

INTRODUCTION

Electrochemistry is a branch of chemistry that deals with the relationship between electricity and chemical reactions. It involves the study of the interconversion of electrical energy and chemical energy, as well as the application of electrical energy to drive non-spontaneous chemical reactions.

1. **Electrochemical Cell:** An electrochemical cell consists of two electrodes, an anode (where oxidation occurs) and a cathode (where reduction occurs), immersed in an electrolyte solution. There are two main types of electrochemical cells: galvanic cells (also known as voltaic cells) and electrolytic cells.
2. **Oxidation and Reduction:** Electrochemical reactions involve oxidation and reduction half-reactions. Oxidation is the loss of electrons, while reduction is the gain of electrons. These reactions are coupled, meaning electrons released from the oxidation half-reaction are used in the reduction half-reaction.
3. **Electrode Reactions:** At the anode, oxidation occurs, and electrons are released, resulting in the production of positively charged ions. At the cathode, reduction occurs, and electrons are consumed, leading to the formation of negatively charged ions or the deposition of metals.
4. **Cell Potential:** The cell potential, also known as the electromotive force (EMF) or cell voltage, is a measure of the driving force for electron flow in an electrochemical cell. It is typically measured in volts (V). The cell potential is influenced by the nature of the electrode materials and the concentrations of species involved.
5. **Standard Electrode Potential:** The standard electrode potential (E°) is the cell potential measured under standard conditions (25°C, 1 atm pressure, 1 M concentrations). It provides a reference point for comparing the relative tendencies of different half-reactions to undergo reduction or oxidation.
6. **Nernst Equation:** The Nernst equation relates the cell potential to the concentrations of reactants and products in a non-standard electrochemical cell. It allows the calculation of cell potential under non-standard conditions, taking into account the activities (concentrations) of species involved.

7. **Faraday's Laws of Electrolysis:** Faraday's laws describe the quantitative relationship between the amount of substance produced or consumed during electrolysis and the electric charge passed through the cell. These laws provide a basis for understanding the stoichiometry of electrochemical reactions.
8. **Applications of Electrochemistry:** Electrochemistry has various applications, including batteries and fuel cells (for energy storage and conversion), electroplating (depositing a metal coating on a surface), corrosion prevention, electrolysis (e.g., in water splitting for hydrogen production), and sensors (such as pH meters and glucose sensors).
9. **Electrochemical Series:** The electrochemical series arranges different substances in order of their standard electrode potentials. It helps predict the direction of electron flow in redox reactions and the feasibility of a given electrochemical process.
10. **Redox Titration:** Electrochemistry is also involved in redox titrations, which are analytical techniques used to determine the concentration of a substance by measuring the electrical potential change during a redox reaction.

CONDUCTORS AND INSULATORS

Conductors:

- High electrical conductivity.
- Electrons can move freely, allowing easy flow of electric current.
- Examples: Metals (e.g., copper, silver), graphite.
- Used for electrical wiring and conducting electricity in devices.

Insulators:

- Low electrical conductivity.
- Electrons are tightly bound, hindering the flow of electric current.
- Examples: Non-metals (e.g., rubber, plastic), glass, wood.
- Used as insulating materials for electrical insulation and protection.

FARADAY LAW OF ELECTROLYSIS

Electrolysis is a process that involves the chemical decomposition of an electrolyte through the passage of electric current, either in its aqueous solution or molten state. The apparatus used to carry out electrolysis is referred to as an electrolytic cell. Faraday's laws of electrolysis describe the relationship between the quantity of electric charge and the amount of substance deposited at the electrodes. These laws were formulated by Michael Faraday in 1834.

The first law of electrolysis states that the mass of the substance produced at the electrode (either the anode or cathode) in an electrolytic cell is directly proportional to the amount of electricity passed through it. Mathematically, it can be expressed as:

$$m = Z \times Q$$

This implies that,

$m \propto Q$, Q is the quantity of electricity

$M \propto It$, I is current in amperes

$m = ZIt$, t is time in seconds, Z is the constant of proportionality called electrochemical equivalent. (E.C.E.)

If $I = 1$ ampere, $t = 1$ sec, then $m = Z$

Thus, electrochemical equivalent may be defined as the mass of the substance produced by passing 1 ampere of current through the electrolyte for one second..

The second law of electrolysis states that when the same quantity of electricity is passed through multiple electrolytes connected in series, the mass of the substances produced at the electrodes is directly proportional to their equivalent masses or electrochemical equivalents. For example, if the same amount of electricity is passed through electrolytic cells in series, resulting in the production of substances A and B at their respective electrodes, then the masses of A and B will be proportional to their respective equivalent masses.

$$\frac{\text{Mass of A}}{\text{Mass of B}} = \frac{\text{Equivalent mass of A}}{\text{Equivalent mass of B}} = \frac{\text{ECE of A}}{\text{ECE of B}}$$

APPLICATIONS

Electrolysis finds applications in various fields, including

- Determination of equivalent masses of elements
- Electrometallurgy
- Manufacturing non-metals
- Electroplating metals
- Production of compounds
- Electrorefining processes
- Electroplating, which involves the coating of an inferior metal with a superior metal through electrolysis.

CONDUCTIVITY

Conductivity is a property that measures how well a material conducts electric current. It is the inverse of resistance and is denoted by C . Its units are Ω^{-1} or ohm^{-1} or mho or S (*Siemens*)

$$C = \frac{1}{R} = \frac{1}{P} \times \frac{a}{l}$$

SPECIFIC CONDUCTIVITY

Specific conductivity (κ) is a measure of conductivity per unit volume. It represents the conductance of one cubic centimeter of a material or solution. Units are $ohm^{-1} cm^{-1}$ or $\Omega^{-1} cm^{-1}$ or $S cm^{-1}$.

The formula for specific conductivity (κ) is:

$$K = G \left(\frac{1}{A} \right)$$

Where:

- κ is the specific conductivity
- G is the conductance of the material or solution
- A is the cross-sectional area through which the current is flowing

$$K = \frac{1}{P} = \frac{1}{R} \left(\frac{l}{a} \right) \text{ or } C \left(\frac{l}{a} \right)$$

Equivalent conductivity (Λ): It is conductance of a solution containing one gram equivalent of electrolyte such that, the entire solution is placed between two large electrodes at one centimeter apart. units of $ohm^{-1} cm^2 eqi^{-1}$ or $S cm^2 eqi^{-1}$.

$$\Lambda = \frac{k \times 1000}{N}$$

Molar conductivity (μ): It is defined as the conductance of the solution containing one gram-mole of the electrolyte such that the entire solution is placed between two electrodes one centimeter apart. Units of μ are $ohm^{-1} cm^{-1} mol^{-1}$ or $\Omega^{-1} cm^2 mol^{-1}$ or $S - cm^2 mol^{-1}$.

$$\mu = \frac{k \times 1000}{M}$$

Kohlrausch's law.

Kohlrausch's law, also known as Kohlrausch's conductivity law, states that the molar conductivity of an electrolyte at infinite dilution is equal to the sum of the molar conductivities of its constituent ions.

In other words, when an electrolyte is completely dissociated into its ions in a solution, the total conductivity of the solution is determined by the individual contributions of the ions. Kohlrausch's law

allows for the determination of the molar conductivity of individual ions by measuring the conductivity of their corresponding electrolytes at infinite dilution.

Mathematically, Kohlrausch's law can be expressed as:

$$\Lambda^\circ(\text{AB}) = \Lambda^\circ(\text{A}^+) + \Lambda^\circ(\text{B}^-)$$

Where:

- $\Lambda^\circ(\text{AB})$ is the molar conductivity of the electrolyte AB at infinite dilution.
- $\Lambda^\circ(\text{A}^+)$ is the molar conductivity of the cation A^+ at infinite dilution.
- $\Lambda^\circ(\text{B}^-)$ is the molar conductivity of the anion B^- at infinite dilution.

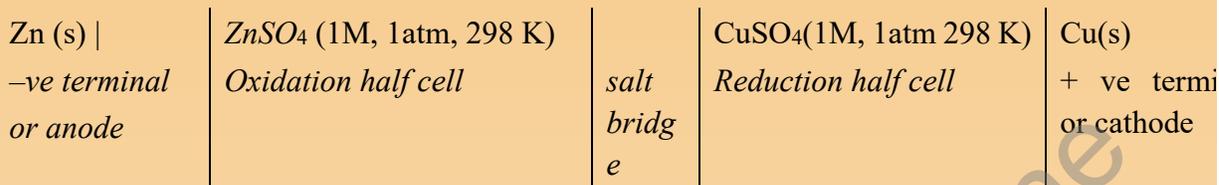
Kohlrausch's law is applicable to strong electrolytes, where complete ionization occurs, and it provides a way to estimate the contribution of individual ions to the overall conductivity of a solution. This law has important applications in various fields, including electrochemistry, analytical chemistry, and chemical engineering. Degree of ionisation of weak electrolyte (α)

$\alpha = \frac{\mu}{\mu^\infty}$, the value of μ^∞ for weak electrolytes and ionic mobilities.

Galvanic or voltaic or Electrochemical cell.

A galvanic cell, also known as a voltaic cell or an electrochemical cell, is a device that uses a spontaneous redox (reduction-oxidation) reaction to convert chemical energy into electrical energy. It consists of two half-cells, each containing an electrode immersed in an electrolyte solution. The two half-cells are connected by a conductive pathway, allowing the flow of electrons.

In a galvanic cell, one half-cell undergoes oxidation (loses electrons) while the other half-cell undergoes reduction (gains electrons). This creates a potential difference between the two electrodes, resulting in the flow of electrons through the external circuit. The spontaneous redox reaction drives the flow of electrons from the anode (site of oxidation) to the cathode (site of reduction). The electrode at the anode is referred to as the negative electrode or the anode electrode, while the electrode at the cathode is referred to as the positive electrode or the cathode electrode. The electrolyte solutions in the two half-cells may be connected by a salt bridge or a porous membrane, which allows ion transfer to maintain electrical neutrality. During operation, the galvanic cell produces a direct current (DC) as electrons flow through the external circuit from the anode to the cathode. This flow of electrons can be utilized to power devices or perform useful work.

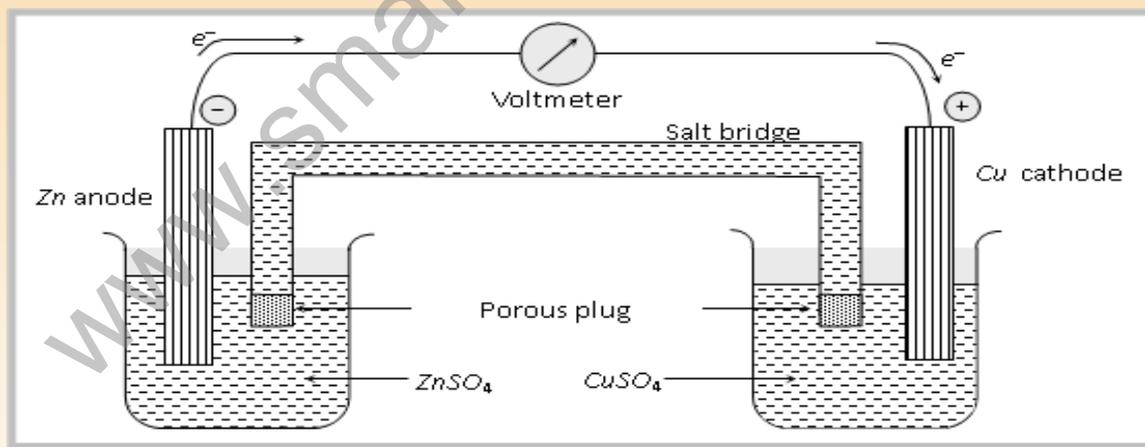


SALT BRIDGE

A salt bridge is a component in a galvanic cell that connects the electrolyte solutions in the two half-cells. It is typically a U-shaped tube filled with an inert electrolyte solution, such as KCl (potassium chloride) or NaNO₃ (sodium nitrate), soaked in a gel or agar-agar. The salt bridge serves two main functions:

1. Maintains Electrical Neutrality: During the operation of a galvanic cell, the oxidation at the anode generates positive ions, while the reduction at the cathode consumes positive ions. This can result in an imbalance of charge in the two half-cells, leading to a buildup of charge and preventing further reaction. The salt bridge allows for the flow of ions between the half-cells, maintaining electrical neutrality and preventing charge buildup.

2. Completes the Circuit: The salt bridge completes the circuit for the flow of current. As electrons flow from the anode to the cathode through the external circuit, the salt bridge allows the corresponding flow of ions in the opposite direction. This completes the circuit and enables the continuous flow of electrons and ions, allowing the galvanic cell to sustain its operation.



Electrode potential.

Electrode potential refers to the electrochemical potential difference that exists between an electrode and the electrolyte solution in which it is immersed. It is a fundamental concept in electrochemistry and represents the ability of an electrode to either gain or lose electrons during a redox reaction.

The electrode potential is a result of the inherent characteristics of the electrode material and its interaction with the surrounding electrolyte solution. Factors such as the composition and structure of the electrode, the concentration of ions in the solution, and the temperature all influence the electrode potential. The measurement of electrode potential is crucial in understanding and predicting the behavior of electrochemical cells. In a galvanic cell, for example, the electrode with a higher electrode potential tends to attract electrons and undergo reduction, becoming the cathode. Conversely, the electrode with a lower electrode potential tends to lose electrons and undergo oxidation, becoming the anode. This potential difference between the electrodes creates an electric potential and drives the flow of electrons through the external circuit. Electrode potentials are often measured relative to a reference electrode, which serves as a point of comparison. The standard hydrogen electrode (SHE) is commonly used as a reference with an assigned electrode potential of 0 volts. By comparing the electrode potential of another electrode with respect to the reference electrode, the relative reactivity and behavior of different electrodes can be determined. E° is an intensive property like temperature or molar volume. This means that E° is same for half cell reaction whether it is represented as, $2X^+ + 2e^- \rightarrow X_2$ or $X^+ + e^- \rightarrow \frac{1}{2} X_2$.

- (1) The tendency of oxidation can be represented by oxidation potential (E_{oxi}).
- (2) The tendency of reduction can be represented by reduction potential (E_{red}).

The reduction potential of the electrode at standard state conditions (1 molar conc. of the ions, 298 K and 1 atm. Pressure) is called **standard reduction potential** (E°).

Reference electrode (Standard hydrogen electrode, SHE).

The Standard Hydrogen Electrode (SHE) is constructed using a glass tube that contains a platinum wire sealed within it. At one end of the platinum wire, a platinum foil is attached. This platinum foil is coated with finely divided platinum particles. To set up the SHE, it is immersed in a beaker filled with an aqueous solution of an acid, typically with a concentration of 1 mole per liter of hydrogen ions (H^+). The solution is maintained at a temperature of 298 Kelvin (25 degrees Celsius).

A continuous stream of hydrogen gas, at a pressure of one atmosphere, is passed through the solution. The hydrogen gas serves as the reactant in the SHE. During the operation of the SHE, oxidation or reduction reactions occur at the surface of the platinum foil. These reactions involve the exchange of electrons with the hydrogen ions in the solution. The platinum acts as a catalyst, facilitating the redox reactions without being consumed in the process. The SHE serves as a reference electrode in electrochemical measurements. Its electrode potential is defined as zero volts, providing a standard against which other electrode potentials can be measured. The use of the SHE as a reference allows for the determination of the electrode potentials of other electrodes relative to the hydrogen electrode.

EMF of the cell or cell voltage.

The EMF of a cell refers to the potential difference between its two terminals in the absence of any current being drawn from the cell.

$$E_{\text{cell}} \text{ or } EMF = [E_{\text{red}}(\text{cathode}) - E_{\text{red}}(\text{anode})] \text{ or } = [E_{\text{red}}(\text{cathode}) + E_{\text{red}}(\text{anode})]$$

$$\text{Similarly, } E_{\text{cell}}^{\circ} \text{ or } EMF^{\circ} = [E_{\text{red}}(\text{cathode}) - E_{\text{red}}(\text{anode})]$$

Nernst Equation.

The Nernst equation is a fundamental equation in electrochemistry that relates the electrode potential of an electrochemical cell to the concentrations of reactants and products involved in the redox reaction. It allows for the calculation of the cell potential under non-standard conditions.

The Nernst equation is expressed as:

$$E = E^{\circ} - \left(\frac{RT}{nF}\right) \times \ln(Q)$$

Where:

- E is the cell potential under non-standard conditions,
- E° is the standard cell potential,
- R is the ideal gas constant (8.314 J/(mol·K)),
- T is the temperature in Kelvin,
- n is the number of moles of electrons transferred in the balanced redox reaction,
- F is the Faraday constant (96,485 C/mol), and
- Q is the reaction quotient, which is the ratio of the concentrations of the products to the concentrations of the reactants, each raised to the power of their stoichiometric coefficients.

The Nernst equation allows us to account for the effect of concentration changes on the cell potential. It states that as the concentrations of reactants and products change, the cell potential will also change. The equation provides a more accurate determination of the cell potential at non-standard conditions, where the concentrations differ from their standard states

$$E = E^{\circ} + \frac{2.303 RT}{nF} \log \frac{[M^{n+}]}{[M]} \quad \text{or} \quad E = E^{\circ} + \frac{2.303 \times 8.3014 \times 298}{n \times 96500} \log \frac{[M^{n+}]}{[M]} \quad \text{oR}$$

$$E = E^{\circ} + \frac{0.059}{n} \log \frac{[M^{n+}]}{[M]}$$

- Relationship between free energy change and cell potential can be written as $\Delta G = -nFE_{\text{cell}}$. For standard state conditions $\Delta G^{\circ} = -nF E_{\text{cell}}^{\circ}$
- Equilibrium constant of net cell reaction is related to the standard EMF as

Electrochemical series.

The electrochemical series is a list of elements arranged based on their standard reduction potentials or standard oxidation potentials when in contact with their respective ions.

Here are the characteristics of the electrochemical series:

1. **Reducing and Oxidizing Agents:** Elements with smaller reduction potentials have a greater ability to act as reducing agents, while elements with larger reduction potentials have a greater tendency to act as oxidizing agents. For example, Li is a strong reducing agent, and F is a strong oxidizing agent.
2. **Redox Reactions:** An element can reduce ions with reduction potentials larger than its own and oxidize elements with reduction potentials lower than its own. The electrochemical series helps determine the feasibility of such redox reactions.
3. **Value Comparison:** The electrochemical series allows for comparisons of reduction potentials among different elements, helping identify their relative abilities to reduce or oxidize other species.
4. **Determination of Cell Potentials:** The series aids in determining the cell potential (voltage) for various combinations of electrodes in electrochemical cells.
5. **Hydrogen Displacement:** Elements positioned above hydrogen in the series can liberate hydrogen gas by reacting with hydrochloric acid or other hydrogen sources. Elements below hydrogen in the series cannot produce hydrogen gas in such reactions. For example, elements like Ag, Au, Pt, and Hg cannot generate hydrogen gas when reacted with HCl.

Cells.

- **Primary cells:** Non-rechargeable cells used once and cannot be recharged, examples include alkaline batteries.
- **Secondary cells:** Rechargeable cells that can be used multiple times, examples include lithium-ion batteries.
- **Fuel cells:** Generate electrical energy through continuous supply of fuel and an oxidizing agent, commonly used in power generation and transportation.

Corrosion.

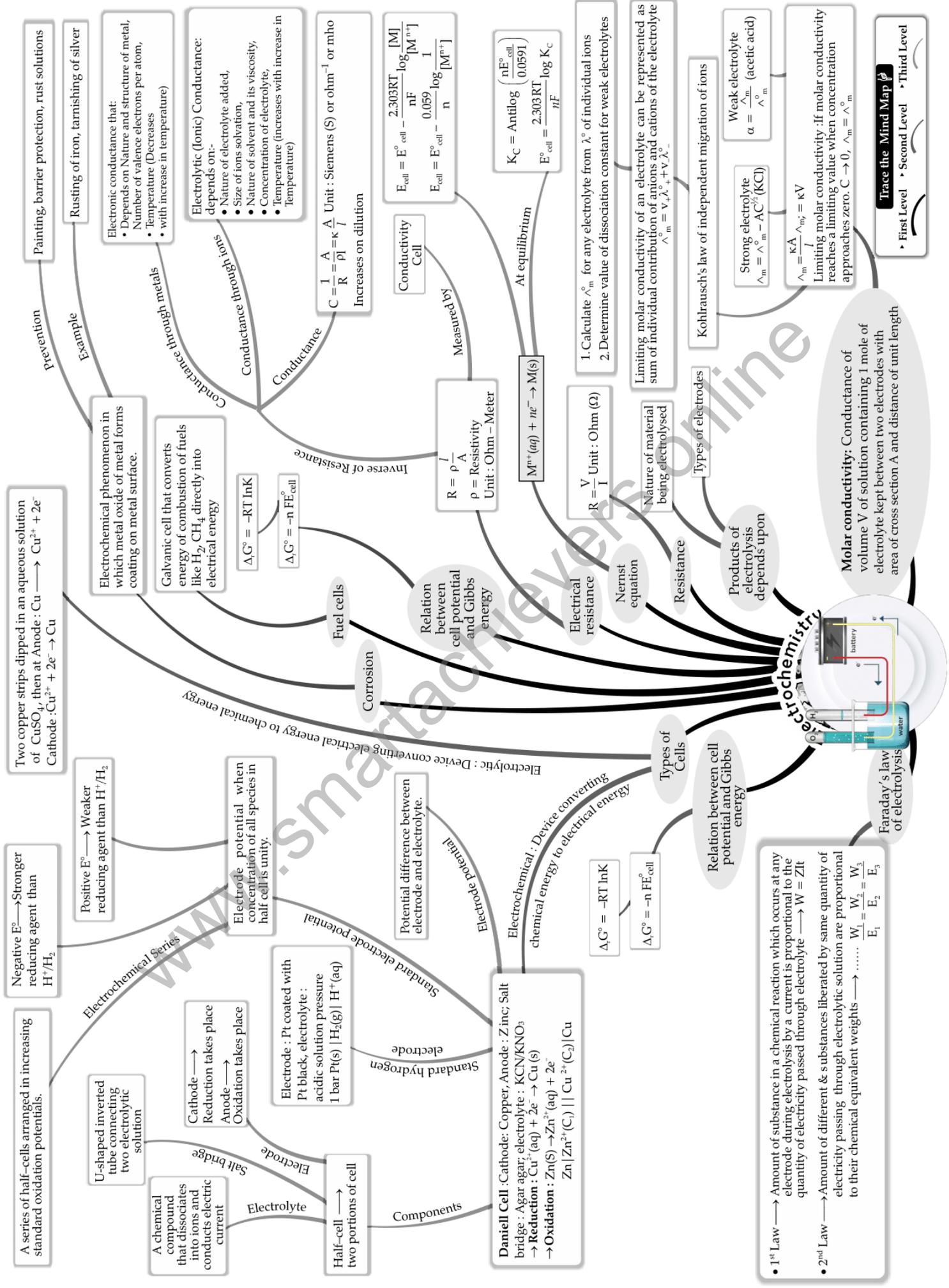
Corrosion is the gradual deterioration or degradation of metals and other materials when they react with their environment. It occurs through an electrochemical process, often influenced by factors like moisture, oxygen, and temperature. Corrosion can lead to structural damage, reduced lifespan, and failure of components. Methods to prevent corrosion include protective coatings, cathodic protection, and material selection.

Factors that enhance corrosion:

1. **Moisture or Water:** Presence of moisture or water increases the likelihood of corrosion, as it provides the necessary electrolyte for the electrochemical reaction to occur.
2. **Oxygen:** Availability of oxygen in the environment accelerates the corrosion process, as it acts as the oxidizing agent in the electrochemical reaction.
3. **Acids and Salts:** Exposure to acids and salts can significantly increase the corrosion rate by providing additional ions and promoting chemical reactions that facilitate corrosion.
4. **Temperature:** Higher temperatures generally increase the rate of corrosion, as chemical reactions tend to occur more rapidly at elevated temperatures.
5. **Humidity:** Higher humidity levels can promote the retention of moisture on the metal surface, increasing the likelihood of corrosion.
6. **pH Levels:** Extremely acidic or alkaline environments can accelerate corrosion by promoting the formation of corrosive species or by affecting the protective properties of passive films on metals.
7. **Presence of Impurities:** Impurities or contaminants, such as sulfur, chlorides, and pollutants, can accelerate corrosion reactions by initiating localized corrosion or by acting as catalysts for corrosion processes.
8. **Galvanic Effects:** When dissimilar metals or alloys are in contact, a galvanic effect can occur, leading to accelerated corrosion of the less noble (more reactive) metal due to electrochemical reactions between the metals.

How corrosion can be prevented?

- Apply protective coatings such as paints or metal plating.
- Use barrier films or corrosion inhibitors on metal surfaces.
- Implement cathodic protection by using sacrificial anodes or applying external electrical currents.
- Choose corrosion-resistant alloys or metals for specific applications.
- Control the environment by reducing humidity, controlling temperature, and avoiding exposure to corrosive substances.
- Incorporate corrosion-resistant design features into structures or equipment.
- Regularly inspect and maintain metal surfaces to detect and address corrosion early.
- Ensure compatibility between different metals to prevent galvanic corrosion.
- Be aware of the specific corrosive elements present in the environment and take preventive measures accordingly.



PRACTISE QUESTIONS

1. Which of the following represents the amount of charge required to obtain one mole of Al from Al^{3+} ?

- a) 96500 C b) 2×96500 C c) 3×96500 C d) $96500/2$ C

2. If a certain current liberates 0.504 g of hydrogen in 2 hours, how many grams of copper can be liberated by the same current flowing for the same time in a $CuSO_4$ solution?

- a) 12.7 g b) 16 g c) 31.8 g d) 63.5 g

3. If the standard cell potential (E_{cell}°) for a given reaction is negative, which of the following relationships correctly describes the values of ΔG° and K_{eq} ?

- a) $\Delta G^\circ > 0$; $K_{eq} < 1$ b) $\Delta G^\circ > 0$; $K_{eq} > 1$
c) $\Delta G^\circ < 0$; $K_{eq} > 1$ d) $\Delta G^\circ < 0$; $K_{eq} < 1$

4. The Edison storage cell is represented as:



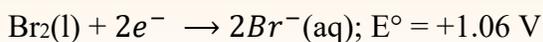
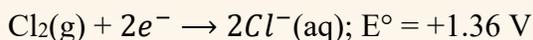
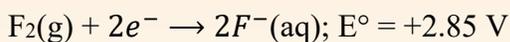
The half-reactions are:

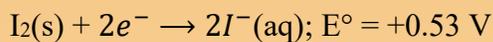


Choose the incorrect statement.

- a) E_{anode} increases with an increase in the concentration of OH^-
b) $E_{cathode}$ decreases with an increase in the concentration of OH^-
c) $E_{cell}^\circ = 1.27 \text{ V}$
d) E_{cell} increases with an increase in the concentration of FeO

5. The standard reduction potentials (E°) of the half-reactions are given below:

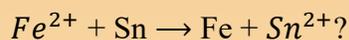




Which of the following pairs represents the strongest oxidizing and reducing agents, respectively?

- a) F_2 and I^- b) Br_2 and Cl^- c) Cl_2 and Br^- d) Cl_2 and I_2

6. The standard reduction potentials for Fe^{2+}/Fe and Sn^{2+}/Sn electrodes are -0.44 V and -0.14 V , respectively. What is the standard electromotive force (e.m.f.) for the cell reaction



- a) $+0.30 \text{ V}$ b) 0.58 V c) $+0.58 \text{ V}$ d) -0.30 V

7. In an electrochemical cell, which electrode is associated with the oxidation process?

- a) Anode b) Cathode
c) Both anode and cathode d) Neither anode nor cathode

8. Which of the following is a non-spontaneous electrochemical reaction?

- a) Discharging a battery b) Charging a battery
c) Rusting of iron d) Dissolution of zinc in hydrochloric acid

9. The SI unit of electric charge is:

- a) Coulomb b) Ampere c) Volt d) Ohm

10. Faraday's law of electrolysis is related to the:

- a) Conservation of mass b) Conservation of energy
c) Conservation of charge d) Conservation of momentum

11. Which of the following is an example of a redox reaction?

- a) Dissolving sugar in water b) Burning of wood
c) Melting of ice d) Mixing of salt and water

12. The process of plating one metal onto another metal by passing an electric current through a solution of metal ions is called:

- a) Electrolysis b) Electroplating c) Galvanization d) Oxidation

13. Which of the following is not a strong electrolyte?

- a) Sodium chloride (NaCl) b) Hydrochloric acid (HCl)
c) Ethanol (C₂H₅OH) d) Sulfuric acid (H₂SO₄)

14. The standard hydrogen electrode (SHE) is used as a reference electrode to measure:

- a) Cell potential b) Current c) Resistance d) Voltage

15. Which of the following statements is true for a spontaneous redox reaction?

- a) $\Delta G > 0$ b) $\Delta G < 0$ c) $\Delta G = 0$
d) ΔG can be positive or negative depending on the reaction conditions

16. The process of converting electrical energy into chemical energy is called:

- a) Electrolysis b) Electroplating
c) Electrochemical cell d) Galvanization

17. Which of the following factors does not affect the rate of an electrochemical reaction?

- a) Temperature b) Concentration of reactants
c) Surface area of electrodes d) Pressure

18. The Nernst equation relates the cell potential to the:

- a) Concentration of reactants b) Temperature
c) Pressure d) Charge of ions

19. Which of the following is an example of a non-spontaneous redox reaction?

- a) Burning of gasoline
- b) Corrosion of iron
- c) Electrolysis of water
- d) Photosynthesis

20. Which of the following is a common application of electrolysis?

- a) Purification of metals
- b) Battery charging
- c) Generation of electricity
- d) Corrosion prevention

21. Which of the following is an example of a primary battery?

- a) Alkaline battery
- b) Lithium-ion battery
- c) Fuel cell
- d) Zinc-carbon battery

22. The standard reduction potential of a half-cell is +0.80 V. What is the value of the standard oxidation potential for the same half-cell?

- a) -0.80 V
- b) +0.80 V
- c) -0.40 V
- d) +0.40 V

23. Which of the following metals would be the best reducing agent based on their standard reduction potentials?

- a) Cu
- b) Zn
- c) Ag
- d) Fe

24. Which statement about electrolytic cells is correct?

- a) They use a spontaneous redox reaction to generate electricity.
- b) They use a non-spontaneous redox reaction to generate electricity.
- c) They convert electrical energy into chemical energy.
- d) They do not involve any redox reactions.

25. The Nernst equation relates the standard reduction potential (E°) to the cell potential (E) under nonstandard conditions. Which of the following represents the Nernst equation?

- a) $E = E^\circ - \left(\frac{RT}{nF}\right)\ln(Q)$ b) $E = E^\circ + \left(\frac{RT}{nF}\right)\ln(Q)$
c) $E^\circ = E - \left(\frac{RT}{nF}\right)\ln(Q)$ d) $E = E^\circ - \left(\frac{RT}{nF}\right)\ln(Q)$

26. Which of the following conditions would increase the voltage of an electrochemical cell?

- a) Increasing the concentration of the electrolyte.
b) Decreasing the concentration of the electrolyte.
c) Increasing the temperature of the system.
d) Adding an inert gas to the system.

27. Which substance acts as the oxidizing agent in the following reaction:



- a) HCl b) Zn c) ZnCl_2 d) H_2

28. The standard hydrogen electrode (SHE) is often used as a reference electrode. What is the standard reduction potential of the SHE?

- a) -0.34 V b) +0.34 V c) -1.36 V d) +1.36 V

29. Which of the following processes occurs at the anode during electrolysis?

- a) Reduction b) Oxidation c) Dissolution d) Precipitation

30. Which of the following is NOT a characteristic of a concentration cell?

- a) Both electrodes are made of the same material.
b) The cell potential is directly proportional to the concentration difference.
c) The cell potential can be zero.
d) The electrolytes are the same on both sides.

31. What is the oxidation number of oxygen in H_2O_2 ?
- a) +1 b) -1 c) -2 d) 0
32. The standard reduction potential of a half-cell can be used to predict:
- a) The rate of the reaction.
b) The direction of the electron flow.
c) The concentration of the electrolyte.
d) The stoichiometry of the reaction.
33. Which of the following is NOT a function of a salt bridge in an electrochemical cell?
- a) Maintaining electrical neutrality in the half-cells
b) Allowing the flow of ions between the half-cells
c) Balancing the charges in the half-cells
d) Providing a conducting path for electrons
34. Which of the following conditions will decrease the cell potential of an electrochemical cell?
- a) Increasing the concentration of the cathode solution
b) Increasing the concentration of the anode solution
c) Decreasing the surface area of the cathode
d) Decreasing the temperature of the system
35. Which of the following statements about Faraday's laws of electrolysis is true?
- a) Faraday's first law states that the mass of a substance deposited at an electrode is directly proportional to the current.
b) Faraday's second law states that the mass of a substance deposited at an electrode is inversely proportional to the current.
c) Faraday's first law states that the mass of a substance deposited at an electrode is inversely proportional to the time.
d) Faraday's second law states that the mass of a substance deposited at an electrode is directly proportional to the time.

36. What is the product formed at the cathode during the electrolysis of molten sodium chloride?

- a) Sodium metal
- b) Chlorine gas
- c) Sodium hydroxide
- d) Hydrogen gas

37. The concentration of Ag^+ in a silver half-cell is 0.10 M. What is the solubility product constant (K_{sp}) of AgCl ?

- a) 1.0×10^{-10}
- b) 1.0×10^{-5}
- c) 1.0×10^{-3}
- d) 1.0×10^2

38. Which of the following is NOT a factor that affects the rate of electrochemical reactions?

- a) Temperature
- b) Concentration of reactants
- c) Surface area of electrodes
- d) Pressure of the system

39. Which of the following statements about the Daniell cell is correct?

- a) Zinc metal oxidizes to form Zn^{2+} ions at the cathode.
- b) Copper metal reduces Cu^{2+} ions at the anode.
- c) The anode is the site of reduction in the cell.
- d) The cell potential is zero when the concentrations of Zn^{2+} and Cu^{2+} ions are equal.

40. Which of the following is a characteristic of a galvanic cell?

- a) It requires an external power source to operate.
- b) It has a positive cell potential.
- c) It converts electrical energy into chemical energy.
- d) It is used for the electrolysis of water.

41. For a cell reaction involving a two-electron change, the standard emf of the cell is found to be 0.295 V at 25°C. The equilibrium constant of the reaction at 25 °C will be

- a) 1×10^{-10}
- b) 29.5×10^{-2}
- c) 10
- d) 1×10^{10}

45. In acidic medium MnO_4^- is converted to Mn^{2+} . The quantity of electricity in faraday required to reduce 0.5 mole of MnO_4^- to Mn^{2+} would be
- a) 2.5 b) 5 c) 1 d) 0.5
46. During electrolysis of water the volume of O_2 liberated is 2.24dm^3 . The volume of hydrogen liberated, under same conditions will be
- a) 2.24 dm^3 b) 1.12 dm^3 c) 4.48 dm^3 d) 0.56 dm^3
47. The amount of electricity required to liberate 1 g-equiv of Cu is
- a) 96500 F b) 1 F c) 1 C d) 96500 A
48. Which of the following is correct?
- a) Zinc acts as cathode in Daniell cell
 b) In a Li – Zn couple, zinc acts as anode
 c) Copper will displace iron in solution
 d) Zinc displaces tin from its solution
49. The number of electrons involved in redox reactions when a faraday of electricity is passed through an electrolyte in solution is :
- a) 6×10^{23} b) 8×10^{19} c) 69500 d) 6×10^{-23}
50. During electrolysis of fused sodium chloride, the reaction of the electrodes are:
- | Anode | Cathode |
|---|--|
| a) $\text{Na}^+ + e \rightarrow \text{Na}$ | $\text{Cl}^- \rightarrow \frac{1}{2}\text{Cl}_2 + e$ |
| b) $\text{Na} \rightarrow \text{Na}^+ + e$ | $\frac{1}{2}\text{Cl}_2 + e \rightarrow \text{Cl}^-$ |
| c) $\text{Cl}^- \rightarrow \frac{1}{2}\text{Cl}_2 + e$ | $\text{Na}^+ + e \rightarrow \text{Na}$ |
| d) $\frac{1}{2}\text{Cl}_2 + e \rightarrow \text{Cl}^-$ | $\text{Na} \rightarrow \text{Na}^+ + e$ |
- Which one is correct about conductivity water?
- a) The water whose own conductance is very small
 b) The water obtained after 7-8 times distillation
 c) Kohlrausch prepared the conductivity water for the first time
 d) All of the above
52. Blocks of magnesium metal are often strapped to the steel hulls of ocean-going ships in order to:
- a) Provide cathodic protection
 b) Protect oxidation of steel
 c) Both (a) and (b) are correct
 d) Neither (a) nor (b) is correct

53. Given the limiting molar conductivity as
 $\Lambda_m^0(\text{HCl}) = 425.9 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$
 $\Lambda_m^0(\text{NaCl}) = 126.4 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$
 $\Lambda_m^0(\text{CH}_3\text{COONa}) = 91 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$
 The molar conductivity, at infinite dilution, of acetic acid (in $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) will be
 a) 481.5 b) 390.5 c) 299.5 d) 516.9
54. If the standard electrode potential of $\text{Cu}^{2+} / \text{Cu}$ electrode is 0.34 V, what is the electrode potential at 0.01 M concentration of Cu^{2+} ?
 ($T = 298 \text{ K}$)
 a) 0.399 V b) 0.281 V c) 0.222 V d) 0.176 V
55. If the ΔG° of Acell reaction,
 $\text{AgCl} + e^- \rightarrow \text{Ag}^+ + \text{Cl}^-$ is -21.20 kJ ;
 The standard emf of the cell is
 a) 0.220 V b) -0.220 V c) 0.229 V d) -0.110 V
56. For the cell reaction, $\text{Cu}_2^{2+}(\text{aq}) + \text{Zn}(\text{s}) \rightarrow \text{Zn}_2^{2+}(\text{aq}) + \text{Cu}(\text{s})$, the change in free energy (ΔG) at a given temperature is a function of :
 a) $\ln c_1$ b) $\ln (c_2/c_1)$ c) $\ln (c_1 + c_2)$ d) $\ln c_2$
57. Consider the following cell reaction
 $2\text{Fe}(\text{s}) + \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) \rightarrow$
 $2\text{Fe}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l}), E^\circ = 1.67 \text{ V}$
 At $[\text{Fe}^{2+}] = 10^{-3} \text{ M}$, $P(\text{O}_2) = 0.1 \text{ atm}$ and $\text{pH} = 3$, the cell potential at 25°C is
 a) 1.47 V b) 1.77 V c) 1.87 V d) 1.57 V
58. Aluminium oxide may be electrolysed at 1000°C to furnish aluminium metal (atomic mass = 27 u; 1 F = 96500 C). The cathode reaction is
 $\text{Al}^{3+} + 3e^- \rightarrow \text{Al}^0$
 To prepare 5.12 kg of aluminium metal by this method would require
 a) $5.49 \times 10^1 \text{ C}$ of electricity b) $5.49 \times 10^4 \text{ C}$ of electricity
 c) $1.83 \times 10^7 \text{ C}$ of electricity d) $5.49 \times 10^7 \text{ C}$ of electricity
59. The standard potentials at 25°C for the following half reactions are given ahead,
 $\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn}; E^\circ = -0.762 \text{ V}$
 $\text{Mg}^{2+} + 2e^- \rightarrow \text{Mg}; E^\circ = -2.37 \text{ V}$
 When zinc dust is added to the solution of MgCl_2 :
 a) ZnCl_2 is formed
 b) Zinc dissolves in the solution
 c) No reaction takes place
 d) Mg is precipitated

HINTS AND SOLUTIONS



The charge required = $3 \times 96500 \text{ C}$



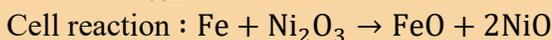
$$\therefore \frac{0.504}{1} = \frac{W}{63.5/2}$$

$$\therefore W_{\text{Cu}} = 16 \text{ g}$$



$\therefore \Delta G^{\circ} = +ve$, E° will be $-ve$ and $K_{eq} < 1$; one should not write $\Delta G^{\circ} > 0$.

4. (d): $E^{\circ}_{\text{cell}} = 0.87 + 0.40 = 1.27 \text{ V}$



5. (a): The given values are E°_{RP} . More is E°_{RP} more is the tendency to gain electron or to show reduction or to show strong oxidant nature.

6. (d): $E^{\circ}_{\text{cell}} = E^{\circ}_{OP_{\text{Sn}}} + E^{\circ}_{RP_{\text{Fe}}} = 0.14 + (-0.44)$
 $= -0.30$

7. a): Anode

Explanation: The anode is the electrode where oxidation occurs. It loses electrons and is negatively charged.

8. b) Charging a battery

Explanation: Charging a battery is a non-spontaneous process that requires an external energy source to drive the reaction against its natural direction.

9 a) Coulomb

Explanation: Coulomb is the SI unit of electric charge, named after the French physicist Charles-Augustin de Coulomb.

10. a) Conservation of mass

Explanation: Faraday's law of electrolysis states that the amount of substance transformed at an electrode during electrolysis is directly proportional to the quantity of electric charge passed through the electrolyte. It is based on the principle of conservation of mass.

11. b) Burning of wood

Explanation: The burning of wood involves the transfer of electrons from the wood (reducing agent) to oxygen (oxidizing agent), making it a redox reaction.

12. b) Electroplating

Explanation: Electroplating is the process of depositing a layer of metal onto a surface by using electrolysis. It is commonly used to enhance the appearance and protect against corrosion.

13. c) Ethanol (C₂H₅OH)

Explanation: Ethanol is a weak electrolyte as it dissociates into ions to a lesser extent compared to strong electrolytes like sodium chloride (NaCl) and hydrochloric acid (HCl).

14. a) Cell potential

Explanation: The standard hydrogen electrode (SHE) is used as a reference electrode to measure the cell potential or voltage of an electrochemical cell.

15. b) $\Delta G < 0$

Explanation: A spontaneous redox reaction has a negative Gibbs free energy (ΔG) value, indicating that the reaction is energetically favorable.

16. c) Electrochemical cell

Explanation: An electrochemical cell is a device that converts electrical energy into chemical energy through redox reactions.

17. d) Pressure

Explanation: Pressure does not significantly affect the rate of an electrochemical reaction. Factors such as temperature, concentration of reactants, and surface area of electrodes have a more pronounced impact.

18. a) Concentration of reactants

Explanation: The Nernst equation relates the cell potential of an electrochemical cell to the concentration of reactants (or ions) involved in the redox reaction.

19. c) Electrolysis of water

Explanation: Electrolysis of water is a non-spontaneous redox reaction that requires an external source of energy to break water molecules into hydrogen and oxygen gases.

20. a) Purification of metals

Explanation: Electrolysis is commonly used for the purification of metals, where impure metal is made the anode and a pure metal is deposited on the cathode.

21. d) Zinc-carbon battery

Explanation: A zinc-carbon battery is an example of a primary battery that uses zinc as the anode and carbon (manganese dioxide) as the cathode to generate electrical energy through a chemical reaction.

22. a) -0.80 V

Explanation: The standard oxidation potential for a half-cell is the negative of the standard reduction potential. Therefore, if the standard reduction potential is +0.80 V, the standard oxidation potential will be -0.80 V.

23. b) Zn

Explanation: The best reducing agent is the one with the most negative standard reduction potential. Among the given metals, zinc (Zn) has the most negative standard reduction potential, indicating its strong reducing ability.

24. b) They use a non-spontaneous redox reaction to generate electricity.

Explanation: Electrolytic cells use a non-spontaneous redox reaction and an external power source to drive the reaction in the opposite direction, producing electricity.

25. b) $E = E^\circ + \left(\frac{RT}{nF}\right) \ln(Q)$

Explanation: The Nernst equation relates the cell potential (E) to the standard reduction potential (E°) and the reaction quotient (Q) under nonstandard conditions.

26. c) Increasing the temperature of the system.

Explanation: Increasing the temperature generally increases the cell voltage in an electrochemical cell. This is due to the temperature dependence of the reaction equilibrium and the reaction rates.

27. b) Zn

Explanation: In the given reaction, Zn is oxidized (loses electrons) to form Zn^{2+} ions, making it the oxidizing agent

28. b) +0.34 V

Explanation: The standard reduction potential of the standard hydrogen electrode (SHE) is defined as 0.00 V. Therefore, the standard reduction potential of the SHE is +0.34 V.

29. b) Oxidation

Explanation: During electrolysis, oxidation occurs at the anode, where electrons are lost and ions or molecules are converted into their oxidized forms.

30. a) Both electrodes are made of the same material.

Explanation: In a concentration cell, the electrodes are made of the same material, and the cell potential arises from the concentration difference between the two half-cells.

31. b) -1

Explanation: In H_2O_2 (hydrogen peroxide), the oxidation number of oxygen is -1.

32. b) The direction of the electron flow.

Explanation: The standard reduction potential of a half-cell can be used to predict the direction of the electron flow in a redox reaction.

33. a) Maintaining electrical neutrality in the half-cells

Explanation: The main function of a salt bridge in an electrochemical cell is to maintain electrical neutrality in the half-cells by allowing the flow of ions.

34. b) Increasing the concentration of the anode solution

Explanation: Increasing the concentration of the anode solution decreases the cell potential of an electrochemical cell.

35. a) Faraday's first law states that the mass of a substance deposited at an electrode is directly proportional to the current.

Explanation: Faraday's first law of electrolysis states that the amount of substance deposited or liberated at an electrode during electrolysis is directly proportional to the amount of electric charge (current) passing through the cell.

36. a) Sodium metal

Explanation: During the electrolysis of molten sodium chloride (NaCl), sodium metal is formed at the cathode.

37. c) 1.0×10^{-3}

Explanation: The solubility product constant (K_{sp}) of AgCl can be calculated using the concentration of Ag^+ ions, which is 0.10 M.

38. d) Pressure of the system

Explanation: Pressure does not significantly affect the rate of electrochemical reactions. Factors such as temperature, concentration of reactants, and surface area of electrodes are more influential.

39. b) Copper metal reduces Cu^{2+} ions at the anode.

Explanation: In the Daniell cell, copper metal (Cu) is oxidized to form Cu^{2+} ions at the anode.

40. b) It has a positive cell potential.

Explanation: A galvanic cell, also known as a voltaic cell, produces electrical energy from a spontaneous redox reaction and has a positive cell potential. It converts chemical energy into electrical energy.

41. (d): $E_{cell}^{\circ} = \frac{2.303RT}{nF} \log K_{eq}$

$$0.295 = \frac{0.0591}{2} \log K_{eq}$$

$$\therefore \log K_{eq} = 10$$

$$\therefore K_{eq} = 10^{10}$$

42. (c): $k = \frac{1}{R} \times \frac{1}{a} = \frac{1}{32} \times \frac{1.8}{5.4} = 0.0104$

And $\lambda = k \times V = 0.0104 \times 10,000 = 104$

43. (d) $E^{\circ} = \frac{0.059}{n} \log K$;

44. (c): $E^{\circ} = \frac{0.059}{n} \log K_c$

$$\therefore 0.295 = \frac{0.059}{2} \log K_c$$

$$\therefore K_c = 10^{10}$$

46. (a) High value for E_{red}° . Shows more electronegativity *i. e.*, Zn is more electropositive than Fe. ($E_{Zn^{2+}/Zn}^{\circ} < E_{Fe^{2+}/Fe}^{\circ}$)

44 (b)

According to Nernst equation.

$$E_{cell} = E_{Cell}^{\circ} + \frac{0.0591}{2} \log \frac{[Cu^{2+}]}{[Zn^{2+}]}$$

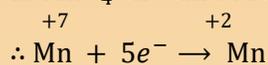
$$E_{cell} = E_{Cell}^{\circ} - \frac{0.0591}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

Or $y = c + (-m)x$

Thus, the slope is negative.

45. (a)

In MnO_4^- the oxidation number of Mn is + 7.



In the reaction, 5 electrons are involved hence 5 Faraday will be needed for the reduction of 1 mole of MnO_4^- .

Therefore, for 0.5 mole of MnO_4^- , number of Faradays required = 2.5 F

46 (c): During electrolysis, volumes of O_2 and H_2 liberated are in the ratio of 1 : 2 Hence, volume of H_2 liberated will be $4.48 dm^3$.

47 (b): When 1 F electricity is passed through the solution. 1 g-equivalent of Cu is liberated.

48 (d): Zn is placed above Sn in electrochemical series.

49 (a): 1 faraday involves charge of 1 mole electrons.

50 (c): Oxidation of Cl^- at anode and reduction of Na^+ at cathode.

51 (d): These are characteristic of conductivity water.

52 (c): These are the facts about use of Mg in protecting iron against corrosion.

53 (b): Sum of molar conductivity of reactants = sum of molar conductivity of products
Therefore, for the reaction



$$\Lambda_m^0 CH_3COOH = \Lambda_m^0 CH_3COONa + \Lambda_m^0 HCl - \Lambda_m^0 NaCl$$

$$= 91 + 425.9 - 126.4$$

$$= 390.5 \Omega^{-1} cm^2 mol^{-1}$$

54 (b)

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} + \frac{0.059}{n} \log[M^{n+}]$$

$$E_{\text{cell}} = 0.34 + \frac{0.059}{2} \log 10^{-2}$$

$$= 0.34 + \frac{0.059}{2} \times -2$$

$$= +0.281 \text{ V}$$

55 (a)

We know that, $\Delta G^{\circ} = -nF \cdot E^{\circ}$

Where, $n = 1$ (number of transferred electron in the cell reaction)

$F = 96500 \text{ C}$ (Faraday's constant)

$E^{\circ} = ?$ (the standard electrode potential of cell)

$\Delta G^{\circ} = -21.20 \text{ kJ}$ (standard free energy)

$$\therefore -21.20 \times 1000 \text{ J} = -1 \times 96500 \times E^{\circ}$$

$$\text{Or } E^{\circ} = \frac{21200}{96500} = 0.220 \text{ V}$$

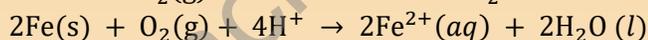
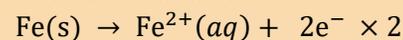
56 (b)

$$-\Delta G = nEF = nE^{\circ}F + RT \ln \frac{[\text{Cu}^{2+}]}{[\text{Zn}^{2+}]}$$

$\therefore \Delta G$ is function of $\ln(c_2/c_1)$.

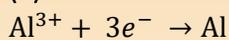
57 (d)

The half reactions are



$$E = E^{\circ} - \frac{0.059}{4} \log \frac{(10^{-3})^2}{(10^{-3})^4(0.1)} = 1.57 \text{ V}$$

58 (d)



$$w = ZQ$$

Where, w = amount of metal

$$w = 5.12 \text{ kg}$$

$$= 5.12 \times 10^3 \text{ g}$$

Z = electrochemical equivalent

$$Z = \frac{\text{equivalent weight}}{96500} = \frac{\text{atomic mass}}{\text{electrons} \times 96500}$$

$$Z = \frac{27}{3 \times 96500}$$

$$5.12 \times 10^3 = \frac{27}{3 \times 96500} \times Q$$

$$Q = \frac{5.12 \times 10^3 \times 3 \times 96500}{27} \text{ C}$$

$$= 5.49 \times 10^7 \text{ C}$$

59. (c)

E_{OP}° of Mg $>$ E_{OP}° of Zn