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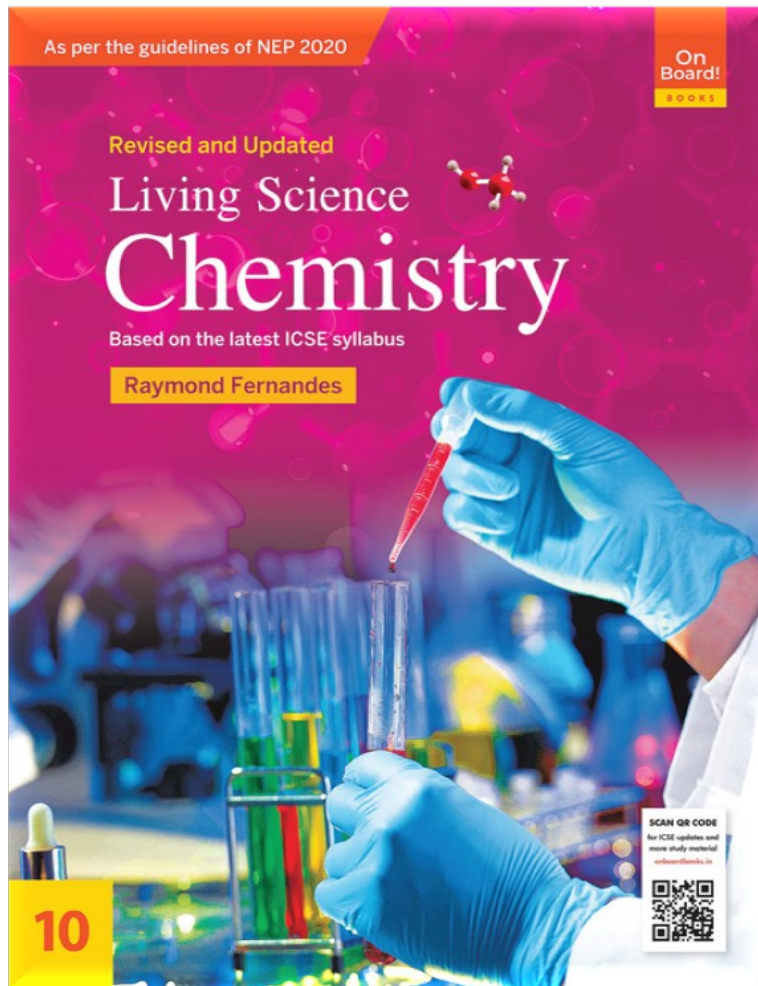
ICSE

Living Science

Chemistry

Class 10

Chapter-6 Electrolysis



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 Electrolytes

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

Applications of electrolysis

What is Electrolysis?

The decomposition of an electrolyte into its constituent ions, 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.

Terms used in electrolysis

Electrolysis: The decomposition of an electrolyte in its aqueous or fused state by the passage of a direct electric current is called electrolysis.

Electrolytes: The chemical compounds that either in fused (or molten) state or in aqueous solution conduct electricity are called electrolytes. The solutions of all electrolytes contain ions. The electrolytes fall into three categories—acids, bases and salts. They are polar compounds.

Non-electrolytes: These are chemical compounds that do not conduct electricity either in their fused state or in aqueous state. The solution of a non-electrolyte contains only molecules. These are non-polar compounds. For example, pure water, alcohol, kerosene and carbon disulphide (CS_2). Most organic compounds are nonelectrolytes.

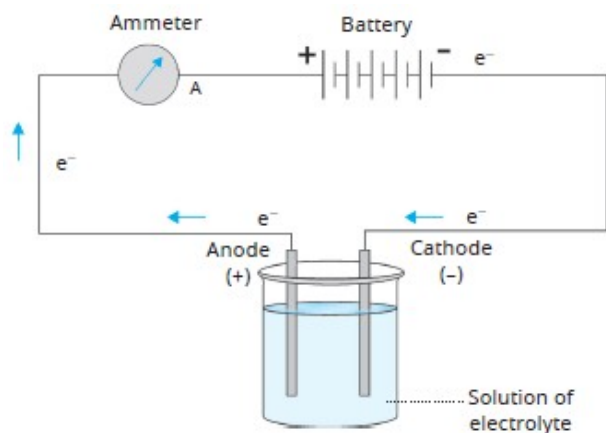
Strong electrolytes: These are chemical compounds that dissociate completely into ions in their aqueous solution or in fused state. They allow a large amount of electricity to flow through them, and hence, are considered good conductors of electricity. The solution of a strong electrolyte contains only free ions. Examples are all strong acids like HCl , H_2SO_4 , HBr , HI and HNO_3 , strong alkali solutions like NaOH , KOH and all salt solutions of strong acids and alkalis like NaCl , Na_2SO_4 and CaCl_2 .

Weak electrolytes

These are chemical compounds that dissociate partially into ions in their aqueous or fused state. They allow a small amount of electricity to flow through them, and hence, are poor conductors of electricity. The solution of a weak electrolyte contains free ions and unionized molecules. Examples are H_2CO_3 (carbonic acid), CH_3COOH (acetic acid), HCOOH (formic acid) and NH_4OH (ammonium hydroxide). Weak electrolytes undergo partial ionization in solutions, while strong electrolytes dissociate completely in solutions.

Electrolytic cell

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.



Electrodes: Conducting rods, which allow the electric current to enter and leave the electrolytic solution, are called electrodes. In electrolysis, platinum and carbon (graphite) are generally used as electrodes because of their low reactivity. They react neither with the electrolyte nor with the products of the electrolysis. These are also called inert electrodes.

Anode: The electrode connected to the positive terminal of a battery is called anode. It acquires positive charge as electrons leave the electrolyte through this electrode and current enters the electrolytic cell through the anode. Therefore, the negatively charged ions migrate to the anode during electrolysis. The negatively charged ions or anions lose excess electrons to the anode and are oxidized to neutral atoms. Loss of electrons by an atom or an ion is called oxidation. Thus, oxidation takes place at the anode or it can be said that anions are oxidized at the anode. Hence, the anode is the oxidizing electrode.

Cathode: The electrode connected to the negative terminal of a battery is called cathode. It acquires negative charge as electrons enter the electrolyte through this electrode and current leaves the electrolytic cell through the cathode. Therefore, the positively charged ions migrate to the cathode during electrolysis.

The positively charged ions or cations gain electrons from the cathode and are reduced to neutral atom. Gain of electrons by an atom or an ion is called reduction. Thus, reduction takes place at the cathode or it can be said that cations are reduced at cathode. Hence, the cathode is the reducing electrode.

Ions: Atoms or groups of atoms that carry a charge (either positive or negative) are called ions. An ion can lose or gain an electron depending on whether it is negatively or positively charged.

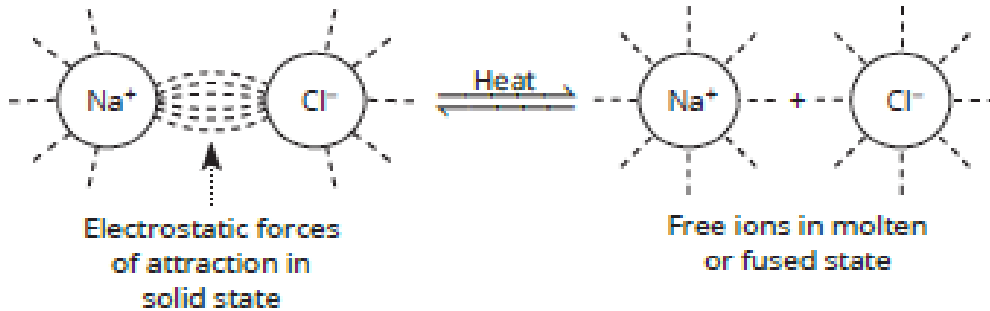
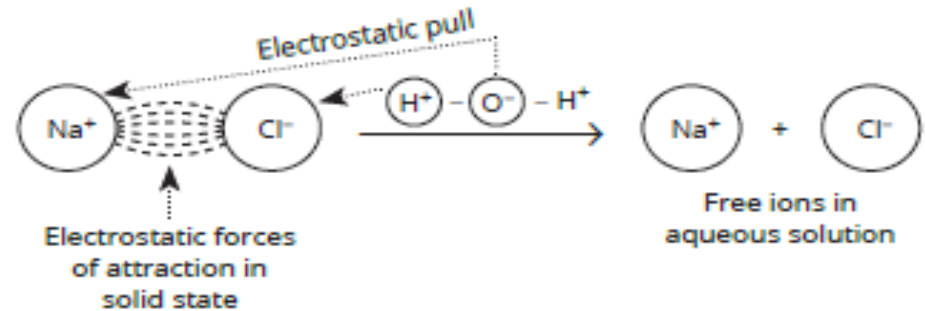
Anions: Negatively charged ions are called anions. They are negatively charged due to the gain of electrons. During electrolysis, they migrate to the anode and get discharged at it by losing excess electrons.

Cations: Positively charged ions are called cations. They are positively charged due to the 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.

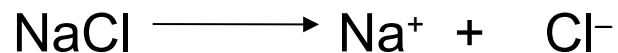
Theory of electrolysis

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.

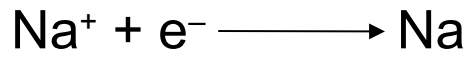
Mechanism of electrolysis

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

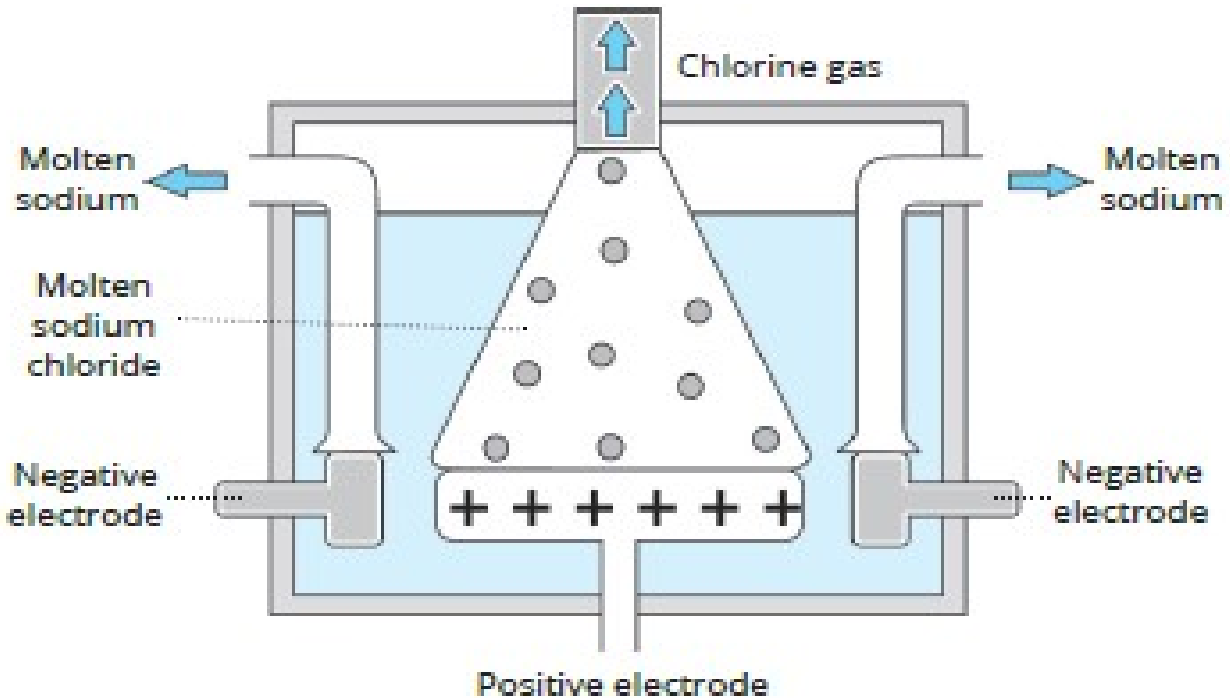


When an electric current is passed through the electrolyte, the ions migrate towards their respective electrodes and get discharged either by gaining or losing electrons.

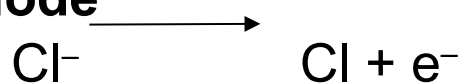
At the cathode



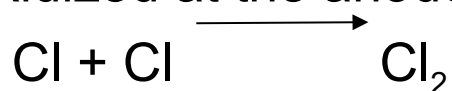
The metal ions gain electrons and get converted to their respective atoms. Since gain of electrons is classified as a reduction reaction, therefore, the metal ions are reduced at the cathode and get deposited on it.



Electrolysis of molten sodium chloride

At the anode

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.



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.

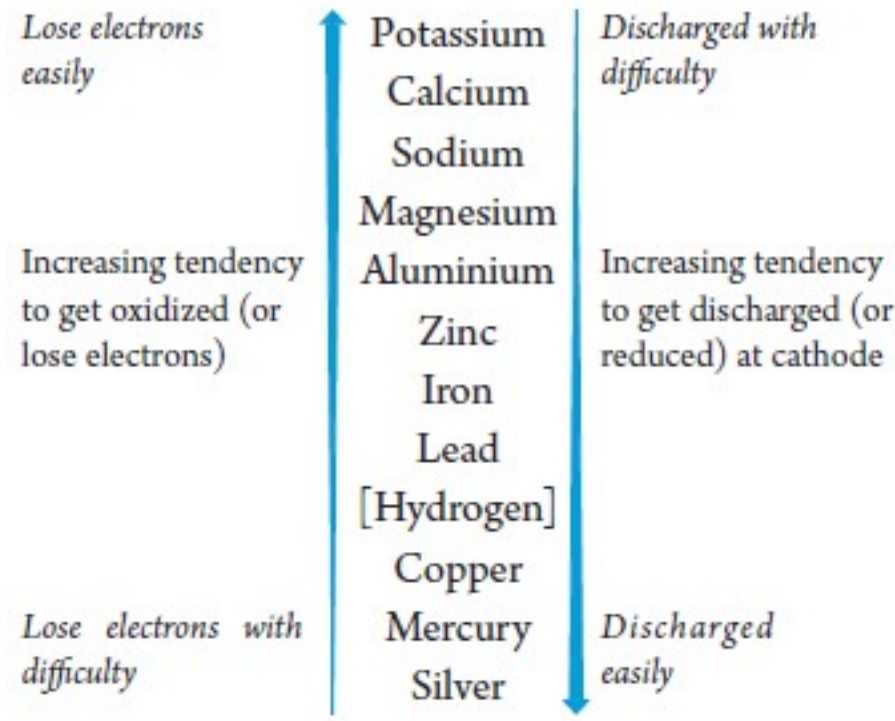
Characteristics of Electrolysis

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.

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

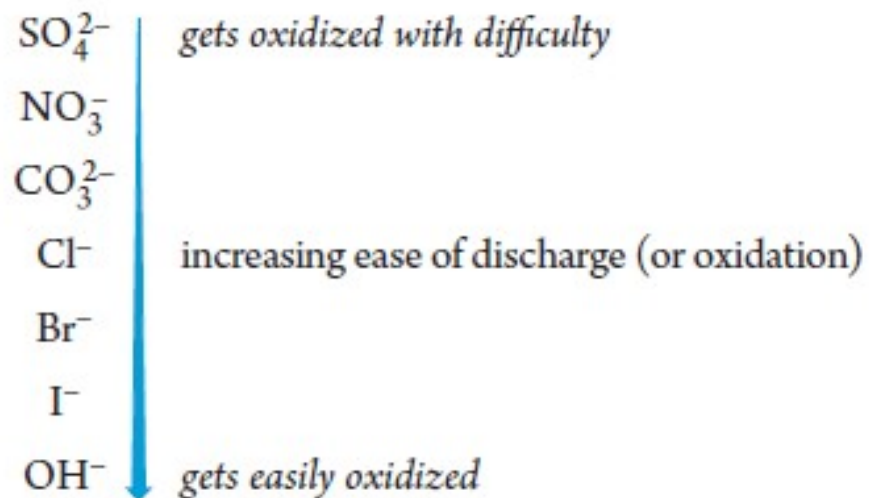
Electrochemical Series

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 118-119 and Table 6.5 of the book.

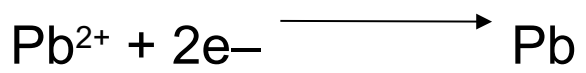
Electrolysis of Some Specific Electrolytes

Molten lead bromide

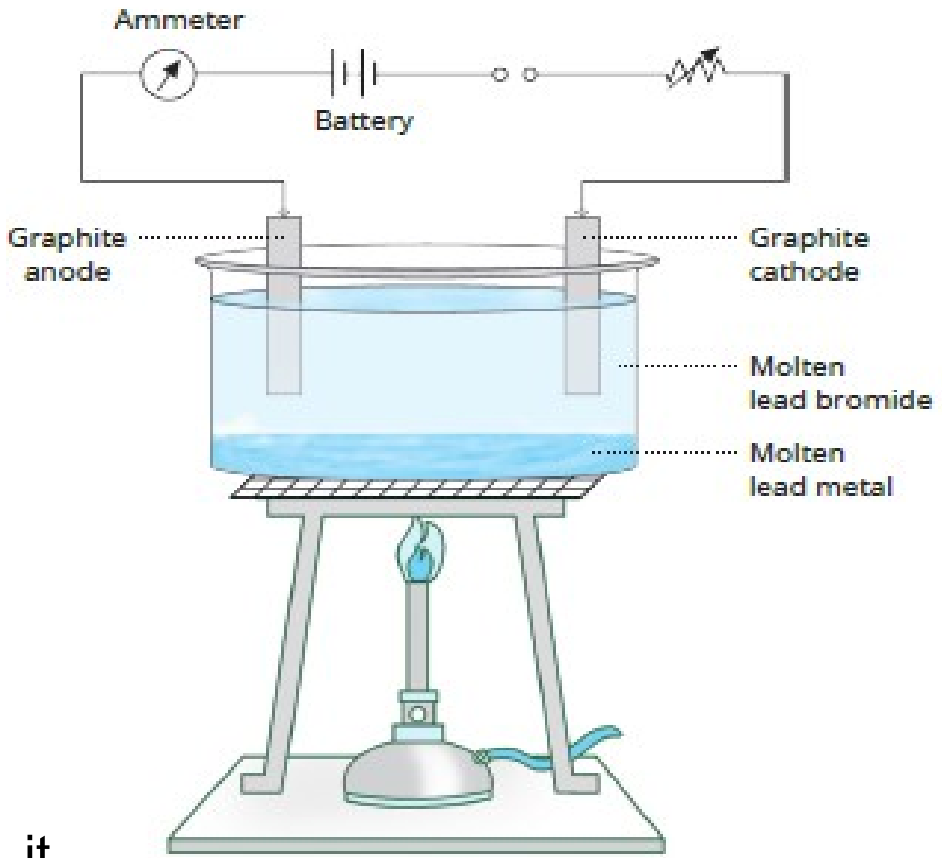
Lead bromide conducts electricity in the molten state. Molten lead bromide contains lead ions as positively charged ions and bromide ions as negatively charged ions.

Reaction at cathode

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



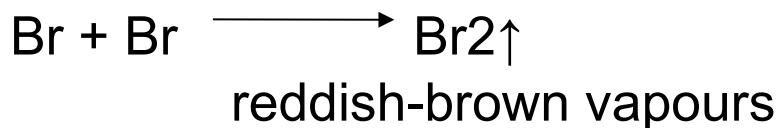
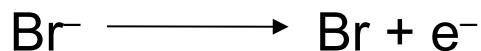
As Pb^{2+} gains or accepts two electrons, it undergoes reduction. The lead atoms are deposited at the cathode and form a layer of grey lead metal.



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.

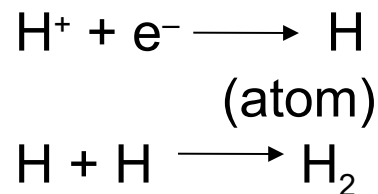


Acidified water

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.

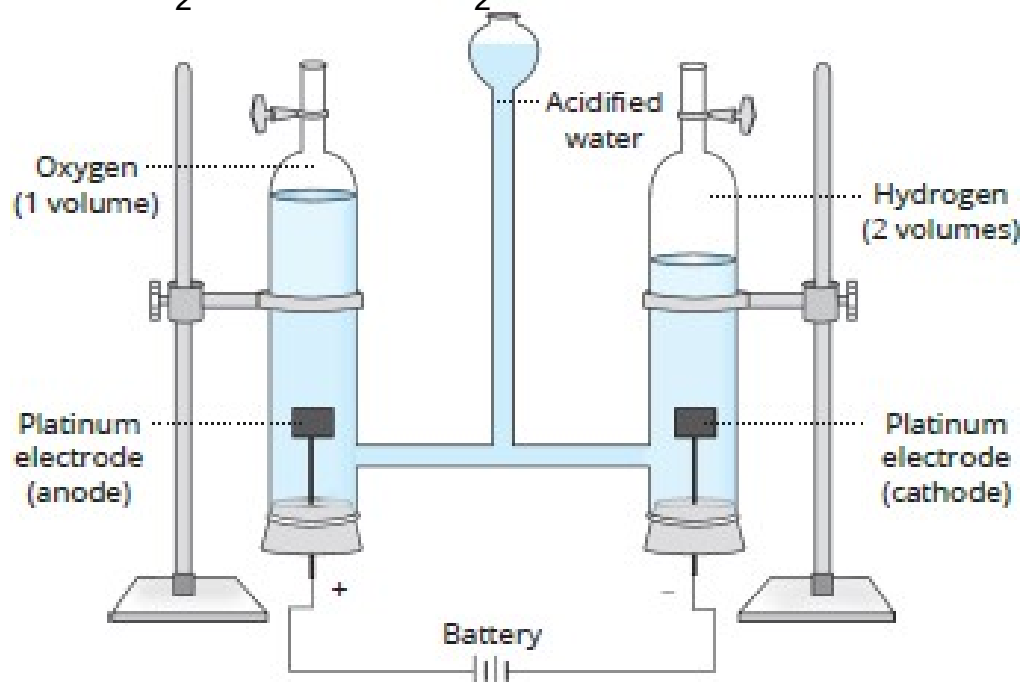
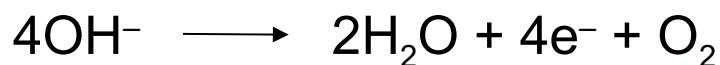
Reaction at cathode

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.



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 of OH which react among themselves to give H₂O and O₂.

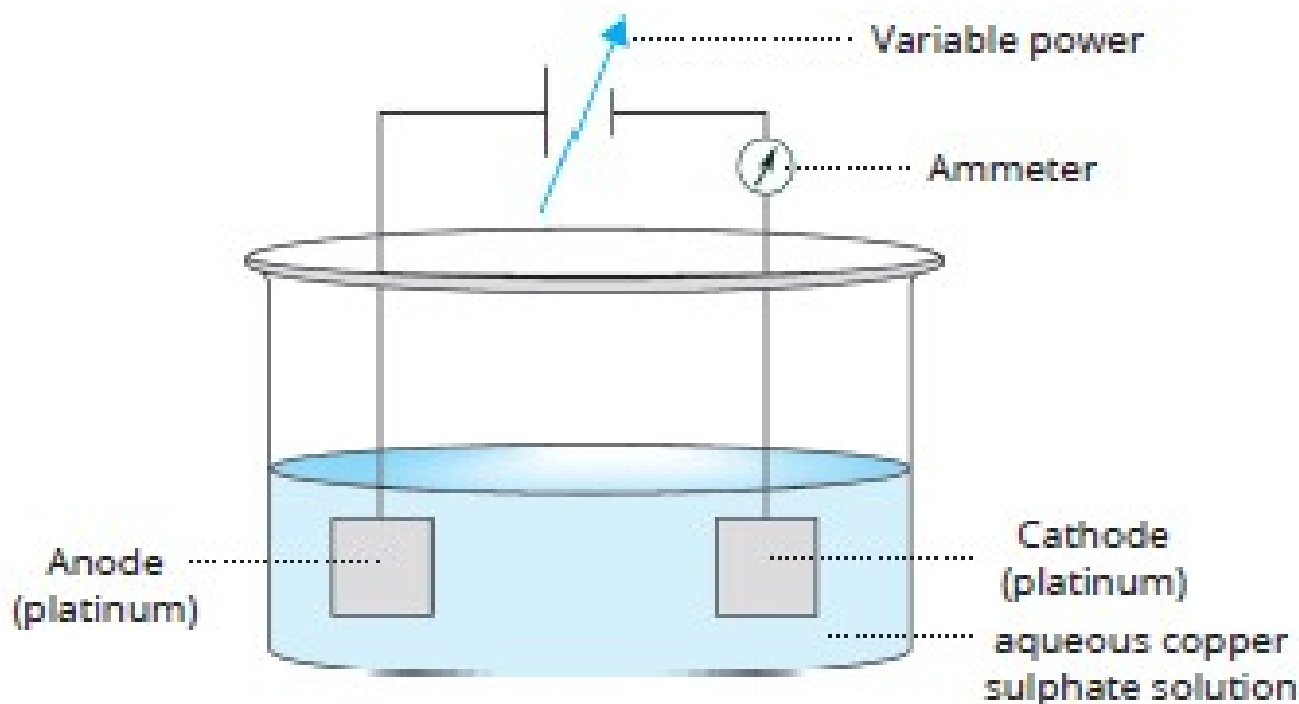


Electrolysis of acidified water using platinum electrodes

Aqueous copper sulphate solution

Using inert electrodes

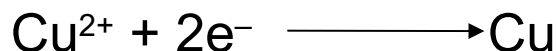
Aqueous copper sulphate solution is blue in colour. It is prepared by dissolving CuSO_4 in distilled water with a small amount of concentrated sulphuric acid so as to increase the electrical conductivity of CuSO_4 solution and to prevent hydrolysis of the electrolyte. When it is electrolysed using inert 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

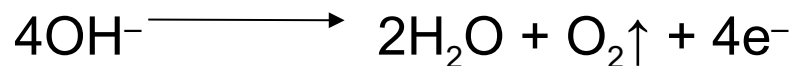
Reaction at cathode

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.



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.

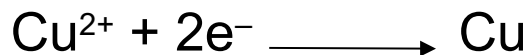


Using active electrodes

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.

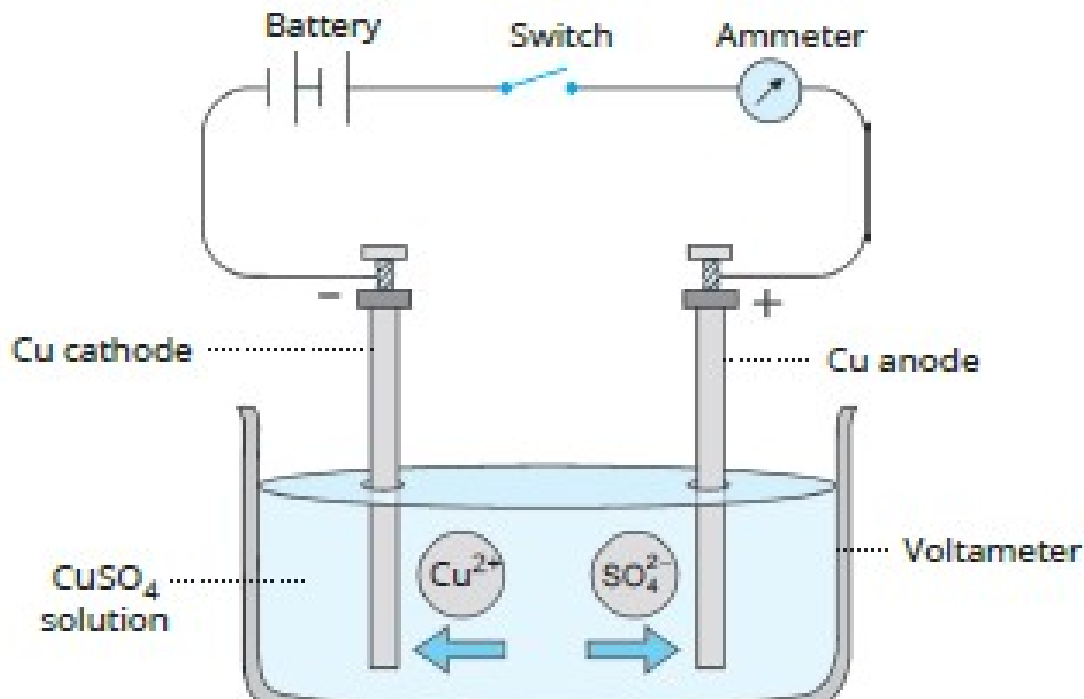
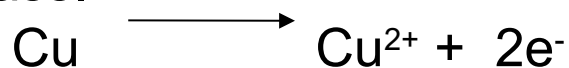
Reaction at cathode

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.



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.



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.

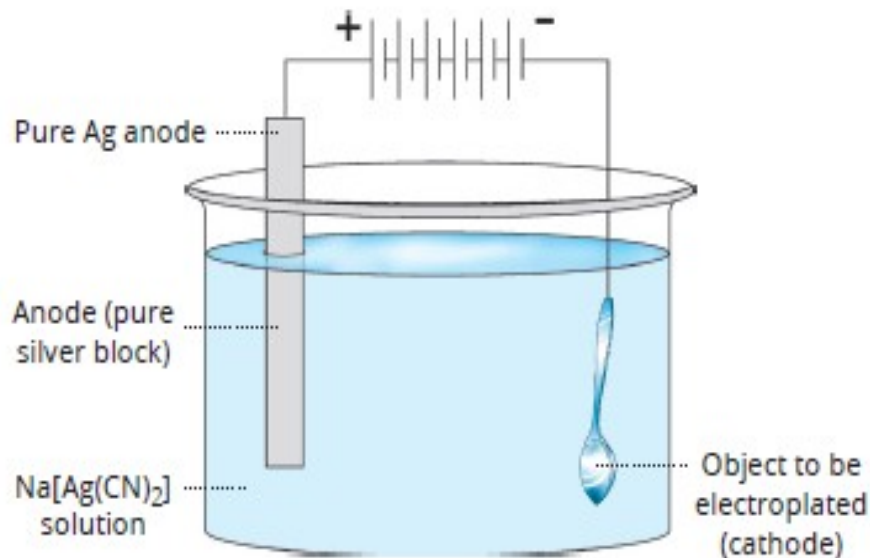
Conditions for electroplating:

1. The article to be electroplated should be made the cathode and the anode must be made of the pure metal which is to be electroplated on the article.
2. The metal to be electroplated should be replaced periodically because when electric current is passed, the metal from the anode dissolves by forming the metal ions which migrate towards the cathode.
3. The electrolyte should contain the ions of the metal which is to be electroplated on the article.
4. For effective electroplating, a low direct current is passed at a constant rate through the electrolyte.

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.

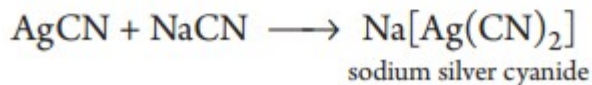
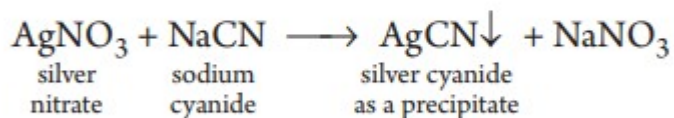
2. Prevention of corrosion: Iron equipment and objects are electroplated with zinc or chromium or nickel for preventing them from corrosion.



Electroplating of an object with silver

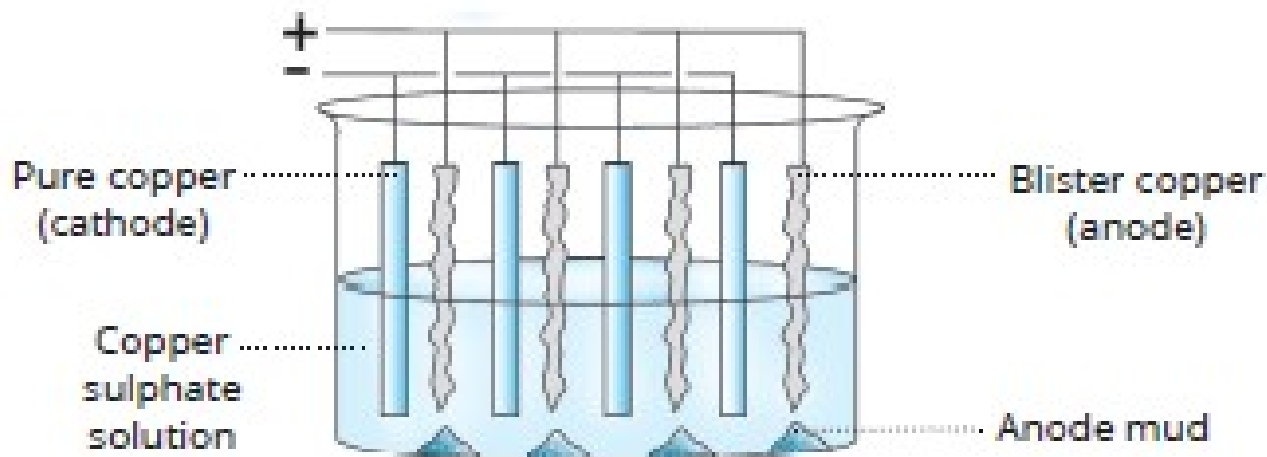
Electrolyte: $\text{Na}[\text{Ag}(\text{CN})_2]$ sodium argentocyanide
 $\text{HCN}/\text{H}_2\text{O}$

This can be prepared as:



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.

TABLE 6.6 Some examples for extraction of metals

Element	Electrolyte	Electrolytic dissociation	Reaction at cathode	Reaction at anode
Potassium	Fused potassium bromide (KBr)	$\text{KBr} \longrightarrow \text{K}^+ + \text{Br}^-$	$\text{K}^+ + \text{e}^- \longrightarrow \text{K}$	$2\text{Br}^- \longrightarrow 2\text{Br} + 2\text{e}^-$ $\text{Br} + \text{Br} \longrightarrow \text{Br}_2 \uparrow$
Sodium	Fused sodium chloride (NaCl)	$\text{NaCl} \longrightarrow \text{Na}^+ + \text{Cl}^-$	$\text{Na}^+ + \text{e}^- \longrightarrow \text{Na}$	$\text{Cl}^- \longrightarrow \text{Cl} + \text{e}^-$ $\text{Cl} + \text{Cl} \longrightarrow \text{Cl}_2$
Magnesium	Fused magnesium chloride (MgCl_2)	$\text{MgCl}_2 \longrightarrow \text{Mg}^{2+} + 2\text{Cl}^-$	$\text{Mg}^{2+} + 2\text{e}^- \longrightarrow \text{Mg}$	$\text{Cl}^- \longrightarrow \text{Cl} + \text{e}^-$ $\text{Cl} + \text{Cl} \longrightarrow \text{Cl}_2$
Aluminium	Pure Alumina (Al_2O_3), cryolite (Na_3AlF_6) and fluorspar (CaF_2)	$\text{Al}_2\text{O}_3 \longrightarrow 2\text{Al}^{3+} + 3\text{O}^{2-}$	$2\text{Al}^{3+} + 6\text{e}^- \longrightarrow 2\text{Al}$ Here, gas carbon lining of electrolytic cell acts as the cathode.	$3\text{O}^{2-} \longrightarrow 3[\text{O}] + 6\text{e}^-$ $3[\text{O}] + 3[\text{O}] \longrightarrow 3\text{O}_2$ Here, graphite rod acts as the anode.

SUMMARY

1. Electrolysis of molten sodium chloride

Electrolytic equation $\text{NaCl} \rightleftharpoons \text{Na}^+ + \text{Cl}^-$

At the cathode $\text{Na}^+ \longrightarrow \text{Na} + \text{e}^-$

At the anode $\text{Cl}^- \longrightarrow \text{Cl} + \text{e}^-$



2. Electrolysis of molten lead bromide

Electrolytic equation $\text{PbBr}_2 \longrightarrow \text{Pb}^{2+} + 2\text{Br}^-$

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

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



3. Electrolysis of acidified water

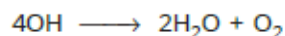
Electrolytic equations $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$



At the cathode $\text{H}^+, 2\text{H}^+$



At the anode $\text{OH}^-, \text{SO}_4^{2-}$



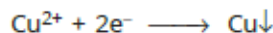
4. Electrolysis of aqueous copper sulphate solution

Using inert electrodes

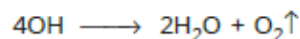
Electrolytic equations $\text{CuSO}_4 \longrightarrow \text{Cu}^{2+} + \text{SO}_4^{2-}$



At the cathode $\text{Cu}^{2+}, \text{H}^+$



At the anode $\text{OH}^- \longrightarrow \text{OH} + \text{e}^-$

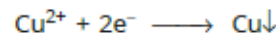


Using active electrodes

Electrolytic equations $\text{CuSO}_4 \longrightarrow \text{Cu}^{2+} + \text{SO}_4^{2-}$



At the cathode $\text{Cu}^{2+}, \text{H}^+$



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

5. Silver plating

Electrolytic equations



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

At the anode $\text{Ag} \longrightarrow \text{Ag}^+ + \text{e}^-$

6. Nickel plating

Electrolytic equations $\text{NiSO}_4 \longrightarrow \text{Ni}^{2+} + \text{SO}_4^{2-}$



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

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

7. Copper refining

Electrolytic equations $\text{CuSO}_4 \longrightarrow \text{Cu}^{2+} + \text{SO}_4^{2-}$



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

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

THANK YOU