Unit 4: Electrochemistry

Syllabus

☐ Introduction
☐ Electrolysis; strong and weak electrolyte
☐ Arrehenius theory of ionization
☐ Faraday's laws of electrolysis
☐ Criteria of product formation during electrolysis
☐ Electrolytic conduction, equivalent and molar conductivities
☐ Variation of conductivity with concentration
☐ Electrode potential, standard electrode potential, standard hydrogen electrode and its applications
☐ Eletrochemical series and its use to predict the feasibility of redox reactions
☐ Electrochemical cell (Galvanic cell)
☐ EMF of electrochemical cell in the standard state (Solving related numerical problems)

Some important terms, concepts and formulae

1. **Faradays first law:** "The amount of substance deposited at electrodes during electrolysis is directly proportional to the quantity of charge passed". i.e. $w = zIt$.

2. **Faraday's second law:** "When same quantity of charge is passed through different voltameter connected in series the amount of substance liberated at electrodes is directly proportional to their chemical equivalent.

3. Electrochemical equivalent (z) is the mass of substance deposited when one coulomb of charge is passed through it's solution.

4. One Faraday is equal to the charge carried by one mole of electrons. i.e. $1F = 96500$ C.

5. Electrochemical equivalent is related to chemical equivalent as: $z = \dfrac{E}{F}$.

6. The conductance given by one centimeter cube of a solution is called specific conductance (k).

7. A galvanic cell converts chemical energy into electrical energy.

8. When a metal strip is dipped into a solution of it's own metal ions, an electrode potential is developed between metal solution interface. This is called single electrode potential.

9. Standard hydrogen electrode is a reference electrode. It's standard reduction potential is arbitrarily taken as zero.

10. EMF of cell $= E^0_{Cathode} - E^0_{Anode}$

Read the above mentioned various definitions, explanations and formulae carefully. Then go through the following solved examples. After doing the solved examples, try to solve the other similar questions independently.

Subject Matter

Very Short Questions-Answers

Q.1. Define Faraday's first law of electrolysis.

Ans: According to Faraday's first law of electrolysis *"The mass of a substance deposited at respective electrodes during electrolysis is directly proportional to the quantity of charge passed through it"*. If w is the mass of a substance in gram deposited when Q coulomb of charge is passed through its solution, then according to Faraday's first law of electrolysis.

$$W \alpha Q$$

or, $\quad W = ZQ$

Where, Z = Electrochemical equivalent (a proportionality constant)

or, $\quad W = ZIt \ldots \ldots \ldots (i)$

Where, $\quad Q = It$

$\quad\quad\quad I = $ Current in ampere

$\quad\quad\quad t = $ time in second

Q.2. State Faraday's second law of electrolysis.

Ans: According to Faraday's second law of electrolysis *"When same quantity of charge is passed across different voltameters connected in series, the mass of substances deposited at respective electrodes is directly proportional to its chemical equivalent."*, i.e.

$$W \alpha E$$

or, $\quad W = A \times E$
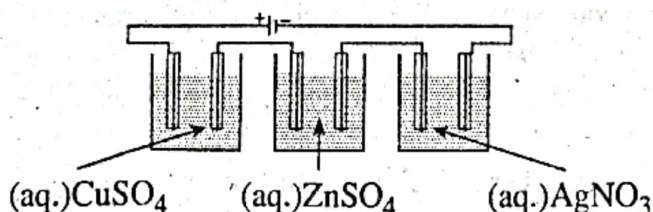
or, $\quad \dfrac{W}{E} = A \ldots \ldots \ldots (i)$

Where,

$\quad\quad\quad W = $ Mass of a substance deposited

$\quad\quad\quad E = $ Equivalent weight of that substance

$\quad\quad\quad A = $ Proportionality constant

Let's suppose, same quantity of charge Q is passed through different voltameters, containing $CuSO_4$, $ZnSO_4$ and $AgNO_3$ solutions respectively and connect in series.

(aq.)$CuSO_4$ (aq.)$ZnSO_4$ (aq.)$AgNO_3$

Fig : Verification of Faraday's Second Law of Electrolysis

According to Faraday's second law,

$$\frac{\text{Mass of Cu-deposited}}{\text{Eq.wt. of Cu}} = \frac{\text{Mass of Zn-deposited}}{\text{Equivalent wt. of Zn}} = \frac{\text{Mass of Ag-deposited}}{\text{Eq.wt. of Ag}} \ldots \ldots (ii)$$

Q.3. What is meant by ECE?

Ans: ECE stands for Electrochemical Equivalent. It is defined as mass of a substance in gram deposited at respective electrodes when one coulomb of charge is passed through an electrolyte solution.

Q.4. *Establish the relationship between ECE and chemical Equivalent.*

Ans: We know, .

1 F charge will deposit eq.wt. (E) of any substance.

or, 96500 charge will deposit eq.wt. (E) of any substance.

∴ 1 C charge will deposit $\dfrac{E}{96500}$ of any substance.

But, the mass of a substance deposited when 1C of charge is passed through its solution is equal to its electrochemical equivalent (Z). So,

Electrochemical equivalent $(Z) = \dfrac{E}{96500}$

or, $\boxed{Z = \dfrac{E}{F}}$ .... (i)

This is the well known relationship between electrochemical equivalent and chemical equivalent.

Q.5. *What do you mean by one ampere current is passing through a solution?*

Ans: One ampere current passing through a solution means one coulomb of charge is passing through the solution per second. In terms of electron, it means 6.25×10^{18} electrons are passing through the solution per second, since 96500 coulomb charge carried by 6.023×10^{23} electrons·

1 coulomb charge carried by $\dfrac{6.023 \times 10^{23}}{96500}$

$= 6.25 \times 10^{18}$ electrons.

Q.6. *What is one Faraday?*

Ans: Charge carried by one mole of electrons is called one faraday. It is represented by F and is numerically equal to 96500 coulomb approximately. The exact charge in one faraday can be calculated as:

∵ 1 electron posses 1.60219×10^{-19} coulomb of charge.

∵ 1 mole (6.023×10^{23}) electrons posses $(6.023 \times 10^{23} \times 1.60219 \times 10^{-19})$ coulomb of charge.

$= 96499.9$ coulomb/mole.

Q.7. *What is standard hydrogen electrode?*

Ans: Standard hydrogen electrode abbreviated as SHE is a reference electrode whose standard electrode potential is arbitrarily assigned to be zero volt. It is prepared by immersing a platinized platinum in a solution of hydrochloric acid containing 1.18M HCl at 25°C through which hydrogen gas at one atmospheric pressure is passed continuously.

Q.8. *State the terms: (i) specific conductance (ii) Equivalent conductance.*

Ans: (i) **Specific conductance:** It is defined as the conductance of a solution placed between two parallel electrodes each having 1 square centimeter area and placed apart 1 cm. Alternatively, we can define it as conductance of 1 centimeter cube of a solution. It's unit is $S\ cm^{-1}$.

(ii) **Equivalent conductance:** Conductance or conductivity of a solution containing one gram equivalent of an electrolyte when it is placed between two parallel electrodes separated 1 cm apart and larger enough to hold the whole solution is called equivalent conductivity. It is represented by cap (Λ) and calculated as,

Equivalent conductance (Λ) = Specific conductance (K) × Vol^m of sol^n(V)

If the concentration of the solution is expressed in normality, then

$$\Lambda = K \times \dfrac{1000}{C_N}\ ....(i)$$

Where, C_N = Concentration of solution in normality.

Q.9. *Why do specific conductance decrease and equivalent conductance increase with dilution?*

Ans: Specific conductance of a solution is conductance by number of ions per unit volume of a solution. With dilution, number of ions per unit volume decreases significantly in comparison to increase in total number of ions due to dilution. Hence, specific conductivity decreases with dilution.

Equivalent conductance, on the other hand, is conductance of total no. of ions present in a certain volume of solution due to ionization of 1 gram equivalent of the electrolyte. With dilution, the mobility of ions increases and also the number of ions for weak electrolytes. Hence, equivalent conductance increases with dilution.

Q.10. *Why do iron get rusted faster in saline solution?*

Ans: Rusting of iron in saline water is quicker because of the presence of ions. The conductivity of saline water is more than ordinary water. Hence, in a miniature electrochemical cell (which is responsible for rusting) flow of electrons (current) will increase, consequently rusting of iron is increased provided CO_2 is available in H_2O.

Q.11. *Differentiate between electrolytic and voltaic cells.*

**Ans:** Two differences between Galvanic cell and electrolytic cell are:

Galvanic or voltaic cell	Electrolytic cell
1. It is a device where electric current is produced as a result of spontaneous chemical reaction taking place in it.	1. It is a device in which electrical energy is passed to bring about certain chemical changes.
2. In this cell two different electrolytes are present in two different voltameters.	2. In this cell only one electrolyte is kept.

Q.12. *CuSO₄ solution should not be stored in a vessel made up of Nickel. Why?*
Given, $E^\circ_{Ni^{2+}/Ni} = -0.25V$
$E^\circ_{Cu^{2+}/Cu} = +0.34V$

Ans: From the data given above we find that Cu^{2+} ions are reduced more easily than Ni^{2+}. Furthermore, if they are brought together, Nickel will oxidize itself to reduce Cu^{2+} forming a galvanic cell where Ni will act as anode and Cu will act as cathode.

$$Ni/Ni^{2+} \quad // \quad Cu^{2+}/Cu$$
Anode   Salt   · Cathode
bridge
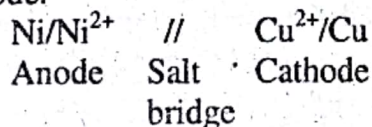
∴   Standard EMF of the cell = E° cathode – E° anode
$$= 0.34 - (-0.25)$$
$$= 0.59 \text{ V.}$$

The positive value of EMF of the cell also shows that the reaction is spontaneous. So, whenever $CuSO_4$ solution is stored in a Ni-vessel, Cu^{2+} ion will oxidize Ni spontaneously resulting in corrosion of vessel. Hence, we should not store $CuSO_4$ solution in a vessel made up of Nickel.

Q.13. *Predict, whether the reaction* $Ag^+ + Cu \longrightarrow Cu^{2+} + Ag$ *will occur or not. Given,* $E^0_{Ag^+/Ag} = +0.80 \text{ V}$ *and* $E^0_{Cu^{2+}/Cu} = +0.34 \text{ V}.$

Ans: This reaction will be possible if E^0_{cell} of the reaction is greater than zero. According the reaction, the cell notation for the reaction can be given as:
$$Cu|Cu^{2+}||Ag^+|Ag$$
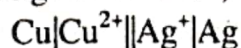
or,   EMF of the cell $(E^0_{cell}) = E^0_{cathode} - E^0_{anode}$

$$= 0.80 \text{ V} - 0.34 \text{ V}$$

$$= 0.46 \text{ V}.$$

Since, E^0_{cell} is greater than zero, the given reaction is possible.

Short Questions-Answers

**Q.14.** *Mention one important application of standard hydrogen electrode giving example.*

Ans: Standard hydrogen electrode can be used to find out the relative standard electrode potential of other electrodes. For instance, standard electrode potential of zinc can be calculated with the help of a voltmeter by combining zinc electrode at it's standardard state to the standard hydrogen electrode through salt bridge. Diagrammatically, it can be represented as given below:
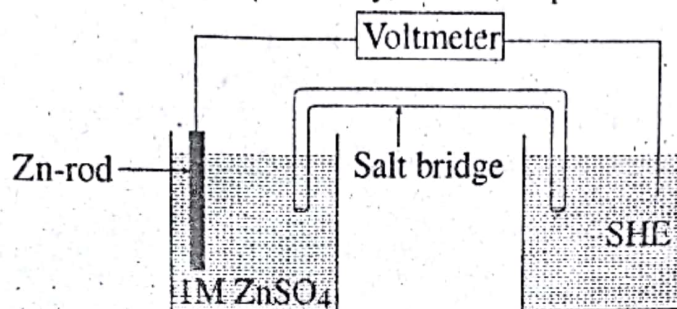
Fig:. A Daniel cell of Zn-electrode and H-electrode

Electrode reduction potential of SHE is arbitrarily taken as zero so the reading shown in the voltameter will be equal to the standard electrode potential of Zn-electrode. As Zn-electrode is acting like anode, the electrode potential should have negative value.

Q.15. *What is meant by standard electrode potential ? The standard electrode potential for the following electrode are;*
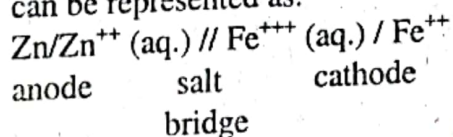
$$Zn^{++} + 2e^- \longrightarrow Zn, \; E° = -0.76V$$

$$Fe^{+++} - e^- \longrightarrow Fe^{++}, \; E° = +0.77V$$
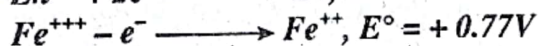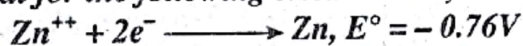
i) *Represent a suitable galvanic cell and point out which one will be cathode?*

ii) *With 1M solutions of the ions what will be emf?*

iii) *Will the reaction $Zn^{2+} + 2Fe^{2+} \longrightarrow Zn + 2Fe^{3+}$ occur? Give reason.*

Ans: **First part:** The potential of an electrode i.e. "potential difference between the electrodes and the electrolyte solution having concentration 1M measured under standard state i.e. at 25°C and 1 atmospheric pressure (for gases)" is known as standard electrode potential. It is represented by E^0.

The standard electrode potential of any metal electrode can be obtained by connecting it with standard hydrogen electrode.

(i) Since the standard reduction potential of Fe^{+++} is greater than Zn^{++}, Fe^{+++} will acts as cathode where reduction occurs. The galvanic cell can be represented as:

$$\underset{\text{anode}}{Zn/Zn^{++} (aq.)} // \underset{\substack{\text{salt} \\ \text{bridge}}}{} \underset{\text{cathode}}{Fe^{+++} (aq.) / Fe^{++}}$$

(ii) Emf of cell $= E^0_{Cathode} - E^0_{Anode}$

$$= +0.77 - (-0.76)$$

$$= 1.53 \text{ V}$$

(iii)   In the given reaction zinc is reduced and Fe^{2+} is oxidized which is not possible since the standard reduction potential of Fe^{+++}/Fe^{++} is greater than Zn^{++}/Zn. So, the given reaction will not occur.

**Q.16.** *Standard reduction potential of Cu^{2+}/Cu and Fe^{2+}/Fe are + 0.34V and -0.44V respectively.*

(a) *Construct a galvanic cell with proper indication of anode and cathode.*

(b) *Write down the cell reaction and also calculate the standard EMF of the cell.*

Ans: (a) The standard reduction potential of Cu^{2+}/Cu (+0.34v) is higher in comparison to Fe^{2+}/Fe here. It shows Cu^{2+} is more easily reduced than Fe^{2+}. So, if any Galvanometer is formed by their combination, Cu^{2+}/Cu will act as cathode and Fe/Fe^{2+} will act as anode. The Galvanic cell with proper notation of anode and cathode can be constructed as:
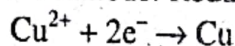
$$Fe/Fe^{2+} \text{ (aq)} \quad // \quad Cu^{2+} \text{ (aq)}/Cu$$
$$\text{anode} \qquad \text{Salt} \quad \text{Cathode}$$
$$\text{bridge}$$
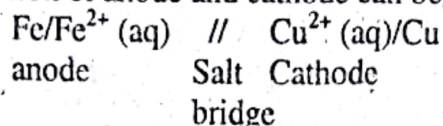
(b) The cell reaction is given as:

(i)   At anode: oxidation takes place here:
$$Fe \rightarrow Fe^{2+} + 2e^-$$
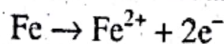
(ii)   At cathode: Reduction takes place here:
$$Cu^{2+} + 2e^- \rightarrow Cu$$

The overall cell reaction is given as:
$$Fe + Cu^{2+} \rightarrow Fe^{2+} + Cu$$
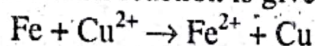
Standard EMF of the cell $= E°$ cathode $- E°$ anode
$$= +0.34 - (-0.44)$$
$$= +0.34 + 0.44$$
$$= +0.78 \text{ V}$$

∴   The standard EMF of the cell is 0.78V.

Q.17. *When 0.5 amperes of current was passed for 30 minutes through a $CuSO_4$ solution, 0.2964 g of Cu was deposited. Calculate the atomic weight of copper.*

Sol^n: Given,

Current (I) = 0.5 amperes

Time (t) = 30 min
$$= 30 \times 60 = 1800 \text{ sec.}$$

∴   Total charge (Q) = It
$$= 0.5 \times 1800$$
$$= 900 \text{ C}$$

Weight deposited (w) = 0.2964 g

Now,

∵   900C of charge deposited 0.2964 g of Cu.

1C of charge deposited $\dfrac{0.2964}{900}$ g of Cu.

∴   96500C of charge deposited $\dfrac{0.2964}{900} \times 96500$ g of Cu.
$$= 31.78 \text{ g of Cu.}$$

But, the mass of a substance deposited by passing 96500C of charge is equal to its equivalent wt. So, equivalent wt. of Cu is 31.78 here, i.e.

Eq.wt. (E) = 31.78

Valency (V) = charge on ion = 2

∴   atomic wt. (A) = ?

We know that,

atomic wt. = Eq. wt. × Valency = 31.78 × 2 = 63.65

∴ Atomic weight of Cu here is 63.65 g.

Long Questions-Answers

Q.18. *State and explain Faraday's Laws of Electrolysis. How many grams of silver could be plated out on a serving tray by passing electricity through a solution on Ag(1) salt for 8 hours at a current of 9 amperes ? What is the area of the tray, if the thickness of the silver platting is 0.002 cm? Density of Ag is 10 gm/cm³. (Atomic Mass of Ag = 107.8).*

Ans: For first part see the answer to Q.N. 1 and 2 on Page No. 32.

Numerical

Time (t) = 8 hours = 8 × 60 × 60 seconds = 28800 sec.

Current (I) = 9 ampere.

Thickness of silver platting (Th) = 0.002 cm

Density of silver (Ag) = 10 g/cm³

Atomic mass of silver = 107.8

Valency of silver = 1

∴ Eq. mass of silver $= \dfrac{\text{Atomic mass}}{\text{valency}} = \dfrac{107.8}{1} = 107.8$

Now, let W is weight of silver deposited, then

W = ZIt

$= \dfrac{E}{F} It \qquad \left[\because Z = \dfrac{E}{F} \right]$

Where, F = Faraday constant

$= \dfrac{107.8 \times 9 \times 28800}{96500} = 289.5$ gm.

Again, Mass of silver (W) = 289.5 g

Volume of silver (V) = ?

We know density $= \dfrac{\text{Mass}}{\text{volume}}$

∴ Volume $= \dfrac{\text{Mass}}{\text{density}} = \dfrac{289.5}{10} = 28.95$ cm³

Again, Let A be the area of silver deposited then, we know

volume = Area × thickness

∴ Area (A) $= \dfrac{\text{Volume}}{\text{Thickness}} = \dfrac{28.95}{0.002} = 144775.6$ cm²

Since, the silver is plated on the tray, the area of tray is also 144775.6 cm².

Q.19. *State and explain Faraday's laws of electrolysis. How long would it take to deposit 100 g of aluminium from an electrolytic cell containing Al₂O₃ at a current of 125 A?*

Ans: First part: See Very Short Q.No. 1 & 2 on Page No. 32.

Numerical:

Given, Mass (w) = 100 g

Current (I) = 125 A

Eq. wt. of A/(E) $= \dfrac{\text{At. wt}}{\text{Valency}} = \dfrac{27}{3} = 9$

Time taken (t) = ?

We know, according to Faraday's 1st law,

W = Z It

$W = \dfrac{E}{F} It$

or, $t = \dfrac{W \times F}{E \times I} = \dfrac{100 \times 96500}{9 \times 125} = 8577.85 = 2.38$ hr.

Hence, it requires 2.38 hr.

Q.20. *Write short notes on:*

    (a)   *Faraday's laws of Electrolysis*

    (b)   *Variation of electrolytic conductance with dilution.*

Ans: **(a)**   **Faraday's laws of Electrolysis:** See the answer to Q.No.1 and Q.No.2, Page No. 32.
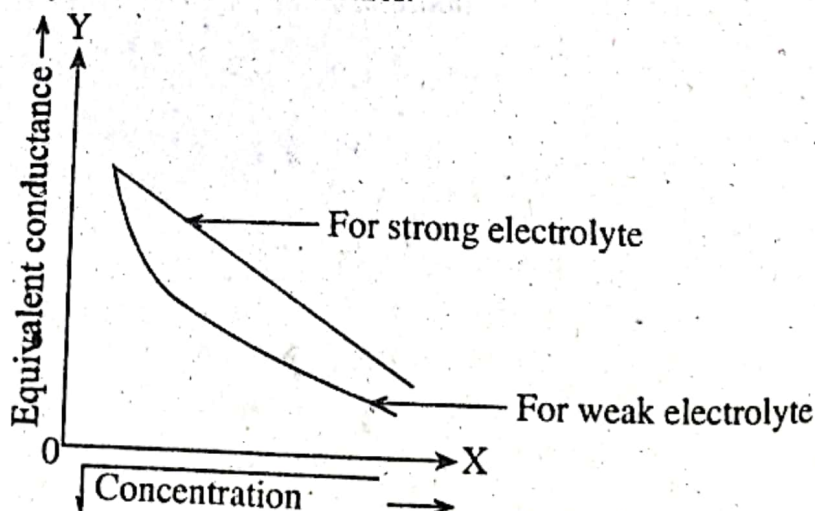
    (b)   **Variation of electrolytic conductance with dilution:** Conductance of an electrolyte solution is highly dependent on its concentration. It changes along with dilution that can be described as given below:

    (i)   **Specific conductance:** Conductance of ions per unit volume of a solution is called specific conductance. When a solution is diluted there is no significant increase in number of ions for strong electrolyte. In contrast, the number of ions per unit volume decreases. In case of weak electrolyte, these are no doubt that number of ions increases, however, it is very insignificant. In overall, number of ions per-unit volume here also decreases. So, due to decrease in number of ions per-unit volume, specific conductance decreases with dilution.
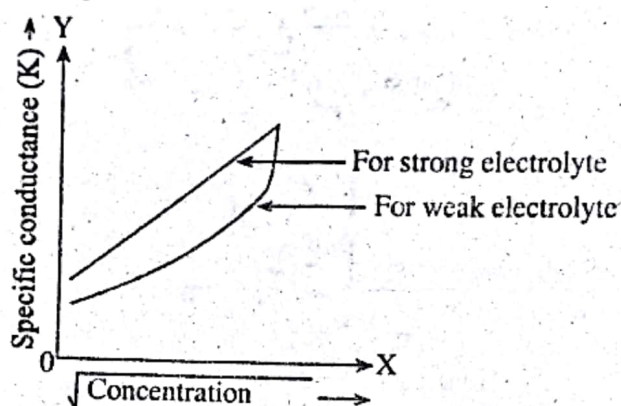
Fig.: Variation of specific conductance with dilution

    (ii)   **Equivalent conductance:** Conductance offered by ions in certain volume of a solution containing one gram equivalent of an electrolyte placed between two parallel electrodes that are 1 cm apart and large enough to contain the whole solution. With dilution, mobility of ions increases for strong electrolyte. In case of weak electrolyte, number of ions in the solution also increases along with increase in its mobility. Hence, with dilution, electrolytic conductance increases.

Fig: Variation of electrolytic conductance with dilution