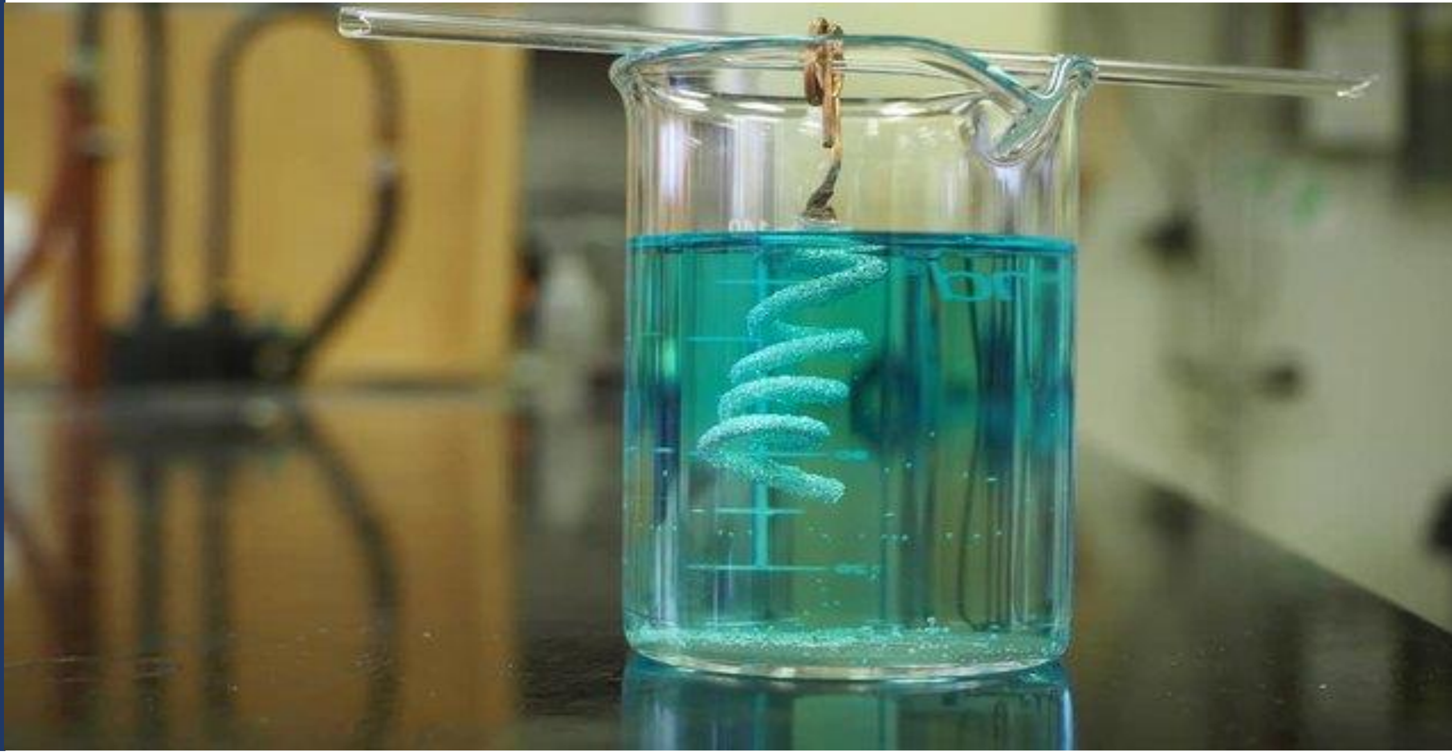
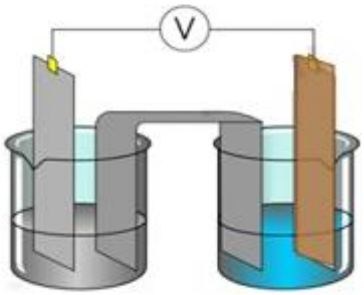
ELECTROCHEMISTRY



CHAPTER – 3

ELECTROCHEMISTRY

INTRODUCTION



- Electrochemistry refers to the conversion of chemical energy to electrical energy and vice versa. It is basically the study of Production of electricity from energy released during spontaneous reaction and use of electrical energy to bring about non-spontaneous chemical transformation.
- A spontaneous chemical reaction is a reaction which happens on its own and releases free energy. This reaction produces electric energy from chemical reaction. For example, burning of coal, rusting of iron, melting of ice, etc.
- On the other hand non-spontaneous reaction occurs by providing an external source like electricity. For example, Hydrolysis of water.
- Electrochemistry is used for the following purposes.
- Production of metals like sodium hydroxide, chlorine, fluorine and many other chemicals.
- It is also used for purification of metals.
- The process is used in batteries as well as fuel cells which converts the chemical energy into electrical energy and is used in several instruments and devices.
- This process is used in electroplating.
- The reactions carried out using the process of electrochemistry are energy effective and less polluting.

Electrochemistry:

Electrochemistry is a branch of chemistry related to the interaction of electrical and chemical changes caused by the passage of energy.

OR

Electrochemistry is the study of the production of electricity from energy released during an automatic chemical reaction and the use of electrical energy to bring about an impossible chemical transformation. Electrochemical reactions can be energy efficient and less polluting.

The primary principle of electrochemistry provides a link between electrical production and the corresponding chemical changes in response and vice versa.

Conductors:

The objects that allow electricity to pass through are known as conductors.

Metallic conductor:

These are metals that contain a free electron to conduct electricity that is why a metallic conductor is a good conductor of heat and electricity.

The best metal conductors are copper, silver, tin, etc.

Electrolytic Conductor:

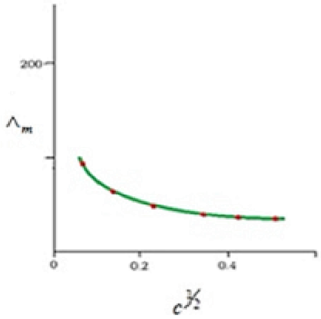
The substance is conducting medium in which the flow of current is accompanied by the movement of matter in the form of ions. any substance that dissociates into ions when dissolved in a suitable medium or melted and thus forms a conductor of electricity.

Example: All metals, Metal salts in an aqueous medium.

The types of electrolytic conductors are:

Weak electrolyte:

- A substance which forms ions in an aqueous solution do not dissociate completely at moderate concentrations is known as weak electrolyte.
- For example, HC2H3O2 (acetic acid), H2CO3 (carbonic acid), etc.
- The conductance of the solution increases with dilution of solution.
- The interionic forces of attraction are not strong at a low concentration.
- The slope for Λm vs c1/2 is not linear even at a lower concentrations.



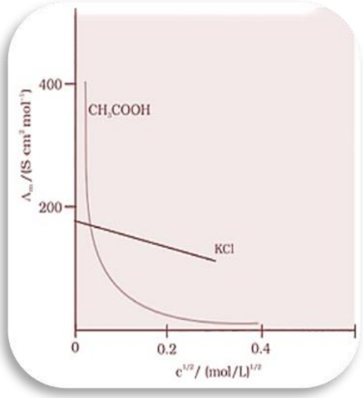
- These electrolytes have lower degree of dissociation at higher concentrations.
- The value of Λm changes with dilution due to increase in the degree of dissociation.
- Ëm increases sharply on dilution exclusively at lower concentrations.
- At infinite dilutionwhen concentration approaches to zero, the electrolyte dissociates completely. But at lower concentration the conductivity of a solution is low to an extent that cannot be even measured.

Strong electrolyte:

- A solute or substances that completely ionize or dissociates in a solution are known as strong electrolyte. These ions are good conductors of electricity in the solution.
- For example, HCl, HBr, HI, HNO3, NaOH, KOH, etc.
- For strong electrolytes, Λm increases slowly with dilution and can berepresented by the equation:

$$\wedge_m = E^{o}_{m} - Ac^{\frac{1}{2}}$$

- It dissociates completely at moderate concentrations.
- The conductance of the solution increases with dilution of solution.
- There exist strong interionic forces of attraction at moderate concentrations.
- The slope for Λm vs c1/2 is linear at low concentrations.



Electrochemical cell:

An electrochemical cell is a device that can generate electrical energy through chemical reactions or use electrical energy to induce chemical reactions.

Some Basic definitions:

Oxidation: loss of electrons $Zn \rightarrow Zn^{2+} + 2e^-$
Reduction: gain of electrons $Cu^{+2} + 2e^- \rightarrow Cu$
Electrolyte: a solution that contains ions is called electrolyte. Electrolyte is an ionic conductor.
Electrode: surface at which oxidation or reduction takes place.
Redox reaction: an oxidation-reduction reaction.
$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

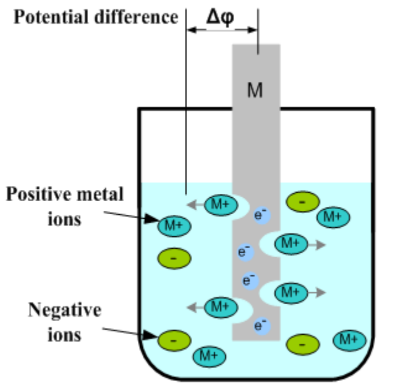
Electrode Potential:

Electrode potential is the electromotive force of a galvanic cell built from a standard reference electrode and another electrode to be characterized. By convention, the reference electrode is the standard hydrogen electrode (SHE). It is defined to have a potential of zero volts.

OR

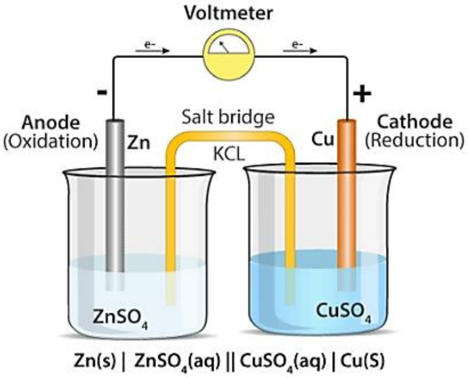
When an electrode contacts a solution of its half-ions ions, it has a tendency to lose or gain electrons known as electrode strength. It is expressed in volts. It is a deep asset, that is, independent on the number of species in reaction.

Single electrode cell (half-cell)



Galvanic or voltaic cells

The Voltaic Cell (also known as the Galvanic Cell) is an electrochemical molecule that utilizes a direct redox reaction to generate electricity.



Spontaneous than ΔG = -ve

In this device ΔG of spontaneous redox reaction is converted into electrical work (which may be used for running a motor, fan, heater etc.)

Construction: it consists of two metallic electrodes dipping in electrolytic solution. The solution in two compartment is connected through an inerted U shaped tube containing a mixture of agar-agar jelly and an electrolyte like KCl, KNO_3 etc.

This tube is called salt bridge.

Salt bridge function:

A salt bridge acts as an electrical contact between the two half cells.

It prevents mechanical flow of solution, but it provides a free path for the migration of ions, to maintain an electric current through the electrolyte solution. It prevents the accumulation of charges.

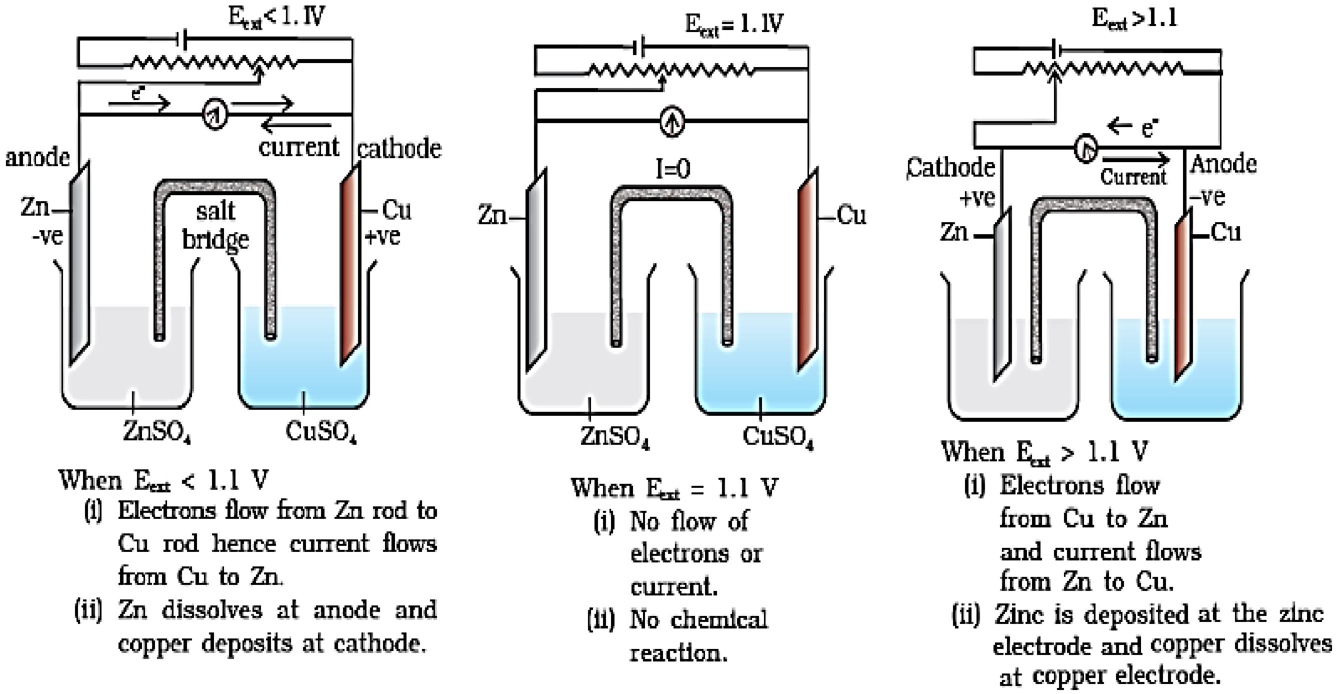
A salt bridge helps in maintaining the charge balance in the two half cells.

A salt bridge minimizes or eliminates the liquid junction potential.

- Maintains electrical neutrality by providing ion flow.
- It avoids the possibility of dispersing solutions between partial cells.
- The electrolyte does not absorb in any type of chemical reaction and does not react with a solution concentrated in two part cells.
- Most often salts such as KCl, KNO3, NH4NO3 are used as electrolyte.

Electrolytic Cell:

If an external opposite potential is applied in the cell and is increased slowly, the reaction continues to take place till the opposing voltage reaches the value 1.1 V when the reaction stops altogether and no current flows through the cell. Any further increase in the external potential starts the reaction again but in the opposite direction. It now functions as an electrolytic cell. In an electrolytic cell, oxidation occurs at the anode but it is a positive plate and reduction occurs at the cathode, which is a negative plate.



When E_{ext} < 1.1 V
(i) Electrons flow from Zn rod to Cu rod hence current flows from Cu to Zn.
(ii) Zn dissolves at anode and copper deposits at cathode.

When E_{ext} = 1.1 V
(i) No flow of electrons or current.
(ii) No chemical reaction.

When E_{ext} > 1.1 V
(i) Electrons flow from Cu to Zn and current flows from Zn to Cu.
(ii) Zinc is deposited at the zinc electrode and copper dissolves at copper electrode.

Functioning of Daniell Cell when External Voltage (E_{ext}) Opposing the Cell Potential is Applied.

Note: Electrochemical or voltaic (galvanic) cells produce electricity as a result of chemical reactions, while in electrolytic cells, electricity is used to produce a non-spontaneous chemical change.

Daniell cell: The Daniell cell consists of two electrodes of dissimilar metals, Zn and Cu; each electrode is in contact with a solution of its own ion; Zinc sulphate and copper sulphate respectively.

The Daniell cell can be conventionally represented as

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

Two half-cell reactions are

Ion Zn/ZnSO4 half-cell, oxidation reaction occurs.

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

Ion Cu/CuSO4 half-cell, reduction reaction occurs.

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

The net cell reaction is

$Zn + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu$

Cell is represented as

$Zn/Zn^{2+} \,||\, Cu^{2+}/Cu$

Differences between Electrochemical cell and electrolytic cell

A galvanic cell converts chemical energy into electricity. Here, the redox reaction is spontaneous and responsible for the production of electrical energy.

The electrolytic cell converts electrical energy into chemical energy. The redox reaction is not automatic and electrical power must be provided to start the reaction. Both electrodes are placed in the same container in the solution of the molten electrolyte.

Typical representation of electrochemical cell:

$M1(s)|$ $M1^{n+}(aq)$ $||$ $M2^{n+}(aq)$ $| M2(s)$

Anode Oxidation Salt Reduction Cathode

Half-cell Half-cell

	cathode	Anode
Sign	Positive due to consumption of electrons	Negative due to release of electrons
Reaction	Reduction	Oxidation
Movement of electrons	Into the cell	Out of cell

Other features of Electrochemical cell are:

- No heat dissipation.
- The solution remains neutral on both sides.

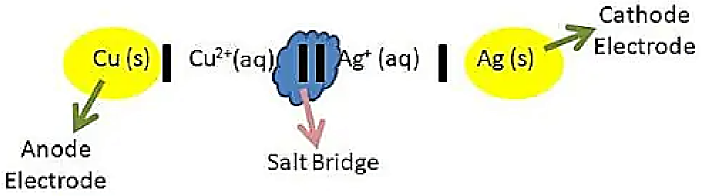
Note: (i) when the concentration of all the species involved in a half cell is unity then the electrode potential in known as standard electrode potential.

(ii) IUPAC convention: standard reduction potential is SEP.

(iii) Cell potential: The cell potential is the measure of potential difference between two half cells in an electrochemical cell. It is represented by the symbol E_{cell}.

$E_{cell} = E_{cathode} - E_{anode} = E_{right} - E_{left}$ [Cell : Anode half cell || cathode half cell]

For a reaction:



Oxidation reaction occurs: $Ag \rightarrow Ag^{2+} + 2e^-$

Reduction reaction occurs: $Cu^{2+} + 2e^- \rightarrow Cu$

The net cell reaction: $Ag + Cu^{2+} \Leftrightarrow Ag^{2+} + Cu$

Cell is represented as: $Ag|Ag^{2+} \,||\, Cu^{2+}|Cu$

Oxidation potential:

The tendency to lose electrons in the above situation is known as oxidation. The oxidation potential of the half-cell equates to ion concentrations in solution.

Reduction potential:

Reduction potential (Eo) is defined as the tendency of a chemical to be reduced by electron degradation and is defined by the electrochemical hydrogen reference, which is given worldwide by zero reduction power.

It is not possible to determine the total amount of electrode power. In this case a reference electrode is required. The electrode strength is the only difference between the two electrodes that we can measure by combining them to give a complete cell.

Standard electrode potential:

The potential difference developed between the metal electrode and the ion solution of the molarity unit (1M) at 1 atm pressure and 25 ° C (298 K) is called the normal electrode strength. Defined by E °. The known power electrode is called the reference electrode.

Reference electrode:

The reference electrode is an electrode with a stable and well-known electrode potential. The simplest is when a reference electrode is used as part of a cell to form an electrochemical cell. This allows the energy of another part of the cell to be cut off.

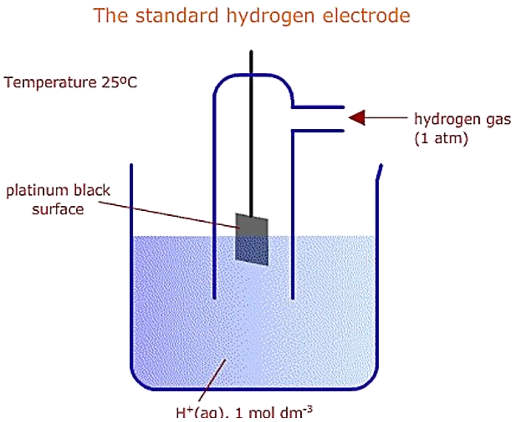
Standard Hydrogen Electrode (SHE) - A reference electrode that measures the electrode strength of all electrodes. When Hydrogen gas at 1 atm-pressure is advertised over a platinum electrode immersed in 1M HCl at 25⁰C, it is a normal hydrogen electrode and its power is, E_0 = ± 0 volt.

At SHE, over platinum, any of the following may be possible:

$$2H^+(ag) + 2e^- \rightarrow H_2G \text{ Reduction}$$

$$H_2(g) \rightarrow 2H^+(ag) + 2e^- \text{ Oxidation}$$

SHE's electrical power is set to zero at all temperatures.



Drawbacks of SHE are:

- Hard to move.
- It is difficult to build and maintain.
- It is difficult to maintain the pressure of hydrogen gas and the concentration of an acid solution taken as HCl.
- It is difficult to find pure hydrogen gas.

Q1. The pressure of H_2 required to make the potential of H_2-electrode zero in pure water at 298 K is

$$-\log[H^+] = 7 \Rightarrow [H^+] = 10^{-7}$$

$$2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{2}\log\frac{p_{H_2}}{[H^+]^2}$$

$$0 = 0 - \frac{0.0591}{2}\log\frac{p_{H_2}}{(10^{-7})^2}$$

$$\log\frac{p_{H_2}}{(10^{-7})^2} = 0$$

$$\Rightarrow \quad \frac{p_{H_2}}{(10^{-7})^2} = 1 \; [\because \log 1 = 0]$$

$$p_{H_2} = 10^{-14}\text{ atm}$$

Q2. The standard electrode potentials of Zn and Ni respectively are −0.76 V and −0.25 V. Then the standard emf of the spontaneous cell by coupling these under standard conditions is:

S2. The standard electrode potential of Zn (E^0_{anode})=−0.76 V

The standard electrode potential of Ni ($E^0_{cathode}$)=−0.25

For spontaneous reaction E_{cell} should be positive.

So, the reaction should be:

$$Zn(s) \div Ni^{2+}(aq) \rightarrow Zn^{2\div}(aq) + Ni(s)$$

$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

$$= -0.25 - (-0.76) = +0.51V$$

Electromotive force (emf) of the cell:

The electromotive force of a cell or EMF of a cell is the maximum potential difference between two electrodes of a cell. It can also be defined as the net voltage between the oxidation and reduction half-reactions. The EMF of a cell is mainly used to determine whether an electrochemical cell is galvanic or not.

Normal emf of the cell:

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

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

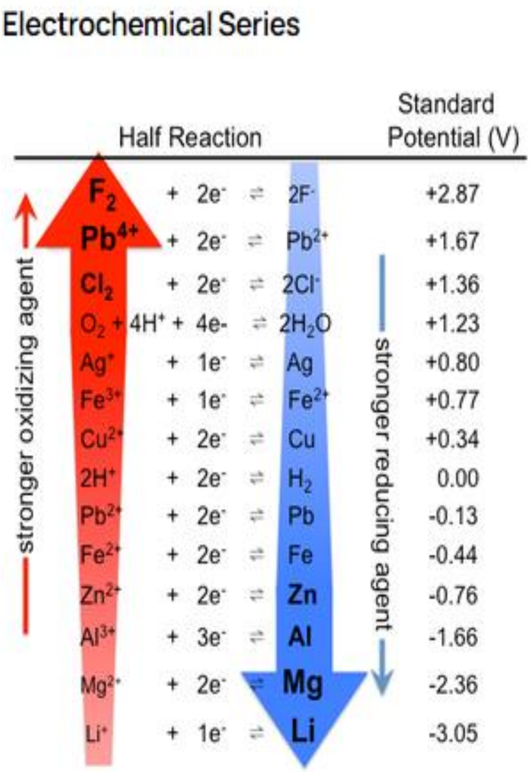
Electrical energy = Emf (volts) x Value of electricity (coulombs)

EMF of Daniell cell: Cell: $Zn|Zn^{2+}$ (1 M)||Cu^{2+} (1 M)|Cu

E^0_{cell} = 0.34 V – (-0.76V) = 1.10 V

Electrochemical Series:

The sequence of events in terms of increasing energy prices is called the 'Electrochemical series'. Also called 'Series Series', of standard electrodes.



Applications of Electrochemical series:

(1) Oxidizing and reducing strengths:
Electrochemical series helps to identify fine oxidizing agents and reducing agents. (top of the series - good reducing agents)

(2) Displacement reactions:
The upper bouts featured two cutaways, for easier access to the higher frets.

(3) Predicting Liberation of H2 gas from acids by metals:
All negative energy metals show a greater tendency to lose electrons compared to hydrogen.

(4) Feasibility of redox reaction

(5) EMF calculation for all.

Q1. Predict whether the following reaction will occur spontaneously or not:
$Fe^{3+} + 2Cl^{-} \rightarrow Fe^{2+} + Cl_2$
$E^0_{Fe^{+2}/Fe} = -0.440$ volt ; $E^0_{Cl/Cl^{-}} = 1.36$ volt

S1. $E^0_{cell} = E^0_{cathode} - E^0_{anode}$
Since chlorine has higher reduction potential than iron therefore at cathode reduction of chlorine occurs and oxidation of iron occurs at the anode.
$E^0_{cell} = 1.36 - (-0.440) = 1.80$ volts
The positive value of E0Cell implies that reaction occurs spontaneously.

Q2. The standard oxidation potential, E0 for the half-reactions are as follows,
$Cu \rightarrow Cu^{2+} + 2e^{-}$; $E^0 = -0.34$ volts
$Fe \rightarrow Fe^{2+} + 2e^{-}$; $E^0 = 0.41$ volts
Calculate the emf of the cell, $Cu^{2+} + Fe \rightarrow Cu + Fe^{2+}$

S2. E^0_{cell} = (standard reduction potential of reduction half-cell) – (standard reduction potential of oxidation half-cell)
E^0_{cell} = -(standard oxidation potential of reduction half-cell) – (-standard oxidation potential of oxidation half-cell)
$E^0_{cell} = -0.34-(-0.41)$
$E^0_{cell} = 0.07$ volt.

Nernst equation:

The Nernst Equation enables cell power validation under abnormal conditions and correlates the measured cell power with the response quotient and allows for accurate measurement of equilibrium.
The figure was named after German physicist Walther Nernst.

$$E = E^{\circ}_{M^{n+}/M} + \frac{RT}{nF} \ln [M^{n+}]$$

For an electrochemical cell for which the overall reaction is:

$$aA + bB \rightleftharpoons cC + dD.$$

$$E_{cell} = E^{\circ}_{cell} - \frac{2{\cdot}303RT}{nF} \log \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

At 298 K, $\frac{2{\cdot}303RT}{nF} = \frac{0{\cdot}0591}{n}$

Then equation becomes

$$E_{cell} = E^{o}_{cell} - \frac{0.0591}{n} \log \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

The equilibrium constant A of a cell can be relate to standard emf of cell

$$E^{\circ}_{cell} = \frac{2{\cdot}303RT}{nF} \log K_c = \frac{0{\cdot}0591}{n} \log K_c \text{ at } 298\,K.$$

$$\Delta G^{o} = -nFE^{\circ}_{cell} = -2{\cdot}303\, RT \log K_c$$

Equilibrium Constant with Nernst Equation

When the reactants and the products of the electrochemical cell reach equilibrium, the value of ΔG becomes 0. At this point, the reaction quotient and the equilibrium constant (Kc) are the same. Since ΔG = -nFE, the cell potential at equilibrium is also 0.

Substituting the values of Q and E into the Nernst equation, the following equation is obtained.

$0 = E^0_{cell} - (RT/nF) \ln Kc$

The relationship between the Nernst equation, the equilibrium constant, and Gibbs energy change is illustrated below.

Converting the natural logarithm into base-10 logarithm and substituting T=298K (standard temperature), the equation is transformed as follows.
$E^0_{cell} = (0.0592V/n) \log Kc$
Rearranging this equation, the following equation can be obtained.
$\log K_c = (n\, E^0_{cell})/0.0592V$

Thus, the relationship between the standard cell potential and the equilibrium constant is obtained. When K_c is greater than 1, the value of E^0_{cell} will be greater than 0, implying that the equilibrium favours the forward reaction. Similarly, when K_c is less than 1, E^0_{cell} will hold a negative value which suggests that the reverse reaction will be favoured.

Q1. The standard electrode potential of zinc ions is 0.76V. What will be the potential of a 2M solution at 300K?

S1. The Nernst equation for the given conditions can be written as follows;
$E_{Mn+/M} = E^0 - [(2.303RT)/nF] \times \log 1/[Mn^{+}]$
Here,
E° = 0.76V
n = 2
F = 96500 C/mole
$[Mn^{+}] = 2$ M
R =8.314 J/K mole

T =300 K

Substituting the given values in the Nernst equation, we get,

$E_{Zn^{2+}/Zn}$ = 0.76 – [(2.303 × 8.314 × 300)/(2×96500)] × log 1/2 = 0.76 – [0.0298 × (-0.301)]

= 0.76 + 0.009 = 0.769V

Therefore, the potential of a 2M solution at 300K is 0.769V.

Q2. From the following standard potentials, arrange the metals in the order of their increasing, reducing power.

$Zn^{2+}_{(aq)} + 2e^- \rightarrow Zn(s)$: E° = -0.76 V

$Ca^{2+}_{(aq)} + 2e^- \rightarrow Ca(s)$: E° = -2.87 V

$Mg^{2+}_{(aq)} + 2e^- \rightarrow Mg(s)$: E° = -2.36 V

$Ni^{2+}_{(aq)} + 2e^- \rightarrow Ni(s)$: E° = -0.25 V

$Ni_{(s)} \rightarrow Ni^{2+}_{(aq)} + 2e^-$: E° = +0.25 V

Reducing power of a metal increases with its ability to give up electrons, i.e., lower standard potentials. Arranging the reduction potentials in the decreasing order gives the increasing order of reducing the power of metals.

Increasing order of reduction potentials is Ni (-0.25V) < Zn (-0.76V) < Mg(-2.36V) < Ca(-2.87).

Q3. What is the Cell Potential of the electrochemical cell in which the cell reaction is: $Pb^{2+} + Cd \rightarrow Pb + Cd^{2+}$; Given that E^0_{cell} = 0.277 volts, temperature = 25⁰C, $[Cd^{2+}]$ = 0.02M, and $[Pb^{2+}]$ = 0.2M.

S3. Since the temperature is equal to 25⁰C, the Nernst equation can be written as follows;

$E_{cell} = E^0_{cell} - (0.0592/n) \log_{10}Q$

Here, two moles of electrons are transferred in the reaction. Therefore, n = 2. The reaction quotient (Q) is given by $[Cd^{2+}]/[Pb^{2+}]$ = (0.02M)/(0.2M) = 0.1.

The equation can now be rewritten as:

$E_{cell} = 0.277 - (0.0592/2) \times \log_{10} (0.1) = 0.277 - (0.0296)(-1) = 0.3066$ Volts

Thus, the cell potential of this electrochemical cell at a temperature of 25⁰C is 0.3066 volts.

Resistance:

Resistance is a measure of the resistance to current flow in an electrical circuit. Resistance is measured in ohms, symbolized by the Greek letter omega (Ω). Ohms was named after Georg Simon Ohm (1784-1854), a German physicist who studied the relationship between voltage, current and resistance.

$$R \propto \frac{\ell}{A} \quad = R = S\frac{\ell}{A}$$

Where S is specific resistance or resistivity.

Resistivity:

The conductor resistance is defined as the resistance provided by the unit by the length of the cross-section unit. Resistivity is a material asset and depends on temperature and pressure. The resistivity of the conductors is low compared to the resistivity of the insulators.

$$S = \frac{RA}{\ell}$$

The SI unit of resistivity of a substance is Ohm-metre (Ωm)

Conductance:

Conductance (also known as electrical conductance) is defined as the force that an object conducts electricity. Conduct is a measure of the fact that electrical energy (i.e. charging flow) can easily pass through objects. Conductance is the opposite (or parallel) of an electrical resistance, represented as 1 / R.

The operating unit is ohm-1 or mho or Siemen (S).

Q1. Why does the conductivity of a solution decrease with dilution?

S1. The conductivity of a solution is related with the number of ions present per unit volume of the solution. When the solution is diluted, the number of ions per unit volume of solution decreases. Hence, conductivity of the solution also decreases.

Q2. The electrical resistance of a column of 0.05 M NaOH solution of diameter 1 cm and length 50 cm is 5.55×10^3 ohm. Calculate its resistivity, conductivity and molar conductivity.

$$A = \pi r^2 = 3.14 \times (0.5)^2 = 0.785 cm^2, l = 50 cm$$

$$R = \frac{\rho l}{A}\rho = \frac{AR}{l} = \frac{5.55 \times 10^{-3} \times 0.785}{50}$$

$$\rho = 87.18\ \Omega cm$$

$$\text{Conductivity, } K = \frac{1}{\rho} = 0.01147 S cm^{-1}$$

$$\text{Molar Conductivity} = \frac{1000 \times K}{C} = \frac{0.01147 \times 1000}{0.05}$$

$$\Lambda_m = 229.4\ S cm^2 mol^{-1}$$

$$\text{Molar conductivity, } \Lambda_m = 229.4\ S cm^2 mol^{-1}$$

Specific conductance:

Specific Conductance is the ability of an object to conduct electricity. It is a reversal of some resistance. The specific conductance is defined as the operating capacity of the molten electrolyte solution and the entire solution is placed between two 1 sq. Electrodes. cm and 1 cm long.

A specific conductance unit is $ohm^{-1}\ cm^{-1}$ or $S\ cm^{-1}$.

Molar conductance:

It is the process of all ions that are given a single molecule of electrolyte present at a precise volume of solution.

Molar conductivity increases with purification. Molar conductance = K / M. K = Direct behaviour. M = Electrolyte concentration.

The unit of molar conductance is $\Omega^{-1}\ cm^2\ mol^{-1}$ or $S\ cm^2\ mol^{-1}$

Q1. Calculate the molar conductivity of the KCl solution?

Given:

Molarity (M) = 0.30M

Conductivity at 298 K (k) = 0.023 $S\ cm^{-1}$

S2. Molar conductivity = (1000 × k) /M
= (1000 × 0.023) / 0.30
= 76.66 $cm^2\ mol^{-1}$
Molar conductivity of the KCl solution is 76.66 $cm^2\ mol^{-1}$.

Q2. Conductivity of 0.02 M solution of KCl at 298 K is 0.0248 $S\ cm^{-1}$. Calculate the molar conductivity?
Given:
Molarity (M) = 0.20M
Conductivity at 298 K (k) = 0.0248 $S\ cm^{-1}$

S2. Molar conductivity = (1000 × k) /M
= (1000 × 0.0248) / 0.20
= 124 $cm^2\ mol^{-1}$
Molar conductivity of the KCl solution is 124 $cm^2\ mol^{-1}$

Effect of Dilution on:

Equivalent Conductance: The equilibrium behaviour of a solid electrolyte increases with purification, because its value is equal to the frequency of K_υ and the volume of the solution. By dilution the volume of the solution increases which also increases the amount of the same conductivity.

Specific Conductance: Solution production increases in purification. The specific conductivity decreases in mixing. The same conductivity and molar conductivity increase with purification. Equivalent and molar conductivity tends to accumulate in high volume with increasing dilution.

Molar conductance: When the solution is diluted, there are more ions and more space to move, i.e. ions are farther away from each other and more ion flow leads to increased molar performance of the solution. Therefore, when the solution is diluted, the conductivity decreases and the molar conductivity increases.

Variation of molar conductance with concentration:

Strong electrolytes:

conductance at infinite dilution (Λ_m^∞)

$\Lambda_m = \Lambda_m^\infty$ when $C \to 0$

The variation of Λ_m with concentration is given by

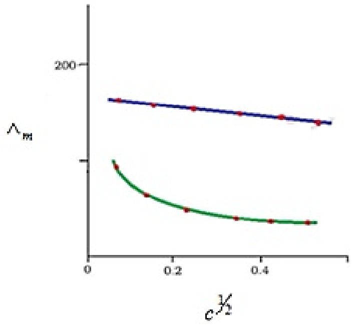
$\Lambda_m = \Lambda_m^\infty - b\sqrt{C}$ where b = constant

Weak electrolytes:

The variation of Λ_m with $\sqrt{C}$ is very large and so much so that we cannot obtain molar conductance at infinite dilution (Λ_m^∞) by extrapolation of the Λ_m Vs. $\sqrt{C}$ plots.

Kohlrausch Law:

Kohlrausch's law of independent ion migration states that limiting the molar activity of an electrolyte can be represented as the sum of each anion offerings and the electrolyte cation.



Equivalent molar conductivity of electrolyte total algebraic limits the molar equivalent conductivity of its partial ions.
Mathematically:

$$\Lambda_o^{electrolyte} = \lambda_o^+ + \lambda_o^-$$

When λ_o^+ = limits the same local conductivities
λ_o^- = limit the same antivirus conductivities.

Degree of dissociation: The degree of dissociation is the phenomenon of generating current carrying free ions, which are dissociated from the fraction of solute at a given concentration.

Faraday's law of electrolytes:

First Rule:
The amount of material inserted or released from the electrode is directly proportional to the electricity transmitted to the electrolyte.
Statistically:

$Q \propto I \times t$
$m = ZIt$
I = current in amperes
t = time in seconds, and
Z = constant called electrochemical equivalent.

When m = quantity of items inserted or released

Rule 2:

When the same amount of electricity is transferred to different electrolyte solutions, the weight of the different material placed or released on the appropriate electrode is equal to their chemical weight.

Note: $Ag^+(aq) + e^- \rightarrow Ag$ [one mole of electron is required for the reduction of one mole of Ag^+ ion.]
Charge on 1 mole of electron = 1 Faraday = N_A x (1.6021 x 10^{-19} c) ≅ 96500 C/mol

Q1. When 0.1M MnO_4^{2-} is oxidized to MnO_4^-, the quantity of electricity required is
a) 96500C b) 2 × 96500C c) 9650C d) 96.50C
$MnO_4^{2-} \rightarrow MnO_4^- + e^-$
1mole of MnO_4^{2-} lose 1 mole of electrons or 96500C
∵ 0.1 mole of MnO_4^{2-} lose 0.1mole of electrons or 9650C

Q2. How much electricity in terms of Faraday is required to produce
(i) 20.0 g of Ca from molten $CaCl_2$?
(ii) 40.0 g of Al from molten Al_2O_3?

(i) $Ca^{2+} + 2\ e^- \rightarrow Ca$

One mole of Calcium ions gains two moles of electrons or 2 Faraday charge to produce one mole of calcium.
Molecular weight of Calcium is 40.
So, 20 gm of calcium shall need one Faraday of electricity.

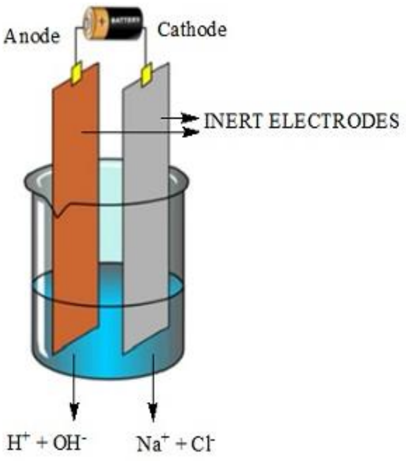
(ii) $Al^{3+} + 3\ e^- \rightarrow Al$
One mole of Aluminium ions gains two moles of electrons or 3 Faraday charge to produce one mole of aluminium.
Molecular weight of Aluminium is 27.
So, 40 gm of Aluminium ion shall need
40 x 3 / 27
Faraday of electricity= 4.44F

Q3. A solution of $Ni(NO_3)_2$ is electrolyzed between platinum electrodes using a current of 5 amperes for 20 minutes. Calculate the weight of nickel reduced on the cathode.
Mass of nickel deposited = EIT/96500
Equivalent eight of nickel = Atomic weight/2 =58.7/2
Mass = 58.7 x 5 x 20 x 60 / 2 x 96500
= 1.83gm

Faraday constant: The well-known Faraday constant of 96,485 C / mol marked F, or also called 1 F, corresponds to the amount of electricity carried by 1 mol of electrons.

Products of Electrolysis

- The product of electrolysis produced depends on the nature of material being that is being electrolyzed as well as the type of electrodes that is being used.
- An inert electrode e.g., platinum or gold does not participate in chemical reaction and acts as a source or sink for electrons.
- Whereas a reactive electrode participates in the electrode reaction.
- It also depends on the different oxidizing as well as reducing species that are present in the electrolytic cell and their standard electrode potentials.
- Electrolysis of molten NaCl results in the production of sodium metal and Cl2



Net reactions may be summarized as:

$NaCl\ (aq) \rightarrow Na^+{}_{(aq)} + Cl^-{}_{(aq)}$
Cathode: $H_2O + e^- \rightarrow \frac{1}{2}\ H_{2\,(g)} + OH^-{}_{(aq)}$
Anode: $Cl^-{}_{(aq)} \rightarrow \frac{1}{2}\ Cl_{2(g)} + e^-$
Net reaction:
$NaCl_{(aq)} + H_2O_{(l)} \rightarrow Na^+{}_{(aq)} + OH^-{}_{(aq)} + \frac{1}{2}H_{2(g)} + \frac{1}{2}Cl_{2(g)}$

Battery:

A battery can be defined as an electrochemical device (consisting of one or more electrochemical cells) that can be charged electrically and can be charged whenever needed. Batteries are usually devices made of multiple electrochemical cells connected to external inputs and outlets.
Battery is a collection of two or more batteries connected in series.
It is of two types:
Primary battery
Secondary battery

Primary batteries:

The reaction in a primary battery occurs only once.

The battery becomes dead after used once and cannot be reused

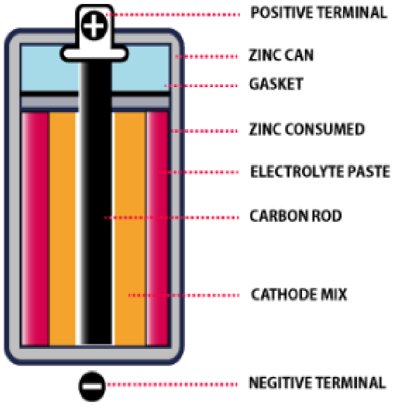
Example of primary cell is dry cell and mercury cell.

The dry cell consists of a zinc anode and the carbon (graphite) cathode surrounded by powdered manganese dioxide and carbon.

Leclanche cell: [Dry cell]

Anode: zinc container
Cathode: carbon rod [surrounded by MnO_2^+ carbon]

The space between electrodes is filled by a moist paste of NH_4Cl and $ZnCl_2$.



At Anode

$Zn_{(s)} \rightarrow Zn^{2+}{}_{(aq)} + 2e^-$

At Cathode

$2e^- + 2\ NH_4^+{}_{(aq)} \rightarrow 2\ NH_{3\,(g)} + H_{2\,(g)}$
$2\ NH_{3\,(g)} + Zn^{2+}{}_{(aq)} \rightarrow [Zn\ (NH_3)_2]^{2+}{}_{(aq)}$
$H_{2\,(g)} + 2\ MnO_{2\,(S)} \rightarrow Mn_2O_{3\,(S)} + H_2O_{\,(l)}$

Thus, the overall cell equation is:
$Zn_{(s)} + 2\ NH_4^+{}_{(aq)} + 2\ MnO_{2\,(S)} \rightarrow [Zn(NH_3)_2]^{2+}{}_{(aq)} + Mn_2O_{3\,(S)} + H_2O_{\,(l)}$

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 batteries:

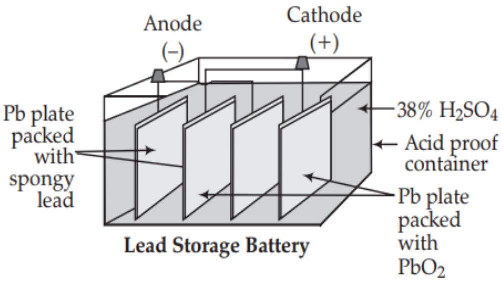
Secondary batteries are those batteries that can be recharged in excess of electricity and can be used repeatedly, e.g., lead battery.

OR

Rechargeable batteries, also called accumulators or secondary batteries are separated from the primary batteries by the recharge feature. Remarkably, both, the accumulators and the main batteries contain all the chemical reactants within the cell boundaries.

The second cell or battery is the one that can be recharged electrically after being used in its original discharge state, by passing gas in a cycle in the opposite direction from the current outlet.

Lead storage battery: it is the most commonly secondary cell commonly used in automobiles and invertors.



Lead Storage Battery

Anode; lead [Pb]
Cathode: a grid of lead with PbO_2
Electro;yte: 30% H_2SO_4 solution (by mass)

At Anode

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

$Pb + SO_4^{2-} \rightarrow PbSO_{4(electrode)} + 2e^-$

At Cathode

$2e^- + PbO_2 + 4H^+ \rightarrow Pb^{2+} + 2H_2O$

$2e^- + PbO2 + 4H^+ + SO_4^{2-} \rightarrow PbSO_{4\,(electrode)} + 2H_2O$

Overall reaction: $Pb(s) + PbO_{2\,(s)} + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O_{(l)}$

Electrical cells:

An electrical cell is a “source of electrical energy”. It converts stored chemical energy into potential electrical energy, allowing direct charges to flow from the positive terminal to the negative through an external circuit. In fact, any charged particle will do the job.

A typical example of an electrochemical cell is a standard 1.5-volt cell used to power many electrical objects such as TV remote controls and clocks. Such cells are capable of producing energy from chemical reactions that occur in their care called Galvanic cells or Voltaic cells.

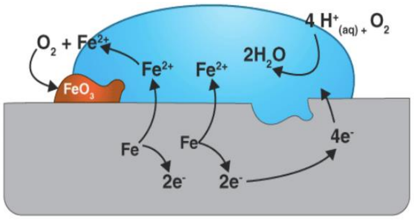
The types of electrical cells are: Solar cell, electrolytic cell, electro chemical cell.

Corrosion of metals:

Degradation of metals due to their interaction with nature is called rust. Rust occurs in the open. When the top layer of metal rusts, then the interior of the metal is exposed, and the rust continues to a certain depth.

OR

Rust is often described as the breakdown of metals due to electrochemical processes. The rust formation on the metal, the silver rust, and the blue patina growing on the brass are all examples of rust.



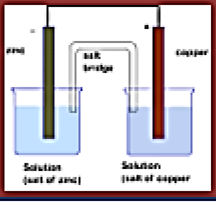
SUMMARY

An electrochemical cell consists of two metallic electrodes dipping in electrolytic solutions. Thus an important component of the electrochemical cell is the ionic conductor or electrolyte. Electrochemical cells are of two types. In galvanic cell, the chemical energy of a spontaneous redox reaction is converted into electrical work, whereas in an electrolytic cell, electrical energy is used to carry out a non-spontaneous redox reaction. The standard electrode potential for any electrode potential of hydrogen electrode taken as zero. The standard potential of the cell can be obtained by taking the difference of the standard potential of cathode and anode. The standard potential of the cells are related to standard Gibbs free energy. And equilibrium constant of the reaction taking place in the cell. Concentration dependence of the potential of the electrodes and the cells are given by Nernst equation.

The conductivity, k, of an electrolytic solution depends on the concentration of the electrolyte, nature of the solvent and temperature. Molar conductivity is defined by = k/c where c is the concentration. Conductivity decreases but molar conductivity increase with decrease in concentration for strong electrolytes while the increase is very steep for weak electrolytes in very dilute solutions. Kohlrauach found that molar conductivity at infinite dilution for an electrolyte is sum of the contribution of the molar conductivity of the ions in which it dissociates. It is known as law of independent migration of ions and has many applications. Ions conduct electricity through the solution but oxidation and reduction of the ions take place at the electrodes in an electrochemical cell. Batteries and fuel cells are very useful forms of galvanic cell. Corrosion of metals is essentially an electrochemical phenomenon. Electrochemical principles are relevant to the Hydrogen economy.

MIND MAP

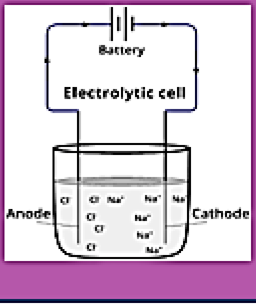
- **Electrochemistry**
  - **Daniell/Galvanic cell**
    - Chemical Energy → Electrical energy



    - Electrode potential
      - At any concentration
        - Nernst equation
          - Equilibrium constant
            - Gibbs free energy
      - At 1 M concentration
        - Standard electrode potential
          - Standard hydrogen electrode
    - Applications
      - Batteries
        - Primary
        - Secondary

      - Fuel cells
      - Corrosion

  - **Electrolytic cell**
    - Electrical energy → Chemical energy



    - Conductance → Conductivity
      - Molar conductivity
        - Weak electrolyte
        - Strong electrolyte
      - Kohlrausch law → Weak electrolyte, Strong electrolyte
    - Quantitative aspects → Faraday's laws of electrolysis
    - Qualitative aspects → Product of electrolysis

MULTIPLE CHOICE QUESTIONS

1. Standard solution of KNO_3 is used to make a salt bridge because
(a) Velocity of K^+ is greater than that of NO^{3-}
(b) Velocity of NO_3^- is greater than that of K^+.
(c) Velocity of both K^+ and NO_3^- are nearly same
(d) KNO_3 is highly soluble in water.

2. Galvanised iron sheets are coated with
(a) Carbon
(b) Copper
(c) Zinc
(d) Nickel

3. How many coulombs are required for the oxidation of 1 mole of H_2O to O_2?
(a) 1.93×10^5 C
(b) 9.65×10^4 C
(c) 3.86×10^5 C
(d) 4.825×10^5 C

4. Rust is a mixture of
(a) FeO and Fe $(OH)_3$
(b) FeO and Fe $(OH)_2$
(c) Fe_2O_3 and Fe $(OH)_3$
(d) Fe_3O_4 and Fe $(OH)_3$

5. Standard electrode potential data are useful for understanding the suitability of an oxidant in a redox titration. Some half-cell reactions and their standard potentials are given below:

MNO_4^- (aq) + $8H^+$ (aq) + 5e– → Mn^{2+} (aq) + 4H2O (1) E° = 1.51 V

$Cr2O_7^{2-}$ (aq) + $14H^+$ (aq) + $6e^-$ → 2 Cr^{3+} (aq) + 7H2O (1) E° = 1.38 V

Fe^{3+} (aq) + e^- → Fe^{2+} (aq) E° = 0.77 V

Cl_2 (g) + $2e^-$ → 2Cl– (aq) E° = 1.40 V

Identify the only incorrect statement regarding the quantitative estimation of aqueous Fe $(NO_3)_2$.
(a) MnO_4^- can be used in aqueous HCl.
(b) $Cr2O_7^{2-}$ can be used in aqueous HCl.
(c) MnO_4^- can be used in aqueous H_2SO_4.
(d) $Cr2O_7^{2-}$ can be used in aqueous H_2SO_4.

6. The standard reduction potentials of Cu^{2+}/Cu and Cu^{2+}/Cu^+ are 0.337 and 0.153 respectively. The standard electrode potential of Cu^+/Cu half-cell is
(a) 0.184 V
(b) 0.827 V
(c) 0.521V
(d) 0.490 V

7. The standard reduction potentials of X, Y, Z metals are 0.52, -3.03, -1.18 respectively. The order of reducing power of the corresponding metals is:
(a) $Y > Z > X$
(b) $X > Y > Z$
(c) $Z > Y > X$
(d) $Z > X > Y$

8. Which of the following is not a good conductor?
(a) Cu
(b) NaCl (aq)
(c) NaCl (molten)
(d) NaCl(s)

9. The volume of H2 gas at NTP obtained by passing 4 amperes through acidified H_2O for 30 minutes is:
(a) 0.0836 L
(b) 0.0432 L
(c) 0.1672 L
(d) 0.836 L

10. 4.5 g of aluminium (at. mass 27 amu) is deposited at cathode from Al^{3+} solution by a certain quantity of electric charge. The volume of hydrogen produced at STP from H^+ ions in solution by the same quantity of electric charge will be:
(a) 44.8 L
(b) 11.2 L
(c) 22.4 L
(d) 5.6 L

11. The amount of electricity required to deposit 1 mol of aluminium from a solution of $AlCl_3$ will be
(a) 0.33 F
(b) 1 F
(c) 3 F
(d) 1 ampere

12. A current of 2.0 A passed for 5 hours through a molten metal salt deposits 22.2 g of metal (at. wt. = 177). The oxidation state of the metal in the metal salt is
(a) +1
(b) +2
(c) +3
(d) +4

13. On the basis of information available from the reaction. 4/3 Al + O_2 → 2/3 $Al2O_3$,? G = – 827 kj mol-1 of O_2 the minimum emf required to carry out the electrolysis of Al_2O_3 is
(a) 2.14 V
(b) 4.28 V
(c) 6.42V
(d) 8.56V

14. For a cell reaction involving two electron change the standard emf of the cell is found to be 0.295 V at 25°C. The equilibrium constant for the reaction at 25°C will be:
(a) 2.95×10^2
(b) 10
(c) 1×10^{10}
(d) 1×10^{-10}

15. If Zn^{2+}/Zn electrode is diluted 100 times, then the change in emf is
(a) increase of 59 mV
(b) decrease of 59 mV
(c) increase of 29.5 mV
(d) decrease of 29.5 mV.

16. If the equivalent conductance of 1 M benzoic acid is 12.8 ohm^{-1} cm^2 and if the conductance of benzoate ion and H^+ ion are 42 and 288.42 ohm^{-1} cm^2 respectively, its degree of dissociation is:
(a) 39%
(b) 3.9%
(c) 0.35%
(d) 0.039%

17. An aqueous solution containing one mole per litre of each of $Cu(NO_3)_2$, $AgNO_3$, Hg $(NO_3)_2$ and Mg $(NO_3)2$ is being electrolysed using inert electrodes. The values of standard electrode (reduction) potentials in volts are Ag/Ag^+ = + 0.80, Hg/ Hg^{2+} = 0.79, Cu/Cu^{2+} = 0.34, Mg/Mg^{2+} = -2.37.

With increasing voltage, the sequence of deposition of metals on cathode will be
(a) Ag, Hg, Cu, Mg
(b) Mg, Cu, Hg, Ag
(c) Ag, Hg, Cu
(d) Cu, Hg, Ag
(e) Cu, Hg, Ag, Mg.

18. The highest electrical conductivity of the following aqueous solutions is of?
(a) 0.1 M acetic acid
(b) 0.1 M chloro acetic acid
(c) 0.1 M fluoroacetic acid
(d) 0.1 M difluoro acetic acid

19. If 96500 coulomb electricity is passed through $CuSO_4$ solution, it will liberate
(a) 63.5 gm of Cu (b) 31.76 gm of Cu
(c) 96500 gm of Cu (d) 100 gm of Cu

20. Fused NaCl on electrolysis gives ………….. on cathode.
(a) Chlroine (b) Sodium
(c) Sodium amalgam (d) Hydrogen

21. Which of the following is a secondary cell?
(a) Leclanche cell
(b) Lead storage battery
(c) Concentration cell
(d) All of these

22. For a certain redox reaction, E° is positive. This means that
(a) ΔG° is positive, K is greater than 1
(b) ΔG° is positive, K is less than 1
(c) ΔG° is negative, K is greater than 1
(d) ΔG° is negative, K is less than 1

23. Cell reaction is spontaneous, when
(a) E^0red is negative (b) ΔG° is negative
(c) E^0oxid is Positive (d) ΔG° is positive

24. Equilibrium constant K is related to E^0_{cell} and not E_{cell} because
(a) E^0_{cell} is easier to measure than E_{cell}
(b) E_{cell} becomes zero at equilibrium point but E^0cell remains constant under all conditions
(c) At a given temperature, E_{cell} changes hence value of K can't be measured
(d) Any of the terms E_{cell} or E^0cell can be used

25. Electrical conductance through metals is called metallic or electronic conductance and is due to the movement of electrons. The electronic conductance depends on
(a) the nature and structure of the metal
(b) the number of valence electrons per atom
(c) change in temperature
(d) all of these

26. Faraday's law of electrolysis is related to
(a) Atomic number of cation
(b) Speed of cation
(c) Speed of anion
(d) Equivalent weight of electrolyte

27. The molar conductivity is maximum for the solution of concentration
(a) 0.004 M (b) 0.002 M
(c) 0.005 M (d) 0.001 M

28. How long would it take to deposit 50 g of Al from an electrolytic cell containing Al_2O_3 using a current of 105 ampere?
(a) 1.54 h (b) 1.42 h
(c) 1.32 h (d) 2.15 h

29. How much electricity in in terms of Faraday is required to produce 100 g of Ca from molten $CaCl_2$?
(a) 1F (b) 2F
(c) 3F (d) 5F

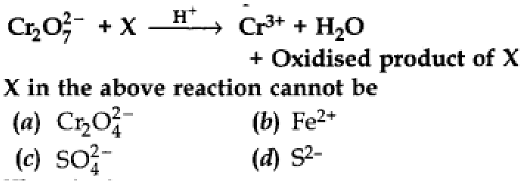
30. A current of 1.40 ampere is passed through 500 mL of 0.180 M solution of zinc sulphate for 200 seconds. What will be the molarity of Zn^{2+} ions after deposition of zinc?
(a) 0.154 M (b) 0.177 M
(c) 2 M (d) 0.180 M

31. How much time is required to deposit 1×10^{-3} cm thick layer of silver (density of 1.05 g cm^{-3}) on a surface of area 100 cm^2 by passing a current of 5 A through $AgNO_3$ solution?
(a) 125 s (b) 115 s
(c) 18.7 s (d) 27.25 s

32. If limiting molar conductivity of Ca^{2+} and Cl^- are 119.0 and 76.3 S cm^2 mol^{-1}, then the value of limiting molar conductivity of $CaCl_2$ will be
(a) 195.3 S cm^2 mol^{-1}
(b) 271.6 S cm^2 mol^{-1}
(c) 43.3 S cm^2 mol^{-1}
(d) 314.3 S cm^2 mol^{-1}.

33. NH_4NO_3 is used in salt bridge because
(a) it forms a jelly like material with agar-agar.
(b) it is a weak electrolyte.
(c) it is a good conductor of electricity.
(d) the transport number of NH_4^+ and NO_3^- ions are almost equal.

34.



$$Cr_2O_7^{2-} + X \xrightarrow{H^+} Cr^{3+} + H_2O + \text{Oxidised product of X}$$

X in the above reaction cannot be
(a) $Cr_2O_4^{2-}$ (b) Fe^{2+}
(c) SO_4^{2-} (d) S^{2-}

35. The reaction, $3ClO^-$ (aq) → ClO_3 (aq) + $2Cl^-$ (aq) is an example of
(a) Oxidation reaction
(b) Reduction reaction
(c) Disproportionation reaction
(d) Decomposition reaction

36. The standard emf of a galvanic cell involving cell reaction with n = 2 is formed to be 0.295 V at 25° C. The equilibrium constant of the reaction would be
(a) 1.0×10^{10} (b) 2.0×10^{11}
(c) 4.0×10^{12} (d) 1.0×10^2
[Given F = 96500 (mol-1); R = 8.314 JK-1 mol-1]

37. The emf of the cell:
Ni / Ni^{2+} (1.0 M) // Au^{3+} (1.0 M) / Au (E° = -0.25 V for Ni^{2+}/Ni; E° = 1.5 V for Au^{3+}/Au) is
(a) 1.25 V (b) -1.25 V
(c) 1.75 V (d) 2.0 V

38. Which of the following reaction is used to make fuel cell?
(*a*) $Cd\ (s) + 2Ni(OH)_3\ (s) \longrightarrow CuO\ (s) + 2\ Ni(OH)_2\ (s) + H_2O\ (l)$
(*b*) $Pb\ (s) + PbO_2\ (s) + 2H_2SO_4\ (aq) \longrightarrow 2PbSO_4\ (s) + 2H_2O\ (l)$
(*c*) $2H_2\ (g) + O_2\ (g) \longrightarrow 2H_2O\ (l)$
(*d*) $2Fe\ (s) + O_2\ (g) + 4H^+\ (aq) \longrightarrow 2Fe^{2+}\ (aq) + 2H_2O\ (l)$

39. The cell reaction of the galvanic cell.
$Cu(s) / Cu^{2+}\ (aq) // Hg^{2+}\ (aq) / Hg\ (l)$ is
(*a*) $Hg + Cu^{2+} \longrightarrow Hg^{2+} + Cu$
(*b*) $Hg + Cu^{2+} \longrightarrow Cu^{+} + Hg^{+}$
(*c*) $Cu + Hg \longrightarrow CuHg$
(*d*) $Cu + Hg^{2+} \longrightarrow Cu^{2+} + Hg$

40. Effect of dilution on conductivity of solution:
(a) Increases
(b) Decreases
(c) Unchanged
(d) None of these

41. Which shows electrical conductance?
(a) Sodium (b) Diamond
(c) Potassium (d) Graphite

42. Time required to deposit one millimole of aluminium metal by the passage of 9.65 amperes through aqueous solution of aluminium ion is
(a) 30 s (b) 10 s
(c) 30000 s (d) 10000 s

43. The products formed when an aqueous solution of NaBr is electrolysed in a cell having inert electrodes are:
(a) Na and Br_2 (b) Na and O_2
(c) H_2, Br_2 and NaOH (d) H_2 and O_2

44. What flows in the internal circuit of galvanic cell?
(a) ions
(b) electrons
(c) electricity
(d) atoms

45. Which of the following statements about galvanic cell incorrect
(a) anode is positive
(b) oxidation occurs at the electrode with lower reduction potential
(c) cathode is positive
(d) reduction occurs at cathode

46. Which device converts chemical energy of a spontaneous redox reaction into electrical energy?
(a) Galvanic cell
(b) Electrolytic cell
(c) Daniell cell
(d) Both a and c

47. The volume of oxygen gas liberated at NTP by passing a current of 9650 coulombs through acidified water is
(a) 1.12 L
(b) 2.24 L
(c) 11.2 L
(d) 22.4 L

48. The electric charge for electrode decomposition of one gram equivalent of a substance.
(a) one ampere per second
(b) 96500 coulombs per second
(c) one ampere for one hour
(d) charge on one mole of electron

49. In electrolysis of dilute H_2SO_4 using platinum electrodes
(a) H_2 is evolved at cathode
(b) NH_2 is produced at anode
(c) Cl_2 is obtained at cathode
(d) O_2 is produced

50. The reference electrode is made by using
(a) $ZnCl_2$
(b) $CuSO_4$
(c) $HgCl_2$
(d) Hg_2Cl_2

ASSERTION AND REASON

Q1. **Assertion:** The resistivity for a substance is its resistance when it is one meter long and its area of cross section is one square meter.
Reason: The SI units of resistivity is ohm metre (m).
(a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
(b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
(c) If the Assertion is correct but Reason is incorrect.
(d) If both the Assertion and Reason are incorrect.

2. **Assertion:** Galvanised iron does not rust.
Reason: Zinc has a more negative electrode potential than iron.
(a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
(b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
(c) If the Assertion is correct but Reason is incorrect.
(d) If both the Assertion and Reason are incorrect.

3. **Assertion:** On increasing dilution, the specific conductance keep on increasing.
Reason: On increasing dilution, degree of ionisation of weak electrolyte increases and molality of ions also increases.
(a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
(b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
(c) If the Assertion is correct but Reason is incorrect.
(d) If both the Assertion and Reason are incorrect.

4. **Assertion:** Cu is less reactive than hydrogen.
Reason: E^0 Cu^{2+} /Cu is negative.
(a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
(b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
(c) If the Assertion is correct but Reason is incorrect.
(d) If both the Assertion and Reason are incorrect.

TRUE AND FALSE

1. In an electrochemical cell, in the inner circuit current is carried by ions and in the external circuit, current of electrons flows through the metal conductors.
(a) True (b) False

2. The electrical energy released from an electrochemical cell can do useful work.
(a) True (b) False

3. The cell voltage is a quantitative measure of the driving force of the cell reaction.
(a) True (b) False.

PRACTICE QUESTIONS (MCQ)

1. A cathode and an anode are the most common components of an electrochemical cell. Which of the following claims about the cathode is correct?
(a) Oxidation occurs at the cathode
(b) Electrons move into the cathode
(c) Usually denoted by a negative sign
(d) Is usually made up of insulating material

2. Which of the following claims about electrochemical cells is true?
(a) Cell potential is an extensive property
(b) Cell potential is an intensive property
(c) The Gibbs free energy of an electrochemical cell is an intensive property
(d) Gibbs free energy is undefined for an electrochemical cell

3. Which of the following about the main cell is correct?
(a) An example of a primary cell is a mercury cell
(b) An example of a primary cell is a nickel-cadmium storage cell
(c) The electrode reactions can be reversed
(d) It can be recharged

4. In a dry cell, which of the following is the electrolyte?
(a) Potassium hydroxide
(b) Sulphuric acid
(c) Ammonium chloride
(d) Manganese dioxide

5. The conductivity of electrolytic conductors is due to ________
(a) Flow of free mobile electrons
(b) Movement of ions
(c) Either movement of electrons or ions
(d) Cannot be said

6. Which of the following statements about a lead storage cell (or a lead-acid battery) is false?
(a) It is a primary cell
(b) The cathode is made up of lead(IV) oxide
(c) The anode is made up of lead
(d) The electrolyte used is an aqueous solution of sulphuric acid

7. In a fuel cell, which of the following can be utilized as a fuel?
(a) Nitrogen (b) Argon
(c) Hydrogen (d) Helium

8. Which of the following is given to a fuel cell's cathode?
(a) Hydrogen (b) Nitrogen
(c) Oxygen (d) Chlorine

9. The cell constant of a conductivity cell
(a) Changes with change of electrolyte.
(b) Changes with change of concentration of electrolyte.
(c) Changes with temperature of electrolyte.
(d) Remains constant for a cell.

10. In an electrochemical process, a salt bridge is used:
(a) as a reducing agent
(b) as an oxidizing agent
(c) to complete the circuit so that current can flow
(d) None

11. Electrical conductance through metals is called metallic or electronic conductance and is due to the movement of electrons. The electronic conductance depends on
(a) the nature and structure of the metal
(b) the number of valence electrons per atom
(c) change in temperature
(d) all of these

12. If 96500 coulomb electricity is passed through $CuSO_4$ solution, it will liberate

(a) 63.5 gm of Cu (b) 31.76 gm of Cu
(c) 96500 gm of Cu (d) 100 gm of Cu

13. Which of the following does not cause rusting of iron?

(a) Moisture (b) Vacuum
(c) SO_2 (d) CO_2

14. In which of the following the corrosion of iron will be most rapid?

(a) In pure water
(b) In pure oxygen
(c) In air and moisture
(d) In air and saline water

15. Which of the following is not essential for rusting to take place?

(a) Metal (like iron) (b) Oxygen
(c) Moisture (d) Light

16. What is the preferred electrode when it is not allowed to take part in the chemical reaction?

(a) Gold (b) Silver
(c) Copper (d) Graphite

17. What is the electrolyte used in the electroplating of gold?

(a) Molten gold (b) $[AgCN_2]^-$
(c) AuCN (d) $AuCl_3$

18. What is the product formed at the cathode in the electrolysis of aqueous $CuSO_4$?

(a) Copper metal (b) Oxygen gas
(c) Hydrogen gas (d) Sulphur

19. What is the product formed at the cathode in the electrolysis of molten NaCl?

(a) Chlorine gas (b) Sodium metal
(c) Hydrogen gas (d) Oxygen gas

20. What are the two electrodes used in Daniell cell?

(a) Pt and Cu (b) Al and Zn
(c) Al and Pt (d) Zn and Cu

21. Which of the following is not a method of prevention of corrosion?

(a) Galvanization
(b) Anti-rust solution
(c) Cathodic protection
(d) Heating

22. Which of the following statements is false?

(a) Salt water decelerates the rate of corrosion
(b) Magnesium is more active than iron
(c) During galvanization, $ZnCO_3 . Zn(OH)_2$ is formed which prevent further corrosion
(d) Anti-rust solutions are used in car radiators to prevent rusting of iron parts of the engine

23. Which of the following is not essential for rust to form?

(a) Water (b) Iron
(c) Oxygen (d) CO_2

24. Which of the following methods is suitable for preventing an iron frying pan from rusting?

(a) Applying grease
(b) Applying paint
(c) Applying a coating of zinc
(d) All of the above

25. Which of the following methods is employed to prevent rusting?

(a) Refining (b) Alloying
(c) Greasing (d) Both (b) and (c)

26. Corrosion cannot be prevented by which of the following method?

(a) Galvanisation
(b) Create a barrier between the object being corrode and oxygen
(c) Painting
(d) Exposing to sunlight

27. Which of the following methods is suitable for preventing an iron vessel from rusting ?

(a) Applying grease
(b) Applying paint
(c) Applying a coat of zinc
(d) All of these

8. Which of the following metal does not corrode?

(a) Iron (b) Zinc
(c) Copper (d) Magnesium

9. What is the method of protection of iron by coating it with zinc called?

(a) Tinning
(b) Cathodic protection
(c) Galvanization
(d) Anti-rust solutions

10. Which of the following statements regarding corrosion is true?

(a) Corrosion does not depend on the reactivity of the metal
(b) Presence of impurities does not affect the rate of corrosion
(c) Strains in metals affect the rate of corrosion
(d) Presence of electrolytes does not affect the rate of corrosion

ASSERTION AND REASON

1. **Assertion:** Copper sulphate can be stored in zinc vessel.
Reason: Zinc is less reactive than copper.

(a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
(b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
(c) If the Assertion is correct but Reason is incorrect.
(d) If both the Assertion and Reason are incorrect.

2. **Assertion:** Current stops flowing when ECell = 0.
Reason: Equilibrium of the cell reaction is attained.
(a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
(b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
(c) If the Assertion is correct but Reason is incorrect.
(d) If both the Assertion and Reason are incorrect.

3. **Assertion:** For measuring resistance of an ionic solution an AC source is used.
Reason: Concentration of ionic solution will change if DC source is used.
(a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
(b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
(c) If the Assertion is correct but Reason is incorrect.
(d) If both the Assertion and Reason are incorrect.

4. **Assertion:** Electrolysis of NaCl solution gives chlorine at anode instead of O2.
Reason: Formation of oxygen at anode requires overvoltage.
(a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
(b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
(c) If the Assertion is correct but Reason is incorrect.
(d) If both the Assertion and Reason are incorrect.

5. **Assertion:** Mercury cell does not give steady potential.
Reason: In the cell reaction, ions are not involved in solution.
(a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
(b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
(c) If the Assertion is correct but Reason is incorrect.
(d) If both the Assertion and Reason are incorrect.
(e) Assertion is false but reason is true.

TRUE AND FALSE

1. A cell works if its e.m.f. is negative.
(a) True
(b) False

2. The redox reaction involved in galvanic cell is a non-spontaneous process.
(a) True
(b) False

3. Salt bridge is used to eliminate liquid junction potential.
(a) True
(b) False

SOLUTIONS MULTIPLE CHOICE

1. **(c)** velocity of both K^+ and NO_3^- are nearly same

For a good salt bridge, the velocities of ions should be same. If the velocities are not same, then the ions would not be able to neutralize the charge equally in both half cells. Consequently, an opposite force would be developed that restricts the flow of current. For KNO_3, the velocities of K^+ and NO_3^- are nearly same. Therefore, it is used to make salt bridges.

2. **(c)** Zinc

Galvanization is the process of applying a protective zinc coating to steel or iron in order to prevent it from rusting.

3. **(a)** 1.93 x 10^5 C

$$H_2O \rightarrow 2H^{\oplus} + 2e^- + \frac{1}{2}O_2$$

$$2\,F \equiv 1\,\text{mol of } H_2O = \frac{1}{2}\,\text{mol of } O_2$$

$$\therefore\ 2 \times 96500\,C = 1.93 \times 10^5\,C$$

4. **(c)** Fe_2O_3 and Fe $(OH)_3$

On corrosion ferric hydroxide (Fe $(OH)_3$) is formed and it forms rust Fe_2O_3 x H_2O.

5. **(a)** MnO_4^- can be used in aqueous HCl.

MnO_4^- cannot be used for oxidation of Fe^{2+} in HCl medium because the following reaction is spontaneous :

$MnO_4^- + cl^- \rightarrow Mn^{2\div} + cl_2, E^o = 1.51 - 1.40 = 0.11V$

In all other cases, the redox process between oxidising agent and medium (HCl or H_2SO_4) are non-spontaneous, would not interfere oxidation of Fe^{2+}

6. **(c)** 0.521 V

$Cu^{2\div} + 2e^- \rightarrow Cu$ ...(i)$E^{\ominus}$

$Cu^{2\div} + e^- \rightarrow Cu^{\oplus}$ ...(ii)$E_2^{\ominus}$

Net equation $(Cu^{\oplus} + e^- \rightarrow Cu)$ ...(iii)

$E_3^{\ominus} = \frac{n_1E_1^{\ominus} - n_2E_2^{\ominus}}{n_3} = \frac{2\times0.337 - 1\times0.153}{1} = 0.521$

7. **(a)** Y > Z > X

Reducing power depends on how easily the ions themselves get oxidised. Since we have the reduction potential values, we need to flip their sign to get oxidation potential values and arrange them in descending order.

This gives us Y (3.303)> Z (1.18)> X (-0.52)

8. **(d)** NaCl(s)

Solid NaCl does not conduct electricity due to absence of free ions.

9. **(d)** 0.836 L

Quantity of electricity passed

$= 4\,A \times (30 \times 60s) = 7200\,C$

$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$

$2 \times 96500\,C$ liberate $H_2 = 22.4L$ at STP

$7200\,C$ will liberate $= \frac{22.4}{2\times96500} \times 7200\,C$

$= 0.836\,L$

10. **(d)** No. of moles of Aluminium deposited = $\frac{45}{27} = \frac{1}{6}$ mole

$2Al \rightarrow Al^{-3} + 6e^-$

$6H^+6e^- \rightarrow 3H_2$

$\Rightarrow\ 2Al \div 6H^+ \rightarrow 3H_2 \div 2Al^{-3}$

2moles of Aluminium produce 3 moles of hydrogen.

so, moles of Al → 3 moles of H_2

$\frac{1}{6}$ moles of Al $\frac{1}{4}$ moles of H_2.

So, 1 ole of H_2 →22.4 Litre

$$\frac{1}{4}\ mole\ of\ H_2 = \frac{22.4}{4} = 5.6L$$

11. **(c)** 3F

The number of electrons involved in the reaction are three as shown below

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

It means the conversion of every aluminium ion to aluminium atom requires three electrons.

Therefore, the amount of electricity required for one mole of Al^{3+} ions =3F.

12. **(c)** +3

Weight = $\frac{E\chi_i\chi t}{F} = \frac{M\ it}{n-factor\times F}\ lE = \frac{M}{n-factor}$

$\Rightarrow 22.2 = \frac{177\times5\times2\times60\times60}{n-factor\times96500}$

$\therefore$ n-factor = 2.97 $\simeq$ 3

Hence oxidation state of metal = ÷ 3

13. **(a)** 2.14 V

$\frac{4}{3}Al + O_2 \rightarrow \frac{2}{3}Al_2O_3$

ΔG = - 827 kJ mol^{-1}

ΔG = nEF^0 (n = 4)

-827 × 10^3 J -4 × E^0 × 96500

E = $\frac{827\times10^3}{4\times96500}$

E^0 = 2.14 V

14. **(c)** 1 x 10*10

Using the relation,

$$E^{\circ}_{cell} = \frac{2.303\ RT}{nF} \log K_c = \frac{0.0591}{n} \log K_c$$

$$\therefore 0.295\ V = \frac{0.0591}{2} \log K_c$$

$$\text{or} \log K_c = \frac{2 \times 0.295}{0.0591} = 10$$

$$\text{or } K_c = 1 \times 10^{10}$$

15. **(b)** decreases of 59 mV

We know;

$E_{cell} = \frac{0.059}{2} \log \frac{1}{c}$

Where ; c = 100 times

$E_{cell} = -\frac{0.059}{2} \log \frac{1}{100}$

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

0.059 V = 59 mV

Thus, if the Zn^{2+}/Zn electrode is diluted to 100 times than the emf is increase of 59 mV.

16. **(b)** 3.9%

$\wedge_m^0 (C_6COOH) = \wedge^0_{(C_6H_5COO^-)} + \wedge^0_{(H^+)}$

= 42 + 288.42 = 330.42

Now we have,

$\alpha = \frac{\wedge_m^c}{\wedge_m^0} = \frac{12.8}{330.42} = 3.90$

17. **(c)** Ag, Hg, Cu

In aqueous solution, only those ions who are less electropositive than hydrogen ($E^0 > 0$) would be deposited.

Therefore, in the present case, only Ag, Hg and Cu would be deposited on passing electricity through aqueous solution of these ions, Mg will not be deposited.

Also, higher the value of E^0, easier will be their reduction, therefore, the sequence in which ions will be deposited on increasing voltage across the electrodes is :

Ag, Hg, Cu

18. **(d)** 0.1 M difluoro acetic acid

Difluoroacetic acid is stronger than fluoroacetic acid or chloroacetic acid or acetic acid. Therefore, 0.1M difluoroacetic acid will have highest electrical conductivity.

19. **(b)** At eh cathode

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

At the anode

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

Faraday's constant = 96500C/ mol

To deposit 1 mole of copper, we need 2 × 96500 so, will deposit 0.5 moles of copper

= 0. × 63.5 31.75g

20. **(b)** Sodium

During electrolysis of fused NaCl:

At cathode:

$Na^+ + e^- \rightarrow Na(s)$

So, we get solid sodium metal at the cathode during this process.

21. **(b)** Lead storage battery

Dry cell (Leclanche cell) and Mercury cell are primary voltaic cells. They cannot be recharged. Hence, none of the given options is a secondary cell.

Lead accumulator (lead storage battery) is a secondary cell.

22. **(c)** ΔG° is negative, K is greater than 1

$\Delta G^0 = -nFE^0 \ \ldots.(i)$

$\Delta G^0 = -2.303\ RT \log K_{eq} \ \ldots\ldots(ii)$

From eq (i) if E^0 is positive

Then ΔG^0 is negative in equation (ii), ΔG^0 is negative

So, log K > 0 ⇒ K > 1

23. **(b)** ΔG° is negative

Gibbs energy and standard electrode potential relation is given by $\Delta G = -nFE_{cell}$.

Explanation:

Part: 1

E_{cell} is an intensive parameter but ΔG is an extensive property. Thus depends on n.

Part: 2

If the electrode potential is assumed to be positive then,

When ΔG<0, the cell reaction is spontaneous.

When ΔG>0, the cell reaction is non-spontaneous.

When ΔG=0, the reaction is in equilibrium.

24. **(b)** E_{cell} becomes zero at equilibrium point but E^0_{cell} remains constant under all conditions

At equilibrium, E_{cell} becomes zero which means no current is generated by the cell at this point. E^0_{cell} remains constant hence equilibrium constant is related to E^0_{cell}

25. **(d)** all of these

Electronic conductance depends upon-

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.

Concentration of the solution: The molar conductance of electrolytic solution varies with the concentration of the electrolyte. In general, the molar conductance of an electrolyte increases with decrease in concentration or increase in dilution nature of the Temperature: The conductivity of an electrolyte depends upon the temperature. With increase in temperature, the conductivity of an electrolyte increases.

Valence electrons per atom present in metal describe the electric conductance of it. Nature and structure is also a significant factor which influences electrical conductance.

26. **(d)** Equivalent weight of electrolyte
Faraday's law of electrolysis is related to equivalent weight of electrolytes as -the number of Faraday's passed is equal to the number of gram equivalent of electrolytes discharged.

27. **(d)** 0.001 M

$$\Lambda_m = \frac{\kappa \times 1000}{M}$$

Lower the molarity higher the molar conductivity

28. **(b)** 1.42 h
Faraday's First Law of Electrolysis states that only, According to this law, the chemical deposition due to flow of current through an electrolyte is directly proportional to the quantity of electricity (coulombs) passed through it.
The reaction of Al is,

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

Now as n=3, Equivalent weight of Al$=\frac{27}{3} = 9$

As per Faraday's first law,

$$W = Z \times I \times t \Rightarrow Z = \frac{Eq.wt}{96500}$$

$$\Rightarrow t = \frac{W \times 96500}{Eq.wt \times 1} = \frac{50 \times 96500}{9 \times 105} = 5102.2 \text{ or } 1.42 \text{ hours}$$

29. **(d)** 5F
We have to note that one mole of electron charge is equivalent to one Faraday.
Given reaction,
$CaCl_2 \rightarrow Ca^{2+} + 2Cl^-$
Ca is undergoing oxidation; $Ca^{2+} + 2e^- \rightarrow Ca$
We can observe that 40g of Ca takes $2e^-$ charge,
So,1 mole of Ca(40g)≡2F
Now, 100g of Ca≡5F

30. **(b)** 0.177 M
Amount of charge passed = 1.40 × 200
= 280
No. of moles of Zn deposited by passing 280 C of charge
$= \frac{1}{2\times 96500} \times 280 = 0.00145$
Molarity of zinc after deposition of zinc
$= 0.180 - \frac{0.00145\times 1000}{500}$
= 0.180 – 0.0029
= 0.177 M

31. **(c)** 18.7 s
Mass of Ag in coated layer = V × d
= $1 \times 10^{-3} \times 100 \times 1.05$
= 0.105g
W = $\frac{\text{Ɪ}\times t\times Eq.\backslash \text{Ʊ}t.}{96500}$
t = $\frac{w\times 9500}{\text{Ɪ}\times Eq.\text{Ʊ}t.}$
= $\frac{0.105\times 96500}{5\times 108}$
= 18.7 s

32. **(b)** 271.6 S cm2 mol-1

$$\Lambda^\circ m(CaCl_2) = \Lambda^\circ\left(Ca^{2+}\right) + 2\Lambda^\circ\left(Cl^-\right)$$

33. **(d)** the transport number of NH_4^+ and NO_3^- ions are almost equal.

Because the ionic velocity of the ammonium ion (NH_4^+) and the nitrate ions are the same, ammonium nitrate is used in salt bridge.

The salt bridge replaces the ions lost or created in the two half cells by supplying cations and anions. As a result, it does not interfere with the cell's neutrality, but rather helps to maintain it.

For example, if an excess negative charge is formed as a result of extra ions, a significant amount of positive ions will migrate from the salt bridge to this half-cell. This cancels out the surplus charge and renders the system electrically neutral.

34. **(c)** SO_4^{2-} cannot be oxidised since S is present in it in its highest oxidation state (+6).

35. **(c)** Disproportionation reaction
It is an example of disproportionation reaction because the same species (CIO^-)is being oxidised to CIO^- as well as reduced to Cl^-

36. **(a)** 1.0×10^{10}
For a cell reaction in equilibrium at 298K
$E^0_{cell} = \frac{0.0591}{n} logK_e$
$\Rightarrow logK_c = \frac{E^0_{cell}\times n}{0.0591}$
Substitute the given values of E^0_{cell} and I the above equation we get
Log $K_c = \frac{0.295\times 2}{0.0591}$
logK_c = 10
$\Rightarrow K_c = 1 \times 10^{10}$

37. **(c)** 1.75 V
We have given, the cell representation from which, we can write the half cell reactions:
At anode (oxidation):
$Ni \rightarrow Ni^{2+} \; 2e^-$ E^0 (anode) = -0.25V ...(1)
At cathode (Reduction):
$Au^3 + 3e^- \rightarrow Au$ E^0 (cathode) = 1.15V ...(2)

Now multiply the equation (1) by 3 and equation (2) by 2, then add;
The overall cell reaction is:
$3Ni + 2Au^{3+}(aq) \rightarrow Au + ni^{2\div}(aq)$
$E^0_{cell} - E^0_{cathode} - E^0_{anode}$
$E^0_{cell} = 1.5 - (-0.25)$
$E^0_{cell} = 1.75\ V$
From the **Nernst equation:**
$E_{cell} = E^0_{cell} - \frac{0.059}{n} \log \frac{[N_2^{2+}]^a}{[Au^{a+}]^2}$
Where 'n' is no. of electrons gained or loss in cell reaction.
Given, $[Ni^{2+}] = 1.0M\ and\ [Au^{3\div}]$=1.0 and n=6
$E_{cell} = 1.75 - \frac{0.059}{6} \log \frac{(1.0)^3}{(1.0)^2}$
$E_{cell} = 1.75 - \frac{0.059}{6} log 1$
E_{cell} = 1.75 – 0 [∵ log 1=0]
E_{cell} = 1.75V
Therefore, the **e.m.f. of cell** is 1.75 Volt.

38. **(c)** Fuel cells are galvanic cells in which chemical energy of fuels is directly converted into electrical energy.

39. **(d)** $\underbrace{Cu(s)|Cu^2_{aq}|}_{anode}\ \underbrace{[Hg^{2\div}]Hg_{(J)}}_{cathode}$
In anode oxidation takes place Cu → $Cu^{2\div} + 2e^-$
In cathode reduction takes place $Hg^{2+} \div 2e^- \rightarrow Hg$
Overall: Cu +$Hg^{2\div}Hg$

40. **(a)** Increases
The conductivity of a weak electrolyte increases with an increase dilution. As the dilution increases the number of ion increases and they get free from their co-ions and can move independently from each other. So by increasing dilution the rate of conductivity increases as more ions are available for conductance.

41. **(d)** Graphite
In graphite, since pi-electrons are free to move throughout the entire layers so graphite is a good conductor of electricity. Its conductivity increases with temperature.

42. **(a)** 30 s
[HINT]: $Al^{3+} + 3e^- \rightarrow Al$
1 mole requires =3×96500 coulomb
1 millimole requires =3×96500x 10^{-3} coulomb
We know that, Q = it
t = Q/i

43. **(c)** H_2, Br_2 and NaOH
$NaBr \rightleftharpoons Na^+ \div Br^-$

$2H_2O \div 2e \rightarrow H_2 + 2OH^-$

$Na^+ + OH^- \rightarrow NaOH$ At cathode

$Br^- \rightarrow Br + e^-$

$Br + Br \rightarrow Br_2$ At anode

So the products are H_2 and NaOH (at cathode) and Br_2 (at anode).

44. **(a)** Ions
Ions flows in the internal circuit of the galvanic cell.

45. **(a)** anode is positive
Anode has negative polarity in galvanic cell.

46. **(a)** A galvanic cell or voltaic cell is a type of electrochemical cell where spontaneous redox reactions take place when deriving electrical energy

47. **(a)** Q = 1 × .9650
Q = .9650
Amount of 02
$\frac{1\times9650}{2\times96500}$ = 1 mol o_2
= 0.05 mol
Vol"+ of O_2 at NTP = 0.05 × 22.4
= 1.12 mol

48. **(d)** charge on one mole of electron
Charge on one mole of electrons is equal to one Faraday, so one gram equivalent of a substance will be deposited by one mole of electrons.
1 g equivalent of a substance means one equivalent of substance which have total charge of one mole of electron.

49. **(a)** H_2 is evolved at cathode
When platinum electrodes are dipped in dilute solution H_2SO_4 then H_2 is evolved at cathode.

50. **(d)** Hg_2Cl_2
In saturated calomel electrode which is a reference electrode is made up of Hg_2Cl_2 .

ASSERTION AND REASON

1. **(b)** we know, R ∝ l/A pr R = ρ(l/A), where proportional constant ρ is called resistivity. If l = 1 m and A = 1 m^2 then R = ρ i.e., resistance = resistivity.

2. **(a)** More -ve electrode potential of Zn means less reduction potential or high oxidation potential. Hence, Zn is more easily oxidized than Fe.

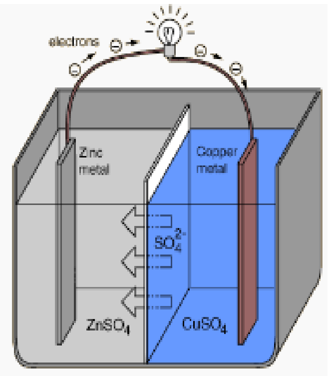
3. **(b)** K = Gσ
On dilution G decreases K decreases.
Distance between cation and anion increases force of attraction between cation and anion decreases.

On dilution, degree of ionisation increases.
No of ions increases
Mobility of ions increases

4. **(c)** Standard electrode potential of $E^o_{Cu^{2-},Cu}$ = 034$V\ and\ E^o_{H/H}$ = 0.00V. This shows that copper is less reactive than hydrogen and $E^0_{cell} of$ Cu is positive

TRUE AND FALSE

1. **(a)** From figure it can be seen that, in an electrochemical cell, in the inner circuit current is carried by ions and in the external circuit, current of electrons flows through the metal conductors.



2. **(a)** The given statement is True.

The electrical energy released from an electrochemical cell can do useful work.

The reversible electrical work done in a galvanic cell by cell reaction is equal to decrease in Gibbs energy.

Electrical work = $-\Delta G = nFE_{cell}$

3. **(a)** The cell voltage, or the electromotive force (emf), is also called the cell potential. The magnitude of the emf is a quantitative measure of the driving force or thermodynamic tendency for the reaction to occur.

As higher is the emf, higher is the tendency of the reaction to occur.

PRACTICE SOLUTIONS

1. **(b)** Metal electrodes are commonly used as cathodes. It is on this electrode that reduction occurs. In a galvanic cell, the cathode is the positive electrode, while in an electrolytic cell, it is the negative electrode. The cathode attracts electrons.

2. **(b)** Because cell potential is independent of the amount of material present, it is an intense attribute. Gibbs free energy is a property that is defined for an electrochemical cell and is a broad characteristic because it is dependent on the amount of material present.

3. **(a)** A primary cell is one in which the electrode reactions only happen once and cannot be reversed with electrical energy. As a result, primary cells are unable to be recharged. A main cell, such as a mercury cell, is different from a secondary cell, such as a nickel-cadmium storage cell.

4. **(c)** In a dry cell, the electrolyte is ammonium chloride, which is applied as a moist paste close to the zinc anode. Ammonium chloride is replaced by sodium chloride in some “heavy-duty” dry cells by zinc chloride.

5. **(b)** The flow of free mobile electrons causes conductance in metallic conductors, while the movement of ions in a fused electrolyte solution causes conductance in electrolytic conductors.

6. **(a)** A secondary cell with a grid of lead packed with finely separated spongy lead for an anode and a grid of lead packed with lead(IV) oxide for a cathode is known as a lead storage cell. An aqueous solution of sulphuric acid is utilized as the electrolytic solution in a lead-acid battery.

7. **(c)** The simplest element is hydrogen. It’s also widely available throughout the universe. Although hydrogen has a lot of energy, an engine that runs on it produces nearly no pollutants. As a result, it’s used in a fuel cell.

8. **(c)** An anode, cathode, and electrolyte membrane make up a fuel cell. In a normal fuel cell, hydrogen is passed through the anode and oxygen is passed via the cathode.

9. **(d)** The cell constant, K, is equal to the distance in cm between the probe's electrodes divided by the surface area of the electrodes in cm^2. For solutions with low conductivities the electrodes can be placed closer together or made larger so that the cell constant is less than one.

For a particular conductivity cell the cell constant remains same even if-

Electrolyte is changed.

Concentration of electrolyte is changed.

Temperature of electrolyte is changed.

10. **(c)** In an electrochemical process, a salt bridge is used to complete the circuit so that current can flow.

A salt bridge, in electrochemistry, is a laboratory device used to connect the oxidation and reduction half-cells of a galvanic cell (voltaic cell), a type of electrochemical cell.

It maintains electrical neutrality within the internal circuit, preventing the cell from rapidly running its reaction to equilibrium.

So that current can flow in two-compartment viz anode and cathode.

11. **(d)** Electronic conductance depends upon-

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.

Concentration of the solution: The molar conductance of electrolytic solution varies with the concentration of the electrolyte. In general, the molar conductance of an electrolyte increases with decrease in concentration or increase in dilution. Nature of the Temperature: The conductivity of an electrolyte depends upon the temperature. With increase in temperature, the conductivity of an electrolyte increases.

Valence electrons per atom present in metal describe the electric conductance of it. Nature and structure is also a significant factors which influences electrical conductance.

12. **(b)** At the cathode

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$$

At the anode 4OG-(aq) $\rightarrow 2H_2O(1) + O_2(g) \div 4e^-$
Faraday's constant = 96500C/mol
To deposit 1 mole of copper, we need 2 x 96500C.
So, 96500C will deposit 0.5 moles of copper = 0.5 x 63.5 = 31.75g

13. **(b)** Air and moisture accelerate corrosion. The most important factor in atmospheric corrosion, overriding pollution or lack of it, is moisture. Presence of gases like SO_2 and CO_2 in air catalyse the process of corrosion. Iron, when placed in vacuum, does not rust.

14. **(d)** The corrosion of iron indicates a chemical change in the metal. Rust (hydrous oxide) is an example of this change that results when the iron is exposed to water or damp air. A thin film of oxide forms on the iron; this actually protects the metal from further corrosion by slowing the rate of oxidation.

Where salt is present, electrochemical corrosion occurs, and the protective oxide film does not form, thus the corrosion (buildup of rust) continues unchecked. Hence corrosion is faster in saline water.

15. **(d)** Rust is a general term for a series of iron oxides, usually, reddish-brown oxides, formed by the reaction of iron with oxygen in the presence of water or moisture. Water is usually present in the form of water vapour and oxygen is always present in the normal atmosphere. The oxygen needs moisture as a catalyst and reactant to accelerate the reaction, so in the absence of moisture, iron won't rust.

16. **(d)** Electrodes which do not take part in the chemical reaction during electrolysis are known as inert electrodes. Gold, silver and graphite do not take part in the process, but graphite is preferred because gold and silver electrodes are expensive.

17. **(c)** The electrolyte in electrolysis should contain the metal to be coated, gold in this case. AuCN is used because it is exceptionally stable and doesn't resist the flow of Au^+ ions from anode to cathode.

18. **(a)** In the electrolysis of aqueous $CuSO_4$, Cu^{2+}, SO_4^{2-}+, H^+ and OH^- are the ions formed after dissociation. Copper ions have much higher reduction potential than water. Hence, these ions are easily reduced and deposited as Cu at the cathode.

19. **(b)** In the electrolysis of NaCl, if the electrolyte is molten NaCl, then the only ions formed after dissociation are Na^+ and Cl^- ions. The cathode being a negatively charged electrode attracts the positive Na^+ ions and neutralizes it to form Sodium metal.

20. **(d)** The two electrodes that are used in a Daniell cell are zinc (as anode) and copper (as cathode) electrodes which are dipped in a solution containing its own ions, generally zinc sulphate and copper sulphate.

21. **(d)** Galvanization is the process of coating iron with zinc to prevent its oxidation. Anti-rust solutions are alkaline phosphate and alkaline chromate solutions. The alkalinity prevents the availability of hydrogen ions. Cathodic protection is the process of connecting the iron object to be protected to a more active metal either directly or through a wire.

22. **(a)** Saline medium has extra salts such as sodium chloride dissolved in water. It has a greater concentration of electrolyte than ordinary medium. The ions present will favour the formation of more electrochemical cells and favour the transfer of hydrogen ions and will thus promote rusting or corrosion.

23. **(d)** The presence of water and oxygen is essential for the rusting of iron. Iron does not rust in presence of carbon dioxide.

24. **(c)** Applying paint and grease are not suitable solutions to prevent an iron frying pan from rusting as the paint can melt by flame and can be destroyed in repeated use.

Applying a coating of zinc is a better option as it forms a coating of corrosion-resistant zinc which prevents corrosive substances from reaching the more delicate part of the metal.

25. **(d)** The rusting of iron can be prevented by greasing or alloying but refining is method to obtain pure metal from it's ore

26. **(d)** Corrosion can be prevented by creating a barrier between the object and oxygen. Galvanisation is a process to prevent corrosion and so is painting. However, exposing to sunlight is not a method to prevent corrosion.

27. **(d)** The rusting of iron can be prevented by painting, greasing or galvanising which is a process of applying a coat of zinc.

28. **(c)** Magnesium and zinc are highly active. Hence, they corrode at a faster rate than iron. Iron undergoes rusting in the presence of oxygen and moisture. Copper, a noble metal that occurs naturally in its elemental form, is almost totally impervious to corrosion.

29. **(c)** Rusting of iron is one of the most common forms of corrosion. To prevent iron from rusting, generally, more active metals are coated on it. The metal which is often used for coating iron is zinc (which is more active) and this process is called galvanization.

30. **(c)** More active metals are readily corroded. Presence of impurities in metals enhances the chances of corrosion. Corrosion takes place rapidly at bends, scratches, nicks and cuts in the metal. Electrolytes, if present, also increase the rate of corrosion.

ASSERTION AND REASON

1. **(a)** Electropositive elements like zinc precipitate copper from a solution of copper sulphate and finally forms a complex.

$CuSO_4 + Zn \rightarrow Cu + SO_{4(aq)} \rightarrow [Zn(H_2O)_4]SO_4$

2. **(a)** At each electrode-electrolyte interface there is a tendency of metal ions from the solution to deposit on the metal electrode trying to make it positively charged. At the same time, metal atoms of the electrode have a tendency to go into the solution as ions and leave behind the electrons at the electrode trying to make it negatively charged. At equilibrium, there is a separation of charges and depending on the tendencies of the two opposing reactions, the electrode may be positively or negatively charged with respect to the solution. A potential difference develops between the electrode and the electrolyte which is called electrode potential.

Hence, at equillibrium there is no opposition of charges at any of the electrode and it implies $E^0_{cell} = 0$

3. **(a)** Concentration of ionic solution changes on using DC current as a source of energy while on passing AC current concentration does not change. Hence AC source is used for measuring resistances.

4. **(a)** At the anode, the following oxidation reactions are possible:

$Cl^-(aq) \rightarrow \frac{1}{2}Cl_2(g) + e^-; E = 136V$

$2H_2O(1) \rightarrow O_2(g) + 4H^+(aq) + 4e^-; E - 1.23\ V$

Lower value of E_{cell} is preferred but due to overvoltage chlorine is liberated at anode.

5. **(e)**

TRUE AND FALSE

1. **(b)** A cell works when its Gibbs free energy is negative means reaction is spontaneous. Hence, EMF should be positive.

2. **(b)** The redox reaction involved in galvanic cell is a spontaneous process, like in Daniell cell

3. **(a)** The above statement is true. Salt bridge prevents liquid-liquid junction-potential, i.e., the potential difference which arises between two solutions when in contact with each other.