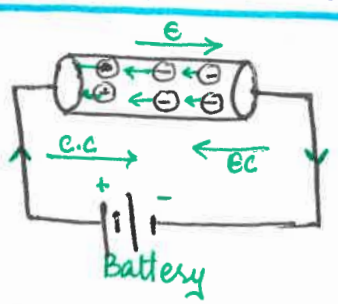
6. ELECTROLYSIS

- CONDUCTORS AND NON-CONDUCTORS:
  - Conductors are materials or substances which allow the passage of electric current.
    Most metallic elements like copper, aluminium, iron, some alloys whether in solid state or in molten state, allow an electric current to pass through them without undergoing any chemical change.
  - Non-conductors are materials or substances which do not allow the passage of electric current.
    Eg: Non-metals.

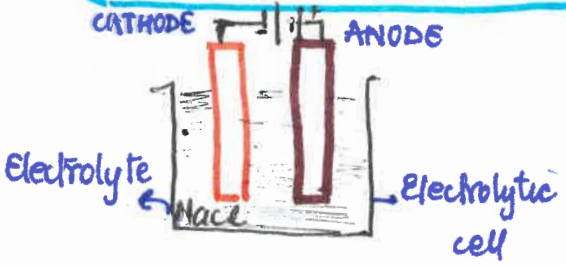
CONDUCTORS

METALLIC CONDUCTORS



- Flow of current consists of a single stream of electrons flowing from the -ve pole to the +ve pole.
- Current carrying particles are electrons which are extremely small
- This is a physical process as no change of form or composition occurs during conduction of electricity.
- Metals both in solid and liquid state are good conductors of electricity.

ELECTROLYTIC CONDUCTORS



- Flow of current consists of two streams, one of the +ve cations flowing towards the -ve cathode and -ve anions flowing towards the +ve anode.
- Current carrying particles are ions
- New products are formed at the electrodes. This involves chemical changes
- Electrolytes are good conductors only in aqueous solution or in molten state.

• **ELECTROLYSIS :** It is a process of decomposition of a chemical compound in aqueous solution or in molten state accompanied by a chemical change using direct electric current.

• **Electrolytes :** They are compounds which either in aqueous solutions or in molten state allow electric current to pass through them.

ELECTROLYTES

STRONG ELECTROLYTES

- Electrolytes which allow a large amount of electricity to flow through them.
- They are almost, completely dissociated in fused or in aqueous state. These solutions contain only free ~~ions~~ mobile ions.

Eg: Acids – HCl, H_2SO_4, HNO_3

Bases – NaOH, KOH (aq. or molten state)

Salts – NaCl (molten or aqueous)
$PbBr_2$ (molten), $CuCl_2$ (aq), $CuSO_4$ (aq)

WEAK ELECTROLYTES

- Electrolytes which allow small amount of electricity to flow through them.
- These are partially dissociated in fused or aqueous solution state. These solutions contain ions as well as molecules.

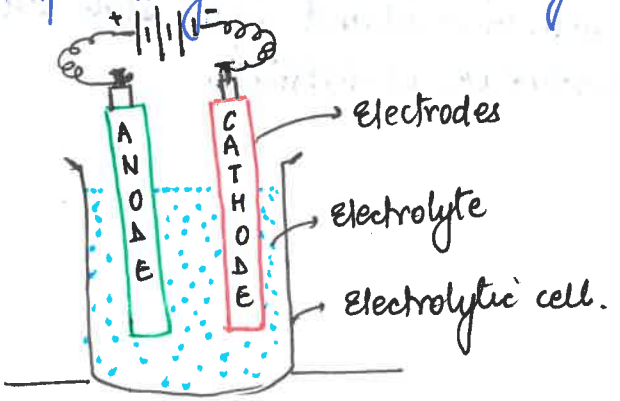
Eg: Acids: H_2CO_3, CH_3COOH, Oxalic acid

Bases – NH_4OH, $Cu(OH)_2$

Salts – $(CH_3COO)_2Pb$, $(NH_4)_2CO_3$

• **NON-ELECTROLYTES :** It is a compound which neither in solution nor in molten state allows an electric current to pass through it.
Eg: Distilled water, alcohol, kerosene, glucose, urea etc.

• **ELECTROLYTIC CELL (VOLTAMETER)** A non-conducting vessel containing two electrodes immersed in a solution of electrolytes used to bring about a chemical reaction.



• **ELECTROCHEMICAL CELL:** It is a device used to convert chemical energy into electrical energy.

Eg: Daniel cell, Simple voltaic cell.

• **ELECTRODES:** Two metal plates or wires or graphite rods or gas carbon rods immersed in the electrolyte through which the current enters and leaves the electrolytic cell are called electrodes.

Electrodes

Anode
- positive electrode
- Anions migrate to the anode
- It is an oxidising electrode. Oxidation takes place at anode
- Anions → -vely charged ions

Cathode
- negative electrode
- cations migrate to the cathode
- It is a reducing electrode. Reduction takes place at cathode.

Cations → +vely charged

• **OXIDATION:** A chemical process which involves addition of oxygen or removal of hydrogen or loss of electron from an atom or ion.

Eg:
$$C + O_2 \longrightarrow CO_2$$
$$Mg + O_2 \longrightarrow MgO$$
$$H_2S + Cl_2 \longrightarrow 2HCl + S$$
$$Zn \longrightarrow Zn^{+2} + 2e^-$$

OXIDISING AGENT: An oxidising agent is one that oxidises other substances by either accepting electrons or by providing oxygen or an electronegative ion.

Examples: MnO_2, PbO, H_2O_2, conc. HNO_3, H_2SO_4, O_2, O_3, Cl_2, etc.

REDUCTION: Reduction is defined as a chemical process which involves removal of oxygen or addition of hydrogen or gain of electron by an atom or ion.

Eg:
$$CuO + H_2 \longrightarrow Cu + H_2O$$
$$Cl_2 + H_2S \longrightarrow 2HCl + S$$
$$Cu^{+2} + 2e^- \longrightarrow Cu$$
$$Fe^{+3} + e^- \longrightarrow Fe^{+2}$$

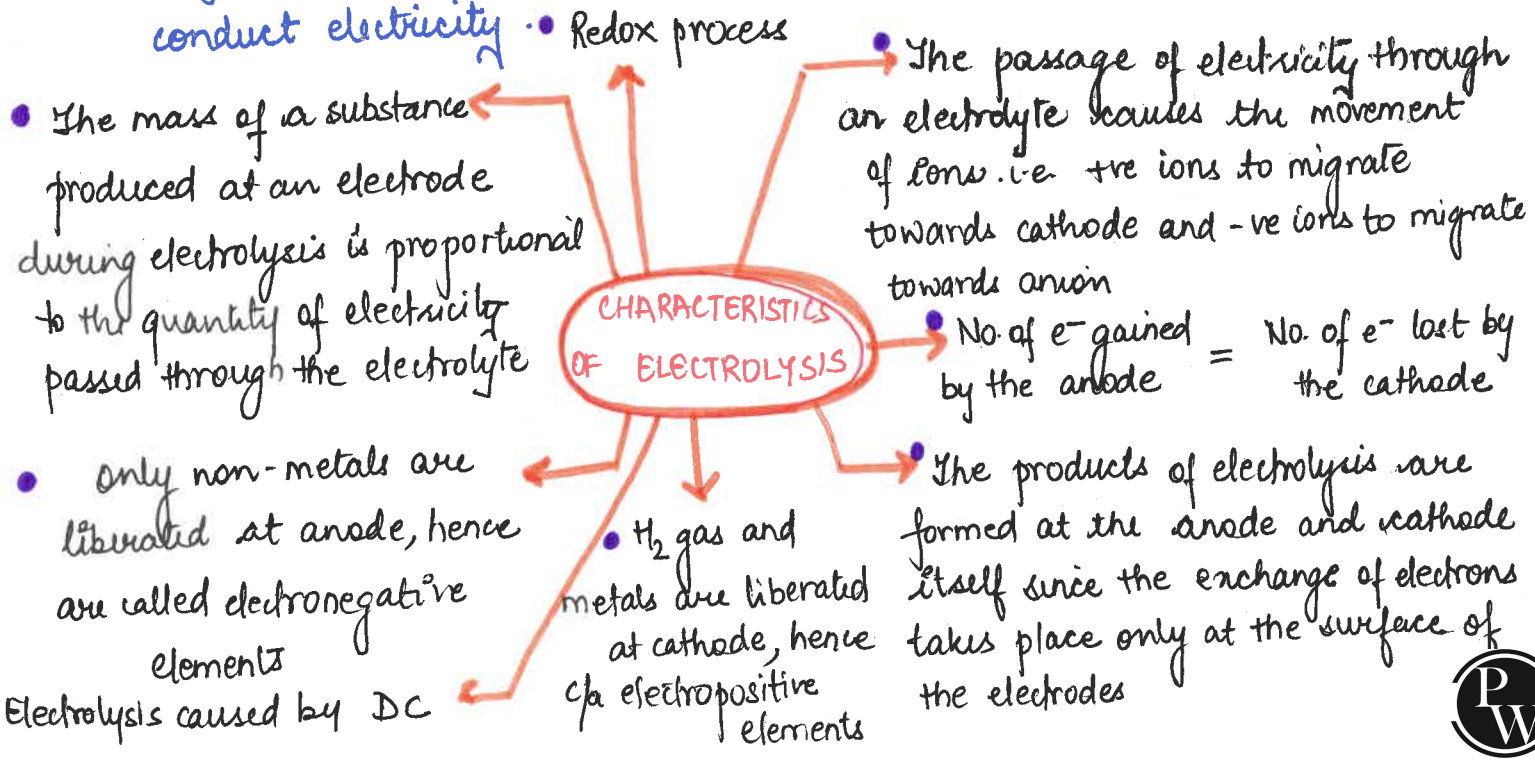
- **REDUCING AGENTS:** A reducing agent is one that reduces other substances by providing electrons, or by providing hydrogen or an electropositive ion.

  Example: Carbon, stannous chloride, H_2O_2, HI, H_2S, CO, SO_2

- **THEORY OF ELECTROLYTIC DISSOCIATION:** "Arrhenius"

1. Electrolyte $\underset{\text{current}}{\overset{\text{Electric}}{\rightleftharpoons}}$ cation (+ve) + anion (−ve) ..... they allow the flow of an electric current through it
2. conductivity ∝ conc of ions in the solution
3. No. of +ve charges = No. of −ve charges.
4. In non-electrolytes, such as sugar solution, benzene etc. there is no ionisation and therefore only molecules are present in solution.
5. The degree of dissociation is the extent to which an electrolyte dissociates or breaks up into ions.

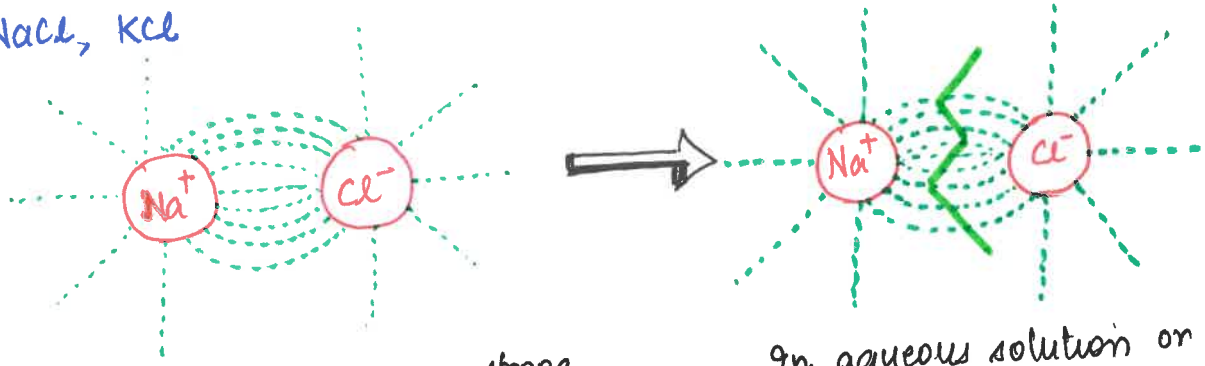
- **CONDUCTION IN COMPOUNDS:**
  - Electrovalent compounds are aggregates of oppositely charged ions held together by strong electrostatic forces of attraction.
  - When the electrovalent compounds are melted or dissolved in water the forces of attraction b/w their ions are broken, the ions are free to conduct electricity



ELECTROLYTIC DISSOCIATION AND IONISATION :

- Dissociation → It is the separation of ions which are already present in an ionic compound.
- Electrovalent compounds show dissociation.

Eg: NaCl, KCl



In solid state, ions are held by strong electrostatic forces of attraction

In aqueous solution or in molten state, the force of attraction weakens b/w the particles and the ions are set free.

IONISATION :

Formation of positively or negatively charged ions from molecules which are not initially in the ionic state. Polar covalent compounds show ionisation.

Eg: NH_4OH, HCl

$$H^{\delta+}-Cl^{\delta-} + O^{\delta-}\begin{matrix}/ H^{\delta+} \\ \backslash H^{\delta+}\end{matrix} \rightleftharpoons (H_3O)^+ + Cl^-$$

Hydronium ion, chloride ion

- ELECTROCHEMICAL SERIES :

Based on the ease with which atoms of metals lose electrons to form positively charged ions, the metals are arranged in a series known as Electrochemical series.

- K^+ Ca^{+2} Na^+ Mg^{+2} Al^{+3} Zn^{+2} Fe^{+3} Ni^{+2} Sn^{+4} Pb^{+2} H^+ Cu^{2+} Hg^{+2} Ag^+ Au^{+3} Pt^{4+}

Increasing ease of discharge at cathode

- K Ca Na Mg Al Zn Fe Ni Sn Pb H Cu Hg Ag Au Pt

Decreasing reactivity of metals

- About Electrochemical series of metals :

1. A metal with a higher position in the series displaces the one with a lower position
2. Metals below hydrogen cannot displace hydrogen from acids.
3. Elements lower in the series gets discharged more easily at the cathode during electrolysis because their cations can easily gain electrons
4. Metal atoms which form their ions most easily, will accept the electrons back to form the atoms with greatest difficulty.

⇒ Electrochemical Series of Anions :

SO_4^{2-} NO_3^- Cl^- Br^- I^- OH^- ⟶ Increasing ease of discharge at anode

- Lower the position of the anion in the series, more easily it gets discharged at anode
- Higher the position of an anion in the series, more difficult for it to lose electrons or get oxidised.

POTENTIAL OR SELECTIVE DISCHARGE OF IONS AT ELECTRODES :

- When two or more ions of the same charge are present in a solution of an electrolyte, under identical conditions and are competing for discharge at the same electrode, one of them gets preferentially discharged.

Selective discharge of ions depends on 3 factors :
- The relative position of ions in the electrochemical series
- The relative concentration of ions
- The nature of the electrodes.

4. ELECTROLYSIS OF AQUEOUS COPPER SULPHATE USING COPPER ELECTRODES:

Electrolyte : Aq. $CuSO_4$ + dil. H_2SO_4

Electrode : copper

$CuSO_4 \rightleftharpoons Cu^{+2} + SO_4^{-2}$

$H_2O \rightleftharpoons H^+ + OH^-$

At anode: $Cu - 2e^- \longrightarrow Cu^{+2}$ [SO_4^{-2} and OH^- ions migrate to anode but neither of them get discharged due to the nature of the electrode (anodi).]

At cathode: $Cu^{+2} + 2e^- \longrightarrow Cu$ [Both Cu^{+2} and H^+ ions migrate to the cathode Cu^{+2} ions discharged as neutral copper atoms]

Product at Anode — Copper anode keeps dissolving during the reaction.

Product at Cathode — Pinkish or Reddish brown copper is deposited.

1. The blue colour of aq. copper (II) sulphate solution remains unchanged during its electrolysis due to the copper electrodes, because for every Cu^{+2} discharged at the cathode as neutral atom, a copper ion Cu^{+2} is released or added to the solution by the anode. ∴ Total Cu^{+2} ions remains same. Therefore, blue colour does not fade.
2. The cathode will become thicker and anode will become thinner.

Since, SO_4^{-2} ions migrate to the anode and H^+ ions have been discharged, the conc. of H_2SO_4 will decrease at cathode.

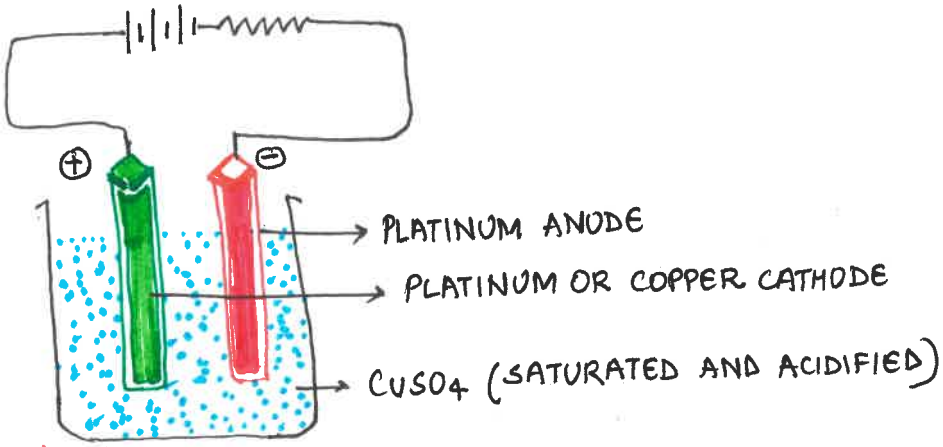
At Anode: The discharge of OH^- disturbs the ionic equilibrium of H_2O and to maintain it, more H_2O ionises.

$H_2O \rightarrow H^+ + OH^-$ .... The excess of H^+ ions, thus produced and the SO_4^{-2} ions present increase the conc. of H_2SO_4 at anode.

'

- Electrolysis of water gives 2 volumes of H_2 and 1 volume of O_2

3. ELECTROLYSIS OF $CuSO_4$ SOLUTION USING PLATINUM ANODE AND COPPER OR PLATINUM CATHODE:



$CuSO_4 \rightleftharpoons Cu^{+2} + SO_4^{-2}$

$H_2O \rightleftharpoons H^+ + OH^-$

At cathode:

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

Copper atoms deposit on the cathode (Pink or reddish brown copper)

At Anode:

SO_4^{-2} and OH^- ions both migrate to the anode. OH^- ions being lower in electrochemical series as compared to SO_4^{-2} ions.

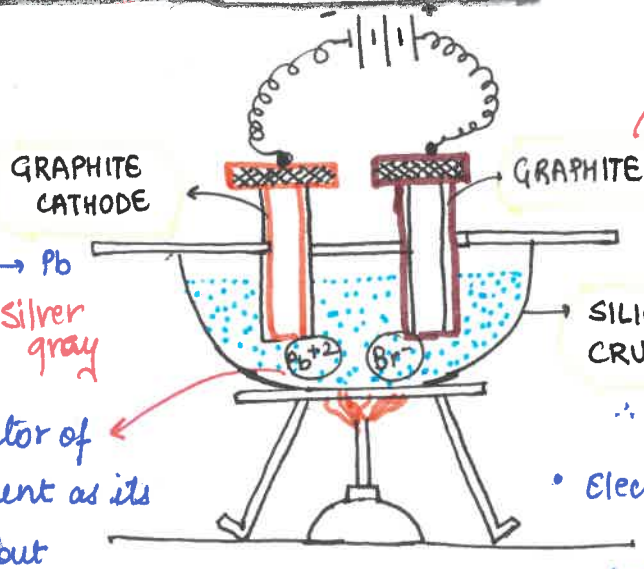
$4OH^- - 4e^- \rightarrow 4OH$

$2OH + 2OH \rightarrow 2H_2O + O_2$ At anode

The blue colour of the Cu^{+2} ions in the electrolyte solution fades due to decrease in Cu^{+2} ions and finally the solution becomes colourless.

• ELECTROLYSIS OF MOLTEN LEAD BROMIDE :

Graphite anode is preferred as it is unaffected by Br_2 vapours.



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

Silver gray

$Br^- \longrightarrow Br + e^-$

$Br + Br \longrightarrow Br_2$

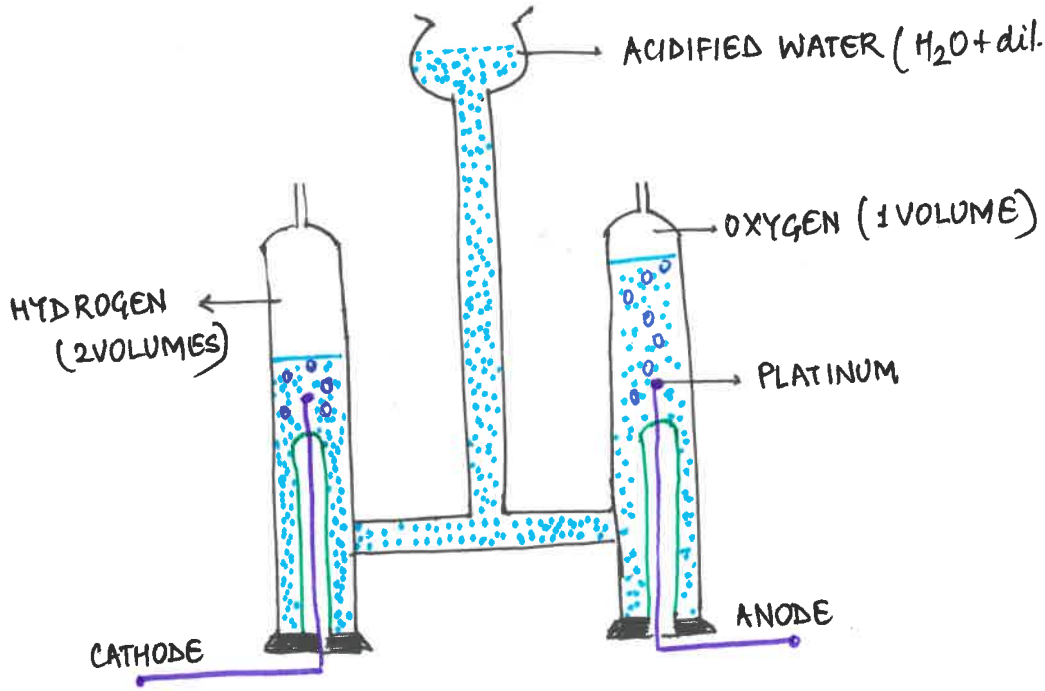
Dark Reddish fumes

$\therefore PbBr_2(\ell) \longrightarrow Pb(s) + Br_2(g)$

$PbBr_2$ (solid) → Non-conductor of electric current as its ions are not free but held together by electrostatic force of attraction.

• Electrolytic cell is made of silica as it can withstand high temperature and is a non-conductor of electricity.

2) ELECTROLYSIS OF ACIDIFIED WATER USING PLATINUM ELECTRODES :



At cathode At Anode

$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{-2}$

$H_2O \rightleftharpoons H^+ + OH^-$

At cathode : $H^+ + e^- \longrightarrow H$

$H + H \longrightarrow H_2$

At Anode : SO_4^{-2} and OH^- both migrate but OH^- is preferentially discharged.

$OH^- \longrightarrow OH + e^-$

$OH + OH \longrightarrow H_2O + O$ $\therefore O + O \longrightarrow O_2 \uparrow$

	ELECTROLYTE	DISSOCIATION OF ELECTROLYTES	IONS MIGRATING TO CATHODE	REACTION AT CATHODE	IONS MIGRATING TO ANODE	REACTION AT ANODE
1.	1. DILUTE $CuSO_4$ SOLUTION USING INERT ELECTRODES	$CuSO_4 \rightarrow Cu^{+2} + SO_4^{-2}$ $H_2O \rightleftharpoons H^+ + OH^-$	Cu^{+2}, H^+	$Cu^{+2} + 2e^- \rightarrow Cu$	SO_4^{-2}, OH^-	$4OH^- - 4e^- \rightarrow 4OH$ $2OH + 2OH \rightarrow 2H_2O + O_2$
2.	DILUTE $CuSO_4$ SOLUTION USING COPPER ELECTRODE	$CuSO_4 \rightarrow Cu^{+2} + SO_4^{-2}$ $H_2O \rightleftharpoons H^+ + OH^-$	Cu^{+2}, H^+	$Cu^{+2} + 2e^- \rightarrow Cu$	SO_4^{-2}, OH^-	$Cu - 2e^- \rightarrow Cu^{+2}$
3.	DILUTE NaCl SOLUTION	$NaCl \rightarrow Na^+ + Cl^-$ $H_2O \rightleftharpoons H^+ + OH^-$	Na^+, H^+	$H^+ + e^- \rightarrow H$ $H + H \rightarrow H_2$	Cl^-, OH^-	$4OH^- - 4e^- \rightarrow 4OH$ $2OH + 2OH \rightarrow 2H_2O + O_2$

- NATURE OF ELECTRODES:

↓ Electrolysis can be done by use of either can inert electrode or active electrode.

- If inert electrodes like graphite and platinum are used they will not take part in the electrolytic reaction.

Electrolysis will depend on :

(1) Position in the electrochemical series

(2) Concentration of ions.

- Active electrodes like Copper, Nickel, Silver, if used, take part in the electrolytic reaction.

Eg: On Electrolysis of $CuSO_4$:

Active electrode: Copper

At cathode: Copper atom

At Anode: Copper ions

Inert electrode: Platinum

At cathode: Copper

At Anode: $O_2 \uparrow$

APPLICATIONS OF ELECTROLYSIS

- Electroplating with metals
  - Electroplating with Silver
  - Electroplating with Nickel
- Electrorefining of metals
  - Refining of copper
- Electrometallurgy

I. ELECTROPLATING : A process in which a thin film of a metal gets deposited on another metallic article with the help of electricity.

REASONS : Decoration, To protect from corrosion

CONDITIONS FOR ELECTROPLATING

CONDITION 1 : Article to be electroplated is always placed at the cathode

REASON : During electrolysis the metal is always deposited at the cathode by the gain of electrons

CONDITION 2: The metal to be plated on the article is always made the anode and has to be periodically replaced

REASON : The metal anode continuously dissolves as ions in solution and is to replaced periodically

CONDITION 3: Electrolyte must contain ions of the metal which is to be plated on the article

REASON : Electrolyte dissociate into ions of the metal which migrate towards the cathode and are deposited as neutral metallic atoms on the cathode

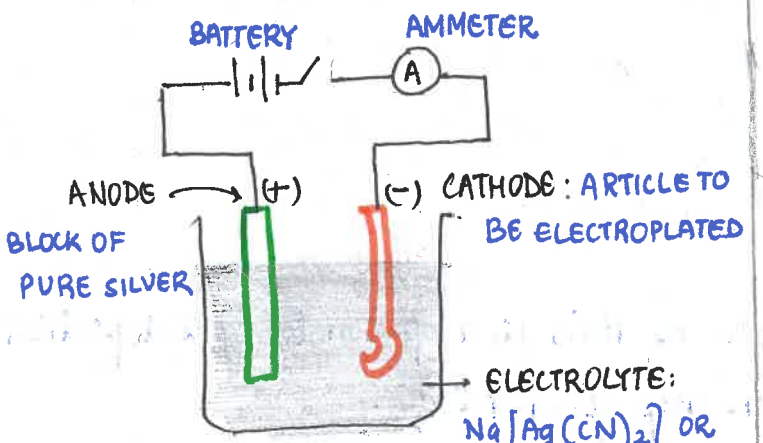
CONDITION 4: A low current for a longer time should be used

Reason: Higher current causes uneven deposition of the metal. Longer time and low current initiates a thicker uniform deposition

CONDITION 5 : A DC to be used instead of AC.

REASON : A.C causes discharge and ionisation to alternate at the cathode thus giving no effective coating.

ELECTROPLATING AN ARTICLE WITH SILVER



- PREPARATION OF ELECTROLYTE:

$$AgNO_3 + NaCN \longrightarrow AgCN\downarrow + NaNO_3$$

$$AgCN + NaNO_3 \longrightarrow Na[Ag(CN)_2]$$

sodium argentocyanide

At cathode: Article to be electroplated is duly cleaned.

$$Ag^+ + e^- \longrightarrow Ag$$

(from electrolyte)

At Anode:

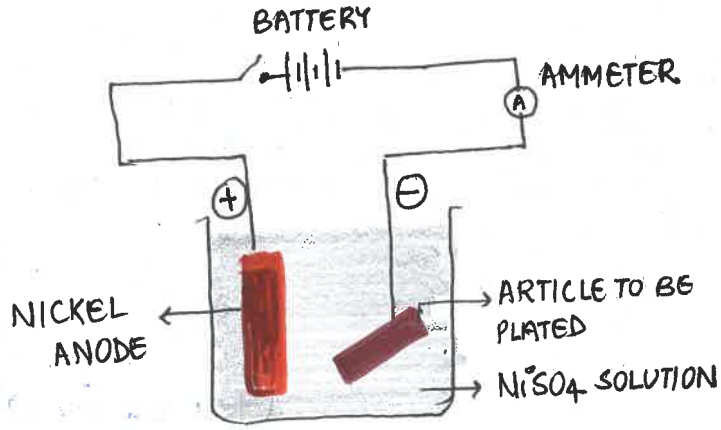
$$Ag - e^- \longrightarrow Ag^+$$

(from anode) (goes into electrolyte) (due to the use of active electrode)

KEY POINTERS:

1) The thickness of the coating will depend on the duration of the current passed.
2) In the process the anode dissolves
3) The electrolyte solution maintains the same concentration, thus if it is coloured, the intensity of the colour remains the same
4) If $AgNO_3$ is used directly instead of $Na[Ag(CN)_2]$ the deposition of silver will be very fast and hence not very smooth and uniform.

ELECTROPLATING AN ARTICLE WITH NICKEL



- ELECTROLYTE: Aqueous solution of $NiSO_4$

$$NiSO_4 \rightleftharpoons Ni^{+2} + SO_4^{-2}$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

At cathode:

$$Ni^{+2} + 2e^- \longrightarrow Ni \text{ (deposited)}$$

At Anode:

$$Ni - 2e^- \longrightarrow Ni^{+2}$$

(due to the use of active electrode)

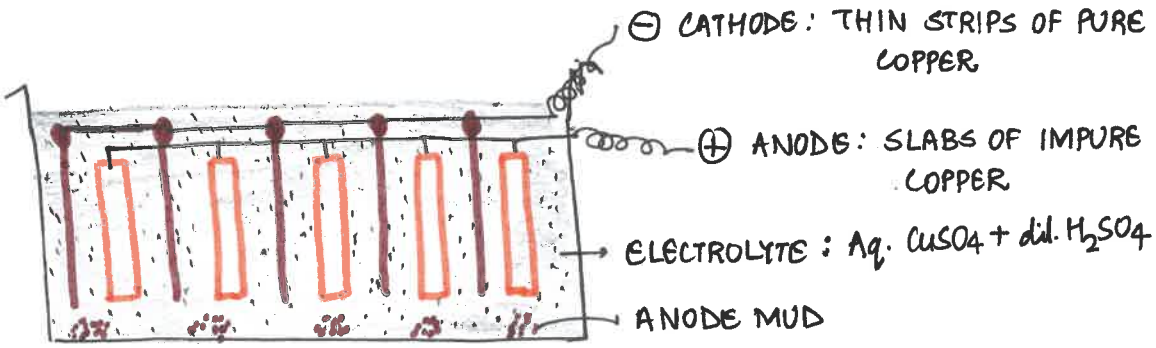
KEY POINTERS:

1) Article to be plated is always kept at the cathode
2) The electrolyte must be a solution of a salt of metal to be electroplated
3) The anode is made of a strip of metal to be plated.

ELECTROLYTIC REFINING OF METALS:

It is a process by which metals containing impurities are purified electrolytically to give a pure metal.

- REFINING OF COPPER:



Reaction:

At cathode: $Cu^{+2} + 2e^- \longrightarrow Cu$

At Anode: $Cu - 2e^- \longrightarrow Cu^{+2}$

These copper ions migrate to the cathode and gain electrons and then gets deposited at cathode. The net result is that, gradually the impure slab of copper gets finished and thin strips of pure copper build up.

- Some impurities gets dissolved in the acid while others namely silver and gold which are insoluble gets deposited below anode as "ANODE MUD"

ELECTRO METALLURGY:

- It is the process of extraction of metals by electrolysis
- Metals which are higher in electrochemical series such as potassium, calcium sodium etc. are extracted by electrolysis
  - ↳ These metals have high affinity for oxygen, their oxides are stable and cannot be reduced by using common reducing agents such as CO and H_2.
  - ↳ Reactive metals are extracted from their halides by electrolytic reduction using inert electrodes.
    - cathode: Iron
    - Anode: Graphite

Eg: $KBr \underset{\text{(Fused)}}{\rightleftharpoons} K^+ + Br^-$

At cathode: $K^+ + e^- \longrightarrow K$

At Anode: $Br^- \longrightarrow Br + e^-$

$Br + Br \longrightarrow Br_2$

② $Al_2O_3 \rightleftharpoons 2Al^{+3} + 3O^{-2}$

At cathode: $2Al^{+3} + 6e^- \longrightarrow 2Al$

At Anode: $3O^{-2} - 6e^- \longrightarrow 3[O]$

$3[O] + 3[O] \longrightarrow 3O_2$