ELECTRO CHEMISTRY

TOPIC-1
Conductance in electrolytic solutions

VERY SHOR ANSWER QUESTIONS

1. **What is electrolysis? Illustrate?**

Ans: The substances whose aqueous solutions allow the passage of electric current and are chemically decomposed, are termed electrolytes. The process of decomposition of an electrolyte in to its corresponding ions, when current is passed through that is called electrolysis.

Electrolysis of sodium chloride solution: The solution of sodium chloride besides Na^+ and Cl^- ions possesses H^+ and OH^- ions due to ionization of water. However, the number is small as water is a weak electrolyte. When potential difference is established across the two electrodes, Na^+ and H^+ ions move towards cathode and Cl^- and OH^- ions move towards anode. At cathode H^+ ions are discharged in preference to Na^+ ions as the discharge potential of H^+ ions is lower than Na^+ ions. Similarly at anode, Cl^- ions are discharged in preference to OH^- ions.

$$NaCl <--> Na^+ + Cl^-$$

$$H_2O <--> H^+ + OH^-$$

At cathode	**At Anode**
$H^+ + e^- \rightarrow H$	$Cl^- \rightarrow Cl + e^-$
$2H \rightarrow H_2$	$2Cl \rightarrow Cl_2$

Thus, Na^+ and OH^- ions remain in solution and the solution when evaporated yields crystals of sodium hydroxide.

2. **What products are obtained in the electrolysis of fused KCl and aqueous KCL between Pt electrodes?**

Ans: Electrolysis of **molten** KCl liquid between Pt electrodes, the following reactions occur.

$$\mathbf{2}\ KCl <--> 2K^+ + 2Cl^-$$

At cathode	**At Anode**

$2 K^+ + 2e^- \rightarrow 2K$ $\qquad$ $2Cl^- \rightarrow Cl_2 + 2e^-$

Thus, KCl decomposes to form K and Cl_2 gas.

Electrolysis of **molten** KCl aqueous solution between Pt electrodes, the following reactions occur.

$$KCl \leftrightarrow K^+ + Cl^-$$

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

At cathode $\qquad$ **At Anode**

$4H_2O + 4e^- \rightarrow 2H_2 + 4e$ $\qquad$ $4Cl^- \rightarrow 2Cl_2 + 4e^-$

Thus, K^+ and OH^- ions remain in solution and the solution when evaporated yields crystals of Potassium hydroxide.

SHORT ANSWER QUESTIONS

1. **Explain metallic conductors?**

Ans:

Metallic or electronic conductors: Conductors which transfer electric current by transfer of electrons, without transfer of any matter, are known as metallic or electronic conductors. Metals such as copper, silver, aluminum, etc., non-metals like carbon (graphite - an allotropic form of carbon) and various alloys belong to this class. These materials contain electrons which are relatively free to move. The passage of current though these materials have no observable effect other than a rise in their temperature.

2. **Explain electrolytic conductors?**

Ans: Electrolytic conductors:

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.

LONG ANSWER QUESTIONS

1. Explain Electrolysis and Electrolytic cell?

Electrolysis and Electrolytic cell

Preferential Discharge Theory: If an electrolytic solution consists of more than two ions and the electrolysis is done, it is observed that all the ions are not discharged at the electrodes simultaneously but certain ions are liberated at the electrodes in preference to others. This is explained by preferential discharge theory. It states that if more than one type of ions is attracted towards a particular electrode, then the one discharged is the ion which requires least energy. The potential at which the ion is discharge or deposition potential. The values of discharge potential are different for different ions. For example, the discharge potential of H+ ions is lower than Na+ ions when platinum or most of the other metals* are used as cathodes. Similarly, discharge potential of Cl^- ions is lower than that of OH^- ions. This can be explained by some examples given below:

(i) Electrolysis of sodium chloride solution: The solution of sodium chloride besides Na^+ and Cl^- ions possesses H^+ and OH^- ions due to ionization of water. However, the number is small as water is a weak electrolyte. When potential difference is established across the two electrodes, Na^+ and H^+ ions move towards cathode and Cl^- and OH^- ions move towards anode. At cathode H^+ ions are discharged in preference to Na^+ ions as the discharge potential of H^+ ions is lower than Na^+ ions. Similarly at anode, Cl^- ions are discharged in preference to OH^- ions.

$$NaCl <--> Na^+ + Cl^-$$

$$H_2O <--> H^+ + OH^-$$

At cathode	At Anode
$H^+ + e^- \rightarrow H$	$Cl^- \rightarrow Cl + e^-$
$2H \rightarrow H_2$	$2Cl \rightarrow Cl_2$

Thus, Na^+ and OH^- ions remain in solution and the solution when evaporated yields crystals of sodium hydroxide.

(ii) Electrolysis of copper sulphate solution using platinum electrodes:

$$CuSO_4 \text{ <--> } Cu^{2+} + SO_4^{2-}$$

$$H_2O \text{ <--> } H^+ + OH^-$$

At cathode	**At Anode**
$Cu^{2+} + 2e^- \text{ --> } Cu$	$2OH^- \text{ --> } H_2O + O + 2e^-$
	$O + O \text{ --> } O_2$

Copper is discharged at cathode as Cu^{2+} ions have lower discharge potential than H^+ ions. OH^- ions are discharged at anode as these have lower discharge potential than ions. 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.

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

$$\rho = a/l.R \qquad \text{or} \qquad 1/\rho = 1/(a.l/R)$$

$K = (l/a) \times C$ (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,

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

$$= I \times t$$

$$\textbf{So} \quad W \propto 1 \times t$$

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

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.

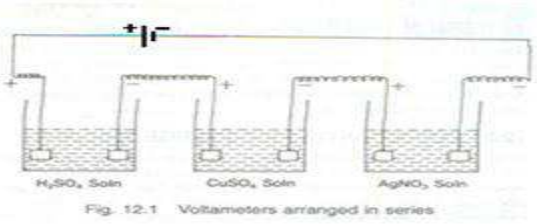


Fig. 12.1 Voltameters arranged in series

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).

$$\textbf{Thus, } E = Z \times 96500$$

$$\textbf{or} \quad Z = E/96500$$

$$z_1/z_2 = E_1/E_2$$

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.

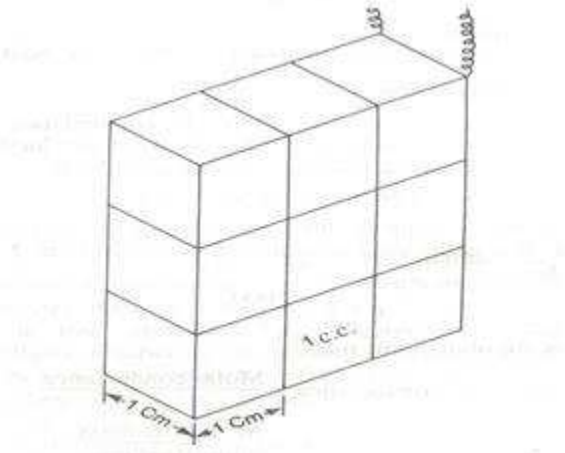


Fig. 12.3

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,

$$\mathbf{\Lambda = k \times V} \qquad \text{..... (v)}$$

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

$$\mathbf{\Lambda = k \times 1000/c} \qquad \text{..... (vi)}$$

$$\mathbf{\Lambda = k \times 1000/N}$$

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,

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

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,

$$\lambda_c = ku_c$$

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

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.,

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

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.,

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

Where ρ is called the specific resistance

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

$$\mathbf{R = \rho} \qquad \text{..... (iii)}$$

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,

$$\mathbf{\kappa = 1/\rho,\ \kappa = kappa - the\ specific\ conductance} \qquad \text{..... (iv)}$$

Specific conductance is also called conductivity.

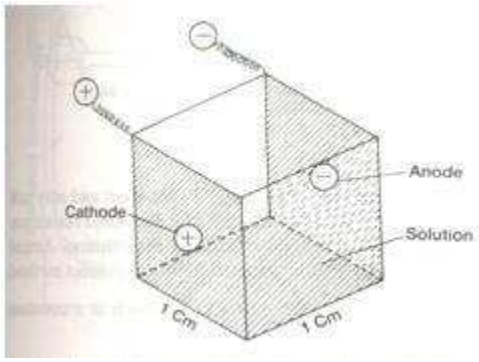
From Eq. (ii), we have

$$\mathbf{\rho = a/l.R \quad or\ 1/\rho = 1/a.1/R}$$

$$\mathbf{K = 1/a \times C \qquad (l/a = cell\ constant)}$$

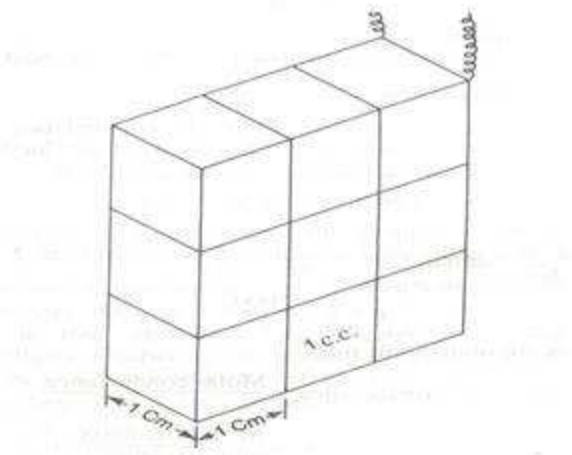
or Specific conductance = Conductance × cell constant

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 × k

In general,

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

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

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

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

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 $\mu = k \times V$ **.... (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

$$\mu = k \times 1000/c$$

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

Equivalent conductance = (Molar conductance)/n

where 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,

$$/\backslash_\infty = \lambda_a + \lambda_c$$

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

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

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

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

$\lambda^{\infty}_{AlCl_3} = \frac{1}{3}\lambda^{\infty}_{Al^{3+}} + \frac{1}{1}\lambda^{\infty}_{Cl^-}$ .... (iii)

$\lambda^{\infty}_{Al_2(SO_4)_3} = \frac{1}{3}\lambda^{\infty}_{Al^{3+}} + \frac{1}{2}\lambda^{\infty}_{SO_4^{2-}}$ ....(iv)

Molar conductance at infinite dilution

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

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

Where m and n are number of ions formed.

$\mu^{\infty}_{Al_2(SO_4)_3} = 2\lambda^{\infty}_{Al^{3+}} + 3\lambda^{\infty}_{SO_4^{2-}} = 6\Lambda^{\infty}_{Al_2(SO_4)_3}$

$\lambda_{BaCl_2} = \lambda^{\infty}_{Ba^{2+}} + 2\lambda^{\infty}_{Cl^-} = 2\Lambda^{\infty}_{BaCl_2}$

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

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

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

For weak electrolyte, $\alpha << 1$

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

Thus equation (i) can be written as

$$K = C\alpha^2$$

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

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

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

$\wedge_e^C$, $\wedge_m^C$ = 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

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

Similarly,

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

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,

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

$$= I \times t$$

$$\text{So} \quad W \propto 1 \times t$$

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

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

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.

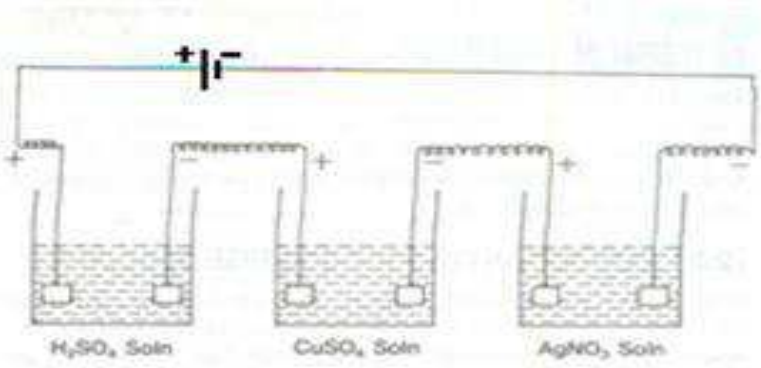


Fig. 12.1 Voltameters arranged in series

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,

$$\mathbf{W = Z \times Q}$$

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

Thus, $E = Z \times 96500$

or $Z = E/96500$

$$\mathbf{z_1/z_2 = E_1/E_2}$$

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

$$\therefore \text{Conductance (C)} = \frac{1}{R} = \frac{1}{702}\ \Omega^{-1}$$

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

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

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

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

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

$\therefore$ **Cell constant** $= \quad \mathbf{103.9\ m^{-1}.}$

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

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

$$\text{Equivalent conductance } (\wedge) = \frac{K \times 1000}{N}$$

$$= \frac{0.14807 \times 1000}{0.1}$$

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

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:

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

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

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

$$\therefore \quad \alpha = \frac{\hat{}c}{\hat{}-} = \frac{1.162 \times 10^{-3}}{0.03873} = \mathbf{0.03}$$

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

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

At. wt of Al = 27

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

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

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.

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

At. wt of Al = 27

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

Valency = ? m = 0.09g

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

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

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

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

$$m = \frac{E \text{ x } c \text{ x } 1}{96500}$$

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

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 $AgNo_3$ and $Al_2(SO4)3$ 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) ($E^0 = -0.762v$)**

$$E = E^0 + \frac{0.059}{n} \log (0.1) \text{ M} \qquad \{ n = 2, Zn^{++} + 2e^- \leftrightarrow Zn \}$$

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

$$= \quad -0.762 \ + \quad 0.0295 \text{ x } (-1)$$

$$= \quad \mathbf{-\ 0.762V.}$$

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

Sol:

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

$$\therefore n = 2$$

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

$$E = 0{:}337 + 0.03 \text{ x } (-2)$$

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

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

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 ,½ Cl_2/Cl^-(0.01)M,

$E^0_{zn^{2+}/zn} = -0.762V$; $E_{½\ Cl2/Cl^-} = +1.36V$.

Sol:

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

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

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

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

$$E_{½\ Cl\ 2/Cl} = E^0 - \frac{0.059}{1} \log [Cl]$$

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

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

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

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

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

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

$$= 0.648\text{g}$$

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

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

C = 2 amp t = ? m = 18g

$$m = \frac{E\ c\ t}{96500} \Rightarrow 18 = \frac{9 \times 2 \times t}{96500} \Rightarrow$$

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

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:

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

$E_1 = 1.008, \quad E_2 = 108$

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

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

$$= 54g$$

13. Calculate E0cell of the following?

$Zn \mid Zn^{2+} \parallel Cu^{2+} \mid Cu$

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

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

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

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

$$= 0.799 - 0.120$$

$$\therefore E = +0.679V$$

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

{E^0 = + 1.36V}.

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

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

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

$$\therefore E = 1.48V$$

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

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

At. wt of Cu = 63.6

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

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

= 0.2224g

17. Calculate the current in amperes required to deposit electrolitically 10g of Ag in 2 hours (At. wt of Ag = 108) from $AgNo_3$ aq. Solution?

Sol: As per first law of Faraday

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

Ag atomic weight = 108 camp = ?

t = 2 x 60 x 60 seconds;

m = 10g

Ag valency = 1

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

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

$$= 1.24 \text{ amp.}$$

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

Ni | Ni $^{2+}$ (0.01M) || Cl $^{-}$ (0.1M) Cl2. Pt ? $E^0_{Ni^{2+}/Ni} = -0.250V$, $E^0_{\frac{1}{2}Cl2/Cl}$ = 1.360V

Sol:

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

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

$$= -0.250 - 0.06$$

$$= -0.31 \text{ V}$$

$$E_{\frac{1}{2}Cl2/Cl} = E^0 - \frac{0.059}{1} \log C = 1.36 - \frac{0.059}{1} \log (10^{-})$$

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

$$= 1.36 + 0.059$$

$$= 1.42 \text{ V}$$

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

$$= 1.42 - (-0.31)$$

$$E \text{ cell} = +1.73 \text{ V}$$

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, $E_{\frac{1}{2}Cl2\backslash Cl}$ = + 1.36V

Sol:

$$\frac{0.059}{}$$

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

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

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

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

$$= 1.36 + 0.06 \times 2$$

$$= 1.36 + 0.12 = 1.48V$$

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

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

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_3COOH?

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:

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

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

$$\hat{}c = \mathbf{16.3}\ \text{ohm}^{-1}\ \text{cm}^2.\ \text{eq}^{-1}$$

22. $\hat{}c$ of acetic acid at 25^o C is 16.3 $\text{ohm}^{-1}\ \text{cm}^2.\ \text{eq}^{-1}$. The ionic conductances of H^+ and $CH_3\ COO^-$ are 349.83 and 40.89 ohm^{-1} . What is α $CH_3\ COOH$?

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

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

$$\hat{}_0 = \lambda_0^{H+} + \lambda^{CH3\ COOH}$$

$$\hat{}_0 = 349.83 + 40.89 = 390.72$$

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

ELECTRO CHEMISTRY

TOPIC-2
Electrolytic and redox reactions

VERY SHORT ANSWER QUESTIONS

1. What is electrochemical cell ?

Ans: It s a device in which a redox reaction takes place indirectly and the decrease in potential energy of the reaction appears as electrical energy.

2. What is cell notation?

Ans:

- Cell notation in chemistry is a shorthand way of expressing a certain reaction in an electrochemical cell.
- The cell anode and cathode (half-cells) are separated by two bars or slashes representing a salt bridge.
- The anode on the left and cathode on the right.
- Individual solid, liquid or aqueous phases within each half-cell are separated by a single bar.
- Concentrations of dissolved species, in each phase written in parentheses and the state of each phase (usually s (solid), l (liquid), g (gas) or aq. (aqueous solution)) is included in a subscript after the species name.
-

Example: For a Daniel cell

Zn (s) | ZnSO4 (aq) || CuSO4 (aq) | Cu (s)

(anode)----------(cathode)

3. Write Cell reactions for

a) Ni / Ni^{+} // Cu^{++} / Cu

b) Cu^{++} / Cu // Cl^{-} / ½ Cl_2.....?

Ans:

a) Ni / Ni^{+} // Cu^{++} / Cu:

At left hand side electrode: $Ni \rightarrow Ni^{++} + 2e$ (Oxidation)

At right hand side electrode: $Cu^{++} + 2e \rightarrow Cu$ (Reduction)

Net Cell reaction $Ni + Cu^{++} \rightarrow Ni^{++} + Cu$

---

b) $Cu^{++} / Cu \ // \ Cl^- / \frac{1}{2} Cl_2$:

At left hand side electrode: $Cu^{++} + 2e \rightarrow Cu$ (Reduction)

At right hand side electrode: $2Cl^- \rightarrow Cl_2 + 2e$ (Oxidation)

Net Cell reaction $Cu^{++} + 2Cl^- \rightarrow Cu + Cl_2$

---

4. What is electrolytic cell?

Ans: Electrolytic cell: It is a device in which electrolysis (chemical reaction involving oxidation and reduction) is carried out by using electricity or in which conversion of electrical energy into chemical energy is done.

5. What is electrochemical cell?

Ans: Electrochemical cell is a system or arrangement in which two electrodes are fitted in the same electrolyte or in two different electrolytes which are joined by a salt bridge. Electrochemical cells are of two types:

(a) Electrolytic cell

(b) Galvanic or voltaic cell

6. What is Galvanic cell?

Ans: Galvanic or voltaic cell: It is a device in which a redox reaction is used to convert chemical energy into electrical energy, i.e., electricity can be obtained with the help of oxidation and reduction reaction. The chemical reaction responsible for production of electricity takes place in two separate compartments. Each compartment consists of a suitable electrolyte solution and a metallic conductor. The metallic conductor acts as an electrode. The compartments containing the electrode and the solution of the electrolyte are called half-cells. When the two compartments are connected by a salt bridge and electrodes are joined by a wire through galvanometer the electricity begins to flow. This is the simple form of voltaic cell.

7. What is salt Bridge?

Ans: Salt Bridge is usually an inverted U-tube filled with concentrated solution of inert electrolytes. An inert electrolyte is one whose ions are neither involved in any electrochemical change nor do they react chemically with the electrolytes in the two half-cells. Generally salts like KCl, $KN0_3$, NH_4N0_3, etc., are used. For the preparation of salt bridge, gelatin or agar-agar is dissolved in a hot concentrated aqueous solution of an inert electrolyte and the solution thus formed is filled in the U-tube. On cooling the solution sets in the form of a gel in the U-tube. The ends of the U-tube are plugged with cotton wool as to minimize diffusion effects. This is used as a salt bridge.

8. What is the Significance of Salt Bridge?

Ans: Significance of salt bridge: The following are the functions of the salt bridge:

(i) It connects the solutions of two half-cells and completes the cell circuit.

(ii) It prevents transference or diffusion of the solutions from one half-cell to the other.

(iii) It keeps the solutions in two half-cells electrically neutral. In anodic half cell, positive ions pass into the solution and there shall be accumulation of extra positive charge in the solution around the anode which will prevent the flow of electrons from anode. This does not happen because negative ions are provided by salt bridge. Similarly, in cathodic half-cell negative ions will accumulate around cathode due to deposition of positive ions by reduction. To neutralize these negative ions, sufficient number of positive ions is provided by salt bridge. Thus, salt bridge maintains electrical neutrality.

(iv) It prevents liquid-liquid junction-potential, i.e., the potential difference which arises between two solutions when in contact with each other.

A broken vertical line or two parallel vertical lines in a cell reaction indicates the salt bridge.

$$Zn|Zn^{2+}||Cu^{2+}|Cu$$

Salt bridge can be replaced by a porous partition which allows the migration of ions without allowing the solutions to intermix.

9. What is Standard Electrode potential?

Ans: **STANDARD ELECTRODE POTENTIAL**: In order to compare the electrode potentials of various electrodes, it is necessary to specify the concentration of the ions present in solution in which the electrode is dipped and the temperature of the half-cell. The potential difference developed between metal electrode and the solution of its ions of unit molarity (1M) at 25°C (298 K) is called standard electrode potential.

According to the IUPAC convention, the reduction potential alone be called as the electrode potential (E^O), i.e., the given value of electrode potential be regarded as reduction potential unless it is specifically mentioned that it is oxidation potential. Standard reduction potential of an electrode means that reduction reaction is taking place at the electrode. If the reaction is reversed and written as oxidation reaction, the numerical value of electrode potential will remain same but the sign of standard potential will have to be reversed. Thus

Standard reduction potential = - (Standard oxidation potential)

or Standard oxidation potential = - (Standard reduction potential

SHORT ANSWER QUESTIONS

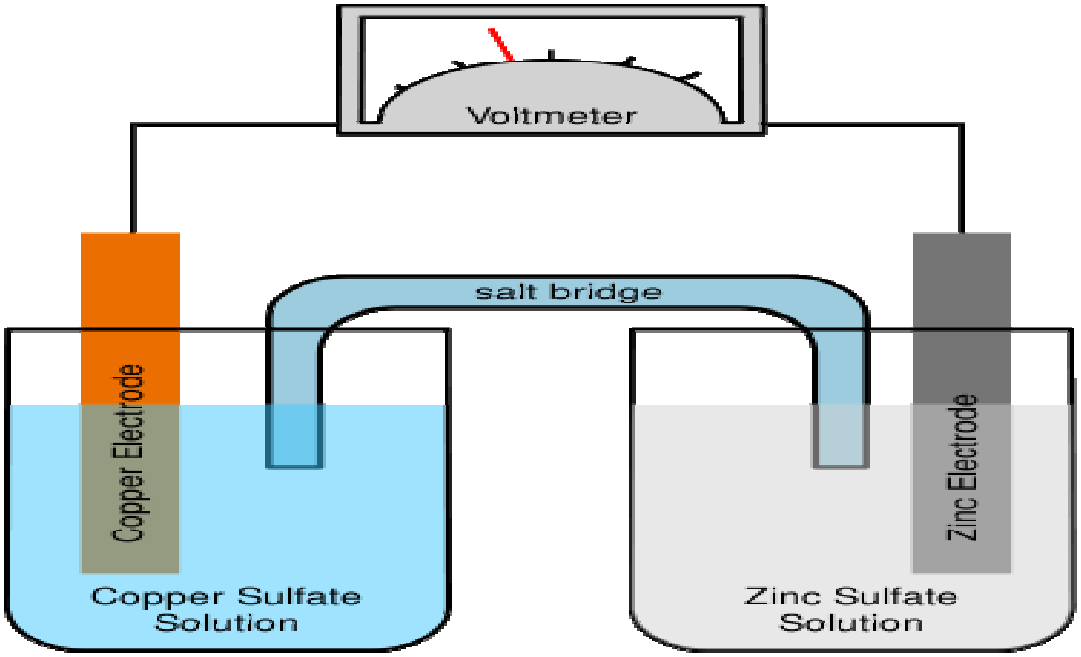
1. What are galvanic cells/ give two examples?

Ans:

Galvanic or voltaic cell: It is a device in which a redox reaction is used to convert chemical energy into electrical energy, i.e., electricity can be obtained with the help of oxidation and reduction reaction. The chemical reaction responsible for production of electricity takes place in two separate compartments. Each compartment consists of a suitable electrolyte solution and a metallic conductor. The metallic conductor acts as an electrode. The compartments containing the electrode and the solution of the electrolyte are called half-cells. When the two compartments are connected by a salt bridge and electrodes are joined by a wire through galvanometer the electricity begins to flow. This is the simple form of voltaic cell.

Examples are 1) Daniel Cell 2) Voltaic Cell\

1) Daniel cell



The Daniel cell consists of Zn rod dipped in ZnSo4 solution and Cu rod dipped in CuSO4 solutions of desired concentrations and the two electrodes are connected externally to a volt meter and a load. The containers are connected by a suitable salt bridge. Thus Daniel cell is formed It gives an emf of 1.1 V.

The galvanic cell, as the one shown in the figure, are conventionally described using the following notation:

Zn (s) | ZnSO4 (aq) || CuSO4 (aq) | Cu (s)

(anode)----------(cathode)

The Half reaction of Daniel Cell is shown below. Reduction potential of Zn is less than copper, hence Zn acts as anode and copper as cathode.

At anode $Zn \rightarrow Zn^{2+} + 2e^-$ (Oxidation)

At cathode $Cu^{2+} + 2e^- \rightarrow Cu$ (Reduction)

Cell reaction $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

---

2. What is Single electrode potential and write Nernst equation for single electrode potentials?

Ans: When a metal is placed in a solution of its ions, the metal acquires either a positive or negative charge with respect to the solution. On account of this, a definite potential difference is developed between the metal and the solution. This potential difference is called electrode potential or single electrode potential.

For example, when a plate of zinc is placed in a solution having Zn^{2+} ions, it becomes negatively charged with respect to solution and thus a potential difference is set up between zinc plate and the solution. This potential difference is termed the electrode potential of zinc. Similarly, when copper is placed in a solution having Cu^{2+} ions, it becomes positively charged with respect to solution. A potential difference is set up between the copper plate and the solution. The potential difference thus developed is termed as electrode potential of copper. The potential difference is established due to the formation of electrical double layer at the

$$M(s) \rightarrow M^{n+} + ne^-$$

The potential difference developed between metal electrode and the solution of its ions of unit molarity (1M) at 25°C (298 K) is called standard electrode potential. According to the IUPAC convention, the reduction potential alone be called as the electrode potential (E^O), i.e., the given value of electrode potential be regarded as reduction potential unless it is specifically mentioned that it is oxidation potential.

The General Nernst Equation

The general Nernst equation correlates the Gibb's Free Energy ΔG and the EMF of a chemical system known as the galvanic cell.

For the reaction,

$$a\,A + b\,B = c\,C + d\,D$$

Reaction Quotient 'Q; is given by,

$$Q = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

It has been shown and we know that,

$$\Delta G = \Delta\, G^\circ + R\,T \ln Q$$

and

$$\Delta G = -\,n\,F E. \quad \text{and} \quad \Delta G^\circ = -\,n\,F\,E^\circ$$

Therefore,

$$-\,n\,F\,E = -\,n\,F\,E^\circ + R\,T \ln Q$$

where, R= gas constant (8.314 J mol-1 K-1),
T= temperature (in K),
Q= reaction quotient
and, F = Faraday constant (96,500 C)

$$E = E^\circ - \frac{R\,T}{n\,F} \ln \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

This is known as the *Nernst* equation.
The equation allows us to calculate the cell potential of any galvanic cell for any concentrations. Some examples are given in the next section to illustrate its application.

Substituting all the values in the equation (R, T and F) the equation for metallic electrode becomes

$$E = E^\circ - \frac{0.059}{n} \log c$$

Where,

C= concentration of electrolyte solution

For non metallic electrode is given by

$$E = E^\circ - \frac{0.059}{n} \log \frac{\text{(Oxidised form)}}{\text{(Reduced form)}}$$

This equationis useful in calculation of elelctrode potentials of metal and non-metal electrodes.

LONG ANSWER QUESTIONS

1. What are galvanic cells? How are these represented? What is cell reaction and how is it written? Illustrate your answer?

Ans: **Galvanic or voltaic cell**: It is a device in which a redox reaction is used to convert chemical energy into electrical energy, i.e., electricity can be obtained with the help of oxidation and reduction reaction. The chemical reaction responsible for production of electricity takes place in two separate compartments. Each compartment consists of a suitable electrolyte solution and a metallic conductor. The metallic conductor acts as an electrode. The compartments containing the electrode and the solution of the electrolyte are called half-cells. When the two compartments are connected by a salt bridge and electrodes are joined by a wire through galvanometer the electricity begins to flow. This is the simple form of voltaic cell.

Daniell Cell: Chemical energy is converted into electrical energy.

The net reaction is the sum of two half-cell reactions. The reaction is Daniel cell can be represented as

Oxidation half reaction, $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

Reduction half reaction, $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Net reaction $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

REPRESENTATION OF AN ELECTROCHEMICAL CELL (GALVANIC CELL)

The following universally accepted conventions are followed in representing an electrochemical cell:

(i) The anode (negative electrode) is written on the left hand side and cathode (positive electrode) on the right hand side.

(ii) A vertical line or semicolon (;) indicates a contact between two phases. The anode of the cell is represented by writing metal first and then the metal ion present in the electrolytic solution. Both are separated by a vertical line or a semicolon. For example,

$Zn|Zn^{2+}$ or $Zn;Zn^{2+}$

The molar concentration or activity of the solution is written in brackets after the formula of the ion. For example:

$Zn|Zn^{2+}(1\ M)$ or $Zn \mid Zn^{2+}(0.1\ M)$

(iii) The cathode of the cell is represented by writing the cation of the electrolyte first and then metal. Both are separated by a vertical line or semicolon. For example,

$Cu^{2+}|Cu$ or $Cu^{2+};Cu$ or $Cu^{2+}(1\ M)|Cu$

(iv) The salt bridge which separates the two half-cells is indicated by two parallel vertical lines.

(v) Sometimes negative and positive signs are also put on the electrodes.

The Daniell cell can be represented as:

$Zn|ZnS0_4(aq)||CuS0_4(aq)|C^+u$

Anode Salt bridge Cathode

Oxidation half-cell Reduction half-cell

or $Zn|Zn^{2+}||Cu^{2+}|Cu$

or $Zn|Zn^{2+}(1\ M)||Cu^{2+}(1\ M)|Cu$

2. What is Nernst equation? Calculate the EMF of the galvanic cell?

$Zn \mid ZN^{2+}\ (1.0M) \parallel Cu^{2+}\ (1.0M) \mid Cu$

$E°_{zn2+/zn} = -0.766V$

$E°_{cu2+/cu}$ = + 0.327 V

Ans: The general Nernst equation correlates the Gibb's Free Energy ΔG and the EMF of a chemical system known as the galvanic cell.

For the reaction,

a A + b B = c C + d D

Reaction Quotient 'Q; is given by,

$$Q = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

It has been shown and we know that,

$$\Delta G = \Delta\, G° + R\,T \ln Q$$

and

$$\Delta G = -\,n\,FE. \quad \text{and} \quad \Delta G° = -\,n\,F\,E°$$

Therefore,

$$-\,n\,F\,E = -\,n\,F\,E° + R\,T \ln Q$$

where, R= gas constant (8.314 J mol-1 K-1),
T= temperature (in K),
Q= reaction quotient
and, F = Faraday constant (96,500 C)

$$E = E° - \frac{R\,T}{n\,F} \ln \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

This is known as the *Nernst* equation.
The equation allows us to calculate the cell potential of any galvanic cell for any concentrations. Some examples are given in the next section to illustrate its application.

Substituting all the values in the equation (R, T and F) the equation for metallic electrode becomes

$$E = E^\circ - \frac{0.059}{n} \log c$$

Where,

C= concentration of electrolyte solution

For non metallic electrode is given by

$$E = E^\circ - \frac{0.059}{n} \log \frac{\text{(Oxidised form)}}{\text{(Reduced form)}}$$

This equationis useful in calculation of elelctrode potentials of metal and non-metal electrodes.

$$E^\circ_{zn2+/zn} = E^\circ + \frac{0.059}{2} \log (1.0) = 0.766 + 0 = -0.766V$$

$$E^\circ_{cu2+/cu} = E^\circ + \frac{0.059}{2} \log (1.0) = +0.327 + 0 = -0.327V$$

$Zn^{2+}/Zn//Cu^{2+/}Cu$

(-0.766V)(+ 0. 327V)

EMF of galvanic cell = $E_{cell} = E_{cu2+/cu} - E_{zn2+/zn}$ = 0.327 - (- 0.766)

$\therefore$ E_{cell} = 1.093 V

ELECTRO CHEMISTRY

TOPIC-4
Faraday's laws of electrolysis and applications

VERY SHORT ANSWER QUESTIONS

1.Explain Faraday's First law of elelctrolysis?

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 = current in amperes × time in seconds

$= I \times t$

So $W \propto I \times t$

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

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

2. **Explain faraday's Second law of elelctrolysis?**

Ans: 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.

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 $Z = E/96500$

$z_1/z_2 = E_1/E_2$

3. **Explain how fundamental unit of charge can be found out?**

Ans: Fundamental unit of charge: As one g-equivalent of an ion is liberated by 96500 coulomb, it follows that charge carried by one g-equivalent of an ion is 96500 coulomb. If the valency of an ion is 'n', then one mole of these ions will carry a charge of nF coulomb. One g-mole of an ion contains 6.02×10^{23} ions.

Then,

The charge carried by an ion = $nF/(6.02 \times 10^{23})$ coulomb

For n = 1,

The fundamental unit of charge = $F/(6.02 \times 10^{23})$

i.e., $96500/(6.02 \times 1023) = 1.6 \times 10^{-19}$ coulomb

or 1 coulomb*=6.24×10^{18} electrons

The rate of following of electric charge through a conductor is called the electric current.

4. Find the charge in coulomb on 1 g-ion of?

Solution: Charge on one ion of N^{3-}

$= 3 \times 1.6 \times 10^{-19}$ coulomb

Thus, charge on one g-ion of N^{3-}

$= 3 \times 1.6\ 10^{-19} \times 6.02 \times 10^{23}$

$= 2.89 \times 10^{5}$ coulomb

5. How much charge is required to reduce (a) 1 mole of Al^{3+} to Al and (b)1 mole of to Mn^{2+}?

Solution: (a) The reduction reaction is

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

1 mole 3 mole

Thus, 3 mole of electrons are needed to reduce 1 mole of Al^{3+}.

$Q = 3 \times F$

$= 3 \times 96500 = 289500$ coulomb

(b) The reduction is

$Mn_4^- + 8H + 5e^- \rightarrow MN^{2+} + 4H_2O$

1 mole 5 mole

$Q = 5 \times F$

$= 5 \times 96500 = 48500$ coulomb

LONG ANSWER QUESTIONS

1. Explain the Faraday's Law of Electrolysis?

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 = current in amperes × time in seconds

$= I \times t$

So $W \propto I \times t$

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

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.

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.

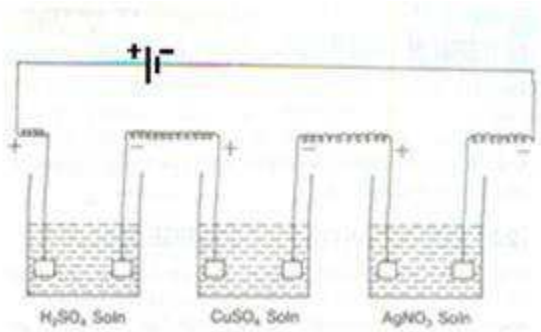


Fig. 12.1 Voltameters arranged in series

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 $Z = E/96500$

$$z_1/z_2 = E_1/E_2$$

2. Explain the applications of Faraday's Laws of electrolysis?
Ans:

Applications of Electrolysis

The phenomenon of electrolysis has wide application. The important ones are:

(1) Determination of equivalent masses of elements:

According to second law of electrolysis when the same quantity of electronic current is passed through solutions of salts of two different cells, the amounts of the metals deposited on the cathodes of the two cells are proportional to their equivalent masses of the respective metals. If the amounts of the metals deposited on the cathodes be W_A and W_B respectively, then

$$W_A/W_B = \text{(Equivalent mass of A)/(Equivalent mass of B)}$$

Knowing the equivalent mass of one metal, the equivalent mass of the other metal can be calculated from the above relationship. The equivalent masses of those non-metals which are evolved at anodes can also be determined by this method.

(2) Electron metallurgy:

The metals like sodium, potassium, magnesium, calcium aluminum, etc., are obtained by electrolytes of fused electrolytes.

Fused electrolyte	**Metal isolated**
$NaCl + CaCl_2 + KF$	Na
$CaCl_2 + CaF_2$	Ca
Al_2O_3 + cryolite	Al
$MgCi_2$ (35%) + NaCl (50%) + $CaCl_2$ (15%)	Mg
NaOH	Na
$KCl + CaCl_2$	K

(3) Manufacture of non-metals:

Non-metals like hydrogen, fluorine, chlorine are obtained by electrolysis.

(4) Electro-refining of metals:

The metals like copper, silver, gold, aluminum, tin, etc., are refined by electrolysis.

(5) Manufacture of compounds:

Compounds like NaOH, KOH, Na_2CO_3 $KClO_3$, white lead, $KMnO_4$, etc., are manufactured by electrolysis.

(6) Electroplating:

The process of coating an inferior metal with a superior metal by electrolysis is known as electroplating.

The aims of electroplating are:

(i) To prevent the inferior metal from corrosion.

(ii) To make it more attractive in appearance.

The object to be electroplated is made the cathode and block of the metal to be deposited is made the anode in an electrolytic bath containing a solution of a salt of the anodic metal. On passing electric current in the cell, the metal of the anode dissolves out and is deposited on the cathode-article in the form of a thin film. The following are the requirements for fine coating:

(i) The surface of the article should be free from greasy matter and its oxide layer. The surface is cleaned with chromic acid or detergents.

(ii) The surface of the article should be rough so that the metal deposited sticks permanently.

(iii) The concentration of the electrolyte should be so adjusted as to get smooth coating.

(iv) Current density must be the same throughout.

For electroplating	Anode	Cathode	Electrolyte
With copper	Cu	Object	$CuSo_4$ + dilute H_2So_4
With silver	Ag	Object	$KAg(CN)_2$
With nickel	Ni	Object	Nickel ammonium sulphate
With gold	Au	Object	$KAu(CN)_2$
With zinc	Zn	Iron objects	$ZnSO_4$
With thin	Sn	Iron objects	$SnSO_4$

Thickness of coated layer

Let the dimensions of metal sheet to be coated be (a cm × b cm).

Thickness of coated layer = c cm

Volume of coated layer = (a × b × c) cm^3

Mass of the deposited substance = Volume × density

$$= (a \times b \times c) \times d \text{ g}$$

$$\Rightarrow \quad (a \times b \times c) \times d = (I \times t \times E)/96500$$

Using above relation we may calculate the thickness of coated layer.

Solved Examples on Faraday's Laws of Electrolysis

Some Solved Examples

Example 1. Find the charge in coulomb on 1 g-ion of

Solution: Charge on one ion of N^{3-}

$= 3 \times 1.6 \times 10^{-19}$ coulomb

Thus, charge on one g-ion of N^{3-}

$= 3 \times 1.6\ 10^{-19} \times 6.02 \times 10^{23}$

$= 2.89 \times 10^{5}$ coulomb

Example 2. How much charge is required to reduce (a) 1 mole of Al^{3+} to Al and (b)1 mole of to Mn^{2+}?

Solution: (a) The reduction reaction is

$Al^{3+} + 3e^{-} \text{ --> } Al$

1 mole 3 mole

Thus, 3 mole of electrons are needed to reduce 1 mole of Al^{3+}.

$Q = 3 \times F$

$= 3 \times 96500 = 289500$ coulomb

(b) The reduction is

$Mn_4^{-} + 8H + 5e^{-} \text{ --> } MN^{2+} + 4H_2O$

1 mole 5 mole

$Q = 5 \times F$

$= 5 \times 96500 = 48500$ coulomb

Example 3. How much electric charge is required to oxidise (a) 1 mole of H_2O to O_2 and (b)1 mole of FeO to Fe_2O_3?

Solution: (a) The oxidation reaction is

$H_2O \rightarrow 1/2\ O_2 + 2H^+ + 2e^-$

1 mole 2 mole

$Q = 2 \times F$

$= 2 \times 96500 = 193000$ coulomb

(b) The oxidation reaction is

$FeO + 1/2\ H_2O \rightarrow Fe_2O_3 + H^+ + e^-$

$Q = F = 96500$ coulomb

Example 4 Exactly 0.4 faraday electric charge is passed through three electrolytic cells in series, first containing AgNO3, second CuSO4 and third FeCl3 solution. How many gram of rach metal will be deposited assuming only cathodic reaction in each cell?

Solution: The cathodic reactions in the cells are respectively.

$Ag^+ + e^- \rightarrow Ag$

1 mole 1 mole

108 g 1 F

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

1 mole 2 mole

63.5 g 2 F

and $Fe^{3+} + 3e^- \rightarrow Fe$

1 mole 3 mole

56 g 3 F

Hence, Ag deposited = 108 × 0.4 = 43.2 g

Cu deposited = 63.5/2×0.4 = 12.7 g

and Fe deposited = 56/3×0.4 = 7.47 g

Example 5 An electric current of 100 ampere is passed through a molten liquid of sodium chloride for 5 hours. Calculate the volume of chlorine gas liberated at the electrode at NTP.

Solution: The reaction taking place at anode is

$2Cl^- \rightarrow Cl_2 + 2e^-$

71.0 g 71.0 g 2 × 96500 coulomb

1 mole

Q = I × t = 100 × 5 × 600 coulomb

The amount of chlorine liberated by passing 100 × 5 × 60 × 60 coulomb of electric charge.

= 1/(2×96500)×100×5×60×60 = 9.3264 mole

Volume of Cl_2 liberated at NTP = 9.3264 × 22.4 = 208.91 L

Example 6. A 100 watt, 100 volt incandescent lamp is connected in series with an electrolytic cell containing cadmium sulphate solution. What mass of cadmium will be deposited by the current flowing for 10 hours?

Solution: We know that

Watt = ampere × volt

100 = ampere × 110

Ampere = 100/110

Quantity of charge = ampere × second

= 100/110×10×60×60 coulomb

The cathodic reaction is

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

112.4 g 2 × 96500 C

Mass of cadmium deposited by passing 100/110×10×60×60

Coulomb charge = 112.4/(2×96500)×100/110×10×60×60 = 19.0598 g

Example 7. In an electrolysis experiment, a current was passed for 5 hours through two cells connected in series. The first cell contains a solution gold salt and the second cell contains copper sulphate solution. 9.85 g of gold was deposited in the first cell. If the oxidation number of gold is +3, find the amount of copper deposited on the cathode in the second cell. Also calculate the magnitude of the current in ampere.

Solution: We know that

(Mass of Au deposited)/(Mass f Cu deposited)=(Eq.mass of Au)/(Eq.Mass of Cu)

Eq. mass of Au = 197/3 ; Eq. mass of Cu 63.5/2

Mass of copper deposited

= 9.85 × 63.5/2×3/197 g = 4.7625 g

Let Z be the electrochemical equivalent of Cu.

E = Z × 96500

or Z = E/96500 = 63.5/(2×96500)

Applying W = Z × I × t

T = 5 hour = 5 × 3600 second

4.7625 = 63.5/(2×96500) × I × 5 × 3600

or I = (4.7625 × 2 × 96500)/(63.5 × 5 × 3600) = 0.0804 ampere

Example 8. How long has a current of 3 ampere to be applied through a solution of silver nitrate to coat a metal surface of 80 cm2 with 0.005 cm thick layer? Density of silver is 10.5 g/cm^3.

Solution: Mass of silver to be deposited

= Volume × density

= Area ×thickness × density

Given: Area = 80 cm^2, thickness = 0.0005 cm and density = 10.5 g/cm^3

Mass of silver to be deposited = $80 \times 0.0005 \times 10.5$

$= 0.42$ g

Applying to silver $E = Z \times 96500$

$Z = 108/96500$ g

ELECTRO CHEMISTRY

TOPIC-5

Galvanic and voltaic cells, Cell notation with and with out salt bridge, salt bridge and its applications

VERY SHORT ANSWER QUESTIONS

1. What are galvanic cells?

It is a device in which a redox reaction is used to convert chemical energy into electrical energy, i.e., electricity can be obtained with the help of oxidation and reduction reaction. The chemical reaction responsible for production of electricity takes place in two separate compartments. Each compartment consists of a suitable electrolyte solution and a metallic conductor. The metallic conductor acts as an electrode. The compartments containing the electrode and the solution of the electrolyte are called half-cells. When the two compartments are connected by a salt bridge and electrodes are joined by a wire through galvanometer the electricity begins to flow. This is the simple form of voltaic cell.

2. **What are electrolytic cells?**

Ans: It is a device in which electrolysis (chemical reaction involving oxidation and reduction) is carried out by using electricity or in which conversion of electrical energy into chemical energy is done.

It is a device in which electrolysis (chemical reaction involving oxidation and reduction) is carried out by using electricity or in which conversion of electrical energy into chemical energy is done.

3. What is electrochemical cell?

ELECTROCHEMICAL CELL: Electrochemical cell is a system or arrangement in which two electrodes are fitted in the same electrolyte or in two different electrolytes which are joined by a salt bridge. Electrochemical cells are of two types:

(a) Electrolytic cell

(b) Galvanic or voltaic cell

4. **What is Salt Bridge?**

Ans: SALT BRIDGE: Salt bridge is usually an inverted U-tube filled with concentrated solution of inert electrolytes. An inert electrolyte is one whose ions are neither involved in any electrochemical change nor do they react chemically with the electrolytes in the two half-cells. Generally salts like KCl, $KN0_3$, NH_4N0_3, etc., are used. For the preparation of salt bridge, gelatin or agar-agar is dissolved in a hot concentrated aqueous solution of an inert electrolyte and the solution thus formed is filled in the U-tube. On cooling the solution sets in the form of a gel in the U-tube. The ends of the U-tube are plugged with cotton wool as to minimize diffusion effects. This is used as a salt bridge.

SHORT ANSWER QUESTIONS

1. What is the significance of Salt Bridge?

Ans: Significance of salt bridge: The following are the functions of the salt bridge:

(i) It connects the solutions of two half-cells and completes the cell circuit.

(ii) It prevents transference or diffusion of the solutions from one half-cell to the other.

(iii) It keeps the solutions in two half-cells electrically neutral. In anodic half cell, positive ions pass into the solution and there shall be accumulation of extra positive charge in the solution around the anode which will prevent the flow of electrons from anode. This does not happen because negative ions are provided by salt bridge. Similarly, in cathodic half-cell negative ions will accumulate around cathode due to deposition of positive ions by reduction. To neutralize these negative ions, sufficient number of positive ions is provided by salt bridge. Thus, salt bridge maintains electrical neutrality.

(iv) It prevents liquid-liquid junction-potential, i.e., the potential difference which arises between two solutions when in contact with each other.

A broken vertical line or two parallel vertical lines in a cell reaction indicates the salt bridge.

$$Zn|Zn^{2+}||Cu^{2+}|Cu$$

Salt bridge can be replaced by a porous partition which allows the migration of ions without allowing the solutions to intermix.

2. What are the electrode signs used in an electrochemical cell?

Ans: Electrode Signs

The signs of the anode and cathode in the voltaic or galvanic cells are opposite to those in the electrolytic cells (Fig. 12.8).

ELECTROLYTIC CELL **VOLTAIC OR GALVANIC CELL**

(e.m.f. is applied to cell) (e.m.f. is generated by cell)

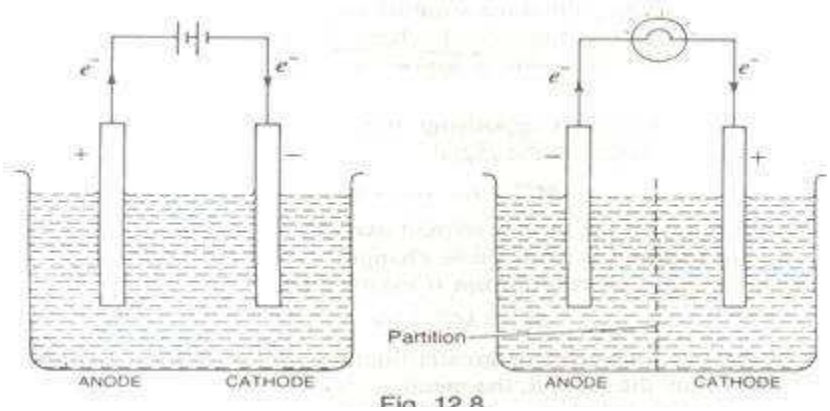


Fig. 12.8

	Electrolytic cell		Voltaic or Galvanic cell	
	Anode	**Cathode**	**Anode**	**Cathode**
Sign	+	-	-	+
Electron flow	Out	in	Out	in
Half-reaction	Oxidation	reduction	Oxidation reduction	

3. How an electrochemical cell is represented?

REPRESENTATION OF AN ELECTROCHEMICAL CELL (GALVANIC CELL)

The following universally accepted conventions are followed in representing an electrochemical cell:

(i) The anode (negative electrode) is written on the left hand side and cathode (positive electrode) on the right hand side.

(ii) A vertical line or semicolon (;) indicates a contact between two phases. The anode of the cell is represented by writing metal first and then the metal ion present in the electrolytic solution. Both are separated by a vertical line or a semicolon. For example,

$$\mathbf{Zn|Zn^{2+} \quad or \ Zn; Zn^{2+}}$$

The molar concentration or activity of the solution is written in brackets after the formula of the ion. For example:

$$Zn|Zn^{2+}(1\ M) \quad or \quad Zn \mid Zn^{2+}(0.1\ M)$$

(iii) The cathode of the cell is represented by writing the cation of the electrolyte first and then metal. Both are separated by a vertical line or semicolon. For example,

$$\mathbf{Cu^{2+}|Cu \quad or \quad Cu^{2+};Cu \quad or \quad Cu^{2+}(1\ M)|Cu}$$

(iv) The salt bridge which separates the two half-cells is indicated by two parallel vertical lines.

(v) Sometimes negative and positive signs are also put on the electrodes

4. How a Daniel cell is represented?

Ans: The Daniel cell can be represented as:

$$Zn|ZnS0_4(aq)||CuS0_4(aq)|C^{+}u$$

Anode Salt bridge Cathode

Oxidation half-cell Reduction half-cell

or $Zn|Zn^{2+}||Cu^{2+}|Cu$

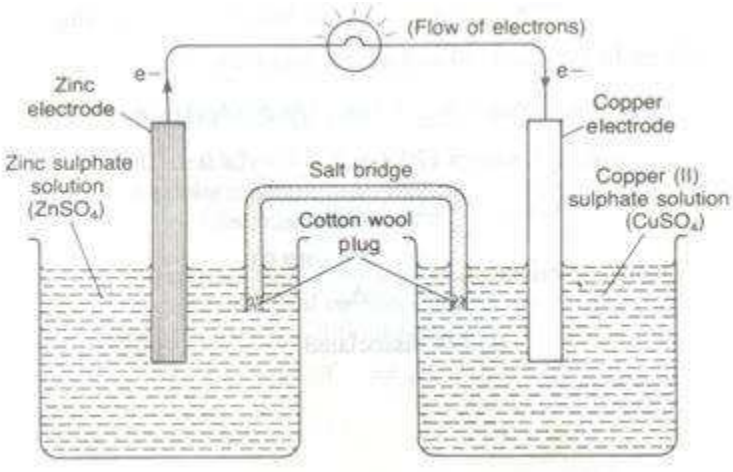
or $Zn|Zn^{2+}(1\ M)||Cu^{2+}(1\ M)|Cu$

LONG ANSWER QUESTIONS

1. Explain Daniel Cell.?

Ans: DANIEL CELL

It is designed to make use of the spontaneous redox reaction between zinc and cupric ions to produce an electric current (Fig.12.7). It consists of two half-cells. The half-cells on the left contains a zinc metal electrode dipped in $ZnSO_4$ solution.



The half-cell on the right consists of copper metal electrode in a solution $CuSO_4$. The half-cells are joined by a salt bridge that prevents the mechanical mixing of the solution.

When the zinc and copper electrodes are joined by wire, the following observations are made:

(i) There is a flow of electric current through the external circuit.

(ii) The zinc rod loses its mass while the copper rod gains in mass.

(iii) The concentration of ZnSO4 solution increases while the concentration of copper sulphate solution decreases.

(iv) The solutions in both the compartments remain electrically neutral.

During the passage if electric current through external circuit, electrons flow from the zinc electrode to the copper electrode. At the zinc electrode, the zinc metal is oxidized to zinc ions which go into the solution. The electrons released at the electrode travel through the external circuit to the copper electrode where they are used in the reduction of Cu^{2+}

ions to metallic copper which is deposited on the electrode. Thus, the overall redox reaction is:

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

Thus, indirect redox reaction leads to the production of electrical energy. At the zinc rod, oxidation occurs. It is the anode of the cell and is negatively charged while at copper electrode, reduction takes, place; it is the cathode of the cell and is positively charged.

Thus, the above points van be summed up as:

(i) Voltaic or Galvanic cell consists of two half-cells. The reactions occurring in half-cells are called half-cell reactions. The half-cell in which oxidation taking place in it is called oxidation half-cell and the reaction taking place in it is called oxidation half-cell reaction. Similarly, the half-cell occurs is called reduction half-cell and the reaction taking place in it is called reduction half-cell reaction.

(ii) The **electrode where oxidation occurs is called anode** and the **electrode where reduction occurs is termed cathode.**

(iii) Electrons flow from anode to cathode in the external circuit.

iv) Chemical energy is converted into electrical energy.

(v) The net reaction is the sum of two half-cell reactions. The reaction is Daniel cell can be represented as

Oxidation half reaction, $\mathbf{Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-}$

Reduction half reaction, $\mathbf{Cu^{2+}(aq) + 2e^- \rightarrow Cu\ (s)}$

Net reaction $\mathbf{Zn(s) + Cu^{2+}\ (aq) \rightarrow Zn^{2+}(aq) + Cu(s)}$

ELECTRO CHEMISTRY

TOPIC-6

Standard electrodes and electrochemical series, characteristics and applications

VERY SHORT ANSWER QUESTIONS

1. What is electrode potential?

When a metal is placed in a solution of its ions, the metal acquires either a positive or negative charge with respect to the solution. On account of this, a definite potential difference is developed between the metal and the solution. This potential difference is called electrode potential.

2. What is oxidation and reduction?

(a) Oxidation: It is process in which **m**etal ions pass from the electrode into solution leaving an excess of electrons and thus a negative charge on the electrode.

(b) Reduction: It is process in which Metal ions in solution gain electrons from the electrode leaving a positive charge on the electrode.

3. What is standard electrode potential?

Ans: In order to compare the electrode potentials of various electrodes, it is necessary to specify the concentration of the ions present in solution in which the electrode is dipped and the temperature of the half-cell. The potential difference developed between metal electrode and the solution of its ions of unit molarity (1M) at 25°C (298 K) is called **standard electrode potential.**

SHORT ANSWER QUESTIONS

1. Explain what are reversible and irreversible cells?

Ans: Daniel cell has the emf value 1.09 volt. If an opposing emf exactly equal to 1.09 volt is applied to the cell, the cell reaction,

$$Zn + Cu^{2+} \text{ --> } Cu + Zn^{2+}$$

stops but if it is increased infinitesimally beyond 1.09 volt, the cell reaction is reversed.

$$Cu + Zn^{2+} \text{ --> } Zn + Cu^{2+}$$

Such a cell is termed a **reversible cell**. Thus, the following are the two main conditions of reversibility:

(i) The chemical reaction of the cell stops when an exactly equal opposing emf is applied.

(ii) The chemical reaction of the cell is reversed and the current flows in opposite direction when the opposing emf is slightly greater than that of the cell.

Any other cell which does not obey the above two conditions is termed as irreversible. A cell consisting of zinc and copper electrodes dipped into the solution of sulphuric acid is **irreversible**. Similarly, the cell

$$Zn|H_2S0_4(aq)|Ag$$

is also irreversible because when the external emf is greater than the emf of the cell, the cell reaction,

$$Zn + 2H^+ \text{ --> } Zn^{2+} + H_2$$

is not reversed but the cell reaction becomes

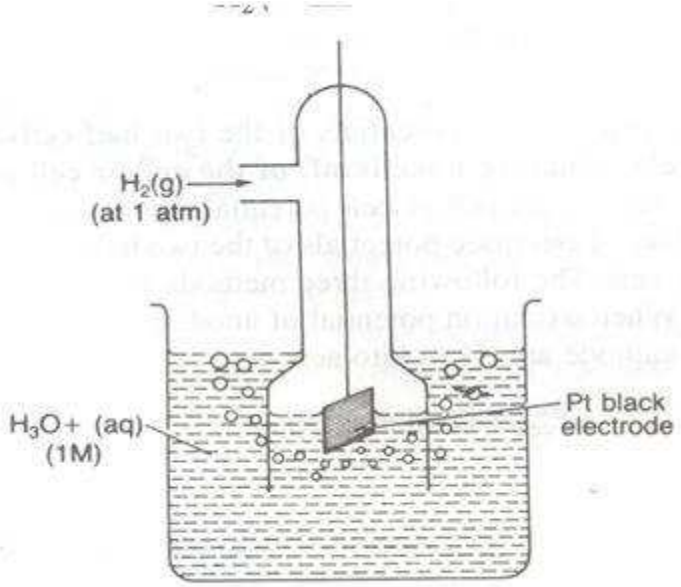
$$2Ag + 2H^+ \text{ --> } 2Ag^+ + H_2$$

2. Explain Standard Hydrogen Electrode?

Ans: STANDARD HYDROGEN ELECTRODE, (SHE OR NHE)

Hydrogen electrode is the primary standard electrode. It consists of a small platinum strip coated with platinum black as to adsorb hydrogen gas. A platinum wire is welded to the platinum strip and sealed in a glass tube as to make contact with the outer circuit through mercury. The platinum strip and glass tube is surrounded by an outer glass tube which has an inlet for hydrogen gas at the top and a number of holes at the base for the escape of excess of hydrogen gas. The platinum strip is placed in an acid solution which has H^+ ion concentration 1 M. Pure hydrogen gas is circulated at one atmospheric pressure. A part of the gas is adsorbed and the rest escapes through holes. This gives equilibrium between the adsorbed hydrogen and hydrogen ions in the solution.

$$\mathbf{H_2 \text{ <--> } 2H^+ + 2e^-}$$



The temperature of the cell is maintained at 25^0C. By international agreement the standard hydrogen electrode is arbitrarily assigned a potential of exactly ± 0.000 . .. volt.

The hydrogen electrode thus obtained forms one of two half-cells of a voltaic cell. When this half-cell is connected with any other half-cell, a voltaic cell is constituted. The hydrogen electrode can act as cathode or anode with respect to other electrode.

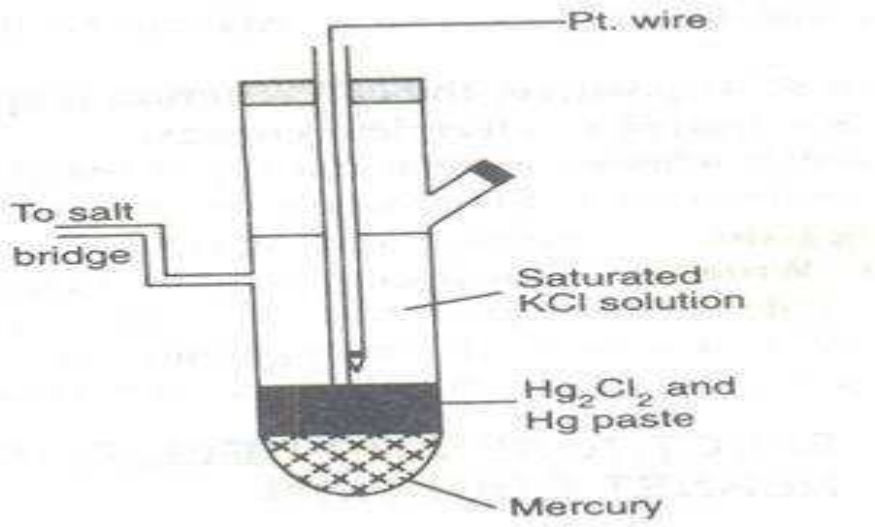
SHE half reaction	**Electrode potential**
$H_2 \text{ --> } 2H^+ + 2e^-$	0.0 V (Anode)
$2H^+ + 2e^- \text{ --> } H_2$	0.0 V (Cathode)

3 . Explain Standard Calomel Electrode?

Calomel electrode: It consists of mercury at the bottom over which a paste of mercury-mercurous chloride is placed. A solution of potassium chloride is then placed over the paste. A platinum wire sealed in a glass tube helps in making the electrical contact. The electrode is connected with the help of the side tube on the left through a salt bridge with the other electrode to make a complete cell.

The potential of the calomel electrode depends upon the concentration of the potassium chloride solution. If potassium chloride solution is saturated, the electrode is known as saturated calomel electrode (SCE) and if the potassium chloride solution is 1 N, the electrode is known as normal calomel electrode (NCE) while for 0.1 N potassium chloride solution, the electrode is referred to as decinormal calomel electrode (DNCE).

The electrode reaction when the electrode acts as cathode is:



1/2 Hg_2Cl_2 + e^- <---> Hg + Cl^-

The reduction potentials of the calomel electrodes on hydrogen scale at 298K are as follows:

Saturated KC1 0.2415 V

1.0NKC1 0.2800 V

0.1NKC1 0.3338 V

The electrode potential of any other electrode on hydrogen scale can be measured when it is combined with calomel electrode. The emf of such a cell is measured. From the value of electrode potential of calomel electrode, the electrode potential of the other electrode can be evaluated.

LONG ANSWER QUESTIONS

1. What is electrochemical series and what are its characteristics and applications?

Ans: ELECTROCHEMICAL SERIES

By measuring the potentials of various electrodes versus standard hydrogen electrode (SHE), a series of standard electrode potentials has been established. When the electrodes (metals and non-metals) in contact with their ions are arranged oh the basis of the values of their standard reduction potentials or standard oxidation potentials, the resulting series is called the **electrochemical** or **electromotive** or **activity series** of the elements.

By international convention, the standard potentials of electrodes are tabulated for reduction half reactions, indicating the tendencies of the electrodes to behave as cathodes towards SHE. Those with positive E° values for reduction half reactions do in fact act as cathodes versus SHE, while those with negative E° values of reduction half reactions behave instead as anodes versus SHE. The electrochemical series is shown in the following table.

Standard Aqueous Electrode Potentials at 25°C 'The Electrochemical Series'

Element	**Electrode Reaction (Reduction)**	**Standard Electrode Reduction potential E^o, volt**
Li	$Li^+ + e^- = Li$	-3.05
K	$K^+ + e^- = K$	-2.925
Ca	$Ca^{2+} + 2e^- = Ca$	-2.87
Na	$Na^+ + e^- = Na$	-2.714
Mg	$Mg^{2+} + 2e^- = Mg$	-2.37
Al	$Al^{3+} + 3e^- = Al$	-1.66
Zn	$Zn^{2+} + 2e^- = Zn$	-0.7628
Cr	$Cr^{3+} + 3e^- = Cr$	-0.74
Fe	$Fe^{2+} + 2e^- = Fe$	-0.44
Cd	$Cd^{2+} + 2e^- = Cd$	-0.403
Ni	$Ni^{2+} + 2e^- = Ni$	-0.25
Sn	$Sn^{2+} + 2e^- = Sn$	-0.14
H_2	$2H^+ + 2e^- = H_2$	0.00

Cu	$Cu^{2+} + 2e^- = Cu$	+0.337
I_2	$I_2 + 2e^- = 2I^-$	+0.535
Ag	$Ag^+ + e^- = Ag$	+0.799
Hg	$Hg^{2+} + 2e^- = Hg$	+0.885
Br_2	$Br_2 + 2e^- = 2Br^-$	+1.08
Cl_2	$Cl_2 + 2e^- = 2Cl^-$	+1.36
Au	$Au^{3+} + 3e^- = Au$	+1.50
F_2	$F_2 + 2e^- = 2F^-$	+2.87

Characteristics of Electrochemical series

(i) The negative sign of standard reduction potential indicates that an electrode when joined with SHE acts as anode and oxidation occurs on this electrode. For example, standard reduction potential of zinc is -0.76 volt. When zinc electrode is joined with SHE, it acts as anode (-ve electrode) i.e., oxidation occurs on this electrode. Similarly, the +ve sign of standard reduction potential indicates that the electrode when joined with SHE acts as cathode and reduction occurs on this electrode.

(ii) The substances which are stronger reducing agents than hydrogen are placed above hydrogen in the series and have negative values of standard reduction potentials. All those substances which have positive values of reduction potentials and placed below hydrogen in the series are weaker reducing agents than hydrogen.

(iii) The substances which are stronger oxidising agents than H^+ ion are placed below hydrogen in the series.

(iv) The metals on the top (having high negative values of standard reduction potentials) have the tendency to lose electrons readily. These are active metals. The activity of metals decreases from top to bottom. The non-metals on the bottom (having high positive values of standard reduction potentials)
have the tendency to accept electrons readily. These are active non-metals. The activity of non-metals increases from top to bottom.

Applications of Electrochemical series

(i) Reactivity of metals:

The activity of the metal depends on its tendency to lose electron or electrons, i.e., tendency to form cation (M^{n+}). This tendency depends on the magnitude of standard reduction potential. The metal which has high negative value (or smaller positive value) of standard reduction potential readily loses the electron or electrons and is converted into cation. Such a metal is said to be chemically active.

The chemical reactivity of metals decreases from top to bottom in the series. The metal higher in the series is more active than the metal lower in the series. For example,

(a) Alkali metals and alkaline earth metals having high negative values of standard reduction potentials are chemically active. These react with cold water and evolve hydrogen. These readily dissolve in acids forming corresponding salts and combine with those substances which accept electrons.

(b) Metals like Fe, Pb, Sn, Ni, Co, etc., which lie a little down in the series do not react with cold water but react with steam to evolve hydrogen.

(c) Metals like Cu, Ag and Au which lie below hydrogen are less reactive and do not evolve hydrogen from water.

(ii) Electropositive character of metals:

The electropositive character also depends on the tendency to lose electron or electrons. Like reactivity, the electropositive character of metals decreases from top to bottom in the electrochemical series. On the basis of standard reduction potential values, metals are divided into three groups:

(a) Strongly electropositive metals: Metals having standard reduction potential near about -2.0 volt or more negative like alkali metals, alkaline earth metals are strongly electropositive in nature.

(b) Moderately electropositive metals: Metals having values of reduction potentials between 0.0 and about -2.0 volt are moderately electropositive. Al, Zn, Fe, Ni, Co, etc., belong to this group.

(c) Weakly electropositive metals: The metals which are below hydrogen and possess positive values of reduction potentials are weakly electropositive metals. Cu, Hg, Ag, etc., belong to this group.

(iii) Displacement reactions:

(a) To predict whether a given metal will displace another, from its salt solution. A metal higher in the series will displace the metal from its solution which is lower in the series, i.e., the metal having low standard reduction potential will displace the metal from its salt's solution which has higher value of standard reduction potential. A metal higher

in the series has greater tendency to provide electrons to the cations of the metal to be precipitated.

(b) Displacement of one nonmetal from its salt solution by another nonmetal: A nonmetal higher in the series (towards bottom side), i.e., having high value of reduction potential will displace another nonmetal with lower reduction potential i.e., occupying position above in the series. The nonmetal's which possess high positive reduction potentials have the tendency to accept electrons readily. These electrons are provided by the ions of the nonmetal having low value of reduction potential. Thus, Cl_2 can displace bromine and iodine from bromides and iodides.

$Cl_2 + 2KI \rightarrow 2KC1 + I_2$

$21^- \rightarrow I_2 + 2e^-$ (Oxidation)

$Cl_2 + 2e- \rightarrow 2C1^-$ (Reduction)

[The activity or electronegative character or oxidising nature of the nonmetal increases as the value of reduction potential increases.]

(c) Displacement of hydrogen from dilute acids by metals: The metal which can provide electrons to H^+ ions present in dilute acids for reduction, evolve hydrogen from dilute acids.

$Mn \rightarrow Mn''^+ + ne^-$ (Oxidation)

$2H^+ + 2e^- \rightarrow H_2$ (Reduction)

The metal having negative values of reduction potential possess the property of losing electron or electrons.

Thus, the metals occupying top positions in the electrochemical series readily liberate hydrogen from dilute acids and on descending in the series tendency to liberate hydrogen gas from dilute acids decreases.

The metals which are below hydrogen in electrochemical series like Cu, Hg, Au, Pt, etc., do not evolve hydrogen from dilute acids.

(d) Displacement of hydrogen from water: Iron and the metals above iron are capable of liberating hydrogen from water. The tendency decreases from top to bottom in electrochemical series.

Alkali and alkaline earth metals liberate hydrogen from cold water but Mg, Zn and Fe liberate hydrogen from hot water or steam.

(iv) Reducing power of metals:

Reducing nature depends on the tendency of losing electron or electrons. More the negative reduction potential, more is the tendency to lose electron or electrons. Thus, reducing nature decreases from top to bottom in the electrochemical series. The power of the reducing agent increases as the standard reduction potential becomes more and more negative.

Sodium is a stronger reducing agent than zinc and zinc is a stronger reducing agent than iron.

Element	Na	Zn	Fe
Reduction potential	-2.71	-0.76	-0.44

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Reducing nature decreases

Alkali and alkaline earth metals are strong reducing agents.

(v) Oxidising nature of nonmetals:

Oxidising nature depends on the tendency to accept electron or electrons. More the value of reduction potential, higher is the tendency to accept electron or electrons. **Thus, oxidising nature increases from top to bottom in the electrochemical series.** The strength of an oxidising agent increases as the value of reduction potential becomes more and more positive.

F_2 (Fluorine) is a stronger oxidant than Cl_2, Br_2 and I_2.

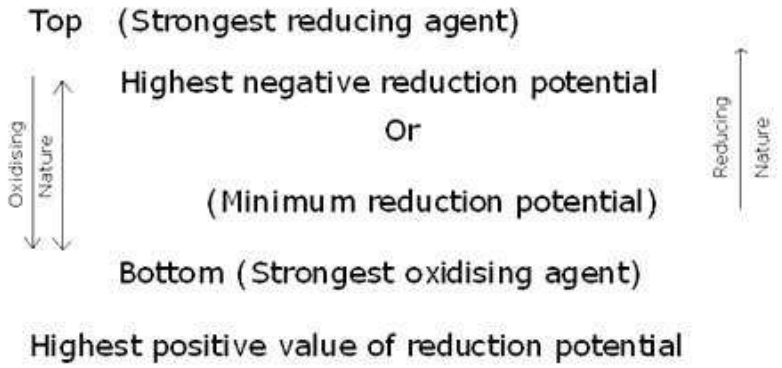
Cl_2 (Chlorine) is a stronger oxidant than Br_2 and I_2.

Element	I_2	Br_2	Cl_2	F_2
Reduction potential	+0.53	+1.06	+1.36	+2.85

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Oxidising nature increases

Thus, in electrochemical series

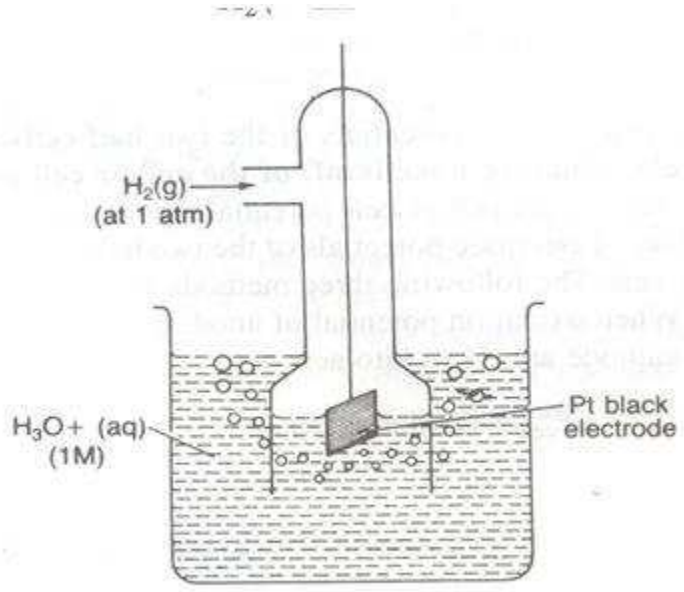


2. What is standard Hydrogen electrode and what are its applications?

Ans: STANDARD HYDROGEN ELECTRODE (SHE OR NHE)

Hydrogen electrode is the primary standard electrode. It consists of a small platinum strip coated with platinum black as to adsorb hydrogen gas. A platinum wire is welded to the platinum strip and sealed in a glass tube as to make contact with the outer circuit through mercury. The platinum strip and glass tube is surrounded by an outer glass tube which has an inlet for hydrogen gas at the top and a number of holes at the base for the escape of excess of hydrogen gas. The platinum strip is placed in an acid solution which has H^+ ion concentration 1 M. Pure hydrogen gas is circulated at one atmospheric pressure. A part of the gas is adsorbed and the rest escapes through holes. This gives equilibrium between the adsorbed hydrogen and hydrogen ions in the solution.

$$\mathbf{H_2 <--> 2H^+ + 2e^-}$$



The temperature of the cell is maintained at 25^0C. By international agreement the standard hydrogen electrode is arbitrarily assigned a potential of exactly ± 0.000 . .. volt.

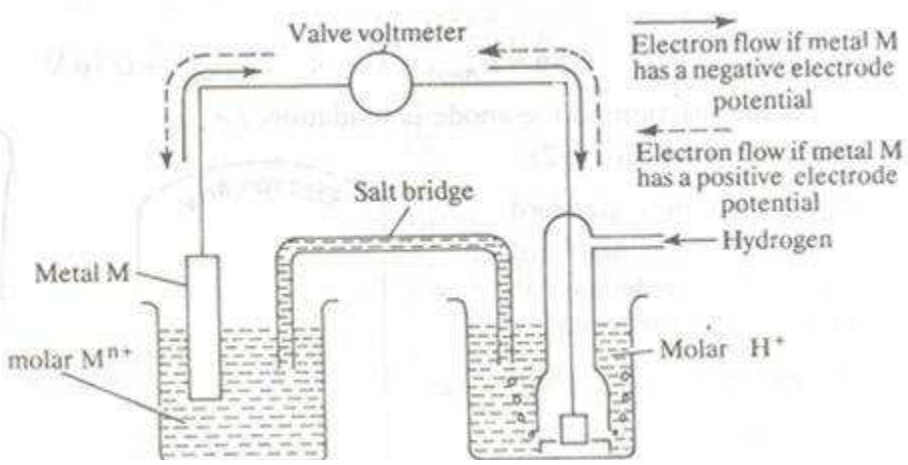
The hydrogen electrode thus obtained forms one of two half-cells of a voltaic cell. When this half-cell is connected with any other half-cell, a voltaic cell is constituted. The hydrogen electrode can act as cathode or anode with respect to other electrode.

SHE half reaction	**Electrode potential**
H_2 --> $2H^+ + 2e^-$	0.0 V (Anode)
$2H^+ + 2e^-$ --> H_2	0.0 V (Cathode)

Applications:

MEASUREMENT OF ELECTRODE POTENTIAL

The measurement of electrode potential of a given electrode is made by constituting a voltaic cell, i.e., by connecting it with a standard hydrogen electrode (SHE) through a salt bridge. 1 M solution is used in hydrogen half-cell and the temperature is



maintained at 25^oC. The emf of the cell is measured either by a calibrated potentiometer or by a high resistance voltmeter, i.e., a valve voltmeter. The reading of the voltmeter gives the electrode potential of the electrode in question with respect to the hydrogen electrode. The standard electrode potential of a metal may be determined as it is the potential difference in volt developed in a cell consisting of two electrodes: the pure metal is contact with a molar solution of one of its ions and the standard hydrogen electrode.

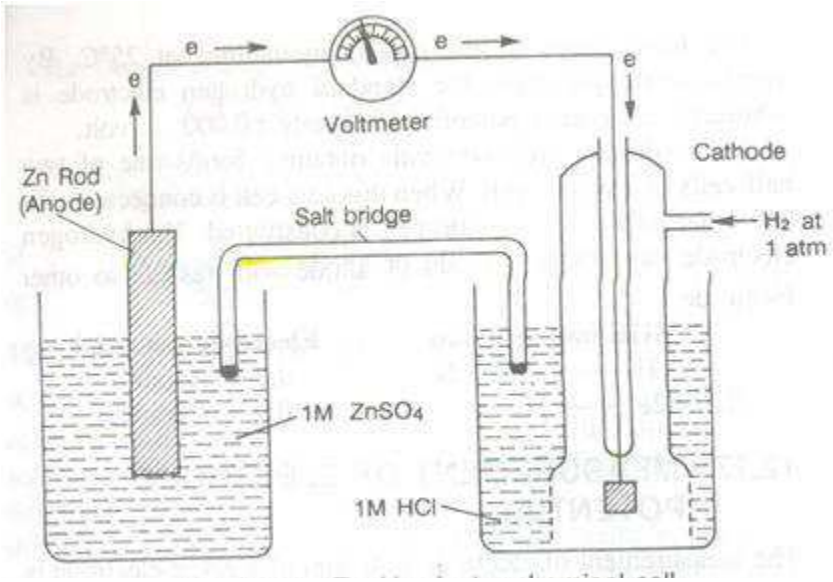
(i) Determination of standard electrode potential of Zn/Zn^{2+} electrode:

A zinc rod is dipped in 1 M zinc sulphate solution. This half-cell is combined with a standard hydrogen electrode through a salt bridge. Both the electrodes are connected with a voltmeter as shown in Fig. 12.12. The deflection of the voltmeter indicates that current is flowing from hydrogen electrode to metal electrode or the electrons are moving from zinc rod to hydrogen electrode. The zinc electrode acts as an anode and the hydrogen electrode as cathode and the cell can be represented as

$$Zn|Zn^{2+}\ (aq)/Anode(-)\ ||\ 2H(aq)|\ H_2\ (g)/Cathode\ (+)$$

$$Zn \rightarrow Zn^{2+} + 2e^-;\ 2H^+ + 2e^- \rightarrow H_2\uparrow$$

(Oxidation) (Reduction)



The emf of the cell is 0.76 volt

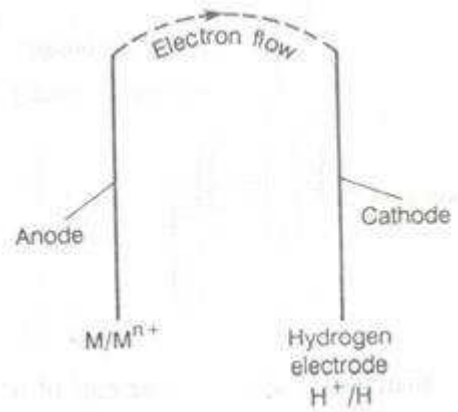
$$E_{Cell} = E^o_{Anode} + E^o_{Cathode}$$

$$0.76 = E^o_{Anode} + 0 \text{ or } E^o_{Anode} = +0.76\ V$$

As the reaction on the anode is oxidation, i.e.,

$$Zn \rightarrow Zn^{2+} + 2e,$$

E^o_{Anode} is the standard oxidation potential of zinc. This potential is given the positive sign.



E^o_{ox} (Zn/Zn^{2+}) = +0.76 volt

So standard reduction potential of Zn, i.e., E^o (Zn/Zn^{2+})

= E^o_{ox} = -(+0.76)

= -0.76 volt

The emf of such a cell gives the positive value of standard oxidation potential of metal M. The standard reduction potential (E^o) is obtained by reversing the sign of standard oxidation potential.

(i) Determination of standard electrode potential of Cu^{2+}/Cu, electrode:

A copper rod is dipped in 1 M solution of CuSO4. It is combined with hydrogen electrode through a salt bridge. Both the electrodes joined through a voltmeter. The deflection of the voltmeter indicates that current is flowing from copper electrode towards hydrogen electrode, i.e., the electrons ate moving from hydrogen to copper electrode. The hydrogen electrode acts as an anode and the copper electrode as a cathode. The cell can be represented as

$$H_2\,(g)|2H^+\,(aq)\,||Cu^{2+}\,(aq)\,|Cu$$

Anode (-) Cathode (+)

$$H_2 \text{ --> } 2H^+ + 2e^- \,;\, Cu^{2+}\, 2e^- \text{ --> } Cu$$

Oxidation Reduction

The emf of the cell is 0.34 volt.

$$\mathbf{E^o_{Cell} = E^o_{Anode} + E^o_{Cathode}}$$

$$\mathbf{0.34 = 0 + E^{o}_{Cathode}}$$

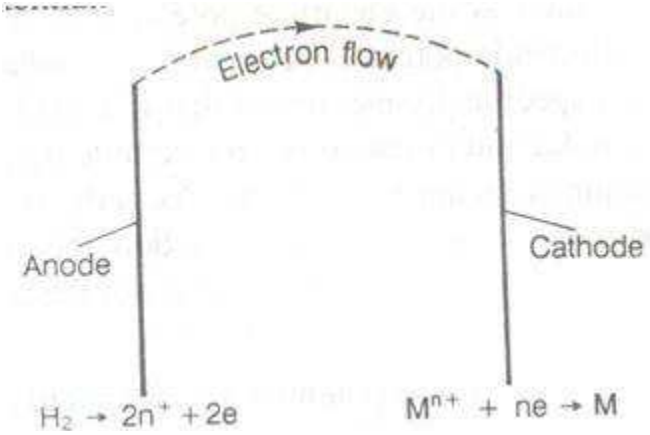
Since the reaction on the cathode is reduction, i.e.,
$Cu^{2+} + 2e^{-}$ --> Cu, $E^{o}_{Cathode}$ is the standard reduction potential of copper. This is given the +ve sign.

E°, i.e., standard reduction potential of Cu^{2+}/Cu = 0.34 volt

So $E°_{x}$ (standard oxidation potential of copper) = -0.34 volt

The emf of such a cell gives positive value of reduction potential of metal electrode. The standard oxidation potential of this electrode is obtained by reversing the sign of standard reduction potential.

The emf of such a cell gives the positive value of standard oxidation potential of metal M. The standard reduction potential (E°) is obtained by reversing the sign of standard oxidation potential.



It is thus concluded that at the metal electrode which acts as anode with respect to hydrogen electrode (cathode), the reduction potential is given the minus sign and at the metal electrode which acts as cathode with respect to hydrogen electrode (anode), the reduction potential is given the positive sign.

The standard electrode potentials (oxidation or reduction) of various elements can be measured by combining the electrode in question with a standard hydrogen electrode and measuring the emf of the cell constituted.

ELECTRO CHEMISTRY

TOPIC-7
Types of cells, primary, secondary and fuel cells, construction and working

VERY SHORT ANSWER QUESTIONS

1. **What is primary cell?**

Ans:

In this cell, once the chemicals have been consumed, further reaction is not possible. It cannot be regenerated by reversing the current flow through the cell using an external direct current source of electrical energy. The most common example of this type is dry cell

2. **What is Secondary cell?**

Ans:

The cell in which original reactants are regenerated by passing direct current from external source, i.e., it is re-charged, is called secondary cell. Lead storage battery is the example of this type.

3. What is Fuel Cell?

Ans:

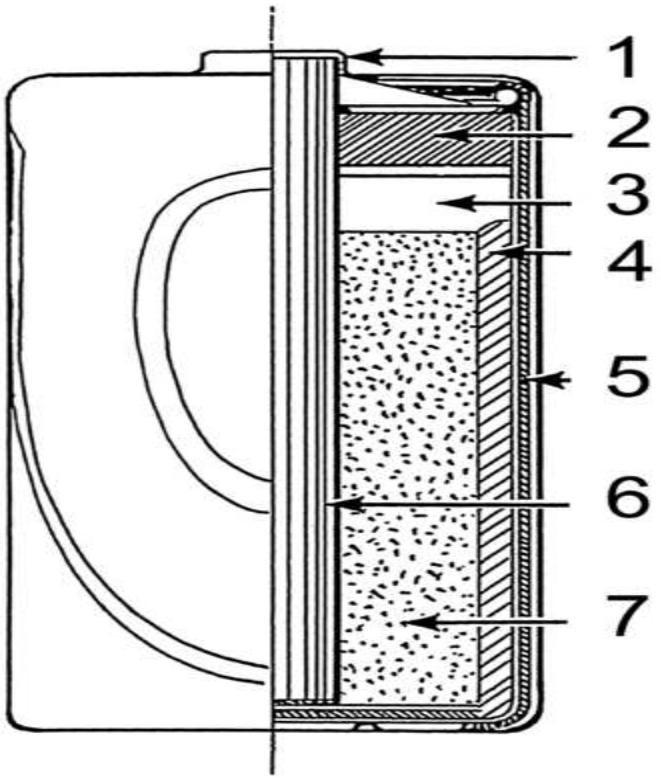
Fuel cells are another means by which chemical energy may be converted into electrical energy. The main disadvantage of a primary cell is that it can deliver current for a short period only. This is due to the fact that the quantity of oxidising agent and reducing agent is limited. But the energy can be obtained indefinitely from a fuel cell as long as the outside supply of fuel is maintained. One of the examples is the hydrogen-oxygen fuel cell.

SHORT ANSWER QUESTIONS

1. Explain a primary voltaic cell?

Ans: PRIMARY VOLTAIC CELL (THE DRY CELL)

In this cell, once the chemicals have been consumed, further reaction is not possible. It cannot be regenerated by reversing the current flow through the cell using an external direct current source of electrical energy. The most common example of this type is dry cell.



1. Brass cap
2. Plastic seal
3. Expansion space
4. Porous cardboard
5. Zinc can
6. Carbon rod
7. Chemical mixture

The container of the dry cell is made of zinc which also serves as one of the electrodes. The other electrode is a carbon rod in the centre of the cell. The zinc container is lined with a porous paper. A moist mixture of ammonium chloride, manganese dioxide, zinc chloride and porous inert filler occupy the space between the paper lined zinc container and the carbon rod. The cell is sealed with a material like wax.

As the cell operates, the zinc is oxidised to Zn^{2+}

$$\mathbf{Zn \ ---> \ Zn^{2+} + 2e^{-} \quad (Anode\ reaction)}$$

The electrons are utilized at carbon rod (cathode) as the ammonium ions are reduced.

$$\mathbf{2NH_4^{+} + 2e^{-} \dashrightarrow 2NH_3 + H_2 \quad (Cathode\ reaction)}$$

The cell reaction is

$$Zn + 2\ NH_4^+ \longrightarrow Zn^{2+} + 2NH_3 + H_2$$

Hydrogen is oxidized by MnO_2 in the cell.

$$2MnO_2 + H_2 \longrightarrow 2MnO(OH)$$

Ammonia produced at cathode combines with zinc ions to form complex ion.

$$Zn^{2+} + 4NH_3 \longrightarrow [Zn(NH_3)_4]_{2+}$$

E_{cell} is 1.6 volt

Alkaline dry cell is similar to ordinary dry cell. It contains potassium hydroxide. The reaction in alkaline dry cell are:

$$Zn + 2OH^- \longrightarrow Zn(OH)_2 + 2e^- \qquad \textbf{(Anode reaction)}$$

$$2MnO_2 + 2H_2O + 2e^- \longrightarrow 2MnO(OH) + 2OH^- \qquad \textbf{(Cathode reaction)}$$

$$Zn + 2MnO_2 + 2H_2O \longrightarrow Zn(OH)_2 + 2MnO(OH) \qquad \textbf{(Overall)}$$

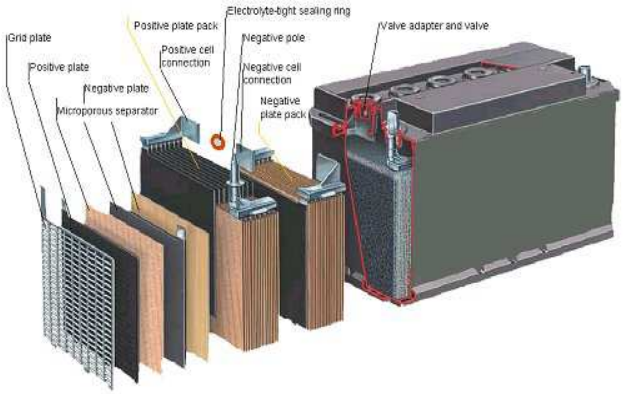
E_{cell} is 1.5 volt.

2. **Explain a secondary voltaic cell?**

Ans:

SECODARY VOLTAIC CELL (LEAD STORAGE BATTERY)

The cell in which original reactants are regenerated by passing direct current from external source, i.e., it is re-charged, is called secondary cell. Lead storage battery is the example of this type.



It consists of a group of lead plates bearing compressed spongy lead, alternating with a group of lead plates bearing leaf dioxide, PbO_2. These plates are immersed in a solution of about 30% H2SO4. When the cell discharges; it operates as a voltaic cell. The spongy lead is oxidized to Pb2+ ions and lead plates acquire a negative charge.

$$\mathbf{Pb \dashrightarrow Pb^{2+} + 2e^-} \qquad \textbf{(Anode reaction)}$$

Pb^{2+} ions combine with sulphate ions to form insoluble lead sulphate, $PbSO_4$, which begins to coat lead electrode.

$$\mathbf{Pb^{2+} + SO_4^{2-} \dashrightarrow PbSO_4} \qquad \textbf{(Precipitation)}$$

The electrons are utilized at PbO_2 electrode.

$$\mathbf{PbO_2 + 4H^+ + 2e^- \dashrightarrow Pb^{2+}\ 2H_2O} \qquad \textbf{(Cathode reaction)}$$

$$\mathbf{Pb^{2+} + SO_4^{2-} \dashrightarrow PbSO_4} \qquad \textbf{(Precipitation)}$$

Overall cell reaction is:

$$\mathbf{Pb + PbO_2 + 4H^+ + 2\ SO_4^{2-} \dashrightarrow 2PbSO_4 + 2H_2O}$$

Ecell is 2.041 volt.

When a potential slightly greater than the potential of battery is applied, the battery can be re-charged.

$$\mathbf{2PbSO_4 + 2H_2O \dashrightarrow\ Pb + PbO_2 + 2H_2SO_4}$$

After many repeated charge-discharge cycles, some of the lead sulphate falls to the bottom of the container, the sulphuric acid concentration remains low and the battery cannot be recharged fully.

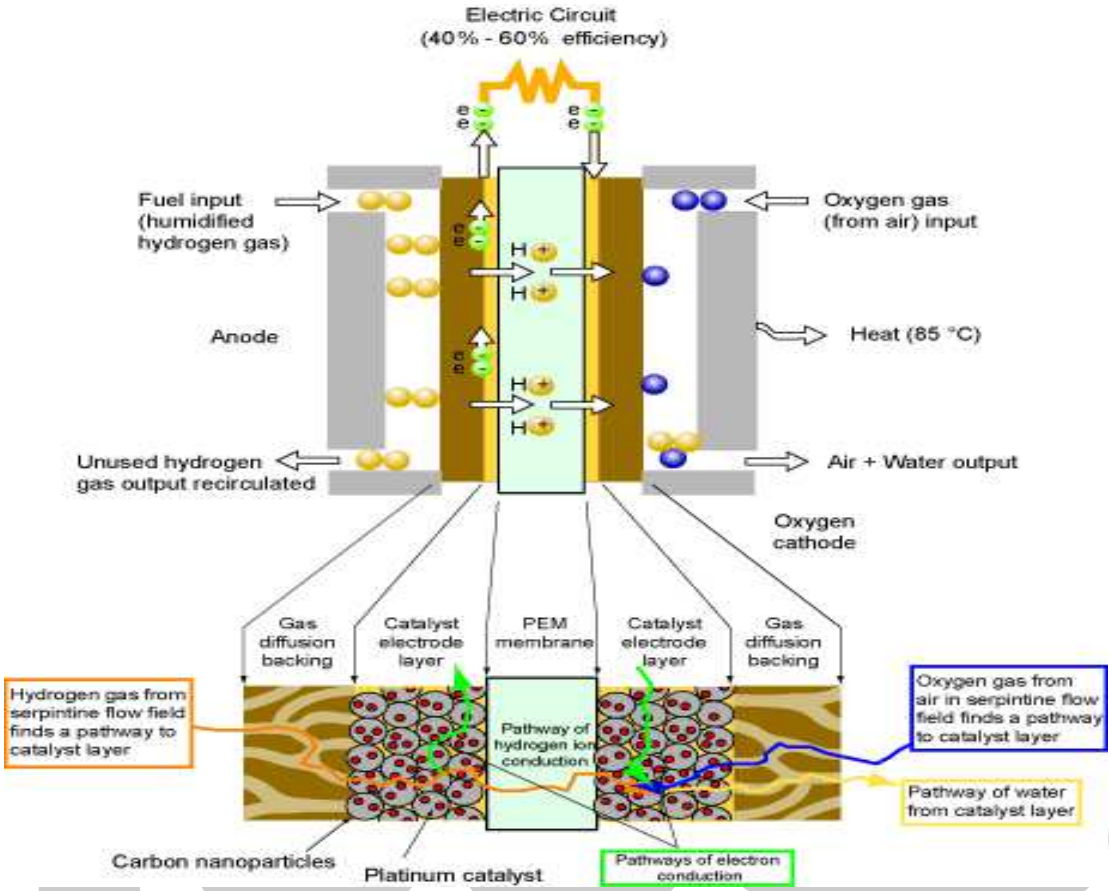
LONG ANSWER QUESTIONS

1. **Explain Construction and working of Fuel Cell?**

Ans:

FUEL CELL

Fuel cells are another means by which chemical energy may be converted into electrical energy. The main disadvantage of a primary cell is that it can deliver current for a short period only. This is due to the fact that the quantity of oxidising agent and reducing agent is limited. But the energy can be obtained indefinitely from a fuel cell as long as the outside supply of fuel is maintained.



One of the examples is the hydrogen-oxygen fuel cell. The cell consists of three compartments separated by a porous electrode. Hydrogen gas is introduced into one compartment and oxygen gas is fed into another compartment. These gases then diffuse slowly through the electrodes and react with an electrolyte that is in the central compartment. The electrodes are made of porous carbon and the electrolyte is a resin containing concentrated aqueous sodium hydroxide solution. Hydrogen is oxidised at anode and oxygen is reduced at cathode. The overall cell reaction produces water. The reactions which occur are:

Anode $[H_2(g) + 2OH^-(aq) \quad ---> \quad 2H_2O(l) + 2e^-] \times 2$

Cathode $\quad O_2(g) + 2H_2O(l) + 4e^- \quad ---> \quad 4OH^-(aq)$

Overall $\quad 2H_2(g) + O_2(g) ---> \quad 2H_20(l)$

These types of cells are used in space-crafts. Fuel cells are efficient and pollution free.

ELECTRO CHEMISTRY

TOPIC-8
Corrosion mechanism, preventions and control, Lead accumulator

VERY SHORT ANSWER QUESTIONS

1. What is corrosion?
Ans:

Corrosion is the disintegration of an engineered material into its constituent atoms due to chemical reactions with its surroundings. In the most common use of the word, this means electrochemical oxidation of metals in reaction with an oxidant such as oxygen. Formation of an oxide of iron due to oxidation of the iron atoms in solid solution is a well-known example of electrochemical corrosion, commonly known as rusting. This type of damage typically produces oxide(s) and/or salt(s) of the original metal.

2. What is passivation?

Ans:
Passivation is the process of making a material "passive", usually by the deposition of a layer of oxide on its surface. In air, passivation affects the properties of almost all metals–notable examples being aluminium, zinc, titanium, and silicon (a metalloid). In the context of corrosion, **passivation** is the spontaneous formation of a hard non-reactive surface film that inhibits further corrosion. This layer is usually an oxide or nitride that is a few nanometers thick.

3. What is galvanic corrosion?
Ans: Galvanic corrosion is an electrochemical process in which one metal corrodes preferentially to another when both metals are in electrical contact and immersed in an electrolyte. The same galvanic reaction is exploited in primary batteries to generate a voltage

SHORT ANSWER QUESTIONS\

1. What is the mechanism of corrosion?
Ans:

Any process of deterioration (or destruction) and consequent loss of a solid metallic material, through an unwanted (or unintentional) chemical or electrochemical attack by its environment, starting at its surface is called corrosion. The most familiar example of corrosion is rusting of iron. Thus corrosion is a process reverse of extraction of metals.

Classification of Corrosion

Based on the mechanism of corrosion, it is classified into two types

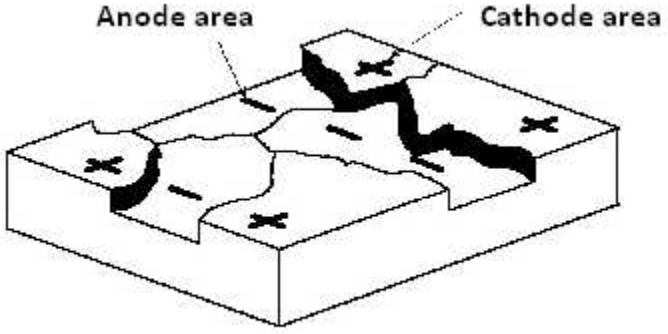
1. Chemical or dry corrosion
2. Electrochemical or wet corrosion

Dry corrosion:

- Corrosion takes place in dry state.
- In occurs due to the direct chemical attack of the metal by the environment.
- Corrosion products accumulate on the same spot, where corrosion occurs.
- Dry corrosion is self controlled.
- It follows absorption mechanism.
- Homogenous metal surface undergoes corrosion observed.
- Uniform corrosions are observed. Example: Formation of mild iron oxide on its surface.

Wet corrosion:

- Corrosion takes place in the presence of moisture.
- It occurs due to the setting up of large numbers of galvanic cells.
- Corrosion products accumulate on cathode.
- Wet corrosion is continuous process.



Wet corrosion

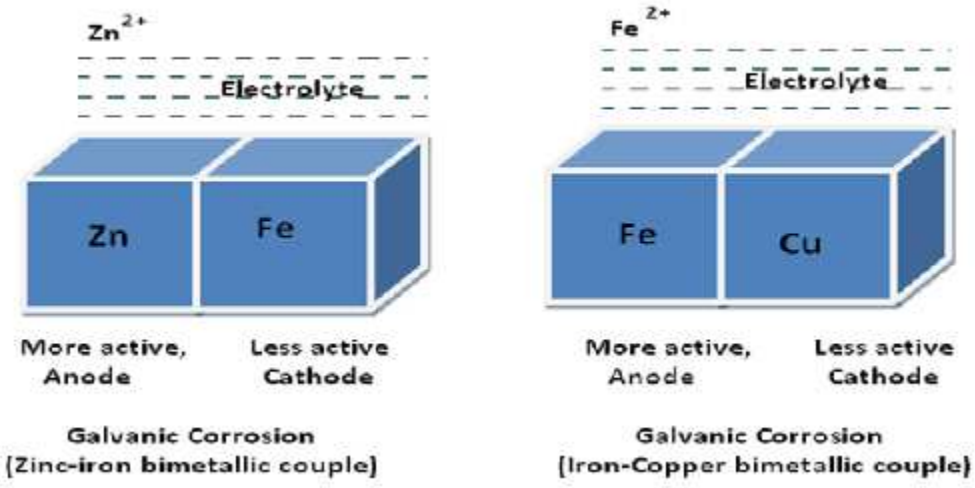
- It follows electrochemical mechanism.
- Heterogeneous metals bimetallic surface is the condition for corrosion.
- Pitting corrosions are observed.

Example: Formation of rust on iron under moist atmosphere.

Some Types of Corrosion

1. **Galvanic or Bimetallic corrosion**

When two dissimilar metals are contact with each other in presence of an electrolyte, the metal higher in electrochemical series undergoes corrosion. This corrosion is known as galvanic corrosion.



Example: Zinc and copper, zinc forms the anode and is attacked and gets dissolved, whereas copper acts as cathode.

2. Granular corrosion

When a molten metal in cast, the solidification starts at many randomly distributed nuclei. Each of them grows in a regular array to form grains. Because of random nucleation, the planes of atoms in neighbouring grains do not match up. Such areas of mismatch between the grains are called grain boundaries.

Example for granular corrosion is welding of stainless steel.

2. Stress corrosion cracking

The cracking of metal alloy by simultaneous action of tensile stress and corrosive environment is known as stress corrosion cracking. The stressed area act as anode and unstressed area act as a cathode. It occurs in certain metal- environment combinations only. Cathodic protection can be applied to delay or stop the failure.

3. Differential aeration corrosion or concentration cell corrosion

This type of corrosion is due to electrochemical or wet attack on the metal surface, exposed to an electrolyte of varying concentrations or of varying aeration. This may be the result of local difference in metal-ion concentrations caused by local temperature differences or slow diffusion of metal-ions produced by corrosion. Poor oxygenated parts are anodic and highly oxygenated parts are cathodic.

2. How Corrosion can be prevented?

Prevention of Corrosion

Iron and steel (alloy of iron) are most easily protected by paint which provides a barrier between the metal and air/water. Moving parts on machines can be protected by a water repellent oil or grease layer. Covering the surface with enamel and lacquers is another method.

Sacrificial Protection

'Rusting' can be prevented by connecting iron to a more reactive metal (e.g., zinc or magnesium). This is referred to as sacrificial protection or sacrificial corrosion, because the more reactive protecting metal is preferentially oxidized away, leaving the protected metal intact.

Alloying

Iron or steel along with other metals can also be protected by 'alloying' or mixing with other metals (e.g., chromium) to make non-rusting alloys. Stainless steel is an example of a non-rusting alloy of iron and carbon. Brass, an alloy containing copper is another metal alloy which is less expensive and non reactive.

Galvanizing

Coating iron or steel with a thin zinc layer is called 'galvanizing'. This layer is produced by electrolytic deposition. Dipping the iron/steel object in molten zinc and using it as the negative cathode zinc is coated on it. Zinc preferentially corrodes or oxidizes to form a zinc oxide layer that does not flake off like iron oxide rust. Also, if the surface is scratched, the exposed zinc again corrodes before the iron and continues to protect it.

Electroplating

Coating the surface with metals like tin, chromium, nickel etc. by electroplating is also utilized to prevent corrosion. Steel cans are protected by relatively un-reacted tin and works well as long as the thin tin layer is complete.

LONG ANSWER QUESTIONS

1. What is corrosion? Explain different types of corrosion and how corrosion can be prevented?

Ans:

Any process of deterioration (or destruction) and consequent loss of a solid metallic material, through an unwanted (or unintentional) chemical or electrochemical attack by its environment, starting at its surface is called corrosion. The most familiar example of corrosion is rusting of iron. Thus corrosion is a process reverse of extraction of metals.

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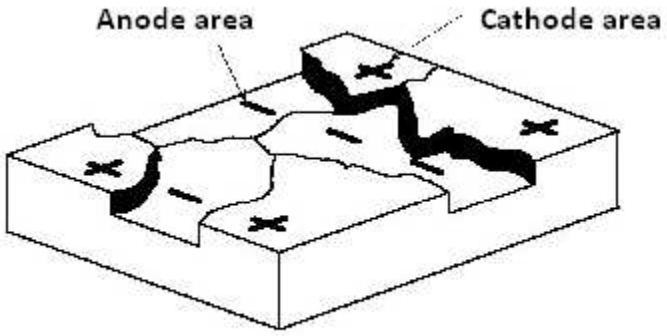
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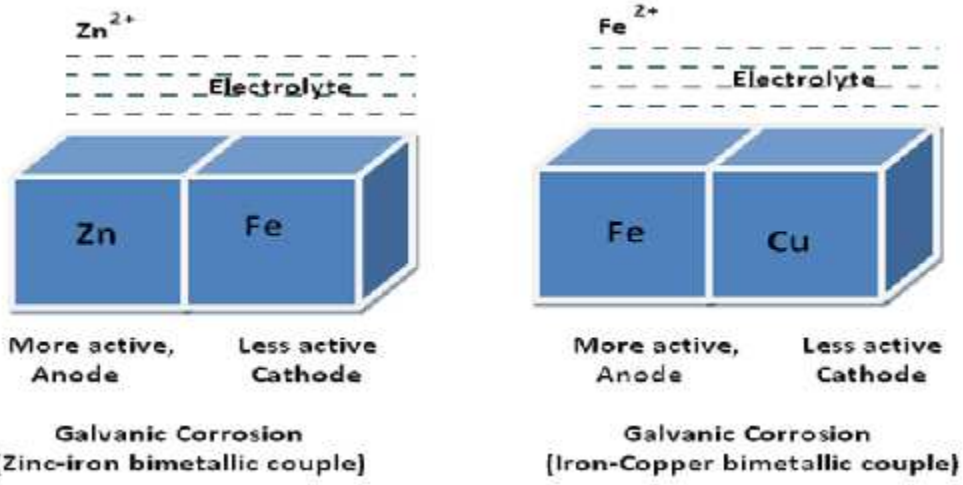
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IMPORTANT QUESTIONS

I. Long answer Questions.

1. What is specific, equivalent and molar conductance? Explain and write the equations?
2. What is Kohlrausch law? Give its applications?
3. What are primary and secondary cells? Explain with examples?
4. What are fuel cells? Explain with examples?
5. What is corrosion and how is it prevented?

II. Short answer Questions

1. State Faraday's laws of electrolysis?

2. What is lead accumulator?

III. Short answer Questions

1. What is corrosion?

2. What is passivity?

3. What is electrolysis? Illustrate.

4. Write equation for specific conductance?

4. What is fuel cell?