

CHEMISTRY

CHAPTER 2: ELECTROCHEMISTRY



ELECTROCHEMISTRY

Classification of Electrolytes**Electrochemistry**

The branch of science which deals with the production of electricity from energy released during spontaneous chemical reactions and the use of electrical energy to bring about non-spontaneous chemical transformations is called electrochemistry.

Redox Reaction

Oxidation is a process which involves loss of electrons and reduction is a process which involves gain of electrons.

The reactions which involve both oxidation and reduction are called redox reactions. In these reactions, electrons are transferred from one reactant to another.

The substance which can lose one or more electrons (i.e., get oxidised) is called reducing agent or reductant while the substance which can gain one or more electrons (i.e., get reduced) is called oxidising agent or oxidant.

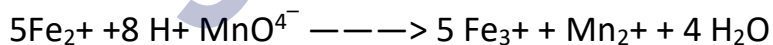
Thus, in a redox reaction, one substance acts as a reducing agent and itself gets oxidised while another substance acts as an oxidising agent and itself gets reduced.

For example: A redox reaction is the reaction between zinc and copper (II) salt occurring in a battery. In this reaction, zinc loses electrons and gets oxidised whereas Cu^{2+} ions gain electrons and get reduced.



Zinc acts as a reducing agent or reductant while Cu^{2+} ions act as oxidising agent or oxidant.

Some other examples of redox reactions are

**Metallic and Electrolytic conductance**

The substances which allow the passage of electric current are called conductors. The best conductors are metals such as copper, silver, tin, etc.

The substances which do not allow the passage of electric current through them are called non-conductors or insulators.

Some common examples of insulators are rubber, glass, ceramics, wood, wax, etc.

Types of Conductors

The conductors are broadly classified into two types:

(1) Metallic conductors or Electronic conductors

These are metallic substances which allow the electricity to pass through them without undergoing any chemical change. Metals and their alloys have very large conductivity and are called conductors.

For example: copper, silver etc.

The flow of electric current through metallic conductors is due to the flow of electrons in the metal atoms. Electrical conductance through metals is called metallic conductance or electronic conductance.

The electronic conductance depends on

- (1) the nature and structure of the metal
- (2) the number of valence electrons per atom
- (3) the density of metal and
- (4) temperature (it decreases with increase of temperature)

(2) Electrolytes or Electrolytic conductors

These are substances which allow the electricity to pass through them in their molten states or in the form of their aqueous solutions and undergo chemical decomposition.

For example: acids, bases and salts are electrolytes.

The flow of electric current through an electrolytic solution is called electrolytic conduction.

In this type of conduction, charge is carried by ions. Therefore, it is also called ionic conductance. The conduction will not occur unless the ions of the electrolyte are free to move.

Therefore, these substances do not conduct electricity in the solid state but conduct electricity in the molten state or in their aqueous solutions due to the movement of ions.

Non-electrolytes: The substances, which do not conduct electricity either in their molten state or through their aqueous solutions are called non-electrolytes.

For example: sugar, glucose, ethyl alcohol, urea, etc.

Metallic conduction Electrolytic conduction

- It is carried by the movement of electrons It is carried by the movement of ions.
- It does not involve the transfer of any matter. It involves the transfer of matter as ions.
- It involves no change in the chemical properties of the conductor. It involves the decomposition of the electrolyte as a result of the chemical reaction.
- It decreases with increase in temperature. It increases with increase in temperature.

Classification of Electrolytes

On this basis, electrolytes are broadly divided into two types: strong electrolytes and weak electrolytes.

(1) Strong electrolytes: The electrolytes which are almost completely dissociated into ions in solution are called strong electrolytes.

For example: NaCl, KCl, HCl, NaOH, NH_4NO_3 etc.

(2) Weak electrolytes: The electrolytes which do not ionise completely in solution are called weak electrolytes.

For example: CH_3COOH , H_2CO_3 , H_3BO_3 , HCN, HgCl_2 , ZnCl_2 , NH_4OH , etc.

In weak electrolytes, an equilibrium is established between the unionised electrolyte and the ions formed in solution.

The extent of ionisation of a weak electrolyte is expressed in terms of degree of ionisation or degree of dissociation. It is defined as the fraction of total number of molecules of the electrolyte which ionise in the solution. It is generally denoted by alpha (α), for strong electrolytes, α is almost equal to 1 and for weak electrolytes, it is always less than 1.

Factors Affecting Electrical Conductivity

The electrical conductivity of the solutions of electrolytes depends upon the following factors:

(i) Interionic attractions: These depend upon the interactions between the ions of the solute molecules, i.e. solute-solute interactions. If the solute-solute interactions are large, the extent of dissociation will be less. These interactions are also responsible for the classification of electrolytes as strong electrolytes and weak electrolytes.

(ii) Solvation of ions: These depend upon the interactions between the ions of the solute and the molecules of the solvent and are called solute-solvent interactions. If the solute-solvent interactions are strong, the ions of the solute will be highly solvated and their electrical conductivity will be low.

(ii) Viscosity of the solvent: The viscosity of the solvent depends upon the solvent-solvent interactions. Larger the solvent-solvent interactions, larger will be the viscosity of the solvent.

The average kinetic energy of the ions of the electrolyte increases with increase in temperature. Consequently, the conductance of electrolytic solutions increases with rise in temperature. The conductance of electronic conductors decreases with increase in temperature.

Conductivity of electrolytic (or ionic) solution depends upon the following factors:

(i) Nature of electrolyte: The conductance of an electrolyte depends upon the number of ions present in the solution. Therefore, the greater the number of ions in the solution, the greater is the conductance. The number of ions produced by an electrolyte depends upon its nature.

The strong electrolytes dissociate almost completely into ions in solutions and therefore, their solutions have high conductance.

Weak electrolytes, dissociate to only small extents and give lesser number of ions. Therefore, the solutions of weak electrolytes have low conductance.

(ii) Nature of the solvent: Electrolytes ionize more in polar solvents. Therefore greater the polarity of the solvent, larger is the ionization and hence greater is the conductance.

(iii) Size of the ions produced and their solvation: If the ions are strongly solvated, their effective size will increase and hence their conductance will decrease.

(iv) Concentration of the electrolytic solution: The molar conductance of electrolytic solution varies with the concentration of the electrolyte. The molar conductance of an electrolyte increases with decrease in concentration or increase in dilution.

(v) Temperature: The conductivity of an electrolyte depends upon the temperature. With increase in temperature, the conductivity of an electrolyte increases.

Electrolytic Conduction

When a voltage is applied to the electrodes dipped into an electrolytic solution, ions of the electrolyte move and, therefore, electric current flows through the electrolytic solution.

The power of the electrolytes to conduct electric current is termed conductance or conductivity. Electrolytic solutions also obey Ohm's law.

Ohm's Law

This law states that the current flowing through a conductor is directly proportional to the potential difference across it, i.e.

$$I \propto V$$

where I is current strength (in amperes) and V is the potential difference applied across the conductor (in volts)

$$I = V/R \text{ or}$$

$$V = IR$$

where R is the constant of proportionality and is known as resistance of the conductor. It is expressed in ohms and is represented as Ω . The strength of current flowing through a conductor is directly proportional to the potential difference applied across the conductor and inversely proportional to the resistance of the conductor.

Resistance

It measures the obstruction to the flow of current. The resistance of any conductor is directly proportional to the length (l) and inversely proportional to the area of cross-section (a) so that

$R \propto l/a$ or

$$R = \rho (l/a)$$

where ρ (Greek, rho) is the constant of proportionality and is called specific resistance or resistivity. The resistance depends upon the nature of the material.

The unit of resistance is ohm (Ω). In terms of SI, base unit is equal to $(\text{kgm}^2/(\text{s}^3\text{A}^2))$

Resistivity or specific resistance

$$R = \rho (l/a)$$

Now, $l=1 \text{ cm}$, $a=1 \text{ cm}^2$, then $R = \rho$

Thus, resistivity is defined as the resistance of a conductor of 1 cm length and having area of cross-section equal to 1 cm².

Resistivity or specific resistance is the resistance between opposite faces of one centimetre cube of the conductor. It is also expressed as resistance when it is 1 m long and its area of cross section is 1 m² i.e., resistance of one metre cube of the conductor

$$1 \Omega \text{ m} = 100 \Omega \text{ cm}$$
 or

$$1 \Omega \text{ cm} = 0.01 \Omega \text{ m}$$

The units of resistivity are

$$\rho = R (a/l) = (\text{ohm cm}^2) / \text{cm} = \text{ohm cm}$$

Its SI units are ohm metre ($\Omega \text{ m}$). But quite often ohm centimeter ($\Omega \text{ cm}$) is also used

Conductance

It is a measure of the ease with which current flows through a conductor. It is expressed as G. It is inverse of the resistance, i.e.

$$G = 1/R$$

The units of conductance are reciprocal ohm (ohm^{-1}) or mho. Ohm is also abbreviated as Ω so that ohm^{-1} may be written as Ω^{-1}

According to S.I. system, the units of electrical conductance are siemens,

$$S \text{ (i.e. } 1S = 1 \Omega^{-1} \text{)}$$

Conductivity

The inverse of resistivity is called conductivity (or specific conductance). It is represented by the symbol, κ (Greek kappa)

The conductance of a solution of 1 cm length and having 1 sq cm as the area of cross-section. Conductivity is the conductance of one centimetre cube of a solution of an electrolyte.

$$\kappa = 1/\rho$$

The units of conductivity are

$$\kappa = 1/\rho$$

$$\kappa = 1/\text{ohm} \cdot \text{cm}$$

$$\kappa = \text{ohm}^{-1} \text{cm}^{-1}$$

$$\kappa = \Omega^{-1} \text{cm}^{-1}$$

Molar Conductivity or Molar Conductance

Molar conductivity is defined as the conducting power of all the ions produced by dissolving one mole of an electrolyte in solution.

It is denoted by Λ_m (lambda).

$$\Lambda_m = \kappa / M$$

where M is the molar concentration. If M is in the units of molarity i.e. moles per litre (mol L^{-1}), then Λ may be expressed as :

$$\Lambda_m = (\kappa \times 1000) / M$$

Units of Molar Conductance

The units of molar conductance can be derived from the formula,

$$\Lambda_m = (\kappa \times 1000) / M$$

The units of κ are S cm^{-1} and units of Λ are

$$\Lambda_m = \text{S cm}^{-1} \times (\text{cm}^3 / \text{mol L}^{-1})$$

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

Equivalent Conductivity

It is defined as the conducting power of all the ions produced by dissolving one gram equivalent of an electrolyte in solution.

It is expressed as Λ_e and is related to specific conductance as

$$\Lambda_e = (\kappa \times 1000) / C$$

where C is the concentration in gram equivalent per litre (or normality). The units of equivalent conductivity are $\text{ohm cm}^2 (\text{g equiv}^{-1})$ as obtained from the formula:

$$\Lambda = (\kappa \times 1000) / C$$

$$\Lambda = [(\text{S cm}^{-1}) \times \text{cm}^3 \text{L}^{-1}] / \text{g equiv L}^{-1}$$

In terms of SI units, the units of equivalent conductivity are $\text{S m}^2 \text{equiv}^{-1}$ and Λ is expressed as:

$$\Lambda = \kappa / C$$

where κ , is in $S\ m^{-1}$ and C is in $g\ equiv\ m^{-3}$.

1) Measurement of Conductance

The conductance of a solution is reciprocal of the resistance, therefore, the experimental determination of the conductance of a solution involves the measurement of its resistance.

It consists of four arms containing the resistance R_1 , R_2 , R_3 and R_4 . R_2 is the variable resistance and R_4 is the unknown resistance. When the current flows through the circuit, the variable resistance is so adjusted to get no current position. This is indicated by no deflection in the galvanometer and is called null point.

At null point

$$R_2/R_4 = R_1 / R_3$$

Knowing the value of R_1 , R_2 , R_3 , unknown resistance R_4 can be calculated.

$$R_4 = (R_2 \times R_3) / R_1$$

Conductivity of Solutions

What is Conductivity?

- Electrical resistance is represented by the symbol 'R', and it is measured in ohm (Ω).
- The electrical resistance of any object is directly proportional to its length (l) and inversely proportional to its area of cross-section (A), i.e.

$$R \propto \frac{l}{A} \quad \text{OR} \quad R = \rho \frac{l}{A}$$

where the constant of proportionality ρ is called resistivity (specific resistance).

- The inverse of resistance, R , is called conductance, G , and we have the relation

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

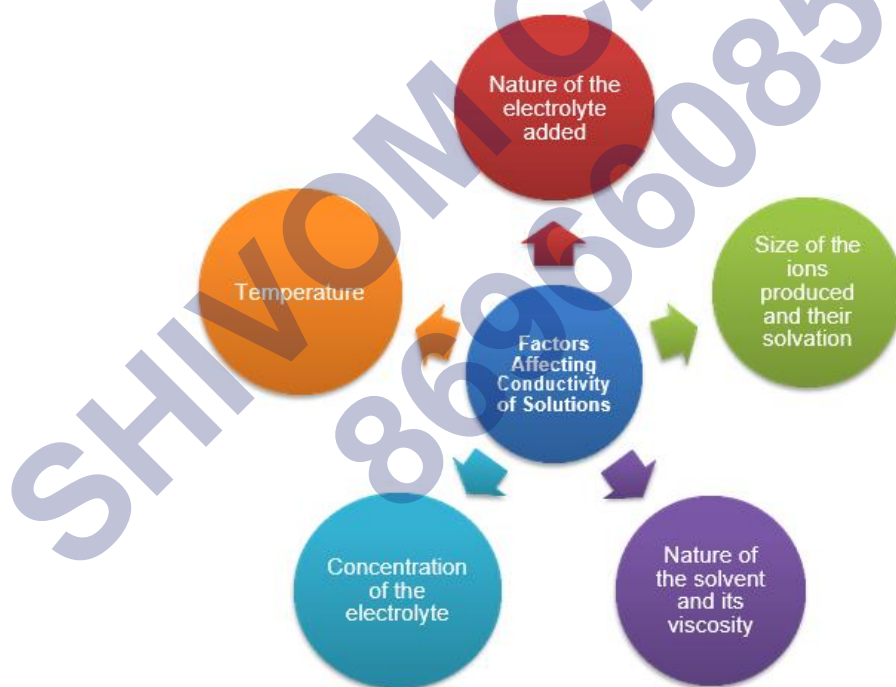
where the constant κ is called conductivity (specific conductance).

- The SI unit of conductance is Siemens, represented by the symbol 'S', and it is equal to ohm^{-1} (also known as mho) or Ω^{-1} . The SI unit of conductivity (κ) is $S\ m^{-1}$.

Conductivity of Electrolytic (Ionic) Solutions

- Very pure water has small amounts of hydrogen and hydroxyl ions ($\sim 10^{-7} \text{M}$) which lend it very low conductivity ($3.5 \times 10^{-5} \text{ S m}^{-1}$).
- When electrolytes are dissolved in water, they dissociate to give their own ions in the solution; hence, its conductivity also increases.

Electrolytic or ionic conductance:
Conductance of electricity by ions present in solutions

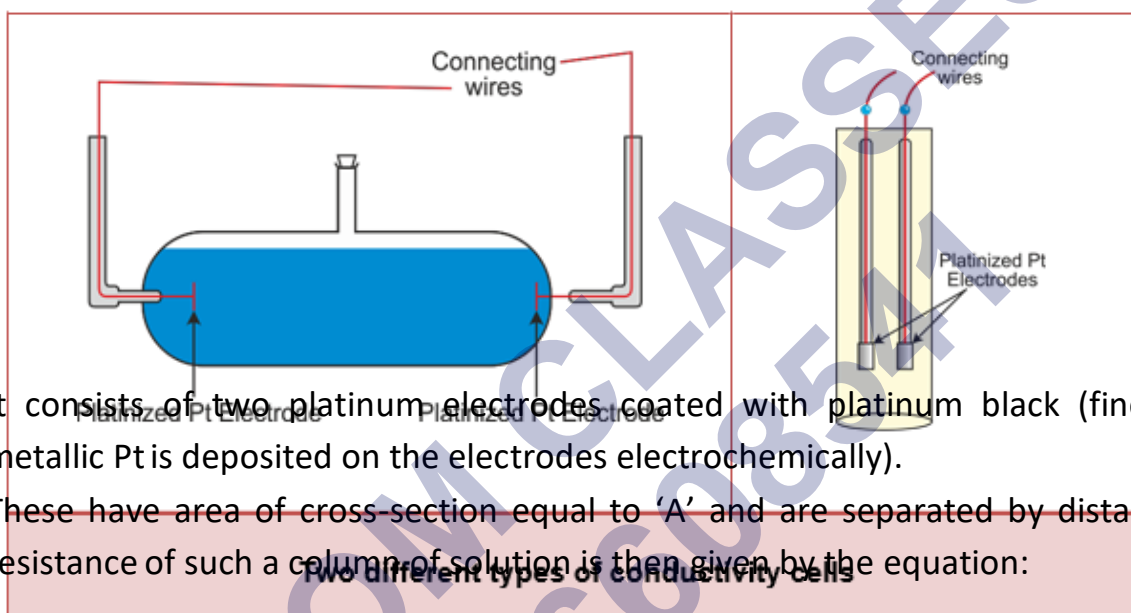


Measurement of Conductivity of Ionic Solutions

- We first need to find the resistance of an ionic solution to measure conductivity.
- We face two problems when measuring the resistance of an ionic solution:
 1. Passing direct current (DC) changes the composition of the solution

2. A solution cannot be connected to the bridge like a metallic wire or other solid conductor
- The first difficulty is resolved by using an alternating current (AC) source of power. The second problem is solved by using a specially designed vessel called **conductivity cell**.

➤ Conductivity Cell:



- It consists of two platinum electrodes coated with platinum black (finely divided metallic Pt is deposited on the electrodes electrochemically).
- These have area of cross-section equal to 'A' and are separated by distance 'l'. The resistance of such a column of solution is then given by the equation:

$$R = \rho \frac{l}{A} = \frac{l}{\kappa A}$$

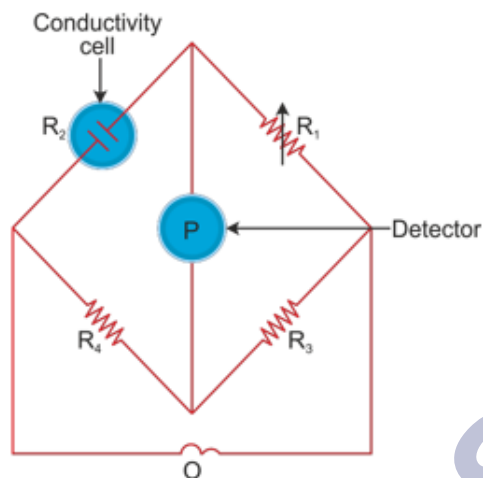
- The quantity 'l/A' is called cell constant and is denoted by the symbol G*. It depends on the distance between the electrodes and their area of cross-section and has the dimension [L⁻¹].
- Hence, the cell constant G* is given by the equation:

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

- When the cell constant is determined, we can use it for measuring the resistance or conductivity of any solution.
- The set up for the measurement of the resistance is nothing but the well-known

Wheatstone bridge.

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Arrangement for measurement of resistance of a solution of an electrolyte

- It consists of two resistances R_3 and R_4 , a variable resistance R_1 and the conductivity cell having the unknown resistance R_2 .
- The Wheatstone bridge is fed by an oscillator O (a source of AC power in the audio frequency range 550–5000 cycles per second).
- P is a suitable detector (a headphone or other electronic device).
- The bridge is balanced when no current passes through the detector.
- Under these conditions,

$$\text{Unknown Resistance, } R_2 = \frac{R_1 R_4}{R_3}$$

- When the cell constant and the resistance of the solution in the cell are determined, the conductivity of the solution is given by the equation:

$$\kappa = \frac{\text{Cell Constant}}{R} = \frac{G^*}{R}$$

Molar Conductivity

- Conductivity of solutions of different electrolytes in the same solvent and at a given temperature differs due to
 1. Charge and size of ions in which they dissociate
 2. Concentration of ions or ease with which the ions move under a potential

gradient

- Therefore, it becomes necessary to define a quantity called molar conductivity denoted by the symbol (λ_m). It is related to the conductivity of the solution by the equation:

$$\text{Molar Conductivity} = \lambda_m = \frac{\kappa}{c}$$

- Unit of λ_m is in $\text{S m}^2 \text{mol}^{-1}$.
- Hence, molar conductivity can be given by the formula

$$\lambda_m (\text{S m}^2 \text{mol}^{-1}) = \frac{\kappa (\text{S m}^{-1})}{1000 \text{L m}^{-3} \times \text{Molarity} (\text{mol L}^{-1})}$$

Variation of Conductivity and Molar Conductivity with Concentration

- Both conductivity and molar conductivity change with the concentration of the electrolyte.
- Conductivity always decreases with a decrease in concentration for both weak and strong electrolytes. It is because the number of ions per unit volume which carry the current in a solution decreases on dilution.
- Molar conductivity increases with a decrease in concentration. This is because the total volume (V) of solution containing one mole of electrolyte also increases.
- The decrease in κ on dilution of a solution is more than compensated by an increase in its volume.

Molar conductivity (λ_m): Conductance of the electrolytic solution kept between the electrodes of a conductivity cell at unit distance but having area of cross section large enough to accommodate sufficient volume of solution which contains one mole of the electrolyte.

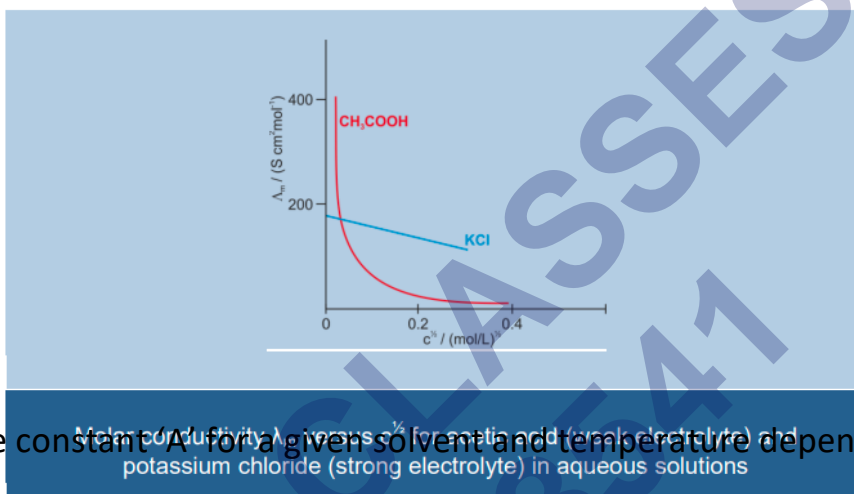
- When concentration approaches zero, the molar conductivity is known as limiting molar conductivity and is represented by the symbol λ_m^0 .
- The variation in λ_m with concentration is different for strong and weak electrolytes.

➤ Strong Electrolytes:

- λ increases slowly with dilution and can be represented by the equation:

$$\lambda_m = \lambda_m^0 - A c^{1/2}$$

- It can be seen that if we plot λ_m against $c^{1/2}$, we obtain a straight line with intercept equal to λ_m^0 and slope equal to $-A$.



- The value of the constant A for a given solvent and temperature depends on the type of electrolyte.

➤ Weak Electrolytes:

- Weak electrolytes such as acetic acid have a lower degree of dissociation at higher concentrations. Hence, for such electrolytes, the change in λ_m with dilution is due to
 1. Increase in the degree of dissociation
 2. The number of ions in total volume of solution which contains 1 mol of electrolyte
- In such cases, λ_m^0 increases steeply on dilution, especially near lower concentrations. Therefore, it cannot be obtained by extrapolating λ_m to zero concentration.
- At infinite dilution, electrolyte dissociates completely ($\alpha = 1$), but at such low concentration, the conductivity of the solution is so low that it cannot be measured accurately. Therefore, λ_m^0 for weak electrolytes is obtained by using Kohlrausch's law of independent migration of ions.
- Thus, at any concentration c , if α is the degree of dissociation, then it can be approximated to the ratio of molar conductivity, λ_m , at the concentration c to limiting molar conductivity λ_m^0 .

$$\therefore \alpha = \frac{\lambda_m}{\lambda_m^0}$$

- But we know that for a weak electrolyte,

$$K_a = \frac{c\alpha^2}{(1-\alpha)}$$

- By putting the value of α in the above equation, we get the equation:

$$K_a = \frac{c\lambda_m^2}{\lambda_m^0 \left(1 - \frac{\lambda_m}{\lambda_m^0}\right)} = \frac{c\lambda_m^2}{\lambda_m^0 (\lambda_m^0 - \lambda_m)}$$

Numerical

- 1) The resistance of a conductivity cell containing 0.001M KCl solution at 298 K is 1500 Ω .

What is the cell constant if conductivity of 0.001M KCl solution at 298K is 0.146×10^{-3}

Scm⁻¹?

Answer :

Given Data:

R = 1500 Ω

$\kappa = 0.146 \times 10^{-3}$ Scm⁻¹

G* = ?

Solution :

The cell constant is given by the equation,

Cell constant = G* = R κ

$$= 1500 \times 0.146 \times 10^{-3}$$

$$= 0.219 \text{ m}^{-1}$$

Hence, cell constant of given conductivity cell is 0.219 m⁻¹

2) Conductivity of 0.00241 M acetic acid is $7.896 \times 10^{-5} \text{ Scm}^{-1}$. Calculate its molar conductivity and if λ_m^0 for acetic acid is $390.5 \text{ Scm}^2 \text{ mol}^{-1}$, what is its dissociation constant?

Answer:

Given Data:

$$\kappa = 7.896 \times 10^{-5} \text{ Scm}^{-1}$$

$$c = 0.00241 \text{ M}$$

$$\lambda_m^0 = 390.5 \text{ Scm}^2 \text{ mol}^{-1}$$

$$\lambda_m = ?$$

$$K_a = ?$$

Solution :

The molar conductivity can be calculated by formula,

$$\lambda_m = \frac{\kappa}{c}$$

$$= \frac{7.896 \times 10^{-5}}{0.00241}$$

$$\therefore \lambda_m = 327.63 \times 10^{-4} \text{ Sm}^2 \text{ mol}^{-1}$$

The dissociation constant of acetic acid can be given by,

$$K_a = \frac{c \lambda_m^2}{\lambda_m^0 (\lambda_m^0 - \lambda_m)}$$

$$= \frac{0.00241 \times (327.63 \times 10^{-4})^2}{390.5 (390.5 - 327.63 \times 10^{-4})}$$

$$\therefore K_a = 1.696 \times 10^{-11} \text{ molL}^{-1}$$

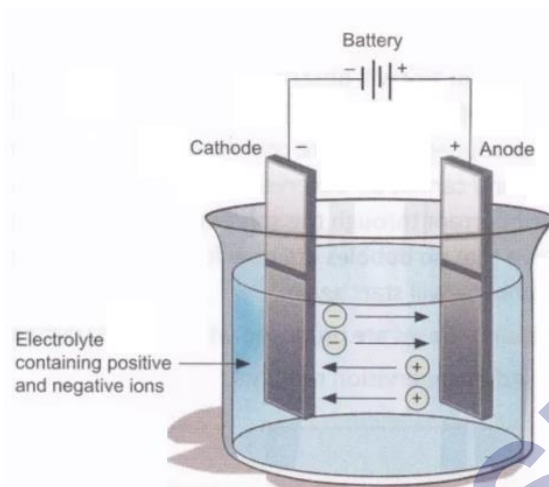
Hence, the molar conductivity of given solution is $327.63 \times 10^{-4} \text{ Sm}^2 \text{ mol}^{-1}$ and dissociation constant is $1.696 \times 10^{-11} \text{ molL}^{-1}$.

Electrolytic Cells

Electrolytic cells

Electrolysis is a process in which chemical changes take place by the passage of electric current. The cells used to carry out electrolysis are electrolytic cells

Process of electrolysis



- 1) The process of electrolysis is carried out by taking the solution of an electrolyte in a suitable vessel. The vessel is called electrolytic tank.
- 2) It is made up of either glass or of a material which is a bad conductor of electricity.
- 3) Two metallic rods or plates are suspended in the electrolytic solution. These are connected to the terminal of a battery with the help of metallic wires.
- 4) These metallic rods or plates allow the passage of current and are called electrodes. The electrode connected to the positive terminal of the battery is called anode while the electrode connected to the negative terminal of the battery is called cathode.

When an electrolyte is dissolved in water, it splits up into negative and positive ions. The positively charged ions are called cations and negatively charged ions are called anions.

On passing electric current through the solution, the ions are attracted by the oppositely charged electrodes. As a result, cations move towards cathode while anions move towards anode. This movement of ions in solution is known as electrolytic or ionic conduction and constitutes flow of current through the solution.

The anions on reaching the anode give up their electrons. On the other hand, cations take up the electrons from the cathode. Therefore, cations and anions get discharged at the respective electrodes and are converted to neutral particles. This is known as primary change. The primary products may be collected as such or they undergo further changes to form molecules or compounds. These are called secondary products and the change is known as secondary change.

According to ionic theory, the electrolytes are present as ions in solution and the function of electricity is only to direct these ions to their respective electrodes. The electrolytes can be electrolysed only in the dissolved or molten state.

Faraday's Laws of Electrolysis

1) Faraday's first law of electrolysis

The amount of any substance deposited or liberated at any electrode is directly proportion to the quantity of electricity passed through the electrolytic solution. The amount of any substance obtained gives the amount of chemical reaction which occurs at any electrode during electrolysis.

Thus, if w gram of the substance is deposited on passing Q coulombs of electricity, then

$$w \propto Q$$

$$w = ZQ$$

where Z is a constant of proportionality and is called electrochemical equivalent. If a current of I amperes is passed for t seconds, then

$$Q = I \times t$$

$$W = Z \times Q = Z \times I \times t$$

$$Q = 1 \text{ coulomb}$$

$I = 1$ ampere and $t = 1$ second, then

$$w = Z \times 1 \times 1$$

$$w = Z$$

Electrochemical equivalent of a substance may be defined as the mass of the substance deposited when a current of one ampere is passed for one second, i.e. a quantity of electricity equal to one coulomb is passed.

2) Faraday's second law of electrolysis

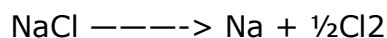
It states that when same quantity of electricity is passed through different electrolytic solutions connected in series, the weights of the substances produced at the electrodes are directly proportional to their chemical equivalent weights.

For example: When same current is passed through two electrolytic solutions, containing copper sulphate (CuSO_4) and silver nitrate (AgNO_3) connected in series, the weights of copper and silver deposited are :

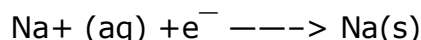
According to Faraday's law, the amount of chemical change occurred i.e. the moles of substances deposited or liberated is proportional to the number of moles of electrons exchanged during the oxidation-reduction reactions that occur.

By knowing the amount of electricity passed, we can easily calculate the number of moles of products formed from the appropriate electrode reaction. From the moles of the products formed, we can calculate the masses their volumes if they are gases.

During the passage of electric current through molten NaCl , sodium gets deposited at cathode and chlorine is liberated at anode.

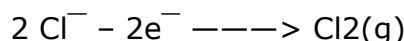
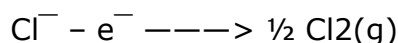


During electrolysis, sodium ions move towards cathode, accept electrons and get deposited as:



The passage of one electron produces one sodium atom. The passage of 1 mol of electrons produce 1 mol of sodium (or 23 g).

Similarly, at anode, chloride ions give up electrons and produce Cl atoms as:



2 mol of electrons produce 1 mol of Cl₂ or 1 mol of electrons produce 1/2 mol of Cl (35.5 g)

Charge on an electron = 1.602×10^{-19} C

Now 1 mole of electrons = 6.022×10^{23} electrons

Charge on 1 mole of electrons = $6.022 \times 10^{23} \times 1.602 \times 10^{-19}$ C

The charge on one mole of electrons is called 1 Faraday, F.

Thus 1F = 96485 C or approximately 96500 C.

Thus, charge on n mol of electrons will be equal to

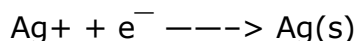
$$Q = nF$$

Now, the production of 1 mol of sodium or 23.0 g by reduction of sodium ions require 1 mol of electrons.

Therefore, amount of charge required,

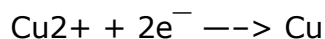
$$Q = nF = 1 \times 96500 \text{ C} = 96500 \text{ C}$$

Similarly, 1 mol of Cl₂ is obtained by 2 mol of electrons or 2×96500 C of charge during electrolysis of NaCl. Similarly, in the reaction

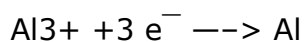


One mole of electrons is required for the reduction of 1 mol of silver ions. Therefore, the quantity of electricity required for reduction of 1 mol of Ag⁺ ions is 96500 C or 1 Faraday.

Now 1 mole of copper will be produced by 2 mol of electrons or 2×96500 C of charge:



The amount of substance deposited or evolved can be calculated. For example: aluminium gets deposited as:



Thus, 1 mol of Al will be deposited by 3 mol of electrons or 3 Faraday of electricity.

When the same quantity of electricity is passed through different electrolyte solutions, connected in series, the weights of different substances produced at the electrodes can be calculated from the mole ratios of their electrode reactions.

Battery

A Battery is a device consisting of one or more electrical cells that convert chemical energy into electrical energy. Every battery is basically a galvanic cell where redox reactions take place between two electrodes which act as the source of the chemical energy.



Battery types

Batteries can be broadly divided into two major types.

- Primary Cell / Primary battery
- Secondary Cell / Secondary battery

Based on the application of the battery, they can be classified again. They are:

Household Batteries

These are the types of batteries which are more likely to be known to the common man. They find uses in a wide range of household appliances (such as torches, clocks, and cameras).

These batteries can be further classified into two subcategories:

- Rechargeable batteries Nickel
Examples: Cadmium batteries, Lithium-Ion
- Non-rechargeable batteries

Examples: Silver oxide, Alkaline & carbon zinc

Industrial Batteries

These batteries are built to serve heavy-duty requirements. Some of their applications include railroad, backup power and more for big companies. Some examples are:

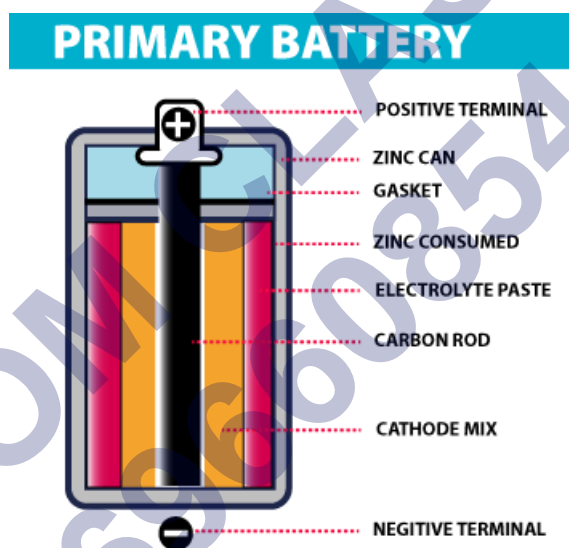
Nickel Iron

Wet Nickel Cadmium (NiCd)

Vehicle Batteries

These are more user-friendly and a less complicated version of the industrial batteries. They are specifically designed to power cars, motorcycles, boats & other vehicles. An important example of a vehicle battery is the Lead-acid battery.

Primary Cell



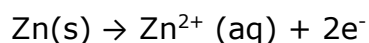
Types Of Battery- Primary battery

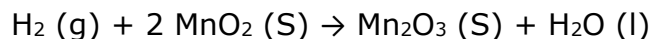
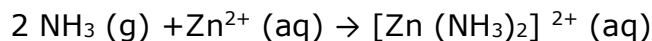
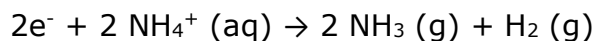
These are batteries where the redox reactions proceed in only one direction. The reactants in these batteries are consumed after a certain period of time, rendering them dead. A primary battery cannot be used once the chemicals inside it are exhausted.

An example of a primary battery is the dry cell – the household battery that commonly used to power TV remotes, clocks, and other devices. In such cells, a zinc container acts as the anode and a carbon rod acts as the cathode. A powdered mixture of manganese dioxide and carbon is placed around the cathode. The space left in between the container and the rod are filled with a moist paste of ammonium chloride and zinc chloride.

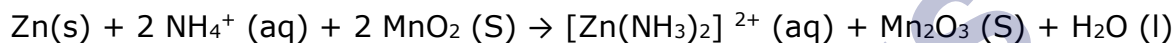
The redox reaction that takes place in these cells is:

At Anode



At Cathode

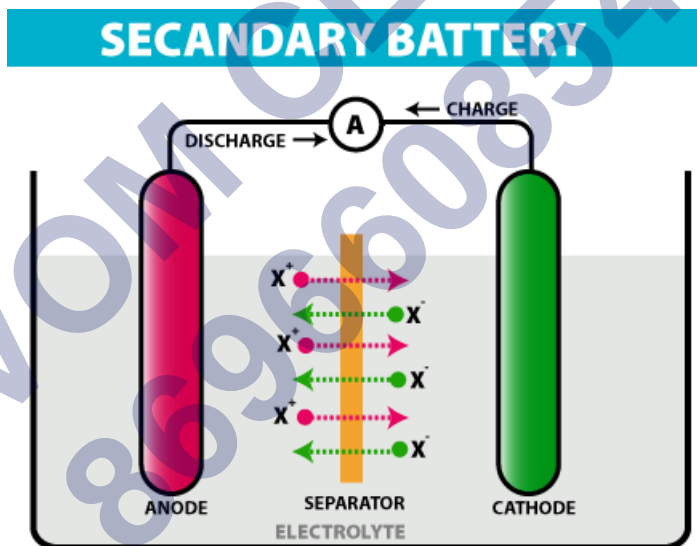
Thus, the overall cell equation is:



Another example of the primary cell is the mercury cell, where a zinc-mercury amalgam is used as an anode and carbon is used as a cathode. A paste of HgO is used as an electrolyte. These cells are used only in devices that require a relatively low supply of electric current (such as hearing aids and watches).

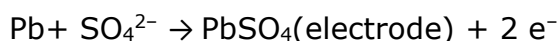
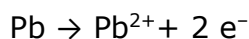
Secondary Cell

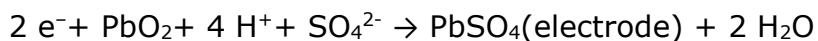
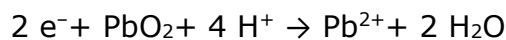
These are batteries that can be recharged after use by passing current through the electrodes in the opposite direction, i.e. from the negative terminal to the positive terminal.



Types Of Battery – Secondary Cell

For example, a lead storage battery that is used in automobiles and inverters can be recharged a limited number of times. The lead storage battery consists of a lead anode and the cathode is a lead grid packed with lead dioxide. Sulphuric acid with a concentration of 38% is used as an electrolyte. The oxidation and reduction reactions involved in this process are listed below.

At Anode**At Cathode**



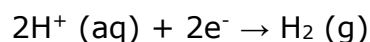
In order to recharge these batteries, the charge is transferred in the opposite direction and the reaction is reversed, thus converting PbSO_4 back to Pb and PbO_2 .

Another example of the secondary cell is the nickel-cadmium cell. These cells have high storage capacities and their lifespan is relatively long (compared to other secondary cells). However, they are difficult to manufacture and maintain.

Standard Hydrogen Electrode

The Standard Hydrogen Electrode is often abbreviated to SHE, and its standard electrode potential is declared to be 0 at a temperature of 298K. This is because it acts as a reference for comparison with any other electrode.

The half cell reaction of SHE can be written as follows:



The reaction given above generally takes place on a platinum electrode. The pressure of the hydrogen gas present in this half cell equals 1 bar.

Uses of Platinum in the Standard Hydrogen Electrode

Platinum is used in the Standard Hydrogen Electrode due to the following reasons:

- Platinum is a relatively inert metal which does not corrode easily.
- Platinum has catalytic qualities which promote the proton reduction reaction.
- The surface of platinum can be covered with platinum black, a fine powder of platinum. This type of platinum electrode is called a platinized platinum electrode.
- Platinum also improves the reaction kinetics by adsorbing hydrogen at the interface.

Standard Hydrogen Electrode Construction

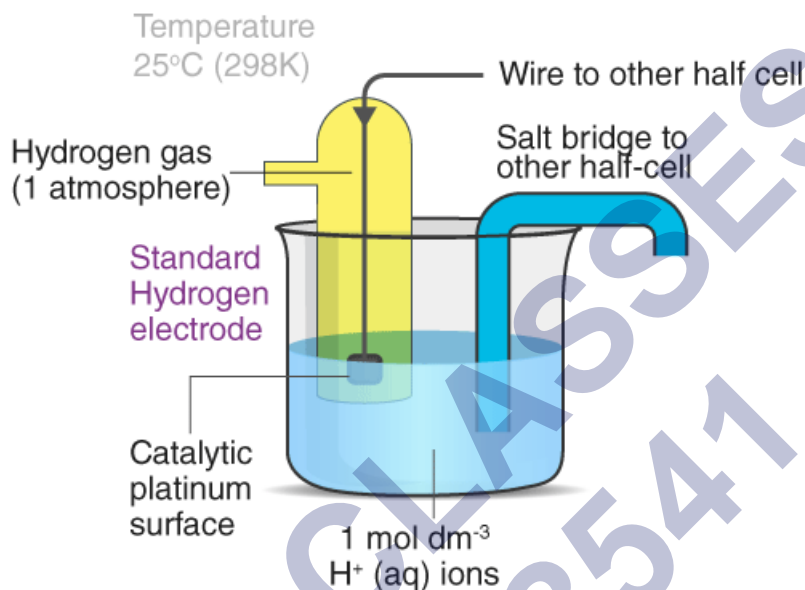
The parts that make up a Standard Hydrogen Electrode are listed below.

- A platinum electrode is covered in finely powdered platinum black (platinized platinum electrode).
- A hydrogen blow.
- A solution of acid having an H^{+} molarity of 1 mole per cubic decimeter.
- SHE also contains a hydroseal which is used to prevent the interference of oxygen.
- The other half-cell of the entire Galvanic cell must be attached to the Standard Hydrogen Electrode through a reservoir in order to create an ionically conductive path. This can be done through a direct connection, through a narrow tube, or even through

the use of a salt bridge.

Standard Hydrogen Electrode Diagram

A labelled diagram of a standard hydrogen electrode is provided below. In SHE, a salt bridge is used to link SHE with the other half cell.



The platinized platinum surface has a very high adsorption activity. Therefore, this surface must be protected from atmospheric oxygen as well as from organic substances. Substances such as arsenic and sulphur compounds can deactivate or poison the catalyst.

Standard Electrode Potential

Standard electrode potential is a measurement of the potential for equilibrium. There is a potential difference between the electrode and the electrolyte called the potential of the electrode. When unity is the concentrations of all the species involved in a semi-cell, the electrode potential is known as the standard electrode potential.

Under standard conditions, the standard electrode potential occurs in an electrochemical cell say the temperature = 298K, pressure = 1atm, concentration = 1M. The symbol ' E°_{cell} ' represents the standard electrode potential of a cell.

Significance of Standard Electrode Potential

- All electrochemical cells are based on redox reactions, which are made up of two half-reactions.
- The oxidation half-reaction occurs at the anode and it involves a loss of electrons.
- Reduction reaction takes place at the cathode, involving a gain of electrons. Thus, the electrons flow from the anode to the cathode.

- The electric potential that arises between the anode and the cathode is due to the difference in the individual potentials of each electrode (which are dipped in their respective electrolytes).
- The cell potential of an electrochemical cell can be measured with the help of a voltmeter. However, the individual potential of a half-cell cannot be accurately measured alone.
- It is also important to note that this potential can vary with a change in pressure, temperature, or concentration.
- In order to obtain the individual reduction potential of a half-cell, the need for standard electrode potential arises.
- It is measured with the help of a reference electrode known as the standard hydrogen electrode (abbreviated to SHE). The electrode potential of SHE is 0 Volts.
- The standard electrode potential of an electrode can be measured by pairing it with the SHE and measuring the cell potential of the resulting galvanic cell.
- The oxidation potential of an electrode is the negative of its reduction potential. Therefore, the standard electrode potential of an electrode is described by its standard reduction potential.
- Good oxidizing agents have high standard reduction potentials whereas good reducing agents have low standard reduction potentials.
- For example, the standard electrode potential of Ca^{2+} is -2.87 V . and that of F_2 is $+2.87\text{V}$. This implies that F_2 is a good oxidizing agent whereas Ca is a reducing agent.

Galvanic Cell (Voltaic Cell)

An electrochemical cell that converts the chemical energy of spontaneous redox reactions into electrical energy is known as a galvanic cell or a voltaic cell.

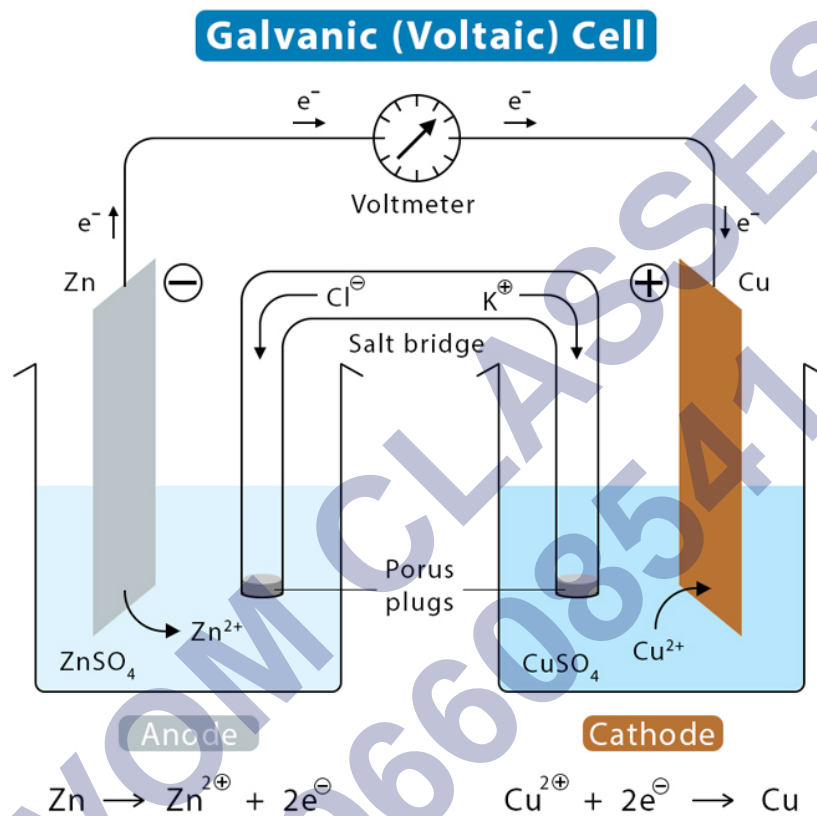
Galvanic cell Voltaic cell is an electrochemical cell that makes use of chemical reactions to generate electrical energy.

Let us understand how a voltaic or galvanic cell is created.

In oxidation-reduction reactions, electrons are moved from one species to another species. Energy is released if the reaction occurs spontaneously. Therefore, the released energy is used to do useful work. To tackle this energy, it is required to split the reaction into two separate half-reactions viz. oxidation and reduction. With the help of two different containers and wire, the reactions are put into them to drive the electrons from one end to the other end. This creates a voltaic cell.

Principle of Galvanic (Voltaic) Cell

Electric work done by a galvanic cell is mainly due to the Gibbs energy of spontaneous redox reaction in the voltaic cell. It generally consists of two half cells and a salt bridge. Each half cell further consists of a metallic electrode dipped into an electrolyte. These two half-cells are connected to a voltmeter and a switch externally with the help of metallic wires. In some cases, when both the electrodes are dipped in the same electrolyte, a salt bridge is not required.



Galvanic Cell (Voltaic Cell) Diagram

Parts of Galvanic Cell

Anode – Oxidation occurs at this electrode.

Cathode – Reduction occurs at this electrode.

Salt bridge – Contains electrolytes which are required to complete the circuit in a galvanic cell.

Half-cells – reduction and oxidation reactions are separated into compartments.

External circuit – Conducts the flow of electrons between electrodes

Load – A part of the circuit utilizes the electron to flow to perform its function.

Working of Galvanic Cell

- In a galvanic cell, when an electrode is exposed to the electrolyte at the electrode-electrolyte interface, the atoms of the metal electrode have a tendency to generate ions in the electrolyte solution leaving behind the electrons at the electrode. Thus, making the

metal electrode negatively charged.

- While at the same time metal ions in the electrolyte solution too, have a tendency to deposit on a metal electrode. Thus, making the electrode positively charged.
- Under equilibrium condition, charge separation is observed and depending on the tendencies of two opposing reactions, the electrode can be positively or negatively charged. Hence, a potential difference is developed between the electrode and electrolyte. This potential difference is known as electrode potential.
- Out of two electrodes, the electrode at which oxidation takes place is called anode while the electrode at which reduction takes place is called cathode.
- The anode has a negative potential with respect to the solution while the cathode has a positive potential with respect to the solution.
- Thus, a potential difference develops between two electrodes of the galvanic cell. This potential difference is known as cell potential.
- When no current is drawn from the galvanic cell, cell potential is known as the electromotive force of the galvanic cell.
- When the switch is set on, due to the potential difference, electrons flow from the negative electrode to the positive electrode.

Electrolytic Cell

An electrolytic cell can be defined as an electrochemical device that uses electrical energy to facilitate a non-spontaneous redox reaction. Electrolytic cells are electrochemical cells that can be used for the electrolysis of certain compounds. For example, water can be subjected to electrolysis (with the help of an electrolytic cell) to form gaseous oxygen and gaseous hydrogen. This is done by using the flow of electrons (into the reaction environment) to overcome the activation energy barrier of the non-spontaneous redox reaction.

The three primary components of electrolytic cells are:

Cathode (which is negatively charged for electrolytic cells)

Anode (which is positively charged for electrolytic cells)

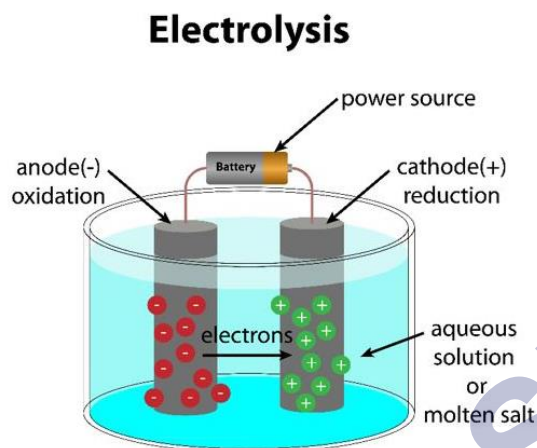
Electrolyte

The electrolyte provides the medium for the exchange of electrons between the cathode and the anode. Commonly used electrolytes in electrolytic cells include water (containing dissolved ions) and molten sodium chloride.

Diagram and Working of an Electrolytic Cell

Molten sodium chloride (NaCl) can be subjected to electrolysis with the help of an electrolytic

cell, as illustrated below.



Here, two inert electrodes are dipped into molten sodium chloride (which contains dissociated Na^+ cations and Cl^- anions). When an electric current is passed into the circuit, the cathode becomes rich in electrons and develops a negative charge. The positively charged sodium cations are now attracted towards the negatively charged cathode. This results in the formation of metallic sodium at the cathode.

Simultaneously, the chlorine atoms are attracted to the positively charged anode. This results in the formation of chlorine gas (Cl_2) at the anode (which is accompanied by the liberation of 2 electrons, finishing the circuit). The associated chemical equations and the overall cell reaction are provided below.

Reaction at Cathode: $[\text{Na}^+ + \text{e}^- \rightarrow \text{Na}] \times 2$

Reaction at Anode: $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$

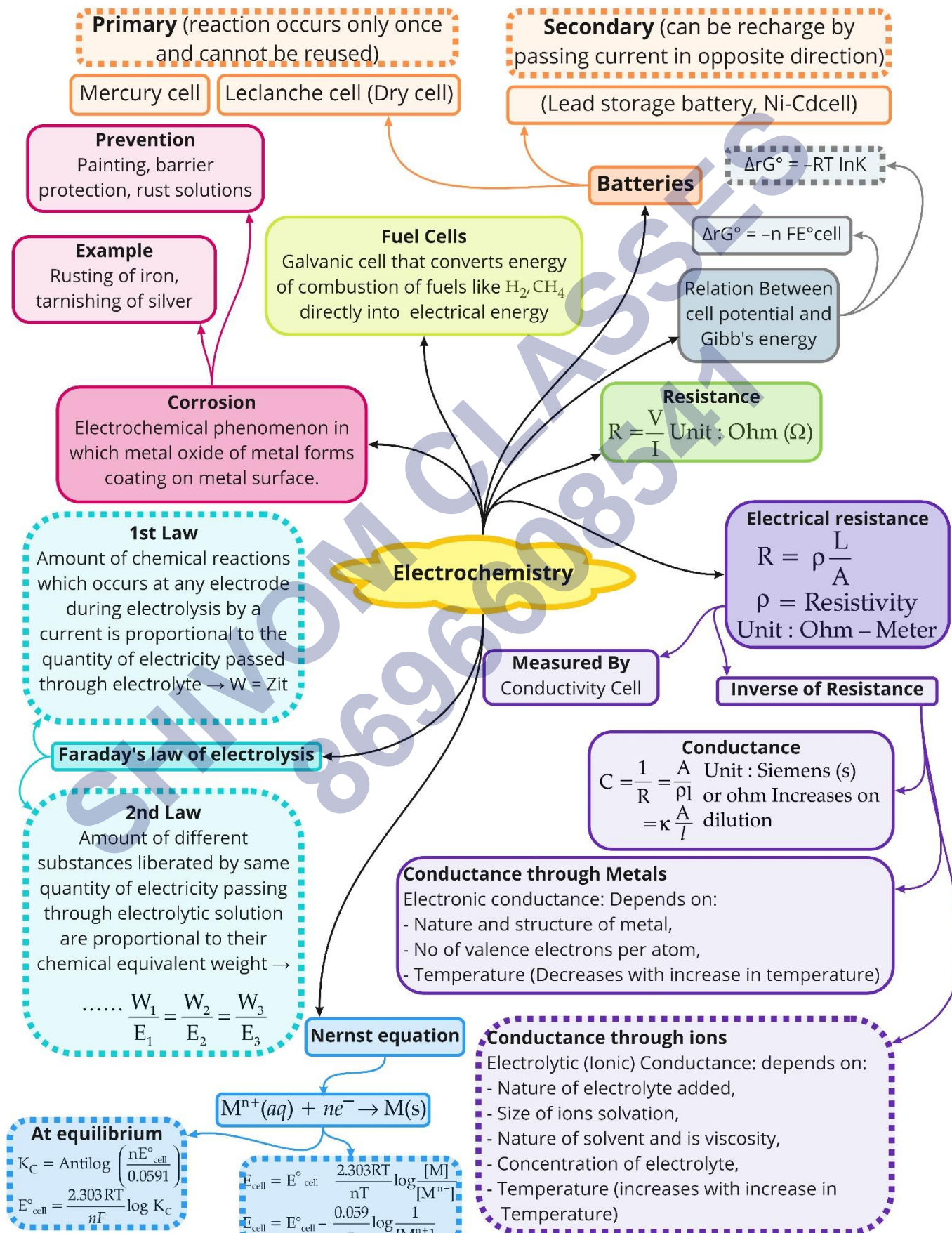
Cell Reaction: $2\text{NaCl} \rightarrow 2\text{Na} + \text{Cl}_2$

Thus, molten sodium chloride can be subjected to electrolysis in an electrolytic cell to generate metallic sodium and chlorine gas as the products.

Applications of Electrolytic Cells

- The primary application of electrolytic cells is for the production of oxygen gas and hydrogen gas from water. They are also used for the extraction of aluminium from bauxite.
- Another notable application of electrolytic cells is in electroplating, which is the process of forming a thin protective layer of a specific metal on the surface of another metal.
- The electrorefining of many non-ferrous metals is done with the help of electrolytic cells. Such electrochemical cells are also used in electrowinning processes.
- It can be noted that the industrial production of high-purity copper, high-purity zinc, and high-purity aluminium is almost always done through electrolytic cells.

Class : 12th Chemistry
Chapter-3 : Electrochemistry (Part_1)



Class : 12th Chemistry
Chapter-3 : Electrochemistry (Part_2)

Strong electrolyte
 $\Lambda_m = \Lambda_m^\circ - Ac^{1/2}$ (KCl)

Weak electrolyte
 $\alpha = \frac{\Lambda_m}{\Lambda_m^\circ}$ (acetic acid)

Kohlrausch law of independent migration of ions

Limiting molar conductivity of an electrolyte can be represented as sum of individual contribution of anions and cations of the electrolyte

$$\Lambda_m^\circ = \nu_+ \lambda_+^\circ + \nu_- \lambda_-^\circ$$

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

Limiting molar conductivity : If molar conductivity reaches a limiting value when concentration approaches zero. $C \rightarrow 0$,
 $\Lambda_m = \Lambda_m^\circ$

1. Calculate Λ_m° for any electrolyte from λ° of individual ions
2. Determine value of dissociation constant for weak electrolytes

Molar conductivity: Conductance of volume V of solution containing 1 mole of electrolyte kept between two electrodes with area of cross section A and distance of unit length

Electrochemistry

Types of Cells

Electrochemical: Device Converting chemical energy to electrical energy

Electrolytic: Device Converting electrical energy to chemical energy

Daniell Cell: cathode: Copper, anode: Zinc; Salt bridge : Agar agar; electrolyte : KCN/KNO₃ → Reduction: $Cu^{2+} + 2e^- \rightarrow Cu$; Oxidation: $Zn(s) \rightarrow Zn^{2+} + 2e^-$; $Zn|Zn^{2+}(C_1) || Cu^{2+}(C_2)|Cu$

Two copper strips dipped in an aqueous solution of $CuSO_4$ → Anode: $Cu \rightarrow Cu^{2+} + 2e^-$ cathode: $Cu^{2+} + 2e^- \rightarrow Cu$

Electrode Potential

Potential difference between electrode and electrolyte

Standard Electrode Potential

Electrode potential when concentration of all species in half-cell is unity

Standard Hydrogen Electrode

Electrode: Pt coated with Pt black, **Electrolyte:** acidic solution pressure 1 bar $Pt(s) | H_2(g) | H^+(aq)$

Components

Half-cell → two portions of cell

Positive $E^\circ \rightarrow$ Weaker reducing agent than H^+/H_2

Negative $E^\circ \rightarrow$ Weaker reducing agent than H^+/H_2

Electrochemical Series

A series of half-cells arranged in increasing standard oxidation potentials.

Electrolyte

A chemical compound that dissociates into ions and conducts electric

Salt bridge

U shaped inverted tube connecting two electrolytic solution

Electrode

Cathode → Reduction takes place
Anode → Oxidation takes place

Important Questions

Multiple Choice questions-

Question 1. If the conductivity and conductance of a solution is same then its cell constant is equal to:

- (a) 1
- (b) 0
- (c) 10
- (d) 1000

Question 2. The units of conductivity are.

- (a) ohm^{-1}
- (b) $\text{ohm}^{-1} \text{cm}^{-1}$
- (c) $\text{ohm}^{-2} \text{cm}^2 \text{equiv}^{-1}$
- (d) $\text{ohm}^{-1} \text{cm}^2$

Question 3. The resistance of 0.1 N solution of acetic acid is 250 ohm, when measured in a cell of cell constant 1.15cm^{-1} . The equivalent conductance (in $\text{ohm}^{-1} \text{cm}^2 \text{equivalent}^{-1}$) of 0.1 N acetic acid is

- (a) 18.4
- (b) 0.023
- (c) 46
- (d) 9.2

Question 4. In infinite dilution of aqueous solution of BaCl_2 , molar conductivity of Ba^{2+} and Cl^- ions are = $127.32 \text{S cm}^2/\text{mol}$ and $76.34 \text{S cm}^2/\text{mol}$ respectively. What is Λ^∞ for BaCl_2 at same dilution?

- (a) $280 \text{ S cm}^2 \text{ mol}^{-1}$
- (b) $330.98 \text{ S cm}^2 \text{ mol}^{-1}$
- (c) $90.98 \text{ S cm}^2 \text{ mol}^{-1}$
- (d) $203.6 \text{ S cm}^2 \text{ mol}^{-1}$

Question 5. The specific conductance of 0.1 M NaCl solution is $1.06 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$. Its molar conductance in $\text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ is

- (a) 1.06×10^2
- (b) 1.06×10^3
- (c) 1.06×10^4
- (d) 53

Question 6. The limiting molar conductivities A° for NaCl, KBr and KCl are 126, 152 and 150 $\text{S cm}^2 \text{ mol}^{-1}$ respectively. The A° for NaBr is

- (a) $278 \text{ S cm}^2 \text{ mol}^{-1}$
- (b) $976 \text{ S cm}^2 \text{ mol}^{-1}$
- (c) $128 \text{ S cm}^2 \text{ mol}^{-1}$
- (d) $302 \text{ S cm}^2 \text{ mol}^{-1}$

Question 7. $\lambda(\text{ClCH}_2\text{COONa}) = 224 \text{ ohm}^{-1} \text{ cm}^2 \text{ gm eq}^{-1}$, $\lambda(\text{NaCl}) = 38.2 \text{ ohm}^{-1} \text{ cm}^2 \text{ gm eq}^{-1}$. $\lambda(\text{HCl}) = 203 \text{ ohm}^{-1} \text{ cm}^2 \text{ gm eq}^{-1}$, what is the value of $\lambda(\text{ClCH}_2\text{COOH})$?

- (a) $288.5 \text{ ohm}^{-1} \text{ cm}^2 \text{ gm eq}^{-1}$
- (b) $289.5 \text{ ohm}^{-1} \text{ cm}^2 \text{ gm eq}^{-1}$
- (c) $388.8 \text{ ohm}^{-1} \text{ cm}^2 \text{ gm eq}^{-1}$
- (d) $59.5 \text{ ohm}^{-1} \text{ cm}^2 \text{ gm eq}^{-1}$

Question 8. The limiting molar conductivities of HCl, CH₃COONa and NaCl are respectively 425, 90 and 125 mho cm² mol⁻¹ at 25 °C. The molar conductivity of 0.1 M CH₃COOH solution is 7.8 mho cm² mol⁻¹ at the same temperature. The degree of dissociation of 0.1 M acetic acid solution at the same temperature is

- (a) 0.10
- (b) 0.02
- (c) 0.15
- (d) 0.03

Question 9. The values of limiting ionic conductance of H and HCOO⁻ ions are respectively 347 and 53 S cm² mol⁻¹ at 298 K. If the molar conductance of 0.025 M methanoic acid at 298 K is 40 S cm² mol⁻¹, the dissociation constant of methanoic acid at 298 K is

- (a) 1×10^{-5}
- (b) 2×10^{-5}
- (c) 1.5×10^{-4}
- (d) 2.5×10^{-4}

Question 10. The ionisation constant of a weak electrolyte is 2.5×10^{-5} and molar conductance of its 0.01 M solution is 19.6 S cm² mol⁻¹. The molar conductance at infinite dilution (S cm² mol⁻¹) is

- (a) 402
- (b) 392
- (c) 306
- (d) 39.2

Very Short Question:

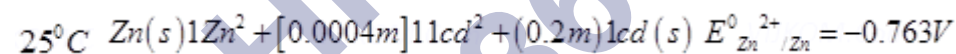
- Question 1. Can you store AgCl solution in Zinc pot?
- Question 2. Define the term – standard electrode potential?
- Question 3. What is electromotive force of a cell?
- Question 4. Can an electrochemical cell act as electrolytic cell? How?
- Question 5. Single electrode potential cannot be determined. Why?
- Question 6. What is SHE? What is its electrode potential?
- Question 7. What does the positive value of standard electrode potential indicate?
- Question 8. What is an electrochemical series? How does it predict the feasibility of a certain redox reaction?
- Question 9. Give some uses of electrochemical cells?
- Question 10. State the factors that affect the value of electrode potential?

Short Questions:

Question 1. What is the cell potential for the cell at 25°C $\text{Cr} / \text{Cr}^{3+}(0.1\text{m}) // \text{Fe}^{2+}(0.01\text{m}) / \text{Fe}$

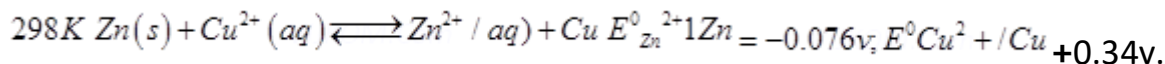
$$E^{\circ}_{\text{Cr}^{3+}/\text{Cr}} = -0.74\text{V}, E^{\circ}_{\text{Fe}^{2+}/\text{Fe}} = -0.44\text{V}$$

Question 2. Calculate ΔG° for the reaction



$$E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} = +0.34\text{V}, F = 96500 \text{ C Mol}^{-1} \quad R = 8.314 \text{ J/K}$$

Question 3. Calculate Equilibrium constant K for the reaction



Question 4. For what concentration of $\text{Ag}^{+}(aq)$ will the emf of the given cell be zero at 25°C

if the concentration of $\text{Cu}^{2+}(aq)$ is 0.1 M ? $\text{Cu}(s) / \text{Cu}^{2+}(0.1\text{M}) // \text{Ag}^{+}(aq) / \text{Ag}(s)$

$$E^{\circ}_{\text{Ag}^{+}/\text{Ag}} = +0.80\text{V}; E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ V}$$

Question 5. Calculate the standard free energy change for the cell- reaction.

$Fe^{2+}(aq) + Ag^+(s) \rightleftharpoons Fe^3+(aq) + Ag(s)$ How is it related to the equilibrium

constant of the reaction? $E^0_{Fe^{3+}/Fe^{2+}} = +0.77V$, $E^0_{Ag^+/Ag} = +0.08V$ $F = 96500 C/mol$.

Question 6. How much charge is required for the following reductions:

- (i) 1 mol of to Al.
- (ii) 1 mol of to Cu.
- (iii) 1 mol of to .

Question 7. How much electricity in terms of Faraday is required to produce

- (i) 20.0 g of Ca from molten .
- (ii) 40.0 g of Al from molten

Question 8. How much electricity is required in coulomb for the oxidation of

- (i) 1 mol of to .
- (ii) 1 mol of FeO to

Question 9. A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using a current of 5 amperes for 20 minutes. What mass of Ni is deposited at the cathode?

Question 10. Depict the galvanic cell in which the reaction takes place. Further show:

- (i) Which of the electrode is negatively charged?
- (ii) The carriers of the current in the cell.
- (iii) Individual reaction at each electrode.

Long Questions:

Question 1. Explain construction and working of standard Hydrogen electrode? (b) Write any two differences between amorphous solids and crystalline solids.

Question 2.

The molar conductivity of 0.025 mol L⁻¹ methanoic acid is 46.1 S cm² mol⁻¹. Calculate its degree of dissociation and dissociation constant. Given $\lambda^\circ_{H^+} = 349.6 S cm^2 mol^{-1}$ and $\lambda^\circ(HCOO^-) = 54.6 S cm^2 mol^{-1}$

Question 3. Explain how rusting of iron is envisaged as setting up of an electrochemical cell.

Question 4. Calculate the standard cell potentials of galvanic cells in which the following reactions take place:

Question 5. Write the Nernst equation and emf of the following cells at 298 K:

Question 6. Define conductivity and molar conductivity for the solution of an electrolyte. Discuss their variation with concentration.

Assertion and Reason Questions:

1. In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- Assertion and reason both are correct statements and reason is correct explanation for assertion.
- Assertion and reason both are correct statements but reason is not correct explanation for assertion.
- Assertion is correct statement but reason is wrong statement.
- Assertion is wrong statement but reason is correct statement.

Assertion: At the end of electrolysis using platinum electrodes, an aqueous solution of copper sulphate turns colourless.

Reason: Copper in CuSO_4 is converted to Cu(OH)_2 during the electrolysis.

2. In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

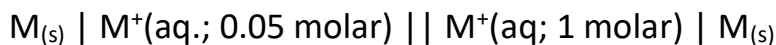
- Assertion and reason both are correct statements and reason is correct explanation for assertion.
- Assertion and reason both are correct statements but reason is not correct explanation for assertion.
- Assertion is correct statement but reason is wrong statement.
- Assertion is wrong statement but reason is correct statement.

Assertion: Zinc displaces copper from copper sulphate solution.

Reason: E^\ominus of zinc is -0.76V and that of copper is $+0.34\text{V}$.

Case Study Questions:

1. The concentration of potassium ions inside a biological cell is at least twenty times higher than the outside. The resulting potential difference across the cell is important in several processes such as transmission of nerve impulses and maintaining the ion balance. A simple model for such a concentration cell involving a metal M is,



The following questions are multiple choice questions. Choose the most appropriate answer:

(i) For the above cell,

- a) $E_{\text{cell}} < 0; \Delta G > 0$
- b) $E_{\text{cell}} > 0; \Delta G < 0$
- c) $E_{\text{cell}} < 0; \Delta G^\circ > 0$
- d) $E_{\text{cell}} > 0; \Delta G^\circ < 0$

(ii) If the 0.05 molar solution of M^+ is replaced by a 0.0025 molar M^+ solution, then the magnitude of the cell potential would be:

- a) 130mV
- b) 185mV
- c) 154mV
- d) 600mV

(iii) The value of equilibrium constant for a feasible cell reaction is:

- a) < 1
- b) $= 1$
- c) > 1
- d) Zero

(iv) What is the emf of the cell when the cell reaction attains equilibrium?

- a) 1
- b) 0
- c) > 1
- d) < 1

(v) The potential of an electrode change with change in:

- a) Concentration of ions in solution.
- b) Position of electrodes.
- c) Voltage of the cell.
- d) All of these.

2. All chemical reactions involve interaction of atoms and molecules. A large number of atoms/molecules are present in a few gram of any chemical compound varying with their

atomic/ molecular masses. To handle such large number conveniently, the mole concept was introduced. All electrochemical cell reactions are also based on mole concept. For example, a 4.0 molar aqueous solution of NaCl is prepared and 500mL of this solution is electrolysed. This leads to the evolution of chlorine gas at one of the electrode. The amount of products formed can be calculated by using mole concept.

The following questions are multiple choice questions. Choose the most appropriate answer:

(i) The total number of moles of chlorine gas evolved is:

- a) 0.5
- b) 1.0
- c) 1.5
- d) 1.9

(ii) If cathode is a Hg electrode, then the maximum weight of amalgam formed from this solution is:

- a) 300g
- b) 446g
- c) 396g
- d) 296g

(iii) The total charge (coulomb) required for complete electrolysis is:

- a) 186000
- b) 24125
- c) 48296
- d) 193000

(iv) In the electrolysis, the number of moles of electrons involved are:

- a) 2
- b) 1
- c) 3
- d) 4

(v) In electrolysis of aqueous NaCl solution when Pt electrode is taken, then which gas is liberated at cathode?

- a) H₂gas
- b) Cl₂gas

- c) O₂ gas
- d) None of these.

Answers key

MCQ answers:

1. Answer: (a) 1
2. Answer: (b) ohm⁻¹ cm⁻¹
3. Answer: (c) 46
4. Answer: (a) 280 S cm² mol⁻¹
5. Answer: (a) 1.06 × 10²
6. Answer: (c) 128 S cm² mol⁻¹
7. Answer: (c) 388.8 ohm⁻¹ cm² gm eq⁻¹
8. Answer: (b) 0.02
9. Answer: (d) 2.5 × 10⁻⁴
10. Answer: (b) 392

Very Short Answers:

1. No. We can't store AgCl solution in Zinc pot because standard electrode potential of Zinc is less than silver..
2. When the concentration of all the species involved in a half-cell is unity, then the electrode potential is called standard electrode potential.
3. Answer: Electromotive force of a cell is also called the cell potential. It is the difference between the electrode potentials of the cathode and anode.

$$E_{cell} = E_{cathode} - E_{anode}$$

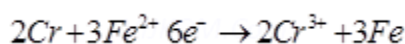
4. Answer: Yes, An electrochemical cell can be converted into electrolytic cell by applying an external opposite potential greater than its own electrical potential.

5. Answer: A single half cell does not exist independently as reduction and oxidation occur simultaneously therefore single electrode potential cannot be measured.
6. Answer: SHE stands for standard Hydrogen electrode. By convention, its electrode potential is taken as 0 (zero).
7. Answer: The positive value of standard electrode potential indicates that the element gets reduced more easily than ions and its reduced form is more stable than Hydrogen gas.
8. The arrangement of metals and ions in increasing order of their electrode potential values is known as electrochemical series. The reduction half reaction for which the reduction potential is lower than the other will act as anode and one with greater value will act as cathode. Reverse reaction will not occur.
9. Electrochemical cells are used for determining the
 - pH of solutions
 - solubility product and equilibrium constant
 - in potentiometric titrations
10. Factors affecting electrode potential values are –
 - Concentration of electrolyte
 - Temperature.

Short Answers:

1. Answer

The cell reaction is



Nernst Equation –

$$\begin{aligned}
 E_{cell} &= \left(E_{Fe^{2+}/Fe}^0 - E_{Cr^{3+}/Cr}^0 \right) - \frac{0.059}{6} \log \frac{[Cr^{3+}]^2}{[Fe^{2+}]^3} \\
 &= (-0.44V - (-0.74V)) - \frac{0.059}{6} \log \frac{(0.10)^2}{(0.01)^3} \\
 &= 0.3V - \frac{0.059}{6} \log 10^4
 \end{aligned}$$

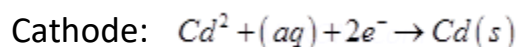
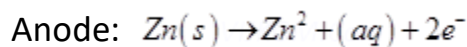
=

$$= 0.3\text{V} - 0.0394\text{V}$$

$$= +0.2606\text{V}$$

2. Answer:

The half-cell reactions are



Nernst Equation

$$E_{\text{cell}} = (E^{\circ}_{\text{Cathode}} - E^{\circ}_{\text{Anode}}) - \frac{0.059}{n} \log \frac{[\text{Zn}^{2+}]}{[\text{Cd}^{2+}]}$$

$$= (-0.403 - (-0.763)) -$$

$$= 0.36\text{V} - 0.0798\text{V} = 0.4398\text{V}$$

$$\Delta G^{\circ} = -n F E^{\circ}_{\text{cell}}$$

$$= \frac{-2\text{mol} \times 96500\text{C}}{\text{mol} \times 0.4398\text{V}}$$

$$= -8488\text{J mol}^{-1}$$

3. Answer:

From the reaction, $n = 2$

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} - E^{\circ}_{\text{Zn}^{2+}/\text{Zn}}$$

$$= +0.34\text{V} - (-0.76\text{V}) = 1.10\text{V}$$

$$E^{\circ}_{\text{cell}} = \frac{2.303RT}{nF} \log k_c$$

$$\text{At } 298\text{K, } E^{\circ}_{\text{cell}} \times \frac{n}{0.059} \log k_c$$

$$\log k_c = E^{\circ}_{\text{cell}} \times \frac{n}{0.059}$$

$$1.10 \times \frac{2}{0.059} = 37.29$$

$$K_c = \text{Antilog } 37.29$$

$$= 1.95 \times 10^{37}$$

4. Answer:

$$[Ag^+] = 5.3 \times 10^{-9} M$$

5. Answer :

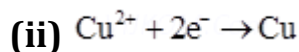
$$E_{cell}^{\circ} = 0.03V$$

6. Answer

(i)

Therefore, Required charge = 3 F

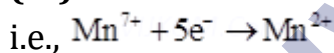
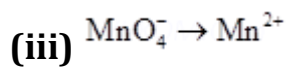
$$= 289461 C$$



Therefore, Required charge = 2 F

$$= 2 \times 96487 C$$

$$= 192974 C$$



Therefore, Required charge = 5 F

$$= 5 \times 96487 C$$

$$= 482435 C$$

7. Answer:

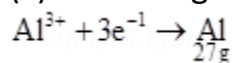
(i) According to the question,

Electricity required to produce 40 g of calcium = 2 F

Therefore, electricity required to produce 20 g of calcium =

$$= 1 F$$

(ii) According to the question,



Electricity required to produce 27 g of Al = 3 F

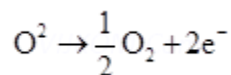
Therefore, electricity required to produce 40 g of Al = $\frac{3 \times 40}{27} F$

$$= 4.44 F$$

8. Answer:

(i) According to the question,

Now, we can write:

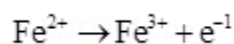


Electricity required for the oxidation of 1 mol of H_2O to $O_2 = 2 F$

$$= 2 \times 96487 \text{ C}$$

$$= 192974 \text{ C}$$

(ii) According to the question



Electricity required for the oxidation of 1 mol of FeO to $Fe_2O_3 = 1 F$

$$= 96487 \text{ C}$$

9. Answer :

Given,

Current = 5A

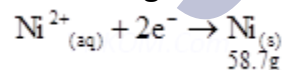
Time = $20 \times 60 = 1200 \text{ s}$

Therefore, Charge = current \times time

$$= 5 \times 1200$$

$$= 6000 \text{ C}$$

According to the reaction,



Nickel deposited by $2 \times 96487 \text{ C} = 58.71 \text{ g}$

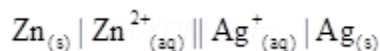
Therefore, nickel deposited by 6000 C = $\frac{58.71 \times 6000}{2 \times 96487} \text{ g}$

$$= 1.825 \text{ g}$$

Hence, 1.825 g of nickel will be deposited at the cathode.

10. Answer :

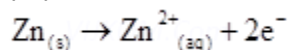
The galvanic cell in which the given reaction takes place is depicted as:



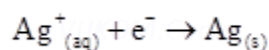
(i) Zn electrode (anode) is negatively charged.

(ii) Ions are carriers of current in the cell and in the external circuit, current will flow from silver to zinc.

(iii) The reaction taking place at the anode is given by,



The reaction taking place at the cathode is given by,

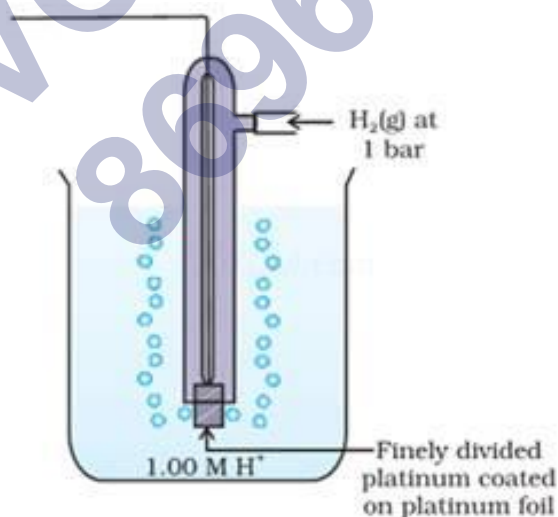


Long Answers:

1. Answer:

Construction: SHE consists of a platinum electrode coated with platinum black. The electrode is dipped in an acidic solution and pure Hydrogen gas is bubbled through it. The concentration of both the reduced and oxidized forms of Hydrogen is maintained at unity i.e) pressure of gas is 1 bar and concentration of Hydrogen ions in the solution is 1 molar.

Working – The reaction taking place in SHE is At 298 K, the emf of the cell constructed by taking SHE as anode and other half-cell as cathode, gives the reduction potential of the other half cell whereas for a cell constructed by taking SHE as anode gives the oxidation potential of other half cell as conventionally the electrode potential of SHE is zero.



2. Answer:

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

$$\lambda^\circ(\text{H}^+) = 349.6 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\lambda^\circ(\text{HCOO}^-) = 54.6 \text{ S cm}^2 \text{ mol}^{-1}$$

$$A_m^\circ(\text{HCOOH}) = \lambda^\circ(\text{H}^+) + \lambda^\circ(\text{HCOO}^-)$$

$$= 349.6 + 54.6 = 404.2 \text{ S cm}^2 \text{ mol}^{-1}$$

Now, degree of dissociation:

$$\alpha = \frac{A_m(\text{HCOOH})}{A_m^\circ(\text{HCOOH})}$$

$$= \frac{46.1}{404.2} = 0.114 \text{ (approximately)}$$

Thus, dissociation constant:

$$K = \frac{c \alpha^2}{(1 - \alpha)}$$

$$= \frac{(0.025 \text{ mol L}^{-1})(0.114)^2}{(1 - 0.114)}$$

$$= 3.67 \times 10^{-4} \text{ mol L}^{-1}$$

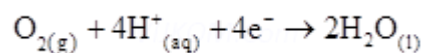
3. Answer:

In the process of corrosion, due to the presence of air and moisture, oxidation takes place at a particular spot of an object made of iron. That spot behaves as the anode. The reaction at the anode is given by,

Electrons released at the anodic spot move through the metallic object and go to another spot of the object.

There, in the presence of ions, the electrons reduce oxygen. This spot behaves as the cathode. These H^+ ions come either from , which are formed due to the dissolution of carbon dioxide from air into water or from the dissolution of other acidic oxides from the atmosphere in water.

The reaction corresponding at the cathode is given



The overall reaction is: $2\text{Fe}_{(\text{s})} + \text{O}_{2(\text{g})} + 4\text{H}^+_{(\text{aq})} \rightarrow 2\text{Fe}^{2+}_{(\text{aq})} + 2\text{H}_2\text{O}_{(\text{l})}$

Also, ferrous ions are further oxidized by atmospheric oxygen to ferric ions. These ferric ions combine with moisture, present in the surroundings, to form hydrated ferric oxide ($\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$)

i.e., rust.

Hence, the rusting of iron is envisaged as the setting up of an electrochemical cell.

4. **Answer (i)** $E^{\circ}_{\text{Cr}^{3+}/\text{Cr}} = 0.74\text{V}$

$$E^{\circ}_{\text{Cd}^{2+}/\text{Cd}} = 0.40\text{V}$$

The galvanic cell of the given reaction is depicted as: $\text{Cr}_{(s)} | \text{Cr}^{3+}_{(aq)} || \text{Cd}^{2+}_{(aq)} | \text{Cd}_{(s)}$

Now, the standard cell potential is $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{R}} - E^{\circ}_{\text{L}}$

$$= 0.40 - (-0.74)$$

$$= +0.34\text{V}$$

$$\Delta_r G^{\circ} = -nFE^{\circ}_{\text{cell}}$$

In the given equation,

$$n = 6$$

$$F = 96487\text{C mol}^{-1}$$

$$E^{\circ}_{\text{cell}} = +0.34\text{V}$$

$$\text{Then, } \Delta_r G^{\circ} = -6 \times 96487\text{C mol}^{-1} \times 0.34\text{V}$$

$$= -196833.48\text{CV mol}^{-1}$$

$$= -196833.48\text{J mol}^{-1}$$

$$= -196.83\text{kJ mol}^{-1}$$

$$\text{Again, } \Delta_r G^{\circ} = -RT \ln K$$

$$\Delta_r G^{\circ} = -2.303RT \ln K$$

$$\log K = -\frac{\Delta_r G^{\circ}}{2.303RT}$$

$$= \frac{196.83 \times 10^3}{2.303 \times 8.314 \times 298}$$

$$= 34.496$$

$$\text{Therefore, } K = \text{antilog}(34.496)$$

$$= 3.13 \times 10^{34}$$

(ii) $E^{\circ}_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.77\text{V}$

$$E^{\circ}_{\text{Ag}^+/\text{Ag}} = 0.80\text{V}$$

The galvanic cell of the given reaction is depicted as: $\text{Fe}^{2+}_{(aq)} | \text{Fe}^{3+}_{(aq)} || \text{Ag}^+_{(aq)} | \text{Ag}_{(s)}$

Now, the standard cell potential is $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{R}} - E^{\circ}_{\text{L}}$

$$= 0.80 - 0.77$$

$$= 0.03\text{V}$$

Here, $n = 1$.

$$\text{Then, } \Delta_r G^{\circ} = -nFE^{\circ}_{\text{cell}}$$

$$= -1 \times 96487 \text{ C mol}^{-1} \times 0.03 \text{ V}$$

$$= -2894.61 \text{ J mol}^{-1}$$

$$= -2.89 \text{ kJ mol}^{-1}$$

Again, $\Delta_r G^\ominus = 2.303 RT \ln K$

$$\log K = -\frac{\Delta_r G}{2.303 RT}$$

$$= \frac{-2894.61}{2.303 \times 8.314 \times 298}$$

$$= 0.5073$$

Therefore, $K = \text{antilog}(0.5073)$

$$= 3.2 \text{ (approximately)}$$

5. Answer (i) For the given reaction, the Nernst equation can be given as:

$$E_{\text{cell}} = E_{\text{cell}}^\ominus - \frac{0.0591}{n} \log \frac{[\text{Mg}^{2+}]}{[\text{Cu}^{2+}]}$$

$$= \{0.34 - (-236)\} - \frac{0.0591}{2} \log \frac{.001}{.0001}$$

$$= 2.7 - \frac{0.0591}{2} \log 10$$

$$= 2.7 - 0.02955$$

$$= 2.67 \text{ V (approximately)}$$

(ii) For the given reaction, the Nernst equation can be given as:

$$E_{\text{cell}} = E_{\text{cell}}^\ominus - \frac{0.0591}{n} \log \frac{[\text{Fe}^{2+}]}{[\text{H}^+]^2}$$

$$= \{0 - (-0.44)\} - \frac{0.0591}{2} \log \frac{0.001}{1^2}$$

$$= 0.44 - 0.02955(-3)$$

$$= 0.52865 \text{ V}$$

$$= 0.53 \text{ V (approximately)}$$

(iii) For the given reaction, the Nernst equation can be given as:

$$E_{\text{cell}} = E_{\text{cell}}^\ominus - \frac{0.0591}{n} \log \frac{[\text{Sn}^{2+}]}{[\text{H}^+]^2}$$

$$\begin{aligned}
 &= \{0 - (-0.14)\} - \frac{0.0591}{2} \log \frac{0.050}{(0.020)^2} \\
 &= 0.14 - 0.0295 \times \log 125 \\
 &= 0.14 - 0.062 \\
 &= 0.078 \text{ V} \\
 &= 0.08 \text{ V (approximately)}
 \end{aligned}$$

(iv) For the given reaction, the Nernst equation can be given as:

$$\begin{aligned}
 E_{\text{cell}} &= E_{\text{cell}}^{\ominus} - \frac{0.0591}{n} \log \frac{1}{[\text{Br}^-]^2 [\text{H}^+]^2} \\
 &= (0 - 1.09) - \frac{0.0591}{2} \log \frac{1}{(0.010)^2 (0.030)^2} \\
 &= -1.09 - 0.02955 \times \log \frac{1}{0.00000009} \\
 &= -1.09 - 0.02955 \times \log \frac{1}{9 \times 10^{-8}} \\
 &= -1.09 - 0.02955 \times \log (1.11 \times 10^7) \\
 &= -1.09 - 0.02955(0.0453 + 7) \\
 &= -1.09 - 0.208 \\
 &= -1.298 \text{ V}
 \end{aligned}$$

Assertion and Reason Answers:

1. (c) Assertion is correct statement but reason is wrong statement.

Explanation:

Cu^{2+} ions are deposited as Cu.

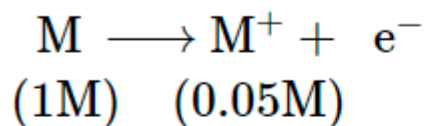
2. (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

Case Study Answers:

1. Answer :

i. (b) $E_{\text{cell}} > 0$; $\Delta G < 0$

Explanation:



For concentration cell, $E_{\text{cell}} = \frac{0.059}{1} \log \frac{0.05}{1}$

$$E_{\text{cell}} = \frac{0.059}{1} \log(5 \times 10^{-2})$$

$$E_{\text{cell}} = \frac{0.059}{1} [(-2) + \log 5] - 0.059(-2 + 0.698)$$

$$= -0.059(-1.302) = 0.0768$$

$$\Delta G = -nFE_{\text{cell}}$$

If E_{cell} is positive, ΔG is negative.

ii. (c) 154mV

Explanation:

$$\frac{E_1}{E_2} = \frac{\log 0.05}{\log 0.0025}$$

$$\frac{E_1}{E_2} = \frac{\log 5 \times 10^{-2}}{\log 25 \times 10^{-4}}$$

$$E_1 = 0.0768$$

$$\frac{0.0168}{E_2} = \frac{-1.3}{-2.6} = \frac{1}{2} \text{ or } E_2 = 154\text{mV}$$

iii. (c) > 1

Explanation:

$$K = \text{antilog} \left(\frac{nE^\circ}{0.0591} \right)$$

For feasible cell, E° is positive,
hence from the above equation,
 $K > 1$ for a feasible cell reaction.

iv. (b) 0

v. (a) Concentration of ions in solution.

2. Answer :

i. (b) 1.0

Explanation:

$$n_{\text{NaCl}} = \frac{4 \times 500}{1000} = 2 \text{ mol}$$

$$\therefore n_{\text{Cl}_2} = 1 \text{ mol}$$

ii. (b) 446g

Explanation:

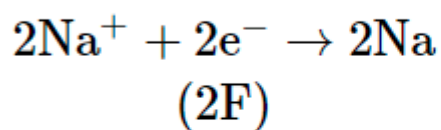
$$n_{\text{Na deposited}} = 2 \text{ mol}$$

$$\therefore n_{\text{Na-Hg formed}} = 2 \text{ mol}$$

$$\therefore \text{Mass of amalgam formed} = 2 \times 223 = 446 \text{ g}$$

iii. (d) 193000

Explanation:



Total charge required = $2F = 2 \times 96500 = 193000\text{C}$

iv. (a) 2

v. (a) H_2 gas

SHIVOM CLASSES
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