Narsee Monjee Educational Trust's
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Chemistry std10

ELECTROLYSIS

Important terms in Electrolysis

1) **Electrolysis**: it is the process of decomposition of a chemical compound in aqueous solution or fused state by the passage of a direct electric current resulting in the discharge of ions as neutral atoms at the respective electrodes
2) **Electrolyte**: it is a compound which either in aqueous solution or molten state allows a current to pass through it. It decomposes into ions and finally neutral atoms at the two electrodes.

Electrolytes are:

*Ionic compounds in which positive and negative ions are held together by strong electrostatic forces of attraction

*These compounds conduct electricity in their aqueous or molten state.

*Polar covalent compounds conduct electricity in their aqueous state.

*Non-conductors in solid state because the ions are not free to conduct electricity.

Examples:

ACIDS: H_2SO_4, HNO_3, H_3PO_4, HCl

BASES: NaOH, KOH, NH_4OH, $Ca(OH)_2$

SALTS: NaCl, $CuSO_4$, $PbBr_2$

Electrolytes are classified into two types

	Strong electrolyte		Weak electrolyte
1	They allow a large amount of electricity to pass through them	1	Allows small amount of electricity to flow through them
2	Good conductors of electricity	2	Poor conductors of electricity
3	Almost completely dissociated in fused or aqueous solution state	3	Partially dissociated in fused or aqueous solution state
4	These solutions contains almost only free mobile ions	4	Contains Ions as well as molecules
5	Strong electrolyte allows a bulb to grow brightly	5	Allow bulb to glow dimly

	ACIDS: H_2SO_4, HCl, HNO_3,HBr BASES: NaOH, KOH, LiOH SALTS: NaCl, $CuSO_4$, $PbBr_2$, $CuCl_2$		ACIDS: Carbonic acid ,acetic acid, Oxalic acid BASES: NH_4OH, $Ca(OH)_2$ SALTS: Sodium carbonate ,Potassium bicarbonate

Non electrolyte: It is a compound which neither in solution nor in the molten state allows an electric current to pass through it.

They do not have ions but only molecules in them

Example: Distilled water, alcohol, kerosene, carbon disulphide, Cane sugar, benzene, glucose, urea.

Electrolytic cell/ voltameter: it is the vessel in which electrolysis is carried out.

Electrochemical Cell: It is a device used to convert chemical energy to electrical energy

Examples: Simple voltaic cell, Daniel 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 cell are called electrodes.

Anode: electrode connected to the positive pole of the battery

Cathode: Electrode connected to the negative pole of the battery

Note: When the current is on, the cathode becomes the negative electrode by which electrons enter the electrolyte and the anode becomes the positive electrode by which electrons leave the electrolyte.

Difference between cathode and Anode

	Anode		**Cathode**
1	Electrode connected to the Positive terminal of the battery	1	Electrode connected to the Negative terminal of the battery
2	Anions migrate to anode	2	Cations migrate to cathode
3	Anions are oxidised at the anode	3	Cations are reduced at the cathode

Ions: are atom or groups of atoms which carry a positive or negative charge

Cations:Ions which carry a positive charge

Anions::Ions which are negatively charged

Difference between cations and anions

	Cations		**Anions**
1	Positively charged ions	1	Negatively charged ions
2	Migrate to the cathode	2	Migrate to the Anode

3	Gains electrons from the cathode and get reduced	3	Lose electrons to the anode and get oxidised

Q. Why do the electrovalent compounds conduct electricity in the fused state or in the aqueous state only?

In the electrovalent compounds the ions are held by strong electrostatic forces of attraction between the ions on melting or dissolving the forces of attraction are broken and the ions then can move about conducting electricity

Q. How do covalent molecules conduct electricity?

Covalent compounds which are polar in nature ,Eg:HCl,NH_3, and H_2O ionise in aqueous solution and conduct electricity

Q. Why is the process of electrolysis a redox reaction?

The reaction at the cathode involves reduction of cations as they gain electrons to become neutral atoms, while at the anode oxidation takes place which involves loss of electrons by the anions to become neutral atoms.

<u>Difference between Ionisation and Dissociation</u>

	Ionisation		Dissociation
1	Formation of positively or negatively charged ions from molecules which are not initially in Ionic state	1	Separation of ions which are already present in an ionic compound
2	Polar covalent compounds and metals undergo ionisation	2	Electrovalent compounds show Dissociation
	$HCl \xrightarrow{H_2O} H^+ + Cl^-$ or $Mg - 2e^- \rightarrow Mg^{+2}$		$KCl \rightarrow K^+ + Cl^-$

<u>Difference in conduction of electricity in a metal and electrolyte</u>

	Metal	Electrolyte
1	Flow of electricity takes place by flow of electrons	Flow of electricity takes place by flow of ions.
2	No decomposition of parent metal.	Decomposition of the electrolyte solutions.
3	Good conductors in solid state and in molten state	Conduct electricity in the aqueous state or molten state.
4	No transfer of matter takes place	Transfer of ions takes place.

Electrochemical Series of Metals:

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 the activity series or electrochemical series

Increasing each of discharge at the cathode

Increasing ease of reduction (↑)

K^{+}

Ca^{+2}

Na^{+2}

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 (↓)

Electrochemical series of Anions:

SO_4^{-2}	↓	Increasing
NO_3^{1-}	↓	ease
Cl^{-}	↓	of discharge
Br^{-1}	↓	at anode
I^{-}	↓	
OH^{-}	↓	

Q.Can we store $CuSO_4$ in an Iron vessel?

It cannot be stored in an Iron vessel since Cu is below iron in the activity series; Iron displaces copper from copper sulphate

Q.What is preferential discharge of ions?

When two or more ions of the same charge are present in a solution of an electrolyte under identical conditions are competing for discharge at the same electrode, one of them is preferentially discharged this is known as selective discharge of ions

Q.What does Selective discharge of ions depends on?

- ❖ Relative positions of ions in the electrochemical series:

If all other factors are constant, any ions lower in the electrochemical series gets discharged at the relevant electrode in preference to those above it.

- ❖ Relative concentration of ions:

If an electrolyte has a much higher concentration of a particular ion then that ion will be discharged at the relevant electrode in preference to those ions which are lower in the electrochemical series

For example: Electrolysis of conc Sodium Chloride (aq)

$NaCl \rightarrow Na^+ + Cl^-$ $H_2O \rightarrow H^+ + OH^-$

At cathode At Anode

$H^+ + 1e^- \rightarrow H_2$ $Cl^- - 1e^- \rightarrow Cl + Cl \rightarrow Cl_2$

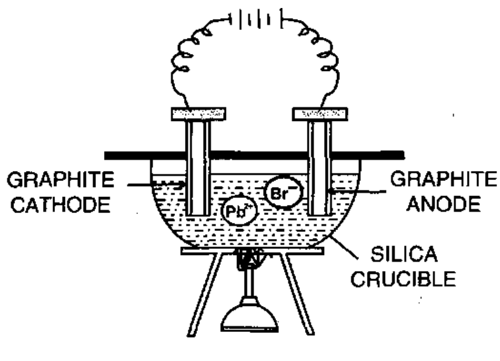
- ❖ Nature of electrode:

In the **electrolysis of Copper (II) sulphate solution**, copper atoms are deposited at the cathode and copper ions are formed at the anode if copper anode and cathode are used, **oxygen is formed at the anode if platinum anode is used**.

Reaction: $CuSO_4 \rightarrow Cu^{+2} + SO_4^{-2}$ $H_2O \rightarrow H^+ + OH^-$	
Cathode is Copper and Anode are Copper	
Cathode: $Cu^{+2} + 2e^- \rightarrow Cu$	Anode: $Cu - 2e^- \rightarrow Cu^{+2}$
Cathode is Copper Anode is Platinum	
Cathode: $Cu^{+2} + 2e^- \rightarrow Cu$	Anode: $4OH^- - 4e^- \rightarrow 2H_2O + O2$

Example of electrolysis:

Electrolysis of Molten lead bromide($PbBr_2$)



Electrolysis of molten lead bromide.

Electrolyte: Molten Lead bromide

Temperature:Above 380 ^{0}C

Electrolytic Cell: Crucible made of Silica

Electrodes: Cathode-Graphite   Anode: Graphite

Current:12v,3amp battery

Electrode Reactions:

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

Anode $Br^- + 1e^- \rightarrow Br$

$Br + Br \rightarrow Br_2$

Overall Reaction $PbBr_2 \rightarrow Pb(s) + Br_2(g)$

Observations: Dark reddish fumes of Br_2 gas at anode .

Greyish black lead metal accumulates at the cathode.

Q.Silica is the material used in the electrolytic cell. Why?

It can withstand high temperature and almost a non conductor of electricity

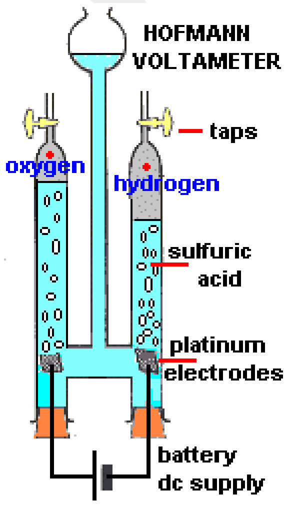
Q. Solid $PbBr_2$ is a non-conductor. Why?

The ions of solid $PbBr_2$ are not free hence it has to be heated to make the ions free from electrostatic forces of attraction.

Q. Graphite is preferred over other inert anode.

Graphite is preferred since it does not react with the reactive Bromine vapours.

Electrolysis of Acidified Water:



Electrolyte: Distilled water acidified with Dil H_2SO_4

Electrolytic cell: Hoffman's Voltameter

Electrodes: Platinum foils

Current:12volts

Electrode reactions

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

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

Cathode: $H^+ + 1e^- \rightarrow H \times 4$

$2H + 2H \rightarrow 2H_2$

Anode: $OH^- - 1e^- \rightarrow OH$

$4OH \rightarrow 2H_2O + O_2$

Note: Since OH^- is discharged at the anode in preference to SO_4^{2-}. The concentration of sulphate ions increases at the anode and decreases at the cathode but the total concentration of H_2SO_4 remains since it is the H^+ and OH^- ions that are discharge at the cathode and anode.

Q. What is the ratio of hydrogen and oxygen and why?

Since the formation of 1 molecule of oxygen at the anode releases 4 electrons and there is no build up of electrons in any part of the circuit ,the reaction of the cathode must take up 4 electrons

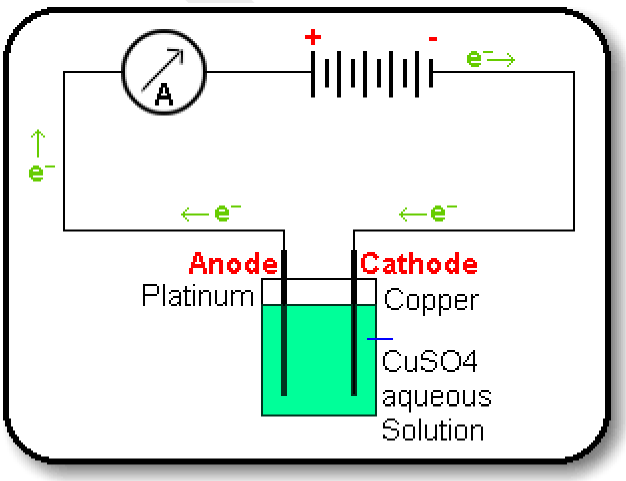
$4H^+ + 4e^- \rightarrow 2H_2$

This shows the number of molecules of hydrogen is twice that of oxygen molecules.

Electrolysis of $CuSO_4$ (aq)

CASE 1:

Electrolysis of $CuSO_4$ using Platinum anode and Copper cathode



Elctrolytic Cell: Glass voltameter

Electrolyte: Aq $CuSO_4$

Electrode: Cathode-Copper

Anode-Platinum

Electrode Reaction: $CuSO_4 \rightarrow Cu^{2+} + SO_4^{2-}$

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

Reaction at Cathode- $Cu^{2+} + 2e^- \rightarrow Cu$ (Reddish brown copper seen at the cathode)

Anode- $OH^- - 1e^- \rightarrow OH$

$4OH \rightarrow 2H_2O + O_2$(Bubbles of a colourless gas which rekindles a glowing splinter are seen)

The sulphate and hydroxyl ions both travel to the anode but OH^- gets discharged .The neutral OH radicals reunite to form water and oxygen

Note: The blue colour of the copper ions fade due to the decrease in the number of copper ions and it finally becomes colourless

Case II

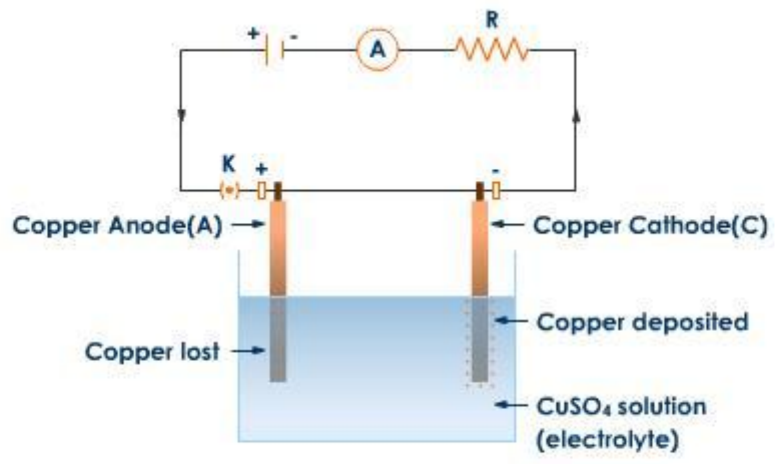
Electrolysis of $CuSO_4$ with copper cathode and anode

Electrolytic Cell: Iron crucible

Electrolyte: Aqueous Copper Sulphate

Electrode: Cathode: Cu Anode: Cu

Current: 12 Volt and Current 3 Amps



Dissociation of Aqueous copper sulphate :

$CuSO4 \rightleftharpoons Cu^{+2} + SO_4^{-2}$

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

Reaction at Cathode : $Cu^{+2} + 2e^- \longrightarrow Cu$

(Reddish brown copper seen at the cathode the mass of the cathode increases)

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

Obs:The anode decreases in mass as copper ions dissolve and get added to the electrolyte.

Q. The blue colour of $CuSO_4$ remains unchanged in the electrolysis.

A For every copper ion discharged at the cathode as neutral copper atoms, a copper ion is added to the solution at the anode and hence the total number of copper ions remains the same. Therefore the blue colour does not fade.

Applications of Electrolysis:

1. Electroplating with metals.
2. Electro-refining of metals
3. Extractions of metals.

I)Def^n Electroplating of metals: Electroplating is an electrolytic process of depositing a thin film of a metal like gold, silver, nickel, chromium etc on another inferior metallic article with the help of electricity.

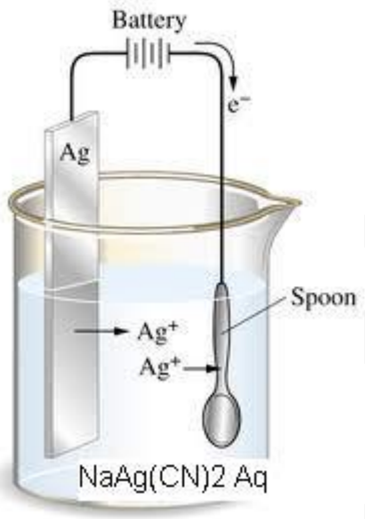
Reasons for electroplating:-

1. Decorative purposes; brass objects are plated with silver to give them the appearance of silver article.
2. To protect from rusting and corrosion. Iron articles are often electroplated.

Conditions for electroplating:-

1. The article to be electroplated is always the cathode. Why the metal is always deposited at the cathode.
2. The metal to be plated on the article is always made as the anode since the anode continuously dissolves as ions in solution.
3. Electrolyte must have ions of the metal which is to be plated on the article. Electrolyte dissociates into ions of the metals which migrate towards the cathode and are deposited as neutral metallic atoms.
4. A low current for a longer time is used. Longer time and low current initiate a thicker uniform deposition.
5. A (DC) direct current and not a an (AC) alternating current is used. AC current causes discharge and ionisation to alternate at the cathode thus giving no effective coating.

Electroplating of a brass spoon with Silver:-



Electrolyte: Sodium argentocyanide or Potassium argento cyanide

$Na(Ag(CN)_2) \rightleftharpoons Na^+ + Ag^+ + 2CN^-$

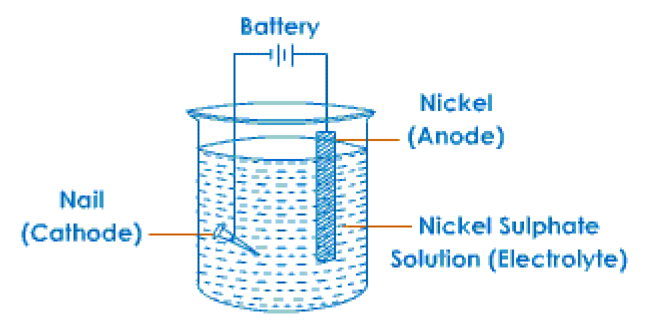
$H_2O \rightleftharpoons H^+ + OH^-$

Cathode: $Ag^+ + 1e^-$ Ag

Anode: Ag $- 1e^-$ Ag^+

If Silver Nitrate solution is used the deposition of silver is very fast and hence not very smooth and uniform.

Electroplating with Nickel



Electroplating with nickel

Electrolyte: Aqueous solution of $NiSO_4$

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

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

Cathode: cleaned article to be electroplated

Anode: Block of nickel metal

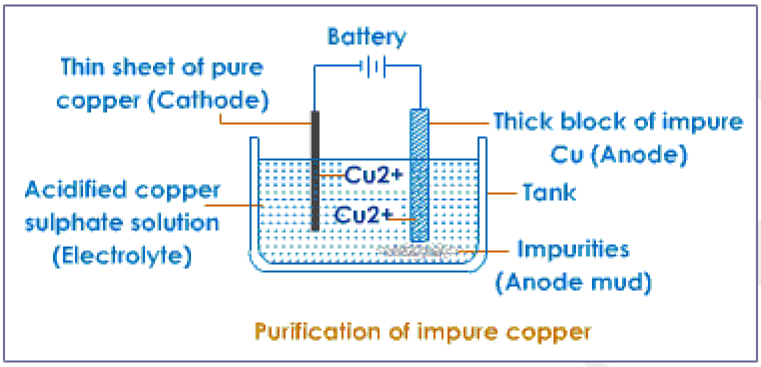
Reaction at Cathode: $Ni^{+2} + 2e^- \longrightarrow Ni$

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

II)Electro-refining of metals:

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

Electrorefining of Copper:



Electolyte: A solution of $CuSO_4$
Cathode: Thin Strip of pure copper
Anode: Impure copper
Reaction: $CuSO_4 \rightarrow Cu^{+2} + SO_4^{-2}$
Cathode: $Cu^{+2} + 2e- \rightarrow Cu$
Anode: $Cu - 2e- \rightarrow Cu^{+2}$

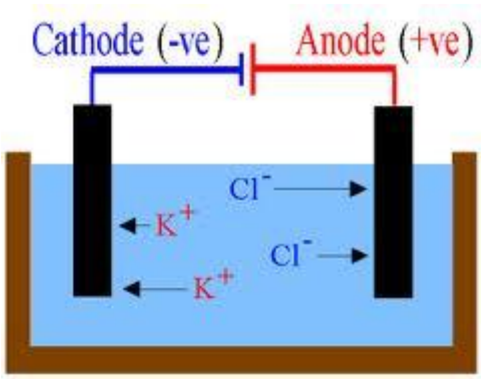
Gradually the impure slabs of copper gets finished and thin strips of pure copper becomes thicker and thicker. The copper deposited has a purity of 99.9% pure.

Q.What is electrode mud?

Some impurities get dissolved with the acid used, while others namely silver and gold which are insoluble fall down near the anode (anode mud) and are recovered later.

Note: Metals like zinc, lead, mercury, silver and copper are refined by electrolysis.The metals extracted by electrolysis are not generally purified.

Electrometallurgy:



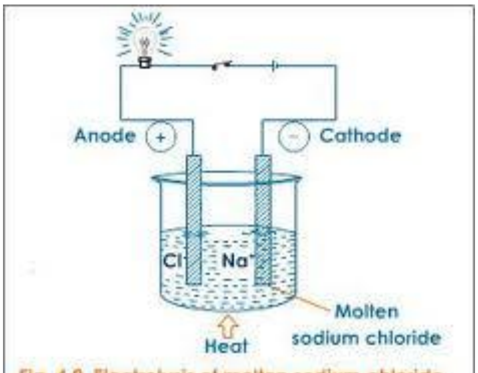


Fig. 4.9 Electrolysis of molten sodium chloride

Electrolysis of Molten KCl

1. Sodium, potassium, Calcium and magnesium are extracted by electrolysis of their fused chlorides when cathode is made of iron and anode of a graphite rod.

For example: $CaCl_2 \rightarrow Ca^{+2} + 2Cl^-$

Cathode: $Ca^{+2} + 2e^- \rightarrow Ca$

Anode: $Cl^- - 1e^- \rightarrow Cl$, $Cl + Cl \rightarrow Cl_2$

2. Aluminium is extracted by electrolysis of Al_2O_3 Gas carbon lining is cathode and thick carbon rods are made anode.

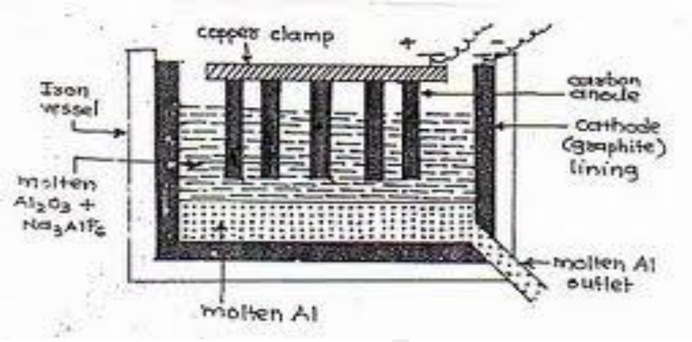
Reaction : $Al_2O_3 \rightarrow 2Al + 3O^{-2}$

Cathode: gas carbon lining

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

Anode: Thick carbon rods

$3O^{-2} - 6e^- \rightarrow 3\ O + 3O \rightarrow 3O_2$



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