ELECTROCHEMISTRY

ELECTROLYTIC CELLS AND ELECTROLYSIS

ELECTROLYTIC CELL AND ELECTROLYSIS AND FARADAY'S LAW: -

ELECTROLYTIC CELL: -

This cell converts electric energy into chemical energy. The entire assembly except that of the external battery is known as the electrolytic cell.



Cell reaction :

 $\operatorname{Zn} + \operatorname{Cu}^{+2} \longrightarrow \operatorname{Zn}^{+2} + \operatorname{Cu}$

Representation of Galvanic cell.



Chemistry

ELECTROLYSIS: -

- 1. Electrolyte is a combination of cations and anions which in fused state can conduct electricity.
- 2. This is possible due to the movement of ions from which it is made of and electrolyte.
- 3. The process of using an electric current to bring about chemical change is called electrolysis.
- 4. Electrolysis is a process of oxidation and reduction due to current in the electrolyte.

The product obtained during electrolysis depends on following factors.

- > The nature of the electrolyte
- The concentration of electrolyte
- > The charge density flowing during electrolysis.
- > The nature of the electrode

ACTIVE v/s INACTIVE ELECTRODES

- 1. The metal electrodes in the cell that are active because the metals themselves are components of the half reactions.
- As the cell operates, the mass of the zinc electrode gradually decreases, and the [Zn²⁺] in the anode half cell increases. At the same time, the mass of the copper electrode increases and the [Cu²⁺] in the cathode half cell decreases; we say that the Cu²⁺ "plates out" on the electrode.
- 3. For many redox reactions, however, there are no reactants or products capable of serving as electrodes. Inactive electrodes are used, most commonly rods of graphite or platinum, materials that conduct electrons into or out of the cell but cannot take part in the half -reactions.
- 4. In a voltaic cell based on the following half reactions, for instance, the species cannot act as electrodes :

 $2I^{-}(aq) \rightarrow I_{2}(s)$ $2e^{-}[anode; oxidation]$

 $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(\ell)$ [cathode ; reduction]

Therefore, each half – cell consists of inactive electrodes immersed in an electrolyte solution that contains all the species involved in that half -reaction. In the anode half-cell, I⁻ ions are oxidized to solid I₂. The electrons released flow into the graphite anode, through the wire, and into the graphite cathode. From there, the electrons are consumed by MnO_4 - ions as they are reduced to Mn^{2+} ions.

Chemistry

Examples of Electrolysis

➤ Using inert (pt/graphite) electrodes Cathode (red) : Pb²⁺ + 2e⁻ → Pb(s) E⁰ = 0.126 v Anode : 2Br → Br₂ + 2e⁻E⁰ = -1.08 V E_{cell} = -0.126 - (0.108) × 10 = -1.206 v E_{ext} > 1.206 V

Electrolysis of CuSO₄ molten

 $\begin{array}{ll} \mbox{Cathode: } \mbox{Cu}^{2+} + 2e^- \rightarrow \mbox{Cu} & \mbox{E}^0 = +0.34 \ \nu \\ \mbox{Anode: } 2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^- & \mbox{E}^0 = -2.05 \ \nu \\ \mbox{H}_2S_2\mbox{H}_8 - \mbox{Marshall's acid peroxy disulphuric acid.} \\ \mbox{E}_{cell} = 0.34 - (2.05) = -1.71 \nu & (negative \div \mbox{not feasible}) \end{array}$

$$H - O - S - O - O - S - O - H$$

Electrolysis of aq CuSO₄

Cathode :	$Cu^{2+} + 2e^- \rightarrow Cu(s)$	$E^0 = 0.34 v$
	$2e + 2H_2O(\ell) \to H_2(g) + 2OH - (aq)$	$E^0 = -0.83 v$
Anode:	$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^-$	$E^0 = -2.05 v$
	$2H_2O(\ell) \rightarrow O_2 + 4H^+ + 4e^-$	$E^0 = -1.23 v$

➢ Electrolysis of aq NaBr solution (initially PH = 7)
Cathode: Na⁺(aq) + e⁻ → Na(s)
E⁰ = -2v
2e⁻ + 2H₂O(ℓ) → H₂ + 2OH⁻
E⁰ = -0.83v

Anode:	$2Br_r \rightarrow Br_2 + 2e^-$	$E_{Ox}^0 = -1.08v$
	$2H_2O(\ell) \rightarrow O_2 + 4H^+ + 4e^-$	$E_{Ox}^{0} = -1.23\nu$

Electrolysis of aq NaCl

Cathode: $Na^+ + e^- \rightarrow Na$	$E^0 = -2v$
$2e^{-} + 2H_2O(\ell) \rightarrow H_2) + 2OH^{-}$	$E^0 = -0.83 v$

Chemistry

Anode:	$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$	$E_{OX}^0 = -1.30 v$
	$2H_2O(\ell) \rightarrow O_2 + 4H^+ + 4e^-$	$E_{OX}^{0} = -1.23 v$

Rate of production of Cl_2 is more than rate of production of O_2 gas.

Electrolysis using attackable (reactive) electrodes.

Electrolysis of aq. CuSO ₄ using Cu electrode.	
Cathode (reduction) : $Cu^{2+} + 2e^- \rightarrow Cu$	$E^0 = -0.83v$
$2\mathrm{H}_2\mathrm{O}(\ell) + 2\mathrm{e}^- \rightarrow \mathrm{H}_2\mathrm{g}) + 2\mathrm{OH}^-$	$E^0 = -0.83v$
Anode (oxidation): $SO_4^{2-} \to S_2O_8^{2-} + 2e^-$	$E_{OX}^0 = -2.05v$
$2H_2O(\ell) \rightarrow O_2 + 2H^+ + 4e^-$	$E^0 = -1.23 v$
$Cu(s) \rightarrow Cu^{2+} + 2e -$	$\mathrm{E}^{\mathrm{0}}=-0.34~\nu$
electrolytic refining	

AgNO₃(aq) using Cu cathode & Ag anode.

Cathode:	$Ag^+ + e^- \rightarrow Ag(s)$	$E^0 = -0.083v$
	$2\mathrm{H}_2\mathrm{O}(\ell) + 2\mathrm{e}^- \rightarrow \mathrm{H}_2\mathrm{g}) + 2\mathrm{OH}^-$	$E^0 = -0.083v$
Anode:	$NO_3 \rightarrow X(No reaction)$	
	$2H_2O(\ell) \rightarrow O_2 + 4H^+ + 4e^-$	$E^0 = -1.23 v$
	$Ag(s) \rightarrow Ag^+(aq) + e^-$	$\mathrm{E}^{\mathrm{0}}=-0.80\nu$

FARADAY'S LAWS OF ELECTROLYSIS:

Michael Faraday deduced two important laws:

(a) FARADAY'S FIRST LAW OF ELECROLYSIS

This law states that "The amount of a substance deposited or dissolved at an electrode is directly proportional to the charge passing through the electrolytes.

If a current of I amperes is passed for t seconds, the quantity of charge Q in coulombs. If W, gram of substances is deposited by Q coulombs of electricity, then

 $W \propto Q \propto It$

$$W = Z It = \frac{E}{96500} It$$

Where Z is constant of proportionality and is known as electrochemical equivalent.

▶ When Q = 1 coulomb, W = Z

thus, electro chemical equivalent may be defined as the weight in grams of an element liberated by the passage of 1 coulomb of electricity

Ex. How many cc of chlorine will be deposited by 100 amp. current flowing for 5 hours through melted NaCl.

Sol. $Q = It = 100 \times 5 \times 60 \times 60 = 18 \times 10^5$

W = ZQ =
$$\frac{E}{96500} \times 18 \times 10^5 = \frac{18E}{96500} \times 10^5 = \frac{18 \times 35.5}{965} \times 10^3 = 662.2g$$

 \therefore Volume of 71g Cl₂ at NTP = 22.4L

: Volume of 662.2 g Cl₂ at NTP = $\frac{22.4}{71} \times 662.2 = 208.9L$

Ex. The time required to coat a metal surface of 80 cm² with 0.005mm thick layer of silver (density = 10.5 g cm^{-3}) with the passage of 3A current through silver nitrate solution is –

Sol. Volume of layer of silver = $0.005 \times 10^{-1} \times 80 = 0.04$ cm³

 \therefore Mass = Density × volume = $10.5 \times 0.04 = 0.42$ g

So

$$w = \frac{E}{96500} \times \text{It} \Rightarrow 0.42 = \frac{108}{96500} \times 3 \times \text{t}$$
$$t = \frac{0.42 \times 96500}{108 \times 3} = 125.09 \text{ seconds.}$$

(b) FARADAY'S SECOND LAW: -

This law states that the amounts of different substances deposited at electrodes by passage of the same quantity of electricity are proportional to their chemical equivalent (E).

 $W \propto E$

If W_1 and W_2 be the amounts of two different substances deposited at electrodes and E_1 and E_2 be the equivalent weights then –

$$\frac{W_1}{W_2} = \frac{E_1}{E_2}$$

Chemistry

combining the two laws

 $W \propto It E W = \frac{ItE}{E}$

Where $\frac{1}{F}$ is proportionality constant and F is called faraday.

when It = F then W = E

Hence faraday (F) is the quantity of charge in coulombs required to deposit one g equivalent of any substance. The Faraday (F) is also the quantity of charge carried by one mole of electrons.

 $F = e \times N = 1.6 \times 10^{-19} \times 6.023 \times 10^{23} = 96500$ coulombs.

PRODUCTS OF ELECTROLYSIS: -

During electrolysis, the reactions occurring at the electrodes are oxidation and reduction reactions. The products of electrolysis depend on the nature of material being electrolysed and the types of electrodes being used. If the electrode is inert such as gold or platinum, it does not take part in the chemical reaction and acts only as a source or sink for electrons.

If the electrode is reactive, it takes part in the electrode reaction. Thus, the products of electrolysis may be different for inert and reactive electrodes.

- 1) The products of electrolysis mainly depend on the different oxidising and reducing species present in the electrolytic cell and their standard electrode potentials.
- 2) Some electrochemical processes, though feasible are so slow kinetically that at lower voltages, these do not seem to occur. The slowness of electrode reaction creates electrical resistance at the electrode surface. Therefore, for the occurrence of such reactions some extra potential or voltage is required than the theoretical value of their standard electrode potential. This extra voltage required is called over voltage.