ELECTROCHEMISTRY

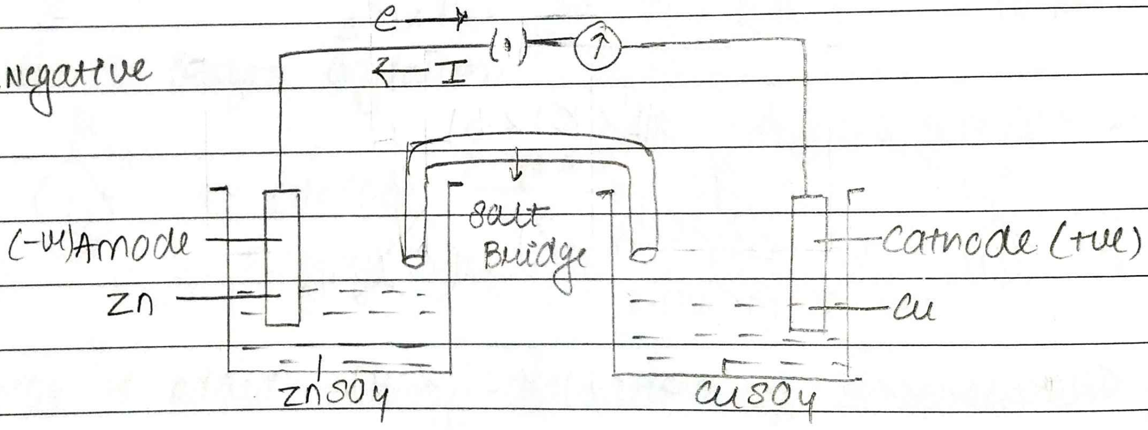
1. A galvanic cell has electrical poential of 1.1 V. What will happen to the cell reaction and current flowing through the cell?

i) An opposing poential of 1.1 V
ii) Opposing poential > 1.1 V is applied?

i) Cell reaction stops completely and no current will flow through the cell.
ii) Electrochemical cell will now work as electrolytic cell, current starts flowing in opposite direction.

- Electrochemical cell converts chemical energy into electrical energy.

Oxidation, Negative
L O A N
Left, Anode



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

Reaction at anode - $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$
Reaction at cathode - $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

2. Write the function of salt bridge?

1. It completes the electrical circuit of electrolytes.
2. It maintains the electrical neutrality of the two half cells by providing ions.

3. Define electrode potential?
The potential difference between the electrode and the electrolyte which is called electrode potential.

Representation of electrochemical cell

Anode ~~Cathode~~ || cathode ~~Anode~~

$Zn_{(s)} | Zn^{2+}_{(aq)} || Cu^{2+}_{(aq)} | Cu_{(s)}$

4. Define cell potential?
The difference between the electrode potential of the two electrodes constituting an electrochemical cell is known as emf or cell potential.

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$ E°_{cell} - standard cell potential

- Electrochemical series

Li
K
Ca
Na
Mg
Al
Zn
Fe
H — 0
Pb
Cu
Ag
Au

Li to Fe: -ve value of reduction potential (Reducing agent) (Oxidise easily)

More -ve value of redn potential it oxidises easily.

More +ve value of redn potential it reduces easily

Pb to Au: +ve value of reduction potential (Oxidising agent) (Reduces easily)

-ve value decreases and oxidising power increases and reducing power decreases

5. Write the uses of electrochemical cell?

i) used for determining the pH of solutions

ii) solubility product

iii) equilibrium constant

iv) for potentiometric titrations.

Nernst equation

$$E_{cell} = E^\circ_{cell} - \frac{2.303RT}{nF} \log \frac{[Anode]}{[Cathode]}$$

At 298 K

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log \frac{[Anode]}{[Cathode]}$$ n- number of electron involved.

At equilibrium

$E_{cell} = 0$

$$\therefore E^\circ_{cell} = \frac{0.0591}{n} \log K_c$$ K_c- Equilibrium constant

$\Delta G = -nFE_{cell}$ ΔG - Extensive (value depends on n)

E_{cell} - Intensive (value does not depend on n)

$\Delta G = -2.303RT \log K_c$

Resistance (R) $= \rho \frac{l}{A}$ S.I unit Ω

Resitivity (ρ) $= \frac{RA}{l}$ S.I unit Ωm

$1 \Omega m = 100 \Omega cm$

Conductance (G) $= \frac{1}{R} = \frac{1}{\rho} \frac{A}{l} = K \frac{A}{l}$ unit Ω^{-1}, Siemen (S)

$$\boxed{G = \frac{KA}{l}}$$

Conductivity $(K) = \frac{1}{P} = \frac{l}{RA}$ unit $\Omega^{-1}m^{-1}$, Scm^{-1}

$1 Scm^{-1} = 100 Sm^{-1}$

$R = \frac{l}{KA}$

$\frac{l}{A} = G^*$

$\therefore R = \frac{G^*}{K}$ $\boxed{G^* = KR}$ G^* - Cell constant

unit - m^{-1} etc.

6. Define molar conductivity.
It is define as the conducting power of all the ions produce by dissolving one mole of an electrolyte.

$\Lambda m = \frac{K}{C}$ C - Concentration K - Conductivity

$$\Lambda m (Sm^2mol^{-1}) = \frac{K(Sm^{-1})}{1000 Lm^{-3} \times M (mol L^{-1})}$$

$$\Lambda m (Scm^2 mol^{-1}) = \frac{K (Scm^{-1}) \times 1000 cm/L}{M (mol L^{-1})}$$

7. Variation of conductivity on dilution.
Conductivity always decreases with decrease in concentration for both strong and weak electrolyte because the number of ions per unit volume that carry the current in a solution decreases on dilution.

8. Variation of molar conductivity on dilution

i) ~~Fron~~ for strong electrolyte

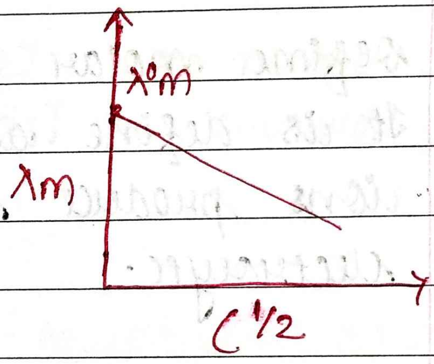
ii) For weak electrolyte.

i) Molar conductivity increases with dilution because the total volume V of a solution containing one mole of electrolyte increases.

$$\lambda m = KV$$

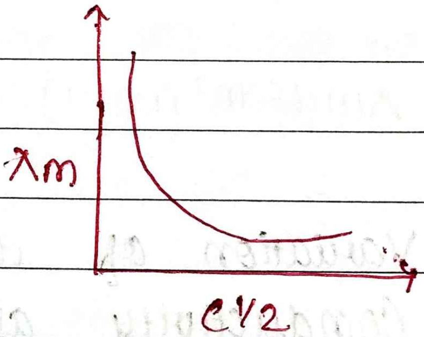
i) For strong electrolyte, molar conductivity increases slowly with dilution.

$$\lambda_m = \lambda^\circ_m - AC^{1/2}$$



ii) For weak electrolyte, molar conductivity increases on dilution because with increase in dilution the degree of dissociation increases.

$$\alpha = \frac{\lambda^c_m}{\lambda^\circ_m}$$



α - Degree of dissociation

λ^c_m - Molar conductivity at any concentration.

9. Define limiting molar conductivity

The limiting molar conductivity of an electrolyte is defined as its molar conductivity when the concentration of the electrolyte in the solution approaches zero.

10. State Kohlrausch law :

It states that at infinite dilution when the dissociation is complete each ion makes a definite contribution towards molar conductivity of the electrolyte irrespective of the nature of other ion with which it is associated.

$$\lambda^\circ = +ve\ \lambda^\circ + \ + \ -ve\ \lambda^\circ -$$

11. Calculate $\lambda^\circ m$ for $CaCl_2$ and $MgSO_4$.

$\lambda^\circ m\ (CaCl_2) = \lambda^\circ Ca^{2+} + 2\lambda^\circ Cl^-$

$= 119.0\ Scm^2 mol^{-1} + 2(76.3)\ Scm^2 mol^{-1}$

$= 119.0 + 152.6 = 271.6\ Scm^2\ mol^{-1}$

$\lambda^\circ m\ (MgSO_4) = \lambda^\circ_{Mg^{2+}} + \lambda^\circ_{SO_4^{2-}}$

$= 106.0\ Scm^2 mol^{-1} + 160.0\ Scm^2 mol^{-1}$

$= 266\ Scm^2 mol^{-1}$

12. $\lambda^\circ m$ for NaCl, HCl and NaAc are 126.4, 425.9 and 91.0 $Scm^2 mol^{-1}$ respectively. Calculate λ° for HAc

$\lambda^\circ(HAC) = \lambda^\circ_{H^+} + \lambda^\circ_{AC} = \lambda^\circ_{HCl} + \lambda^\circ_{NaAC} - \lambda^\circ_{NaCl}$

$= 425.9 + 91.0 - 126.4$

$= 390.5\ Scm^2 mol^{-1}$

$$K_a = \frac{C\alpha^2}{(1-\alpha)} = \frac{C(\lambda^c)^2}{\lambda^\circ(\lambda^\circ - \lambda^c)}$$ where Ka - Dissociation constant

13. State Faraday's laws of electrolysis

Faraday's first law - The amount of any substance deposited or liberated at any electrode is directly proportional to the amount of electricity pass through the electrolytic solution.

$$w = ZQ$$

- Faraday's second law - when same quantity of electricity is passed through different electrolytic solutions connected in series the weights of the substance produced at the electrode are directly proportional to their chemical equivalent weight.

$$\frac{\text{Amount of } 1^{st} \text{ substance deposited}}{\text{Amount of } 2^{nd} \text{ substance deposited}} = \frac{\text{Eq wt of } 1^{st}}{\text{Eq wt of } 2^{nd}}$$

- Charge on one mole of e^- is called one Faraday.

1 mole of e^- = 1 Faraday = 96500 C

14. How many coulombs are required to deposit 50g of aluminium when the electrode reaction is

$Al^{3+} + 3e^- \rightarrow Al$

1 mole of Al = 27g

27g of Al = 3x96500 C

$$50g \text{ of Al} = \frac{\overset{1}{\cancel{3}} \times 96500 \times 50g}{\cancel{27}\,9}$$

$$= \frac{4825000}{9} = 525000\ C$$

15. How many electrons flow through a metallic wire if a current of 0.5A is passed for 2hour?

Q = ixt

= 0.5 x 2 x 60 x 60 = 30 x 2 x 60 = 8600 C

96500 C deposite ^{1} mole

$$3600\ C = \frac{36\cancel{0}\cancel{0}}{965\cancel{0}\cancel{0}} = 0.037\ mol$$

$1\ mol = 6.023 \times 10^{23}\ e^-$

$0.037\ mole = 0.037 \times 6.023 \times 10^{23}\ e^-$

$= 22.46 \times 10^{21}$ electrons.

16. A steady current of 2 amperes was passed through two electrolytic cells X and Y connected in series containing electrolytes $FeSO_4$ and $ZnSO_4$ until 2.8g of Fe deposited at the cathode of cell X. How long did the current flow? Calculate the mass of Zn deposited at the cathode of cell Y.

(Molar mass of Fe = 56 g, Zn = 65.3 g, 1F = 96500 C)

17. There are two possible reactions for cathode in the electrolysis of aqueous $ZnCl_2$:

$Zn^{2+} + 2e^- \rightarrow Zn$ $E = -0.76\ V$

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ $E = -0.83\ V$

At cathode higher value of $E^\circ cell$ will be preferred so $Zn^{2+} + 2e^- \rightarrow Zn$ reaction will take place at cathode.

18. On the basis of E° values, O_2 gas should be liberated at anode but is Cl_2 gas which is liberated in the electrolysis of aqueous NaCl.
For the substance to be deposited at anode it should have low value of E° but due to overpoential of O_2, Cl_2 gas will be liberated at anode.

19. Write the difference between primary and secondary battery?

	Primary battery		Secondary battery
1.	Reactions occur only once. and cannot be reused again	1.	can be recharged by passing current, can be used again.
2.	Ex- Leclanche cell.	2.	Ex- Lead storage battery

20. A Leclanche cell is also called dry cell. why?
Leclanche cell consist of zinc anode and carbon cathode. The electrolyte is a moist paste of MnO_2, $ZnCl_2$, NH_4Cl and carbon black. Because there is no free liquid in the cell it is called dry cell.

Leclanche cell is used in transistors and clocks

Reaction at anode : $Zn \rightarrow Zn^{2+} + 2e^-$

Reaction at cathode : $MnO_2 + NH_4^+ + e^- \rightarrow MnO(OH) + NH_3$

21. Name the cell used for low current devices like hearing aids , watches etc. Also give the half cell reactions for such a cell?

Mercury cell .

Reaction at anode : $Zn(Hg) + 2OH^- \rightarrow ZnO + H_2O + 2e^-$

Reaction at cathode : $HgO + H_2O + 2e^- \rightarrow Hg + 2OH^-$

22. Why is the voltage of a mercury cell constant during its working ?

Because as all the products and reactants are in solid or liquid state, their concentration does not change with the use .

28. Write the reaction taking place during charging and discharging of lead storage battery ?

Lead storage battery is used in automobiles and invertors .

during discharging

Reaction at anode : $Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^-$

Reaction at cathode : $PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O$

during charging

$2PbSO_4 + 2H_2O \rightarrow Pb + PbO_2 + 2H_2SO_4$

24. What are fuel cells ?

Fuel cell is the cell which converts the energy of combustion of fuels directly into electrical energy .

25. Write the reaction taking place at fuel cell?

Reaction at anode: $2H_2 + 4OH^- \longrightarrow 4H_2O + 4e^-$

Reaction at cathode: $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$

26. Write the advantages of using fuel cell over other cells?

1. High efficiency
2. Continuous source of energy
3. Pollution free

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

Methane, Methanol.

28. What do you understand by corrosion.

It is an electrochemical phenomenon in which metal gets decomposed in the presence of air and water and forms compound like oxide.

29. Rusting of iron is quicker in saline water than in ordinary water. Explain.

Saline water consist of greater number of ions than normal water which increases the electrochemical reaction.

30. Name the two metals that can be used for cathodic protection of iron?

Magnesium and zinc