

ELECTROCHEMISTRY

It is a branch of chemistry that deals with the relationship between chemical energy and electrical energy and their inter conversions.

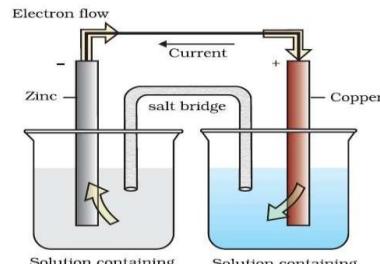
ELECTROCHEMICAL CELLS

These are devices that convert chemical energy of some redox reactions to electrical energy. They are also called Galvanic cells or Voltaic cells. An example for Galvanic cell is Daniel cell.

It is constructed by dipping a Zn rod in $ZnSO_4$ solution and a Cu rod in $CuSO_4$ solution. The two solutions are connected externally by a metallic wire through a voltmeter and a switch and internally by a salt bridge.

A salt bridge is a U-tube containing an inert electrolyte like $NaNO_3$ or KNO_3 in a gel-like substance. The functions of a salt bridge are:

1. To complete the electrical circuit
2. To maintain the electrical neutrality in the two half cells.



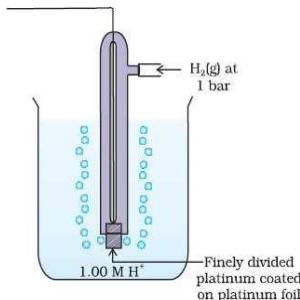
Electrode Potential

The tendency of a metal to lose or gain electron when it is in contact with its own solution is called **electrode potential**. When the concentrations of all the species involved in a half-cell is unity then the electrode potential is known as **standard electrode potential**. According to IUPAC convention, **standard reduction potential is taken as the standard electrode potential**.

The **cell potential** is the difference between the electrode potentials (reduction potentials) of the cathode and anode.

The cell **electromotive force (emf)** of the cell is the potential difference between the two electrodes, when no current is flow through the cell.

$$\text{i.e. } E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} \quad \text{Or} \quad E_{\text{cell}} = E_R - E_L .$$



Measurement of Electrode Potential

The potential of individual half-cell cannot be measured.

We can measure only the difference between the two half-cell potentials that gives the emf of the cell.

For this purpose a half-cell called **Standard Hydrogen Electrode (SHE)** or **Normal Hydrogen Electrode (NHE)** is used.

Electrochemical series

It is a series in which various electrodes are arranged in the decreasing order of their reduction potential. In this table, fluorine is at the top indicating that fluorine gas (F_2) has the maximum tendency to get reduced to fluoride ions (F^-). Therefore fluorine gas is the strongest oxidising agent and fluoride ion is the weakest reducing agent.

Lithium has the lowest electrode potential indicating that lithium ion is the weakest oxidising agent while lithium metal is the most powerful reducing agent in an aqueous solution.

Nernst Equation

Nernst proposed an equation to relate the electrode potential of an electrode (or, emf of a cell) with the

electrolytic concentration.

He showed that for the electrode reaction:

$$E_{\text{Cell}} = E_{\text{cell.}}^0 + \frac{2.303RT}{nF} \log [M^{n+}]$$

Where E is constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), F is Faraday constant (96500 C mol^{-1}), T is temperature in Kelvin and $[M^{n+}]$ is the concentration of the species, M^{n+} .

For a general electrochemical reaction of the type:



Nernst equation can be written as:

$$E_{\text{cell}} = E_{\text{cell.}}^0 + \frac{0.0591}{n} \log \frac{[A]^a[B]^b}{[C]^c[D]^d}$$

Equilibrium Constant from Nernst Equation

For a Daniel cell, the emf of the cell at 298K is given by:

$$E_{\text{cell}} = E_{\text{cell.}}^0 + \frac{0.0591}{2} \log \frac{[\text{Cu}^{2+}]}{[\text{Zn}^{2+}]}$$

When the cell reaction attains equilibrium, $E_{\text{cell}} = 0$

$$E_{\text{cell.}}^0 = \frac{0.0591}{n} \log K_c \text{ at } 298 \text{ K}$$

Electrochemical Cell and Gibbs Energy of the Reaction

Electrical work done in one second is equal to electrical potential multiplied by total charge passed.

Also the reversible work done by a galvanic cell is equal to decrease in its Gibbs energy. Therefore, if the emf of the cell is E and nF is the amount of charge passed,

then the Gibbs energy of the reaction, $\Delta G = -nFE$

If the concentration of all the reacting species is unity, then $E_{\text{cell}} = E_{\text{cell.}}^0$. So, $\Delta G^0 = -nFE_{\text{cell.}}^0$

Thus, from the measurement of $E_{\text{cell.}}^0$, we can calculate the standard Gibbs energy of the reaction.

Conductance of Electrolytic Solutions

Resistance (R): The electrical resistance is the hindrance to the flow of electrons. Its unit is ohm (Ω). The resistance of a conductor is directly proportional to the length of the conductor (l) and inversely proportional to the area of cross-section (A) of the conductor.

i.e. $R \propto l/A$

or, $R = \text{constant} \times l/A$

or, $R = \rho \times l/A$, where ρ (rho) is a constant called resistivity. Its unit is ohm-metre ($\Omega \text{ m}$) or ohm-centimetre ($\Omega \text{ cm}$).

$1 \Omega \text{ m} = 100 \Omega \text{ cm}$, $1 \Omega \text{ cm} = 10^{-2} \Omega \text{ m}$

Resistivity is defined as the resistance offered by a conductor having unit length and unit area of cross- section.

Conductance (G): It is the inverse of resistance.

i.e. $G = 1/R$.

Its unit is ohm^{-1} or mho or Siemens (S)

Or, $G = \frac{1}{R} \times A$

P l

Or, $G = k \times A/l$

Where, k is called **conductivity**. It is defined as the conductance of a conductor having unit length and unit area of cross-section.

Its unit is $\text{ohm}^{-1} \text{ m}^{-1}$ or mho m^{-1} or S m^{-1} .

$1 \text{ S cm}^{-1} = 100 \text{ S m}^{-1}$ $1 \text{ S m}^{-1} = 10^{-2} \text{ S cm}^{-1}$

There are of two types of Conductance - electronic or metallic conductance and electrolytic or ionic

conductance.

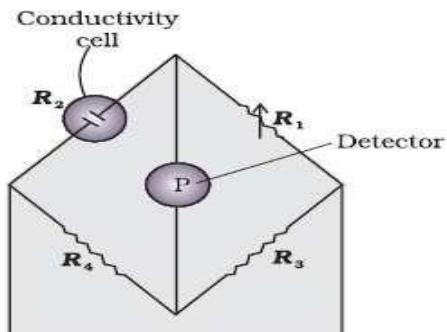
Measurement of the conductivity of ionic solutions

We know that, conductivity $G = k \times A/l$ So conductivity, $k = G \times l/A$

The quantity l/A is called **cell constant** (G^*). It depends on the distance between the electrodes and their area of cross-section. Its unit is m^{-1} .

i.e. conductivity = conductance x cell constant

So in order to determine the conductivity of an electrolytic solution, first determine the resistance by using a Wheatstone bridge. It consists of two resistances R_3 and R_4 , a variable resistance R_1 and the conductivity cell having the unknown resistance R_2 . It is connected to an AC source (an oscillator, O) and a suitable detector (a headphone or other electronic device, P). Direct current (DC) cannot be used since it causes the decomposition of the solution.



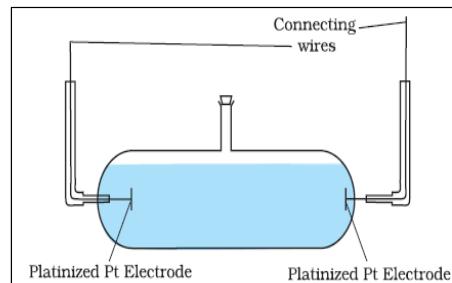
Conductivity cell

The bridge is balanced, when no current passes through the detector. Under this condition,

$$R_1/R_2 = R_3/R_4$$

$$\text{Therefore, the unknown resistance, } R_2 = \frac{R_1 R_4}{R_3}$$

By knowing the resistance, we get the value of conductance and conductivity.



It consists of two platinum electrodes coated with platinum black. The electrodes are separated by a distance l and their area of cross-section is A .

The cell constant of a conductivity cell is usually determined by measuring the resistance of the cell containing a solution whose conductivity is already known (e.g. KCl solution).

Molar conductivity (λ_m)

It is the conductivity of 1 mole of an electrolytic solution kept between two electrodes with unit area of cross section and at a distance of unit length. It is related to conductivity of the solution by the equation, $\lambda_m = k/C$ (where C is the concentration of the solution) Or, $\lambda_m =$

$1000 f_i/M$ (where M is the molarity)

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

$$1 \text{S m}^2 \text{ mol}^{-1} = 10^4 \text{ S cm}^2 \text{ mol}^{-1}$$

$$1 \text{S cm}^2 \text{ mol}^{-1} = 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$$

Variation of conductivity and Molar conductivity with concentration (dilution)

Both conductivity and molar conductivity change with the concentration of the electrolyte.. *For both strong and weak electrolytes, conductivity always decreases with dilution.* This is because conductivity is the conductance of unit volume of electrolytic solution. As dilution increases, the number of ions per unit volume decreases and hence the conductivity decreases.

For both strong and weak electrolytes, the molar conductivity increase with dilution (or decrease with increase in concentration), but due to different reasons.

For strong electrolytes, as dilution increases, the force of attraction between the ions decreases and hence the

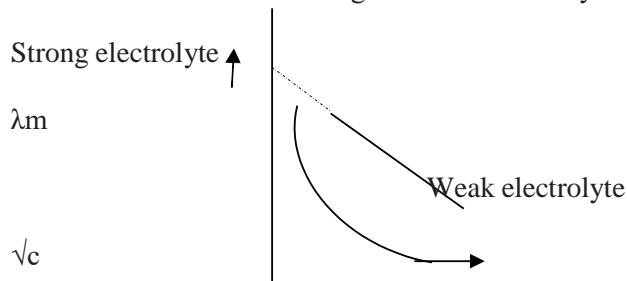
ionic mobility increases. So, molar conductivity increases. When dilution reaches maximum or concentration approaches zero, the molar conductivity becomes maximum and it is called the limiting molar conductivity (λ^0_m).

For strong electrolytes, the relation between λ_m and concentration can be given as: $\lambda_m = \lambda^0 m - A\sqrt{c}$

Where 'c' is the concentration and A is a constant depends on temperature, the nature of the electrolyte and the nature of the solvent. All electrolytes of a particular type have the same value for 'A'.

For weak electrolytes, as dilution increases, the degree of dissociation increases. So the number of ions and hence the molar conductivity increases.

The variation of λ_m for strong and weak electrolytes is shown in the following graphs:



For strong electrolytes, the value of $\lambda^0 m$ can be determined by the extrapolation of the graph. But for weak electrolytes, it is not possible since the graph is not a straight line. So their $\lambda^0 m$ values are calculated by applying Kohlrausch's law of independent migration of ions.

Kohlrausch's law of independent migration of ions

The law states that the limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and the cation of the electrolyte.

Thus if an electrolyte on dissociation gives $n_{(+)}$ cations and $n_{(-)}$ anions, its limiting molar conductivity is given as:

$$\lambda^0 m = n_{(+)} \lambda^0 (+) + n_{(-)} \lambda^0 (-) \quad \text{For NaCl, } \lambda^0 m_{(NaCl)} = \lambda^0_{(Na^+)} + \lambda^0_{(Cl^-)} \quad \text{For CaCl}_2, \lambda^0 m_{(CaCl_2)} = \lambda^0_{(Ca^{2+})} + 2 \times \lambda^0_{(Cl^-)}$$

Applications of Kohlrausch's law

1) Determination of $\lambda^0 m$ of weak electrolytes

By knowing the λ^0m values of strong electrolytes, we can calculate λ^0m of weak electrolytes. For e.g. we can determine the λ^0m of acetic acid (CH_3COOH) by knowing the λ^0m of CH_3COONa , NaCl and HCl as follows:

$$\lambda^0_m (\text{CH}_3\text{COONa}) = \lambda^0\text{CH}_3\text{COO}^- + \lambda^0\text{Na}^+ \quad (1)$$

$$\lambda^0 m(HCl) = \lambda^0 H+ + \lambda^0 Cl \quad (2)$$

$$\begin{aligned}\lambda^0 m (\text{CH}_3\text{COONa}) + \lambda^0 m (\text{HCl}) - \lambda^0 m (\text{NaCl}) &= \lambda^0 \text{CH}_3\text{COO}^- + \lambda^0 \text{Na}^+ + \lambda^0 \text{H}^+ + \lambda^0 \text{Cl}^- - \lambda^0 \text{Na}^+ - \lambda^0 \text{Cl}^- \\ &= \lambda^0 \text{CH}_3\text{COOH}\end{aligned}$$

Determination of degree of dissociation of weak electrolytes

By knowing the molar conductivity at a particular concentration (λ^c) and limiting molar conductivity

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

(λ^0_m), we can calculate the degree of dissociation (α) as,

Electrolytic Cells and Electrolysis

$$\alpha = \frac{\lambda^c m}{\lambda^0 m}$$

In an electrolytic cell, the electrical energy is converted to chemical energy. The dissociation of an electrolyte by the passage of electricity is called electrolysis.

For e.g. when CuSO_4 solution is electrolysed by Cu electrodes, Cu is deposited at the cathode and Cu^{2+} ions are liberated from the anode.

Quantitative Aspects of electrolysis – Faraday's laws

1) Faraday's first law

It states that the amount of substance deposited or liberated at the electrodes (m) is directly proportional to the quantity of electricity (Q) flowing through the electrolyte.

Mathematically, $m \propto Q$
Or, $m = zQ$

Where z is a constant called electrochemical equivalent (ECE). Z = equivalent weight/96500

But quantity of electricity is the product of current in ampere (I) and time in second (t).

i.e. $Q = It$

Therefore, $m = zIt$

1 Faraday is the charge of 1 mole of electron or it is the amount of electricity required to deposit one gram equivalent of any substance. Its value is 96500 C/mol.

For the deposition of 1 mole of Na, the amount of charge required = 1 F (Since $\text{Na}^+ + e^- \rightarrow \text{Na}$)

For Ca, $Q = 2F$ (since $\text{Ca}^{2+} + 2e^- \rightarrow \text{Ca}$)

2) Faraday's second law

It states that *when same quantity of electricity is passed through solutions of different substances, the amount of substance deposited or liberated is directly proportional to their chemical equivalence.*

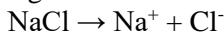
For e.g. when same quantity of electricity is passed through solutions of two electrolytes A and B, then

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

Products of electrolysis

The products of electrolysis depend on the following factors:

i) *The nature of the electrolyte:* The electrolyte may be in molten state or in aqueous solution state. For e.g. if molten NaCl is electrolysed, Na is deposited at the cathode and chlorine is liberated at the anode.



At cathode: $\text{Na}^+ + e^- \rightarrow \text{Na}$ At anode: $\text{Cl}^- \rightarrow \frac{1}{2} \text{Cl}_2 + e^-$

If NaCl solution is electrolysed, we get H₂ gas at the

cathode and Cl₂ gas at the anode. NaCl solution

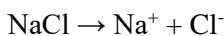
contains 4 ions – Na⁺, Cl⁻, H⁺ and OH⁻

Cathode reaction: $\text{H}^+ + e^- \rightarrow \frac{1}{2} \text{H}_2$ Anode reaction: $\text{Cl}^- \rightarrow \frac{1}{2} \text{Cl}_2 + e^-$

NaOH is formed in the solution. Products of electrolysis

The products of electrolysis depend on the following factors:

ii) *The nature of the electrolyte:* The electrolyte may be in molten state or in aqueous solution state. For e.g. if molten NaCl is electrolysed, Na is deposited at the cathode and chlorine is liberated at the anode.



At cathode: $\text{Na}^+ + e^- \rightarrow \text{Na}$

Anode: $\text{Cl}^- \rightarrow \frac{1}{2} \text{Cl}_2 + e^-$

If NaCl solution is electrolysed, we get H₂ gas at the cathode and Cl₂ gas at the anode. NaCl

solution contains 4 ions – Na⁺, Cl⁻, H⁺ and OH⁻

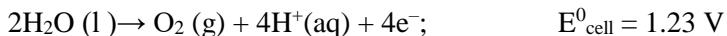
Cathode reaction: $\text{H}^+ + e^- \rightarrow \frac{1}{2} \text{H}_2$

Anode reaction: $\text{Cl}^- \rightarrow \frac{1}{2} \text{Cl}_2 + e^-$

iii) *The type of electrodes used:* If the electrode is inert (e.g. Pt, gold, graphite etc.), it does not participate in the electrode reaction. While if the electrode is reactive, it also participate in the electrode reaction.

iv) *The different oxidising and reducing species present in the electrolytic cell and their standard electrode potentials.* Some of the electrochemical processes are very slow and they do not take place at lower voltages. **So some extra potential (called overpotential) has to be applied, which makes such process more difficult to occur.**

For e.g. during the electrolysis of NaCl solution, the possible reactions at anode are:



At anode, the reaction with lower value of E_{cell}^0 is preferred and so water should get oxidised in preference to $\text{Cl}^-(\text{aq})$. However, on account of overpotential of oxygen, the first reaction is preferred and hence Cl_2 is formed at anode.

Batteries

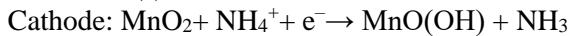
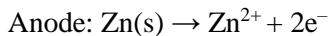
A battery is basically a galvanic cell in which the chemical energy of a redox reaction is converted to electrical energy. They are of mainly 2 types – primary batteries and secondary batteries.

a) Primary cells:

These are cells which cannot be recharged or reused. Here the reaction occurs only once and after use over a period of time, they become dead. E.g. Dry cell, mercury button cell etc.

1. Dry Cell

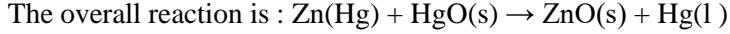
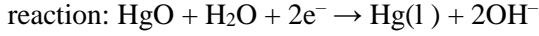
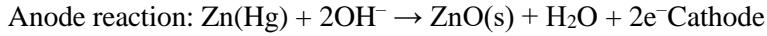
It is a compact form of Leclanche cell. It consists of a zinc container as anode and a carbon (graphite) rod surrounded by powdered manganese dioxide (MnO_2) and carbon as cathode. The space between the electrodes is filled by a moist paste of ammonium chloride (NH_4Cl) and zinc chloride (ZnCl_2). The electrode reactions are:



Ammonia produced in this reaction forms a complex with Zn^{2+} and thus corrodes the cell. The cell has a potential of nearly 1.5 V.

2. Mercury cell

Here the anode is zinc – mercury amalgam and cathode is a paste of HgO and carbon. The electrolyte is a paste of KOH and ZnO . The electrode reactions are:



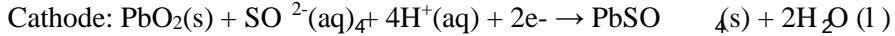
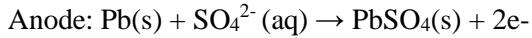
The cell has a constant potential of 1.35 V, since the overall reaction does not involve any ion in solution.

b) Secondary cells

A secondary cell can be recharged and reused again and again. Here the cell reaction can be reversed by passing current through it in the opposite direction. The most important secondary cell is lead storage cell, which is used in automobiles and invertors.

It consists of lead as anode and a grid of lead packed with lead dioxide (PbO_2) as the cathode. The electrolyte is 38% H_2SO_4 solution.

The cell reactions are:



The overall cell reaction is: $\text{Pb}(\text{s}) + \text{PbO}_2(\text{s}) + 2\text{H}_2\text{SO}_4(\text{aq}) \rightarrow 2\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{l})$

On charging the battery, the reaction is reversed and $\text{PbSO}_4(\text{s})$ on anode and cathode is converted into Pb and PbO_2 , respectively.

Another example for a secondary cell is nickel – cadmium cell. Here the overall cell reaction is

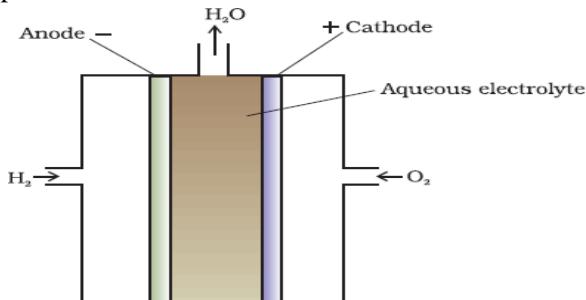


Fuel cells

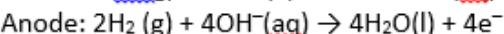
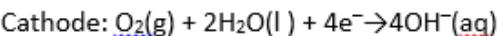
These are galvanic cells which convert the energy of combustion of fuels like hydrogen, methane, methanol, etc. directly into electrical energy.

One example for fuel cell is **Hydrogen – Oxygen fuel cell**, which is used in the Apollo space programme.

Here hydrogen and oxygen are bubbled through porous carbon electrodes into concentrated aqueous sodium hydroxide solution. To increase the rate of electrode reactions, catalysts like finely divided platinum or palladium metal are filled into the electrodes.



The electrode reactions are:



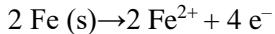
Advantages of Fuel cells

1. The cell works continuously as long as the reactants are supplied.
2. It has higher efficiency as compared to other conventional cells.
3. It is eco-friendly (i.e. pollution free) since water is the only product formed.
4. Water obtained from H₂ – O₂ fuel cell can be used for drinking.

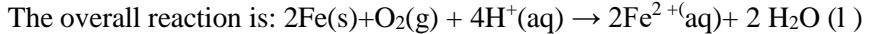
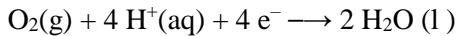
Corrosion

It is the process of formation of oxide or other compounds of a metal on its surface by the action of air, water-vapour, CO₂ etc. Some common examples are: The rusting of iron, tarnishing of silver, formation of green coating on copper and bronze (verdigris) etc.

Most familiar example for corrosion is rusting of iron. It occurs in presence of water and air. It is a redox reaction. At a particular spot of the metal, oxidation takes place and that spot behaves as anode. Here Fe is oxidized to Fe²⁺.



Electrons released at anodic spot move through the metal and go to another spot on the metal and reduce oxygen in presence of H⁺. This spot behaves as cathode. The reaction taking place at this spot is:



The ferrous ions (Fe²⁺) are further oxidised to ferric ions (Fe³⁺) and finally to hydrated ferric oxide (Fe₂O₃. x H₂O), which is called rust.

Methods to prevent corrosion

1. By coating the metal surface with paint, varnish etc.
2. By coating the metal surface with another electropositive metal like zinc, magnesium etc. The coating of metal with zinc is called galvanisation and the resulting iron is called galvanized iron.
3. By coating with anti-rust solution.
4. An electrochemical method is to provide a sacrificial electrode of another metal (like Mg, Zn, etc.) which corrodes itself but saves the object (sacrificial protection).

Mind map

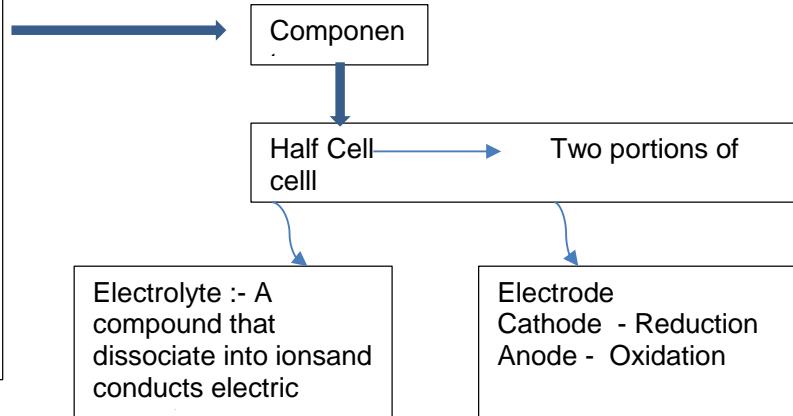
Types of Cells

Electrochemical cell:- The electrodes are fitted in same electrolyte or different electrolytes joined by a salt

Electrolytic cell :- Device in which conversion of electrical energy into chemical energy is done.

Galvanic cell:- It involves a redox reaction for the conversion of chemical energy into electrical energy

Daniell cell:-
Cathod :- copper metal
Anode :- Zinc metal
Electrolyte :- Aqueous salt solution of the metal involved
Cell reaction
Reduction :- $Cu^{2+} + 2 e^- \rightarrow Cu(s)$ (cathode)
Oxidation:- $Zn(s) \rightarrow Zn^{2+} + 2 e^-$ (anode)
Cell representation
 $Zn|Zn^{2+}(1M)||Cu^{2+}(1M)|Cu$
Anode salt cathode
bridge



Electrode

Salt Bridge :- U- shape inverted tube connecting two electrolytic solution

Standard electrode potential- Electrode potential when concentration of all species in half cell is unity at 298 K.

Potential difference between electrode

Positive E^0 – weaker reducing agent than $H+/H_2$

Negative E^0 – strong reducing agent than $H+/H_2$

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

Electrochemical series:- A series of half cells arranged in increasing order of standard electrode potential.

Nernst Equation



$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{2.303RT}{nF} \log \frac{[\text{M}]}{[\text{M}^{n+}]}$$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{1}{[\text{M}^{n+}]}$$

At equilibrium

$$E_{\text{cell}}^{\circ} = \frac{2.303RT}{nF} \log K_c$$

or,

$$E_{\text{cell}}^{\circ} = \frac{0.0591}{n} \log K_c \text{ at } 298 \text{ K}$$

Relation between cell potential and Gibb's energy

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

Relation between Equilibrium constant and Gibb's energy

$$\Delta G^{\circ} = - \frac{2.303RT}{n} \log K_c$$

Electrical Resistance:- $R = \frac{1}{P} \times \frac{A}{l}$

Unit : ohm ; P= resistivity unit: Ohm-metre

Measured by conductivity cell

Conductance (G) : Inverse of resistance

$$G = \frac{1}{R} \text{ unit : Simenes}$$

R
Increasing on dilution of solution

Molar conductivity (Λ_m): $\Lambda_m = \frac{k}{C}$ k is in $\text{Sm}^{-1} \text{ C}^{-1}$
 $= \text{mol m}^{-3}$

$$\Lambda_m = \text{Sm}^2 \text{ mol}^{-1} \quad \text{or} \quad \text{Scm}^2 \text{ mol}^{-1}$$

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

Limiting molar conductivity (Λ_m^0)
If molar conductivity reaches a limiting value when $c \rightarrow 0$, $\Lambda_m = \Lambda_m^0$

$$\text{Strong electrolyte} \quad \Lambda_m = \Lambda_m^0 - Ac^{1/2}$$

$$\text{Weak electrolyte} \quad \alpha = \frac{\Lambda_m}{\Lambda_m^0}$$

Kohlrausch's law of independent migration of ions:

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

$$\Lambda_m^0 (\text{CH}_3\text{COONa}) = \lambda^0 \text{CH}_3\text{COO}^- + \lambda^0 \text{Na}^+ \quad \Lambda_m^0 (\text{NaCl}) = \lambda^0 \text{Cl}^- + \lambda^0 \text{Na}^+ \quad \Lambda_m^0 (\text{MgCl}_2) = \lambda^0 \text{Cl}^- + \lambda^0 \text{Mg}^{2+}$$

Application :- (i) To calculate Λ_m^0 for any electrolyte from λ^0 of individual ion.

(ii) To determine value of degree of dissociation and dissociation constant for weak electrolytes.

(iii) To calculate Λ_m^0 for weak electrolyte using Λ_m^0 of strong electrolyte

$$\begin{aligned} \lambda^0 \text{CH}_3\text{COOH} &= \lambda^0 \text{m} (\text{CH}_3\text{COONa}) + \lambda^0 \text{m} (\text{HCl}) - \lambda^0 \text{m} (\text{NaCl}) \\ &= \lambda^0 \text{CH}_3\text{COO}^- + \lambda^0 \text{Na}^+ + \lambda^0 \text{H}^+ + \lambda^0 \text{Cl}^- - \lambda^0 \text{Na}^+ - \lambda^0 \text{Cl}^- \end{aligned}$$

Faraday's Law of

First law $m = Zit$ Where Z is electrochemical equivalent

$$\text{Second law} : \frac{m_1}{m_2} = \frac{E_1}{E_2}$$

Where E = $\frac{\text{atomic mass}}{\text{valency}}$

Products of electrolysis

- (i) Nature of material being electrolysed
- (ii) Type of electrodes
- (iii) Concentration of electrolyte

Corrosion

Electrochemical phenomenon in which metal oxide or metal forms coating on the metal surface.

Rusting of Iron , Tarnishing of silver

Methods of prevention of Rusting

1. Barrier Protection : Painting, oiling and greasing
2. Sacrificial protection : Galvanization process
3. Electrical or Cathodic protection for underground pipes
4. Using Anti-rust solutions : Alkaline Phosphate or alkaline chromate solutions.

Batteries

Primary Batteries reaction occurs only once and cannot be reused.
Mercury cell. Leclanche cell or dry cell

Secondary batteries can be recharged by passing current in opposite direction and can be reused. Lead storage Battery, Nickel- cadmium cell.

MCQ (1x10)

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) $1.93 \times 10^5 \text{ C}$
 - (b) $9.65 \times 10^4 \text{ C}$
 - (c) $3.86 \times 10^5 \text{ C}$
 - (d) $4.825 \times 10^5 \text{ C}$
4. The standard reduction potentials of Cu^{2+}/Cu and $\text{Cu}^{2+}/\text{Cu}^+$ 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
5. 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) $\text{Y} > \text{Z} > \text{X}$
 - (b) $\text{X} > \text{Y} > \text{Z}$
 - (c) $\text{Z} > \text{Y} > \text{X}$
 - (d) $\text{Z} > \text{X} > \text{Y}$
6. For a spontaneous reaction,? ΔG , equilibrium constant K and E°_{cell} will be respectively.
 - (a) - ve > 1, + ve
 - (b) + ve > 1 - ve
 - (c) -ve, < 1, -ve
 - (d) -ve, > 1, -ve
7. 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
8. Standard electrode potentials are Fe^{2+}/Fe , $E^\circ = -0.44$; $\text{Fe}^{3+}/\text{Fe}^{2+}$, $E^\circ = 0.77 \text{ V}$. Fe^{2+} , Fe^{3+} and Fe blocks are kept together then
 - (a) Fe^{3+} increases
 - (b) Fe^{3+} decreases
 - (c) $\text{Fe}^{2+}/\text{Fe}^{3+}$ remains unchanged
 - (d) Fe^{2+} decreases?
9. The $E^\circ_{\text{M}^{3+}/\text{M}^{2+}}$ values for Cr, Mn, Fe and Co are -0.41, + 1.57, + 0.77 and +1.97 V respectively. For which one of the metals, the change in oxidation state from +2 to +3 is easiest?
 - (a) Cr
 - (b) Mn
 - (c) Fe
 - (d) Co
10. 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

2-mark Questions

1. Electrolysis of KBr(aq) gives Br₂ at anode but does not give F₂. Give a reason.
2. For the standard cell, Cu(s) | Cu²⁺ (aq) || (aq Ag⁺ | Ag(s), E°_{Cu2+/Cu} = + 0.34V E°_{Ag+/Ag} = 0.80 V,
 - (i) Identify the cathode and the anode as the current is drawn from the cell.
 - (ii) Write the reaction taking place at the electrodes.
 - (iii) Calculate the standard cell potential
3. The cell reaction as written is spontaneous if the overall EMF of the cell is positive. Comment on this statement.
4. Write any three differences between potential difference and e.m.f.
5. State Kohlrausch law of independent migration of ions. Why does the conductivity of a solution decreases with dilution?

3-Mark Questions

1. If a current of 0.5 ampere flows through a metallic wire for 2 hours, then how many electrons would flow through the wire?
2. Write the chemistry of recharging the lead storage battery, highlighting all the materials that are involved during recharging.
3. Calculate Equilibrium constant K for the reaction at 298K Zn(s) + Cu²⁺ (aq) ⇌ Zn²⁺ (aq) + Cu E°_{Zn²⁺/Zn} = -0.076V, E°_{Cu²⁺/Cu} = +0.34V.
4. What is the cell potential for the cell at 25°C Cr / Cr³⁺ 10.1 m] // Fe²⁺ (0.01m) / Fe
 $E^0_{Cr+/Cr} = -0.74V, E^0_{Fe^{2+}/Fe} = -0.44V$.

5-Mark Questions

1. (a) The conductivity of 0.20 mol L⁻¹ solution of KC1 is 2.48 X 10⁻² S cm⁻¹. Calculate its molar conductivity and degree of dissociation
 (a). Given λ[°](k⁺) = 73.5 S cm² mol⁻¹ and λ[°](cl⁻) = 76.5 S cm² mol⁻¹.
 (b) What type of battery is mercury cell? Why is it more advantageous than dry cell?
2. (a) State Faraday's first law of electrolysis. How much charge in terms of Faraday is required for the reduction of 1 mol of Cu²⁺ to Cu?
 (b) Calculate emf of the following cell at 298 K:
 Mg(s) | Mg²⁺(0.1 M) || Cu²⁺(0.01) | Cu(s) [Given E°_{cell} = + 2.71 V, 1 F = 96500 C mol⁻¹]

Assertion and Reason Type Questions

In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the following choices:

- (a) Both Assertion and Reason are true and the Reason is the correct explanation for Assertion.
- (b) Both Assertion and Reason are true and the Reason is not correct explanation for Assertion
- (c) Assertion is true but the Reason is false.
- (d) Both Assertion and Reason are false.
- (e) Assertion is false but Reason is true.

1. Assertion (A): Cu is less reactive than hydrogen.
Reason (R): $E^\circ_{Cu^{2+}/Cu}$ is negative.
2. Assertion (A): E cell should have a positive value for the cell to function.

Reason (R). $E_{\text{cadlode}} - E_{\text{anode}}$

3. Assertion (A): Conductivity of all electrolytes decreases on dilution.
Reason (R): On dilution number of ions per unit volume decreases.
4. Assertion (A): Mercury cell does not give steady potential.
Reason (R): In the cell reaction, ions are not involved in solution.
5. Assertion (A): Electrolysis of NaCl solution gives chlorine at anode instead of O₂.
Reason (R): Formation of oxygen at anode requires overvoltage.

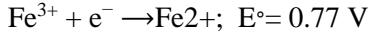
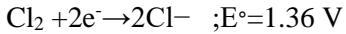
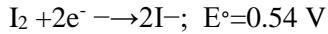
Case based question

1. Read the passage given below and answer the following questions:

Standard electrode potentials are used for various processes:

- (i) It is used to measure relative strengths of various oxidants and reductants.
- (ii) It is used to calculate standard cell potential.
- (iii) It is used to predict possible reactions.

A set of half-reactions (in acidic medium) along with their standard reduction potential, E° (in volt) values are given below



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

(i) Which of the following statements is correct?

- (a) Cl⁻ is oxidised by O₂
- (b) Fe²⁺ is oxidised by iodine
- (c) I⁻ is oxidised by chlorine.
- (d) Mn²⁺ is oxidised by chlorine

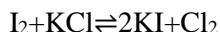
(ii) Mn³⁺ is not stable in acidic medium, while Fe³⁺ is stable because

- (a) O₂ oxidises Mn²⁺ to Mn³⁺
- (b) O₂ oxidises both Mn²⁺ to Mn³⁺ and Fe²⁺ to Fe³⁺
- (c) Fe³⁺ oxidises H₂O to O₂
- (d) Mn³⁺ oxidises H₂O to O₂

(iii) The strongest reducing agent in the aqueous solution is

- (a) I⁻
- (b) Cl⁻
- (c) Mn²⁺
- (d) Fe²⁺

(iv) The emf for the following reaction is



- (a) -0.82 V
- (b) + 0.82 V
- (c) -0.73 V
- (d) +0.73

2. Read the passage given below and answer the following questions:

The concentration of potassium ions inside a biological cell is at least twenty times higher than the outside. The resulting potential difference across the cell is important in several processes such as transmission of nerve impulses and maintaining the ion balance. A simple model for such a concentration cell involving a metal M is $M_{(s)} | M^+(aq.; 0.05 \text{ molar}) || M^+(aq.; 1 \text{ molar}) | M_{(s)}$.

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

(i) For the above cell,

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

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

- (a) < 1 (b) $= 1$ (c) > 1 (d) zero

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

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

(iv) The potential of an electrode change with change in

- | | |
|---------------------------------------|----------------------------|
| (a) concentration of ions in solution | (b) position of electrodes |
| (c) voltage of the cell | (d) all of these |

MCQ (1x10)

1. Answer: (c) Velocity of both K^+ and NO_3^- are nearly same
2. Answer: (c) Zinc
3. Answer: (a) $1.93 \times 10^5 C$
4. Answer: (c) 0.521V
5. Answer: (a) $Y > Z > X$
6. Answer: (a) -ve > 1 , +ve
7. Answer: (c) 3 F
8. Answer: (b) Fe^{3+} decreases
9. Answer: (a) Cr
10. Answer: (d) 0.1 M difluoro acetic acid

2 Mark Questions

1. Ans: Oxidation takes place at anode. Now higher the oxidation Potential, easier to oxidize. Oxidation potential of Br^- , H_2O , F^- are in the following order. $Br^- < H_2O < F^-$. Therefore in aq Solution of KBr. Br^- ions are oxidized to Br_2 in preference to H_2O . On the other hand, in aqueous solution of KF, H_2O is oxidized in preference to F^- . Thus in this case oxidation of H_2O at anode gives O_2 and no F_2 is produced.

2. Ans: (i) From the cell representation, Ag / Ag^+ electrode is cathode and Cu / Cu^{2+} an electrode is anode.

ii. Ans: At anode: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$, At cathode $Ag^+(aq) + 2e^- \rightarrow Ag(s)$

iii. $E^0_{cell} = E^0_{cathode} - E^0_{anode}$, $E^0_{cell} = E^0_{Ag^+|Ag} - E^0_{Cu^{2+}|Cu}$,

$$E^0_{cell} = 0.80V - (+0.34V) = 0.46V$$

3. Ans :- If the e.m.f of a cell is positive, then the Gibbs free energy of the overall reaction is less than zero.

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

Therefore, if E_{cell} is positive, then the cell reaction is spontaneous.

4. Ans.

E.M.F	POTENTIAL DIFFERENCE
1. It is the difference between the electrode potential of two electrodes when no current is flowing through the circuit.	1. It is the difference of potential between the electrodes in a closed circuit.
2. It is the maximum voltage obtained from a cell.	2. It is less than the maximum voltage obtained from a cell.

$$\begin{aligned}
E_{cell} &= \left(E_{Fe}^{0^-} + /_{Fe} - E_{Cr}^{0^+} /_{Cr} \right) - \frac{0.059}{6} \log \frac{[Cr^{3+}]^2}{[Fe^{2+}]^3} \\
&\quad - \frac{0.059}{6} \log \frac{(0.10)^2}{(0.01)^3} \\
&= (-0.44V - (-0.74V)) - \\
&\quad 0.3V - \frac{0.059}{6} \log 10^4 \\
&= 0.3V - 0.0394V \\
&= +0.2606 V
\end{aligned}$$

5-Mark Questions

a. answer

(a) $M = 0.20 \text{ mol L}^{-1}$, $\kappa = 2.48 \times 10^{-2} \text{ S cm}^{-1}$, $\Lambda_m = ?$, $\alpha = ?$

$$\lambda_{(K+)}^\circ = 73.5 \text{ S cm}^2 \text{ mol}^{-1}, \lambda_{(Cl^-)}^\circ = 76.5 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\Lambda_{(KCl)}^\circ = \lambda_{(K+)}^\circ + \lambda_{(Cl^-)}^\circ = 73.5 + 76.5 = 150.0 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\text{Now, } \Lambda_m = \frac{1000 \kappa}{M} = \frac{1000 \times 2.48 \times 10^{-2}}{0.20}$$

$$\Rightarrow \Lambda_m = \frac{248}{2} = 124 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\therefore \alpha = \frac{\Lambda_m}{\Lambda_m^\circ} = \frac{124}{150.0} = 8.26 \times 10^{-1}$$

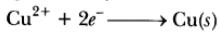
$$\Rightarrow \alpha = 8.26 \times 10^{-1} \times 10^2 = 82.6\%$$

(b) Mercury cell is primary cell because it is not rechargeable.

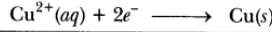
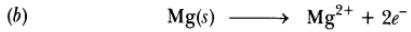
Its efficiency is higher than dry cell. Its voltage remains constant over long period of time.

b. answer

(a) It states that the mass of the substance deposited is directly proportional to charge passed through electrolyte.



2 Faraday of charge is required to deposit 1 mole of copper, i.e. 63.5 g of Cu.



$$E_{cell} = E_{cell}^\circ - \frac{0.0591}{2} \log \frac{[Mg^{2+}]}{[Cu^{2+}]} = 2.71 \text{ V} - \frac{0.0591}{2} \log \frac{0.1}{0.01}$$

$$\Rightarrow E_{cell} = 2.71 \text{ V} - \frac{0.0591}{2} \log 10 = 2.71 \text{ V} - 0.0295 = 2.68 \text{ V.}$$

Assertion and Reason Type Questions

1. Solution: (c) Cu is less reactive than hydrogen because $E^\circ_{Cu^{2+}/Cu}$ is positive.
2. Solution: (c) $E_{cell} = E_{cathode} - E_{anode}$. To have positive value of E_{cell} , $E_{cathode} > E_{anode}$.
3. Solution: (a) Conductivity depends on number of ions per unit volume which decreases on dilution of electrolytes.
4. Solution: (e) Mercury cell gives a steady potential because in the cell reaction ions are not involved in the solution.
5. Solution: (a) Formation of oxygen has lower value of E° than formation of chlorine even though it is not formed because it requires overvoltage.

Case based question

Answer 1:

- i. Ans (c) : The half cell having the higher reduction potential will undergo reduction process.
- ii. Ans- (d) : Electrode potential of Mn^{3+} is higher than O_2 .
- iii. Ans; - (a) I⁻ Due to least electrode potential value

iv. Ans: (a) -0.82V

Answer 2:

- i. Ans- (b)
- ii. Ans- (c)
- iii. Ans- b
- iv. Ans (a)