ELECTRO CHEMISTRY

TOPIC-2
Specific, equivalent and molar conductance, Kohlrauch Law

VERY SHORT ANSWER QUESTIONS

1.   What is Faraday's first law?
Ans: When an electric current is passed through an electrolyte, the amount of substance deposited is proportional to the quantity of electric charge passed through the electrolyte.

If **W** be the mass of the substance deposited by passing **Q** coulomb of charge, then according to the law, we have the relation:

$$W \propto Q$$

A coulomb is the quantity of charge when a current of one ampere is passed for one second. Thus, amount of charge in coulombs,

$$Q = \text{current in amperes} \times \text{time in seconds}$$

$$= I \times t$$

$$\text{So} \quad W \propto I \times t$$

$$\text{or} \quad W = z \times 1 \times t$$

2. **Write the equation for specific conductance?**

Ans: The reciprocal of specific resistance is termed the specific conductance or it is the conductance of one centimeter cube of a conductor.

It is denoted by the symbol. Thus,

K= $1/\rho$, K = kappa - the specific conductance

Specific conductance is also called conductivity.

From Eq. (ii), we have

ρ = a/l.R   or   1/ρ = 1/(a.l/R)

K = (l/a)×C   (l/z = cell constant)

or Specific conductance = Conductance × cell constant

3. **Give equation for equivalent conductance?**

Ans: Equivalent conductance is defined as the conductance of all the ions produced by one gram equivalent of an electrolyte in a given solution. It is denoted by **Λ.**

$$\Lambda = k \times 1000/N$$

where N = normality

k = Specific conductance

The unit of equivalent conductance is ohm^{-1} cm^{-2} equi^{-1}

SHORT ANSWER QUESTIONS

1. What are electrolytes? Distinguish between metallic electrodes and electrolytes?

Conductors like aqueous solutions of acids, bases and salts in which the flow of electric current is accompanied by chemical decomposition are known as electrolytic conductors. The substances whose aqueous solutions allow the passage of electric current and are chemically decomposed, are termed electrolytes.

In order to pass the current through an electrolytic conductor (aqueous solution or fused electrolyte), two rods or plates (metallic conductors) are always needed which are connected with the terminals of a battery. These rods or plates are known as electrodes. The electrode through which the current enters the electrolytic solution is called the anode (positive electrode) with the electrode through which the current leaves the electrolytic solution is known as cathode (negative electrode). The electrolytic solution conductors electricity not by virtue of the electrolytic as in metallic conductors but as a result of movement of charged particles called ions towards the respective oppositely charged electrodes. The ions which carry positive charge and move towards cathode are termed cations while ions carrying negative charge which move towards anode are called anions. When these ions reach the boundary between a metallic and an electrolytic conductor, electrons are being either attached to or removed from the ions. Removal of electrons is termed oxidation (de-electronation) which occurs at anode while addition of electrons is called reduction (electronation) that takes place at cathode. Hence, flow of electrons through the outer circuit from anode to cathode across the boundary is accompanied by oxidation and reduction.

The differences between metallic and electrolytic conductors is given as below.

Metallic Conduction	Electrolytic Conduction
Passage of Charge by electrons	Passage of charge by ions in molten and aqueous state.
Passage of charge brings about only physical changes. Does not involve transfer of matter	Brings about physical and chemical changes. Involves transfer of matter in the form of ions
Resistance increases with temperature because of obstacles of vibrating kernels	Resistance decreases with temperature because viscosity decreases
Conducting power is high	Conducting power is low

2. State Faraday's laws of electrolysis?

Ans: **Faraday's First Law :** When an electric current is passed through an electrolyte, the amount of substance deposited is proportional to the quantity of electric charge passed through the electrolyte.

If W be the mass of the substance deposited by passing Q coulomb of charge, then according to the law, we have the relation:

$$W \propto Q$$

A coulomb is the quantity of charge when a current of one ampere is passed for one second. Thus, amount of charge in coulombs,

$$Q = \text{current in amperes} \times \text{time in seconds}$$

$$= I \times t$$

So $\quad$ **$W \propto 1 \times t$**

or $\quad$ **$W = z \times 1 \times t$**

where **z** is a constant, known as electro-chemical equivalent, and is characteristic of the substance deposited.

Faraday's Second Law: When the same quantity of charge is passed through different electrolytes, then the masses of different substances deposited at the respective electrodes will be in the ratio of their equivalent masses.

Fig. 12.1 Voltameters arranged in series
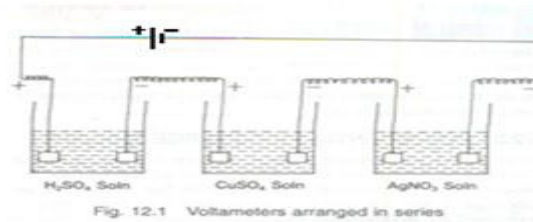
The law can be illustrated by passing same quantity of electric current through three voltametres containing solutions of H_2SO_4, $CuSO_4$ and $AgNO_3$ respectively as shown in Fig.12.1. In the first voltameter, hydrogen and oxygen will be liberated; in the

Again according to first law,

$$W = Z \times Q$$

Then Q = 96500 coulomb, W becomes gram equivalent mass (E).

Thus, E = Z×96500

or   Z = E/96500

$$z_1/z_2 = E_1/E_2$$

3. What is equivalent conductance?

Ans: Equivalent conductance: One of the factors on which the conductance of an electrolytic solution depends is the concentration of the solution. In order to obtain comparable results for different electrolytes, it is necessary to take equivalent conductance's.
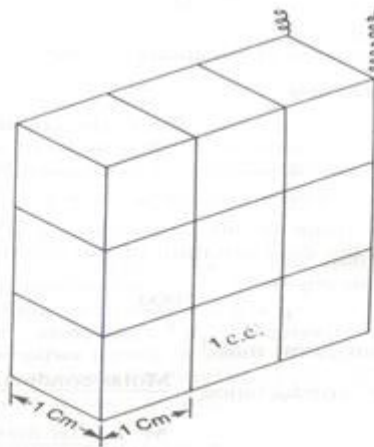

Fig. 12.3

Equivalent conductance is defined as the conductance of all the ions produced by one gram equivalent of an electrolyte in a given solution. It is denoted by **Λ**.

To understand the manning of equivalent conductance, imagine a rectangular trough with two opposite sides made of metallic conductor (acting as electrodes) exactly 1 cm apart, If 1 cm^3 (1 mL) solution containing 1 gram equivalent of an electrolyte is places in this container is measured.

According to definitions,

Conductance = Specific conductance (K)

= Equivalent conductance (Λ)

In general,

$$\Lambda = k \times V \qquad\qquad ..... (v)$$

where V is the volume in mL containing 1 g equivalent of the electrolyte.

In case, if the concentration of the solution is c g equivalent per litre, then the volume containing 1 g equivalent of the electrolyte will be 1000/e.

So equivalent conductance

$$\Lambda = k \times 1000/c \qquad\qquad ..... (vi)$$

$$\Lambda = k \times 1000/N$$

where N = normality

The unit of equivalent conductance is ohm^{-1} cm^{-2} equi^{-1}.

4. What is Kohlrauch's Law?

Ans: KOHLRAUSCH'S LAW: "At infinite dilution, when dissociation is complete, each ion makes a definite contribution towards equivalent conductance of the electrolyte irrespective of the nature of the ion with which it Is associated and the value of equivalent conductance at infinite dilution for any electrolyte is the sum of contribution of its constituent ions", i.e., anions and cations. Thus,

$$\Lambda_{\infty} = \lambda_a + \lambda_c$$

The λ_a and λ_c are called the ionic conductance of cation and anion at infinite dilution respectively. The ionic conductances are proportional to their ionic mobilities. Thus, at infinite dilution,

$$\lambda_c = ku_c$$

$$\text{and} \quad \lambda_a = ku_a$$

where u_c and u_a are ionic mobilities of cation and anion respectively at infinite dilution. The value of k is equal to 96500 c, i.e., one Faraday.

Thus, assuming that increase in equivalent conductance with dilution is due to increase in the degree of dissociation of the electrolyte; it is evident that the electrolyte achieves the degree of dissociation as unity when it is completely ionized at infinite dilution. Therefore, at any other dilution, the equivalent conductance is proportional to the degree of dissociation. Thus,

Degree of dissociation

$$\alpha = \Lambda/(\Lambda_\infty)$$

= (Equivalent conductance at a given concentration)/(Equivalent conductance at infinite dilution)

LONG ANSWER QUESTIONS

1. **What are Specific, Equivalent and Molar conductances? Explain and write the equations?**

Ans: Electrolytic Conductance: - The conductance is the property of the conductor (metallic as well as electrolytic) which facilitates the flow of electricity through it. It is equal to the reciprocal of resistance i.e.,

$$\text{Conductance} = 1/\text{Resistance} = 1/R \qquad \qquad \text{..... (i)}$$

It is expressed on the unit called reciprocal ohm (ohm^{-1} or mho) or siemens.

Specific conductance or conductivity:

The resistance of any conductor varies directly as its length (l) and inversely as its cross-sectional area (a), i.e.,

$$R \propto 1 \text{ or } \rho \propto 1/a \qquad \qquad \text{..... (ii)}$$

Where ρ is called the specific resistance

If l = 1 cm and a = 1 cm^2, then

R = ρ   **..... (iii)**

The specific resistance is, thus, defines as the resistance of one centimeter cube of a conductor.

The reciprocal of specific resistance is termed the specific conductance or it is the conductance of one centimeter cube of a conductor.

It is denoted by the symbol **κ** Thus,

κ = 1/ρ, κ = kappa - the specific conductance   **...... (iv)**

Specific conductance is also called conductivity.

From Eq. (ii), we have

$$ρ = a/l.R \quad or \quad 1/ρ = 1/a.1/R$$
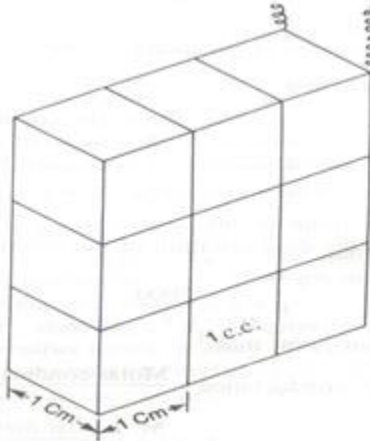
$$K = 1/a×C \quad (l/a = cell\ constant)$$

or Specific conductance = Conductance × cell constant

In the case of electrolytic solutions, the specific conductance is defined as the conductance of a solution of definite dilution enclosed in a cell having two electrodes of unit area separated y one centimeter apart as shown in Fig. 12.2.
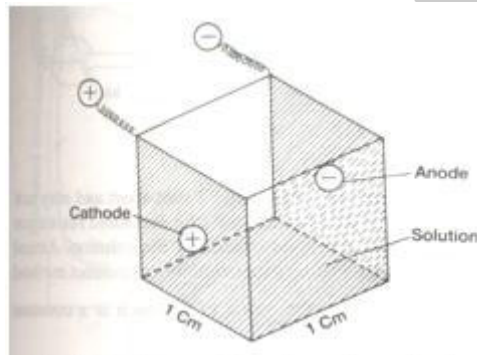
The unit of specific conductance is ohm^{-1} cm^{-}

Equivalent conductance: One of the factors on which the conductance of an electrolytic solution depends is the concentration of the solution. In order to obtain comparable results for different electrolytes, it is necessary to take equivalent conductances.

Equivalent conductance is defined as the conductance of all the ions produced by one gram equivalent of an electrolyte in a given solution. It is denoted by A.

To understand the manning of equivalent conductance, imagine a rectangular trough with two opposite sides made of metallic conductor (acting as electrodes) exactly 1 cm apart, If 1 cm^3 (1 mL) solution containing 1 gram equivalent of an electrolyte is places in this container is measured.

According to definitions,

Conductance = Specific conductance (K)

= Equivalent conductance (Λ)

If the solution is diluted to say (9 cm^3) (9 mL), the conductance of the solution will be the same but specific conductance becomes $1/9^{th}$ as it contains nine cubes. The conductance is also equal to the equivalent because the solution still has 1 g equivalent of the electrolyte. This is shown in Fig. 12.3. Thus,

Equivalent conductance (A) = $9 \times k$

In general,

$$\Lambda = k \times V \qquad\qquad ..... (v)$$

where V is the volume in mL containing 1 g equivalent of the electrolyte.

In case, if the concentration of the solution is c g equivalent per litre, then the volume containing 1 g equivalent of the electrolyte will be 1000/e.

So equivalent conductance

$$\Lambda = k \times 1000/c \qquad\qquad ..... (vi)$$

$$\Lambda = k \times 1000/N$$

where N = normality

The unit of equivalent conductance is $ohm^{-1}\ cm^{-2}\ equi^{-1}$.

Molar conductance: The molar conductance is defined as the conductance of all the ions produced by ionization of 1 g mole of an electrolyte when present in V mL of solution. It is denoted by **μ**.

Molar conductance $\quad \mathbf{μ = k \times V} \qquad\qquad$ **.... (vii)**

where V is the volume in mL containing 1 g mole of the electrolyte. If c is the concentration of the solution in g mole per litre, then

$$\mathbf{μ = k \times 1000/c}$$

It units are $ohm^{-1}\ cm^2\ mol^{-1}$.

Equivalent conductance = (Molar conductance)/n

where $\qquad\qquad$ n = (Molecular mass)/(Equivalent mass)

2. What is Kohlrauschlaw? Give its applications.

Ans: KOHLRAUSCH'S LAW: "At infinite dilution, when dissociation is complete, each ion makes a definite contribution towards equivalent conductance of the electrolyte irrespective of the nature of the ion with which it Is associated and the value of equivalent conductance at infinite dilution for any electrolyte is the sum of contribution of its constituent ions", i.e., anions and cations. Thus,

$$\Lambda_\infty = \lambda_a + \lambda_c$$

The λ_c and λ_a are called the ionic conductance of cation and anion at infinite dilution respectively. The ionic conductances are proportional to their ionic mobilities. Thus, at infinite dilution,

$$\lambda_c = ku_c$$

$$\text{and }\ \lambda_a = ku_a$$

where u_c and u_a are ionic mobilities of cation and anion respectively at infinite dilution. The value of k is equal to 96500 c, i.e., one Faraday.

Thus, assuming that increase in equivalent conductance with dilution is due to increase in the degree of dissociation of the electrolyte; it is evident that the electrolyte achieves the degree of dissociation as unity when it is completely ionized at infinite dilution. Therefore, at any other dilution, the equivalent conductance is proportional to the degree of dissociation. Thus,

Degree of dissociation

$$\alpha = \Lambda/(\Lambda_\infty)$$

=(Equivalent conductance at a given concentration)/(Equivalent conductance at infinite dilution)

Applications

1. **Calculation of absolute ionic mobilities:?**

It has been experimentally found that ionic conductance is directly proportional to ionic mobilities.

$$\lambda_+ \propto u_+$$

$$\lambda_- \propto u_-$$

where u_+ and u_- are ionic mobilities of cations and anions.

$\lambda_+ = Fu_+$ where F = Faraday

$\lambda_- = Fu_-$ = 96500 coulomb

Ionic mobility= (Ionic velocity)/(Potential gradient)

= (Ionic velocity (cm/sec))/(Potential gradient (volt)/electrode separation)

Relation between equivalent and molar conductance at infinite dilution

$$\Lambda^{\infty} = \frac{1}{z^+}\lambda_+^{\infty} + \frac{1}{z^+}\lambda_-^{\infty} \qquad \dots\dots(i)$$

where z+ and z− are corresponding charges on the ions,

e.g., $\qquad \lambda_{BaCl_2}^{\infty} = \frac{1}{2}\lambda_{Ba^{2+}}^{\infty} + \frac{1}{1}\lambda_{Cl^-}^{\infty} \qquad \dots (ii)$

$$\lambda_{AlCl_3}^{\infty} = \frac{1}{3}\lambda_{Al^{3+}}^{\infty} + \frac{1}{1}\lambda_{Cl^-}^{\infty} \qquad \dots (iii)$$

$$\lambda_{Al_2(SO_4)_3}^{\infty} = \frac{1}{3}\lambda_{Al^{3+}}^{\infty} + \frac{1}{2}\lambda_{SO_4^{2-}}^{\infty} \qquad \dots(iv)$$

Molar conductance at infinite dilution

Λ_m^{∞} or μ^{∞} = Molar conductance at infinite dilution

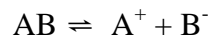$\qquad\qquad = m\lambda_+^{\infty} + n\lambda_-^{\infty}$

Where m and n are number of ions formed.

$$\mu_{Al_2(SO_4)_3}^{\infty} = 2\lambda_{Al^{3+}}^{\infty} + 3\lambda_{SO_4^{2-}}^{\infty} = 6\Lambda_{Al_2(SO_4)_3}^{\infty}$$
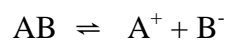
$$\lambda_{BaCl_2} = \lambda_{Ba^{2+}}^{\infty} + 2\lambda_{Cl^-}^{\infty} = 2\Lambda_{BaCl_2}^{\infty}$$

2. THEORY OF WEAK ELECTROLYTES

(i) Weak electrolytes are not completely ionized when dissolved in a polar medium like water. There exists equilibrium between ions and unionized molecules.

$$AB \rightleftharpoons A^+ + B^-$$

(ii) Concept of chemical equilibrium and law of mass action can be applied to ionic equilibrium also.

$$AB \rightleftharpoons A^+ + B^-$$

t =0   C   0   0

t_{eq} $C-C_\alpha$ C_α C_α

$$K = ([A^+][B^-])/[AB] = (C_\alpha \times C_\alpha)/C(1-\alpha)$$

$$K = (C\alpha^2)/(1-\alpha) \qquad \text{....... (i)}$$

For weak electrolyte, $\alpha \ll 1$

$$(1-\alpha) \approx 1$$

Thus equation (i) can be written as

$$K = C\alpha^2$$

$$\alpha = \sqrt{(K/C)} \qquad \text{....... (ii)}$$

From (ii) it is clear that on dilution concentration decreases, as a result of which degree of ionization ' ' increases. At high degree of ionization bot equivalent and molar conductance increase.

(iii) Degree of ionization can be calculated as

$$\alpha = (\wedge_e^C)/(\wedge_e^\infty) = (\wedge_m^C)/(\wedge_m^\infty) \qquad \text{....... (iii)}$$

$\wedge_e^C$, $\wedge_m^C$ = Equivalent and molar conductance at concentration 'C'.

$\wedge_e^\infty$, $\wedge_m^\infty$ = Equivalent and molar conductance at infinite dilution.

Subtracting the values of ' ' from (ii) in (i), we get

$$K = \frac{c \times \left(\frac{\wedge_e^C}{\wedge_e^\infty}\right)}{1 - \frac{\wedge_e^C}{\wedge_e^\infty}} = \frac{c(\wedge_e^C)^2}{\wedge_e^C(\wedge_e^\infty - \wedge_e^C)} \qquad \text{......... (iv)}$$

Similarly,

$$K = \frac{c(\wedge_m^C)^2}{\wedge_m^C(\wedge_m^C - \wedge_m^C)} \qquad \text{........ (v)}$$

Equations (iv) and (v) are called Ostwald equations.

3. State Faraday's laws of Electrolysis and explain?

Ans: The relationship between the quantity of electric charge passed through an electrolyte and the amount of the substance deposited at the electrodes was presented by Faraday in 1834, in the form of laws of electrolysis.

(i) Faraday's First Law

When an electric current is passed through an electrolyte, the amount of substance deposited is proportional to the quantity of electric charge passed through the electrolyte.

If W be the mass of the substance deposited by passing Q coulomb of charge, then according to the law, we have the relation:

$$W \propto Q$$

A coulomb is the quantity of charge when a current of one ampere is passed for one second. Thus, amount of charge in coulombs,

$$Q = \text{current in amperes} \times \text{time in seconds}$$

$$= I \times t$$

So $W \propto 1 \times t$

or $W = z \times 1 \times t$

where z is a constant, known as electro-chemical equivalent, and is characteristic of the substance deposited.

When a current of one ampere is passed for one second, i.e., one coulomb (Q = 1), then

$$W = Z$$

Thus, electrochemical equivalent can be defined as the mass of the substance deposited by one coulomb of charge or by one ampere of current passed for one second. For example, when a charge of one coulomb is passed through silver nitrate solution, the amount of silver deposited is 0.001118 g. this is the value of electrochemical equivalent of silver.

(ii) Faraday's Second Law

When the same quantity of charge is passed through different electrolytes, then the masses of different substances deposited at the respective electrodes will be in the ratio of their equivalent masses.
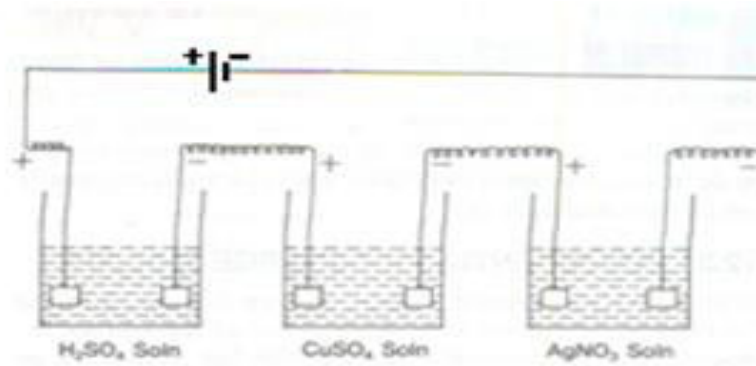
Fig. 12.1 Voltameters arranged in series

The law can be illustrated by passing same quantity of electric current through three voltametres containing solutions of H_2SO_4, $CuSO_4$ and $AgNO_3$ respectively as shown in Fig.12.1. In the first voltameter, hydrogen and oxygen will be liberated; in the second, copper will be deposited and in the third, silver will be deposited.

(Mass of hydrogen)/(Mass of copper) = (Equivalent mass of hydrogen)/
(Equivalent mass of copper)

or (Mass of copper)/(Mass of silver) = (Equivalent mass of copper)/
(Equivalent mass of silver)

or (Mass of silver)/(Mass of hydrogen) = (Equivalent mass of silver)/
(Equivalent mass of hydrogen)

It is observed that by passing one coulomb of electric charge.

Hydrogen evolved = 0.00001036 g.

Copper deposited = 0.0003292 g.

and   Silver deposited = 0.001118 g

These masses are in the ratio of their equivalent masses. From these masses, the amount of electric charge required to deposit one equivalent of hydrogen or copper or silver can be calculated.

For hydrogen = 1/0.0001036= 96500 coulomb

For copper = 31.78/0.0003292= 96500 coulomb

For silver = 107.88/0.001118 = 96500 coulomb

This follows that 96500 coulomb at electric charge will deposit one g equivalent of any substance. 96500 coulomb us termed as one Faraday and is denoted by F.

Again according to first law,

$$W = Z \times Q$$

Then Q = 96500 coulomb, W becomes gram equivalent mass (E).

Thus, $E = Z \times 96500$

or $Z = E/96500$

$$z_1/z_2 = E_1/E_2$$

NUMERICALS OF ELECTROCHEMISTRY

NUMERICAL PROBLEMS:

1. The resistance of 0.1 N KCL solution is found 702Ω when measured in a conductivity cell. The specific conductance of 0.1 N KCL is 0.14807 Ω^{-1} m^{-1}. Calculate the equivalent conductance?

Sol: Given, resistance (R) = 702Ω

$\therefore$ Conductance (C) = $\dfrac{1}{R}$ = $\dfrac{1}{702}$ Ω^{-1}

Specific conductance (K) = 0.14807 Ω^{-1} m^{-1}.

$\therefore$ Cell constant = $\dfrac{\text{Specific conductance}}{\text{Conductance}}$

$$= \dfrac{0.14807 \ \Omega^{-1} \ m^{-1}.}{\dfrac{1}{702} \ \Omega^{-1}}$$

$$= \quad 0.14807 \times 702 \text{ m}^{-1}.$$

$$= \quad 103.9 \text{ m}^{-1}.$$

∴ **Cell constant** $\qquad = \qquad$ **103.9 m^{-1}.**

2. The specific conductance of 0.1 N KCL Solution is 0.14807 Ω^{-1} m^{-1}. Calculate the equivalent conductance?

Sol:

Given, Specific conductance (K) $\quad = 0.14807 \ \Omega^{-1}$ m^{-1}.

$\qquad$ Normality (N) $\quad = \quad$ 0.1 N

Equivalent conductance (^) $\qquad = \quad \dfrac{\text{K} \times 1000}{\text{N}}$

$$= \quad \dfrac{0.14807 \times 1000}{0.1}$$

$$= \quad \textbf{1.4807} \times \textbf{10}^3 \ \boldsymbol{\Omega}^{-1} \ \textbf{.m}^2\textbf{./ equivalent}$$

3. The equivalent conductance of 0.02 M acetic is 1.162 x 10^3 ohm^{-1} mol^{-1} m^2 . What is 'α' of CH3COOH ?(^-CH3COOH is 0.03873 ohm^{-1} mol^{-1} m^2)

Sol:

$\qquad$ Given $\quad$ ^c $\quad = \quad$ 1.162 x 10^3 ohm^{-1} mol^{-1} m^2

$\qquad$ ^- $\quad = \quad$ 0.03873 ohm^{-1} mol^{-1} m^2

$$\alpha \quad = \quad \dfrac{\text{^c}}{\text{^-}}$$

$$\therefore \ \alpha \ = \ \frac{\wedge_c}{\wedge_-} \ = \ \frac{1.162 \ \times \ 10^{-3}}{0.03873} = \textbf{0.03}$$

4. The electrode protential of cu^{++} / cu and Ag$^+$ /Ag electrode are + 0.33 V and + 0.8 V respectively. What is the EMF of the cell constructed from these electrodes?

Sol:

Cell is: Cu / Cu $^{++}$ // Ag$^+$ /Ag

Given Electrode potential of   Cu $^{++}$/ Cu   = + 0.33 V and

Electrode potential of Ag$^+$ /Ag   =   + 0.8 V

EMF of the cell   = [$E_{RHS} - E_{LHS}$]

= (0.8 – 0.33) V

=   **0.47 V**

5. The E^0 value of Zn^{++} /Zn electrode is - 0.77 v. What is the E value of the electrode containing 0.01 M Zn^{++} ions?

Sol:

$$E \ = \ E^0 + \frac{0.059}{n} \ \log c$$

Given, $E^0 \ = \ - \ 0.77$ v   [$Zn^{2+} + 2e \ \leftrightarrow Zn$]

n = 2 $\therefore$ n = 2

C = Concentration = 0.01 M

$$E \ = \ E^0 + \frac{0.059}{n} \ \log c \ = \ 0.77 + \frac{0.059}{2} \log (0.01)$$

$$= 0.77 + \frac{0.059}{2} \log(10^{-2})$$

$$= 0.77 + \frac{0.059}{2} (-2)$$

= 0.77 − 0.059 = −0.829V

Additional Numericals with Solutions

1. A current of 10amp is passed through molten $AlCl_3$ for 96.5 seconds. Calculate the mass of Al deposited at the cathode. ?(At. wt of Al = 27)

Sol: As per first law of Faraday

$$m = \frac{At.wt. \times c \times t}{valency \times 96500}$$

At. wt of Al = 27

c = 10 amp.   t = 96.5   seconds valency = 3

$$m_{Al} = \frac{27 \times 10 \times 96.5}{3 \times 96500} g = 0.09$$

2. 9.65 amp. current is passed through molten $AlCl_3$ for one minute forth seconds during electrolysis. The mass of Al deposited is 0.09g at the cathode. What is the valency of Al?

Sol: As per first law of Faraday.

$$m = \frac{At.wt. \times c \times t}{valency \times 96500}$$

At. wt of Al = 27

C = 9.65 amp: t = { (1 x 60) + 40}} = 100 secs

Valency = ?   m = 0.09g

$$m = \frac{At.wt. \times c \times t}{valency \times 96500}$$

$$0.09 = \frac{27. \times 9.65 \times 100}{valency \times 96500}$$

$$\therefore \text{ valency } = \frac{27. \times 9.65 \times 100}{0.09 \times 96500} = 3$$

3**. How much time (in hours) is required for a current of 2 amp to decompose electrolytically 18g of water.?**

Sol:
        As per first law of Faraday

$$m = \frac{E \times c \times 1}{96500}$$

E = Chemical equivalent = $\frac{18}{2}$ = 9g

C = 2 amp: t =? m = 18g

$$18 = \frac{9 \times 2 \times 1}{96500}$$

$$t = \frac{18 \times 96500}{9 \times 2} \text{ sec.}$$

$$t = \frac{18 \times 96500}{9 \times 2 \times 60 \times 60} \text{ hrs} = 26.8 \text{ hours}$$

4. What is the ratio of weights of Ag and Al deposited at the respective cathodes when the same current is passed for same period through aqueous AgNo₃ and Al₂(SO4)3 Solutions?

Sol:

As per second law of Faraday

$$\frac{\text{mass of Ag}}{\text{mass of Al}} = \frac{\text{Equivalent weight of Ag}}{\text{Equivalent weight of Al}}$$

$$\frac{m_{Ag}}{m_{Al}} = \frac{108}{9} = 12 : 1$$

5. **Calculate the potential of single electrode Zn^{++}$_{(aq)}$/Zn ? (0.1M) (E^0 = −0.762v)**
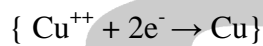
$$E = E^0 + \frac{0.059}{n} \log (0.1) \text{ M} \qquad \{ n = 2, Zn^{++} + 2e^- \leftrightarrow Zn\}$$

$$= -0.762 + \frac{0.059}{2} \log (10^{-1})$$

$$= -0.762 + 0.0295 \times (-1)$$

$$= -0.762V.$$

6. **Calculate the electrode potential of the single electrode? Cu^{++} (aq) [c = 0.01M}/ Cu? ; $E^0 = +0.337$ V]**

Sol:

$$E = E^0 + \frac{0.059}{n} \log c \qquad \{ Cu^{++} + 2e^- \rightarrow Cu\}$$

$$\therefore n = 2$$

$$E = E^0 + \frac{0.059}{2} \log(10^{-2})$$

$$E = 0:337 + 0.03 \times (-2)$$

$$E = +0.337 - 0.06 = 0.277V.$$

7. **Calculate the EMF of the cell formed from Ag and Ni electrodes**
   $E^0_{Ag+/Ag} = +0.799$ V; $E^0_{Ni^{+2}/Ni} = -0.250$V.

 Sol: Cell is Ni/Ni^{++}(aq) // Ag^{++}(aq) / Ag

$$E^0 = E^0_{Ag} - E^0_{Ni}$$

$$= 0.799 - (-0.250)$$

$$E^0 = +0.799 + 0.250 = 1.049V$$

8. Write the cell reaction of the cell constructed from Sn^{2+}/Sn ; Pb^{2+}/Pb electrodes. E^0

Values are $E^0_{Sn^{2+}/Sn} = -0.140v$, $E^0_{Pb++/Pb} = -0.126v$.

Sol: The cell is written as $Sn/Sn^{++}_{(aq)}//Pb^{++}_{(aq)}/Pb$

LHS electrode reaction; oxidation $Sn \leftrightarrow Sn^{++}_{(aq)} + 2e^-$

RHS electrode reaction; reduction $Pb^{++}_{(aq)} + 2e^- \leftrightarrow Pb$

Cell reaction $Sn + Pb^{++} \leftrightarrow Sn^{++} + Pb$

9. Calculate the electrode potentials of Zn^{++} (0.1M) / Zn , $\frac{1}{2}$ Cl_2/Cl^-(0.01)M,

$E^0_{zn^{2+}/zn} = -0.762V$; $E_{\frac{1}{2}Cl2/Cl^-} = +1.36V$.

Sol:

$$E^0_{zn^{++}/zn} = E^0 + \frac{0.059}{n} \log[Zn^{++}]$$

$$E = -0.762 + \frac{0.059}{2} \log(10^{-1})$$

$$= -0.762 + 0.03 \times (-1)$$

$$= -0.762 - 0.03 = -0.792V$$

$$E_{\frac{1}{2}Cl2/Cl} = E^0 - \frac{0.059}{1} \log[Cl]$$

$$= +1.36 - \frac{0.059}{1} \log 10^{-2}$$

$$= 1.36 - 0.06 \text{ x } (-2)$$

$$E = 1.36 + 0.12 = 1.48 \text{ V.}$$

10. A current of 0.965 amp. is passed through an aq. Solution of Ag No3 for 10 minutes during electrolysis. Calculate the mass of Ag deposited at the cathode. (At.wt of Ag = 108 g)

Sol:

At. wt of Ag = 108, valency = 1, c = 0.965 amp,

t = 10 x 60 = 600 seconds

$$m_{Ag} = \frac{\text{At.wt. x c x t}}{\text{valency x 96500}}$$

$$m_{Ag} = \frac{108 \text{ x } 0.965 \text{ x } 10 \text{ x } 60}{1 \text{ x } 96500}$$

$$= 0.648g$$

11. How much time is required for a current of 2 amp to decompose electrolytically 18g of water?

$$E = \text{Chemical equivalent} = \frac{18}{2} = 9g$$

C = 2 amp   t = ?   m = 18g

$$m = \frac{E \text{ c } t}{96500} \quad \Rightarrow \quad 18 = \frac{9 \text{ x } 2 \text{ x } t}{96500} \quad \Rightarrow$$

$$t = \frac{18 \times 96500}{9 \times 2} = 96500 \text{sec.}$$

12. Certain quantity of electricity liberates 0.504g of H_2. Calculate the amount of Ag deposited for the passage of same quantity of electricity?

Sol:

$m_1 = 0.504$g, $m_2 = ?$

$E_1 = 1.008$, $E_2 = 108$

$$\frac{m_1}{m_2} = \frac{E_1}{E_2}$$

$$\Rightarrow m_2 = m_1 \times \frac{E_2}{E_1} = \frac{0.540 \times 108}{1.008}$$

$$= 54\text{g}$$

13. Calculate E0cell of the following?

Zn | Zn²⁺ || Cu²⁺ | Cu

$E^0_{zn^{++}/zn} = -0.762V$, $E^0_{cu^{++}/cu} = +0.337$ V

Sol:

$$E^0_{cell} = E_{RHS} - E_{LHS} = E^0_{cu} - E^0_{zn}$$

$$= +0.337 - (-0.762)$$

$$\therefore E^0_{cell} = 1.099V$$

14. **Calculate the electrode potential of the single electrode Ag$^+$ (0.01M)/ Ag?**

   $\{E^0 = 0.799V\}$.

Sol:

$$E^0 = 0.799 \text{ V}, \ C = 0.01M = 10^{-2} \text{ M}, n = 1(Ag^+ + e^- \rightarrow Ag)$$

$$E = E^0 + \frac{0.059}{n} \log C = 0.799 + \frac{0.059}{1} \log 10^{-2}$$

$$= 0.799 + 0.059 \ (-2)$$

$$= 0.799 - 0.120$$

$$\therefore \ E = +0.679V$$

15. **Calculate the single electrode potential of Pt. Cl_2/Cl^- (0.01M)?**

   $\{E^0 = +1.36V\}$.

Sol: $E^0 = +1.36V, \ C = 0.01 \text{ M} = 10^{-2} \text{ M}, \ n = 1 \ [\frac{1}{2} Cl_2 + e^- \rightarrow Cl^-]$

$$E = E^0 - \frac{0.059}{n} \log C = 1.36 - \frac{0.059}{1} (10^{-2})$$

$$= 1.36 - 0.056 \ (-2) = 1.36 + 0.12$$

$$\therefore \ E = 1.48V$$

16. **A current of 0.25 amp. is passed through CuSo$_4$ solution for 45 minutes. Calculate the mass of copper deposited on the cathode? (At. wt of Cu = 63.6)**

Sol: As per first law of Faraday

$$m = \frac{At.wt. \times c \times t}{valency \times 96500}$$

At. wt of Cu = 63.6

C = 0.25amp;   t = 45 x 60 sec;   valency = 2

$$m_{Cu} = \frac{63.6. \times 0.25 \times 45 \times 60}{2 \times 96500}$$

= 0.2224g

17. Calculate the current in amperes required to deposit electrolitically 10g of Ag in 2 hours   (At. wt of Ag = 108) from AgNo₃ aq. Solution?

Sol: As per first law of Faraday

$$m = \frac{At.wt. \times c \times t}{valency \times 96500}$$

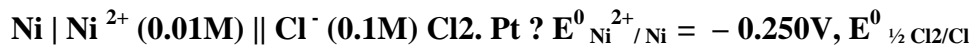Ag atomic weight = 108   camp = ?

t = 2 x 60 x 60 seconds;

 m = 10g

Ag valency = 1

$$10 = \frac{108. \times c \times 2 \times 60 \times 60}{2 \times 96500}$$

$$C = \frac{10.\ x\ 1\ x\ 96500}{108.\ x\ 2\ x\ 60\ x\ 60}$$

$$= 1.24\ amp.$$

18. **Calculate the EMF of the Cell**

   Ni | Ni $^{2+}$ (0.01M) || Cl^{-} (0.1M) Cl2. Pt ? E^0 $_{Ni}^{2+}$$_{/\ Ni}$ = $-$ 0.250V, E^0 $_{½\ Cl2/Cl}$

   = 1.360V

Sol:

$$E_{Ni}{}^{2+}{}_{/\ Ni} = E^0 + \frac{0.059}{2}\ log\ C\ =\ -\ 0.250 + 0.03\ log\ (10^{-2})$$

$$= -\ 0.250 + 0.03\ (-2)$$
$$= -\ 0.250 - 0.06$$

$$= -\ 0.31\ V$$

$$E_{½\ Cl2/Cl} = E^0 - \frac{0.059}{1}\ log\ C\ =\ 1.36 - \frac{0.059}{1}\ log\ (10^{-})$$

$$= 1.36\ -\ 0.059\ (-\ 1)$$

$$= 1.36\ +\ 0.059$$

$$= 1.42\ V$$

   $\therefore$ EMF of the cell (E cell) $=$ [E$_{RHS}$ $-$ E$_{LHS}$]

   $$=\ 1.42\ -\ (-\ 0.31)$$

   $$E\ cell\ =\ +\ 1.73\ V$$

19. **Calculate the e.m.f. of the cell Cu || Cu^{++} (0.1M) || Cl $^{-}$½ Cl$_2$ (0.1M), Pt E^0 $_{cu}^{2+}$$_{/\ cu}$**
    = + 0.337V, E $_{½\ Cl2\backslash\ Cl}$= + 1.36V

Sol:

$$0.059$$

$$E^0_{cu^{2+}/cu} = E^0 + \frac{\text{------------}}{n} \log 10^{-1} = 0.337 + 0.03 \times (-1)$$

$$= + 0.337 - 0.03 = + 0.0307$$

$$E_{\frac{1}{2}Cl2\backslash Cl^-} = E^0 + \frac{0.059}{1} \log 10^{-2}$$

$$= 1.36 - 0.06 \times (-2)$$

$$= 1.36 + 0.06 \times 2$$

$$= 1.36 + 0.12 = 1.48V$$

$$E^0_{cell} = E_{\frac{1}{2}Cl2\backslash Cl^-} - E^0_{cu^{2+}/cu}$$

$$= 1.48 - 0.307 = + 1.073V$$

20.   At 25° C the equivalent conductance of sodium acetate, hydrochloric acid, and sodium chloride at infinite dilution respectively are 91.0, 426.16, 126.45 ohm^{-1} cm^2. What is A$_o$ of CH$_3$COOH?

Sol:

$$A_o^{CH3COOH} = A_o^{CH3COONa} + A_o^{Hcl} - A_o^{Nacl}$$

$$= 91.0 + 426.16 - 126.45$$

$$A_o^{CH3COOH} = 390.71 \text{ ohm}^{-1} \text{ cm}^2. \text{ eq}^{-1}$$

21. **At 25° C the specific conductance of acetic acid of 0.01 N concentrations is 0.000163 ohm^{-1} cm^2. What is ^c at this concentration?**

Sol:

$$\text{^c} = \frac{k \times 1000}{N}$$

$$= \frac{0.000163 \times 1000}{0.01}$$

$\wedge c = 16.3$ ohm^{-1} cm^2. eq^{-1}

22. $\wedge c$ of acetic acid at 25° C is 16.3 ohm^{-1} cm^2. eq^{-1}. The ionic conductances of H$^+$ and CH$_3$ COO$^-$ are 349.83 and 40.89 ohm^{-1}. What is α CH$_3$ COOH?

$$\alpha = \frac{\wedge c}{\wedge \alpha}$$

$\therefore \wedge^{CH3\ COOH} = \lambda_0^{H+} + \lambda_0^{CH3\ COOH}$

$\wedge_0 = \lambda_0^{H+} + \lambda^{CH3\ COOH}$

$\wedge_0 = 349.83 + 40.89 = 390.72$

$$\mu = \frac{16.3}{390.72} = 0.04072$$