ELECTROCHEMISTRY

Electrochemistry: Study of relationship between chemical energy and electrical energy and how one can be converted into another.

Electrolytic cell: Electrical energy → Chemical energy

Electrochemical cell : chemical energy → Electrical energy (Galvanic cell/ voltaic cell / Daniel cell)

Electrode Potential: Potential difference between the electrode and the electrolyte.

Standard electrode potential : Potential difference developed in a cell when the gives electrode which is in contact with its ions having concentration 1 mol L^{-1} is coupled with standard hydrogen electrode.

Cell potential : Potential difference between the 2 electrodes of a galvanic cell.

EMF : Potential difference between the 2 electrodes of a galvanic cell when no current is drawn through the cell.

$$E_{cell} = E_R - R_L = E_{cathode} - E_{anode.}$$

Cell Reaction : $Cu(s) + 2Ag^+(aq) \rightarrow Cu^{+2}(aq) + 2Ag(s)$

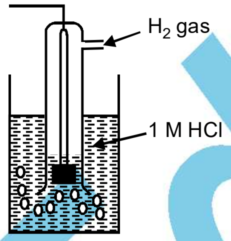
At Cathode(Reduction) : $2Ag^+(aq) + 2e \rightarrow 2Ag(s)$

At anode (Reduction) : $Cu(s) \rightarrow Cu^{+2}(aq) + 2e^-$

Cell Representation : $Cu \mid Cu^{+2} \mid\mid Ag^+ \mid Ag$

$$E_{cell} = E_{Ag^+/Ag} - E_{Cu^{+2}/Cu}$$

SHE : Standard hydrogen electrode



$$H^+(aq) + e^- \rightarrow \frac{1}{2} H_2(g)$$

$$E^o_{H^+/H_2} = 0$$

Electrochemical Series : The arrangement of metal (or species) in their increasing reducing power (or decreeing E^o) is known as electrochemical series.

Nernst Equation: To calculate electrode potential at any concentration.

$$M^{n+}_{(aq)} + ne \rightarrow M_{(s)}$$

$$E_{M^{n+}/M} = E^o_{M^{n+}/M} - \frac{RT}{nF} \ln \frac{[M_{(s)}]}{[M^{n+}]}$$

But concentration of solid M is taken as unity

$$E'_{M^{n+}/M} = E^o_{M^{n+}/M} - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]}$$

Or $$E_{M^{n+}/M} = E^{o}_{M^{n+}/M} + \frac{RT}{nF}\ln\left[M^{n+}\right]$$

F = 96487 C mol^{-1}

R = 8.314 Jk^{-1} mol^{-1}

$[M^{n+}]$ = concentration of species.

T = 298 k

n = no of moles of e indicated in balanced eq^{n}-

$$E_{M^{n+}/M} = E^{o}_{M^{n+}/M} + \frac{0.059}{n}\ln\left[M^{n+}\right]$$

In Daniel cell

(1) Zn | Zn^{+2}||Cu^{+2} | Cu

$$E_{Cell} = E^{o}_{cell} + \frac{0.059}{2}\log\frac{\left[Cu^{+2}\right]}{\left[Zn^{+2}\right]}$$

(2) Ni | Ni^{+2} || Ag^{+1} | Ag

$$E_{Cell} = E^{o}_{cell} + \frac{0.059}{2}\log\frac{[Ag^{+1}]^2}{[Ni^{+2}]}$$

For general electrochemical reaction

$$aA + bB \xrightarrow{ne^-} cC + dD$$

$$E_{cell} = E^{o}_{cell} - \frac{RT}{nF}\ln\frac{[C]^c[D]^d}{[A]^a[B]^b}$$

At equilibrium condition

$$E_{Cell} = 0, \qquad \frac{[C]^c[D]^d}{[A]^a[B]^b} = K_C$$

$$\therefore \qquad 0 = E^o - \frac{RT}{nF}\ln K_C = \frac{2.303}{nF}RT\log K_C$$

$$E^o = \frac{RT}{nF}\ln K_C$$

Electrochemical cell and Gibbs energy of the reaction

$\Delta G = -nFE$ Total Charge = nF, E = EMF

$\Delta G = -RT\ln K_C$

Conductance (G) – The inverse or reciprocal or R

The case with which current flows through a conductor.

$$G = \frac{1}{R} \text{ SI unit} \Rightarrow \text{Siemen} = \text{ohm}^{-1}$$

Conductivity (k) – The reciprocal of resistivity

$$k = \frac{1}{\rho} = \frac{l}{RA} \text{ SI unit } Sm^{-1}$$

Cell constant (G^*) The quantity $\frac{\ell}{A}$ is called cell constant. $k = \frac{G^*}{R}$.

Electronic conductance – electrical conductance though metal.

Electrolytic or ionic conductance – The conductance by ions present in solution.

Conductivity of ionic solution depends on

1. Nature of electrolyte.
2. Size of the ions produced and their solvation.
3. Nature of the solvent and its viscosity
4. Concentration of electrolyte.
5. Temperature (Increases with increase of T)

Molar conductivity.:

$$\Lambda_m = \frac{k}{C} = \frac{k \times 1000}{\text{Molarity}}$$

Equivalent conductivity

$$\Lambda_{eq} = \frac{k \times 1000}{\text{Normality}}$$

Limiting molar conductivity : The molar conductivity of a solution whose concentration approaches zero.

Debye – Huckel Onsanger equation

$\Lambda = \Lambda^o = AC^{1/2}$

Kohlrausch law of independent migration of ions the law states that the limiting molar conductivety of an electrolyte at infinite dilution is opposed as the sum of individual contributions of the anion and cation of the electrolyte.

$$\Lambda^o_{NaCl} = \lambda^o_{Na^+} + \lambda^o_{Cl^-}, \quad \Lambda^0_{CaCl_2} = \lambda^0_{Ca^{+2}} + 2\lambda^0_{Cl^-}$$

In General

$$\Lambda^0_m = \nu_+\lambda^0_+ + \nu_-\lambda^0_-$$

ν_+ & ν_- are the no. of cations and anions performed of electrolyte.

Applications of Kohlrausch Law :

(i) In the calculation of Λ^0_m for weak electrolyte

(ii) In the calculation of degee of dissociation

Degree of Dissociation $\alpha = \frac{\Lambda_m}{\Lambda^\infty_m}$

(iii) In the calculation of dessociation of constant of weak electrolyte.

$$K_a = \frac{c\alpha^2}{(1-\alpha)} = \frac{C\Lambda^2_m}{\Lambda^0_m\left(\Lambda^0_m - \Lambda_m\right)}$$

Faradays laws of electrolysis

First law – It states that the amount of any substance produced at any electrode during electrolysis is directly proportional to the quantity of charge passed.

$W \propto Q$, $W = zit$

Second law – When the same quantity of electricity is passed through a solution of different electrolytes, thus the weight of the substance produced at the respective electrodes are directly proportional to their equivalent weights.

$$\frac{W_A}{W_B} = \frac{\text{Eq.Wt of A}}{\text{Eq.wt of B}}$$

FARADAY : The charge on one mole of electrons is called 1 faraday. Thus 1 faraday = 96487 C

So, charge on n mole of electrons will be Q = nF

Products of electrolysis – depends on nature of materiel electrolysed and the types of electrodes used.

Electrolysis of

(i) Molten NaCl solution → Na + Cl_2

(ii) Aqueous NaCl solution → NaOH + H_2 + Cl_2

(iii) $CuCl_2 \xrightarrow{\text{using Pt electrodes}} Cu + Cl_2$

(iv) $CuCl_2 \xrightarrow{\text{using Cu electrodes}}$ Cu is deposited at cathode and dissolves at anode.

(v) $AgNO_3 \xrightarrow{\text{using Pt electrodes}}$ Silver at Cathode and O_2 at anode

(vi) $AgNO_3 \xrightarrow[\text{Ag electrode}]{\text{using}}$ Silver at Cathode and silver anode will be dissolved slowly.

Commercial Cells: Two type

Primary Cells/Battries :

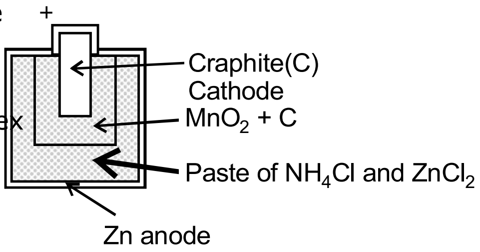
Reaction occurs only once

* Cannot be reused.

* Electrode reaction cannot be reversed by external electric source.

eq. Daniel cell, dry cell, Mercury cell .

Dry cell /Lechlanche cell : At anode $Zn(s) \rightarrow Zn^{+2} + 2e$



At Cathode $MnO_2 + NH_4^+ + e \rightarrow MnO(OH)_2 + NH_3$

NH_3 gas produced reacts with Zn^{+2} to form complex

$2NH_3 + Zn^{+2} \rightarrow [Zn(NH_3)_4]^{2+}$

Cell potential = 1.5 V

Mercury cell - for low current devices eq. hearing aids, watches etc.

Anode - Zn –Hg Amalgam

Cathode – paste of HgO and C.

Electrolyte – paste of KOH and ZnO

Anode: $Zn(Hg) + 2OH^- \rightarrow ZnO(s) + H_2O + 2e$

Cathode : $HgO + H_2O + 2e \rightarrow Hg(l) + 2OH^-$

Overall Reaction : $Zn(Hg) + HgO(s) \rightarrow ZnO(s) + Hg(l)$

Cell potential = 1.35 (Remains constant through out life as the overall reaction does not involve any ion in solution)

Secondary cells: - Can be recharged by passing electric current

eq. Lead storage battery, nickel cadmium cell

Lead storage battery - in Automobiles and invertor.

Anode -Pb

Cathode - Grid of Pb packed with lead dioxide (PbO_2).

Electrolyte : H_2SO_4 (38% by mass)

When battery in use (Discharging)

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

On Recharging -Reaction is reversed

In Recharging process $PbSO_4$ (s) on anode and cathode is converted into Pb and PbO_2 respectively.

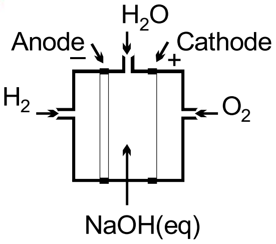
Ni–Cd Cell : It has longer life, more expensive then Pb storage battery but it is light therefore used in calculators, portable power tools.

Overall reaction : $Cd(s) + 2Ni(OH)_3(s) \rightarrow CdO(s) + 2Ni(OH)_2(s) + H_2O$

Fuel Cells : Galvanic Cells that are designed to convert the energy on combustion of fuel like H_2, CH_4 CH_3OH etc directly into electrical energy are called fuel cells.

Catalyst like Pt or palladilum are incorr proated into electrode

- * Efficiency 70%
- * Pollution free



Cathode: $O_2 + 2H_2O + 4e \rightarrow 4OH^-$

Anode : $2H_2 + 4OH^- \rightarrow 4H_2O + 4e$

Overall Reaction : $2H_2 + O_2 \rightarrow 2H_2O(l)$

* H_2–O_2 fuel cells were used in Apollo space program for providing electrical power.

The cell runs continuously as long as reactants are supplied.

Corrosion : In corrosion metal is oxidised by loss of electron to oxygen and formation of oxide.

eq. tarnishing of Ag.

Green coating on Cu and Bronge

rusting of iron. (In presence of O_2 & H_2O)

Anode (Oxidation): $2Fe \rightarrow 2Fe^{+2} + 4e$

Electrons released at anodic sport move through metal and go to another spot on the metal and reduce oxygen in presence of H^+(obtained from H_2CO_3 formed due to disolution of CO_2 into water.)

Cathode : $O_{2(g)} + 4H^+_{(eq)} + 4e \rightarrow 2H_2O$.

The ferrous ions are further oxidised by atmospheric oxygen to ferric ions which come out as rust in the form of hydrated ferric oxide (($Fe_2O_3x\ H_2O$)

Prevention of corrosion : - Covering surface of metal by paint, chemicals (Bisphenol) or other metals (Sn, Zn,) etc, Galvanisation.

SOLVED PROBLEMS

Q.1 Calcualate the potential of hydrogen electrode in contact with a solution whose pH is 10.

Sol. If pH of solution is 10, that means

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

According to Nernst equation

$$E_{H^+/H_2} = E^0_{H^+/H_2} - \frac{0.0591}{n}\log\left[\frac{1}{H^+}\right]$$

$$E_{H^+/H_2} = 0 - \frac{0.0591}{1}\log\left[\frac{1}{10^{-10}}\right] = 0 - 0.0591 \times 10 = 0 - 0.591\ V$$

Q.2 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 $E^{\ominus}_{cell}$ = 1.05 V.

Sol. The oxidation and reduction half reactions are:

$Ni(s) \rightarrow Ni^{2+}(aq) + 2e^-$ (At anode)

$2Ag^+ + 2e^- \rightarrow 2Ag$

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

According to Nernst equation

$$E_{cell} = E^{\ominus}_{cell} - \frac{0.0591}{n}\log\frac{[Anode]}{[Cathode]}$$

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

$$= 1.05 - \frac{0.0591}{2}\log\frac{1.160}{(0.002)^2} = 1.05 - \frac{0.0591}{2}\log(4 \times 10^4)$$

$$E_{cell} = 1.05 - \frac{0.0591}{2} \times 4.6020 = 0.9142\ V.$$

Q.3 The molar conductivity of 0.025 molL^{-1} methanoic acid is 46.1 cm^2 mol^{-1}. Calculate its degree of dissociation and dissociation constant. Give $\Lambda^0_{(H^+)}$ = 349.6 S cm^{2}mol^{-1} and $\Lambda^0_{(HCOO^-)}$ = 54.6 S cm^2 mol^{-1}.

Sol. (I) Calculation of degree of dissociation (α) of methanoic acid

Λ^C_m = 46.15 S cm^2 mol^{-1}

$\Lambda^0_m(HCOOH) = \Lambda^0_m(HCOO^-) + \Lambda^0_m(H^+) = 54.6 + 349.6 = 404.2$ S cm^2 mol^{-1}

$$\alpha = \frac{\Lambda_m^C}{\Lambda_m^0} = \frac{46.15}{404.2}\frac{\text{Scm}^2\,\text{mol}^{-1}}{\text{S cm}^2\,\text{mol}^{-1}} = 0.1140$$

(II) Calculation of dissociation constant (K_C)

$$\text{HCOOH(aq)} \rightleftharpoons \text{HCOO}^-\text{(aq)} + \text{H}^-\text{(aq)}$$

$$\begin{array}{lll} \text{C} & \text{O} & \text{O} \\ \text{C}(1-\alpha) & \text{C}\alpha & \text{C}\alpha \end{array}$$

$$K_\alpha = \frac{[\text{HCOO}^-][\text{H}^+]}{[\text{HCOOH}]} = \frac{C\alpha^2}{1-\alpha}$$

$$K_\alpha = \frac{0.025\times(0.1140)^2}{(1-0.1140)} = 3.67\times10^{-4}\ \text{molL}^-$$

Q.4 **If a current of 0.5 ampere flows through a metallic wire for 2 hours, then how many electrons would flow through the wire ?**

Sol. Charge = I t

Charge =(0.5 A) × (2 × 60 × 60 S) = 3600 AS = 3600 C

No. of electorns flowig through the wire tby passing a charge of one faraday (96500 C)

= 6.022×10^{23} electrons

∵ No. of electrons flowing through the wire by passing charge of 3600 C

$$= 6.022\times10^{23}\times\frac{3600\text{C}}{96500\text{C}} = 2.246\times10^{22}\ \text{electrons}$$

Q.5 **Write the chemistry of recharging the lead storage battery, highlighting all the materials that are involved during reacharging.**

Sol. During recharging the cell is operated like an electrolytic cell i.e., electrical energy is supplied from some externa sources. Electrode reactions are reverse of those during discharging.

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

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

——————————————————————————

$2PbSO_4(s) + 2H_2O(s) \rightarrow Pb(s) + PBO_2(s) + 4H^+ (aq) + 2SO_4^{2-} (aq)$

Q.6 **Depict the galvanic cell in which the reaction**

$Zn(s) + 2Ag^+ (aq) \rightarrow Zn^{2+} (aq) + 2Ag(s)$ takes place.

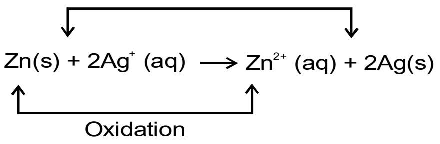
Further show :

(i) Which of the electrodes is negatively charged ?

(ii) The carrier of the current in the cell.

(iii) Individual reactions at each electrode.

Sol.



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

$Zn(s) \mid Zn^{2+}$ (aq) Ag^+ (aq) $\mid$ Ag(s) Daniel cell.

(i) Anode of Zn with negative charge ; cathode of Ag with positive charge.

(ii) Electonrs wil flow from Zn in Cu inouter circuit and current will flow from Cu to Zn.

(iii) Cathode : $Zn \rightarrow Zn^{2+} + 2e^-$; Anode : $2AG^+ + 2e^- \rightarrow Ag(s)$

Q.7 Calculate the standard cell potentials of galvanic cells in which the following reactions takes place :

(i) $2Cr(s) + 3Cd^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + 3Cd(s)$

(ii) Fe^{2+} (sq) + Ag^{+} (aq) ® Fe^{3+} (qq) + Ag(s)

Calculate the ΔrG^{o} and equilibrium constant of the reactions.

Sol. (i) $2Cr \rightarrow 2Cr^{3+} + 6e^{-}$, (Oxidation)

$3Cd^{2} + 6e^{-} \rightarrow 3Cd$, (Reduction)

$$E^{o}_{cell} = E^{o}_{cathode} = E^{o}_{anode}$$

$$= E^{o}_{Cd^{2+}/Cd} - E^{o}_{Cr^{3+}/Cr} = -0.40 - (-0.74) = 0.34\ V$$

Six electrons (n = 6) are used in redox charge

$\Delta_r G^{o} = -nE^{o}F = -6 \times 0.34 \times 96500\ J = -196860\ J$

or $\Delta_r G^{o} = -196.86\ kJ\ mol^{-1}$

Also $\Delta_r G^{o} = -2.303 \times 8.314 \times 298 \log K$

$K = \text{antilog } 34.5014 = 3.173 \times 10^{34}$

(ii) $Fe^{2+} \rightarrow Fe^{3+} + e^{-}$, (Oxidation)

$Ag^{+} + e^{-} \rightarrow Ag_{+}$ (Redution)

$E^{o}_{cell} = E^{o}_{Cathode} - E^{o}_{Anode}$

$$= E^{o}_{Ag^{+}/Ag} - E^{o}_{Fe^{3+}/Fe^{2+}} = 0.80 - 0.77 = 0.03\ V$$

Also $\Delta_r G^{o} = -nFE^{o} = -1 \times 96500 \times 0.03$

or $\Delta_r G^{o} = -2895\ J\ mol^{-1}$

Also $\Delta_r G^{o} = -2.303\ RT \log K$

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

$K = \text{antilog } 0.5074 = 3.22$

Q.8 Write the Nernst equation and emf of the follownig cell at 298 K :

(i) Mg(s) | Mg^{2+} (0.001 M)|| Cu^{2+} (0.0001 M) | Cu(s)

(ii) Fe(s) | Fe^{2+} (0.001 M) || H^{+} (1 M)| H_2(g) (g) (1 bar) Pt(s)

Sol. (i) $E_{cell} = (E^{o}_{Cathode} - E^{o}_{anode}) - \frac{0.059}{n} \log \frac{[Mg^{2+}]}{[Cu^{2+}]}$

$$E_{cell} = (0.34 - (-2.36)) - \frac{0.059}{2} \log \frac{0.001}{0.0001} = 2.68\ V$$

(ii) $E_{cell} = (E^{o}_{cathode} - E^{o}_{anode})$

$$= \frac{0.059}{n} \log \frac{[Fe^{2+}][pH_2]}{[H^{+}]^{2}}$$

$$E_{cell} = (0 - (-0.44)) - \frac{0.059}{2} \log \frac{0.001}{(1)^{2}} = 0.5285\ V$$

Q.9 Conductivity of 0.0241 M acetic acid is 7.896 × 10^{-5} S cm^{-1}. Calculate its molar conductivity. If Λ_m^0 for acetic acid is 390.5 S cm^2 mol^{-1}, what is its dissociation constant?

Sol. $\Lambda_m = \dfrac{K \times 1000}{C} = \dfrac{7.896 \times 10^{-5} \times 1000}{0.00241} = 32.76 \text{ S cm}^2\text{mol}^{-1}$

Also

$$\alpha = \frac{\Lambda_m}{\Lambda_m^0} = \frac{32.76}{390.5} = 0.084 = 8.4 \times 10^{-2}$$

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

Q.10 How much electricity in terms of Faraday ios 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) $CaCl_2 \rightleftharpoons Ca^{2+}\ 2Cl^-$

$Ca^{2+} + \underset{2mol}{2e^-} \rightarrow \underset{1mol}{Ca}$ (1 mole of calcium = 40 cm)

∵ 40 g of calcium requires charge = 2F

∴ 20 g of calcium requires charge = $\dfrac{2F \times 20}{40}$

$$= \frac{2 \times 96500 \times 20}{40} = 96500 \text{ C}$$

(ii) $2Al^{3+} + \underset{6F}{6e^-} \rightarrow \underset{2\times 27g}{2Al,}$

To produce 2 × 27 g Al, Electrictiy required = 6F

∴ To produce 40 g Al, electricity required $= \dfrac{6F}{2 \times 27} \times 40$

$$= \frac{120}{27} = 4.44 \text{ F}$$

Q.11 How much electricity is required in coloumb for the oxidation of
(i) 1 mol of H_2O to O_2 ?
(ii) 1 mol of FeO to Fe_2O_3 ?

Sol. (i) The reaction involved is $H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$

Thus 1 mol of water will require 2 × 96500C = 193000C

(ii) $Fe^{2+} \rightarrow Fe^{3+}\ e^-$

or $2FeO + \frac{1}{2}O_2 \rightarrow Fe_2O_3$

So 1 mol of FeO will require 96500 C.

Q.12 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) $Fe^{3+}(aq)$ and $Br^-(aq)$

(c) $Br_2(aq)$ and $Fe^{2+}(aq)$

Electrode	$E^o_{Fe^{3+}/Fe^{2+}}$	$E^o_{I_2/I^-}$	$E^o_{Br_2/Br}$
E°	0.77V	0.54V	1.09V

Sol. (a) $2Fe^{3+} + 2e^- \rightarrow 2Fe^{2+}$

$2I^- \rightarrow I_2 + 2e^-$

$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$

Thus two half cells are Fe^3/Fe^{2+} and I_2/I^-

$E^o_{cell} = E^o_{cathode} - E^o_{anode}$

$= E^0_{Ag^{3+}/Ag^{2+}} - E^0_{I_2/I^-} = 0.77 - 0.54 = 0.23\ V$

This reaction is feasible as E^o_{cell} is positive

(b) $2Fe^{3+} + 2e^- \rightarrow 2Fe^{2+}$

$2Br^- + 2e^- \rightarrow Br_2$

$Br^- + Fe^{3+} \rightarrow 2Fe^{2+} + \frac{1}{2}Br_2$

$E^o_{cell} = E^o_{cathode} - E^o_{anode}$

$= E^0_{Ag^{3+}/Ag^{2+}} - E^0_{Br_2/Br^-} = 0.77 - 1.09 = -0.32\ V$

The reaction is not feasible as E^o_{cell} is negative.

(c) $Br_2 + 2e^- \rightarrow 2Br^-$

$2Fe^{2+} \rightarrow 2Fe^{3+} + 2e^-$

$Br_2 + 2Fe^{2+} \rightarrow 2Br^- + 2Fe^{3+}$

Thus two half cells are Br_2/Br^- and Fe^{3+}/Fe^{2+}

$E^o_{cell} = E^o_{cathode} - E^o_{anode}$

$= E^0_{Br_2/Br^-} - E^0_{Ag^{3+}/Ag^{2+}} = 1.09 - 0.77 = 0.32\ V$

The reaction is feasible as E^o_{cell} is positive. So the reaction

$Br_2 + 2Fe^{2+} \rightarrow 2Br^- + 2Fe^{3+}$

Q.13 In the electrolysis of acidulated water, it is desired to obtain H_2 at the rate of 1cc per second at NTP condition. What should be the current passed ?

Sol. $2H^+ + 2e^- \rightarrow H_2$

2F 1 mole

22400 cc at NTP

$\therefore$ 22400 cc of H_2 at NTP requires 2F i.e., 2 × 96500 C

$\therefore$ 1 cc of H_2 at NTP requires $\frac{2 \times 96500}{22400} \times 1 = 8.616$ C

Now, $Q = I \times t$

$$I = \frac{Q}{t} = \frac{8.616}{1s} = 8.616 \text{ ampere}$$

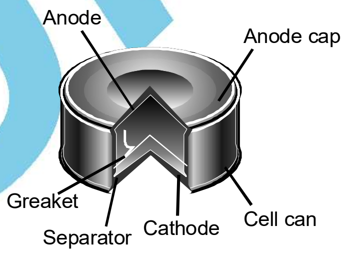
Q.14 Consider the following diagram of mercury cell

(a) Which substance acts as cathode and which acts as anode ?

(b) Mention the electrolyte used in the cell

(c) What is the cell potential of this cell ?

(d) Why does the voltage of mercury cell remain constant throughout in life ?



Sol. (a) Anode – Zinc container, Cathode – Carbon rod

(b) A paste of HgO + KOH

(c) 1.35 V

(d) Because overall cell reaction does not involve any ion whose concentration can change

$Zn(s) + HgO(s) \rightarrow ZnO(s) + Hg(s)$

Q.15 At what pH will hydrogen electrode at 298 K show an electrode potential of – 0.118 V, when H_2 gas is bubbled at 1 atm. pressure.

Sol. The electrode reaction involved is:

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

$$E_{H^+/H_2} = E^0_{H^+/H_2} - \frac{0.0591}{n} \log \frac{1}{[H^+]}$$

$$-0.118 = 0 - \frac{0.0591}{1} \log \frac{1}{[H^+]}$$

$$\log \frac{1}{[H^+]} = \frac{0.118}{0.0591}$$

$$-\log[H^+] = 1.996 \approx 2$$

$$pH = 2$$

EXERCISE – I UNSOLVED PROBLEMS

Q.1 In the buton cell widely used in watches and other devices, the following reaction takes place
$Zn(s) + AgO(s) + H_2O(l) \rightarrow Zn^{2+} (aq) + 2Ag(s) + 2OH^-(aq)$
Determine Δ_rG^o and E^o for the reaction.

Q.2 Define conductivity and molar conductivity for the solution of an electrolyte. Discuss their variation with concentration.

Q.3 The conductivity of 0.20 M solution of KCl at 298 K is 0.0248 S cm^{-1}. Calculate its molar conductivity.

Q.4 How much charge is required from 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+}?

Q.5 A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using a current of 5 amperes for 20 minutes. What mass of Ni is deposited at the cathode?

Q.6 Three electrolytic cells A, B, C containing solution of $ZnSO_4$, $AgNO_3$ and $CuSO_4$, respectively are connected in series. A steady current of 1.5 amperes are 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 of zinc were deposited?

Q.7 What is the function of salt bridge in electrochemical cells?

Q.8 At infinite dilution, the molar conductance of Na^+ and SO_4^{2-} ions are 50 S cm^2 mol^{-1} and 160 Scm^2 mol^{-1} respectively. What will be the molar conductance of sodium sulphate at infinite dilution?

Q.9 Which will have greater molar conductivity?
"Solution having 1 mol of KCl in 200 cc or 1 mol of KCl in 600 cc."

Q.10 What are secndary cels? Give the anode or cathode reaction of Nickel -Cadmium storage cell.

Q.11 What is corrosion ? How is cathodic protection of iron different from its galvanisation?

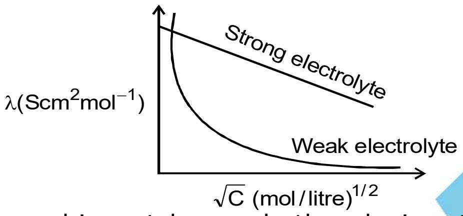
Q.12 What do you mean by e.m.f. of a cell. Calculate the e.m.f. of the cell $Mg(s) | Mg^{2+}(0.2\ M) || Ag^+(1 \times 10^{-3} M) | Ag$, $E^o_{Ag^+/Ag} = 0.80$ V, $E^o_{Mg^{2+}/Ag} = -2.37V$, What will be the effect on e.m.f., if conc. of Mg^{2+} is decreaed to 0.1 M.

EXERCISE – II

BOARD PROBLEMS

Q.1 Conductivity of 0.00247 M acetic acid is 7.896×10^{-5} S cm^{-1}. Calculate its molar conducitvity. If λ^o for acetic aicd is 390.5 S cm^2 mol^{-1}, what is its dissociation constant ? (Ans. 1.85×10^{-5})

Q.2 How does molar conductivty vary with concentration for
(i) weak electrolyte
(ii) strong electrolyte ? Give reason for these variations



Q.3 (a) In the button cell, widely used in watches and other devices the following reaction takes place:
$Zn(s) + Ag_2O(s) + H_2O(l) \rightarrow Zn^{2+}(aq) + 2Ag(s) + 2OH^-(aq)$
Determine E^o and ΔrG^o for the reaction

Given $E^0_{Ag^+/Ag} = +0.80$ V, $E^0_{Zn^{2+}/Zn} = -0.76$ V.

(b) Explain with examples the terms weak and strong electrolytes. How can these be distinguished?

Q.4 Predict the products of electrolysis obtained at the electrodes in each case when the electrodes used are of platinum:
(i) An aqueous solution of $AgNO_3$ (ii) An aqeous solution of H_2SO_4

Q.5 (a) State two advantages of $H_2 - O_2$ fuel cell over ordinary cell.
(b) Silver is electrodeposited on a metallic vessel of total surface area 900 cm^2 by passing a current of 0.5 amp for two hours. Calculate the thickness of silver deposited.
(Density of Ag = 10.5 g cm^{-3} , At. mass of Ag = 108 amu)

Q.6 (a) Give reasons for the following :
(i) Rusing of iron is quicker in saline water than is ordinary water.
(ii) Aluminium metal cannot be produced by the electrolysis of aqueous solution of aluminium salt.

Q.7 (a) Calculate the e.m.f. of the cell
$Mg(s)\ |Mg^{2+}(0.1M||Cu^{2+}(1 \times 10^{-3}\ M)|\ Cu(s)$
Given : E^o Cu^{2+}/Cu = + 0.34 V, E^o Mg^{+2}/Mg = – 2.37 V
(b) Explain with examples the terms weak and strong electrolytes.

Q.8 (a) The resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is 1500 Ω . What is the cell constant, if the conductivity of 0.001 M KCl solution at 298 K is 0.146×10^{-3} S cm^{-1}?
(b) Predict the products of electrolysis in the following :
A solution of H_2SO_4 with platinum electrodes.

Q.9 Conductivity of 0.00241 M acetic acid solution 7896×10^{-5} S cm^{-1}. Calculate its molar conductivity in this solution. If Λ^0_m for acetic acid in 390.5 S cm^2 mol^{-1}, what would be its dissociation constant?

Q.10 The conductivity of a 0.20 M solution of KCl at 298 K is 0.0248 S cm^{-1}. Calculate its molar conductivity.

Q.11 Express the relation between conductivity and molar conductivity of a solution.

Q.12 (a) State Kohlrausch's Laq of independent migration of ions. How can the degree of dissociation of acetic acid in a solution be calculated from its molar conductivity data?

(b) (i) Formulate the electrochemical cell representing the reaction
$2Cr(s) + 3Fe^{+2}(aq) \rightarrow 2Cr^{+3}(aq) + 3Fe(s)$
(ii) Calculate E^o_{cell}
(iii) Calculate E_{cell} at 25ºC if
$[Cr^{3+}] = 0.1$ M and $[Fe^{+2}] = 0.01$ M

Given : $E^0_{Cr^{3+}/Cr} = -0^o74$ V, $E^0_{Fe^{+2}/Fe} = -0.44$ V

Q.13 What is meant by 'limiting molar conductivity' ?

Q.14 Express the relation among the cell constant, the resistance of the solution in the cell and the conductivity of the solution. How is the conductivity of a solution related to its molar conductivity?

Q.15 Given that the standard electrode potentials(E^o) of metals are:
$K^+/K = -2.93$ V, $Ag^+/Ag = 0.80$ V, $Cu^{2+}/Cu = 0.34$ V
$Mg^{2+}/Mg = -2.37$ V, $Cr^{3+}/Cr = -0.74$ V, $Fe^{2+}/Fe = -0.44$ V,
Arrange these metals in an increasing order of their reducing power.

Q.16 Two half-reactions of an electrochemical cell are given below:
$MnO_4^-\,(aq) + 8H^+(aq) + 5\,e^- \rightarrow Mn^{2+}\,(aq) + 4H_2O(l)$, $E^o = +1.51$ V
$Sn^{2+}(aq) \rightarrow Sn^{4+}\,(aq) + 2\,e^-$, $E^o = +0.15$ V.
Construct the redox reaction equation from the two half -reactions and calculate the cell potential from the standard potentials and predict if the reaction is reactant or product favoured.

Q.17 Define the following :
(i) Order of a reaction (ii) Activation energy of a reaction

Q.18 What type of cell is a lead storage battery? Write the anode and the cathode reactions and the overall cell reaction occurring in the use of a lead storage battery.

Q.19 Two half cell reactions of an electrochemical cell are given below:
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$, $E^o = +1.51$ V
$Sn^2(aq) \rightarrow Sn^{4+}\,(aq) + 2e^-$, $E^o = +0.15$ V
construct the redox equation from the two half cell reactions and predict if this reaction favours formation of reactants or product shown in the equation.

Q.20 (a) 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.
(b) Calculate the potential for half-cell containing 0.10 M $K_2Cr_2O_7$(aq, 0.20 M Cr^{3+} (aq) and 1.0×10^{-4} M H^+(aq)
The half -cell reaction is
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}\,(aq) + 7H_2O(l)$,
and the standard electrode potential is given as $E^o = 1.33$ V

Q.21 (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 ? $[Hg(NO_3)_2 = 200.6 \text{ g mol}^{-1}]$
(b) A voltaic cell is set up at 25ºC with the following half-cells Al^{3+}(0.001) and Ni^{2+}(0.50M). Write an equation for the reaction that occurs when the cell generates an electric current and determine the cell potential. (Given : $E^o_{Ni^{2+}/Ni} = -0.25\,V, E^o_{Al^{3+}/Al} = -1.66\,V$)

Q.22 Express the relation among cell constant, resistance of the solution in the cell and conductivity of the solution. How is molar conductivity of a solution related to its conductivity ?

or

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 this solution.

Q.23 The electrical resistance of a column of 0.05 M NaOH solution of diameter 1 cm and length 50 cm is 5.55×10^3 oh. Calculate its resistivity, conductivity and molar conductivity.

Q.24 The standard electrode potential (E°) for Daniell cell is 1.1 V. Calculate the $\Delta G°$ for the reaction
$Zn(s) + Cu^{2+}\,(aq) \longrightarrow Zn^{2+}\,(aq) + Cu\,(s)$ (1 F = 96500 C mol^{-1}).

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