CH3 – ELECTROCHEMISTRY

3.1. How would you determine the standard electrode potential of the system Mg^{2+1} Mg?

Ans: A cell will be set up consisting of Mg/$MgSO_4$ (1 M) as one electrode and standard hydrogen electrode Pt, H, (1 atm)H^+/(l M) as second electrode, measure the EMF of the cell and also note the direction of deflection in the voltmeter. The direction of deflection shows that e^{-1} s flow from mg electrode to hydrogen electrode, i.e., oxidation takes place on magnesium electrode and reduction on hydrogen electrode. Hence, the cell may be represented as follows :

$$Mg \mid Mg^{2+} (1\ M) \parallel H^+ (1\ M) \mid H_2, (1\ atm), Pt$$

$$E^o_{cell} = E^o_{H^+/\frac{1}{2}H_2} - E^o_{Mg^{2+}/Mg}$$

Put $\quad E^o_{H^+/\frac{1}{2}H_2} = 0$

$$\therefore \quad E^o_{Mg^{2+}/Mg} = -E^o_{cell}$$

3.2. Can you store copper sulphate solutions in a zinc pot?

Ans: Zn being more reactive than Cu, displaces Cu from $CuSO_4$ solution as follows:Zn (s) + $CuSO_4$ (aq) –> $ZnSO_4$(ag)+Cu (s)

In terms of EMF, we have

$$Zn \mid Zn^{2+} \parallel Cu^{2+} \mid Cu$$

$$\begin{aligned} E^o_{cell} &= E^o_{Cu^{2+}/Cu} - E^o_{Zn^{2+}/Zn} \\ &= 0.34\ V - (-0.76\ V) \\ &= 1.10\ V \end{aligned}$$

As E^o_{cell} is positive, reaction takes place, i.e., Zn reacts with copper and hence, we cannot store $CuSO_4$ solution in zinc pot.

3.3. Consult the table on standard electrode potentials and suggest three substances that can oxidise Fe2+ ions under suitable conditions.

Ans. The oxidation of Fe2+ ions to Fe3+ ions proceeds as follows :

$Fe^{2+} \rightarrow {}^{3+} + e^-$; E∘OX = – 0·77 V

Only those substances can oxidise Fe^{2+} ions to Fe^{3+} ions which can accept electrons released during oxidation or are placed above iron in electrochemical series. These are : Cl_2(g), Br_2(g) and Cr_2O2−7 ions (in the acidic medium).

3.4. Calculate the potential of hydrogen electrode in contact with a solution whose pH is 10.

Ans. For hydrogen electrode,$H^+ + e^- \longrightarrow 1/2\ H_2$,

Applying Nernst equation,

$$E_{H^+, \frac{1}{2}H_2} = E^o_{H^+/\frac{1}{2}H_2} - \frac{0.0591}{n}\log\frac{1}{[H^+]}$$

$$= 0 - \frac{0.0591}{1}\log\frac{1}{10^{-10}}$$

$$\left\{\begin{array}{l} pH = 10 \\ \Rightarrow [H^+] = 10^{-10} M \end{array}\right\}$$

$$= -0.0591 \times 10$$

$$= -0.591\ V$$

3.5. Calculate the emf of the cell in which the following reaction takes place: $Ni(s) + 2Ag^+\ (0.002\ M) \rightarrow Ni^{2+}\ (0.160\ M) + 2Ag(s)$ Given that $E^{(-)}_{(cell)} = 1.05\ V$.

Ans:

Applying Nernst equation,

$$E_{cell} = E^o_{cell} - \frac{0.0591}{n}\log\frac{[Ni^{2+}]}{[Ag^+]^2}$$

$$= 1.05V - \frac{0.0591}{2}\log\frac{0.160}{(0.002)^2}$$

$$= 1.05 - \frac{0.0591}{2}\log(4 \times 10^4)$$

$$= 1.05 - \frac{0.0591}{2}(4.6021)$$

$$= 1.05 - 0.14\ V$$

$$= 0.91\ V$$

3.6. The cell in which the following reaction occurs: $2Fe^{3+}\ (aq) + 2I^-\ (aq) \longrightarrow 2Fe^{2+}\ (aq) + I^2\ (s)$ has $E^\circ_{cell} = 0.236\ V$ at 298 K. Calculate the standard Gibbs energy and the equilibrium constant of the cell reaction.

Ans:

$2\,Fe^{3+}(aq) + 2I^{-}(aq) \rightarrow 2\,Fe^{2+}(aq) + I_2(s)$

For the given cell, $n = 2$

$$\begin{aligned}\Delta_r G^\circ &= -nF\,E^\circ_{cell}\\ &= -2 \times 96500 \times 0.236\\ &= -45.55\ \text{kJ mol}^{-1}\end{aligned}$$

Also, $\Delta_r G^\circ = -2.303\,RT \log K_C$

$$\Rightarrow \quad \log K_C = \frac{-\Delta_r G^\circ}{2.303RT}$$

$$= \frac{-45.55}{2.303 \times 8.314 \times 10^{-3} \times 298}$$

$$= 7.983$$

$$\Rightarrow \quad K_C = \text{antilog}(7.983)$$

$$= 9.616 \times 10^7$$

3.7. Why does the conductivity of a solution decrease with dilution?

Ans: The conductivity of a solution is linked with the number of ions present per unit volume. With dilution, these decrease and the corresponding conductivity or specific conductance of the solution decreases.

3.8. Suggest a way to determine the value of water.

Ans:

By using Kohlrausch's law, Λ°_m for H_2O can be calculated, we can write,

$\Lambda^\circ_m = \Lambda^\circ_m(HCl) + \Lambda^\circ_m(NaOH) - \Lambda^\circ_m(NaCl)$

Being strong electrolytes, Λ°_m values of HCl, NaOH and NaCl are known. By substituting their values, we can obtain Λ°_m for H_2O.

3.9. The molar conductivity of 0.025 mol L^{-1} methanoic acid is 46.1 S cm^2 mol^{-1}. Calculate its degree of dissociation and dissociation constant Given $\lambda^\circ(H^+)=349.6$ S cm^2 mol^{-1} and$\lambda^\circ(HCOO^-) = 54.6$ S cm^2 mol^{-1}

Ans:

$$\Lambda^{o}_{m}(HCOOH) = \lambda^{o}(H^{+}) + \lambda^{o}(HCOO^{-})$$
$$= 349.6 + 54.6$$
$$= 404.2 \text{ S cm}^2 \text{ mol}^{-1}$$
$$\Lambda^{C}_{m} = 46.1 \text{ S cm}^2 \text{ mol}^{-1}$$
$$\therefore \quad \alpha = \frac{\Lambda^{C}_{m}}{\Lambda^{o}_{m}} = \frac{46.1}{404.2} = 0.114$$

	$HCOOH \rightleftharpoons$	$HCOO^{-}$ +	H^{+}
Initial conc.	c	0	0
at equi,	$c(1-\alpha)$	$c\alpha$	$c\alpha$

$$\therefore \quad K_a = \frac{c\alpha . c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$$
$$= \frac{0.025 \times (0.114)^2}{1-0.114} = 3.67 \times 10^{-4}$$

3.10. If a current of 0.5 ampere flows through a metallic wire for 2 hours, then how many electrons would flow through the wire?

Ans:

We know, $Q = It$
$$= 0.5 \times (2 \times 60 \times 60)$$
$$= 3600 \text{ C}$$

$1F \Rightarrow 96500C \Rightarrow 1$ mole of e^{-1} s
$\Rightarrow 6.02 \times 10^{23}$ e^{-1} s
$\therefore$ 3600 C is equivalent to the flow of e^{-1} s
$$= \frac{6.02 \times 10^{23}}{96500} \times 3600$$
$$= 2.246 \times 10^{22} \text{ } e^{-1} \text{ s}$$

3.11. Suggest a list of metals which can be extracted electrolytically.

Ans: The highly reactive metals having large -ve E° values, which can themselves act as powerful reducing agents can be extracted electrolytically. The process is known as electrolytic reduction. For details, consult Unit-6. For example, sodium, potassium, calcium, magnesium etc.

3.12. Consider the reaction: $Cr_2O_7^{2-}$-+ $14H^+$ + 6e- -> $2Cr_3$+ + $7H_2O$ What is the quantity of electricity in coulombs needed to reduce 1 mol of $Cr_2O_7^{2-}$?

Ans:

From the reaction, 1 mol of $Cr_2O_7^{2-}$ require 6F
$$= 6 \times 96500 = 579000 \text{ C}$$
$\therefore$ 579000 C of electricity are required for reduction of $Cr_2O_7^{2-}$ to Cr^{3+}

3.13. Write the chemistry of recharging the lead storage battery, highlighting all the materials that are involved during recharging.

Ans: A lead storage battery consists of anode of lead, cathode of a grid of lead packed with lead dioxide (PbO_2) and 38% H_2SO_4 solution as electrolyte. When the battery is in use, the reaction taking place are:

Anode : $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$

Cathode : $PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$

Overall Reaction : $Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$

On charging the battery, the reverse reaction takes place, i.e., $PbSO_4$ deposited on electrodes is converted back to Pb and PbO_2 and H_2SO_4 is regenerated.

3.14. Suggest two materials other than hydrogen that can be used as fuels in the fuel cells.

Ans: Methane (CH_4) and methanol (CH_3OH) can also be used as fuels in place of hydrogen in the fuel cells.

3.15. Explain how rusting of iron is envisaged as setting up of an electrochemical cell.

Ans: The water present on the surface of iron dissolves acidic oxides of air like CO_2 , SO_2 , etc. to form acids which dissociate to give H^+ ions :

$$H_2O + CO_2 \rightarrow H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{2-}$$

In the presence of H^+, iron looses e^{-1}s to form Fe^{3+}. Hence, this spot acts as anode:

$$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$$

The e^{-1}s released move through the metal to reach another spot where H^+ ions and dissolved oxygen take up these e^{-1} s and reduction occurs. This spot, thus, acts as cathode :

$$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$$

The overall reactio nis :

$$2Fe(s) + O_2(g) + 4H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O(l)$$

Thus, an electrochemical cell is set up on the surface.

Ferrous ions are further oxidised by atmospheric oxygen to ferric ions which combine with water to form hydrated ferric oxide, $Fe_2O_3 . xH_2O$, which is rust.

NCERT 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

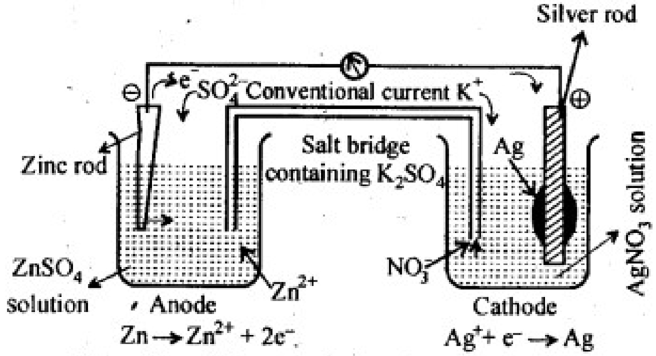
Sol: Mg, Al, Zn, Fe, Cu.

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
$Zn(s) + 2Ag^+(aq) \longrightarrow 7M^{2+}(aq) + 2Ag(s)$ 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) $2Cr(s) + 3Cd^{2+}(aq) \longrightarrow 2Cr^{3+}(aq) + 3Cd(s)$

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

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

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

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

Sol:

(a) Calculation of $E°_{cell}$,

$$E°_{cell} = E°_{cathode} - E°_{anode} = -0{\cdot}40 - (-0{\cdot}74) = \mathbf{+0{\cdot}34\ V}$$

Calculation of $\Delta G°$,

$$\Delta G° = -nF\,E°_{cell} = -(6\ \text{mol}) \times (96500\ \text{C mol}^{-1}) \times (0{\cdot}34\ \text{V})$$
$$= -196860\ \text{CV} = -196860\ \text{J} = \mathbf{-196{\cdot}86\ kJ}$$

Calculation of Equilibrium Constant (K_c)

$$\Delta G° = -2{\cdot}303\ RT \log K_c$$

$$\log K_c = \frac{(-)\,\Delta G°}{2{\cdot}303\ RT} = (-)\frac{(-)\,196860}{2{\cdot}303 \times 8{\cdot}314 \times 298} = 34{\cdot}501$$

$$K_c = \text{Antilog}\ (34{\cdot}501) = \mathbf{3{\cdot}17 \times 10^{34}}$$

(b) Calculation of $E°_{cell}$,

$$E°_{cell} = E°_{cathode} - E°_{anode} = (0{\cdot}80 - 0{\cdot}77) = \mathbf{0{\cdot}03\ V}$$

Calculation of $\Delta G°$,

$$\Delta G° = -nF\,E°_{cell} = -(1\ \text{mol}) \times (96500\ \text{C mol}^{-1}) \times (0{\cdot}03\ \text{V})$$
$$= -2895\ \text{CV} = -2895\ \text{J} = \mathbf{-2{\cdot}895\ kJ}$$

Calculation of Equilibrium Constant (K_c)

$$\Delta G° = -2{\cdot}303\ RT \log K_c$$

$$\log K_c = (-)\frac{(-\Delta G°)}{2{\cdot}303\ RT} = (-)\frac{(-)2895}{2{\cdot}303 \times 8{\cdot}314 \times 298} = 0{\cdot}5074$$

$$K_c = \text{Antilog}\ (0{\cdot}5074) = \mathbf{3{\cdot}22}$$

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

(*i*) **$Mg(s)\,|\,Mg^{2+}\,(0\cdot001\ M)\,||\,Cu^{2+}\,(0\cdot0001\ M)\,|\,Cu(s)$**

(*ii*) **$Fe(s)\,|\,Fe^{2+}\,(0\cdot001\ M)\,||\,H^{+}\,(1M)\,|\,H_2(g)\,(1\ bar)\,|\,Pt(s)$**

(*iii*) **$Sn(s)\,|\,Sn^{2+}\,(0\cdot050\ M)\,||\,H^{+}\,(0\cdot020\ M)\,|\,H_2\,(g)\,(1\ bar)\,|\,Pt\,(s)$**

(*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:

(*iv*) $Pt(s) | Br_2(l) | Br^-(0\cdot010\ M) || H^+(0\cdot030\ M) | H_2(g)(1\ bar) | Pt(s)$

Given $E^{\circ}_{Mg^{2+},Mg} = -2\cdot37V$,

$E^{\circ}_{Cu^{2+},Cu} = +0\cdot34\ V$, $E^{\circ}_{Fe^{2+},Fe} = -0\cdot44\ V$.

$E^{0}_{Sn^{2+}/Sn} = -0.14V$

$E^{0}_{1/2Br_2/Br^-} = +1.08V$

(*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 $Zn \longrightarrow Zn^{2+} + 2e^-, E^\circ = 0.76V$;

$Ag_2O + H_2O + 2e^- \longrightarrow 2Ag + 2OH^-, E^\circ = 0.344$ V.

Sol:

Zn is oxidized and Ag_2O is reduced.

$$E^\circ_{cell} = E^\circ_{Ag_2O, Ag\,(reduction)} - E^\circ_{Zn/Zn^{2+}\,(oxidation)}$$
$$= 0{\cdot}344 + 0{\cdot}76 = 1{\cdot}104\text{ V}$$
$$\Delta G = -nFE_{cell} = -2 \times 96500 \times 1{\cdot}104\text{ J}$$
$$= -2{\cdot}13 \times 10^5\text{ J.}$$

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

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

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 cm^3 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:

$$\Lambda_m = \frac{\kappa \times 1000}{\text{Molarity}} = \frac{0{\cdot}0248\,\text{S cm}^{-1} \times 1000\,\text{cm}^3\text{L}^{-1}}{0{\cdot}20\,\text{mol L}^{-1}}$$

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

3.9. The resistance of a conductivity cell containing 0.001 M 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:

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

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

$$= 0{\cdot}146 \times 10^{-3}\ \text{S cm}^{-1} \times 1500\ \Omega$$

$$= 0{\cdot}219\ \text{cm}^{-1}.$$

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

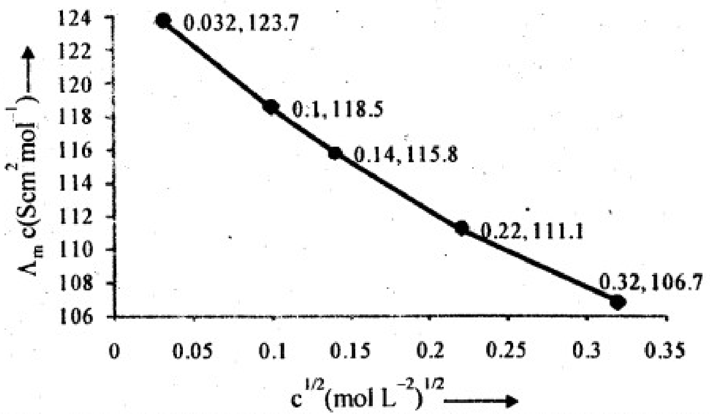
Concentration/M	0·001	0·010	0·020	0·050	0·100
$10^2 \times k$/S m^{-1}	1·237	11·85	23·15	55·53	106·74

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

Sol:

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

Concentration (M)	κ (S m^{-1})	κ (S cm^{-1})	$\Lambda_m = \frac{1000 \times \kappa}{\text{Molarity}}$ (S cm^2 mol^{-1})	$c^{1/2}$(M$^{1/2}$)
10^{-3}	$1{\cdot}237 \times 10^{-2}$	$1{\cdot}237 \times 10^{-4}$	$\frac{1000 \times 1{\cdot}237 \times 10^{-4}}{10^{-3}} = 123{\cdot}7$	0·0316
10^{-2}	$11{\cdot}85 \times 10^{-2}$	$11{\cdot}85 \times 10^{-4}$	$\frac{1000 \times 11{\cdot}85 \times 10^{-4}}{10^{-2}} = 118{\cdot}5$	0·100
2×10^{-2}	$23{\cdot}15 \times 10^{-2}$	$23{\cdot}15 \times 10^{-4}$	$\frac{1000 \times 23{\cdot}15 \times 10^{-4}}{2 \times 10^{-2}} = 115{\cdot}8$	0·141
5×10^{-2}	$55{\cdot}53 \times 10^{-2}$	$55{\cdot}53 \times 10^{-4}$	$\frac{1000 \times 55{\cdot}53 \times 10^{-4}}{5 \times 10^{-2}} = 111{\cdot}1$	0·224
10^{-1}	$106{\cdot}74 \times 10^{-2}$	$106{\cdot}74 \times 10^{-4}$	$\frac{1000 \times 106{\cdot}74 \times 10^{-4}}{10^{-1}} = 106{\cdot}7$	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_{m0}, for acetic acid is 390.5 S cm^2 mol^{-1}, what is its dissociation constant?

Sol:

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

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

$$= 32{\cdot}76\ \text{S cm}^2\ \text{mol}^{-1}$$

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

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

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

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

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

(iii) 1 mol of Mn04- to Mn^{2+}?

Sol: (i) The electrode reaction is $Al^{3+} + 3e$ ——> Al
∴ Quantity of charge required for reduction of 1 mol of Al^{3+}=3F=3 x 96500C=289500C.
(ii) The electrode reaction is $Cu^{2+} + 2e^-$ ———> Cu
∴ Quantity of charge required for reduction of 1 mol of Cu^{2+}=2F=2 x 96500=193000 C.
(iii) The electrode reaction is Mn04- ————> Mn^{2+}.
i.e., $Mn^{7+} + 5e^-$———> Mn^{2+}.
∴ Quantity of charge required = 5F
=5 x 96500 C=4825000.

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 ?
Sol:

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

To produce 40 g of $CaCl_2$, charge needed = 2F
To produce 20 g of $CaCl_2$, charge needed = **1F**

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

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

$$\text{To produce 40 g of Al, charge needed} = \frac{(40\text{g})}{(54\text{g})} \times (6F) = \mathbf{4{\cdot}44F.}$$

3.14. How much electricity is required in coulomb for the oxidation of (i) 1 mol of H_2O to 0_2 (ii) 1 mol of FeO to Fe_20_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

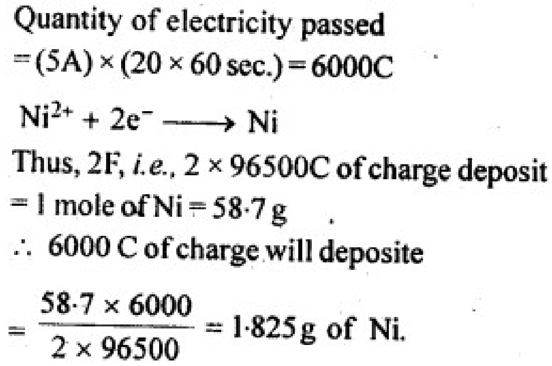
$$FeO + \frac{1}{2}O_2 \longrightarrow \frac{1}{2}Fe_2O_3$$

i.e., $Fe^{2+} \longrightarrow Fe^{3+} + e^-$

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

3.15. A solution of $Ni(N0_3)_2$ 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

$= (5A) \times (20 \times 60 \text{ sec.}) = 6000C$

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

Thus, 2F, *i.e.*, 2 × 96500C of charge deposit

= 1 mole of Ni = 58·7 g

∴ 6000 C of charge will deposite

$$= \frac{58{\cdot}7 \times 6000}{2 \times 96500} = 1{\cdot}825 \text{ g of Ni.}$$

3.16. Three electrolytic cells A, B, C containing solutions of $ZnS0_4$, $AgNO_3$ and $CuS0_4$, 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, $W = \frac{E}{nF} It$

or, $t = \frac{1.45 \times 96500}{1.5 \times 108} = 863.73$ 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 $\frac{W_1}{W_2} = \frac{E_1}{E_2}$

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

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

Similarly, for Zn, $W_1 = 1.45$ 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^{3+}(aq)
(e) Br_2(aq) and Fe^{2+}(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) $I^-(aq) + Fe^{3+}(aq) \longrightarrow Fe^{2+}(aq) + 1/2\ I_2(g)$

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

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

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

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

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

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

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

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

$E^\circ_{cell} = 1{\cdot}08 - 0{\cdot}77 = \mathbf{0{\cdot}31\ V}$ (feasible)

3.18. Predict the products of electrolysis in each of the following.
(i) An aqueous solution of $AgNO_3$ with silver electrodes.
(ii) An aqueous solution of $AgNO_3$ with platinum electrodes.
(iii) A dilute solution of H_2S0_4 with platinum electrodes.
(iv) An aqueous solution of $CuCl_2$ 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*) $H_2SO_4(aq) \longrightarrow 2H^+(aq) + SO_4^{2-}(aq)$

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

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

$H + H \longrightarrow H_2(g)$

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

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

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

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

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

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

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

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

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

$$Cl + Cl \longrightarrow Cl_2(g)$$

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

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