NCERT Solutions for 12th Class Chemistry: Chapter 3-Electrochemistry

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NCERT Solutions for 12th Class Chemistry: Chapter 3-Electrochemistry

NCERT 12th Chemistry Chapter 3, class 12 Chemistry chapter 3 solutions

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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, $Hg^{2+}/Hg = 0.79V$, $Mg^{2+}/Mg=-2.37V$, $Cr^{3+}/Cr=0.74V$.

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

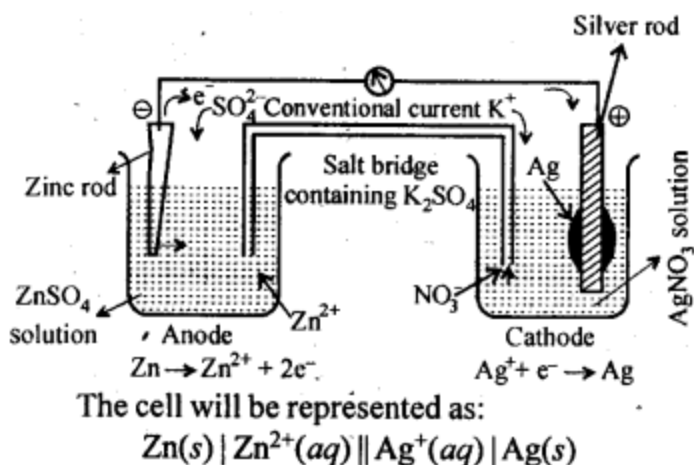**$Zn(s) + 2Ag^+(aq)$ —-> $7M^{2+}(aq) + 2Ag (s)$ takes place. Further show:**

(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:

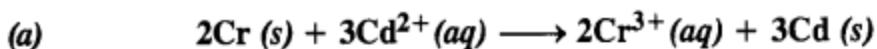$$Zn(s) | Zn^{2+}(aq) \| Ag^+(aq) | Ag(s)$$

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

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

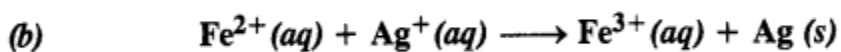(iii) At anode: $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$

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

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

(a) $\qquad$ $2Cr\,(s) + 3Cd^{2+}\,(aq) \longrightarrow 2Cr^{3+}\,(aq) + 3Cd\,(s)$

Given $E^{\circ}_{Cr^{3+}/Cr} = -0{\cdot}74\ V$; $E^{\circ}_{Cd^{2+}/Cd} = -0{\cdot}40\ V$

(b) $\qquad$ $Fe^{2+}\,(aq) + Ag^+\,(aq) \longrightarrow Fe^{3+}\,(aq) + Ag\,(s)$

Given $E^{\circ}_{Ag^+/Ag} = 0{\cdot}80\ V$; $E^{\circ}_{Fe^{3+}/Fe^{2+}} = 0{\cdot}77\ V$

Also calculate ΔG° and equilibrium constant for the reaction. (C.B.S.E. Outside Delhi 2008)

Sol:

(a) $2Cr\ (s) + 3Cd^{2+}(aq) \longrightarrow 2Cr^{3+}(aq) + 3Cd\ (s)$

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

(b) $Fe^{2+}(aq) + Ag^{+}(aq) \longrightarrow Fe^{3+}(aq) + Ag\ (s)$
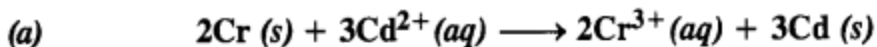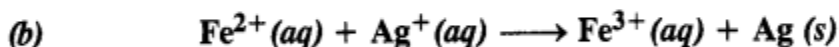
Given $E°_{Ag^{+}/Ag} = 0.80\ V$; $E°_{Fe^{3+}/Fe^{2+}} = 0.77\ V$

(a) Calculation of E°cell,

$$E°_{cell} = E°_{cathode} - E°_{anode} = -0.40 - (-0.74) = +0.34\ V$$

Calculation of ΔG°,

$$\Delta G° = -nF\ E°_{cell} = -(6\ mol) \times (96500\ C\ mol^{-1}) \times (0.34\ V)$$
$$= -196860\ CV = -196860\ J = -196.86\ kJ$$

Calculation of Equilibrium Constant (Kc)

$$\Delta G° = -2.303\ RT\ \log K_c$$

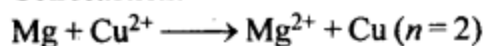$$\log K_c = \frac{(-)\ \Delta G°}{2.303\ RT} = (-)\frac{(-)\ 196860}{2.303 \times 8.314 \times 298} = 34.501$$

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

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

(i) $Mg(s) \mid Mg^{2+} (0 \cdot 001\ M) \parallel Cu^{2+} (0 \cdot 0001\ M) \mid Cu(s)$

(ii) $Fe(s) \mid Fe^{2+} (0 \cdot 001\ M) \parallel H^+ (1M) \mid H_2(g)$ (1 bar) $\mid Pt(s)$

(iii) $Sn(s) \mid Sn^{2+} (0 \cdot 050\ M) \parallel H^+ (0 \cdot 020\ M) \mid H_2(g)$ (1 bar) $\mid Pt(s)$

(i)   Cell reaction:

$Mg + Cu^{2+} \longrightarrow Mg^{2+} + Cu\ (n = 2)$

Nernst equation:

$$E_{cell} = E^{\circ}_{cell} - \frac{0 \cdot 0591}{2} \log \frac{[Mg^{2+}]}{[Cu^{2+}]}$$

$$\therefore E_{cell} = 0 \cdot 34 - (-2.37) - \frac{0 \cdot 0591}{2} \log \frac{10^{-3}}{10^{-4}}$$

$$= 2 \cdot 71 - 0 \cdot 02955 = 2 \cdot 68\ V.$$

(ii) Cell reaction:

$Fe + 2H^+ \longrightarrow Fe^{2+} + H_2\ (n = 2)$

Nernst equation:

$$E_{cell} = E^{\circ}_{cell} - \frac{0 \cdot 0591}{2} \log \frac{[Fe^{2+}]}{[H^+]^2}$$

$$\therefore E_{cell} = 0 - (-0 \cdot 44) - \frac{0 \cdot 0591}{2} \log \frac{10^{-3}}{(1)^2}$$

$$= 0 \cdot 44 - \frac{0 \cdot 0591}{2} \times (-3)$$

$$= 0 \cdot 44 + 0 \cdot 0887 = 0 \cdot 5287\ V.$$

Sol:

IndCareer

(i) Cell reaction:

$Mg + Cu^{2+} \longrightarrow Mg^{2+} + Cu \ (n = 2)$

Nernst equation:

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

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

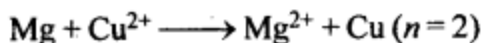$$= 2.71 - 0.02955 = 2.68 \text{ V}.$$

(ii) Cell reaction:

$Fe + 2H^+ \longrightarrow Fe^{2+} + H_2 \ (n = 2)$

Nernst equation:

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

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

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

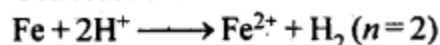$$= 0.44 + 0.0887 = 0.5287 \text{ V}.$$

(iii) Cell reaction:

$Sn + 2H^+ \longrightarrow Sn^{2+} + H_2 \ (n = 2)$

Nernst equation :

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

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{2} \log \frac{0.05}{(0.02)^2}$$

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

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

$$= 0.14 - \frac{0.0591}{2} (2.0969) = 0.078 \text{ V}.$$

(iv) Cell reaction:

$2Br^- + 2H^+ \longrightarrow Br_2 + H_2 \ (n = 2)$

Nernst equation :

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{2} \log \frac{1}{[Br^-]^2 [H^+]^2}$$

$$= (0 - 1.08) - \frac{0.0591}{2} \log \frac{1}{(0.01)^2 (0.03)^2}$$
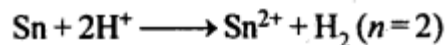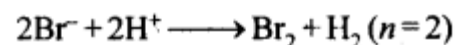
$$= -1.08 - \frac{0.0591}{2} \log (1.111 \times 10^7)$$

$$= -1.08 - \frac{0.0591}{2} (7.0457)$$

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

Thus, oxidation will occur at the hydrogen electrode and reduction will occur on Br_2 electrode.

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

$$Zn(s) + Ag_2O(s) + H_2O(l)$$
$$\longrightarrow Zn^{2+}(aq) + 2\,Ag(s) + 2OH^-(aq)$$
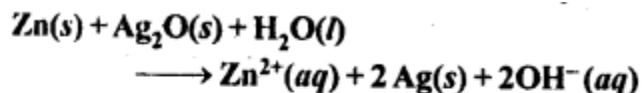
Determine $\Delta_r G^\ominus$ and $E^\ominus$ for the reaction.

Given $Zn \longrightarrow Zn^{2+} + 2e^-, E° = 0\cdot76V;$

$Ag_2O + H_2O + 2e^- \longrightarrow$
$$2Ag + 2OH^-, E° = 0\cdot344\ V.$$
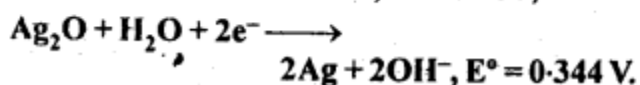
Sol:

Zn is oxidized and Ag_2O is reduced.

$$E°_{cell} = E°_{Ag_2O, Ag\ (reduction)} - E°_{Zn/Zn^{2+}\ (oxidation)}$$
$$= 0\cdot344 + 0\cdot76 = 1\cdot104\ V$$

$$\Delta G = - nFE_{cell} = -2 \times 96500 \times 1\cdot104\ J$$
$$= -2\cdot13 \times 10^5\ J.$$

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 K (kappa). Thus, if K is the specific conductance and G is the conductance of the solution, then

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

Now, if I = 1 cm and A = 1 sq.cm, then K = G.

Hence, conductivity of a solution is defined as the conductance of a solution of 1 cm length and having 1 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 mole of the electrolyte dissolved in V cm³ of the solution when the electrodes are one 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 Δ_m.

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

Since $l = 1$ 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 K 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 S cm⁻¹. Calculate its molar conductivity.

Sol:

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

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

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

Sol:

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

$$= Conductivity \times Resistance$$

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

$$= 0.219\,cm^{-1}.$$

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
$10^2 \times k/S\ m^{-1}$	1·237	11·85	23·15	55·53	106·74

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

Sol:

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

Concentration (M)	κ (S m^{-1})	κ (S cm^{-1})	$\Lambda_m = \dfrac{1000 \times \kappa}{\text{Molarity}}$ (S cm^2 mol^{-1})	$c^{1/2}$(M$^{1/2}$)
10^{-3}	1.237×10^{-2}	1.237×10^{-4}	$\dfrac{1000 \times 1.237 \times 10^{-4}}{10^{-3}} = 123.7$	0.0316
10^{-2}	11.85×10^{-2}	11.85×10^{-4}	$\dfrac{1000 \times 11.85 \times 10^{-4}}{10^{-2}} = 118.5$	0.100
2×10^{-2}	23.15×10^{-2}	23.15×10^{-4}	$\dfrac{1000 \times 23.15 \times 10^{-4}}{2 \times 10^{-2}} = 115.8$	0.141
5×10^{-2}	55.53×10^{-2}	55.53×10^{-4}	$\dfrac{1000 \times 55.53 \times 10^{-4}}{5 \times 10^{-2}} = 111.1$	0.224
10^{-1}	106.74×10^{-2}	106.74×10^{-4}	$\dfrac{1000 \times 106.74 \times 10^{-4}}{10^{-1}} = 106.7$	0.316
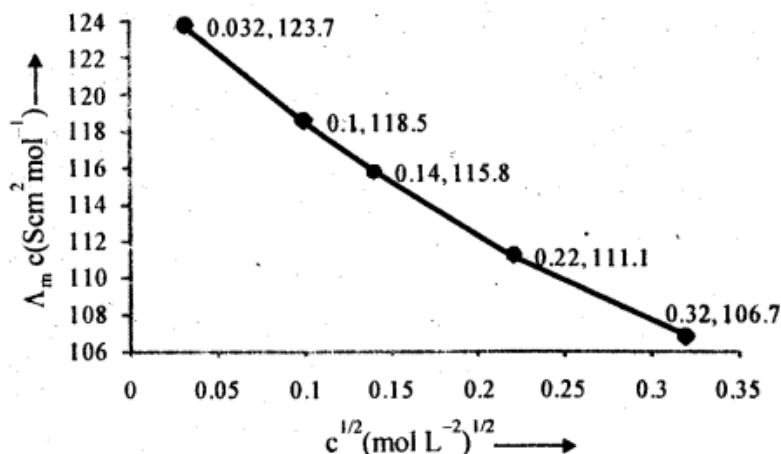
Λ° = Intercept on Λ_m axis = 124.0 S cm^2 mol^{-1}, which is obtained by extrapolation to zero concentration.

3.11. Conductivity of 0.00241 M acetic acid is 7.896 x 10^{-5} S cm^{-1}. Calculate its molar conductivity. If Λ_{mo}, for acetic acid is 390.5 S cm^2 mol^{-1}, what is its dissociation constant?

Sol:

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

$$= \frac{(7 \cdot 896 \times 10^{-5} \, S \, cm^{-1}) \times 1000 \, cm^3 \, L^{-1}}{0 \cdot 00241 \, mol \, L^{-1}}$$

$$\approx 32 \cdot 76 \, S \, cm^2 \, mol^{-1}$$

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^\circ} = \frac{32 \cdot 76}{390 \cdot 5} = 8 \cdot 4 \times 10^{-2}$$

$$K_a = \frac{C\alpha^2}{1-\alpha} = \frac{0 \cdot 0024 \times (8 \cdot 4 \times 10^{-2})^2}{1 - 0 \cdot 084} = 1 \cdot 86 \times 10^{-5}.$$

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

(i) 1 mol of Al³⁺ to Al?

(ii) 1 mol of Cu²⁺ to Cu ?

(iii) 1 mol of Mno4- to Mn²⁺?

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

∴ Quantity of charge required for reduction of 1 mol of Al^{3+}=3F=3 x 96500C=289500C.

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

∴ Quantity of charge required for reduction of 1 mol of Cu^{2+}=2F=2 x 96500=193000 C.

(iii) The electrode reaction is Mno4- ———> Mn²⁺.

i.e., $Mn^{7+} + 5e^- \longrightarrow Mn^{2+}$.
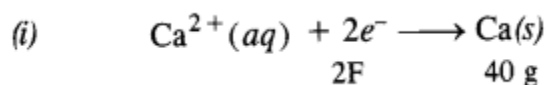
∴ Quantity of charge required = 5F

=5 x 96500 C=4825000.

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3.13. How much electricity in terms of Faraday is required to produce :
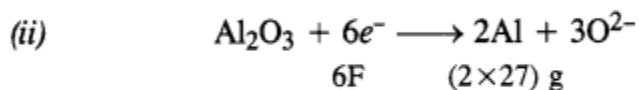
(i) 20·0 g of Ca from molten CaCl$_2$

(ii) 40·0 g of Al from molten Al$_2$O$_3$?

Sol:

(i)
$$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s)$$
$$2F \qquad\qquad 40\ g$$

To produce 40 g of CaCl$_2$, charge needed = 2F

To produce 20 g of CaCl$_2$, charge needed = 1F

(ii)
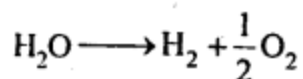$$Al_2O_3 + 6e^- \longrightarrow 2Al + 3O^{2-}$$
$$6F \qquad (2\times27)\ g$$

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

To produce 40 g of Al, charge needed = $\dfrac{(40g)}{(54g)} \times (6F) = $ **4·44F.**

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

Sol:

(*i*) The electrode reaction for 1 mol of H_2O is

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

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

∴ Quantity of electricity required
$= 2F = 2 \times 96500\,C = 193000\,C.$
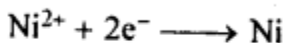
(*ii*) The electrode reaction for 1 mol of FeO is

$$FeO + \frac{1}{2}O_2 \longrightarrow \frac{1}{2}\,Fe_2O_3$$

i.e., $Fe^{2+} \longrightarrow Fe^{3+} + e^-$
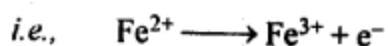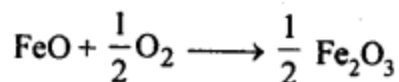
∴ Quantity of electricity required $= 1F = 96500\,C$

3.15. A solution of $Ni(NO_3)_2$ 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
$= (5A) \times (20 \times 60\,sec.) = 6000C$

$Ni^{2+} + 2e^- \longrightarrow Ni$

Thus, 2F, i.e., $2 \times 96500C$ of charge deposit
$= 1$ mole of Ni $= 58\cdot7\,g$

∴ 6000 C of charge will deposite

$= \dfrac{58\cdot7 \times 6000}{2 \times 96500} = 1\cdot825\,g$ 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 call B. How long did the current flow? What mass of copper and zinc were deposited?

Sol:

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

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

or, $W = \dfrac{E}{nF}\,It$

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

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

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

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

$= 0.426\,g$ of Cu.

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

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

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

$\therefore W_2 = \dfrac{1.45 \times 32.65}{108} = 0.438$ 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) Fe³⁺(aq) and Br⁻(aq)

(d) Ag(s) and Fe³⁺(aq)

(e) Br₂(aq) and Fe²⁺(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.

(a) $I^-(aq) + Fe^{3+}(aq) \longrightarrow Fe^{2+}(aq) + 1/2\ I_2(g)$

$E^°_{cell} = 0 \cdot 77 - 0 \cdot 54 = \mathbf{0 \cdot 23\ V}$ (feasible)

(b) $Cu(s) + 2Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$

$E^°_{cell} = (0 \cdot 80 - 0 \cdot 34) = \mathbf{0 \cdot 46\ V}$ (feasible)

(c) $Br^-(aq) + Fe^{3+}(aq) \longrightarrow Fe^{2+}(aq) + 1/2\ Br_2(g)$

$E^°_{cell} = 0 \cdot 77 - (1 \cdot 08) = \mathbf{-0 \cdot 31\ V}$ (not feasible)

(d) $3Ag(s) + Fe^{3+}(aq) \longrightarrow 3Ag^+(aq) + Fe(s)$

$E^°_{cell} = (0 \cdot 77 - 0 \cdot 80) = \mathbf{-0 \cdot 03\ V}$ (not feasible)

(e) $2Fe^{2+}(aq) + Br_2(g) \longrightarrow 2Fe^{3+}(aq) + 2\ Br^-(aq)$

$E^°_{cell} = 1 \cdot 08 - 0 \cdot 77 = \mathbf{0 \cdot 31\ V}$ (feasible)
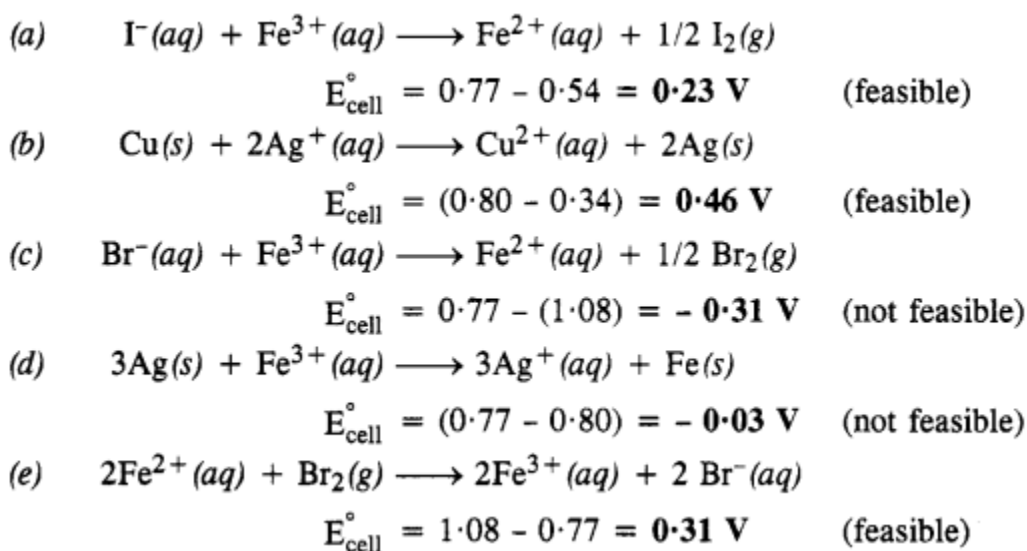
3.18. Predict the products of electrolysis in each of the following.

(i) An aqueous solution of AgNO₃ with silver electrodes.

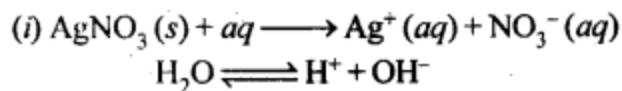**(ii) An aqueous solution of AgNO₃ with platinum electrodes.**

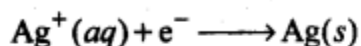**(iii) A dilute solution of H₂So₄ with platinum electrodes.**

(iv) An aqueous solution of CuCl₂ with platinum electrodes.

Sol:

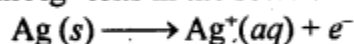(i) $AgNO_3(s) + aq \longrightarrow Ag^+(aq) + NO_3^-(aq)$

$H_2O \rightleftharpoons H^+ + OH^-$

At cathode: Ag^+ ions have lower discharge potential than H^+ ions. Hence, Ag^+ ions will be deposited as Ag in preference to H^+ ions.
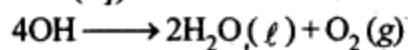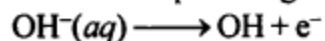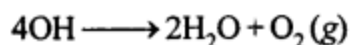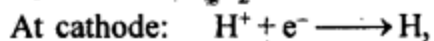
$$Ag^+(aq) + e^- \longrightarrow Ag(s)$$

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

$$Ag(s) \longrightarrow Ag^+(aq) + e^-$$
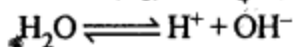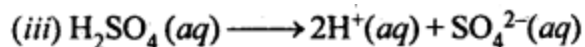
(ii) At cathode: Ag^+ ions have lower discharge potential than H^+ ions. Hence, Ag^+ ions will be deposited as Ag in preference to H^+ ions.

At anode: As 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.

$$OH^-(aq) \longrightarrow OH + e^-$$
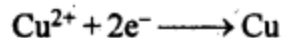$$4OH \longrightarrow 2H_2O(\ell) + O_2(g)$$

(iii) $H_2SO_4 (aq) \longrightarrow 2H^+(aq) + SO_4^{2-}(aq)$

$\qquad\qquad H_2O \rightleftharpoons H^+ + OH^-$

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

$\qquad\qquad\quad H + H \longrightarrow H_2(g)$

At Anode: $OH^- \longrightarrow OH + e^-$

$\qquad\qquad\quad 4OH \longrightarrow 2H_2O + O_2(g)$

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

(iv) $CuCl_2(s) + aq \longrightarrow Cu^{2+}(aq) + 2Cl^-(aq)$

$\qquad\quad H_2O \rightleftharpoons H^+ + OH^-$
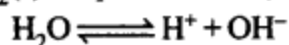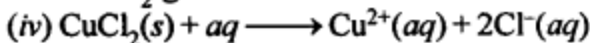
At cathode: Cu^{2+} ions will be reduced in preference to H^+ ions and copper will be deposited at cathode.

$\qquad Cu^{2+} + 2e^- \longrightarrow Cu$

At anode: Cl^- ions will be discharged in preference to OH^- ions which remains in solution.

$\qquad Cl^- \longrightarrow Cl + e^-$

$\qquad Cl + Cl \longrightarrow Cl_2(g)$
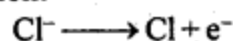
Thus, Cu will be deposited on the cathode and Cl_2 gas will be liberated at the anode.

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