Electrochemistry Important Questions

2015 – Very Short Answer Type Questions [1 Mark]

1. How much charge in Faraday is required for the reduction of 1 mol of Ag^+ to Ag?
Answer: $Ag^+ + e^- \longrightarrow Ag(s)$
1 Faraday of charge is required (charge on 1 mole of electrons).

2. How much charge is required for the reduction of 1 mole of Zn^{+2} to Zn?
Answer: $Zn^{+2} + 2e^- \longrightarrow Zn(s)$
2 Faradays or 2 x 96500 C of charge is required.

3. How much charge in Faradays is required for the reduction of 1 mol of Al^{+3} to Al ?
Answer: 3 Faradays
$Al3^+ + 3e^- \longrightarrow Al(s)$
3 moles of electron have charge = 3 Faradays.

4. Calculate the time to deposit 1.5 g of silver at cathode when a current of 1.5 A was passed through the solution of $AgNO_3$. (Molar mass of Ag = 108 g mol^{-1}, 1 F = 96500 C mol^{-1}).
Answer:

Given: $m = 1.5$ g, $I = 1.5$ A, Molar mass = 108 g mol^{-1}, 1F = 96500 C mol^{-1}

$$\therefore \quad m = Z \times I \times t$$

$$\Rightarrow \quad 1.5 = \frac{108}{1 \times 96500} \times 1.5 \times t$$

$$\Rightarrow \quad t = \frac{96500}{108} = 893 \text{ seconds}$$

Short Answer Type Questions [I] [2 Marks]

5. Calculate the time to deposit 1.17 g of Ni at cathode when a current of 5 A was passed through the solution of $Ni(NO_3)_2$.
(Molar mass of Ni = 58.5 g mol^{-1}, 1 F = 96500 C mol^{-1}).
Answer:

$$m = Z \times I \times t$$

$$\Rightarrow \quad 1.17 = \frac{58.5 \times 5 \times t}{2 \times 96500}$$

$$t = \frac{2 \times 96500 \times 1.17}{58.5 \times 5} = \frac{2 \times 96500}{50 \times 5} = \frac{19300}{25}$$

$$t = 772 \text{ seconds}$$

6. Accounts for the following
(i) Rusting of iron is quicker in saline water than in ordinary water.

(ii) Blocks of magnesium are straped to the steel hubs of ocean going ships.
Answer: (i) Electrolytes present in sea water favour the formation of more electrochemical cells on the surface of iron leading to increase in the rate of rusting.
(ii) Mg is more reactive than iron, therefore, prevents oxidation of steel (rusting of steel)

7. (a) Following reactions occur at cathode during the electrolysis of aqueous sodium chloride solution:
$Na^+(aq) + e^{-1} \longrightarrow Na(s)$ $\quad$ E° = – 2.71 V
$H^+(aq) + e^{-1} \longrightarrow 1/2H2(s)$ $\quad$ E° = 0.00 V
On the basis of their standard reduction electrode potential (E°) values, which reaction is feasible at the cathode and why?
(b) Why does the cell potential of mercury cell remain constant throughout its life?
Answer: (a) $H^+(aq) + e^{-1} \longrightarrow \sim H_2(g)$ will take place at cathode because it has higher reduction potential.
(b) It is because ions are not involved in net cell reaction.

8.(a) Following reactions occur at cathode during the electrolysis of aqueous silver chloride solution:

$Ag^+(aq) + e^{-1}$ -----> Ag(s) $E° = +0.80$ V

$H^+(aq) + e^{-1}$ ----> $1/2H_2(g)$ $E° = 0.00$ V

On the basis of their standard reduction electrode potential (E°) values, which reaction is feasible at the cathode and why?

(b) Define limiting molar conductivity. Why conductivity of an electrolyte solution decreases with the decrease in concentration?

Answer:

(a) $E°_{Cell} = E°_{Ag^+/Ag} - E°_{H^+/½H_2}$

$= +0.80 - 0.00 = +0.80$ V

$$\frac{1}{2}H_2 + Ag^+ \longrightarrow H^+(aq) + Ag(s)$$

This reaction is feasible because $E°_{Cell}$ is +ve.

Therefore, ΔG will be –ve, since $\Delta G° = -nE°F$.

(b) Limiting molar conductivity is the maximum conductivity when solution is infinitely dilute, such that on further dilution there is no increase in Am. Conductivity decreases with decrease in concentration because number of ions per unit volume decrease.

9. Calculate the time to deposit 1.27 g of copper at cathode when a current of 2 A was passed through the solution of CuS04.

(Molar mass of Cu = 63.5 g mol^{-1}, 1 F = 96500 C mol^{-1})

Answer:

$t = ?,\ m = 1.27$ g, $I = 2$ A

$\therefore \quad m = Z \times I \times t$

$\Rightarrow \quad 1.27 = \frac{\text{Eq. Wt}}{96500} \times 2 \times t.$

$\Rightarrow \quad 1.27 \times 96500 = \frac{\text{Atomic Wt}}{\text{Valency}} \times 2 \times t.$ $\quad \left[\text{Eq.Wt} = \frac{\text{Atomic Wt}}{\text{Valency}}\right]$

$\Rightarrow \quad 1.27 \times 96500 = \frac{63.5}{2} \times 2 \times t$

$\Rightarrow \quad t = \frac{1.27 \times 96500}{63.5} = \frac{127 \times 10 \times 96500}{100 \times 635}$

$\therefore \quad t = 2 \times 965 = 1930$ seconds.

10. (a) Following reactions occur at cathode during the electrolysis of aqueous copper (II) chloride solution:

$Cu^{2+}(aq) + 2\ e^{-2}$ ----> Cu(s) $E° = + 0.34$ V

H+(aq) + e^{-1} -----> $1/2H_2(g)$ $E° = 0.00$ V

On the basis of their standard reduction electrode potential (E°) values, which reaction is feasible at the cathode and why ?

(b) State Kohlrausch law of independent migration of ions. Write its one application.

Answer: (a) At cathode $Cu^{2+} + 2e^{-1}$ ———> Cu(s)

The above reaction is feasible at cathode because $E°Cu^{2+}/Cu = + 0.34$, because reduction potential of Cu^{2+} is higher than H^+ as $E^0_{H+/H2} = 0$.

(b) Kohlrausch law: It states that the limiting molar conductivity of an electrolyte is equal to the sum of contribution of cations as well as anions. Application: It helps in calculating A0 (limiting molar conductivities) of weak electrolytes.

Short Answer Type Questions [II] [3 Marks]

11. Calculate E°el1 and ArG° for the following reaction at 25 °C:
$A^{2+}(aq) + B^{+}(aq)$ ---> $A^{5+}(aq) + B(s)$
Given Kc=1010, 1F=96500 C mol^{-1}

Answer:

$$A^{2+} + B^{+} \longrightarrow A^{3+} + B$$

$$E^{\circ}_{cell} = ?\ \Delta_r G^{\circ} = ?\quad K_C = 10^{10},\quad 1\ F = 96500\ C\ mol^{-1}$$

$$A^{2+} \longrightarrow A^{3+} + e^{-}$$
$$B^{+} + e^{-} \longrightarrow B$$
$$A^{2+} + B^{+} \longrightarrow A^{3+} + B$$
$$(n = 1)$$

$$\log K_C = \frac{nE^{\circ}}{0.0591}$$

$$\log 10^{10} = \frac{1 \times E^{\circ}}{0.0591}$$

$$10 = \frac{E^{\circ}}{0.0591}$$

$$E^{\circ} = 0.591\ V$$

$$\Delta_r G^{\circ} = -nE^{\circ}F = -1 \times 0.591\ V \times 96500\ C$$
$$= -57031.5\ J\ mol^{-1} = -57.031\ kJ\ mol^{-1}$$

12. Calculate E°cell for the following reaction at 25 °C:
$A + B^{2+}$ (0.001 M) ---> A^{2+} (0.0001 M) + B
Given : E_{cell} = 2.6805 V, 1 F = 96500 C mol^{-1}
Answer:

$$A \longrightarrow A^{2+}(aq) + 2e^{-}$$
$$B^{2+}(aq) + 2e^{-} \longrightarrow B$$
$$A + B^{2+} \longrightarrow A^{2+} + B \qquad \therefore\ n = 2$$

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

$$2.6805\ V = E^{\circ}_{Cell} - \frac{0.0591}{2} \log \frac{10^{-4}}{10^{-3}} = E^{\circ}_{Cell} + 0.0295 \log 10$$

$$E^{\circ}_{cell} = 2.6805 - 0.0295 = 2.651\ V$$

13. Calculate emf of the following cell at 25 °C:
Fe I Fe^{2+}(0.001 M) 11 H^{+}(0.01 M) I H_2(g) (1 bar) I Pt(s)
E°(Fe^{2+}IFe) = -0.44V, E°(H^{+}IH_2) = 0.00 V

Answer:

$$\begin{array}{rcl} Fe(s) & \longrightarrow & Fe^{2+}(aq) + 2e^- \\ 2H^+(aq) + 2e^- & \longrightarrow & H_2(g) \\ \hline Fe(s) + 2H^+(aq) & \longrightarrow & Fe^{2+}(aq) + H_2(g) \end{array}$$

Here, $n = 2$

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

$$= (E°_{H^+/H_2} - E°_{Fe^{2+}/Fe}) - \frac{0.0591}{2}\log\frac{10^{-3}}{[10^{-2}]^2}$$

$$= [0 - (-0.44\ V)] - \frac{0.0591}{2}\log 10$$

$$= +0.44\ V - 0.0295 = 0.4105\ V.$$

14. Conductivity of 2.5×10^{-4}M methanoic acid is 5.25×10^{-5} S cm^{-1} Calculate its molar conductivity and degree of dissociation.
Given: $\Lambda°(H^+) = 349.5$ S cm^2 mol^{-1} and $\Lambda°(HCOO^-) = 50.5$ S cm^2
Answer:

Given: $\kappa = 5.25 \times 10^{-5}$ S cm^{-1}, $M = 2.5 \times 10^{-4}$ M.

$$\lambda^0_{HCOOH} = \lambda^0_{(HCOO^-)} + \lambda^0_{H^+}$$

$$= 349.5 + 50.5 = 400\ S\ cm^2\ mol^{-1}.$$

$$\therefore \quad \Lambda_m = \frac{1000\,\kappa}{M} = \frac{1000 \times 5.25 \times 10^{-5}}{2.5 \times 10^{-4}} = \frac{1000 \times 525}{10 \times 2.5 \times 100}$$

$$\Rightarrow \quad \Lambda_m = \frac{525}{2.5} = \frac{5250}{25} = 210\ S\ cm^2\ mol^{-1}$$

$$\therefore \quad \alpha = \frac{\Lambda_m}{\Lambda^0_m} = \frac{210}{400} = \frac{21}{40} = 0.525$$

$$\Rightarrow \quad \alpha = 0.525 \times 100\% = 52.5\%$$

15. Calculate the emf of the following cell at 25 °C:
Zn | Zn^{2+} (0.001 M) || H^+(0.01 M) | H_2(g) (1 bar) | Pt(s)
Answer:

$$\begin{array}{rcl} Zn(s) & \longrightarrow & Zn^{2+}(aq) + 2e^- \\ 2H^+(aq) + 2e^- & \longrightarrow & H_2(g) \\ \hline Zn(s) + 2H^+(aq) & \longrightarrow & Zn^{2+}(aq) + H_2(g) \end{array}$$

$n = 2$

$$\text{Now,}\quad E_{cell} = E°_{cell} - \frac{0.0591}{n}\log\frac{[Zn^{2+}]}{[H^+]^2}$$

$$= (E°_{H^+/H_2} - E°_{Zn^{2+}/Zn}) - \frac{0.0591}{2}\log\frac{10^{-3}}{[10^{-2}]^2}$$

$$= [0 - (-0.76\ V)] - \frac{0.0591}{2}\log 10$$

$$\therefore \quad E_{cell} = +0.76\ V - 0.0295 = 0.7305\ V$$

Long Answer Type Questions [5 Marks]

16. (a) The conductivity of 0.20 mol L^{-1} solution of KC1 is 2.48 X 10^{-2} S cm^{-1}. Calculate its molar conductivity and degree of dissociation (a). Given X,°(K^+) = 73.5 S cm2 mol^{-1} and Z°(cr) = 76.5 S cm^2 mol^{-1}.
(b) What type of battery is mercury cell? Why is it more advantageous than dry cell?
Answer:

(a) $M = 0.20 \text{ mol L}^{-1}$, $\kappa = 2.48 \times 10^{-2} \text{ S cm}^{-1}$, $\Lambda_m = ?$, $\alpha = ?$

$\lambda^\circ_{(K+)} = 73.5 \text{ S cm}^2 \text{ mol}^{-1}$, $\lambda^\circ_{(Cl^-)} = 76.5 \text{ S cm}^2 \text{ mol}^{-1}$

$\Lambda^\circ_{(KCl)} = \lambda^\circ_{K^+} + \lambda^\circ_{Cl^-} = 73.5 + 76.5 = 150.0 \text{ S cm}^2 \text{ mol}^{-1}$

Now, $$\Lambda_m = \frac{1000\,\kappa}{M} = \frac{1000 \times 2.48 \times 10^{-2}}{0.20}$$

$$\Rightarrow \quad \Lambda_m = \frac{248}{2} = 124 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\therefore \quad \alpha = \frac{\Lambda_m}{\Lambda_m^\circ} = \frac{124}{150.0} = 8.26 \times 10^{-1}$$

$$\Rightarrow \quad \alpha = 8.26 \times 10^{-1} \times 10^2 = 82.6\%$$

(b) Mercury cell is primary cell because it is not rechargeable.
Its effeciency is higher than dry cell. Its voltage remains constant over long period of time.

17. (a) The conductivity of 0.1 mol L^{-1} solution of NaCl is 1.06 X 10^{-2} S cm^{-1}. Calculate its molar conductivity and degree of dissociation (a).
Given Z°(Na^+) = 50.1 S $cm^2 mol^{-1}$ and 7°(C1-) = 76.5 S cm^2 mol^{-1}.
(b) What is the difference between primary battery and secondary battery? Give one example of each type.
Answer:

(a) $M = 0.1 \text{ mol L}^{-1}$, $\kappa = 1.06 \times 10^{-2} \text{ S cm}^{-1}$, $\Lambda_m = ?$, $\alpha = ?$

$\lambda^\circ_{NaCl} = \lambda^\circ_{Na^+} + \lambda^\circ_{Cl^-} = 50.1 + 76.5 = 126.6 \text{ S cm}^2 \text{ mol}^{-1}$

$$\therefore \quad \Lambda_m = \frac{1000\,\kappa}{M} = \frac{1000 \times 1.06 \times 10^{-2}}{0.1} = 106 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\therefore \quad \alpha = \frac{\Lambda_m}{\Lambda_m^\circ} = \frac{106}{126.6} = 0.8372 = 83.72\%$$

2014

Short Answer Type Questions [I] [2 Marks]

18. Define the following terms:
(t) Molar conductivity (Am)
(it) Secondary batteries
Answer: (i) Molar conductivity: It is defined as the conductance of solution containing 1 mole of electrolyte placed in a cell having electrodes unit distance apart having sufficient area of cross-section to hold electrolyte.
(ii) Secondary battery: Those batteries which can be recharged are called secondary batteries, e.g. lead storage battery, Nickel-cadmium battery.

19. 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? [Given: At. Mass of Ni = 58.7 g mol^{-1}, IF = 96500 C mol^{-1}]
Answer:

Given: $I = 5$ A, $t = 20$ min $\times 60 = 1200$ s, $m = ?$

$$m = Z \times I \times t$$

$$\Rightarrow \quad m = \frac{58.7}{2 \times 96500} \times 1200 \times 5 = \frac{58.7 \times 30}{965} = \frac{1761}{965} = 1.825 \text{ g}$$

20. The resistance of 0.01 M NaCl solution at 25 °C is 200 Ω. The cell constant of conductivity cell is unity. Calculate the molar conductance.
Answer:

$$\Lambda_m = \frac{1}{R} \times \frac{l}{A} \times \frac{1000}{M} = \frac{1}{200} \times 1 \times \frac{1000}{0.01} = 500 \text{ S cm}^2 \text{ mol}^{-1}$$

21. State Kohlrausch law of independent migration of ions. Why does the conductivity of a solution decrease with dilution?
Answer: It states, 'the molar conductance at infinite dilution (A°, limiting molar conductivity) of an electrolyte is equal to the sum of contribution due to cation as well as anion'.

$$\Lambda^0_{NaCl} = \lambda^0_{Na^+} + \lambda^0_{Cl^-}$$

The conductivity of a solution decreases with dilution because number of ions per unit volume decreases.

22. Set up Nemst equation for the standard dry cell. Using this equation show that the voltage of dry cell has to decrease with use.
Answer:

Anode: $Zn(s) \longrightarrow Zn^{2+} + 2e^-$

Cathode: $[MnO_2 + NH_4^+ + e^- \longrightarrow MnO(OH) + NH_3] \times 2$

$Zn(s) + 2MnO_2(s) + 2NH_4^+ \longrightarrow Zn^{2+}(aq) + 2MnO(OH)(s) + 2NH_3(g)$ [Net cell reaction]

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2} \log \frac{[Zn^{2+}][pNH_3]^2}{[NH_4^+]^2}$$

Due to presence of ions in over all reaction, its voltage decreases with time.

23. Define the following terms:
(i) Limiting molar conductivity (A°m) (ii) Fuel cell
Answer: (i) Limiting molar conductivity: It is defined as the maximum molar conductance of an electrolyte when solution is infinitely dilute, i.e. concentration approaches zero when electrolyte solution is kept in cell having electrodes unit distance apart having large area of cross-section . to hold enough electrolyte.
(ii) Fuel cell: It is a cell in which chemical energy of fuel is converted into electrical energy, e.g. H2—02 fuel cell.

Short Answer Type Questions [II] [3 Marks]

24. (a) Calculate ArG° for the reaction:
$Mg(s) + Cu2^{2+}(aq) > Mg^{2+}(aq) + Cu(s)$
Given: E°cell = + 2.71 V, 1 F = 96500 C mol^{-1}

(b) Name the type of cell which was used in Apollo space programme for providing electrical power.
Answer:

(a) $Mg(s) \longrightarrow Mg^{2+}(aq) + 2e^-$

$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

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

$n = 2$

$\Delta_r G^\circ = - nE^\circ F = - 2 \times 2.71 \text{ V} \times 96500 \text{ C} = - 523030 \text{ J mol}^{-1}$

$\Delta_r G^\circ = - 523.030 \text{ kJ mol}^{-1}$

(b) H2—02 Fuel Cell was used in Apollo space programme for providing electrical power.

25. (i) Write two advantages of H2 – 02 fuel cell over ordinary cell.
(ii) Equilibrium constant (Kc) for the given cell reaction is 10. Calculate E°ell.
Answer: (i) (a) Its efficiency is high.
(b) It does not create pollution.
(c) H20 formed can be used by astronauts for drinking.

(ii)

$$A(s) + B^{2+}(aq) \longrightarrow A^{2+}(aq) + B(s)$$

$$A(s) \longrightarrow A^{2+}(aq) + 2e^- \quad \text{At anode}$$

$$B^{2+}(aq) + 2e^- \longrightarrow B(s) \quad \text{At cathode}$$

$$A(s) + B^{2+}(aq) \longrightarrow A^{2+}(aq) + B(s) \quad \text{Net cell reaction}$$

$n = 2$

$$\therefore \quad nE^\circ_{cell}F = 2.303\ RT \log K_c.$$

$$\Rightarrow \quad \log K_c = \frac{nE^\circ_{cell} \times 96500}{2.303 \times 8.314 \times 298} = \frac{n \times E^\circ_{cell}}{0.0591}$$

$$\Rightarrow \quad \log 10 = \frac{2 \times E^\circ_{cell}}{0.0591}$$

$$\therefore \quad E^\circ_{cell} = \frac{0.0591}{2} = 0.0295\ V.$$

Long Answer Type Questions [5 Marks]

26. (a) Define tue following terms:
(i) Limiting molar conductivity (ii) Fuel cell
(b) Resistance of a conductivity cell filled with 0.1 mol L^{-1} KC1 solution is 100 Q. If the resistance of the same cell when filled with 0.02 mol L^{-1} KC1 solution is 520 Q, calculate the conductivity and molar conductivity of 0.02 mol L KC1 solution. The conductivity of 0.1 mol L 1.29 X 10^{-2} CT1 cm^{-1}
Answer: (a) Refer Ans. to Q.23.

(b) $R = 100$ ohms, M = 0.1 mol L^{-1} of KCl

$$\kappa_1 = \frac{1}{R} \times \frac{l}{A}$$

$$\Rightarrow \quad 1.29 \times 10^{-2}\ ohm^{-1}\ cm^{-1} = \frac{1}{100\ ohm} \times \frac{l}{A}$$

$$\Rightarrow \quad \frac{l}{A} = 1.29\ cm^{-1}$$

Again, $\kappa_2 = \frac{1}{R} \times \frac{l}{A} = \frac{1}{520} \times 1.29$

$$= \frac{1.29}{5.20} \times 10^{-2} = 2.48 \times 10^{-3}\ ohm^{-1}\ cm^{-1}$$

Now, $M = 0.02\ mol\ L^{-1}$.

$$\therefore \quad \Lambda_m = \frac{1000\,\kappa_2}{M} = \frac{1000 \times 2.48 \times 10^{-3}}{0.02} = 124 \text{ S cm}^2 \text{ mol}^{-1}$$

27. (a) State Faraday's first law of electrolysis. How much charge in terms of Faraday is required for the reduction of 1 mol of Cu^{2+} to Cu?
(b) Calculate emf of the following cell at 298 K:
Mg(s) I Mg^{2+}(0.1 M) 11 Cu2+ (0.01) I Cu(s)
[Given $E°_{cell}$, = + 2.71 V, 1 F = 96500 C mol^{-1}]
Answer:

(*a*) It states that the mass of the substance deposited is directly proportional to charge passed through electrolyte.

$$Cu^{2+} + 2e^- \longrightarrow Cu(s)$$

· 2Faraday of charge is required to deposite 1 mole of copper, i.e. 63.5 g of Cu.

(*b*)

$$Mg(s) \longrightarrow Mg^{2+} + 2e^-$$
$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$$
$$Mg(s) + Cu^{2+}(aq) \longrightarrow Mg^{2+} + Cu(s) \qquad n = 2$$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2} \log \frac{[Mg^{2+}]}{[Cu^{2+}]} = 2.71 \text{ V} - \frac{0.0591}{2} \log \frac{0.1}{0.01}$$

$$\Rightarrow \quad E_{cell} = 2.71 \text{ V} - \frac{0.0591}{2} \log 10 = 2.71 \text{ V} - 0.0295 = 2.68 \text{ V.}$$

28. (a) Predict the products of electrolysis in each of the following:
(i) An aqueous solution of $AgNO_3$ with platinum electrode.
(ii) An aqueous solution of H_2S0_4 using platinum electrode.
(b) Estimate the minimum potential differences needed to reduce Al_2O_3 at 500°C. The gibbs free energy change for the decomposition reaction

Answer:

(*a*) (*i*)

$$AgNO_3 \longrightarrow Ag^+ + NO_3^-$$
$$H_2O \longrightarrow H^+ + OH^-$$

At cathode $\quad Ag^+ + e^- \longrightarrow Ag(s)$

At Anode $\quad H_2O \longrightarrow 2H^+ + 2e^- + \frac{1}{2}O_2$

(*ii*)

$$H_2SO_4 \longrightarrow 2H^+ + SO_4$$
$$H_2O \longrightarrow H^+ + OH^-$$

At cathode $\quad 2H^+ + 2e^- \longrightarrow H_2(g)$

At Anode $\quad H_2O \longrightarrow 2H^+ + 2e^- + \frac{1}{2}O_2$

(*b*) $\frac{2}{3} \times 2\,Al^{3+} + 4e^- \longrightarrow \frac{4}{3}Al \qquad [n = 4]$

$$\Delta G^\circ = -nE^\circ F$$

$$\Rightarrow 960 \times 1000 \text{ J} = -4 \times E^\circ \times 96500 \text{ C}$$

$$\therefore \quad E^\circ = -\frac{9600}{965 \times 4} = -2.48 \text{ V}$$

2013

Very Short Answer Type Question [1 Mark]

29. Represent the galvanic cell in which the reactions is
Zn(s) + Cu^{2+}(aq) > Zn^{2+}(aq) + Cu(s)
Answer: Zn | ZnS04 (1M) | | CuS04 (1M) | Cu(s).

Short Answer Type Questions [I] [2 Marks]

Very Short Answer Type Question [1 Mark]

29. Represent the galvanic cell in which the reactions is
$Zn(s) + Cu^{2+}(aq) > Zn^{2+}(aq) + Cu(s)$
Answer: Zn | ZnS04 (1M) | | CuS04 (1M) | Cu(s).

Short Answer Type Questions [I] [2 Marks]

30. The conductivity of 0.20 M solution of KC1 at 298 K is 0.025 S cm^{-1}. Calculate its molar conductivity.
Answer:

$$\Lambda_m = \frac{1000 \times \kappa}{M} = \frac{1000 \times 0.025}{0.2} = 125 \text{ S cm}^2 \text{ mol}^{-1}$$

31. The standard electrode potential (E°) for Daniell cell is + 1.1 V. Calculate the AG° for the reaction
$Zn(s) + Cu^{2+}(a<7)$ ---> $Zn^{2+}(aq) + Cu(s)$ (1 F = 96500 C mol^{-1}).

Answer:

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

$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$ At cathode

$n = 2$

$$\Delta G° = -nE°F$$

$$= \frac{-2 \times 1.10 \text{ V} \times 96500 \text{ C}}{1000} = -212.3 \text{ kJ mol}^{-1} \qquad [\text{CV} = \text{J}]$$

Short Answer Type Questions [II] [3 Marks]

32. Calculate the emf of the following cell at 298 K:
Fe(s) I Fe^{2+}(0.001 M) 11 H+ (1 M) I H_2(g) (1 bar), Pt ($) (Given E°eU = – 0.44 V)
Answer:

$Fe(s) + 2H^+(aq) \longrightarrow Fe^{2+}(aq) + H_2(g)$ Net cell reaction

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

At cathode: $2H^+(aq) + 2e^- \longrightarrow H_2(g)$ $[n = 2]$

$$E_{cell} = [E°_{H^+/H_2} - E°_{Fe^{2+}/Fe}] - \frac{0.0591}{2} \log \frac{[Fe^{2+}]}{[H^+]^2}$$

$$= [0 - (-0.44)] - \frac{0.0591}{2} \log \frac{0.001}{(1)^2}$$

$$= +0.44 \text{ V} + \frac{0.1773}{2}$$

$$= 0.44 \text{ V} + 0.0886\text{V} = 0.5286 \text{ V}$$

33. Calculate the emf of the following cell at 25 °C:
Ag(s) I Ag^+ (10^{-3} M) II Cu^{2+} (10^{-1} M) I Cu(s)
Given: $E°_{cell}$ = + 0.46 V and log 10^n = n.
Answer:

33. Calculate the emf of the following cell at 25 °C:
$Ag(s) | Ag^+ (10^{-3} M) || Cu^{2+} (10^{-1} M) | Cu(s)$
Given: $E^\circ_{cell} = + 0.46$ V and $\log 10^n = n$.
Answer:

$$2Ag(s) \longrightarrow 2Ag^+(aq) + 2e^- \quad \text{At anode}$$
$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s) \quad \text{At cathode}$$
$$2Ag(s) + Cu^{2+}(aq) \longrightarrow 2Ag^+(aq) + Cu(s)$$

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

$$E^\circ_{cell} = E^\circ_{Cu^{2+}/Cu} - E^\circ_{Ag^+/Ag} = 0.34\ V - 0.80\ V = -0.46\ V$$

$$= E^\circ_{cell} - \frac{0.0591}{2} \log \frac{[10^{-3}]^2}{[10^{-1}]^2}$$

$$= -0.46\ V - \frac{0.0591}{2} \log \frac{10^{-6}}{10^{-1}}$$

$$= -0.46\ V - \frac{0.0591}{2} \times (-5) = -0.46\ V + 0.14775\ V = -0.3123\ V$$

[Note: The given cell will not work as E°_{Cell} is –ve, ΔG = +ve]

Long Answer Type Questions [5 Marks]

34. (a) Predict the products of electrolysis in each of the following:
(i) An aqueous solution of $AgNO_3$ with platinum electrode.
(it) An aqueous solution of H_2S0_4 using platinum electrode.
(b) Estimate the minimum potential differences needed to reduce Al_20_3 at 500°C. The gibbs free energy change for the decomposition reaction
$2/3\ Al_2O_3 \longrightarrow 4/3\ Al + O_2$
Answer: Refer Ans. to Q.28.

35. (a) State Kohlrausch's law of independent migration of ions. Mention one application of Kohlrausch's law.
(b) The resistance of a conductivity cell containing 10^{-3} M KC1 solution at 25 °C is 1500 Q. What is the cell constant if conductivity of 10^{-3} M KC1 solution at 25 °C is 1.5×10^{-4} S cm^{-1}?
Answer: Refer Ans. to Q.12 (b).

Refer Ans. to Q.12 (*b*).

(*b*) R = 1500 ohm, $C = 10^{-3}$ M

$$\kappa = \frac{1}{R} \times \frac{l}{A}$$

$$1.5 \times 10^{-4}\ S\ cm^{-1} = \frac{1}{1500} \times \frac{l}{A}$$

$$\Rightarrow \quad \text{cell constant} = \frac{l}{A} =$$
$$1500 \times 1.5 \times 10^{-4}\ cm^{-1} = 2.25 \times 10^{-1}\ cm^{-1}$$

36. Calculate emf and AG° for the following cell at 298 K:
Mg(s) IMg^{2+}(10^{-3}M) II CU^{2+}(10^{-3}M)I CU(S)
Given:$E^0_{mg2+/mg}$ = – 2.36 V and$E^0_{cu2+/cu}$ = +0.34 V, [1 F = 96500 C mol^{-1}]
Answer:

$Mg(s) \longrightarrow Mg^{2+}(aq) + 2e^-$		At anode
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$		At cathode
$Mg(s) + Cu^{2+}(aq) \longrightarrow Mg^{2+}(aq) + Cu(s)$		Net cell reaction

$$E^\circ_{cell} = E^\circ_{SRP\ cathode} - E^\circ_{SRP\ anode} = +0.34\ V - (-2.36\ V) = 2.70\ V$$

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

$$= 2.70\ V - \frac{0.0591}{2}\log\frac{10^{-3}}{10^{-4}}$$

$$= 2.70\ V - 0.0295\log 10 = 2.70 - 0.0295 = 2.6705 = 2.67\ V$$

$$\Delta G^\circ = -nE^\circ F = -2 \times 2.67\ V \times 96500\ C$$

$$= -515310\ J = -515.310\ kJ\ mol^{-1}$$

2012

Short Answer Type Questions [I] [2 Marks]

37. What type of a battery is lead storage battery? Write the anode and cathode reactions and the overall cell reaction occurring in the operation of a lead storage battery.
Answer: Lead storage battery. It is a secondary cell. It consists of a lead anode and a grid of lead packed with lead dioxide as cathode. A solution of sulphuric acid (38% by mass) is used as an electrolyte.
The cell reactions when the battery is in use are given below:
Anode: Pb(s) + SO^{-2} (aq) ———> PbS04(s) + e^{-2}

Cathode: Pb02 (s) + $S04^{-2}$(aq) + $4H^+$(aq) + 2 e^- ——> PbS04 (s) + $2H_20$ (/)
The overall cell reaction consisting of cathode and anode reactions is:
Pb(s) + $Pb0_2$(s) + $2H_2SO_4$(aq) ——> $2PbS0_4$(s) + $2H_20$(/)
On recharging the battery, the reaction is reversed.

38. Zinc rod is dipped in 0.1 M solution of ZnS04. The salt is 95% dissociated at this dilution at 298 K. Calculate the electrode potential. Given $E^0_{zn2+/zn}$ = – 0.76 V.
Answer:

$$[Zn^{2+}] = 0.1 \times \frac{95}{100} = 0.095\ M$$

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

$$E_{Zn^{2+}/Zn} = E^\circ_{Zn^{2+}/Zn} - \frac{0.0591}{2}\log\frac{1}{[Zn^{2+}]}$$

$$= -0.76\ V - \frac{0.0591}{2}\log\frac{1}{0.095}$$

$$= -0.76\ V - \frac{0.0591}{2}[\log 1000 - \log 95]$$

$$= -0.76\ V - \frac{0.0591\ V}{2}[3.000 - 1.9777]$$

$$= -0.76\ V - \frac{0.0591\ V}{2} \times 1.0223$$

$$= -0.76\ V - \frac{0.0604}{2}\ V = -0.76\ V - 0.0302\ V = -0.7902\ V$$

39. Express the relation among the cell constant, the resistance of the solution in the cell and the conductivity of the solution. How is molar conductivity of a solution related to its conductivity?
Answer:

$\kappa = \frac{1}{R} \times \frac{l}{A}$, where κ is the conductivity of solution, R is resistance, $\frac{l}{A}$ is cell constant. 'l' is distance between electrodes, a is area of cross-section.

$\Lambda_m = \frac{1000\,\kappa}{M}$ where 'κ' is conductivity in S cm^{-1} and M is the molarity of solution.

Λ_m is molar conductivity in S cm^2 mol^{-1}.

40. The molar conductivity of a 1.5 M solution of an electrolyte is found to be 138.9 S $cm^2 mol^{-1}$. Calculate the conductivity of the solution.
Answer:

$$\Lambda_m = \frac{1000 \times \kappa}{M}$$

$$138.9\ S\ cm^2\ mol^{-1} = \frac{1000 \times \kappa}{1.5}$$

$$\Rightarrow \quad \kappa = \frac{138.9 \times 1.5}{1000} = \frac{208.35}{1000} = 2.0835 \times 10^{-1}\ S\ cm^{-1}.$$

Short Answer Type Questions [II] [3 Marks]

41. A voltaic cell is set up at 25 °C with the following halfcells:
Al/Al^{3+}(0.001 M) and Ni/Ni^{2+}(0.50 M)

Write an equation for the reaction that occurs when the cell generates an electric current and determine the cell potential.
[$E^0_{Ni2+/Ni}$= -0.25 V and$E^0_{al3+/al}$ = – 1.66 V]
Answer:

$Al(s)\ |\ Al^{3+}\ (0.001\ M)\ ||\ Ni^{2+}\ (0.50\ M)\ |\ Ni(s)$

$$[Al(s) \longrightarrow Al^{3+}(aq) + 3e^-] \times 2 \qquad \text{At anode}$$

$$[Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)] \times 3 \qquad \text{At cathode}$$

$$2Al(s) + 3Ni^{2+}(aq) \longrightarrow 2Al^{3+}(aq) + 3Ni(s) \qquad \text{Net cell reaction}$$

$n = 6$

$$E_{cell} = (E^\circ_{Ni^{2+}/Ni} - E^\circ_{Al^{3+}/Al}) - \frac{0.0591}{6} \log \frac{[Al^{3+}]^2}{[Ni^{2+}]^3}$$

$$= [-0.25\ V - (-1.66\ V)] - \frac{0.0591}{6} \log \frac{(10^{-3})^2}{(0.50)^3}$$

$$= 1.41\ V - \frac{0.0591}{6} \log \frac{8 \times 10^{-6}}{1}$$

$$= 1.41\ V - \frac{0.0591}{6} [\log 8 + \log 10^{-6}]$$

$$= 1.41\ V - \frac{0.0591}{6} [0.9031 - 6.0000]$$

$$= 1.41\ V - \frac{0.0591}{6} \times -5.0969$$

$$= 1.41\ V + \frac{0.3012}{6}$$

$$= 1.41\ V + 0.0502\ V = 1.4602\ V = 1.46\ V$$

42. The electrical resistance of a column of 0.05 mol L^{-1} NaOH solution of diameter 1 cm and length 50 cm is 5.55×10^3 ohm. Calculate its resistivity, conductivity and molar conductivity.

Answer:

$$A = \pi r^2 = 3.14 \times (0.5)^2 \text{ cm}^2 = 0.785 \text{ cm}^2$$

$$\rho \text{ (resistivity)} = \frac{R \times A}{l} = \frac{5.55 \times 10^3 \, \Omega \times 0.785 \text{ cm}^2}{50 \text{ cm}} = 87.135 \, \Omega \text{ cm.}$$

$$\kappa = \frac{1}{\rho} = \frac{1}{87.135 \, \Omega \text{ cm}} = 0.01148 \text{ S cm}^{-1}$$

$$\Lambda_m = \frac{\kappa \times 1000}{M} = \frac{0.01148 \times 1000}{0.05 \text{ M}} = 229.6 \text{ S cm}^2 \text{ mol}^{-1}$$

43. A strip of nickel metal is placed in a 1 molar solution of $Ni(NO_3)_2$ and a strip of silver metal is placed in a 1-molar solution of $AgNO_3$. An electrochemical cell is created when the two solutions are connected by a salt bridge and the two strips are connected by wires to a voltmeter.

(I) Write the balanced equation for the overall reaction occurring in the cell and calculate the cell potential.

(ii) Calculate the cell potential, E, at 25 °C for the cell if the initial concentration of $Ni(NO_3)_2$ is 0.100 molar and the initial concentration of $AgNO_3$ is 1.00 molar.

[$E^0_{Ni2+/Ni}$= -0.25 V; $E^0_{ag3+/ag}$ = 0.80 V; log 10^{-1} = -1]

Answer:

(i)

$$Ni(s) \longrightarrow Ni^{2+}(aq) + 2e^-$$

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

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

$$E^\circ_{cell} = E^\circ_{(cathode)} - E^\circ_{(anode)} = +0.80 \text{ V} - (-0.25 \text{ V}) = 1.05 \text{ V}$$

(ii)

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

$$= E^\circ_{cell} - \frac{0.0591}{2} \log \frac{0.1}{(1)^2}$$

$$= 1.05 \text{ V} - \frac{0.0591}{2} \log 10^{-1}$$

$$= 1.05\text{V} - \frac{0.0591}{2} \times -1$$

$$= 1.05\text{V} + \frac{0.0591}{2}$$

$$= 1.05 \text{ V} + 0.0295 = 1.0795\text{V}$$

44. When a certain electrolytic cell was filled with 0.1 M KC1, it has resistance of 85 ohms at 25 °C. When the same cell was filled with an aqueous solution of 0.052 M unknown electrolyte, the resistance was 96 ohms. Calculate the molar conductance of the electrolyte at this concentration.

[Specific conductance of 0.1 M KC1 = 1.29×10^{-2} ohm^{-1}cm^{-1}]

Answer:

$$\kappa = 1.29 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$\kappa = \frac{1}{R} \times \frac{1}{A} \Rightarrow \frac{l}{A} = \kappa \times R = 1.29 \times 10^{-2} \times 85$$

$$= 109.65 \times 10^{-2} = 1.0965 \text{ cm}^{-1}$$

$$\Lambda_m = \frac{1000 \, \kappa}{M} = \frac{1000}{M} \times \frac{1}{R} \times \frac{l}{A}$$

$$\Rightarrow \Lambda_m = \frac{1000 \times 1 \times 1.0965}{0.052 \times 96} = \frac{1096.50}{4.992} = 219.65 \text{ S cm}^2 \text{ mol}^{-1}$$

44. When a certain electrolytic cell was filled with 0.1 M KC1, it has resistance of 85 ohms at 25 °C. When the same cell was filled with an aqueous solution of 0.052 M unknown electrolyte, the resistance was 96 ohms. Calculate the molar conductance of the electrolyte at this concentration.
[Specific conductance of 0.1 M KC1 = $1.29 \times 10^{-2} ohm^{-1}cm^{-1}$]
Answer:

$\kappa = 1.29 \times 10^{-2}\ ohm^{-1}\ cm^{-1}$

$$\kappa = \frac{1}{R} \times \frac{1}{A} \Rightarrow \frac{l}{A} = \kappa \times R = 1.29 \times 10^{-2} \times 85$$

$$= 109.65 \times 10^{-2} = 1.0965\ cm^{-1}$$

$$\Lambda_m = \frac{1000\,\kappa}{M} = \frac{1000}{M} \times \frac{1}{R} \times \frac{l}{A}$$

$$\Rightarrow \quad \Lambda_m = \frac{1000 \times 1 \times 1.0965}{0.052 \times 96} = \frac{1096.50}{4.992} = 219.65\ S\ cm^2\ mol^{-1}$$

Long Answer Type Questions [5 Marks]

45. (a) What type of battery is the lead storage battery? Write the anode and the cathode reactions and the overall reaction occuring in a lead storage battery when current is drawn from it.
(b) In the button cell, widely used in watches, the following reaction takes place:
$Zn(s) + Ag_20(s) + H_20\ (l)$ ——> $Zn^{2+}(aq) + 2Ag(s) + 20H^-\ (aq)$
Determine E° and AG° for the reaction.
(Given: $E^0_{ag+/ag}$= + 0.80 V, $E^0_{zn+2/zn}$ = – 0.76 V)
Answer:

(*a*) **Lead storage battery:** It is a secondary cell. It consists of a lead anode and a grid of lead packed with lead dioxide as cathode. A solution of sulphuric acid (38% by mass) is used as an electrolyte.

The cell reactions when the battery is in use are given below:

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

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

The overall cell reaction consisting of cathode and anode reactions is:

$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l)$

On recharging the battery, the reaction is reversed.

(*b*)

$$Zn\ (s) \longrightarrow Zn^{2+}(aq) + 2e^-$$

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

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

$$E^\circ_{cell} = \left(E^\circ_{SRP\ cathode} - E^\circ_{SRP\ anode}\right)$$

$$= +0.80\,V - (-0.76\,V) = +1.56\,V$$

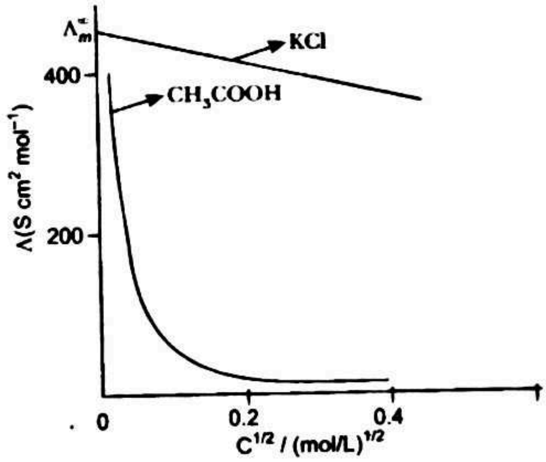
$$\Delta_r G^\circ = -n\ E^\circ F$$

$$\Delta_r G^\circ = -2 \times 1.56\,V \times 96500 = -301080\ J\ mol^{-1}$$

$$= -301.080\ kJ\ mol^{-1}$$

46. (a) Define molar conductivity of a substance and describe how for weak and strong electrolytes, molar conductivity changes with concentration of solute. How is such change explained?
(b) A voltaic cell is set up at 25 °C with the following half-cells:
Ag^+ (0.001 M) I Ag and Cu^{+2} (0.10 M) I Cu What would be the voltage of this cell?
(E^0_{cell}= O.4V)
Answer: (a) Molar Conductivity. It is defined as the conducting power of all the ions produced by one molar solution of an electrolyte. It is denoted by A .(or) It is defined as the conductivity of 1 M electrolytic solution placed between two electrodes 1 cm apart and have enough area of cross section to hold the entire volume.

Variation of molar conductivity with concentration.



Molar conductivity versus $C^{1/2}$ for acetic acid (weak electrolyte) and potassium chloride (strong electrolyte) in aqueous solutions

Molar conductivity increases with decrease in concentration.
This is because both number of ions as well as mobility of ions increase with dilution.
In the case of strong electrolyte, the number of ions does not increase appreciably, only the mobility of ions increases, therefore, Am increases a little as shown in graph as straight line.
In case of weak electrolyte both number of ions and mobility of ions increases, therefore, Affl increases sharply as shown by curve in the figure.

(*b*)

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

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

$$\Rightarrow E_{cell} = 0.46 - \frac{0.0591}{2} \log \frac{0.10}{(0.001)^2}$$

$$= 0.46 - \frac{0.0591}{2} \log (10^5)$$
$$= 0.46 - \frac{0.0591}{2} \times 5$$
$$= 0.46 - \frac{0.2955}{2}$$
$$= 0.46 - 0.1477 = 0.3123 \text{ V.}$$

47. (a) How many moles of mercury will be produced by electrolysing 1.0 M $Hg(NO_3)_2$ solution with a current of 2.00 A for 3 hours?

[$Hg(N0_3)_2$ = 200.6 g mol-1]
(b) A voltaic cell is set up at 25 °C with the following half-cells:
Al^{2+}(0.001 M) and Ni^{2+}(0.50 M)
Write an equation for the reaction that occurs when the cell generates an electric current and determine the cell potential.
(Given;$E_{Ni2+/Ni}$= – 0.25 V, $E_{al3+/al}$= – 1.66 V)
Answer:

(*a*)

$$m = Z \times I \times t$$

$$\Rightarrow m = \frac{200.6 \times 2 \times 3 \times 60 \times 60}{2 \times 96500}$$

$$\Rightarrow m = \frac{43329.6}{1930} = 22.45 \text{ g}$$

$$\text{Number of moles} = \frac{22.45}{200.6} = 0.112 \text{ mole}$$

(*b*)

$$[Al(s) \longrightarrow Al^{3+}(aq) + 3e^-] \times 2$$

$$[Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)] \times 3$$

$$2Al(s) + 3Ni^{2+}(aq) \longrightarrow 2Al^{3+}(aq) + 3Ni(s)$$

Here $n = 6$

$$E_{cell} = (E^\circ_{Ni^{2+}/Ni} - E^\circ_{Al^{3+}/Al}) - \frac{0.0591}{6} \log \frac{[Al^{3+}]^2}{[Ni^{2+}]^3}$$

$$= [-0.25\ V - (-1.66\ V)] - \frac{0.0591}{6} \log \frac{[10^{-3}]^2}{[0.50]^3}$$

$$= 1.41\ V - \frac{0.0591}{6} \log \frac{8 \times 10^{-6}}{1}$$

$$= 1.41\ V - \frac{0.0591}{6} [\log 8 + \log 10^{-6}]$$

$$= 1.41\ V - \frac{0.0591}{6} [0.9031 - 6.0000]$$

$$= 1.41\ V - \frac{0.0591}{6} \times -5.0969$$

$$= 1.41\ V + \frac{0.3012}{6}$$

$$= 1.41\ V + 0.0502\ V$$

$$= 1.4602\ V = 1.46\ V.$$

2011

Very Short Answer Type Questions [1 Mark]

48. Express the relation between conductivity and molar conductivity of a solution held in a cell.
Answer: Λ_m = 1000k/M , where m is molar conductivity, K is conductivity and M is molarity or concentration in mol L^{-1}.

49. Express the relation among the conductivity of solution in the cell, the cell constant and the resistance cf solution in the cell.

Answer: K =1 /R*l/A , where K is conductivity, R is resistance and l/A is cell constant.

Short Answer Type Questions [I] [2 Marks]

50. Express the relation among the cell constant, the resistance of the solution in the cell and the conductivity of the solution. How is molar conductivity of a solution related to its conductivity?
Answer: Refer Ans. to Q.39.

51. Determine the values of equilibrium constant (Kc) and AG° for the following reaction:
$Ni(s) + 2Ag^+(aq) \longrightarrow Ni^{+2}(aq) + 2Ag(s)$,
E° = 1.05 V (IF = 96500 C mol^{-1})
Answer:

$$n = 2$$

$$\Delta G^\circ = -nE^\circ F$$

$$= -2 \times 1.05\ V \times 96500\ C = -202.65\ kJ\ mol^{-1}$$

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

$$-nE^\circ F = -2.303\ RT \log K_C$$

$$\Rightarrow \quad \log K_C = \frac{nE^\circ}{0.0591} = \frac{2 \times 1.05}{0.0591} = \frac{2.10}{0.0591} = 35.5329$$

$\Rightarrow \quad K_c = \text{Antilog of } 35.5329$

$\Rightarrow \quad K_c = 3.411 \times 10^{35}$

52. The chemistry of corrosion of iron is essentially an electrochemical phenomenon. Explain the reactions occurring during the corrosion of iron in the atmosphere.

Answer:

$$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^- \quad \text{oxidation}$$

$$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l) \quad \text{reduction}$$

$$2Fe^{2+}(aq) + 2H_2O(l) + \tfrac{1}{2} O_2(g) \longrightarrow Fe_2O_3(s) + 4H^+(aq)$$

Atmospheric oxidation

The above reaction takes place at the surface of iron and it acts as an electrochemical cell.

53. Two half-reactions of an electrochemical cell are given below:
$MnO4^-(aq) + 8H^+(aq) + 5e^- > Mn^{2+}(aq) + 4H_20(l)$, E° = + 1.51 V
$Sn^{2+}(aq)$ ——> $Sn^{4+}(aq) + 2e^-$, E° = + 0.15 V
Construct the redox equation from the standard potential of the cell and predict the reaction is reactant favoured or product favoured.
Answer:

$Pt|Sn^{2+}(aq)|Sn^{4+}(aq)||MnO_4^-(aq) \mid Mn^{2+}(aq)|Pt$;

$$E^\circ_{cell} = E^\circ_{MnO_4^-/Mn^{2+}} - E^\circ_{Sn^{4+}/Sn^{2+}}$$
$$= 1.51 - (-0.15\ V) = 1.66\ V$$

Since E°_{cell} is +ve, ΔG will be –ve, therefore, the reaction is product favoured.

54. the reactions occurring at (i) anode, (ii) cathode, during working of a mercury cell. Why does the voltage of a mercury cell remain constant during its operation?
Answer: Mercury cell. It consists of zinc mercury amalgam as anode, a paste of HgO and carbon as cathode. The electrolyte is a paste of KOH and ZnO. The reaction of the cell is *
At anode: Zn (amalgam) + $20H^-$ ———> ZnO(s) + H20 + $2e^-$

At cathode: HgO(s) + H_20 + 2 e^{-2}———> Hg(Z) + $20H^-$

The net reaction: Zn (amalgam) + HgO(s) ———> ZnO(s) + Hg(l)
It gives constancy in voltage over long period because no ions are involved in net cell reaction. It is used in watches and hearing aids.

55. Define and express the relation between conductivity and molar conductivity for the solution of an electrolyte.
Answer: Conductivity is defined as ease with which current flows through an electrolyte. It is the reciprocal of resistance.
Molar conductivity is the conductance of all the ions produced by 1 mole of electrolyte when electrodes are unit distance apart and have sufficient area of cross section to hold electrolyte.
AM =1000K /M
where K is conductivity, M is molarity and Am is molar conductivity.