Ratna Sagar

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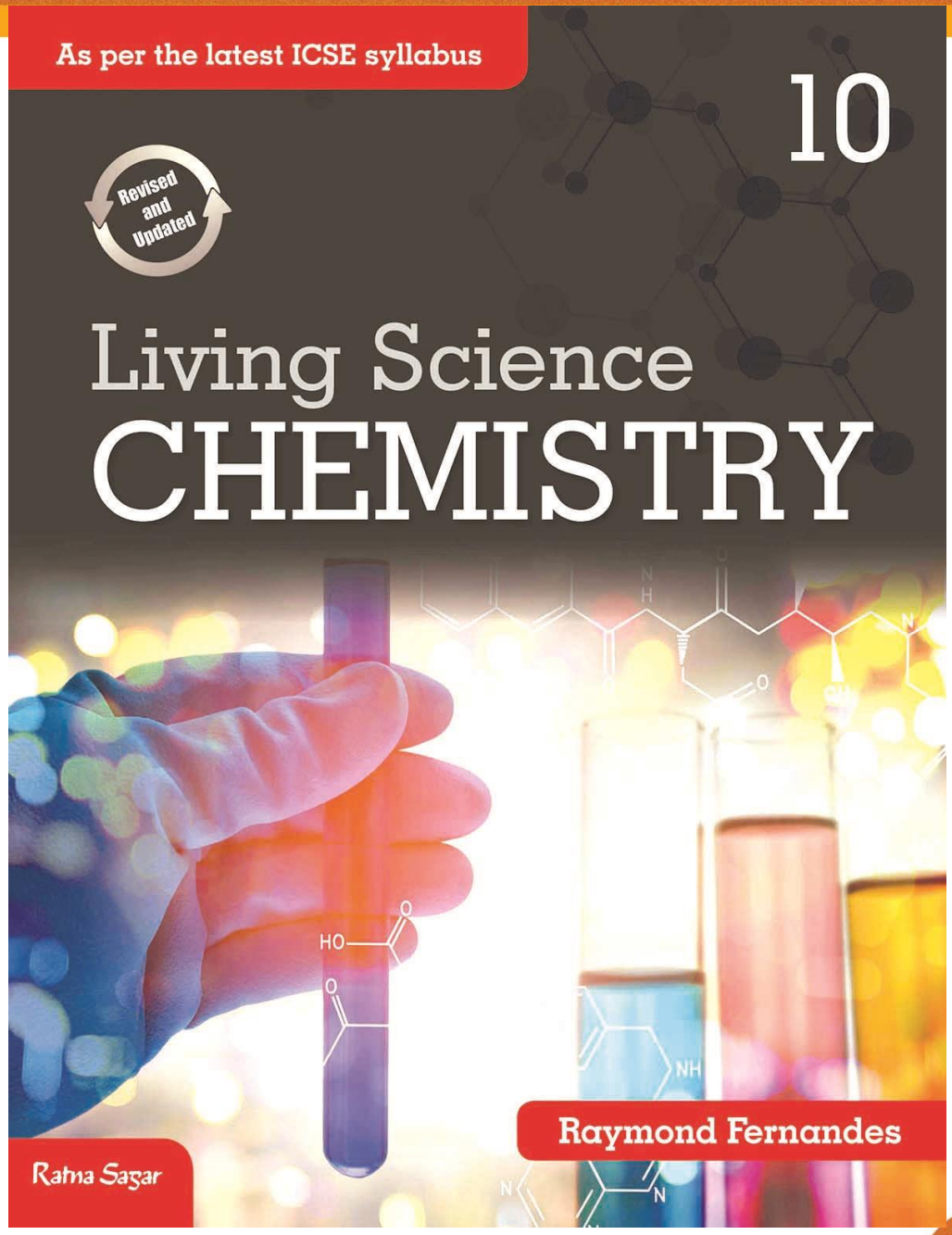
ICSE
Living Science
Chemistry

Class 10

Chapter-6 Electrolysis


As per the latest ICSE syllabus
10
Revised and Updated
Living Science
CHEMISTRY
Raymond Fernandes
Ratna Sagar

LEARNING OBJECTIVES

Electrolysis

- ❖Electrolytes and conductors
- ❖Terms used in electrolysis
- ❖Theory of electrolysis
- ❖Mechanism of electrolysis

Characteristics of electrolysis

Electrochemical series

- ❖Electrochemical series for anions

Selective Discharge of Ions at Electrodes

Electrolysis of Some Specific Electrodes

- ❖Molten lead bromide
- ❖Acidified water
- ❖Aqueous copper sulphate solution

What is Electrolysis?

The decomposition of an electrolyte in its aqueous or fused state by the passage of a direct electric current is called electrolysis. Such substances which conduct electricity in molten or aqueous state are called electrolytes.

Electrolytes and Conductors

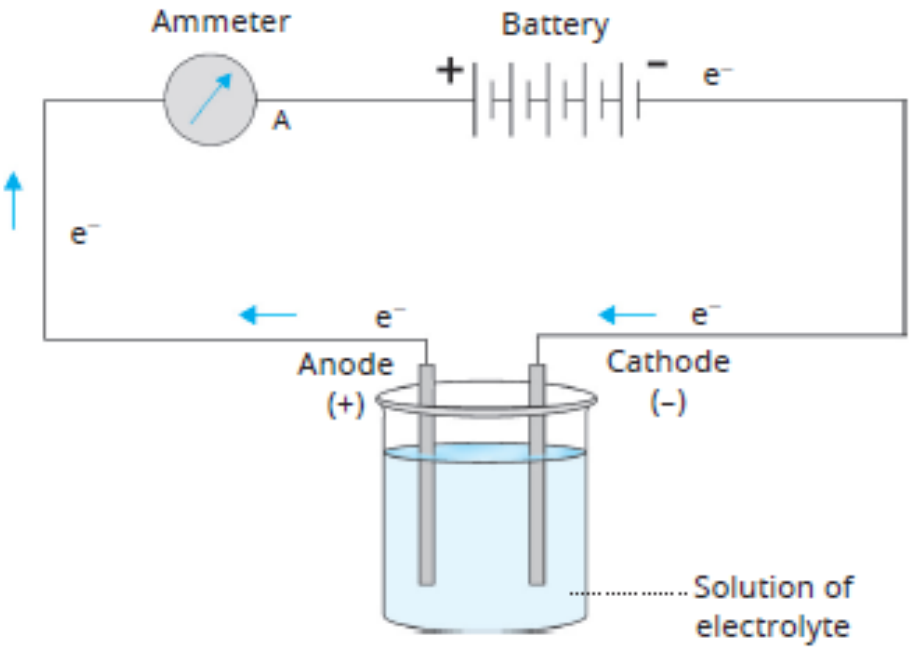
The chemical compounds which either in fused (or molten) state or in aqueous solution conduct electricity are called **electrolytes**.
Substances (like metals) that conduct electricity in their solid state are called **conductors**. Examples of conductors are copper, silver, etc.

Strong and weak electrolytes

Chemical compounds which dissociate completely into ions in their aqueous solution or in fused state and allow a large amount of electricity to flow through them are called **strong electrolytes**. All strong acids, strong alkali solutions and all salt solutions of strong acids and alkalis are strong electrolytes.
Chemical compounds which dissociate partially into ions in their aqueous or fused state and allow a small amount of electricity to flow through them are **weak electrolytes.**

Electrolytic cell and electrodes

The vessel in which electrolysis is carried out is called an **electrolytic cell.** It converts electrical energy into chemical energy. It contains electrodes and solution of electrolytes.



Conducting rods, which allow the electric current to enter and leave the electrolytic solution, are called **electrodes**. The electrode connected to the positive terminal of a battery is called **anode**. The electrode connected to the negative terminal of a battery is called **cathode**.

Ions

Atoms or groups of atoms that carry a charge (either positive or negative) are called **ions.** It can lose or gain an electron depending on whether it is negatively or positively charged. Negatively charged ions are called **anions**. They are negatively charged due to gain of electrons.

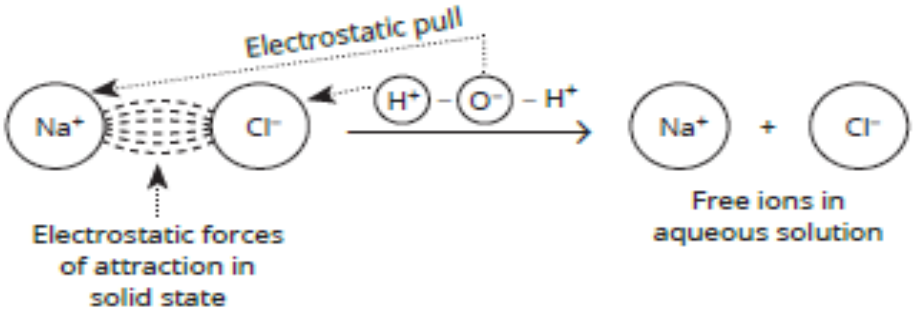
During electrolysis, they migrate to the anode and get discharged at it by losing excess electrons.

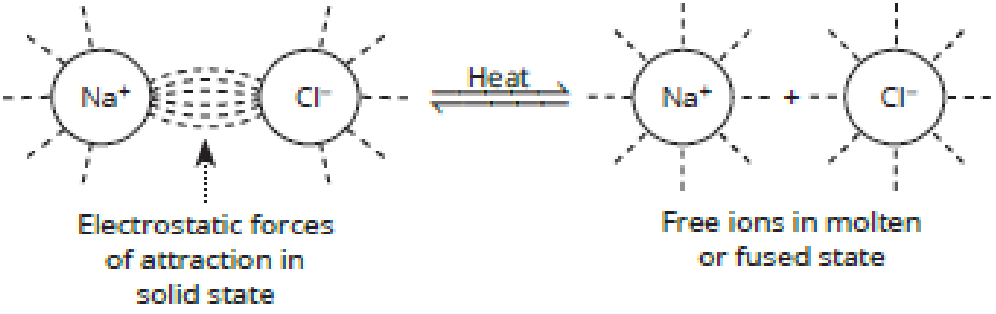
Positively charged ions are called **cations.** They are positively charged due to loss of electrons. During electrolysis, they migrate to the cathode and get discharged at it by gaining electrons.

Electrolytic dissociation

The process by which an ionic (or electrovalent) compound dissociates into its ions in aqueous or fused state on the application of a direct current is called **electrolytic dissociation**.

Electrolytic dissociation of sodium chloride in aqueous solution





Electrolytic dissociation of sodium chloride in molten or fused state

Ionization

Some polar covalent molecules form ions when dissolved in water and hence, conduct electricity. Such molecules are said to be ionized in solution and this process is called **ionization**. Thus, ionization is the process in which polar covalent molecules form ions when dissolved in water.

Theory of electrolysis

The main postulates of the Arrhenius theory are as follows:

1. An electrolyte on dissolving in water dissociates into free ions.

2. This dissociation allows the flow of electric current through the electrolyte.

3. The extent to which the electrolyte breaks up into its ions is called the degree of dissociation.

4. The amount of electricity conducted by the electrolyte depends upon the concentration of ions in solution.

5. The number of cations is always equal to the number of anions and therefore, the solution is in electrolytic equilibrium.

Mechanism of electrolysis

The electrolyte, in its molten or aqueous state, ionizes to form its corresponding ions.

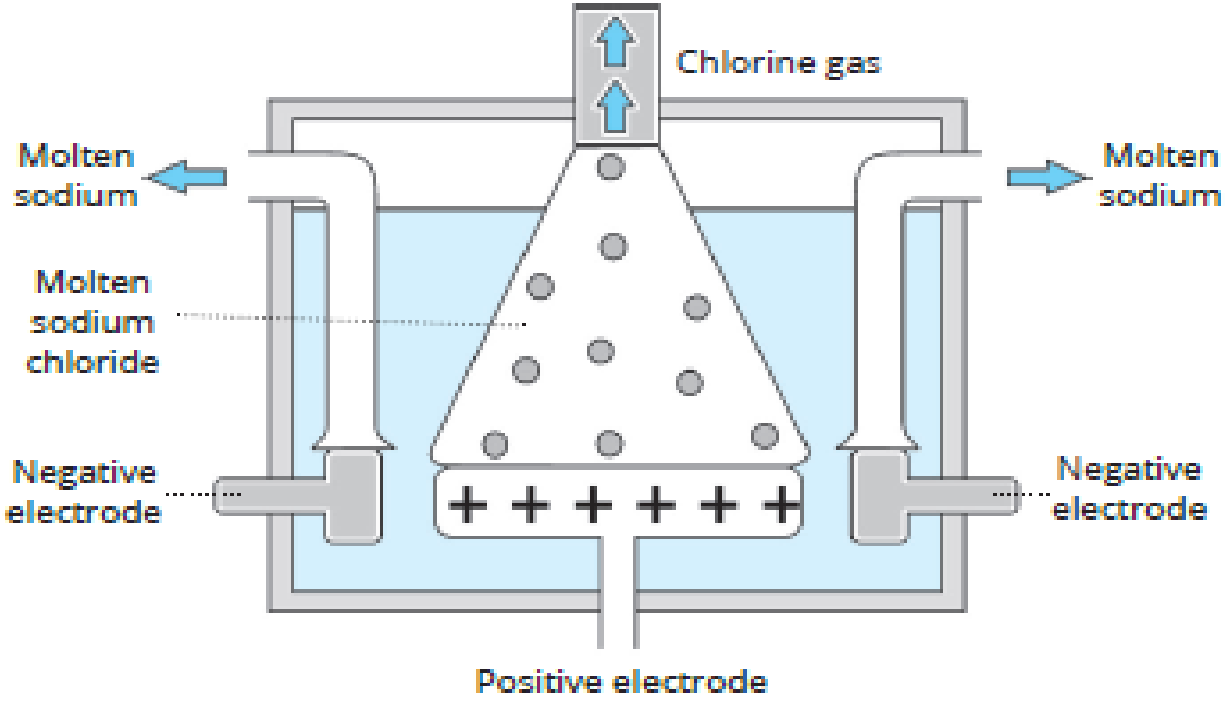
$NaCl \longrightarrow Na^{+} + Cl^{-}$

When an electric current is passed through the electrolyte, the ions migrate towards their respective electrodes and get discharged either by gaining or losing electrons.

At the cathode

$$Na^+ + e^- \longrightarrow Na$$

The metal ions gain electrons and get converted to their respective atoms. Since gain of electrons is classified as a reduction reaction, therefore, the metal ions are reduced at the cathode and get deposited on it.



Electrolysis of molten sodium chloride

At the anode

$$Cl^- \longrightarrow Cl + e-$$

The non-metal ions lose electrons and get converted to their atoms. Since, loss of electrons is classified as an oxidation reaction, therefore, the non-metal ions get oxidized at the anode.

$$Cl + Cl \longrightarrow Cl_2$$

Atoms of non-metals cannot exist on their own, so they combine to form molecules. These molecules are in their gaseous state and are liberated at the anode. Hence, in electrolysis both oxidation and reduction takes place simultaneously.

Characteristics of Electrolysis

1. During electrolysis, the positively charged ions (called cations) move towards the cathode and negatively charged ions (called anions) move towards the anode under the effect of direct current.

2. At anode, anions undergo oxidation by the loss of electrons to the electrode and at cathode, cations undergo reduction by the gain of electrons from the electrode. The number of electrons lost at anode will be equal to the number of electrons gained at the cathode.

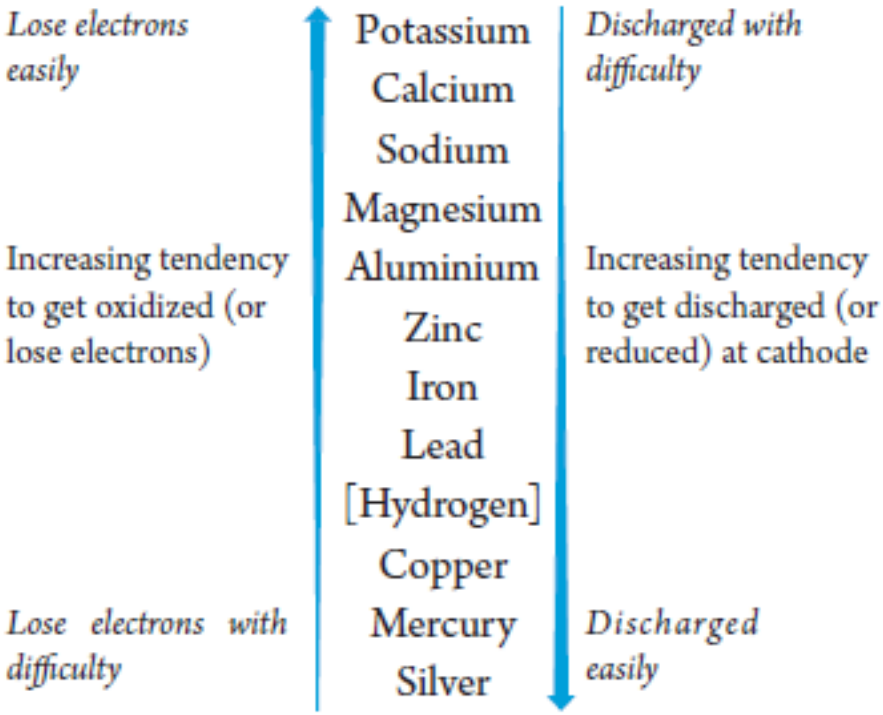
3. During electrolysis, the products are formed at the anode and cathode because the exchange of electrons takes place only at the surface of the electrodes.

4. Generally, the electropositive elements like metals and hydrogen are liberated at cathode and electronegative non-metals are liberated at anode.

5. During electrolysis, the amount of electricity passed through an electrode is directly proportional to the mass of substance deposited at that electrode. This is called **Faraday's Law of electrolysis**.

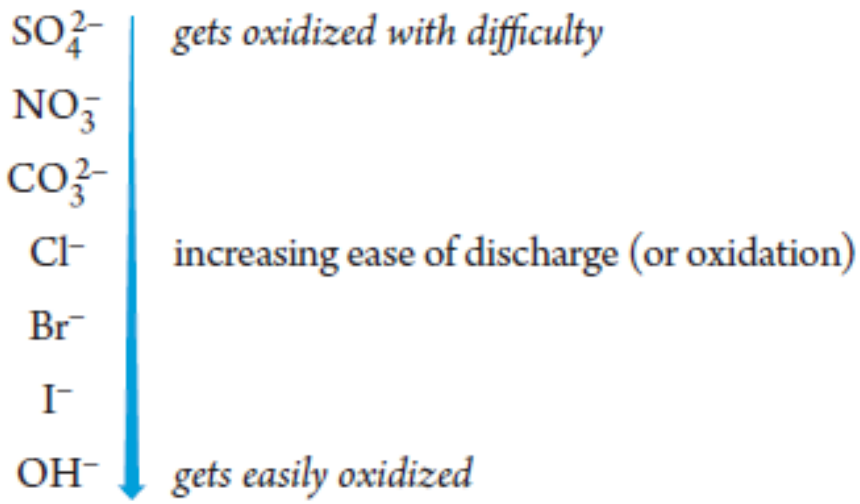
Electrochemical Series

The metals can be arranged in a series in order of their tendency to lose their valence electrons. This series is called **electrochemical series**. This series indicates the ease with which metals lose electrons to form ions in solution. The metal placed higher in the series has a strong tendency to lose electrons readily and exists as a stable ion in solution.



Electrochemical series for anions

Anions migrate towards anode during electrolysis. At anode, they lose their extra electrons and get discharged (or oxidized). The ease with which anions lose their electrons is different for different anions. On the basis of the ease of losing electrons, i.e. to get oxidized and get discharged at the anode, anions can be arranged in the form of series in the increasing order.



Selective Discharge of Ions at Electrodes

The preferential discharge of ions present in an electrolyte at the respective electrodes is called **selective discharge of ions**.

Note: For more for Selective Discharge and Factors influencing the selective discharge of ions, pl. refer to pages 96-97 and Table 6.2 of the book.

Electrolysis of Some Specific Electrolytes

Molten lead bromide

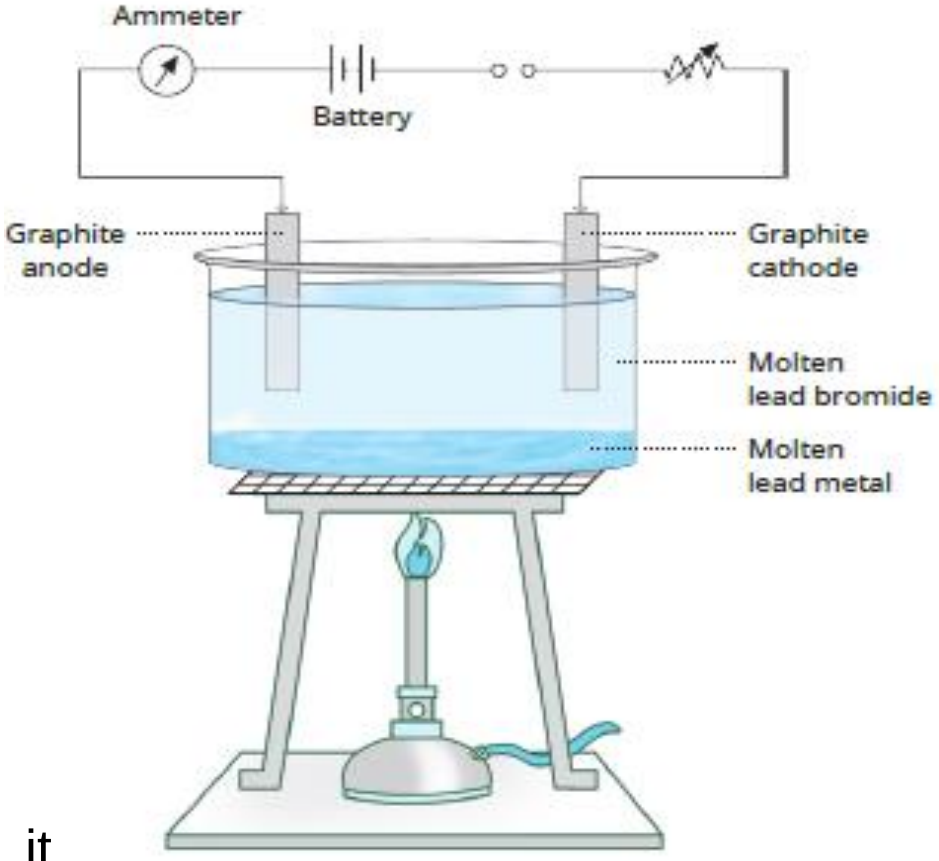
Lead bromide conducts electricity in the molten state. Molten lead bromide contains lead ions as positively charged ions and bromide ions as negatively charged ions.

Reaction at cathode

Lead ions being positively charged migrate towards cathode where they accept two electrons from the cathode and change to lead atom.

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

As Pb^{2+} gains or accepts two electrons, it undergoes reduction. The lead atoms are deposited at the cathode and form a layer of grey lead metal.



Electrolysis of molten lead bromide

Reaction at anode

Bromide ions being negatively charged migrate towards anode where they lose their extra electron and thus get oxidized at the anode by changing into bromine atoms. The bromine atoms combine to give molecules of bromine that escape as reddish-brown vapours at anode.

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

$$Br + Br \longrightarrow Br_2\uparrow$$

reddish-brown vapours

Acidified water

Pure water is a poor conductor of electricity. To electrolyse water, a few drops of dilute sulphuric acid are added. The addition of dilute sulphuric acid initiates the ionization of water. Water ionizes to form hydronium and hydroxyl ions. Sulphuric acid also ionizes to form hydronium and sulphate ions.

Reaction at cathode

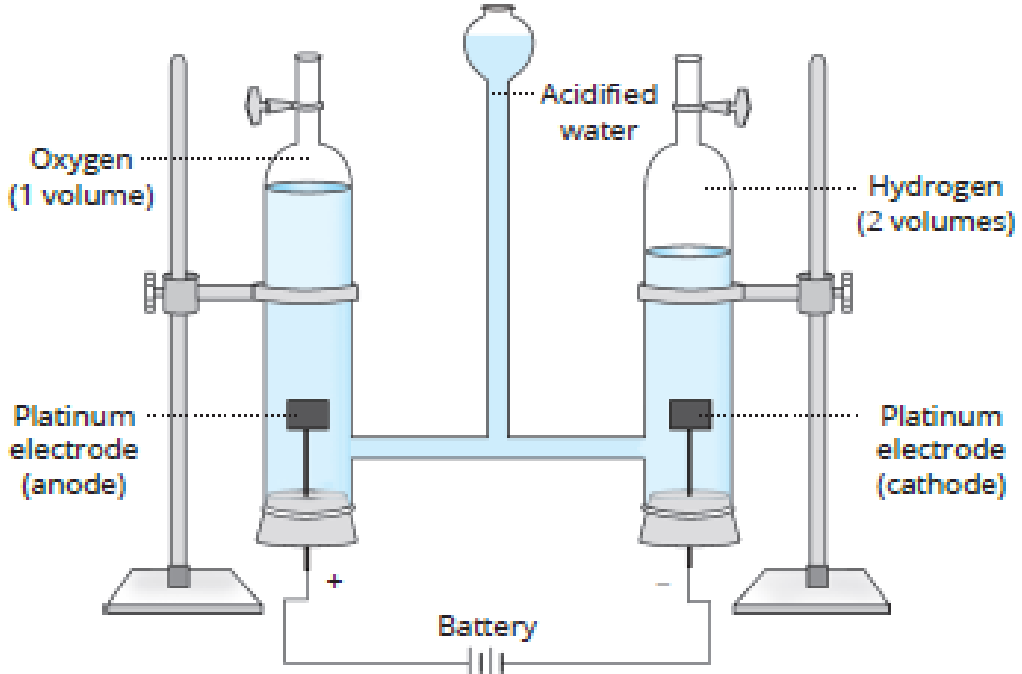
Hydrogen ions being positively charged migrate towards cathode where they accept an electron to form hydrogen atoms. The hydrogen atoms combine to give hydrogen gas.

$$H^+ + e^- \longrightarrow H$$
(atom)
$$H + H \longrightarrow H_2$$

Reaction at anode

Both sulphate ions and hydroxide ions being negatively charged migrate towards anode. But hydroxide ions get discharged first in preference to the sulphate ions. The hydroxide ions lose their electrons and become electrically neutral particles OH which react among themselves to give water and oxygen.

$$4OH^- \longrightarrow 2H_2O + 4e^- + O_2$$

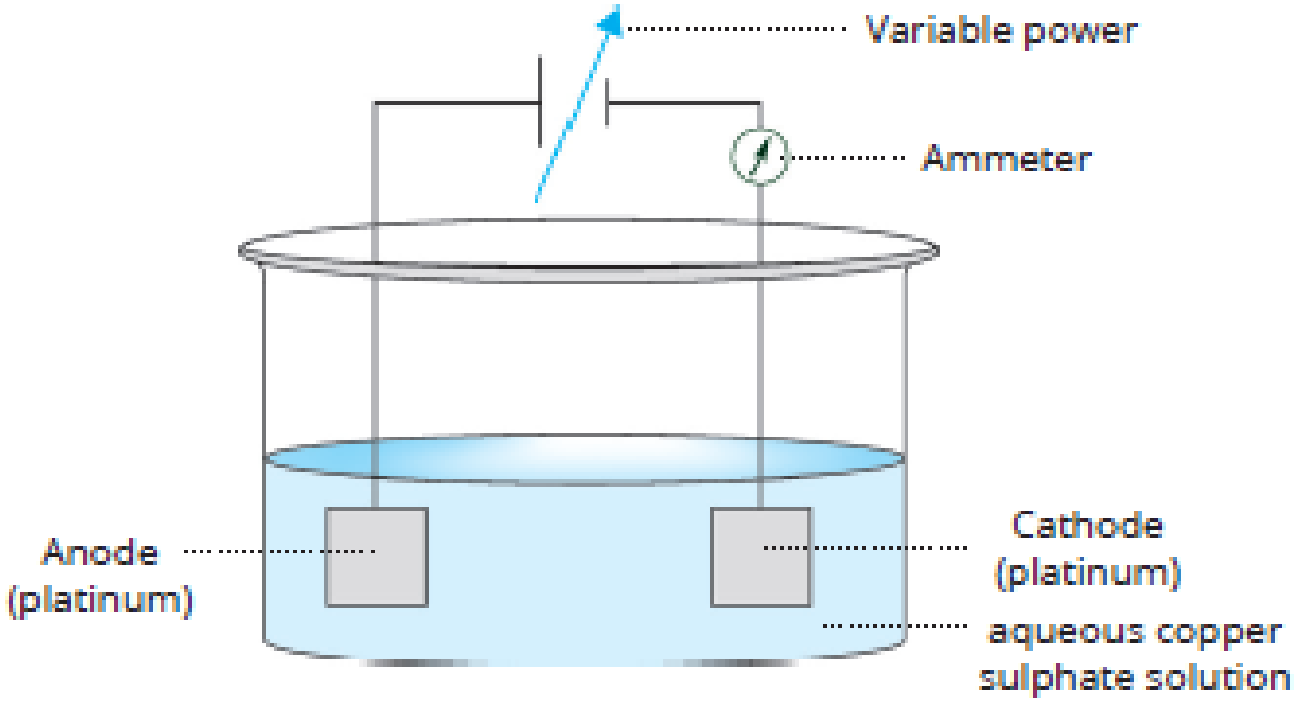


Electrolysis of acidified water using platinum electrodes

Aqueous copper sulphate solution

Using inert electrodes

Aqueous copper sulphate solution is blue in colour. It is prepared by dissolving CuSO4 in distilled water with a small amount of concentrated sulphuric acid so as to increase the electrical conductivity of CuSO4 solution and to prevent hydrolysis of the electrolyte. When it is electrolysed using inert electrodes like platinum, copper ions get discharged at the cathode and are deposited at the cathode as reddish-brown copper metal.



Electrolysis of copper sulphate solution

Reaction at cathode

Both copper and hydrogen ions being positively charged migrate towards cathode. Copper ions being lower in the electrochemical series are preferentially discharged to give copper atoms at the platinum electrode.

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

Reaction at anode

Both sulphate ions and hydroxyl ions being negatively charged migrate towards the anode. Hydroxyl ions are preferentially discharged at the platinum electrode to form neutral OH particles. These neutral OH particles react among themselves to give water and oxygen gas.

$$4OH^{-} \longrightarrow 2H_2O + O_2\uparrow + 4e^{-}$$

Using active electrodes

When aqueous copper sulphate solution (blue) is electrolysed using active electrodes (especially the anode), copper ions get discharged at the cathode and are deposited at the cathode as reddish-brown copper metal.

Reaction at cathode

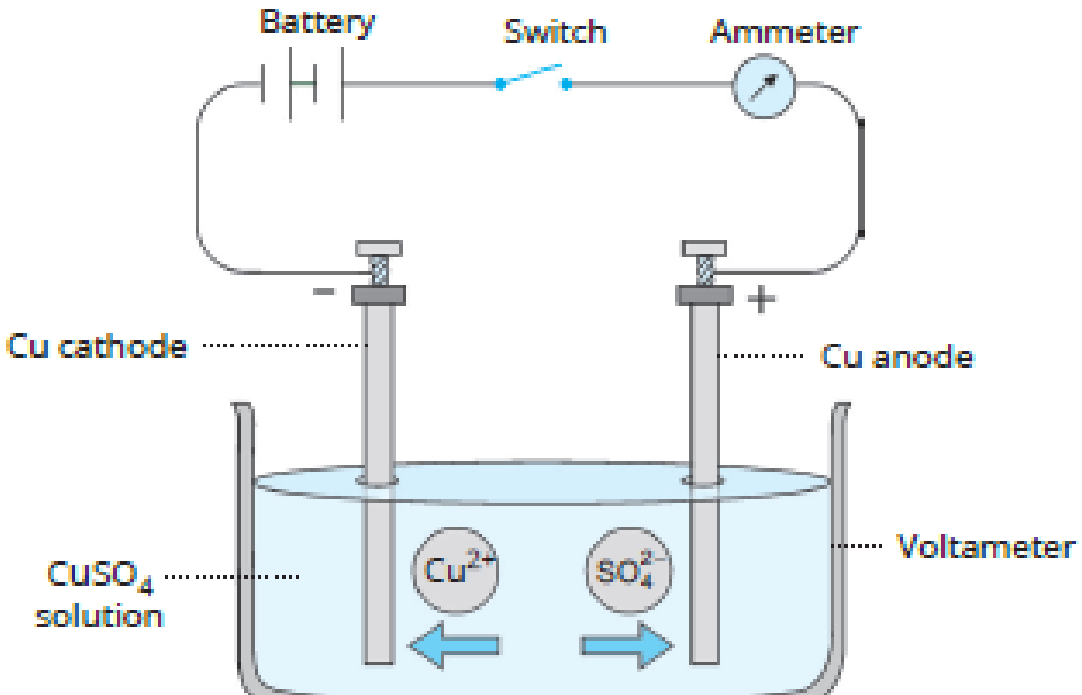
Both copper and hydrogen ions migrate towards the cathode but Cu^{2+} ions would get discharged in preference to hydrogen ions as Cu^{2+} is lower in the series. Copper ions accept two electrons from cathode and are deposited as copper metal.

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

Reaction at anode

Both sulphate (SO_4^{2-}) and hydroxide (OH^-) ions migrate towards the anode but neither is discharged because the copper metal from copper anode loses electrons readily than sulphate and hydrogen ions. Therefore, the atoms of copper change to copper ions that go into the solution. Thus, the copper anode undergoes a loss in mass.

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



Electrolysis of an aqueous solution of $CuSO_4$ using copper electrodes (active electrodes

Applications of Electrolysis

The three main applications of electrolysis are:

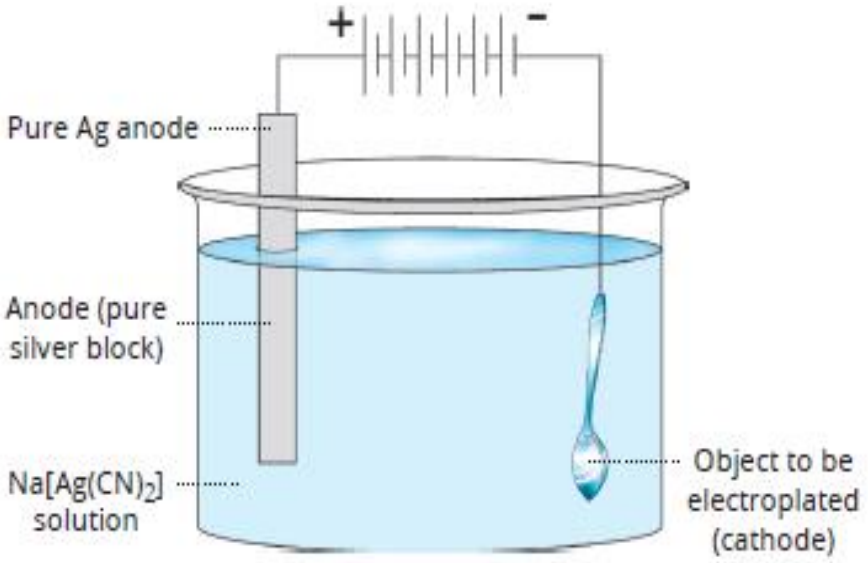
1. Electroplating with metals
2. Electrolytic refining of metals
3. Electrometallurgy (Extraction of metals)

Electroplating

The electrolytic process of depositing a superior metal on the surface of another metal is called electroplating.

Purpose for electroplating

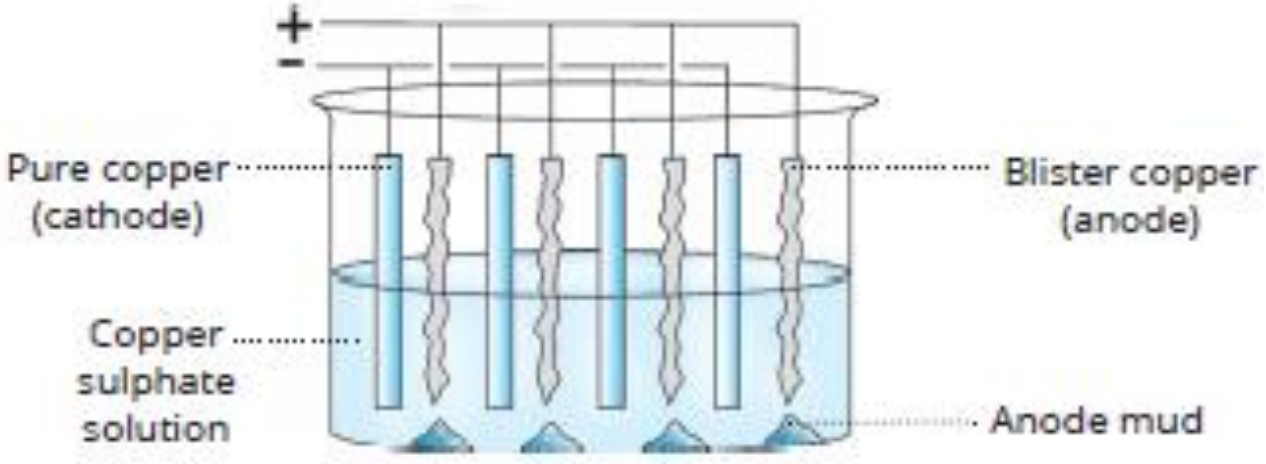
1. **Improving appearance:** Electroplating makes the object look more attractive. For example, an article made of brass is electroplated with silver or gold to impart a shiny appearance to it.
2. **Prevention of corrosion**: Iron equipment and objects are electroplated with zinc or chromium or nickel for preventing them from corrosion .



Electroplating of an object with silver

Electrolytic refining (Electrorefining)

Electrorefining is a process by which metals containing impurities are purified electrically to give pure metal. The impurities like gold and silver that are insoluble in solution, settle down as **anode mud**.



Electrometallurgy

The extraction of metals by electrolysis is called electrometallurgy. Highly electropositive metals like K, Na, Ca, Mg and Al are extracted by electrolysis. The oxides of these metals are very stable and cannot be reduced by conventional reducing agents like coke, carbon monoxide and hydrogen. Such metals are extracted from their halides like chlorides and bromides by electrolysis using graphite and iron electrodes.

SUMMARY

1. **Electrolysis of molten sodium chloride**

Electrolytic equation $NaCl \rightleftharpoons Na^+ + Cl^-$

At the cathode $Na^+ \longrightarrow Na + e^-$

At the anode $Cl^- \longrightarrow Cl + e^-$

$Cl + Cl \longrightarrow Cl_2$

2. **Electrolysis of molten lead bromide**

Electrolytic equation $PbBr_2 \longrightarrow Pb^{2+} + 2Br^-$

At the cathode $Pb^{2+} + 2e^- \longrightarrow Pb$

At the anode $2Br^- \longrightarrow 2Br + 2e^-$

$2Br \longrightarrow Br_2\uparrow$

3. **Electrolysis of acidified water**

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

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

At the cathode $H^+, 2H^+$

$H^+ + e^- \longrightarrow H$

$H + H \longrightarrow H_2\uparrow$

At the anode OH^-, SO_4^{2-}

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

$4OH \longrightarrow 2H_2O + O_2$

4. **Electrolysis of aqueous copper sulphate solution**

Using inert electrodes

Electrolytic equations $CuSO_4 \longrightarrow Cu^{2+} + SO_4^{2-}$

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

At the cathode Cu^{2+}, H^+

$Cu^{2+} + 2e^- \longrightarrow Cu\downarrow$

At the anode $OH^- \longrightarrow OH + e^-$

$4OH \longrightarrow 2H_2O + O_2\uparrow$

Using active electrodes

Electrolytic equations $CuSO_4 \longrightarrow Cu^{2+} + SO_4^{2-}$

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

At the cathode Cu^{2+}, H^+

$Cu^{2+} + 2e^- \longrightarrow Cu\downarrow$

At the anode $Cu \longrightarrow Cu^{2+} + 2e^-$

5. **Silver plating**

Electrolytic equations

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

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

$HCN \rightleftharpoons H^+ + CN^-$

At the cathode $Ag^+ + 1e^- \longrightarrow Ag\downarrow$

At the anode $Ag \longrightarrow Ag^+ + e^-$

6. **Nickel plating**

Electrolytic equations $NiSO_4 \longrightarrow Ni^{2+} + SO_4^{2-}$

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

At the cathode $Ni^{2+} + 2e^- \longrightarrow Ni$

At the anode $Ni \longrightarrow Ni^{2+} + 2e^-$

7. **Copper refining**

Electrolytic equations $CuSO_4 \longrightarrow Cu^{2+} + SO_4^{2-}$

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

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

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

At the anode $Cu \longrightarrow Cu^{2+} + 2e^-$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