3. Electrochemistry

Questions:

Que.-1 Arrange the following metals in order in which they displace each other from the solution of their salts.
Al, Cu, Fe, Mg and Zn.

Ans:

Mg, Al, Zn, Fe, Cu.

Que.-2 Given the standard electrode potentials.

$K^+/K = -2.93V$, $Ag^+/Ag = 0.80V$,
$Mg^{2+}/Mg = -2.37V$, $Hg^{2+}/Hg = 0.79V$,
$Cr^{3+}/Cr = -0.74V$

Arrange these metals in their increasing order of reducing power.

Ans:

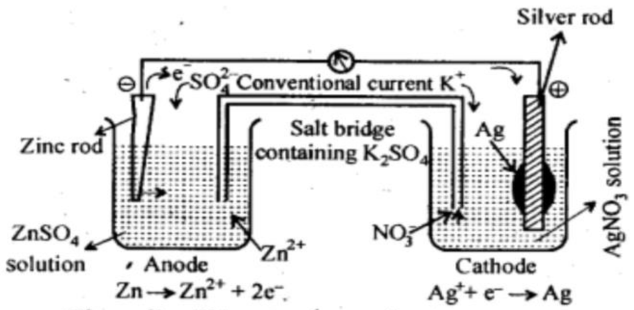
Metals with higher oxidation potential can easily be oxidised and have greater reducing power. Thus, increasing order of reducing power will be Ag<Hg<Cr<Mg<K.

Que.-3 Depict the galvanic cell in which the reaction
$Zn(s) + 2Ag^+(aq) \dashrightarrow Zn^{2+}(aq) + 2Ag(s)$ takes place. Further show:

i.)Which of the electrode is negatively charged?
ii.)The carries of the current in the cell.
iii.)Individual reaction at each electrode.

Ans:

i.) Anode, i.e. zinc electrode will be negatively charged.
ii.)The current will flow from silver to copper in the external circuit.
iii.)At anode: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
At cathode: $2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$
The setup will be similar as shown below:



The cell will be represented as:

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

Que.-4 In the button cells widely used in watches and other devices the following reaction takes place:

$Zn(s) + Ag_2O(s) + H_2O(l) \rightarrow Zn^{2+}(ag) + 2Ag(s) + 2OH^-(aq)$

Determine Δ_r G^- and E^- for the reaction.

Ans:

Zn is oxidised and Ag_2O is reduced:

$E^-_{cell} = E^-_{Ag2O,Ag(reduction)} - E^-_{Zn/Zn*2+(oxidation)}$

$= 0.344 + 0.76 = 1.104V$

Δ G = $-nFE_{cell}$ = -2 x 96500 x 1.104J

= -2.13 x 10^5J

Que.-5 Define conductivity and molar conductivity for the solution of an electrolyte. Discuss their variation with concentration.

Ans:

Conductivity (K): It is the conductance of unit cube of material.

SI unit is S/m. Common unit is S/cm.

The conductivity of an electrolytic solution always decreases with decrease in concentration that is on dilution. This is because with dilution, the degree of dissociation increases and the total no. of current carrying ions increases but the no. of ions per unit volume decreases.

Molar conductivity: It is the ratio of the electrolytic conductivity k to the molar concentration C of the dissolved electrolyte.

$\Lambda = k/C$

The SI unit of molar conductivity is S m^2/ mol

The common unit of molar conductivity is S cm^2/ mol

The molar conductivity of strong and weak electrolytes increases with a dilution. This is b/c with dilution, the degree of dissociation increases and the no. of current carrying ions increases.

Que.-6 The conductivity of 0.20M solution of KCl at 298K is 0.0248 S cm^{-1}. Calculate its molar conductivity.

Ans:

$$\Lambda_m = k \times 1000 / \text{molarity} = \frac{0.0248\,\text{Scm}^{-1} \times 1000\,\text{cm}^3\text{L}^{-1}}{0.20\,\text{molL}^{-1}}$$

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

Que.-7 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+}?

Ans:

i.) The electrode reaction is $Al^{3+} + 3e^- \rightarrow Al$

: Quantity of charge required for reduction of 1 mol of Al^{3+} = 3F = 3 x 95600C = 289500C.

ii.)The electrode reaction is $Cu^{2+} + 2e^- \rightarrow Cu$

: Quantity of charge required for the reduction of 1 mol of Cu^{2+} = 2F 2 x 95600C = 193000C.

iii.)The electrode reaction is $MnO_4^- \rightarrow Mn^{2+}$ I.e., $Mn^{7+} + 5e^- \rightarrow Mn^{2+}$

: Quantity of charge required = 5F = 5 x 95600C = 482500C.

Que.-8 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?

Ans:

i.) $Ca^+ + 2e^- \rightarrow Ca$

Thus, 1 mole of Ca i.e., 40g of Ca require = 2F electricity

: 20 g of Ca require = 1 F of electricity

ii.)$Al^{3+} + 3e^- \rightarrow Al$

Thus, 1 mole of Al i.e., 27g of Al require = 3 F electricity

: 40g of Al require electricity

= 3/27 x 40 = 4.44F of electricity.

Que.-9 How much electricity is required in coulomb for the oxidation of :

i.) 1 mol of H_2O to O_2?

ii.) 1 mol of FeO to Fe_2O_3?

Ans:

i.) The electrode reaction for 1 mole of H_2O is

$H_2O \rightarrow H_2 + ½ O_2$

i.e., $O^{2-} \rightarrow 1/2O_2 + 2e^-$

: Quantity of electricity required

= 2F = 2 x 96500 C = 193000 C

ii.)The electrode reaction for 1 mole of FeO is

$FeO + 1/2O_2 \rightarrow 1/2Fe_2o_3$

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

: Quantity of electricity required = 1F = 96500C.

Que.-10 A solution of $Ni(NO_3)_2$ is electrolysed b/w platinum electrodes using a current of 5 amperes for 20 minutes. What mass of Ni is deposited at the cathode?

Ans:

Quantity of electricity passed = (5A) X (20 x 60 sec) = 6000 C

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

Thus, 2F i.e., 2 x 96500 C of charge deposit = 1 mole of Ni = 58.7 g

: 6000 C of charge will deposit

= 58.7 x 6000/ 2 x 96500 C = 1.825g of Ni

Que.-11 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.

Ans:

i.) $AgNO_3(s) + aq \rightarrow Ag^+(aq) + NO_3^-(aq)$

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

At cathode : Ag^+ ions have lower discharge potential than H^+ ions. Hence, Ag^+ ions will be deposited as Ag in preference to H^+ ions:

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

At anode : As Ag anode is attacked by NO^-_3 ions, Ag of the anode will dissolve to form Ag^+ ions in the solution.

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

ii.)$AgNO_3$ with platinum electrodes:

At cathode: Ag^+ ions have lower discharge potential than H^+ ions. Hence, Ag^+ ions will be deposited as Ag in performance to H^+ ions.

At anode: As anode is not attackable, out of OH^- and NO_3^- ions, OH^- ions have lower discharge potential. Hence OH^- will be discharge in preference to NO_3^- ions, which than decompose to give out O_2.

$OH^-_{(aq)} \rightarrow OH + e^-$

$4OH \rightarrow 2H_2O_{(l)} + O_{2(g)}$

iii.)$H_2SO_{4(aq)} \rightarrow 2H^+_{(aq)} + SO_4^{2-}{}_{(aq)}$

$H_2O \rightarrow H + OH^-$

At cathode: $H^+ + e^- \rightarrow H$

$H + H \rightarrow H_{2(g)}$

At anode: $OH^- \rightarrow OH + e^-$

$4OH \rightarrow 2H_2O + O_{2(g)}$

Thus H_2 gases liberated at the cathode and O_2 gases at the anode.

iv.)$CuCl_{2(s)} + aq \rightarrow Cu^{2+}_{(aq)} + 2Cl^-_{(aq)}$

$H_2O \rightarrow H + OH^-$

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

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

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

$Cl^- \rightarrow Cl + e-$

$Cl + Cl \rightarrow Cl2(g)$

Thus, Cu will be deposited on the cathode and Cl2 gas will be liberated at the anode.

Que.-12 Conductivity of 0.00241 M acetic acid is 7.896 x 10^{-5} S cm^{-1}. Calculate its molar conductivity. If Λ^0_m for acetic acid is 390.5 S cm^2 mol^{-1}. What is its dissociation constant?

Ans:

Λ^c_m = k x 1000/ molarity

$$= \frac{(7.896 \times 10^{-5} S\ cm^{-1}) \times 1000 cm^{-1} L^{-1}}{0.00241\ mol\ L^{-1}}$$

$= 32.76\ S\ cm^2\ mol^{-1}$

$\alpha = \Lambda^c_{m/}\ \Lambda^0_m = 32.76/390.5 = 8.4 \times 10^{-2}$

$K_a = C\ \alpha^2/1 - \alpha = 0.0024 \times (8.4 \times 10^{-2})^2/1 - 0.084$

$= 1.86 \times 190^{-5}$

Que.-13 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 1.45g of silver deposited at the cathode of cell B. How long did the current flow? What mass of copper and zinc were deposited?

Ans:

Given: I = 1.5A, W = 1.5g of Ag, t = ?, E = 108, n = 1

Using Faraday's 1 st law of electrolysis W = Zit or W = E/nF It

or, t = 1.45 x 96500/ 1.5 x 108 = 863.73 seconds.

Now for Cu, W1 = 1.45g of Ag $E_1 = 108$, $W_2 = ?$

$E_2 = 31.75$

Form Faraday's 2nd law of electrolysis $W_1/W_2 = E_1/E_2$

$1.45/W_2 = 108/31.75$

: $W_2 = 1.45 \times 31.75/108 = 0.426$ g of Cu

Similarly, for Zn, $W_1 = 1.45$ g of Ag, $E_1 = 108$,

$W_2 = ?$, $E_2 = 32.65$

Using formula, $W_1/W_2 = E_1/E_2$

$1.45/W_2 = 108/32.65$

: $W_2 = 1.45 \times 32.65/ 108 = 0.438$ 0f Zn.

Que.-14 Calculate the standard cell potential of galvanic cell in which the following reactions take place:

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

ii.) $Fe^{2+}(aq) + Ag^{+}(aq) \rightarrow Fe^{3+}(aq) + Ag(s)$

Calculate the $\Delta_r G^-$ and equilibrium constant of the reactions.

Ans:
i.) $E^{-}cell = E^{-}$ cathode – E^{-} anode
= -0.40V – (-0.74V) = 0.34V
$\Delta_r G^0 = nFE^{-}_{cell}$
= -6 x 96500 C mol^{-1} x 0.34V
= -196860 CV mol^{-1}
= -196860 J mol^{-1}
= -19.86 kJ mol^{-1}
- $\Delta_r G^0$= 2.303 X 8.314 X 298 log K
196860 = 2.303 x 8.314 x 298 log K
Or log K = 34.5014
K = Antilog 34.5014 = 3.172 x 10^{34}
ii.)E^{-}_{cell} = + 0.80 V – 0.77 V = + 0.03 V
$\Delta_r G^0 = nFE^{-}_{cell}$
= -1 x (96500 CV mol^{-1}) x (0.03V)
= -2.895 C V mol^{-1} = -2895 J mol^{-1} = -2.895 k$Jmol^{-1}$
$\Delta_r G^0$ = 2.303 RT log K
-2895 = - 2.303 x 8.314 x 298 x log K
Or log K = 0.5074
Or K = Antilog (0.5074) = 3.22

Que.-15 The resistance of a conductivity cell containing 0.001M KCl solution at 298K is 500ohm. What is the cell constant if conductivity of 0.001M KCl solution at 298 K is 0.146 x 10^{-1}.

Ans:
Cell constant = Conductivity/ Conductance
= Conductivity x Resistance
= 0.146 x 10^{-3} S cm^{-1} x 1500 ohm
= 0.218 cm^{-1}

Que.-16 The conductivity of sodium chloride at 298K has been determined at different concentrations and the result are given below:

Concentration/M	**0.001**	**0.010**	**0.020**	**0.050**	**0.100**
10^2 x k/S m^{-1}	**1.237**	**11.85**	**23.15**	**55.53**	**106.74**

Calculate Λ_m for all concentrations.

Ans:
1S cm^{-1}/100S m^{-1} = 1 (unit conversion factor)

Concentration (M)	K(Sm^{-1})	K(S cm^{-1})	Λ_m = 1000 x k/Molarity (Scm^2 mol^{-1})	$C^{1/2}$ ($M^{1/2}$)
10^{-3}	1.237 x 10^{-2}	1.237 x 10^{-4}	1000 x 1.237 x $10^{-4}/10^{-3}$ = 123.7	0.0316
10^{-2}	11.85 x 10^{-2}	11.85 x 10^{-4}	1000 x 11.85 x $10^{-4}/10^{-2}$=1118.5	0.100
2 x 10^{-2}	23.15 x 10^{-2}	23.15 x 10^{-4}	1000 x 23.15 x $10^{-4}/10^{-2}$ x 2 = 115.8	0.141
5 x 10^{-2}	55.53 x 10^{-2}	55.53 x 10^{-4}	1000 x 55.53 x 10^{-4}/5 x 10^{-2} = 111.1	0.224
10^{-1}	106.74 x 10^{-2}	106.74 x 10^{-4}	1000 X 106.74 x $10^{-4}/10^{-1}$ = 106.7	0.316

Que.-17 Using the standard electrode potentials given in chapter (table-3.1). Predict if the reaction b/w the following is feasible:

- **i.) Fe^{3+}(aq) and I^-(aq)**
- **ii.) Ag^+(aq) and Cu(s)**
- **iii.) Fe^{3+}(aq) and Br^-(aq)**
- **iv.) Ag(s) and Fe^{3+}(aq)**
- **v.) Br_2(aq) and Fe^{2+}(aq).**

Ans:

The reaction is feasible if the emf of the cell reaction is positive.

i.) $Fe^{3+}_{(aq)} + I^-_{(aq)} \rightarrow Fe^{2+}_{(aq)} + ½ I^2(g)$

i.e., $Pt/I_2/I^-_{(aq)}||Fe^{3+}_{(aq)}|Fe^{2+}_{(aq)}|Pt$

$:E^-_{cell} = E^-_{Fe3+,Fe2+} = E^-_{1/2I2,I-}$

= 0.77 – 0.54 = 0.23 V (Feasible)

ii.) $2Ag^+_{(aq)} + Cu_{(s)} \rightarrow 2Ag_{(s)} + Cu^{2+}_{(aq)}$

i.e., $Cu|Cu^{2+}_{(aq)} || Ag^+_{(aq)}|Ag$

$E^-_{cell} = E^-_{Ag+, Ag} – E^-_{Cu2+, Cu}$

= 2.80 – 0.34 = 0.46 V(Feasible)

iii.) $Fe^{3+}_{(aq)} + Br^{-}_{(aq)} \rightarrow Fe^{2+}_{(aq)} + 1/2Br_{2(g)}$

$E^{-}_{cell} = 0.77 – 1.09 = -0.32V$ (not feasible)

iv.) $Ag_{(s)} + Fe^{3+}_{(aq)} \rightarrow Ag^{+}_{(aq)} + Fe^{2+}_{(aq)}$

$E^{-}_{cell} = 0.77 – 0.80 = -0.03V$ (Not feasible)

v.) $\frac{1}{2} Br_{2(g)} + Fe^{2+}_{(aq)} \rightarrow Br^{-}_{(aq)} + Fe^{3+}_{(aq)}$

$E^{-}_{cell} = 1.09 – 0.77 = 0.32V$(Feasible)