NCERT SOLUTIONS

CLASS - 12th



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Class : 12th
Subject : Chemistry
Chapter : 3
Chapter Name : Electrochemistry

Q3.1 How would you determine the standard electrode potential of the system $Mg^{2+}|Mg$?

Answer. The standard electrode potential Of $Mg^{2+}|Mg$ can be measured with respect to the standard hydrogen electrode, represented by $Pt_{(s)}, H_{2(g)}(1atm)\left|H^{+}_{(aq)}(1M)\right.$. A cell, consisting of Mg I $MgSO_4$(aq 1M) as the anode and the standard hydrogen electrode as the cathode, is set up.

$$Mg\left|Mg^{2+}(aq, 1M)\right\|H^{+}(aq, 1M)\left|H_2(g, 1\ bar), Pt_{(s)}\right.$$

Then, the emf of the cell is measured and this measured emf is the standard electrode potential of the magnesium electrode.

$E^{\ominus} = E^{\ominus}_R - E^{\ominus}_l$

Here, E°_R for the standard hydrogen electrode is zero.

$\therefore E^{\theta} = 0 - E^{\circ}_L$

$= -E^{\circ}_l$

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Q3.2 Can you store copper sulphate solutions in a zinc pot?

Answer. Zinc is more reactive than copper. Therefore, zinc can displace copper from its salt solution. If copper sulphate solution is stored in a zinc pot, then zinc Will displace copper from the copper sulphate solution.

$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$

Hence, copper sulphate solution cannot be stored in a zinc pot.

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Q3.3 Consult the table of standard electrode potentials and suggest three substances that can oxidise ferrous ions under suitable conditions.

Answer. Substances that are stronger oxidising agents than ferrous ions can oxidise ferrous ions.

$Fe^{2*} \longrightarrow Fe^{3+} + e^{-1}; E^2 = -0.77V$

This implies that the substances having higher reduction potentials than +0.77 V can oxidise ferozus ions to ferric ions. Three substances that can do so are F_2, Cl_2, and O_2.

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Q3.4 Calculate the potential of hydrogen electrode in contact with a solution whose pH is 10.

Answer.

For hydrogen electrode, $H^{+} + e^{-} \longrightarrow \frac{1}{2} H_2$, it is given that pH = 10

$\therefore [H^+] = 10^{-10}$ M

Now, using Nernst equation:

$$H_{\left(H^{+}/\frac{1}{2}H_2\right)} = E^{\ominus}_{\left(H^{+}/\frac{1}{2}H_2\right)} - \frac{RT}{nF} \ln \frac{1}{[H^+]}$$

$$= E^{\ominus}_{\left(H^{+}/\frac{1}{2}H_2\right)} - \frac{0.0591}{1} \log \frac{1}{[H^+]}$$

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

$= -0.0591 \log 10^{10}$

$= -0.591$ V

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Q3.5 Calculate the emf of the cell in which the following reaction takes place:

$\mathrm{Ni(s)} + 2\mathrm{Ag}^{+}(0.002\mathrm{M}) \rightarrow \mathrm{Ni}^{2+}(0.160\mathrm{M}) + 2\mathrm{Ag(s)}$
Given that $\mathrm{E}^{\ominus}_{(\text{cell})} = 1.05\mathrm{V}$

Answer. $Applying Nernst equation we have$:

$E_{(\text{ cell })} = E^{\circ}_{(\text{cell })} - \frac{0.0591}{n} \log \frac{\left[\mathrm{Ni}^{2+}\right]}{\left[\mathrm{Ag}^{+}\right]^{2}}$

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

$= 1.05 - 0.02955 \log \frac{0.16}{0.000004}$

$= 1.05 - 0.02955 \log 4 \times 10^{4}$

$= 1.05 - 0.02955 (\log 10000 + \log 4)$

$= 1.05 - 0.02955 (4 + 0.6021)$

$= 0.914\mathrm{V}$

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Q3.6 The cell in which the following reaction occurs:
$2\mathrm{Fe}^{3t}(\mathrm{aq}) + 2\mathrm{I}^{-}(\mathrm{aq}) \rightarrow 2\mathrm{Fe}^{2*}(\mathrm{aq}) + \mathrm{I}_{2}(\mathrm{s})$ has $E^{0}_{\text{cell}} = 0.236\mathrm{V}$ at 298 K. Calculate the standard Gibbs energy and the equilibrium constant of the cell reaction.

Answer. Here, n =2 $E^{\circ}_{\text{cell}} = 0.236\mathrm{V}, \mathrm{T} = 298\mathrm{K}$
We know that
$\Delta, \mathrm{G}^{\circ} = -n\mathrm{FE}^{\circ}_{\text{cell}}$
$= -2 \times 96487 \times 0.236$
$= -45541.8643\mathrm{mol}^{-1}$
$= -45.54\mathrm{k}\}\mathrm{mol}^{-1}$
$\Delta, G^{\circ} = -2.303\mathrm{R}T \log K_{\mathrm{c}}$
$\Rightarrow \log K_{\mathrm{e}} = -\frac{\Delta, G^{\circ}}{2.303\mathrm{RT}}$
$= -\frac{-45.54 \times 10^{3}}{2.303 \times 8.314 \times 298} = 7.981$
$\therefore K_{\mathrm{c}} = \text{ Antilog } (7.981)$
$= 9.57 \times 10^{7}$

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Q3.7 Why does the conductivity of a solution decrease with dilution?

Answer. The conductivity Of a solution iS the conductance Of ions present in a unit volume Of the solution. The number Of ions (responsible for carrying current) decreases when the solution is diluted. As a result, the conductivity of a solution decreases with dilution.

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Q3.8 Suggest a way to determine the Λ° m value of water.

Answer. Applying Kohlrausch's law of independent migration of ions, the λ^{0}_{m} be determined as follows:

$\Lambda^{0}_{m(\mathrm{H_2O})} = \lambda^{0}_{\mathrm{H}^{+}} + \lambda^{0}_{\mathrm{OH}^{-}}$

$= \left(\lambda^{0}_{\mathrm{H}^{+}} + \lambda^{0}_{\mathrm{Cl}^{-}}\right) + \left(\lambda^{0}_{\mathrm{Na}^{+}} + \lambda^{0}_{\mathrm{OH}^{-}}\right) - \left(\lambda^{0}_{\mathrm{Na}^{+}} + \lambda^{0}_{\mathrm{Cl}^{-}}\right)$

$\Lambda^{0}_{m(\mathrm{HCl})} + \Lambda^{0}_{m(\mathrm{NaOH})} - \Lambda^{0}_{m(\mathrm{NaCl})}$

Hence, by knowing the Λ^{0}_{m} values of HCl, NaOH, and NaCl, the Λ^{0}_{m} value of water can be determined.

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Q3.9 The molar conductivity of 0.025 mol L^{-1} methanoic acid is 46.1 S $\mathrm{cm}^{2}\mathrm{mol}^{-1}$. Calculate its degree of dissociation and dissociation constant. Given $\lambda^{0}\left(\mathrm{H}^{+}\right)$
$= 349.6\mathrm{Scm}^{2}\mathrm{mol}^{-1}$ and $\lambda^{0}(\mathrm{HCOO}) = 54.6\mathrm{Scm}^{2}\mathrm{mol}^{-1}$

Answer.
$C = 0.025\mathrm{mol}L^{-1}$
$\Lambda_{m} = 46.1\mathrm{Scm}^{2}\mathrm{mol}^{-1}$

$\lambda^0\left(\mathrm{H}^{+}\right)=349.6 \mathrm{Scm}^2 \mathrm{mol}^{-1}$
$\lambda^0\left(\mathrm{HCOO}^{-}\right)=54.6 \mathrm{Scm}^2 \mathrm{mol}^{-1}$
$\begin{aligned}\Lambda_m^0(\mathrm{HCOOH}) & =\lambda^{\circ}\left(\mathrm{H}^{+}\right)+\lambda^0\left(\mathrm{HCOO}^{-}\right) \\ & =349.6+54.6 \\ & =404.2 \mathrm{Scm}^2 \mathrm{mol}^{-1}\end{aligned}$
Now, degree Of dissociation:
$\begin{aligned}\alpha & =\frac{\Lambda_{=}(\mathrm{HCOOH})}{\Lambda_m^{\circ}(\mathrm{HCOOH})} \\ & =\frac{46.1}{404.2} \\ & =0.114(\text { approximately })\end{aligned}$
Thus, dissociation constant:
$\begin{aligned}K & =\frac{c \propto^2}{(1-\alpha)} \\ & =\frac{\left(0.025 \mathrm{molL}^{-1}\right)(0.114)^2}{(1-0.114)} \\ & =3.67 \times 10^{-4} \mathrm{molL}^{-1}\end{aligned}$

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Q3.10 If a current of 0.5 ampere flows through a metallic wire for 2 hours, then how many electrons would flow through the wire?

Answer.
$I=0.5 \mathrm{A}$
$t=2 \text { hours } =2 \times 60 \times 60 \mathrm{s}=7200 \mathrm{s}$
$\text { Thus, } Q=I t$
$=0.5 \mathrm{A} \times 7200 \mathrm{s}$
$=3600 \mathrm{C}$

$\text { We know that } 96487 \mathrm{C}=6.023 \times 10^{23} \text { , number of electrons. Then, } 3600 \mathrm{C}=\frac{6.023 \times 10^{23} \times 3600}{96487} \text { number of electrons } =2.25 \times 10^{22} \text { nun}$

Hence, 2.25×10^{22}number of electrons will flow through the wire.

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Q3.11 Suggest a list of metals that are extracted electrolytically.

Answer. Metals that are on the top of the reactivity senes such as sodium, potassium, calcium, lithium, magnesium, aluminium are extracted electrolyticallv.

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Q3.12 Consider the reaction: $\mathrm{Cr}_2 \mathrm{O}_7^{2-}+14 \mathrm{H}^{+}+6 \mathrm{e}^{-} \rightarrow 2 \mathrm{Cr}^{3+}+7 \mathrm{H}_2 \mathrm{O}$ What is the quantity of electricity in coulombs needed to reduce 1 mol of $\mathrm{Cr}_2 \mathrm{O}_7^{2-}$?

Answer.
$\text { The given reaction is as follows: }$
$\mathrm{Cr}_2 \mathrm{O}^2+14 \mathrm{H}^{+}+6 \mathrm{e}^{-} \rightarrow 2 \mathrm{Cr}^{3+}+7 \mathrm{H}_2 \mathrm{O}$
$\text { Therefore, to reduce 1 mole of } \mathrm{Cr}_2 \mathrm{O}_7^{2-}, \text { the required quantity of electricity will be: }$
$=6 \mathrm{F}$
$=6 \times 96487 \mathrm{C}$
$=578922 \mathrm{C}$

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Q3.13 Write the chemistry of recharging the lead storage battery, highlighting all the materials that are involved during recharging.

Answer.
$\text { A lead storage battery consists of a lead anode, a grid of lead packed with }$
$\text { lead oxide } \left(\mathrm{PbO}_2\right) \text { as the cathode, and a } 38 \% \text { solution of sulphuric acid }$
$\left(H_2 S O_4\right) \text { as an electrolyte. }$

When the battery is in use, the following cell reactions take place:
At anode: $Pb_{(s)} + SO^{2-}4(aq) \rightarrow PbSO_{4(s)} + 2e^-$
At cathode:$\mathrm{PbO_{2(s)} + SO^{2-}_{4(aq)} + 4H^+_{(aq)} + 2e^- \longrightarrow PbSO_{4(s)} + 2H_2O_{(i)}}$
The overall cell reaction is given by,
$\mathrm{Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(aq)} \longrightarrow 2PbSO_{4(s)} + 2H_2O_{(l)}}$
When a battery is charged, the reverse of all these reactions takes place.
Hence, on charging, present at the anode and cathode is converted into and respectively.

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Q3.14 Suggest two materials other than hydrogen that can be used as fuels in fuel cells.

Answer. Methane and methanol can be used as fuels in fuel cells.

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Q3.15 Explain how rusting of iron is envisaged as setting up of an electrochemical cell.

Answer. In the process of corrosion, due to the presence of air and moisture, oxidation takes place at a particular spot of an object made of iron. That spot behaves as the anode. The reaction at the anode is given by,
$\mathrm{Fe_{(,)} \longrightarrow Fe^{2+}_{(aq)} + 2e^-}$
Electrons released at the anodic spot move through the metallic object and go to another
spot of the object. There, in the presence of H^+ ions, the electrons reduce oxygen. This spot behaves as the cathode. These H^+ions come either from $\mathrm{H_2CO_3}$ which are formed due to the dissolution of carbon dioxide from air into water or from the dissolution of other acidic oxides from the atmosphere in water.
The reaction corresponding at the cathode is given by,
$\mathrm{O_{2(g)} + 4H^+_{(aq)} + 4e^- \longrightarrow 2H_2O_{(j)}}$
The overall reaction is:
$\mathrm{2Fe_{(s)} + O_{2(g)} + 4H^+_{(aq)} \longrightarrow 2Fe^{2+}_{(\alpha)} + 2H_2O_{(i)}}$
Also, ferrous ions are further oxidized bv atmospheric oxygen to ferric ions. These ferric ions combine With moisture, present in the surroundings, to forrn hydrated ferric oxide
$\mathrm{(Fe_2O_3, xH_2O)_{\text{i.e., rust.}}}$
Hence, the rusting of iron is envisaged as the setting up of an electrochemical cell.

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Q3.1 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.

Answer. The following is the order in which the given metals displace each other from the solution of theil salts.
Mg, Al, Zn, Fe, Cu

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Q3.2 Given the standard electrode potentials,
$\mathrm{K^+/K = -2.93V, Ag^+/Ag = 0.80V}$
$\mathrm{Hg^{2+}/Hg = 0.79V}$
$\mathrm{Mg^{2+}/Mg = -2.37V. Cr^{3+}/Cr = -0.74V}$
Arrange these metals in their increasing order of reducing power.

Answer. The lower the reduction potential, the higher is the reducing power. The given standard electrode potentials increase in the order of
$\mathrm{K^+/K < Mg^{2+}/Mg < Cr^{3+}/Cr < Hg^{2+}/Hg < Ag^+/Ag}$
Hence, the reducing power of the given metals increases in the following order:
$\mathrm{Ag < Hg < Cr < Mg < K}$

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Q3.3 Depict the galvanic cell in which the reaction
$\mathrm{Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)}$takes place. Further show:
(i) Which of the electrode is negatively charged?
(ii) The carriers of the current in the cell.
(iii) Individual reaction at each electrode.

Answer. The galvanic cell in which the given reaction takes place is depicted as:
$\mathrm{Zn_{(s)} \left| Zn^{2+}_{(aq)} \right\| Ag^+_{(aq)} \left| Ag_{(s)} \right.}$

(i) Zn electrode (anode) is negatively charged.
(ii) Ions are carriers Of current in the cell and in the external circuit, current Will flow from silver to Zinc.
(iii) The reaction taking place at the anode is given by,
$\mathrm{Zn}_{(s)} \longrightarrow \mathrm{Zn}^{2+}_{(aq)} + 2\mathrm{c}^{-}$
The reaction taking place at the cathode is given by,
$\mathrm{Ag}^{+}_{(aq)} + \mathrm{e}^{-} \longrightarrow \mathrm{Ag}_{(s)}$

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Q3.4 Calculate the standard cell potentials of galvanic cell in which the following reactions take place:
(i) $2\mathrm{Cr(s)} + 3\mathrm{Cd}^{2+}\mathrm{(aq)} \rightarrow 2\mathrm{Cr}^{3+}\mathrm{(aq)} + 3\mathrm{Cd}$
(ii) $\mathrm{Fe}^{2+}\mathrm{(aq)} + \mathrm{Ag}^{*}\mathrm{(aq)} \rightarrow \mathrm{Fe}^{3+}\mathrm{(aq)} + \mathrm{Ag(s)}$
Calculate the $\Delta_r G^{\theta}$ and equilibrium constant of the reactions.

Answer.

(i) $E^{\circ}_{Cr^{3+}/Cr} = 0.74\ \mathrm{V}$

$E^{\circ}_{Cd^{2+}/Cd} = -0.40\ \mathrm{V}$

The galvanic cell of the given reaction is depicted as:

$\mathrm{Cr}_{(s)}\left|\mathrm{Cr}^{3+}_{(aq)}\right\|\mathrm{Cd}^{2+}_{(aq)}\left|\mathrm{Cd}_{(s)}\right.$

Now, the standard cell potential is

$E^{\circ}_{cell} = E^{\circ}_{R} - E^{\circ}_{L}$
$= -0.40 - (-0.74)$
$= +0.34\ \mathrm{V}$

$\Delta_r G^{\circ} = -nFE^{\circ}_{cell}$

In the given equation,

$n = 6$

$F = 96487\ \mathrm{C\ mol^{-1}}$

$E^{\circ}_{cell} = +0.34\ \mathrm{V}$

Then, $\Delta_r G^{\circ} = -6 \times 96487\ \mathrm{C\ mol^{-1}} \times 0.34\ \mathrm{V}$
$= -196833.48\ \mathrm{CV\ mol^{-1}}$
$= -196833.48\ \mathrm{J\ mol^{-1}}$
$= -196.83\ \mathrm{kJ\ mol^{-1}}$

Again,

$\Delta_r G^{\circ} = -RT \ln K$

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

$\Rightarrow \log K = -\dfrac{\Delta_r G}{2.303\ RT}$

$= \dfrac{-196.83 \times 10^{3}}{2.303 \times 8.314 \times 298}$

$= 34.496$

$\therefore K = \text{antilog } (34.496)$

$= 3.13 \times 10^{34}$

(ii) $E^{\circ}_{Fe^{3+}/Fe^{2+}} = 0.77\ \mathrm{V}$

$E^{\circ}_{Ag^{+}/Ag} = 0.80\ \mathrm{V}$

The galvanic cell of the given reaction is depicted as:

$\mathrm{Fe}^{2+}_{(aq)}\left|\mathrm{Fe}^{3+}_{(aq)}\right\|\mathrm{Ag}^{+}_{(aq)}\left|\mathrm{Ag}_{(s)}\right.$

Now, the standard cell potential is

$E^{\circ}_{cell} = E^{\circ}_{R} - E^{\circ}_{L}$
$= 0.80 - 0.77$
$= 0.03\ \mathrm{V}$

Here, $n = 1$.

Then, $\Delta_r G^{\circ} = -nFE^{\circ}_{cell}$

$= -1 \times 96487\ \mathrm{C\ mol^{-1}} \times 0.03\ \mathrm{V}$

$= -2894.61\ \mathrm{J\ mol^{-1}}$

$= -2.89\ \mathrm{kJ\ mol^{-1}}$

Again, $\Delta_r G^{\circ} = -2.303\ RT \log K$

$\Rightarrow \log K = -\dfrac{\Delta_r G}{2.303\ RT}$

$= \dfrac{-2894.61}{2.303 \times 8.314 \times 298}$

$= 0.5073$

$\therefore K = \text{antilog } (0.5073)$

$= 3.2$ (approximately)

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Q3.5 Write the Nernst equation and emf of the following cells at 298 K:
(i) $\mathrm{Mg(s)}\left|\mathrm{Mg}^{2+}(0.001\mathrm{M})\right\|\mathrm{Cu}^{2+}(0.0001\mathrm{M})\left|\mathrm{Cu(s)}\right.$
(ii) $\mathrm{Fe(s)}\left|\mathrm{Fe}^{2+}(0.001\mathrm{M})\mathrm{llH}^{+}(1\mathrm{M})\right|\mathrm{H}_2\mathrm{(g)(1bar)}\left|\mathrm{Pt(s)}\right.$
(iii) $\mathrm{Sn(s)}\left|\mathrm{sn}^{2+}(0.050\mathrm{M})\right\|\mathrm{H}^{+}(0.020\mathrm{M})\left|\mathrm{H}_2\mathrm{(g)(1\ bar\ )}\right|\mathrm{Pt(s)}$

(iv) $\mathrm{Pt(s)\,|Br_2(l)|\,Br^-(0.010M)\,\|H^+(0.030M)\,|H_2(g)(1bar)|\,Pt(s)}$

Answer. (i) For the given reaction, the Nernst equation can be given as:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n}\log\frac{\left[\mathrm{Mg^{2+}}\right]}{\left[\mathrm{Cu^{2+}}\right]}$$
$$= \{0.34 - (-2.36)\} - \frac{0.0591}{2}\log\frac{.001}{0001}$$
$$= 2.7 - \frac{0.0591}{2}\log 10$$
$$= 2.7 - 0.02955$$
$$= 2.67\mathrm{V}\ \text{(approximately)}$$

(ii) For the given reaction, the Nernst equation can be given as:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n}\log\frac{\left[\mathrm{Fe^{2+}}\right]}{\left[\mathrm{H^+}\right]^2}$$
$$= \{0 - (-0.44)\} - \frac{0.0591}{2}\log\frac{0.001}{1^2}$$
$$= 0.44 - 0.02955(-3)$$
$$= 0.52865\mathrm{V}$$
$$0.53\mathrm{V}\ \text{(approximately)}$$

(iii) For the given reaction, the Nernst equation can be given as:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n}\log\frac{\left[\mathrm{Sn^{2+}}\right]}{\left[\mathrm{H^+}\right]^2}$$
$$= 0.14 - 0.0295 \times \log 125$$
$$= 0.14 - 0.062$$
$$= 0.078\mathrm{V}$$
$$= 0.08\mathrm{V}\ \text{(approximately)}$$

(iv) For the given reaction, the Nernst equation can be given as:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n}\log\frac{1}{\left[\mathrm{Br^-}\right]^2\left[\mathrm{H^+}\right]^2}$$
$$= (0 - 1.09) - \frac{0.0591}{2}\log\frac{1}{(0.010)^2(0.030)^2}$$
$$= -1.09 - 0.02955 \times \log\frac{1}{0.00000099}$$
$$= -1.09 - 0.02955 \times \log\frac{1}{9 \times 10^{-3}}$$
$$= -1.09 - 0.02955 \times \log\left(1.11 \times 10^{7}\right)$$
$$= -1.09 - 0.02955 \times \log\left(1.11 \times 10^{7}\right)$$
$$= -1.09 - 0.208$$
$$= -1.298\mathrm{V}$$

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Q3.6 In the button cells widely used in watches and other devices the following reaction takes place:
$\mathrm{Zn(s) + Ag_2O(s) + H_2O(\mathit{I}) \rightarrow Zn^{2+}(aq) + 2Ag(s) + 2OH^-(aq)}$
Determine Δ, $G^{\ominus}$ and $E^{\ominus}$ for the reaction.

Answer.

$$\mathrm{Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-\ ;\ E^{\circ} = 0.76V}$$
$$\mathrm{Ag_2O_{(s)} + H_2O_{(\mathit{l})} + 2e^- \longrightarrow 2Ag_{(s)} + 2OH^-_{(aq)}\ ;\ E^{\circ} = 0.344\ V}$$
$$\mathrm{Zn_{(s)} + Ag_2O_{(s)} + H_2O_{(\mathit{l})} \longrightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)} + 2OH^-_{(aq)};\ E^{\circ} = 1.104\ V}$$

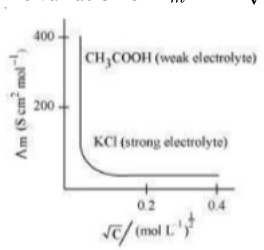
$\therefore E^{\circ} = 1.104\mathrm{V}$
We know that,
$\Delta rG^{\circ} = -n\mathrm{F}E^{e}$
$= -2 \times 96487 \times 1.04$
$= -213043.296\mathrm{J}$
$= -213.04\mathrm{kJ}$

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Q3.7 Define conductivity and molar conductivity for the solution of an electrolyte. Discuss their variation with concentration

Answer. Conductivity of a solution is defined as the conductance of a solution of 1 cm in length and area Of cross-section 1 sq. cm. The inverse Of resistivity is called conductivity or specific conductance. tt is represented by the symbolK. If p is resistivity, then we can write:

$\kappa = \frac{1}{\rho}$
The conductivity of a solution at any given concentration is the conductance (G) of one unit volume of solution kept between two platinum electrodes with the unit area of
cross-section and at a distance of unit length.
I.e., $G = \kappa\frac{a}{l} = \kappa \cdot 1 = K$
Conductivity always decreases With a decrease in concentration, both for weak and
strong electrolytes. This is because the number of ions per unit volume that carry the
current in a solution decreases with a decrease in concentration.
Molar conductivity:
Molar conductivity of a solution at a given concentration is the conductance of volume V of a solution containing t mole Of the electrolyte kept between two electrodes With the
area Of cross-section A and distance Of unit length.
$\Lambda_m = \kappa\frac{A}{l}$
NOW, / and A V (volume containing I mole Of the electrolyte),
$\therefore \Lambda_m = \kappa V$
Molar conductivity increases with a decrease in concentration. This is because the total
volume V of the solution containing one mole of the electrolyte increases on dilution.
The variation of Λ_m with $\sqrt{c}$ for strong and weak electrolytes is shown in the following plot:



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Q3.8 The conductivity of 0.20 M solution of KCl at 298 K is 0.0248 Scm^{-1}. Calculate its molar conductivity

Answer. Given
$\kappa = 0.0248\mathrm{Scm}^{-1}$
$\mathrm{c} = 0.20\mathrm{M}$
$\therefore$ Molar conductivity, $\Lambda_m = \frac{\kappa \times 1000}{\mathrm{c}}$
$= \frac{0.0248 \times 1000}{0.2}$
$= 124\mathrm{Scm}^2\mathrm{mol}^{-1}$

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Q3.9 The resistance of a conductivity cell containing 0.001M KCl solution at 298 K is 1500 Ω. What is the cell constant if conductivity of 0.001M KCl solution at 298 K is 0.146×10^{-3} Scm^{-1}.

Answer.
Given,
Conductivity, $\kappa = 0.146 \times 10^{-3}\mathrm{Scm}^{-1}$
Resistance, $R = 1500\Omega$
$\therefore$ Cell constant $= \kappa \times R$
$= 0.146 \times 10^{-3} \times 1500$
$= 0.219\mathrm{cm}^{-1}$

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Q3.10 The conductivity of sodium chloride 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 \mathrm{k}/\mathrm{Sm}^{-1}$1.23711.8523.1555.53106.74
Calculate Λ_m 'for all concentrations and draw a plot between
Λ_m and $\mathrm{c}1/2$. Find the value of \Lambda _ { m } ^ { 0 }

Answer.
$\mathrm{k} = 1.237 \times 10^{-2}\mathrm{Sm}^{-1}, \mathrm{c} = 0.001\mathrm{M}$
Then, $\kappa = 1.237 \times 10^{-4}\mathrm{Scm}^{-1}, \mathrm{c}1/2 = 0.0316\mathrm{M}^{1/2}$

$\therefore \quad \Lambda_m = \frac{\kappa}{c}$

$= \frac{1.237 \times 10^{-4} \mathrm{Scm}^{-1}}{0.001 \mathrm{molL}^{-1}} \times \frac{1000 \mathrm{cm}^3}{\mathrm{L}}$

$= 123.7 \mathrm{Scm}^2 \mathrm{mol}^{-1}$

Given,

$\kappa = 11.85 \times 10^{-2} \mathrm{Sm}^{-1}, \mathrm{c} = 0.010 \mathrm{M}$

Then, $\kappa = 11.85 \times 10^{-4} \mathrm{Scm}^{-1}, \mathrm{c}//2 = 0.1 \mathrm{M}^{1/2}$

$\therefore \quad \Lambda_m = \frac{K}{c}$

$= \frac{11.85 \times 10^{-4} \mathrm{Scm}^{-1}}{0.010 \mathrm{molL}^{-1}} \times \frac{1000 \mathrm{cm}^3}{\mathrm{L}}$

$= 118.5 \mathrm{Scm}^2 \mathrm{mol}^{-1}$

Given,

$\kappa = 55.53 \times 10^{-2} \mathrm{Sm}^{-1}, \mathrm{c} = 0.050 \mathrm{M}$

Then, $k = 55.53 \times 10^{-4} \mathrm{Scm}^{-1}, \mathrm{c}^{1/2} = 0.2236 \mathrm{M}^{1/2}$

$\therefore \quad \kappa = \frac{\kappa}{c}$

$= \frac{55.53 \times 10^{-4} \mathrm{Scm}^{-1}}{0.050 \mathrm{molL}^{-1}} \times \frac{1000 \mathrm{cm}^3}{\mathrm{L}}$

$= 111.11 \mathrm{Scm}^2 \mathrm{mol}^{-1}$

Given,

$\kappa = 106.74 \times 10^{-2} \mathrm{Sm}^{-1}, \mathrm{c} = 0.100 \mathrm{M}$

Then, $\kappa = 106.74 \times 10^{-4} \mathrm{Scm}^{-1}, \mathrm{c}^{1/2} = 0.3162 \mathrm{M}^{1/2}$

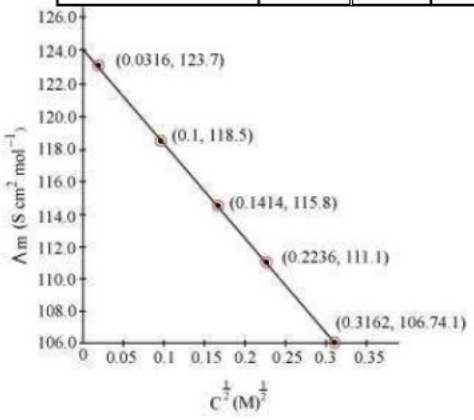
$\therefore \quad \Lambda_m = \frac{\kappa}{c}$

$= \frac{106.74 \times 10^{-4} \mathrm{Scm}^{-1}}{0.100 \mathrm{molL}^{-1}} \times \frac{1000 \mathrm{cm}^3}{\mathrm{L}}$

$= 106.74 \mathrm{Scm}^2 \mathrm{mol}^{-1}$

Now, we have following data:

$C^{1/2}/M^{1/2}$	0.0316	0.1	0.1414	0.2236	0.3162
$\Lambda_m (S\ cm^2\ mol^{-1})$	123.7	118.5	115.8	111.1	106.74



Since the line interrupts Λ_m at $124.0 \mathrm{Scm}^2 \mathrm{mol}^{-1}, \quad \Lambda^0_{m=124.0} \mathrm{Scm}^2 \mathrm{mol}^{-1}$.

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Q3.11 Conductivity Of 0.00241 M acetic acid is 7.896 x $10^{-5} \mathrm{scm}^{-1}$. Calculate its molar conductivity and if $\Lambda^0_{m\ \text{for}}$ acetic is 390.5 $\mathrm{Scm}^2 \mathrm{mol}^{-1}$, what is its dissociation constant ?

Answer.

Given, $\kappa = 7.896 \times 10^{-5} \mathrm{Sm}^{-1}$

$\mathrm{c} = 0.00241 \mathrm{molL}^{-1}$

Then, molar conductivity, $\Lambda_m = \frac{\kappa}{\mathrm{c}}$

$= \frac{7.896 \times 10^{-5} \mathrm{Scm}^{-1}}{0.00241 \mathrm{molL}^{-1}} \times \frac{1000 \mathrm{cm}^3}{\mathrm{L}}$

$= 32.76 \mathrm{Scm}^2 \mathrm{mol}^{-1}$

$\Lambda^0_{m=} = 390.5 \mathrm{Scm}^2 \mathrm{mol}^{-1}$

Now, $\alpha = \frac{\Lambda_m}{A^0_m} = \frac{32.76 \mathrm{Scm}^2 \mathrm{mol}^{-1}}{390.5 \mathrm{Scm}^2 \mathrm{mol}^{-1}}$

=0.084

$\therefore$ Dissociation constant, $\quad K_a = \frac{c\alpha^2}{(1-\alpha)}$

$= \frac{\left(0.00241 \text{molL}^{-1}\right)(0.084)^2}{(1-0.084)}$

$= 1.86 \times 10^{-5} \text{molL}^{-1}$

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Q3.12 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 MnO_4^- to Mn^{2+}

Answer. (i)

(i) $Al^{3+} + 3e^- \longrightarrow Al$

$\therefore$ Required charge $= 3F$

$= 3 \times 96487C$

$= 289461C$

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

$\therefore$ Required charge $= 2F$

$= 2 \times 96487c$

$= 192974C$

(iii) $MnO_4^- \longrightarrow Mn^{2+}$

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

$\therefore$ Required charge $= 5F$

$= 5 \times 96487C$

$= 482435C$

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Q3.13 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

Answer. (i) According to the question,

$Ca^{2*} + 2e^{-1} \longrightarrow Ca_{40g}$

Electricity required to produce 40 g of calcium = 2 F

Therefore, electricity required to produce 20 g of calcium = = $\frac{2\times20}{40}$F = 1F

(ii) According to the question,

$$Al^{3+} + 3e^- \longrightarrow Al$$
$$27 \text{ g}$$

Electricity required to produce 27g of $Al = 3F$

Therefore, electricity required to produce 40 g of Al $= \frac{3\times40}{27}F$

$= 4.44F$

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Q3.14 How much electricity is required in coulomb for the oxidation Of
(i) 1mol of H_2O to O_2
(ii) 1mol of FeO to Fe_2O_3

Answer. (i) According to the question,

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

Now, we can write:

$O^{2-} \quad \longrightarrow \quad \frac{1}{2}O_2 + 2e^-$

Electricity required for the oxidation Of I mol Of H20 to 02

$= 2 \times 96487c$

$= 192974C$

(ii) According to the question,

$Fe^{2*} \quad \longrightarrow \quad Fe^{3+} + e^{-1}$

Electricity required for the oxidation of 1 mol of Feo to $Fe_2O_3 = 1F$

$= 96487c$

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Q3.15 A solution of is electrolysed between platinum electrodes using a current of 5 amperes for 20 minutes. What mass of Ni is deposited at the cathode?

Answer.
Given,
$\text{Current} = 5\text{A}$
$\text{Time } = 20 \times 60 = 1200\text{s}$
$\therefore \text{ Charge } = \text{ current } \times \text{ time}$
$= 5 \times 1200$
$= 6000\text{C}$
According to the reaction,
$\underset{58.7\text{g}}{\text{Ni}^{2+}_{(aq)} + 2\text{e}^- \longrightarrow \text{N}_\text{i}}$
Nickel deposited bv 2 x 96487 C = 58.71 g
Therefore, nickel deposited by 6000 C $= \frac{58.71 \times 6000}{2 \times 96487}\text{g}$
= 1.825 g
Hence, 1.825 g of nickel will be deposited at the cathode.

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Q3.16 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 1.45 g of silver deposited at the cathode of cell B. How long did the current flow? What mass of copper and zinc were deposited?

Answer. According to the reaction
$\underset{108\text{g}}{\text{Ag}^+_{(aq)} + \text{e}^- \longrightarrow \text{Ag}_{(s)}}$
i.e., 108 g of Ag is deposited by 96487 C.
$\text{Therefore, 1.45 g of Ag is deposited by } = \frac{96487 \times 1.45}{108}\text{C}$
$= 1295.43\text{c}$
Given
$\text{Current } = 1.5\text{A}$
$\therefore \frac{1295.43}{1.5}\text{s}$
$= 863.6\text{s}$
$= 864\text{s}$
$= 14.40\text{min}$
Again,
$\underset{63.5\text{g}}{\text{Cu}^{2+}_{(aq)} + 2\text{e}^- \longrightarrow \text{Cu}_{(s)}}$
$2 \times 96487\text{C of charge deposit } = 63.5\text{g of Cu}$
Therefore, 1295.43 C Of charge Will deposit $= \frac{63.5 \times 1295.43}{2 \times 96487} g$
= 0.426 g of Cu
$\underset{63.5\text{g}}{\text{Zn}^{2+}_{(aq)} + 2\text{e}^- \longrightarrow \text{Zn}_{(s)}}$
$\text{i.e., } 2 \times 96487\text{C of charge deposit } = 65.4\text{g of Zn}$
$\text{Therefore, 1295.43c of charge will deposit } = \frac{65.4 \times 1295.43}{2 \times 96487}\text{g}$
$= 0.439\text{g of Zn}$

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Q3.17 Using the standard electrode potentials given in Table 3.1, predict if the reaction between the following is feasible:
(i) $\text{Fe}^{3+}(\text{aq})$ and $\text{I}^-(\text{aq})$
(ii) $\text{Ag}^+(\text{aq})$ and Cu(s)
(iii) $\text{Fe}^{3+}(\text{aq})$ and $\text{Br}^-(\text{aq})$
(iv) Ag(s) and $\text{Fe}^{3+}(\text{aq})$
(v) $\text{Br}_2(\text{aq})$ and $\text{Fe}^{2+}(\text{aq})$

Answer.

(i) $Fe^{3+}_{(aq)} + e^- \longrightarrow Fe^{2+}_{(aq)}$] $\times 2$; $E^\circ = +0.77$ V

$2I^-_{(aq)} \longrightarrow I_{2(s)} + 2e^-$; $E^\circ = -0.54$ V

$2Fe^{3+}_{(aq)} + 2I^-_{(aq)} \longrightarrow 2Fe^{2+}_{(aq)} + I_{2(s)}$; $E^\circ = +0.23$ V

Since E° for the overall reaction is positive, the reaction between $Fe^{3+}_{(aq)}$ and $I^-_{(aq)}$ is feasible.

(ii) $Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}$] $\times 2$; $E^\circ = +0.80$ V

$Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2e^-$; $E^\circ = -0.34$ V

$2Ag^+_{(aq)} + Cu_{(s)} \longrightarrow 2Ag_{(s)} + Cu^{2+}_{(aq)}$; $E^\circ = +0.46$ V

Since E° for the overall reaction is positive, the reaction between $Ag^+_{(aq)}$ and $Cu_{(s)}$ is feasible.

(iii) $Fe^{3+}_{(aq)} + e^- \longrightarrow Fe^{2+}_{(aq)}$] $\times 2$; $E^\circ = +0.77$ V

$2Br^-_{(aq)} \longrightarrow Br_{2(l)} + 2e^-$; $E^\circ = -1.09$ V

$2Fe^{3+}_{(aq)} + 2Br^-_{(aq)} \longrightarrow 2Fe^{2+}_{(aq)}$ and $Br_{2(l)}$; $E^\circ = -0.32$ V

Since E° for the overall reaction is negative, the reaction between $Fe^{3+}_{(aq)}$ and $Br^-_{(aq)}$ is not feasible.

(iv) $Ag_{(s)} \longrightarrow Ag^+_{(aq)} + e^-$; $E^\circ = -0.80$ V

$Fe^{3+}_{(aq)} + e^- \longrightarrow Fe^{2+}_{(aq)}$; $E^\circ = +0.77$ V

$Ag_{(s)} + Fe^{3+}_{(aq)} \longrightarrow Ag^+_{(aq)} + Fe^{2+}_{(aq)}$; $E^\circ = -0.03$ V

Since E° E for the overall reaction is negative, the reaction between $Ag_{(s)}$ and $Fe^{3+}_{(aq)}$ is not feasible.

(iv) $Br_{2(aq)} + 2e^- \longrightarrow 2Br^-_{(aq)}$; $E^\circ = +1.09$ V

$Fe^{2+}_{(aq)} \longrightarrow Fe^{3+}_{(aq)} + e^-$] $\times 2$; $E^\circ = -0.77$ V

$Br_{2(aq)} + 2Fe^{2+}_{(aq)} \longrightarrow 2Br^-_{(aq)} + 2Fe^{3+}_{(aq)}$; $E^\circ = +0.32$ V

Since E° for the overall reaction is positive, the reaction between $Br_{2(aq)}$ and $Fe^{2+}(aq)$and is feasible.

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Q3.18 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_2SO_4 With platinum electrodes.
(iv) An aqueous solution of $CuCl_2$ with platinum electrodes.

Answer. (i) At cathode:
The following reduction reactions compete to take place at the cathode.

$Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}$; $E^\circ = 0.80$V

$H^+_{(aq)} + e^- \longrightarrow \frac{1}{2}H_{2(g)}$; $E^\circ = 0.00$ V

The reaction with a higher value of E°takes place at the cathode. Therefore, deposition of saver will take place at the cathode.
At anode:
The Ag anode is attacked by ions. Therefore, the silver electrode at the anode dissolves in the solution to form Ag^+
(ii) At cathode:
The following reduction reactions compete to take place at the cathode.

$Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}$; $E^\circ = 0.80$V

$H^+_{(aq)} + e^- \longrightarrow \frac{1}{2}H_{2(g)}$; $E^\circ = 0.00$ V

The reaction with a higher value of E' takes place at the cathode. Therefore, deposition of silver will take place at the cathode.
At anode :
Since Pt electrodes are inert, the anode is not attacked bv NO_3^- ions. Therefore, OH^- or NO_3^- can be oxidized at the anode. But OH^- ions having a lower discharge potential
and get preference and decompose to liberate O_2.

$OH^- \longrightarrow OH + e^-$

$4OH^- \longrightarrow 2H_2O + O_2$

(iii) At the cathode, the following reduction reaction occurs to produce H2 gas.

$H^+_{(aq)} + e^- \longrightarrow \frac{1}{2}H_{2(g)}$

At the anode, the following pr«esses are possible.

$2H_2O_{(l)} \longrightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^- \; ; \; E^\circ = +1.23V \qquad (i)$

$2SO^{2-}_{4\,(aq)} \longrightarrow S_2O^{2-}_{6\,(aq)} + 2e^- ; \; E^\circ = +1.96\ V \qquad (ii)$

For dilute sulphuric acid, reaction (i) is preferred to produce 02 gas. But for concentrated sulphuric acid, reaction (ii) occurs.

(iv) At cathode:

The following reduction reactions compete to take place at the cathode.

$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)} \; ; \; E^\circ = 0.34V$

$H^+_{(aq)} + e^- \longrightarrow \frac{1}{2}H_{2(g)} \; ; \; E^\circ = 0.00\ V$

The reaction with a higher value of E" takes place at the cathode. Therefore, deposition of copper will take place at the cathode.

At anode:

The following oxidation reactions are possible at the anode.

$Cl^-_{(aq)} \longrightarrow \frac{1}{2}Cl_{2(g)} + e^{-1} \; ; E^\circ = 1.36\ V$

$2H_2O_{(l)} \longrightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^- \; ; \; E^\circ = +1.23V$

At the anode, the reaction veith a lower value of E^{-0} is preferred. But due to the over- potential of oxygen, Cl- gets oxidized at the anode to produce Cl_2 gas.

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