

# ELECTRO CHEMISTRY

## Short Answer Questions:

**\*1. Give the applications of Kohlrausch law of independent migration of ions?**

**Ans. I. Calculation of molar conductivities of weak electrolytes at infinite dilution:**

Kohlrausch law is helpful in determining the limiting molar conductivities of weak electrolyte. The value of  $\Lambda_m^\infty$  of weak electrolyte cannot be determined directly by the extrapolation of plot of  $\Lambda_m$  versus  $\sqrt{c}$ . But this can be easily calculated with the help of Kohlrausch law.

For example, the value of  $\Lambda_m^\infty$  for acetic acid can be calculated from the knowledge of the molar conductivities at infinite dilution of strong electrolytes like  $CH_3COONa$ ,  $HCl$  and  $NaCl$  as follows -

$$\Lambda_{m(CH_3COOH)}^\infty = \lambda_{CH_3COO^-}^\infty + \lambda_{H^+}^\infty$$

Now add and subtract  $\lambda_{Na^+}^\infty$  and  $\lambda_{Cl^-}^\infty$  to the expression on the right hand side and rearrange thus,

$$\begin{aligned} \Lambda_{m(CH_3COOH)}^\infty &= \Lambda_{m(CH_3COONa)}^\infty + \Lambda_{m(HCl)}^\infty - \Lambda_{m(NaCl)}^\infty \\ &= [\lambda_{CH_3COO^-}^\infty + \lambda_{Na^+}^\infty] + [\lambda_{H^+}^\infty + \lambda_{Cl^-}^\infty] - [\lambda_{Na^+}^\infty + \lambda_{Cl^-}^\infty] \\ &= \lambda_{CH_3COO^-}^\infty + \lambda_{H^+}^\infty \end{aligned}$$

**II. Calculation of dissociation constant of weak electrolyte:**

Dissociation constant of weak electrolyte can be calculated by knowing its degree of dissociation.

for a binary electrolyte AB, dissociation constant K is related to degree of dissociation as  $K = \frac{C\alpha^2}{1-\alpha}$

$$\text{But } \alpha = \frac{\Lambda_m^C}{\Lambda_m^\infty}, \quad K = \frac{C \left( \frac{\Lambda_m^C}{\Lambda_m^\infty} \right)^2}{1 - \frac{\Lambda_m^C}{\Lambda_m^\infty}} = \frac{C(\Lambda_m^C)^2}{\Lambda_m^\infty(\Lambda_m^\infty - \Lambda_m^C)}$$

**\*2. What is electrolysis? Give Faraday's First and second laws of electrolysis?**

**Ans.** The decomposition of a chemical compound in the molten state (or) in the solution state into constituent elements under the influence of an applied EMF is called electrolysis.

**Ex.** When molten NaCl is electrolysed by applying an EMF, it decomposes into sodium metal and  $Cl_2$  gas at the respective electrodes.

**First Law:** It states that "The amount of substance liberated, deposited (or) dissolved at an electrode during the electrolysis of an electrolyte is directly proportional to the quantity of electricity passed through the electrolyte.

If  $m$  = mass of the substance in grams liberated (or) deposited (or) dissolved

$Q$  = quantity of electricity in coulombs, then

$$m \propto Q \quad \text{Or} \quad m = e Q$$

Where 'e' is the electrochemical equivalent. But  $Q = i \times t = \text{current (amp)} \times \text{time (seconds)}$

$$\therefore m = e \times i \times t$$

**Second Law:** If the same quantity of electricity is passed through different electrolytes, then the weight of substances deposited at the respective electrodes are in the ratio of their chemical equivalents.

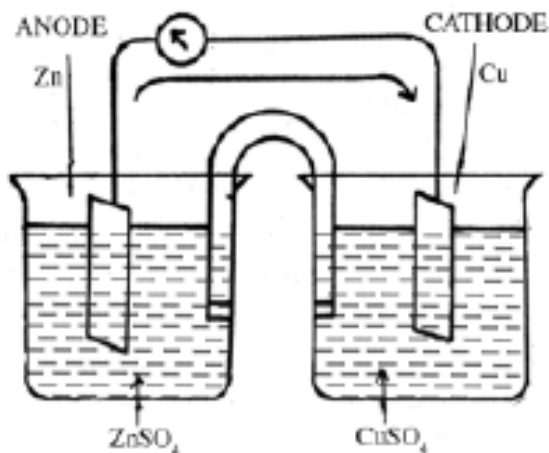
Let the weight of the substance 'A' be  $w_A$  and equivalent weight of 'A' be  $E_A$ . Let the weight of the substance, 'B' be  $w_B$  and equivalent weight of 'B' be  $E_B$ . Then, according to the second law,

$$\frac{w_A}{w_B} = \frac{E_A}{E_B} \quad \text{or} \quad \frac{w_A}{E_A} = \frac{w_B}{E_B}$$

**\*\*3. What are galvanic cells? Explain the working of a galvanic cell with neat sketch taking Daniel cells as example?**

**Ans. Galvanic cell:** A galvanic cell is an electro chemical cell that converts the chemical energy of a spontaneous red-ox reaction into electrical energy.

Daniel cell is an example of galvanic cells



### Working of Daniel cell:

'Zn' rod dipped in  $ZnSO_{4(aq)}$  solution act as 'anode' (-ve electrode)

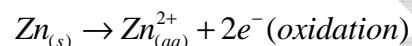
'Cu' rod dipped in  $CuSO_{4(aq)}$  solution act s 'cathode' (+ve electrode)

Both the electrolytic solutions are connected through a 'salt bridge'

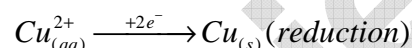
The 'Zn' rod and 'Cu' rod are connected through a metallic wire externally.

Now anodic and cathodic reactions occurs as shown below and hence potential difference between electrodes arises which is taken as the electrode potential of the Daniel cell

### Anode (-ve Electrode):



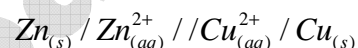
### Cathode (+ve electrode):



i) In the construction of the Daniel cell, oxidation half-cell is written on the left hand side and then reduction half-cell is written on the right hand side

ii) In both sides metal and metal ion are separated by single slash (/)

iii) Both half cells are separated by double slash (//) that is known as salt bridge the cell construction of Daniel cell having salt bridge is



The emf of the cell is calculated by the following formula

$$E_{cell} = E_{cell}^0 - \frac{0.059}{2} \log \left[ \frac{Zn^{2+}}{Cu^{2+}} \right]$$

**4. State and explain Nernst equation with the help of a metallic electrode and a non metallic electrode?**

**Ans. Nernst equation:** An equation used to calculate the potential of metal or a non-metal single electrode at any concentration measured with respect to standard hydrogen electrode is called Nernst equation

**For metal single electrode:** Suppose zinc single electrode is taken in a known concentration (activity) of  $ZnSO_{4(aq)}$  solution and is galvanized with standard hydrogen electrode, then the single electrode potential of metal (zinc) single electrode is calculated by the following formula.

$$E_{M^{n+}/M} = E_{M^{n+}/M}^0 - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]} \Rightarrow E_{Zn^{2+}/Zn} - \frac{RT}{nF} \ln \frac{[Zn]}{[Zn^{2+}]}$$

$$\Rightarrow E_{Zn^{2+}/Zn} = E_{Zn^{2+}/Zn}^0 + \frac{RT}{nF} \ln [Zn^{2+}] \quad (Q [Zn] = 1)$$

$$= E_{Zn^{2+}/Zn}^e + \frac{2.303RT}{nF} \log_{10} [Zn^{2+}]$$

$$\therefore E_{Zn^{2+}/Zn} = E_{Zn^{2+}/Zn}^e + \frac{2.303RT}{nF} \log_{10} [Zn^{2+}]$$

$$(\therefore \text{By substituting R, T, F values } \frac{2.303RT}{F} = 0.059)$$

**For non-metal single electrodes:** Suppose chlorine over pt-electrode (non-metal electrode) is taken in a known concentration of  $HCl_{(aq)}$  solution and is galvanized with standard hydrogen electrode is calculated by the following formula

$$E_{M^{n-}/M} = E_{M^{n-}/M}^0 - \frac{RT}{nF} \ln \frac{[M^{n-}]}{[M]}$$

$$\Rightarrow E_{Cl^- / \frac{1}{2}Cl_2, pt} = E_{Cl^- / \frac{1}{2}Cl_2, pt}^0 - \frac{RT}{nF} \ln \frac{[Cl^-]_{(aq)}}{[Cl_2]}$$

$$\Rightarrow E_{Cl^- / \frac{1}{2}Cl_2, pt}^0 - \frac{RT}{nF} \ln [Cl^-]_{(aq)} \quad [Q [Cl_2] = 1]$$

$$= E_{Cl^- / \frac{1}{2}Cl_2, pt}^0 - \frac{2.303RT}{nF} \log_{10} [Cl^-]_{(aq)}$$

$$= E_{Cl^- / \frac{1}{2}Cl_2, pt}^0 - \frac{0.059}{n} \log_{10} [Cl^-]_{(aq)}$$

$$\therefore E_{Cl^- / \frac{1}{2}Cl_2, pt} = E_{Cl^- / \frac{1}{2}Cl_2, pt}^0 - \frac{0.059}{1} \log_{10} [Cl^-]_{(aq)}$$

$$\therefore E_{Cl^- / \frac{1}{2}Cl_2, pt} = E_{Cl^- / \frac{1}{2}Cl_2, pt}^0 - 0.059 \log_{10} [Cl^-]_{(aq)}$$

5. What are the primary and secondary batteries? Give one example for each?

**Ans. Primary cell (or) Battery:** 'The battery after its use over a period of time become dead and the cell reaction is completed and this can't be reused again is called primary battery.

(Or)

'The battery which is not previously charged up from an external source of current (electricity) but gives the electrical energy by the red-ox reaction of chemical (electrolyte) in it is called primary battery.

In primary batteries there is a regular decrease in the potential and after a long period the potential of the battery becomes zero

**Ex:** Dry cell (Leclanche cell), mercury cell

**Secondary Battery:** A battery in which both charging and discharging takes place is called secondary battery. It can be recharged and used again

During charging it acts as electrolytic cell.

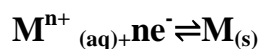
During the discharging it act as an electro chemical cell

Secondary battery produces a constant voltage containing electricity during the discharge

**Ex:** Lead storage battery, nickel – cadmium cell.

## Very Short Answer Questions

1. What is Nernst equation? Write the equation for an electrode with electrode reaction



**Ans. Nernst equation:** An equation used to calculate the potential of metal or a non-metal single electrode, at any concentration measured with respect to standard hydrogen electrode is called Nernst equation.

**Nernst equation** for an electrode with electrode reaction  $M^{n+}{}_{(aq)} + ne^{-} \rightleftharpoons M_{(s)}$  is

$$E_{M^{n+}/M} = E_{M^{n+}/M}^0 + \frac{2.303RT}{nF} \log[M^{n+}]$$

\*2. How is Gibbs free energy related to the emf of the cell mathematically?

**Sol. Gibbs free energy related to the emf of the cell**  $\Delta_r G^{\circ} = -nFE_{\text{cell}}^{\circ}$

Where  $\Delta_r G^{\circ}$  is standard Gibbs energy of the reaction.

$E_{\text{cell}}^{\circ}$  = emf of the cell and  $nF$  = charge passed.

3. Define conductivity of a material .Give its SI units?

**Ans. Conductivity ( $\kappa$ ):** The inverse of resistivity ( $\rho$ ) is called conductivity.

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

[G = conductance,  $l$  = length, A = cross-section area, R = resistance]

If  $l = 1 \text{ cm}$  and  $A = 1 \text{ cm}^2$ , then  $\kappa = G$ .

So, conductivity of an electrolytic solution may be defined as the conductance of a solution of  $1 \text{ cm}$  length with area of cross-section equal to  $1 \text{ cm}^2$ . Its unit is  $\text{ohm}^{-1}$  or  $\text{S cm}^{-1}$ .

#### 4. Define molar conductivity and how it is related to Conductivity?

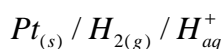
**Ans.** Molar conductivity ( $\Lambda_m$ ) : Molar conductivity of a solution at a given concentration is the conductance of the volume (V) of solution containing one mole of electrolyte kept between two electrodes with area of cross section A and at a distance of unit length.

$$\Lambda_m = \frac{\kappa A}{l}$$

Its unit is  $\text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  or  $\text{S cm}^2 \text{ mol}^{-1}$ .

#### 5. What is a standard hydrogen electrode?

**Ans.** The standard hydrogen electrode consists of a platinum electrode coated with platinum black. The electrode is dipped in a solution of acid (usually  $1 \text{ M HCl}$ ) and pure  $\text{H}_2$  gas is bubbled through it at one atmospheric pressure (or  $1 \text{ bar}$ ) and the concentration of  $\text{H}^+$  is unity ( $1 \text{ M}$ ). This electrode is known as standard hydrogen electrode (S.H.E)



#### \*6. What is a fuel cell? How it is different from a conventional galvanic cell?

**Ans.** Galvanic cells that convert energy of combustion of fuels like hydrogen, methane, methanol etc directly into electrical energy are called fuel cells.

Conventional method of converting chemical energy into electrical energy involves three steps.

**Step I:** Chemical energy  $\longrightarrow$  Heat energy

**Step II:** Heat energy  $\longrightarrow$  Mechanical energy

**Step III:** Mechanical energy  $\longrightarrow$  Electrical energy

The extent of heat converted into mechanical energy (step II) is limited. Hence the Conventional methods are with only 40% efficiency. But in a fuel cell chemical energy is directly converted into electrical energy with a theoretical 100% efficiency.

#### 7. Give the electrode reactions occurring at anode and cathode in $\text{H}_2$ - $\text{O}_2$ fuel cell?

**Ans.** The electrode reactions in  $\text{H}_2$ -  $\text{O}_2$  fuel cell are

**At cathode (reduction):**  $O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-_{(aq)}$

**At anode (oxidation):**  $2H_{2(g)} + 4OH^-_{(aq)} \rightarrow 4e^- + 4H_2O_{(l)}$

The overall reaction is:  $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$

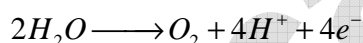
**\*8. What is metallic corrosion? Give one example?**

**Ans.** Natural tendency of conversion of a metal into its mineral compound on interaction with environment is known as corrosion.

**E.g.:** Rusting of iron ( $Fe_2O_3 \cdot xH_2O$ ), tarnishing of silver ( $Ag_2S$ ) and development of green coating on Copper ( $CuCO_3$ ) etc.

**9. Give the chemical reaction corresponding to the oxidation and reduction of liquid water at platinum electrodes?**

**Ans.** The chemical reaction corresponding to the oxidation of liquid water at platinum electrodes is



The chemical reaction corresponding to the reduction of liquid water at platinum electrodes is



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

**Ans.** Quantity of charge (Q) passed = Current (C) X Time (t)

$$= (0.5 \text{ A}) \times (2 \times 60 \times 60 \text{ s})$$

$$= 3600 \text{ Ampere sec} = 3600 \text{ C.}$$

Number of electrons flowing through the wire on passing charge of one Faraday

i.e.  $96500 \text{ coulombs} = 6.023 \times 10^{23}$

Number of electrons flowing through the wire on passing a charge of 3600 coulombs is.

$$= \frac{6.022 \times 10^{23} \times (3600 \text{ C})}{(96500 \text{ C})} = 2.246 \times 10^{22}$$



∴ Number of electrons =  $2.246 \times 10^{22}$ .

11. The molar conductivity of  $0.025 \text{ mol L}^{-1}$  methanoic acid is  $46.1 \text{ S cm}^2 \text{ mol}^{-1}$ . Calculate its degree of dissociation and dissociation constant.

Given,  $\lambda^\circ(\text{H}^+) = 349.6 \text{ S cm}^2 \text{ mol}^{-1}$  and  $\lambda^\circ(\text{HCOO}^-) = 54.6 \text{ S cm}^2 \text{ mol}^{-1}$ .

Ans. Calculation of degree of dissociation ( $\alpha$ ) of HCOOH

$$\Lambda_m^c = 46.1 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\Lambda_m^\circ(\text{HCOOH}) = \lambda_m^\circ(\text{HCOO}^-) + \lambda_m^\circ(\text{H}^+) = (54.6 + 349.6) \text{ S cm}^2 \text{ mol}^{-1} = 404.2 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^\circ} = \frac{(46.1) \text{ S cm}^2 \text{ mol}^{-1}}{(404.2) \text{ S cm}^2 \text{ mol}^{-1}} = 0.1140.$$

Calculation of dissociation constant



Initial conc.	C	0	0
Equilibrium conc.	$C(1-\alpha)$	$C\alpha$	$C\alpha$

$$\text{Dissociation constant, } K_a = \frac{[\text{HCOO}^-][\text{H}^+]}{[\text{HCOOH}]} = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$$

$$\text{Placing values, } K_a = \frac{(0.025 \text{ mol L}^{-1}) \times (0.114)^2}{(1-0.114)} = 3.67 \times 10^{-4} \text{ mol L}^{-1}$$

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