CHAPTER 5
Electrolysis

SYLLABUS – SCOPE OF SYLLABUS – in and after MARCH 2019 – ELECTROLYSIS

I] ELECTROLYTES & NON-ELECTROLYTES.
- ***Definitions & examples.***

II] SUBSTANCES CONTAINING MOLECULES ONLY, IONS ONLY, BOTH MOLECULES AND IONS.
- ***Substances containing molecules only ions only, both molecules & ions.***
- ***Examples; relating their composition with their behaviour as*** strong & weak electrolytes as well as non-electrolytes.

III] DEFINITION & EXPLANATION OF ELECTROLYSIS, ELECTROLYTE, ELECTRODE, ANODE, CATHODE, ANION, CATION, OXIDATION & REDUCTION [ON THE BASIS OF LOSS & GAIN OF ELECTRONS].

IV] AN ELEMENTARY STUDY OF THE MIGRATION OF IONS, WITH REFERENCE TO THE FACTORS INFLUENCING SELECTIVE DISCHARGE OF IONS [REFERENCE SHOULD BE MADE TO THE ACTIVITY SERIES AS INDICATING THE TENDENCY OF METALS, e.g. Na, Mg, Fe, Cu, TO FORM IONS] ILLUSTRATED BY THE ELECTROLYSIS OF:
- ***Molten lead bromide***
- ***Acidified water with platinum electrodes***
- ***Aqueous copper [II] sulphate with copper electrodes; electron transfer at the electrodes.***

The above electrolytic processes can be studied in terms of electrolyte used, electrodes used, ionization reaction, anode reaction, cathode reaction, use of selective discharge theory, wherever applicable.

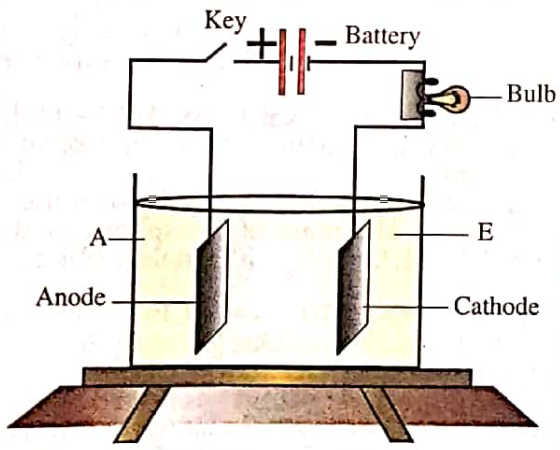
V] APPLICATIONS OF ELECTROLYSIS:
- ***Electroplating with nickel and silver, choice of electrolyte for electroplating.***
- ***Electro refining of copper;***

Reasons & conditions for electroplating; names of the electrolytes & the electrodes used should be given. Equations for the reactions at the electrodes should be given for electroplating, refining of copper.

A. INTRODUCTION

- *Electrolysis* – The word 'electrolysis' can be split into - *electro* [meaning - electricity ie. flow of electrons] & *lysis* [meaning - pertaining to].
- *Electrolytes & non-electrolytes* – Compounds which conduct electricity when dissolved in water or in the molten state are called – *electrolytes* eg. NaCl, $CuSO_4$ etc. while those which do not conduct electricity are called – *non-electrolytes*. e.g. alcohol, sugar soln.

Electrolysis - *Electrolytic cell*



A: Electrolytic cell E: Electrolyte

Electrolytic cell: A non-conducting vessel – containing the electrolyte [in aq. or fused state].

Anode : Electrode connected to the – *positive terminal* of the battery [via a metal wire, bulb and key (switch)].

Cathode : Electrode connected to the – *negative terminal* of the battery.

When the switch is 'on' – the electrolyte starts dissociating. Current remaining the same the glow on the bulb indicates whether the electrolyte is a –
- *Strong electrolyte* - by bright glow of the bulb.
- *Weak electrolyte* - by dim glow of the bulb.
- *Non-electrolyte* - when bulb does not glow.

B. TERMS – Involved in Electrolysis

1. ELECTROLYSIS

Electrolysis is the ***decomposition*** of a chemical compound [electrolyte] – in the ***aqueous or fused*** [molten] state – by the ***passage of a direct electric current*** resulting in ***discharge of ions*** – as ***neutral atoms*** – at the ***respective electrodes.***

- *Decomposition of electrolyte* – in aq. or fused state by passage of electric current
  NaCl [electrolyte] $\rightleftharpoons$ Na^{1+} [cation] + Cl^{1-} [anion]
- *Discharge of ions* – as neutral atoms at the respective electrodes.
  At cathode [negative electrode] : $Na^{1+} + 1e^- \rightarrow Na$ [neutral atom] – Reduction reaction
  At anode [positive electrode] : $Cl^{1-} - 1e^- \rightarrow Cl$ [neutral atom] – Oxidation reaction
- *Electrolysis involves* – a *chemical change* & is a – ***Redox reaction*** [oxidation & reduction].

2a] ELECTROLYTES

Chemical compounds – ***which conduct electricity*** in the fused or in aq. solution state & – *undergo* chemical decomposition due to the flow of current through it.

Electrolytes - *are ionic compounds*

PARTICLES IN ELECTROLYTES
– Ions only or Ions & molecules only

Examples

Acids - dil. HCl, HNO_3, H_2SO_4
Alkalis - KOH, NaOH solutions
Ionic salts - $PbBr_2$ [molten], $CuSO_4$ [aq.]

2b] NON-ELECTROLYTES

Chemical compounds – ***which do not conduct electricity*** in the fused or aq. soln. state & – *do not undergo* chemical decomposition due to the flow of current through it.

Non-electrolytes – *are covalent compounds*

PARTICLES IN NON-ELECTROLYTES
– Molecules only

Examples

Pure or distilled water, Alcohol, Kerosene, Carbon disulphide, liquid carbon tetrachloride, sucrose, glucose, sugar solution.

3a] STRONG ELECTROLYTES

- They are electrolytes which allow – a large amount of electricity to flow through them and hence are – ***good conductors of electricity.***
- Strong electrolytes are – ***almost completely dissociated*** – in fused or aqueous solution state.

PARTICLES IN STRONG ELECTROLYTES
– Mainly *ions only*

Examples - generally all strong acids and bases and most salts of strong acids

Acids - dil. *HCl*, H_2SO_4, HNO_3, *HBr*, *HI*
Bases - NaOH, KOH, LiOH solns.
Salts - Na*Cl* [KCl], Na_2SO_4, $NaNO_3$, $CuCl_2$, $PbSO_4$, $Pb(NO_3)_2$, $PbBr_2$, Ag*I* aq. solns.

3b] WEAK ELECTROLYTES

- They are electrolytes which allow – small amounts of electricity to flow through them and hence are – ***poor conductors of electricity.***
- Weak electrolytes are – ***partially dissociated*** – in fused or aqueous solution state.

PARTICLES IN WEAK ELECTROLYTES
– Ions & unionised molecules
Examples - generally all weak acids and bases and most salts of weak acids

Acids - **Carbonic, acetic, oxalic, formic**
Bases - NH_4OH, $Ca(OH)_2$, $Mg(OH)_2$
Salts - Sodium – **carbonate, bicarbonate, oxalate** and **formate** aq. solns.

4. ELECTROLYTIC CELL

The device in which electrolysis is carried out is called the – ***electrolytic cell*** or voltameter which contains ***electrodes*** [cathode& anode] and the ***electrolytic solution.***

5. ELECTRODES

- Electrodes allow the ***electric current*** to – ***enter*** or ***leave*** the electrolytic solution.
- The electrodes are two in number and are made of – metal or carbon.
- Graphite [carbon] electrodes are used – when the products formed during electrolysis react with the metallic electrode.
- The electrodes are connected to a battery via a key or switch and depending on their connection to the battery are classified as – ***anode*** or ***cathode.***

5a] ANODE [positive electrode]

- It is the electrode connected to the – ***positive terminal [end] of the battery***
- The electrode hence acquires a – positive charge during electrolysis & hence ions which are – vely charged ie. ***anions migrate to the anode.***
- The anions – ***donate*** excess electrons to the anode and are – ***oxidised*** to neutral atoms.

OXIDISING ELECTRODE

- The anode is the ***oxidising*** electrode by which electrons leave the electrolyte

Loss of electrons from an atom or ion is called oxidation, hence ***oxidation*** takes place at the ***anode.***

Anode : $Cl^{1-} - 1e^- \rightarrow Cl$
[anion] [neutral atom]
[anions lose electrons at anode]

5b] CATHODE [negative electrode]

- It is the electrode connected to the – ***negative terminal [end] of the battery.***
- The electrode hence acquires a – negative charge during electrolysis & hence ions which are +vely charged ***ie. cations migrate to the cathode.***
- The cations – ***gain*** excess electrons from the cathode and are – ***reduced*** to neutral atoms.

REDUCING ELECTRODE

The cathode is the ***reducing*** electrode by which electrons enter the electrolyte.

Gain of electrons by an atom or ion is called reduction, hence ***reduction*** takes place at the ***cathode.***

Cathode : $Na^{1+} + 1e^- \rightarrow Na$
[cation] [neutral atom]
[cations gain electrons at cathode]

6. IONS

- They are ***atoms*** [or groups of atoms] which carry a– ***positive*** or ***a negative charge*** and become free and mobile when – an electric current is passed through an aq. solution of a chemical compound.
- Depending on the type of electric charge [+ve or – ve] carried by an ion – an ion is further classified into anions and cations.

6a] ANIONS

- They are – ***negatively charged*** ions.
- They – ***migrate to the anode*** during electrolysis & are discharged at it.
- They – ***donate or lose electrons*** to the anode **[oxidation process]** and get – ***oxidised*** to neutral atoms.

Anode : $Cl^{1-} - 1e^- \rightarrow Cl$
[anion] [neutral atom]

6b] CATIONS

- They are – ***positively charged*** ions.
- They – ***migrate to the cathode*** during electrolysis & are discharged at it.
- They – ***accept or gain electrons*** from the cathode **[reduction process]** and get – ***reduced*** to neutral atoms.

Cathode : $Na^{1+} + 1e^- \Rightarrow Na$
[cation] [neutral atom]

C. MECHANISM – Of Electrolysis

The process or mechanism of electrolysis was first explained by a Swedish chemist ***Avante Arrhenius*** in 1887. The **main** findings or **postulates of his theory** are as follows:

- An electrolyte on dissolving in water dissociates into – free cations [+ve ions] & anions [-ve ions] and allows the flow of electric current through it.
- The *degree of dissociation* – is the extent to which an electrolyte dissociates or breaks up, into ions.
- All ions carry an electric charge and are responsible for the flow of current through the solution. The amount of electricity conducted by the electrolyte – depends upon the concentration of the ions in the solution.
- The number of positive charges on the ions equals – the number of negative charges and thus the solution is in electrolytic equilibrium [an equilibrium is also established between the ions produced & unionized molecules].

1. CHARACTERISTICS – Of Electrolysis

- The passage of electricity through an electrolyte causes the metallic ions [cations] to – migrate towards the cathode and non-metallic ions [anions] to migrate towards the anode.
- The preferential discharge of the ions depends on its position in the electrochemical series.
- The number of electrons gained by the anode – is equal to the number of electrons donated by the cathode.
- The products of electrolysis are formed at the anode and cathode itself – since the exchange of electrons takes place only at the surface of the electrodes.
- Only hydrogen gas and *metals* are liberated at the *cathode* and are hence called – *electropositive elements.*
- Only *non-metals* are liberated at the *anode* and are called – *electronegative elements.*

2. ELECTROLYTIC DISSOCIATION – The Term

- The process due to which an ionic compound – in the fused [molten] state or in aqueous solution state dissociates into – ions by passage of electric current through it is called – *electrolytic dissociation.*

Comparison between – Electrolytic Dissociation & Ionisation

ELECTROLYTIC DISSOCIATION	*IONISATION*
• Electrolytic dissociation is a process which takes place in – ***electrovalent compounds***	• Ionisation is a process which takes place in – ***covalent compounds.***
• It involves – ***separation of ions*** of the ***ions*** which are already present – in an ionic compound. $PbBr_2 \rightleftharpoons Pb^{2+} + 2Br^{1-}$ [ionic]	• It involves – ***formation of charged ions*** from the ***molecules*** which are – not in the ionic state. $HCl\ [aq.] \rightleftharpoons H^{1+} + Cl^{1-}$ [covalent] Ionisation may also involve atoms changing into ions [eg. $Mg \rightarrow Mg^{2+} + 2e^-$]

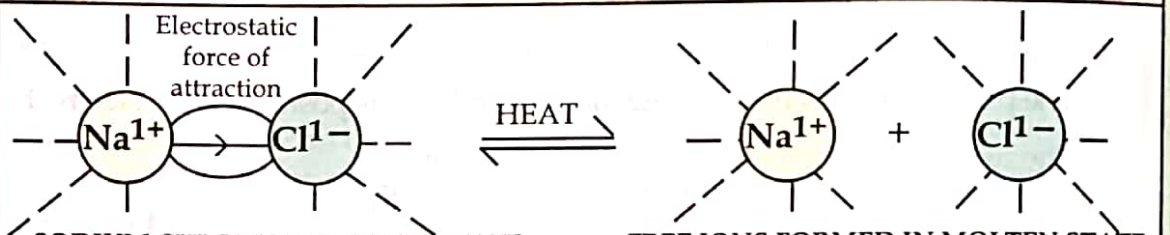
3. ELECTROLYTIC DISSOCIATION – Of Ionic Compounds [NaCl]

Solid sodium chloride is a – non-electrolyte & does not allow electricity to pass through it, but dissociates in the – molten [fused] or in aqueous solution state.
[Thus sodium chloride will conduct electricity only in *fused* or *aqueous solution* state].

a] IN THE MOLTEN STATE [FUSED]

- Ionic compounds [eg. NaCl] contain – positively charged metallic ions [Na^{1+}] & negatively charged non-metallic ions [Cl^{1-}].
- These ***ions are not free*** but held together by – ***strong electrostatic force of attraction.*** Due to this an ionic compound – in the solid state is a bad conductor of electricity since free ions are essential for conducting electricity.
- When an *ionic compound* is *heated strongly* – the ions gain kinetic energy and *break lose* and move freely.
- The molten solution then becomes a – good conductor of electricity.

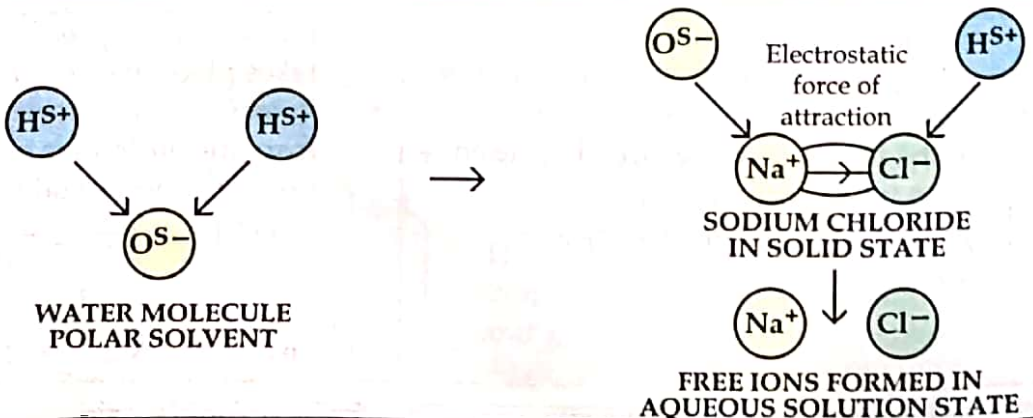
DISSOCIATION OF SODIUM CHLORIDE – IN THE MOLTEN STATE



b] IN THE AQUEOUS SOLUTION STATE

- Water is a – ***polar solvent*** and exhibits – *charge distribution* in its molecule.
- In water each *hydrogen* atom develops a – *slight positive charge* while the oxygen atom develops a *slight negative charge.*
- When *sodium chloride* is dissolved in water it dissociates into – ***sodium ions*** [Na^{1+}] and ***chloride ions*** [Cl^{1-}] which move freely in solution.
- This is due to the fact that the slightly negatively charged oxygen atoms of the water exerts a pull on the positively charged sodium ion. A similar pull is exerted by the slightly positively charged hydrogen atoms of the water on the negatively charged chloride ions. Thus, sodium and chloride ions become free in solution.

DISSOCIATION OF SODIUM CHLORIDE - IN AQUEOUS SOLUTION

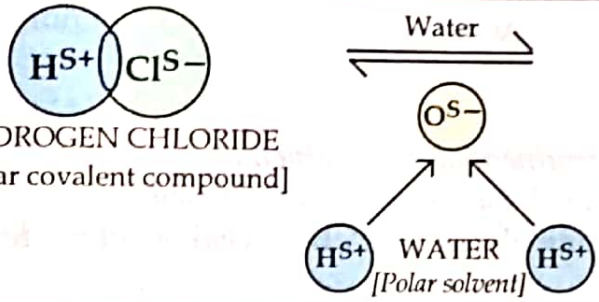


4. IONISATION – Of Covalent Compounds [HCl]

Polar covalent compounds [eg. ammonia, hydrogen chloride] – are non-electrolytes in the gaseous state, but ionise in aqueous solution state.

- Hydrogen chloride in the gaseous state or in the pure liquid state – is unionized and does not conduct an electric current.
- ***Hydrogen chloride*** is however – ***polar covalent*** in nature ie. shows charge distribution in its molecule such that the – hydrogen atom has a slight positive charge & chlorine atom a slight negative charge.
- When hydrogen chloride is added to ***water*** – a ***polar solvent*** – the slightly negatively charged oxygen atom of the water exerts an electrostatic pull on positively charged hydrogen ion of HCl. Thus H^+ ions combine with the water – forming hydronium ions [H_3O^+] and the residual chloride ions remain in solution.
[Hence *ammonia* or *hydrogen chloride* in gaseous or pure liquid state *does not conduct electricity*, but conducts electricity when dissolved in water]

IONISATION OF HYDROGEN CHLORIDE MOLECULE – IN AQUEOUS SOLUTION



H^+ + Cl^-
[hydrogen ion] [chloride ion]

IONISATION

$H^+ + H_2O \rightarrow H_3O^+$ – Hydronium ion

COMPARISON BETWEEN – Metallic conduction & Electrolytic conduction

METAL [eg. Cu]	*ELECTROLYTE* [eg. $CuSO_4$]
1. The *flow of electricity* takes place by– *flow of electrons* – which have negligible mass.	1. The *flow of electricity* takes place by– *flow of ions* – which are denser compared to electrons.
2. There is – *no decomposition* of the *parent metal* and thus the – chemical properties of metal are intact.	2. There is – *decomposition* of the *electrolytic solution* and thus the – chemical properties of electrolyte are altered.
3. Metals are – *good conductors of electricity in the solid state* and in the molten state.	3. Electrolytes are – *good conductors of electricity in aq. soln. or molten state* but not in solid state.
4. During metallic conduction there is – *no transfer of matter.* The flow of electricity only produces heat energy & – *no new products are formed.*	4. During electrolytic conduction there is – *transfer of ions.* The flow of electricity decomposes the electrolyte & – *new products are formed.*

Copper metal – is thus a *good conductor of electricity* – but is a *non-electrolyte*, since – it does not undergo chemical decomposition due to flow of electric current through it.
Copper [II] sulphate – on the other hand is an *electrolyte* – since it decomposes – on passage of electric current forming copper ions and sulphate ions. The Cu^{2+} ions are – discharged at the cathode as Cu metal – when copper electrodes are used during electrolysis.