

# CHAPTER 5

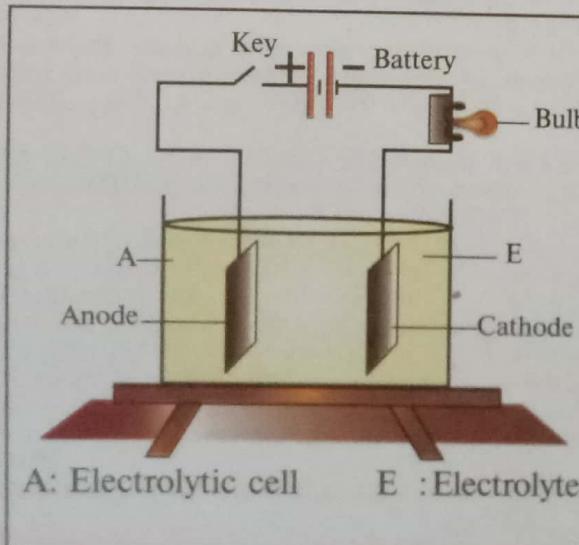
## Electrolysis

| SYLLABUS - SCOPE OF SYLLABUS - in and after MARCH 2021 - ELECTROLYSIS   |   |
|---|---|
| I] ELECTROLYTES & NON-ELECTROLYTES.   | <ul style="list-style-type: none"> <li>• Definitions &amp; examples.</li> </ul>   |
| II] SUBSTANCES CONTAINING MOLECULES ONLY, IONS ONLY, BOTH MOLECULES AND IONS.   | <ul style="list-style-type: none"> <li>• Substances containing molecules only ions only, both molecules &amp; ions.</li> <li>• Examples; relating their composition with their behaviour as strong &amp; weak electrolytes as well as non-electrolytes.</li> </ul>  |
| 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: | <ul style="list-style-type: none"> <li>• Molten lead bromide</li> <li>• Acidified water with platinum electrodes</li> <li>• Aqueous copper [II] sulphate with copper electrodes; electron transfer at the electrodes.</li> </ul> <p>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.</p> |
| V] APPLICATIONS OF ELECTROLYSIS:  | <ul style="list-style-type: none"> <li>• Electroplating with nickel and silver, choice of electrolyte for electroplating.</li> <li>• Electro refining of copper;</li> </ul> <p>Reasons &amp; conditions for electroplating; names of the electrolytes &amp; the electrodes used should be given. Equations for the reactions at the electrodes should be given for electroplating, refining of copper.</p>  |

### 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<sub>4</sub> etc. while those which do not conduct electricity are called - **non-electrolytes**. e.g. alcohol, sugar soln.

### Electrolysis - Electrolytic cell



**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
- $\text{NaCl}$  [electrolyte]  $\rightleftharpoons \text{Na}^{1+}$  [cation] +  $\text{Cl}^{1-}$  [anion]
- Discharge of ions – as neutral atoms at the respective electrodes.
- At cathode :  $\text{Na}^{1+} + 1e^- \rightarrow \text{Na}$  [neutral atom] – Reduction reaction  
[negative electrode]
- At anode :  $\text{Cl}^{1-} - 1e^- \rightarrow \text{Cl}$  [neutral atom] – Oxidation reaction  
[positive electrode]
- 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.  $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$   
Alkalies -  $\text{KOH}$ ,  $\text{NaOH}$  solutions  
Ionic salts -  $\text{PbBr}_2$  [molten],  $\text{CuSO}_4$  [aq.]

### 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.  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ,  $\text{HBr}$ ,  $\text{HI}$   
Bases -  $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{LiOH}$  solns.  
Salts -  $\text{NaCl}$  [ $\text{KCl}$ ],  $\text{Na}_2\text{SO}_4$ ,  $\text{NaNO}_3$ ,  $\text{CuCl}_2$ ,  
 $\text{PbSO}_4$ ,  $\text{Pb(NO}_3)_2$ ,  $\text{PbBr}_2$ ,  $\text{AgI}$  aq. solns.

### 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.

### 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 -  $\text{NH}_4\text{OH}$ ,  $\text{Ca}(\text{OH})_2$ ,  $\text{Mg}(\text{OH})_2$

Salts - Sodium – carbonate, bicarbonate, oxalate and formate aq. solns.

## TERMS – Involved in Electrolysis [Contd.]

### 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

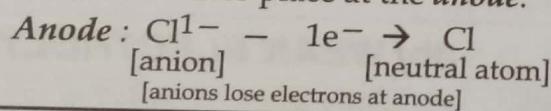
- Electrodes allow the *electric current* to - *enter* or *leave* the electrolytic solution.
- The electrodes are two in number and are made of - metal or carbon.
- Graphite [carbon] electrodes are used - when the products formed during electrolysis react with the metallic electrode.
- The electrodes 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 - very 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*.

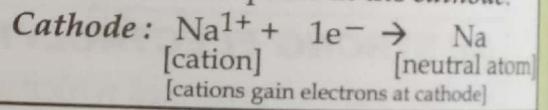


#### 5b] CATHODE [negative electrode]

- 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*.



### 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

#### 6b] CATIONS

## G. 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  |
|--|---|
| <ul style="list-style-type: none"><li>Electrolytic dissociation is a process which takes place in – <i>electrovalent compounds</i></li><li>It involves – <i>separation of ions</i> of the <i>ions</i> which are already present – in an ionic compound.</li></ul> $\text{PbBr}_2 \rightleftharpoons \text{Pb}^{2+} + 2\text{Br}^{1-}$<br>[ionic] | <ul style="list-style-type: none"><li>Ionisation is a process which takes place in – <i>covalent compounds</i>.</li><li>It involves – <i>formation of charged ions</i> from the <i>molecules</i> which are – not in the ionic state.</li></ul> $\text{HCl} \text{ [aq.]} \rightleftharpoons \text{H}^{1+} + \text{Cl}^{1-}$<br>[covalent]<br>Ionisation may also involve atoms changing into ions [eg. $\text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^-$ ] |

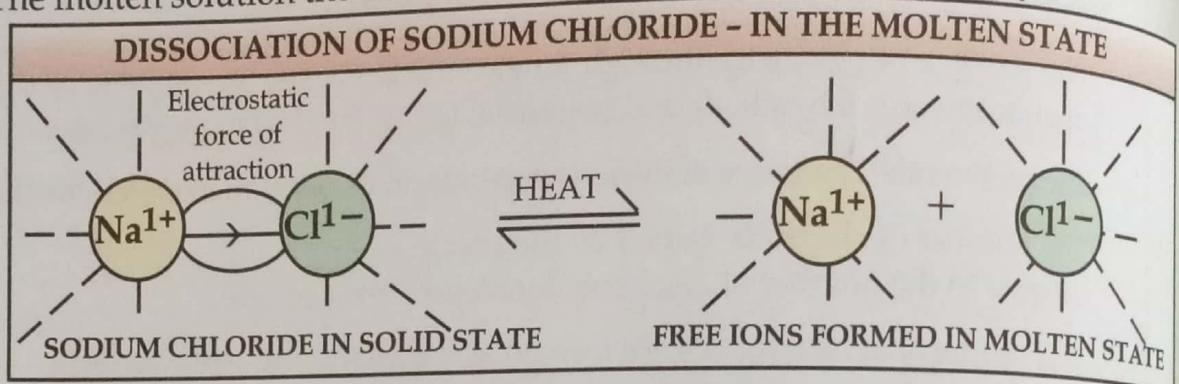
## MECHANISM – Of Electrolytic Dissociation – Of Ionic Compounds [NaCl]

**ELECTROLYTIC DISSOCIATION**

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].

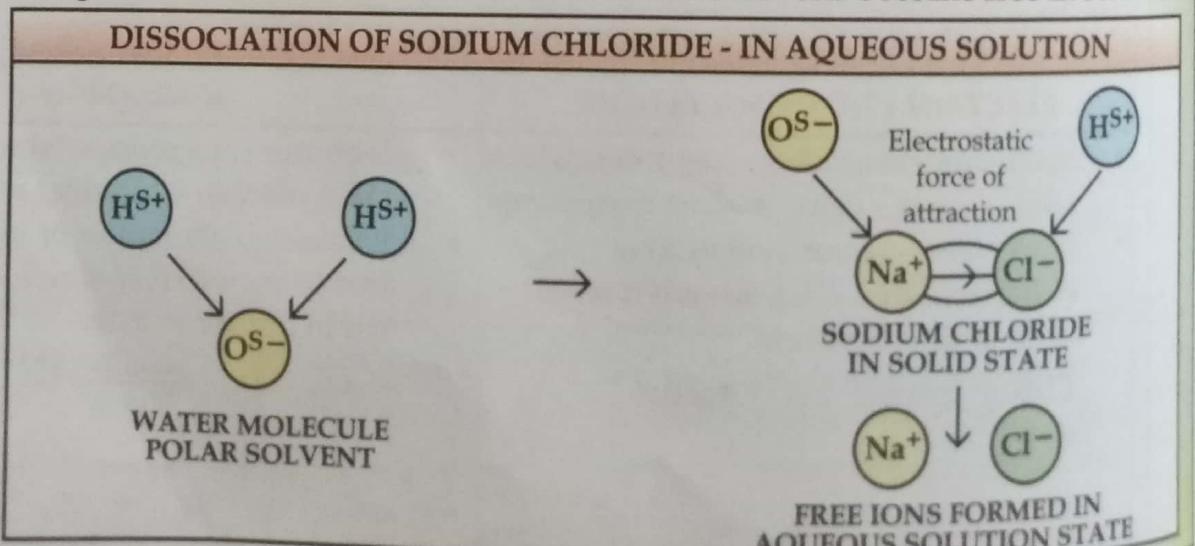
a] IN THE MOLTEN STATE [FUSED]

- Ionic compounds [eg. NaCl] contain - positively charged metallic ions  $[Na^{1+}]$  & negatively charged non-metallic ions  $[Cl^{-}]$ .
  - 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.



**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.



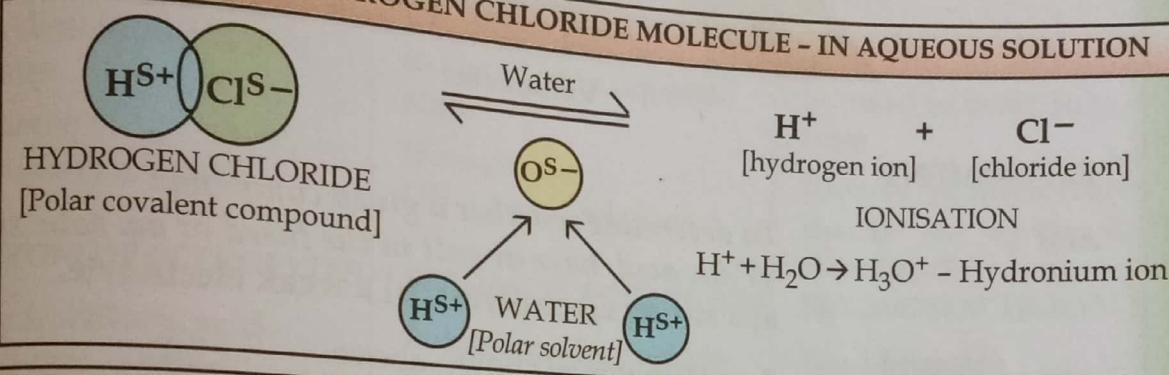
## MECHANISM - Of Electrolysis [Contd.]

### 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

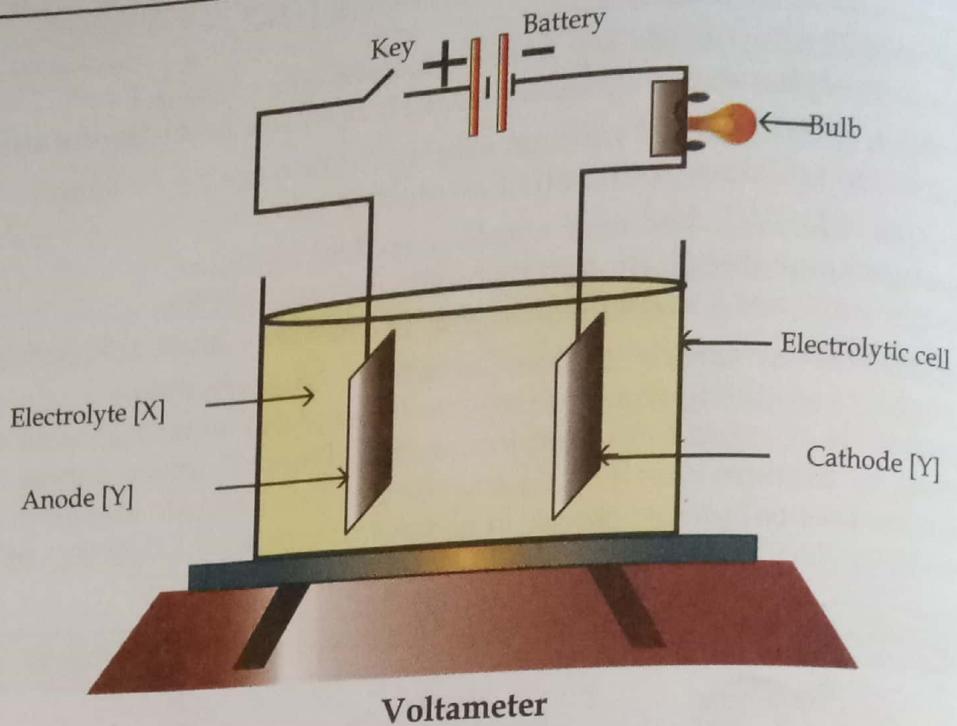


### COMPARISON BETWEEN - Metallic conduction & Electrolytic conduction

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

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.

## D. ACIDS, BASES AND SALTS – as electrolytes



### EXPERIMENT

- AIM** : To determine whether a given compound - 'A' i.e. acid, base or salt in the fused or aq. soln. state is  
a] a strong electrolyte b] a weak electrolyte.
- APPARATUS** : A voltameter as shown above.  
X = Electrolytic solution of the given compound  
Y = Electrodes - graphite electrodes connected to a bulb and a current source through a key.
- PROCEDURE** : The given compound 'A' i.e. acid, base or salt - in the fused or aqueous solution state is placed - in the electrolytic cell and the current is switched on.
- OBSERVATIONS** : The conduction of electricity through the electrolyte - is indicated by the glow of the bulb.  
If the given compound 'A' ie. acid, base or salt solution - is a **strong electrolyte** the **bulb glows brightly** - when the current is switched on.  
If the given compound 'A' - is a **weak electrolyte** the **glow of the bulb is very dim** - when the current is switched on.  
Thus different acids, base [alkalis] and salt solutions - can be classified into strong or weak electrolytes.

# STRONG ELECTROLYTES

# WEAK ELECTROLYTES

*can be classified as -  
strong or weak electrolytes -  
depending on the degree of dissociation.*

- : Compounds which in the fused or in the aqueous solution state are almost completely dissociated and are good conductors of electricity are called - *strong electrolytes*.
- : Compounds which in the fused or in the aqueous solution state are feebly or partially dissociated and are poor conductors of electricity are called - *weak electrolytes*.

Classification of acids, bases and salts into - strong and weak electrolytes

| ACIDS   | BASES [alkalis]   | SALTS  |
|---|---|--|
| Mineral acids ionise -<br>on dissolution in<br>water<br><br>[Furnish -<br>$H^+$ ions in solution] | Bases ionise -<br>in fused or in aq. soln.<br>state<br><br>[Furnish -<br>$OH^-$ ions in solution] | Ionic salts ionise -<br>in fused or in aq. soln.<br>state<br><br>[Furnish - positive ions other<br>than $H^+$ and negative ions<br>other than $OH^-$ ions] |
| <b>STRONG ELECTROLYTES</b>  | <b>STRONG ELECTROLYTES</b>  | <b>STRONG ELECTROLYTES</b>   |
| <b>Hydrochloric acid</b><br>$HCl \rightleftharpoons H^{1+} + Cl^{1-}$<br>[aq.]                    | <b>Potassium hydroxide</b><br>$KOH \rightleftharpoons K^{1+} + OH^{1-}$<br>[aq.]                  | <b>Lead bromide</b><br>$PbBr_2 \rightleftharpoons Pb^{2+} + 2Br^{1-}$<br>[molten]  |
| <b>Nitric acid</b><br>$HNO_3 \rightleftharpoons H^{1+} + NO_3^{1-}$<br>[aq.]                      | <b>Sodium hydroxide</b><br>$NaOH \rightleftharpoons Na^{1+} + OH^{1-}$<br>[aq.]                   | <b>Copper chloride</b><br>$CuCl_2 \rightleftharpoons Cu^{2+} + 2Cl^{1-}$<br>[aq.]  |
| <b>Sulphuric acid</b><br>$H_2SO_4 \rightleftharpoons 2H^{1+} + SO_4^{2-}$<br>[aq.]                | <b>Lithium hydroxide</b><br>$LiOH \rightleftharpoons Li^{1+} + OH^{1-}$<br>[aq.]                  | <b>Silver nitrate</b><br>$AgNO_3 \rightleftharpoons Ag^{1+} + NO_3^{1-}$<br>[aq.]  |
| <b>WEAK ELECTROLYTES</b>  | <b>WEAK ELECTROLYTES</b>  | <b>WEAK ELECTROLYTES</b>   |
| <b>Acetic acid</b><br>$CH_3COOH \rightleftharpoons CH_3COO^{1-} + H^{1+}$<br>[aq.]                | <b>Calcium hydroxide</b><br>$Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^{1-}$<br>[aq.]             | <b>Sodium carbonate</b><br>$Na_2CO_3 \rightleftharpoons 2Na^{1+} + CO_3^{2-}$<br>[aq.]   |
| <b>Formic acid</b><br>$HCOOH \rightleftharpoons HCOO^{1-} + H^{1+}$<br>[aq.]                      | <b>Magnesium hydroxide</b><br>$Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^{1-}$<br>[aq.]           | <b>Potassium bicarbonate</b><br>$KHCO_3 \rightleftharpoons K^{1+} + HCO_3^{1-}$<br>[aq.]   |
| <b>Carbonic acid</b><br>$H_2CO_3 \rightleftharpoons 2H^{1+} + CO_3^{2-}$<br>[aq.]                 | <b>Ammonium hydroxide</b><br>$NH_4OH \rightleftharpoons NH_4^{1+} + OH^{1-}$<br>[aq.]             | <b>Lead acetate</b><br>$(CH_3COO)_2Pb \rightleftharpoons 2CH_3COO^- + Pb^{2+}$<br>[aq.]  |

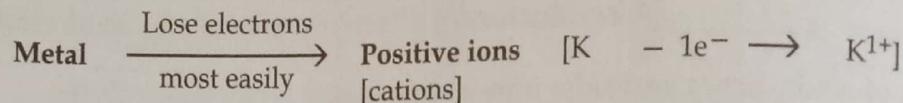
### E. ELECTROCHEMICAL SERIES

Depending on the ease with which the metals lose their electrons and form ions - they are arranged in a series known as - metal activity series or electrochemical series.

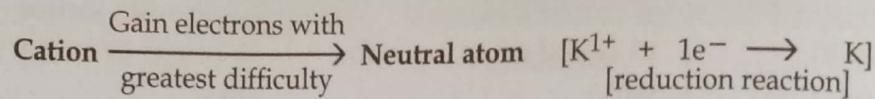
The arrangement is so done that the elements that - ionize most readily [discharged with great difficulty] - are placed at the top of the series and other elements in the descending order.

## AT THE TOP OF THE SERIES

Metals which ionize most readily - are included at the top of the series.

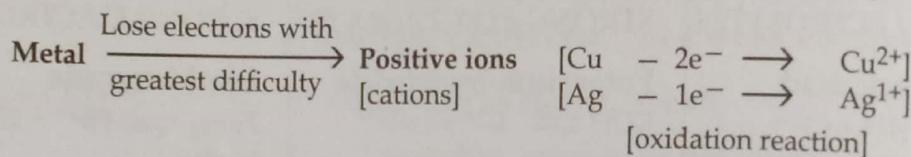


- *Positive ions [cations] formed – are discharged at cathode – with most difficulty.*  
Gain electrons with

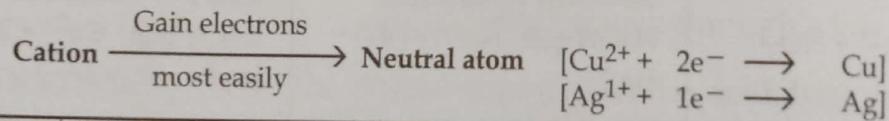


## AT THE LOWER END OF THE SERIES

*Metals which ionize least readily - are included at the lower end of the series*



- Positive ions [cations] formed - are discharged at the cathode - most readily.



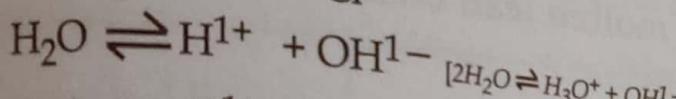
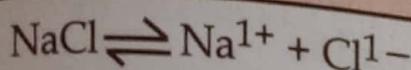
| METAL | CATION    |  |  | ANION       |
|-------|-----------|--|--|-------------|
| K     | $K^{1+}$  | Discharged with -<br><i>most difficulty.</i>   | Discharged with -<br><i>most difficulty.</i>   | $SO_4^{2-}$ |
| Ca    | $Ca^{2+}$ |  |  |             |
| Na    | $Na^{1+}$ |  |  |             |
| Mg    | $Mg^{2+}$ | <i>Positive ions [cations]</i><br>discharged at <i>cathode</i><br>- by <i>gain of electrons.</i>   | <i>Negative ions [anions]</i><br>discharged at <i>anode</i><br>- by <i>loss of electrons.</i>  | $NO_3^{1-}$ |
| Al    | $Al^{3+}$ |  |  | $Cl^{1-}$   |
| Zn    | $Zn^{2+}$ | The tendency of the<br>cations to get -<br><i>reduced</i> at the cathode<br><i>increases</i> on descending<br>the <i>electrochemical series.</i> | The tendency of the<br>anions to get -<br><i>oxidised</i> at the anode<br><i>increases</i> on descending<br>the <i>electrochemical series.</i> | $Br^{1-}$   |
| Fe    | $Fe^{2+}$ |  |  | $I^{1-}$    |
| Pb    | $Pb^{2+}$ |  |  |             |
| [H]   | $H^{1+}$  |  |  |             |
| Cu    | $Cu^{2+}$ |  |  |             |
| Hg    | $Hg^{2+}$ | Discharged -<br><i>most easily.</i>  | Discharged -<br><i>most easily.</i>  | $OH^{1-}$   |
| Ag    | $Ag^{1+}$ |  |  |             |

- Greater - the tendency of the ion-forming element in the electrochemical series -
- the tendency to be liberated - at the respective electrode.

| DISCHARGE OF CATIONS AND ANIONS - at the respective electrodes |  |
|--|--|
| Cations  | a] $\text{Cu}^{2+}$ & $\text{H}^{1+}$ migrate to cathode - $\text{Cu}^{2+}$ ions discharged at cathode.<br>b] $\text{Ag}^{1+}$ & $\text{H}^{1+}$ migrate to cathode - $\text{Ag}^{1+}$ ions discharged at cathode. |
| Anions   | a] $\text{SO}_4^{2-}$ & $\text{OH}^{1-}$ migrate to anode - $\text{OH}^{1-}$ ions discharged at anode.   |

2. CONCENTRATION OF THE IONS - In the Electrolyte
- Higher - the concentration of the ion -
  - Greater - the probability of it being discharged - at the respective electrodes.

### ELECTROLYSIS OF - dil. NaCl soln.



Cathode :  $\text{H}^{1+} \rightleftharpoons \text{H}_3\text{O}^+$  ions discharged  
Anode :  $\text{OH}^{1-}$  ions discharged

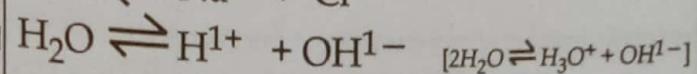
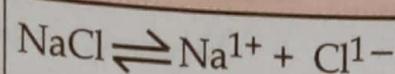
$\text{H}^{1+}$  gains electrons more easily than  $\text{Na}^{1+}$   
•  $\text{OH}^{1-}$  preferentially discharged

[due to lower position in electrochemical series]

Cathode:  $\text{H}_2$  evolved

Anode:  $\text{O}_2$  evolved

### ELECTROLYSIS OF - conc. NaCl soln.



Cathode:  $\text{Na}^{1+} \rightleftharpoons \text{H}^{1+} \rightleftharpoons \text{H}_3\text{O}^+$  ions migrate  
Anode :  $\text{Cl}^{1-} \rightleftharpoons \text{OH}^{1-}$  ions migrate

Despite high conc. of  $\text{Na}^{1+}$ , at a particular conc.  
 $\text{H}^{1+}$  gains electrons more easily than  $\text{Na}^{1+}$ .

•  $\text{Cl}^{1-}$  preferentially discharged

[due to high conc. of  $\text{Cl}^{1-}$  ions]

Cathode:  $\text{H}_2$  evolved

Anode:  $\text{Cl}_2$  evolved

### 3. NATURE OF THE ELECTRODE -

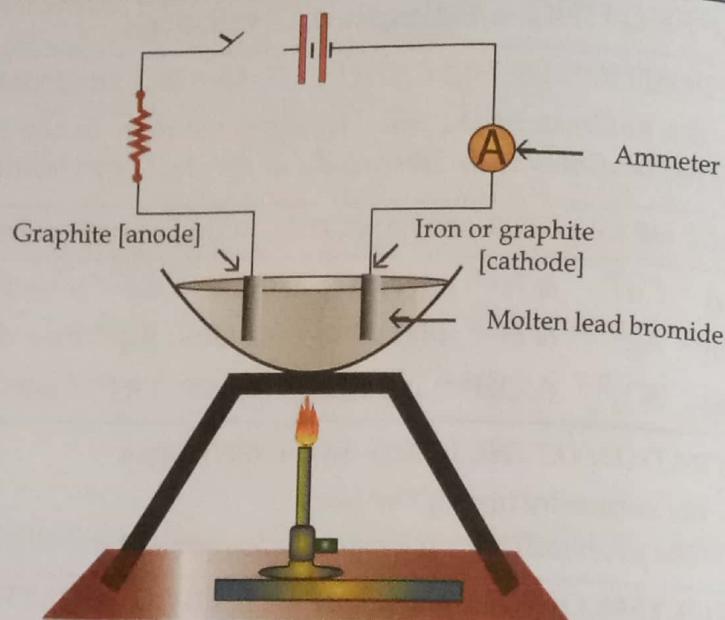
Determines the preferential ion - which will be discharged at the electrode.

- Inert electrodes : Iron, graphite, platinum - do not take part in electrolytic reaction.
- Active electrodes: Copper, nickel, silver - take part in electrolytic reaction.

| ACTIVE ELECTRODE - Cu   | Aq. copper sulphate soln.   | INERT ELECTRODE - Pt  |
|---|---|---|
| <p>Electrolysis of <math>\text{CuSO}_4</math> soln.</p> <p>Electrodes: Cathode - copper<br/>Anode - copper</p> <p>Reaction at anode :<br/> <math>\text{Cu} - 2\text{e}^- \rightarrow \text{Cu}^{2+}</math></p> <p>Product: <math>\text{Cu}^{2+}</math> ions</p> | $\text{CuSO}_4 \rightleftharpoons \text{Cu}^{2+} + \text{SO}_4^{2-}$ $\text{H}_2\text{O} \rightleftharpoons \text{H}^{1+} + \text{OH}^{1-}$ | <p>Electrolysis of <math>\text{CuSO}_4</math> soln.</p> <p>Electrode: Cathode - copper<br/>Anode - platinum</p> <p>Reaction at anode :<br/> <math>\text{OH}^{1-} - 1\text{e}^- \rightarrow \text{OH} \times 2</math><br/> <math>[2\text{OH} \rightarrow \text{H}_2\text{O} + [\text{O}]]</math><br/> <math>4\text{OH} \rightarrow 2\text{H}_2\text{O} + \text{O}_2</math></p> |

## G. EXAMPLES – OF ELECTROLYSIS

### 1. ELECTROLYSIS OF – MOLTEN OR FUSED LEAD BROMIDE



Electrolysis of molten lead bromide

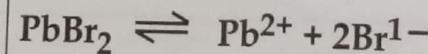
1. ELECTROLYTIC CELL
2. ELECTROLYTE
3. ELECTRODE :
4. TEMPERATURE
5. CURRENT
6. ELECTRODE REACTION

*Dissociation of  $PbBr_2$*

*Reaction at the cathode*

*Reaction at the anode*

Silica crucible  
Molten – lead bromide  
*Cathode : Iron or graphite*  
*Anode : Graphite*  
Above :  $380^\circ C$  [*m.p. of  $PbBr_2$* ]  
*Current : 3 amperes*



$Pb^{2+} + 2e^- \rightarrow Pb$   
•  *$Pb^{2+}$  ions are discharged at the cathode -*  
as neutral lead atoms -  
by accepting electrons

$Br^{1-} - 1e^- \rightarrow Br$   
 $Br + Br \rightarrow Br_2$   
•  *$Br^{1-}$  ions are discharged at the anode -*  
as neutral bromine atoms -  
by giving up electrons.  
• Bromine atoms form a molecule of bromine

[INERT ELECTRODE]  
[INERT ELECTRODE]

*Ions present :*  
 $Pb^{2+}$ ,  $Br^{1-}$  [lead, bromide]

*Product at - cathode :*  
Lead metal.  
[silvery grey deposit]  
[reduction reaction]

*Product at - anode :*  
Bromine vapours  
[reddish brown fumes]  
[oxidation reaction]

[electrolysis of molten lead bromide involves oxidation & reduction reactions & hence is a - redox reaction]

## EXAMPLES - OF ELECTROLYSIS [Contd.]

### ELECTROLYSIS OF - MOLTEN OR FUSED LEAD BROMIDE [Contd.]

1. The electrolytic cell - is made of silica and the crucible heated slowly from outside.

- The crucible is made of silica since it is - non-reactive, withstands high temperature & is almost a non-conductor of electricity.
- Solid lead bromide is a non-conductor of electric current since - its ions are not free but held together by - an electrostatic force of attraction.
- The ions become free - when lead bromide is in the - fused or molten state. Hence the crucible is heated to maintain lead bromide - in the molten state.

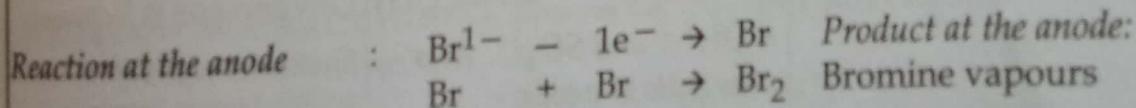
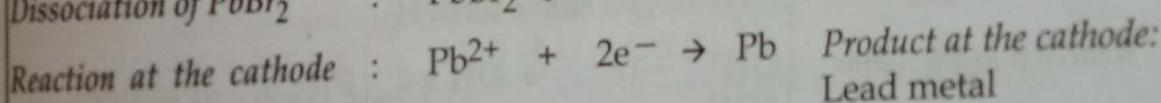
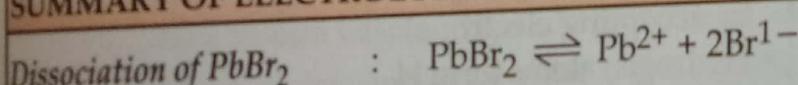
2. The metallic lead ions are discharged at the cathode as lead metal and bromine is liberated at the anode.

- The cathode is an electron donor and metallic lead ions need electrons - to discharge at the cathode as neutral lead atoms or metallic lead.
- Hence the lead ions gain electrons to form metallic lead atoms. The lead atoms are then deposited as a silvery grey deposit around the cathode.
- Bromine ions give up electrons - resulting in formation of neutral bromine atoms.
- The neutral bromine atoms form bromine molecules - by forming a covalent bond between them.
- Reddish brown vapours of bromine are hence seen at the anode - when the molecules of bromine escape from the molten lead bromide and - evolve as bromine vapours.

3. The cathode and anode are - inert in nature and generally made of graphite

- The electrodes are inert - since they should not take part in the reaction - otherwise they would prevent the discharge of the respective ions.
- A graphite anode is preferred - to other inert electrodes such as platinum - since graphite is unaffected by the reactive bromine vapours.

#### SUMMARY OF ELECTROLYTIC REACTIONS OF - FUSED LEAD BROMIDE

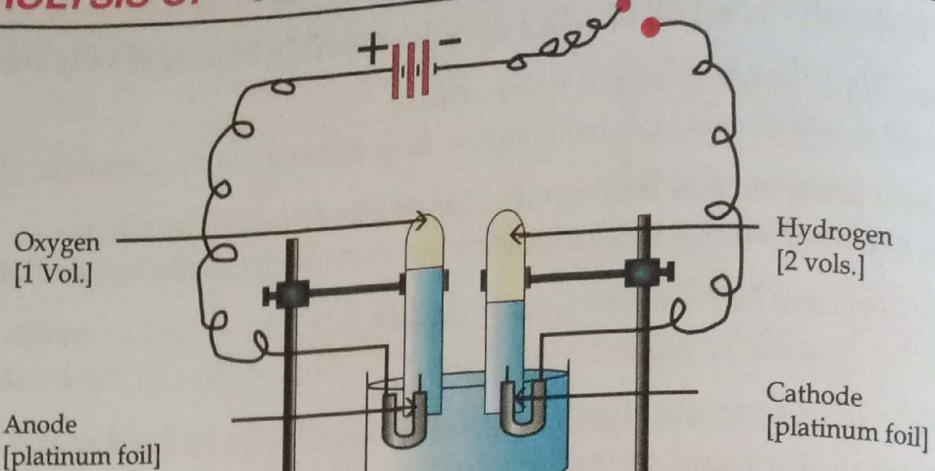


Compound formed between a metal 'X' [e.g. Pb] and a non-metal 'Y' [e.g. Br] - On electrolysis in the molten or aq. soln. state generally liberates or discharges -

- At cathode - Metal 'X' in pure state.
- At anode - Non-metal 'Y' in gaseous or vapour state.

**EXAMPLES – OF ELECTROLYSIS [Contd.]**

**2. ELECTROLYSIS OF – ACIDIFIED WATER – Using platinum electrodes**



Electrolysis of acidified water

|                         |   |   |
|-------------------------|---|---|
| 1. ELECTROLYTIC CELL    | As shown above.   |   |
| 2. ELECTROLYTE          | Acidified water [with dil. $\text{H}_2\text{SO}_4$ ]  |   |
| 3. ELECTRODE            | Cathode : Pt foil<br>Anode : Pt foil  | [INERT ELECTRODE]<br>[INERT ELECTRODE]  |
| 4. TEMPERATURE          | Ordinary temperature  |   |
| 5. CURRENT              | Current : 3 amps  |   |
| 6. ELECTRODE REACTION   | Dissociation of acidified water<br>$\text{H}_2\text{SO}_4 \rightleftharpoons 2\text{H}^{1+} + \text{SO}_4^{2-}$<br>$\text{H}_2\text{O} \rightleftharpoons \text{H}^{1+} + \text{OH}^{1-}$   | Ions present :<br>$\text{H}^{1+}, \text{SO}_4^{2-}, \text{OH}^{1-}$<br>[hydrogen, sulphate, hydroxyl]   |
| Reaction at the cathode | $\text{H}^{1+} + 1\text{e}^- \rightarrow \text{H} \times 4$<br>$2\text{H} + 2\text{H} \rightarrow 2\text{H}_2$<br>• $\text{H}^{1+}$ ions are discharged at the cathode -<br>as neutral hydrogen atoms - by accepting electrons.<br>• Hydrogen atoms form $\text{H}_2$ .   | Product at cathode :<br>Hydrogen gas [2 Volumes]  |
| Reaction at the anode   | $\text{OH}^{1-} - 1\text{e}^- \rightarrow \text{OH} \times 4$<br>$4\text{OH} \rightarrow 2\text{H}_2\text{O} + \text{O}_2$<br>• $\text{OH}^{1-}$ and $\text{SO}_4^{2-}$ ions - migrate to anode.<br>• $\text{OH}^{1-}$ is discharged - at the anode -<br>[lower in electrochemical series]<br>• Unstable OH radical - forms water & oxygen. | Product at anode :<br>Oxygen gas [1 Volume]<br>Since electrolysis of - acidified water involves -<br>• reduction - at cathode [gain of electrons] &<br>• oxidation - at anode [loss of electrons],<br>it is an example of - redox reaction<br>[reduction & oxidation] |

The current is passed for a prolonged period of time - before collection of the gases for the purpose of accurate comparison. This ensures saturation of the gases - in the electrolyte since solubility of oxygen differs from that of hydrogen.

Hydrogen is liberated at the cathode and oxygen at the anode.

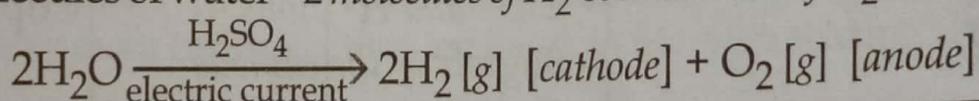
- Cathode      - the  $H^{1+}$  ions migrate to the cathode.
- Anode      - the  $SO_4^{2-}$  &  $OH^{1-}$  ions migrate to the anode.
- At the anode      - the  $OH^{1-}$  ions are discharged in preference to  $SO_4^{2-}$  ions - [ $OH^{1-}$  ions have lower discharge potential than  $SO_4^{2-}$  ions].

Concentration of  $SO_4^{2-}$  ions at the anode increases

Due to presence of excess  $H^{1+}$  &  $SO_4^{2-}$  ions at the anode, the conc. of  $H_2SO_4$  increases at the anode & decreases at the cathode - but the total conc. of  $H_2SO_4$  molecules remains the same since it is the  $- H^{1+}$  ions &  $OH^{1-}$  ions which are actually discharged at the electrodes respectively.

The ratio of hydrogen & oxygen liberated at cathode & anode is - 2:1 by volume.

- As per electrolytic reactions -  $4H^{1+}$  ions are needed at the cathode &  $4OH^{1-}$  at the anode - & two molecules of water are produced - at the anode.
- Hence, for every 2 molecules of water - 2 molecules of  $H_2$  & 1 molecule of  $O_2$  are liberated-



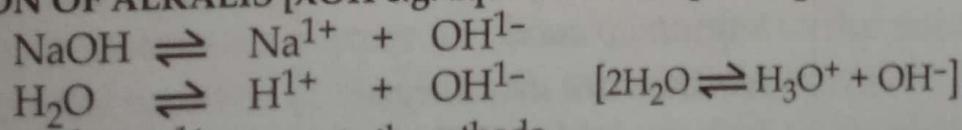
### DISSOCIATION OF ACIDS [e.g. HX]

**Strong acids** - Dissociate almost completely in aq. soln. state to give particles - almost only ions.  
 $HX \rightarrow H^+ + X^-$  ;  $H^+ + H_2O \rightarrow H_3O^+$

Ions present in soln. :  $H_3O^+$ ;  $X^-$  & minimum undissociated molecules of HX.

**Weak acids** - Dissociate partially in aq. soln. state to give particles - ions & undissociated molecules.  
 $HX \rightarrow H^+ + X^-$  ;  $H^+ + H_2O \rightarrow H_3O^+$   
Ions present in soln. :  $H_3O^+$ ;  $X^-$  & undissociated molecules of HX.

### DISSOCIATION OF ALKALIS [XOH e.g. aqueous NaOH] - using inert electrodes



$Na^{1+}$  &  $H^{1+}$  migrate to the cathode

[ $H^{1+}$  discharged - due to lower position in the electrochemical series]

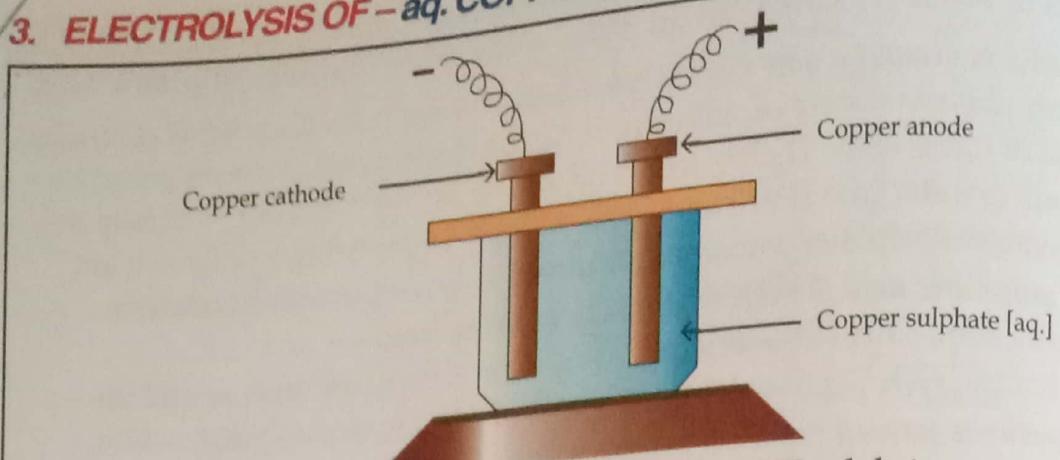
**Cathode:**  $H^{1+} + 1e^- \rightarrow H$   $\times 4$ ;  $2H + 2H \rightarrow 2H_2$  [hydrogen - evolved]

**Anode:**  $OH^{1-} - 1e^- \rightarrow OH \times 4$ ;  $4OH \rightarrow 2H_2O + O_2$  [oxygen - evolved]

[Fused NaOH - however discharges  $Na^{1+}$  at the cathode &  $OH^{1-}$  at the anode]

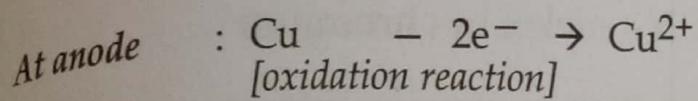
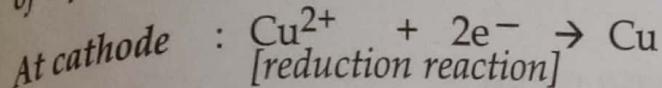
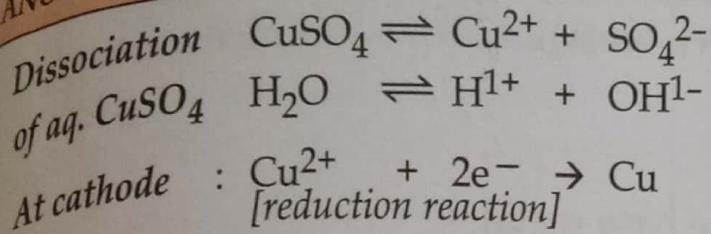
## EXAMPLES - OF ELECTROLYSIS [Contd.]

### 3. ELECTROLYSIS OF - aq. COPPER [II] SULPHATE — Using copper electrodes



|  |  |  |
|--|--|--|
| 1. ELECTROLYTIC CELL   | As shown above.  |  |
| 2. ELECTROLYTE   | Aqueous copper [II] sulphate   | [ACTIVE ELECTRODE]   |
| 3. ELECTRODE:  | Cathode : Copper<br>Anode : Copper   | [ACTIVE ELECTRODE]   |
| 4. TEMPERATURE   | Ordinary temperature   |  |
| 5. CURRENT   | Current : 3 amps.  |  |
| 6. ELECTRODE REACTION  | <p>Dissociation of aqueous copper sulphate</p> $\text{CuSO}_4 \rightleftharpoons \text{Cu}^{2+} + \text{SO}_4^{2-}$ $\text{H}_2\text{O} \rightleftharpoons \text{H}^{1+} + \text{OH}^{1-}$   | <p>Ions present:<br/> <math>\text{Cu}^{2+}, \text{H}^{1+}, \text{SO}_4^{2-}, \text{OH}^{1-}</math><br/>         [copper, hydrogen, sulphate, hydroxyl]</p> |
| Reaction at the cathode  | $\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}$ <ul style="list-style-type: none"> <li>• <math>\text{Cu}^{2+}</math> and <math>\text{H}^{1+}</math> ions - migrate to the cathode</li> <li>• <math>\text{Cu}^{2+}</math> ions are discharged at the cathode - as neutral copper atoms - by accepting electrons.<br/> <math>[\text{Cu}^{2+} \text{ below } \text{H}^{1+} \text{ in the electrochemical series}]</math></li> </ul> | <p>Product at cathode :</p> <p>Copper metal</p>  |
| Reaction at the anode  | $\text{Cu} - 2e^- \longrightarrow \text{Cu}^{2+}$ <ul style="list-style-type: none"> <li>• <math>\text{SO}_4^{2-}</math> and <math>\text{OH}^{1-}</math> ions migrate to anode</li> <li>• Neither are discharged [copper is an active electrode and itself takes part in the reaction].<br/> <math>\text{Copper anode itself ionises to give Cu}^{2+}</math> ions.</li> </ul>  | <p>Product at anode :</p> <p>Nil [<math>\text{Cu}^{2+}</math> ions formed]</p>   |
| <p><i>[The process of oxidation takes place at the anode and hence it is called the oxidising electrode]</i></p> |  |  |

**USING CATHODE : Copper [or platinum or carbon]**  
**ANODE : Copper**



**Product at cathode :** Copper a brownish pink metal is deposited at the cathode during electrolysis of CuSO<sub>4</sub> soln.

**Product at anode:** Nil [Copper ions formed]

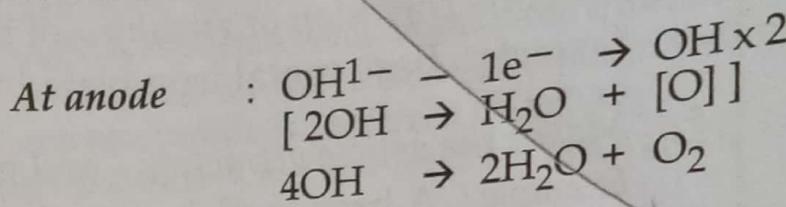
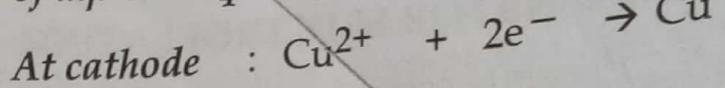
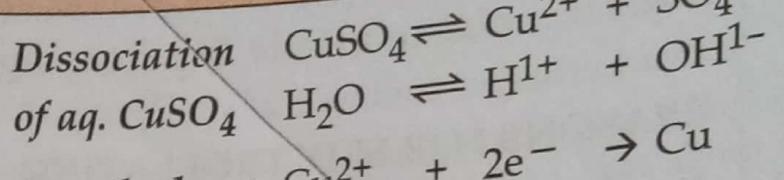
**At cathode :**  
 Cu<sup>2+</sup> ions & H<sup>1+</sup> ions migrate to the cathode  
 Cu<sup>2+</sup> ions are discharged in preference to H<sup>1+</sup>.  
 [Cu<sup>2+</sup> lower in electrochemical series]

**At anode :**  
 SO<sub>4</sub><sup>2-</sup> & OH<sup>1-</sup> ions migrate to the anode  
 but neither are discharged since the -  
 Copper anode loses electrons more easily -  
 than SO<sub>4</sub><sup>2-</sup> & OH<sup>1-</sup>.

[Nature of electrode - copper active electrode]

**Copper anode hence shows -**  
**a loss in mass.**

**CATHODE : Platinum or carbon**  
**ANODE : Platinum or carbon**



**Product at anode: Oxygen gas**

**At cathode :**  
 Cu<sup>2+</sup> ions & H<sup>1+</sup> ions migrate to the cathode  
 Cu<sup>2+</sup> ions are discharged in preference to H<sup>1+</sup>.  
 [Cu<sup>2+</sup> lower in electrochemical series]

**At anode :**  
 SO<sub>4</sub><sup>2-</sup> & OH<sup>1-</sup> ions migrate to the anode  
 but OH<sup>1-</sup> ions are discharged since -  
 they are lower in the electrochemical series.

Oxidation of the OH<sup>1-</sup> ions gives -  
 unstable hydroxyl radical which forms -  
 water with the liberation of oxygen.

3. The blue colour of aq. copper [II] sulphate solution -  
 remains unchanged during electrolysis of aq. CuSO<sub>4</sub> - using copper electrodes -  
 but fades when - platinum electrodes are used

- If copper anode is used - for every copper ion [Cu<sup>2+</sup>] discharged at the cathode as neutral copper atom - a copper ion [Cu<sup>2+</sup>] is added to the solution at the anode. Hence the total number of Cu<sup>2+</sup> ions - remains the same.  
 Therefore the blue colour of CuSO<sub>4</sub> which is due to presence of Cu<sup>2+</sup> ions - does not fade [SO<sub>4</sub><sup>2-</sup> & OH<sup>1-</sup> ions are spectator ions]. [copper anode diminishes in mass]
- If platinum [or carbon] anode is used - the blue colour of CuSO<sub>4</sub> solution fades since - the blue Cu<sup>2+</sup> ions which are discharged at the cathode are not replaced at the anode

## THE TERM

**Electroplating** - is the electrolytic process of deposition of - a *superior metal* [eg. nickel, silver, chromium, gold] on the surface of - a *baser metal or article* [eg. iron, copper, brass].

## REASONS FOR ELECTROPLATING

- Prevents corrosion or rusting - of the base metal.  
*Example :* Base metal iron plated with - nickel or chromium
- Makes the article attractive - and gives it an expensive appearance.  
*Example :* A brass article plated with - silver or gold.

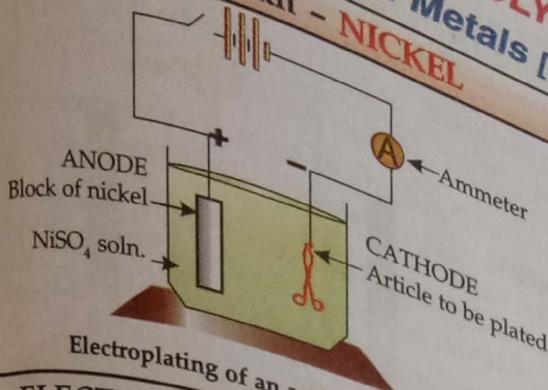
## CONDITIONS - For Electroplating

| Condition  | Reason   |
|--|--|
| 1. The <i>article</i> to be electroplated is always placed at the - <i>cathode</i> .   | During electrolytic reaction - the metal is always deposited at the cathode - by gain of electrons.  |
| 2. The <i>metal</i> to be plated on the article is always made the - <i>anode</i> . It has to be replaced periodically.  | The metal anode continuously dissolves - as ions in solution and is hence - replaced periodically.   |
| 3. The <i>electrolyte</i> - must contain - <i>ions of the metal</i> used for plating on the article. [metal to be electroplated with silver - must contain - ions of the metal silver] | The electrolyte dissociates - into ions of the metal which migrate - towards the cathode and are deposited as neutral metallic atoms on the - cathode [article]. |
| 4. A <i>low current</i> and for a - <i>longer time</i> should be used.   | Higher current causes - uneven deposition of the metal.<br>Low current for a longer time - initiates a smooth, firm, uniform & long lasting deposition.          |
| 5. A <i>direct current</i> and not A.C. current should be used.  | A.C. current causes - discharge and ionisation to alternate at the cathode - thus giving no effective coating.   |

# APPLICATIONS - OF ELECTROLYSIS [Contd.]

## ELECTROPLATING - Of Metals [Contd.]

### a) Electroplating with - NICKEL



#### 1. ELECTROLYTE

Aqueous soln. of - nickel sulphate-



#### 2. NATURE OF ELECTRODE

- Cathode

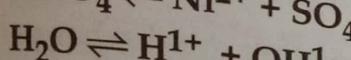
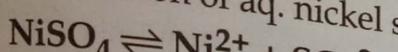
Cleaned article to be electroplated

- Anode - Active electrode

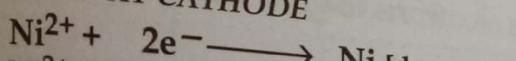
Plate or block of nickel metal

#### 3. ELECTRODE REACTIONS

Dissociation of aq. nickel sulphate

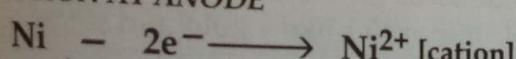


#### REACTION AT CATHODE



- $\text{Ni}^{2+}$  ions move towards the cathode & are discharged as - neutral Ni atoms - by gain of electrons [in preference to  $\text{H}^+$ ]
- Thus nickel is - deposited on the article [cathode].

#### REACTION AT ANODE

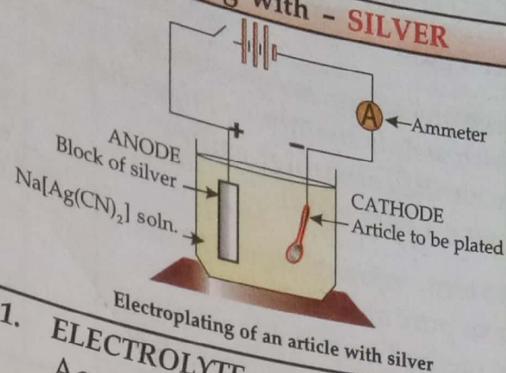


- $\text{SO}_4^{2-}$  and  $\text{OH}^-$  ions migrate - to the anode but neither are discharged
- Instead the nickel anode - loses electrons to give -  $\text{Ni}^{2+}$  ions in soln. [Nature of electrode - Ni active electrode].

Hence anode - diminishes in mass.

[Product at anode - Nil ( $\text{Ni}^{2+}$  ions formed)]

### b) Electroplating with - SILVER



#### 1. ELECTROLYTE

Aq. soln. of - sodium silver cyanide -  $\text{Na[Ag(CN)}_2]$  i.e. sodium argentocyanide.

Migration of  $\text{Ag}^{1+}$  ions from above complex salt soln. is slow compared to that from -  $\text{AgNO}_3$ . Hence even deposition of the metal silver is obtained on the article. Therefore sodium argentocyanide is preferred to  $\text{AgNO}_3$ . [Preparation -  $\text{AgCN} + \text{NaCN} \rightarrow \text{Na[Ag(CN)}_2]$ ]

#### 2. NATURE OF ELECTRODE

- Cathode

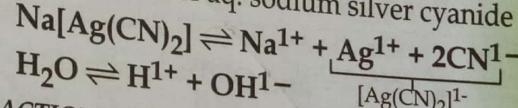
Cleaned article to be electroplated

- Anode - Active electrode

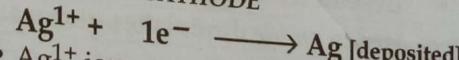
Plate or block of silver metal

#### 3. ELECTRODE REACTIONS

Dissociation of aq. sodium silver cyanide

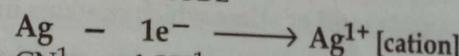


#### REACTION AT CATHODE



- $\text{Ag}^{1+}$  ions move towards the cathode & are discharged as - neutral Ag atoms - by gain of electrons [in preference to  $\text{Na}^{1+}, \text{H}^+$ ]
- Thus silver is - deposited on the article [cathode].

#### REACTION AT ANODE



- $\text{CN}^{1-}$  and  $\text{OH}^-$  ions migrate - to the anode but neither are discharged.
- Instead the silver anode - loses electrons to give -  $\text{Ag}^{1+}$  ions in soln. [Nature of electrode - Ag active electrode].

Hence anode - diminishes in mass.

[Product at anode - Nil ( $\text{Ag}^{1+}$  ions formed)]

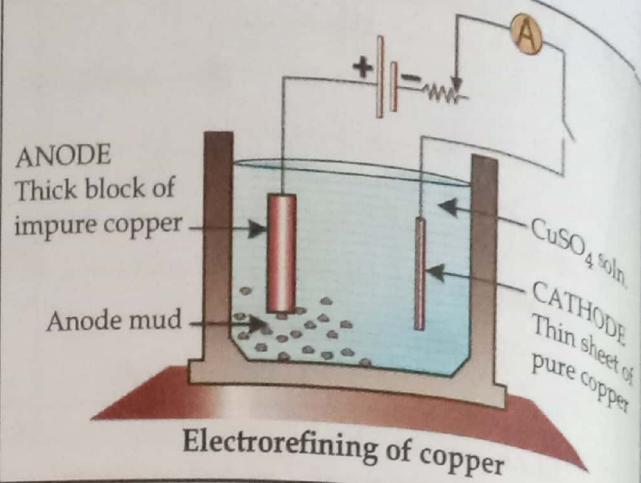
## APPLICATIONS – OF ELECTROLYSIS [Contd.]

### 2. ELECTROREFINING – Of Metals i.e. purification of metals

#### THE TERM

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

The term 'refining' means to - make pure and 'electro' - the method employed to make the metal pure i.e. by electrolysis.



#### Electro-refining of - COPPER

##### 1. ELECTROLYTE

Aqueous copper sulphate solution [acidified]

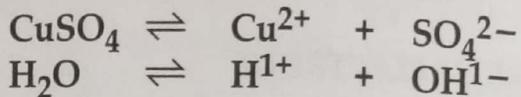
##### 2. NATURE OF ELECTRODE :

**Cathode** : Pure thin sheet of copper

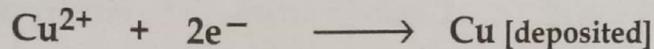
**Anode** : Impure block of copper

##### 3. ELECTRODE REACTION

Dissociation of aqueous copper sulphate

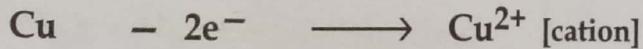


#### Reaction at cathode



- $\text{Cu}^{2+}$  ions are discharged at the cathode - as neutral copper atoms.
- Thus pure copper deposited on the thin sheet of pure copper placed at the cathode.

#### Reaction at anode [Cu - active electrode]



- $\text{SO}_4^{2-}$  and  $\text{OH}^{1-}$  migrate to the anode but - neither are discharged
- Instead the copper anode - itself loses electrons to give  $\text{Cu}^{2+}$  ions in solution.  
Hence anode diminishes in mass.

#### The impure block of copper [anode] gets used up and the impurities settle down

- The pure copper metal dissolves out from the copper anode [impure copper block] - and the  $\text{Cu}^{2+}$  ions formed in solution at the anode are deposited at the cathode - ie. on the thin pure sheet of copper [by gaining electrons].
- The impurities present in impure copper anode settle down as - **anode mud or slime** which contains insoluble impurities like - gold and silver.
- Impurities such as - iron, zinc, etc [higher in the electrochemical series] - ionise and dissolve in the electrolytic copper sulphate solution.

#### Metals generally refined by - electrolysis

- Metals which are extracted by electrolysis i.e. highly electropositive metals - are already deposited at the cathode in the pure state & hence need not be refined further.
- Zinc, lead, copper, mercury and silver - are thus generally refined by electrolysis

# APPLICATIONS - OF ELECTROLYSIS

## ELECTROMETALLURGY - process of extraction of metals by electrolysis. [Reference]

Method of extraction of metals - depends on position of the metal - in the activity series.

| ACTIVITY SERIES | Method of extraction of the metal  | Examples   |
|-----------------|--|--|
| K               | <b>BY ELECTROLYSIS</b> - of their fused salts<br>- Their oxides are - highly stable.<br>- Metal has - strong affinity for oxygen.<br>- On electrolysis - metal is deposited at the cathode.<br>- Metals generally extracted by electrolysis are - K, Na, Ca, Mg, Al. | 1. Electrolyte: <i>fused sodium chloride</i> .<br>$\text{NaCl} \rightleftharpoons \text{Na}^{1+} + \text{Cl}^{1-}$<br>Cathode: $\text{Na}^{1+} + 1\text{e}^- \rightarrow \text{Na}$<br>Anode: $\text{Cl}^{1-} - 1\text{e}^- \rightarrow \text{Cl}$<br>$\text{Cl} + \text{Cl} \rightarrow \text{Cl}_2$            |
| Na              |  | 2. Electrolyte: <i>fused calcium chloride</i> .<br>$\text{CaCl}_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{Cl}^{1-}$<br>Cathode: $\text{Ca}^{2+} + 2\text{e}^- \rightarrow \text{Ca}$<br>Anode: $2\text{Cl}^{1-} - 2\text{e}^- \rightarrow 2\text{Cl} [\text{Cl}_2]$   |
| Ca              |  | 3. Electrolyte: <i>fused alumina</i> .<br>$\text{Al}_2\text{O}_3 \rightleftharpoons 2\text{Al}^{3+} + 3\text{O}^{2-}$<br>Cathode: $2\text{Al}^{3+} + 6\text{e}^- \rightarrow 2\text{Al}$<br>Anode: $3\text{O}^{2-} - 6\text{e}^- \rightarrow 3[\text{O}]$<br>$3[\text{O}] + 3[\text{O}] \rightarrow 3\text{O}_2$ |
| Mg              |  |  |
| Al              | eg. $\text{Al}_2\text{O}_3$ is a highly stable oxide & Al has a strong affinity for oxygen, hence conventional reducing agents like - C, CO & $\text{H}_2$ cannot reduce $\text{Al}_2\text{O}_3$ to Al & hence Al is extracted by electrolysis.                      |  |
| Zn              | <b>By using - Reducing agents</b> - C, CO, $\text{H}_2$<br>- Their oxides are - less stable.<br>- Reducing agents - reduce metallic oxide to metal.  | $\text{CuO} + \text{C} \xrightarrow{\Delta} \text{Cu} + \text{CO}$   |
| Fe              |  |  |
| Pb              |  |  |
| [H]             |  |  |
| Cu              | <b>By - Thermal decomposition</b><br>- Their oxides are - least stable.<br>- Heat alone - can reduce metallic oxide to metal.  | $2\text{HgO} \xrightarrow{\Delta} 2\text{Hg} + \text{O}_2$   |

## SUMMARY OF - Electrode reactions

|                       | MOLTEN LEAD BROMIDE   | ACIDIFIED WATER  | COPPER [II] SULPHATE   |
|-----------------------|---|--|--|
| 1. Electrolyte        | $\text{PbBr}_2$ [molten]  | $\text{H}_2\text{O} [\text{H}_2\text{SO}_4]$   | $\text{CuSO}_4$ [aq.]  |
| 2. Electrode          | Inert - graphite  | Inert - platinum   | Active - copper  |
| 3. Electrode reaction | $\text{PbBr}_2 \rightleftharpoons \text{Pb}^{2+} + 2\text{Br}^{1-}$   | $\begin{aligned} \text{H}_2\text{SO}_4 &\rightleftharpoons 2\text{H}^{1+} + \text{SO}_4^{2-} \\ \text{H}_2\text{O} &\rightleftharpoons \text{H}^{1+} + \text{OH}^{1-} \end{aligned}$ | $\text{CuSO}_4 \rightleftharpoons \text{Cu}^{2+} + \text{SO}_4^{2-}$<br>$\text{H}_2\text{O} \rightleftharpoons \text{H}^{1+} + \text{OH}^{1-}$ |
| 4. Cathode reaction   | $\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}$  | $\begin{aligned} \text{H}^{1+} + 1\text{e}^- &\rightarrow \text{H} \times 4 \\ 2\text{H} + 2\text{H} &\rightarrow 2\text{H}_2 \end{aligned}$   | $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$   |
| • Product             | Lead metal  | Hydrogen gas [2 vols.]   | Copper metal   |
| 5. Anode reaction     | $\begin{aligned} \text{Br}^{1-} - 1\text{e}^- &\rightarrow \text{Br} \\ \text{Br} + \text{Br} &\rightarrow \text{Br}_2 \end{aligned}$ | $\begin{aligned} \text{OH}^{1-} - 1\text{e}^- &\rightarrow \text{OH} \times 4 \\ 4\text{OH} &\rightarrow 2\text{H}_2\text{O} + \text{O}_2 \end{aligned}$                             | $\text{Cu} - 2\text{e}^- \rightarrow \text{Cu}^{2+}$   |
| • Product             | Bromine vapours   | Oxygen gas [1 vol.]  | Nil [ $\text{Cu}^{2+}$ ions]   |

## SUMMARY OF - Applications of electrolysis

|                       | ELECTROPLATING - With  |  | ELECTROREFINING - of   |
|-----------------------|--|--|--|
|                       | NICKEL   | SILVER   | COPPER   |
| 1. Electrolyte        | $\text{NiSO}_4$ [aq. soln.]  | $\text{Na} [\text{Ag}(\text{CN})_2]$ [aq. soln.]   | $\text{CuSO}_4$ [acidified aq. soln.]                                  |
| 2. Electrode          |  |  |  |
| * Cathode used        | Article to be plated   | Article to be plated   | Pure thin sheet of Cu  |
| * Anode used          | Thick block of nickel  | Thick block of silver  | Impure block of Cu   |
| 3. Electrode reaction | $\text{NiSO}_4 \rightleftharpoons \text{Ni}^{2+} + \text{SO}_4^{2-}$   | $\text{Na}[\text{Ag}(\text{CN})_2] \rightleftharpoons \text{Na}^{1+} + \text{Ag}^{1+} + 2\text{CN}^{1-}$ | $\text{CuSO}_4 \rightleftharpoons \text{Cu}^{2+} + \text{SO}_4^{2-}$   |
|                       | $\text{H}_2\text{O} \rightleftharpoons \text{H}^{1+} + \text{OH}^{1-}$ | $\text{H}_2\text{O} \rightleftharpoons \text{H}^{1+} + \text{OH}^{1-}$                                   | $\text{H}_2\text{O} \rightleftharpoons \text{H}^{1+} + \text{OH}^{1-}$ |
| 4. Cathode reaction   | $\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}$                   | $\text{Ag}^{1+} + 1\text{e}^- \rightarrow \text{Ag}$   | $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$                   |
| 5. Anode reaction     | $\text{Ni} - 2\text{e}^- \rightarrow \text{Ni}^{2+}$                   | $\text{Ag} - 1\text{e}^- \rightarrow \text{Ag}^{1+}$   | $\text{Cu} - 2\text{e}^- \rightarrow \text{Cu}^{2+}$                   |