XII UNIT 3

Electrochemistry

Question Bank
Unit 3
- Electrochemistry

Solved Example

Ex.1 The reaction : Zn^{2+} (aq) + 2e⁻ → Zn (s) has a electrode potential of - 0.76 V. This means-

(A) Zn cannot replace hydrogen from acids

(B) Zn is reducing agent

(C) Zn is oxidizing agent

(D) Zn^{2+} is a reducing agent

Sol. (B) Negative electrode potential shows that Zn^{2+} is difficult to be reduced and therefore, Zn acts as reducing agent.

Ex.2 Certain quantity of current is passed through 2V connected in series and containing XSO_4(aq) and Y_2SO_4(aq) respectively. If the atomic masses of X and Y are in the ratio of 2 : 1 the ratio of the masses of Y liberated to that of X is :

(A) 1 : 1

(B) 1 : 2

(C) 2 : 1

(D) 3 : 2

Sol. (A) $X^{2+} + 2e^- \rightarrow X$; $Y^+ + e^- \rightarrow Y$

2 mol e⁻ produce X = 1 mol = 1 × M g

2 mol e⁻ produce Y = 2 mol = 2 × M/2 = M g

Hence, ratio of the masses of Y:X is M:M or 1:1

Ex.3 The equivalent conductivities at infinite dilution of the cation and the anion of a salt A_2B are 140 and 80 ohm⁻¹ cm² eq⁻¹ respectively. The equivalent conductivity of the salt at infinite dilution is-

(A) 160 ohm⁻¹ cm² eq⁻¹

(B) 220 ohm⁻¹ cm² eq⁻¹

(C) 60 ohm⁻¹ cm² eq⁻¹

(D) 360 ohm⁻¹ cm² eq⁻¹

Sol. (B) Λ_{eq}^{∞} (A_2B) = λ_{eq}^{∞} (A) λ_{eq}^{∞} (B^{2-})

= 140 + 80 = 220 ohm⁻¹ cm² eq⁻¹

Ex.4 The specific conductance of a 0.20 mol L⁻¹ solution of an electrolyte at 20ºC is 2.48 x 10⁻⁴ ohm⁻¹ cm⁻¹. The molar conductivity of the solution is -

(A) 1.24 ohm⁻¹ cm² mol⁻¹

(B) 4.96 ohm⁻¹ cm² mol⁻¹

(C) 1.24 ohm⁻¹ cm²

(D) 4.96 ohm⁻¹ cm²

Sol. (A) $L_m = \dfrac{\kappa \times 1000}{M} = \dfrac{2.48 \times 10^{-4} \times 1000}{0.20}$

$= 1.24$ ohm^{-1} cm^2 mol^{-1}

Ex.5 When an electric current is passed through acidulated, water, 112 mL of hydrogen gas at N.T.P. collects at the cathode in 965 seconds. The current passed, in amperes, is-

(A) 1.0

(B) 0.5

(C) 0.1

(D) 2.0

Sol. (A) 22,400 mL of hydrogen at STP(or NTP)=2g

Therefore,112 mL of hydrogen at

STP = $\dfrac{2g \times 112\, mL}{22,400\, mL}$ = 10^{-2} g

Therefore,2H 2e$^-$ → H$_2$

2F 1 mol

$= 2 \times 96,500$ C $= 2$ g, 2 g hydrogen is deposited by $2 \times 96,500$ C

Therefore,10^{-2} g hydrogen will be deposited by = $\dfrac{2 \times 96,500 \times 10^{-2} g}{2g}$ = 965 C

Q = i × t = 965 = i × 965

= i = 1

Ex.6 The charge required to deposit 40.5 g of Al (atomic mass = 27.0 g) from the fused Al$_2$ (SO$_4$)$_3$ is-

(A) 4.34×10^5 C

(B) 43.4×10^5C

(C) 1.44×10^5

(D) None of these

Sol. (A) Al^{3+} + 3e$^-$ → Al

3F 1 mol = 27.0 g

to deposit 27g required charge =3×96,500 C

Therefore,to deposit 40.4g required charge

= $\dfrac{40.5g \times 3mol \times 96,500C\ mol^{-1}}{27.0g}$ = 4.34×10^5 C

Ex.7 The same amount of electricity was passed through two separate electrolytic cells containing solutions of nickel nitrate and chromium nitrate respectively. If 0.3 g of nickel was deposited in the first cell, the amount of chromium deposited is (At. wt. Ni= 59, Cr=52)

(A) 0.1 g

(B) 0.176 g

(C) 0.3 g

(D) 0.6 g

Sol. (B) $\dfrac{m_{Ni}}{m_{Cr}} = \dfrac{Eq.\ mass\ of\ Ni}{Eq.\ mass\ of\ Cr}$

For Ni^{2+} and Cr^{3+}, we have : $\dfrac{0.3\ g}{m_{Cr}} = \dfrac{59\,/\,2}{52\,/\,3}$ $m_{Cr} = \dfrac{0.3g \times \frac{52}{3}}{(59\,/\,2)} = 0.176\ g$

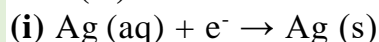**Ex.8 Electrolytic conduction differs from metallic conduction. In case of metallic conduction -**

(A) The resistance increases with increasing temperature

(B) The resistance decreases with increasing temperature

(C) The flow of current does not generate heat

(D) The resistance is independent of the length of electrolytic conductor

Sol. (A) With increase in temperature vibration of Kernal (Cation) increases and therefore, conduction decreases and hence, resistance of the metallic conductor increases.

Ex.9 Three faraday of electricity is passed through molten solutions of $AgNO_3$, $NiSO_4$ and $CrCl_3$ kept in three vessels using inert electrodes. The ratio in mol in which the metals Ag, Ni and Cr will be deposited is-
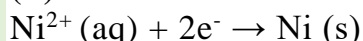
(A) 1 : 2 : 3
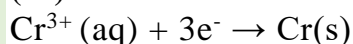
(B) 3 : 2 : 1

(C) 6 : 3 : 2

(D) 2 : 3 : 6

Sol. (C)

(i) $Ag\,(aq) + e^- \rightarrow Ag\,(s)$

1 mol = 1F   1 mol

3F   =   3 mol

(ii)

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

2 mol = 2F   1 mol

3 F = 3/2 mol

(iii)

$Cr^{3+}\,(aq) + 3e^- \rightarrow Cr(s)$
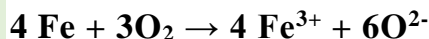
3 mol = 3F   1 mol

The required ratio of moles of Ag, Ni and Cr is :

3 mol Ag : 3/2 mol Ni : 1 mol Cr

or **6 mol Ag : 3 mol Ni : 2 mol Cr.**

Ex.10 In the reaction :

$4\ Fe + 3O_2 \rightarrow 4\ Fe^{3+} + 6O^{2-}$

which of the following statements is correct

(A) A redox reaction

(B) O_2 is reducing agent

(C) Fe^{3+} is an oxidizing agent

(D) Fe is reduced to Fe^{3+}

Sol. (A)

In this reaction, Fe is oxidized to Fe^{3+} and O_2 is reduced to O^{2-}.

Ex.11 Calculate current strength in ampere required to deposit 10 g Zn in 2hrs. At wt. of Zn = 65.

Sol. Q $w = \dfrac{E.i.t.}{96500}$; Therefore, $i = \dfrac{96500 \times w}{E.t.}$ $\left[\begin{array}{l} \because Zn^{2+} + 2e \rightarrow Zn \\ \therefore E = \dfrac{At\ wt.}{2} = \dfrac{65}{2} \end{array} \right]$ $i = \dfrac{96500 \times 10 \times 2}{65 \times 2 \times 60 \times 60} = 4.12$ ampere

Ex.12 How many hour are required for a current of 3.0 ampere to decompose 18 g water.

Sol. $H_2O \rightarrow H_2\ O_2$ $\left[\begin{array}{l} 2H^+ + 2e \rightarrow H_2 \\ O^{2-} \rightarrow \dfrac{1}{2}O_2 + 2e \end{array} \right]$

Therefore, Eq. of $H_2O = \dfrac{i.t}{96500}$ Equivalent weight of $H_2O = 18/2$ as two electrons are used for

1 mole H_2O to decompose in H_2 and O_2.

Therefore, $\dfrac{18}{18/2} = \dfrac{3 \times t}{96500}$

Therefore, t = 64333.3 sec = 1072.2 minute = 17.87 hr

Ex.13 Calculate the Avogadro's number using the charge on the electron 1.60×10^{-19} C and the fact that 96500 C deposits 107.9 g silver from its solution.

Sol. Q 96500 coulomb deposits 107.9 g Ag

Here eq. wt = Atomic weight

because Ag is monovalent. Thus 96500 coulomb charge means charge on N electrons

where N in Av. no.

Thus $N \times e = 96500$

$N = \dfrac{96500}{1.60 \times 10^{-19}}$

$= 6.03 \times 10^{23}$ electrons

Ex.14 Calculate the volume of gases liberated at anode and cathode at NTP from the electrolysis of Na_2SO_4(aq.) solution by a current of 2 ampere passed for 10 minute.

Sol. At cathode : $2H_2O + 2e \rightarrow H_2 + 2OH^-$

At anode : $2H_2O \rightarrow 4H^+ + 4e^- + O_2$

Therefore, At anode $E_{O_2} = \dfrac{32}{4} = 8$ Therefore, $w_{O_2} = \dfrac{E.i.t.}{96500} = \dfrac{32 \times 2 \times 10 \times 60}{4 \times 96500} = 0.0995$ g

At NTP : Volume of $O_2 = \dfrac{0.0995 \times 22.4}{32} = 0.0696$ litre

Similarly at cathode $w_{H_2} = \dfrac{E.i.t.}{96500} = \dfrac{2 \times 2 \times 10 \times 60}{2 \times 96500}$ = 0.0124 g

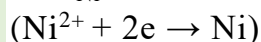At NTP : Volume of H_2 = $\dfrac{0.0124 \times 22.4}{2}$ = 0.139 litre

Ex.15 Fused $Ni(NO_3)_2$ is electrolysed between platinum electrodes using a current of 5 ampere for 20 minute. What mass of Ni is deposited at the cathode ?

Sol. Eq. of Ni deposited

$\dfrac{w}{E} = \dfrac{i.t}{96500} = \dfrac{5 \times 20 \times 60}{96500}$

= 0.0622

or w_{Ni} = 0.0622 × 58.71/2 = 1.825 g

$(Ni^{2+} + 2e \rightarrow Ni)$

Ex.16 A current of 3.7 ampere is passed for 6 hrs. between Ni electrodes in 0.5
litre of 2M solution of $Ni(NO_3)_2$. What will be the molarity of solution at the end of electrolysis ?

Sol. The electrolysis of $Ni(NO_3)_2$ in presence of Ni electrode will bring in following changes :

At anode : $Ni \rightarrow Ni^{2+} + 2e$

At cathode : $Ni^{2+} + 2e \rightarrow Ni$

Eq. of Ni^{2+} formed = Eq. of Ni^{2+} lost

Thus, there will be no change in conc. of $Ni(NO_3)_2$ solution during electrolysis i.e. ,

It will remain 2M

Ex.17 How long a current of 3 ampere has to be passed through a solution of $AgNO_3$ to coat a metal surface of 80 cm^2 with a thickness of 0.005 mm ?Density of Ag is 10.5 g cm^{-3}

Sol. Given , i = 3 ampere

Also Volume covered by

Ag = $80 \times 0.005 \times 10^{-1}$ cm^3 = 0.04 cm^3
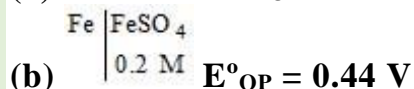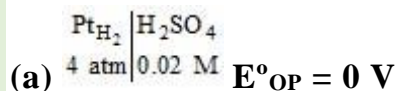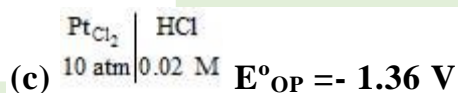
Therefore,Weight of Ag used = 0.04 × 10.5 g

$w_{Ag} = \dfrac{E.i.t.}{96500}$

$0.04 \times 10.5 = \dfrac{108 \times 3 \times t}{96500}$

Therefore,t = 125.09 sec.

Ex.18 Calculate e.m.f of half cells given below :

(a) $Pt_{H_2} \left| \begin{array}{c} H_2SO_4 \\ 4\ atm \end{array} \right| 0.02\ M$ E^o_{OP} = 0 V

(b) $Fe \left| \begin{array}{c} FeSO_4 \\ 0.2\ M \end{array} \right.$ E^o_{OP} = 0.44 V

(c) $Pt_{Cl_2} \mid HCl$ 10 atm | 0.02 M $E°_{OP} = -1.36$ V

Sol. (a) $H_2 \to 2H^+ + 2e$

Therefore, $E_{OP} = E°_{OP} - \dfrac{0.059}{2} \log \dfrac{[H^+]^2}{P_{H_2}}$ [H = 0.02 × 2M]

$= 0 - \dfrac{0.059}{2} \log \dfrac{(0.02 \times 2)^2}{4}$ $E_{OP_{H_2/H^+}} = 0.100$ V

(b) $Fe \to Fe^2\ 2e$ Therefore, $E_{OP} = E°_{OP} - \dfrac{0.059}{2} \log [Fe^2]$

$= 0.44 - \dfrac{0.059}{2} \log[0.2]$ $E_{OP_{Fe/Fe^{2+}}} = 0.4606$ volt.

(c) $2Cl^- \to Cl_2\ 2e$ Therefore, $E_{OP} = E°_{OP} - \dfrac{0.059}{2} \log \dfrac{P_{Cl_2}}{[Cl^-]^2}$

$= -1.36 - \dfrac{0.059}{2} \log \dfrac{10}{(0.02)^2}$ $E_{OP_{Cl^-/Cl_2}} = -1.49$ volt

Ex.19 If the oxidation of oxalic acid by acidified MnO_4^- solution were carried out in a reversible cell, what would be the electrode reaction ? Also calculate the equilibrium constant of the reaction. Given

$E°_{Mn^{7+}/Mn^{2+}} = \textbf{1.51 V and }$ $E°_{CO_2/C_2O_4^{2-}} = \textbf{-0.49 V.}$

Sol. $E°_{RP\ Mn^{7+}/Mn^{2+}} = 1.51$ V $E°_{OP\ Mn^{2+}/Mn^{7+}} = -1.51$ V

$E°_{RP\ CO_2/C_2O_4^{2-}} = -0.49$ V $E°_{OP\ C_2O_4^{2-}/CO_2} = 0.49$ V

More is $E°_{OP}$, more is the tendency to get oxidise

$C_2O_4^{2-} \to 2CO_2\ 2e$; $E°_{OP} = 0.49$ v $MnO_4^-\ 8H\ 5e \to Mn^2\ 4H_2O$; $E°_{RP} = 1.51$ V
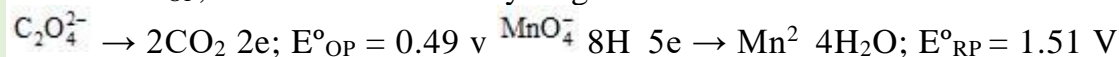
$2MnO_4^-\ 5C_2O_4^{2-}\ 16H \to 10CO_2\ 2Mn\ 8H_2O$; n = 10 Q 10 electron are used in redox change.

Therefore, $E°_{Cell} = E°_{OP}\ E°_{RP} = 0.49\ 1.51 = 2.0$ V Also $E° = \dfrac{0.059}{n} \log K_C$

Therefore, $2 = \dfrac{0.059}{10} \log K_C$ Therefore, $K_C = 10^{338.98}$

Ex.20 The e.m.f. of cell, $Ag|AgI_{(s)}$, 0.05 MKI || 0.05 M $AgNO_3$ | Ag, is 0.788 V.

Sol. K_{sp} of AgI = [Ag] [I⁻] = [Ag] [0.05]

For given cell $E_{Cell} = E_{OPAg}\ E_{RPAg}$ ....(i)

$= E_{OPAg/Ag^+} - \dfrac{0.059}{1} \log [Ag]_{L.H.S.}$ $E_{RP_{Ag^+/Ag}}\ \dfrac{0.059}{1} \log[Ag]_{R.H.S.}$ $E_{Cell} = \dfrac{0.059}{1} \log \dfrac{[Ag^+]_{R.H.S.}}{[Ag^+]_{L.H.S.}}$

$\left[\because E°_{OP_{Ag/Ag^+}} = E°_{RP_{Ag^+/Ag}}\right]$ $0.788 = \log \dfrac{0.05}{[Ag^+]_{LHS}}$ Therefore, $[Ag]_{L.H.S.} = 2.203 \times 10^{-15}$

By equation (i) $K_{sp} = [2.203 \times 10^{-15}] [0.05]$ $K_{spAgI} = 1.10 \times 10^{-16}$