

Electrolysis

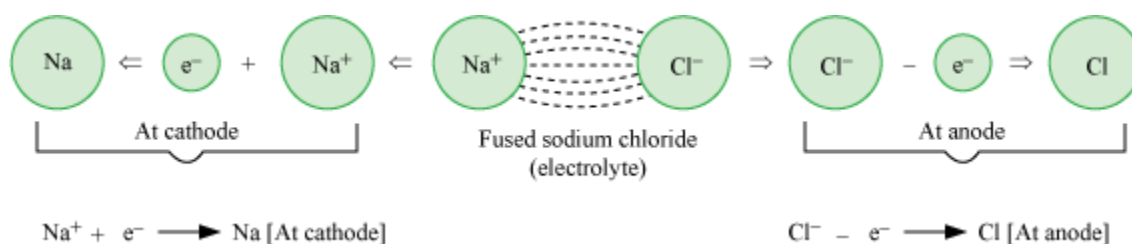
Electrolysis

An ionic compound or electrovalent compound is formed when metallic atoms donate electrons and non-metallic ions accept electrons.

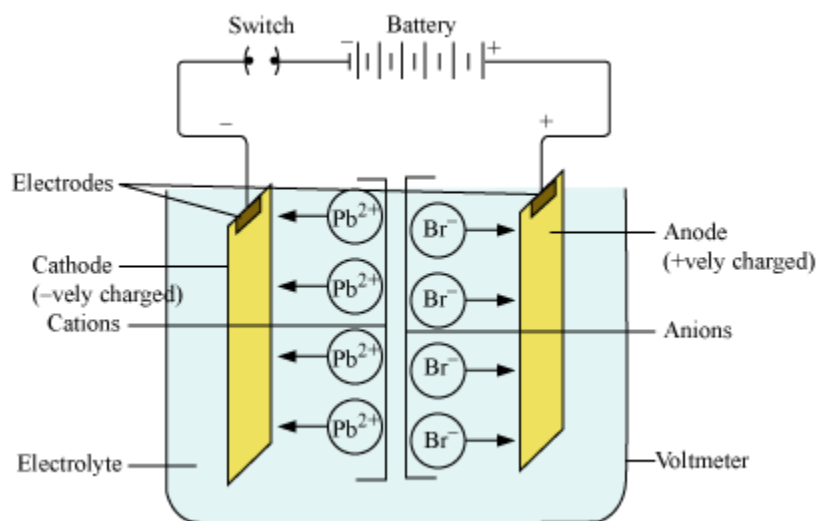
The word electrolysis is made up of two words **electro**, which means the flow of electrons, and **lysis**, which means pertaining to.

Electrolysis is the process by which a chemical compound in the fused state or in aqueous solution undergoes a chemical change on the passage of current.

During electrolysis, a chemical change is brought about by electric energy.



- Electrolytic cell or voltameter is the vessel consisting of glass, containing **two electrodes and an electrolyte**.



- The graphite or metal rods through which electric current enters or leaves from an electrolyte are called **electrodes**.

Therefore, a **cathode** is the electrode which is connected to the negative terminal of the battery. It has an excess of electrons. **An anode** is an electrode which is connected to positive terminal of battery. It has deficiency of electrons.

Difference between cathode and anode

Anode	Cathode
Connected to positive terminal of the battery	Connected to negative terminal of the battery
Migration of anion occurs	Migration of cations occurs
Oxidation occurs	Reduction occurs

Differences between metallic and electrolytic conductors

Metallic Conductors	Electrolytic Conductors
Flow electrons from negative pole to positive pole is responsible for conduction.	Flow of ions in solution to the respective electrodes is responsible for conduction.
Shown by metals and alloys	Shown by aqueous solution of ionic compounds
Present in both solid and liquid state of metals	Present in molten or aqueous solution of the ionic compounds
Physical process	Chemical process

- **Electrolyte** refers to the compound, which in fused state or in aqueous state conducts electric current so that chemical decomposition of the compound takes place.

The electrolytes which allow a large amount of current to flow through them are called strong electrolytes. The strong electrolytes in fused state are completely dissociated and hence, their ions are free to move in any direction.

Examples include an aqueous solution of mineral acid and caustic alkalis.

The electrolytes which allow a very small amount of current to flow through them are called weak electrolytes. The strong electrolytes in fused state are completely dissociated. Hence, their ions are free to move in any direction.

Examples include aqueous solution of acid and bases.

- **Non-electrolyte** is the chemical compound which does not conduct electric current in fused state or in aqueous solution and does not undergo any chemical decomposition.

Examples are carbon tetrachloride, alcohol, ether, pure water, etc.

Differences between strong and weak electrolytes

Strong electrolytes	Weak electrolytes
Allows large amount of electricity to flow through them	Allows small amount of electricity to flow through them
Good conductors	Poor conductors
Undergo complete dissociation in molten or aqueous solution	Undergo partial dissociation in molten or aqueous solution
Contain free mobile ions	Contains ions and molecules
Examples are HCl, H ₂ SO ₄ , HNO ₃ , NaOH, KOH, NaCl, CuSO ₄ , etc.	Examples are H ₂ CO ₃ , CH ₃ COOH, HOOC-COOH, NH ₄ OH, Ca(OH) ₂ , (NH ₄) ₂ CO ₃ , Pb(CH ₃ COO) ₂

Ions

When a chemical compound in fused state or in aqueous solution breaks up into electrically charged atoms or group of atoms, the charged particles are called ions. A positively charged ion is cation. They migrate towards cathode. A negatively charged ion is an anion. They migrate towards anode.

Differences between cation and anion

Cation	Anion
Positively charged	Negatively charged
Migrate to cathode	Migrate to anode
Get reduced to form neutral atom	Get oxidised to form neutral atom
Examples, Na ⁺ , Al ³⁺	Examples, Cl ⁻ , OH ⁻

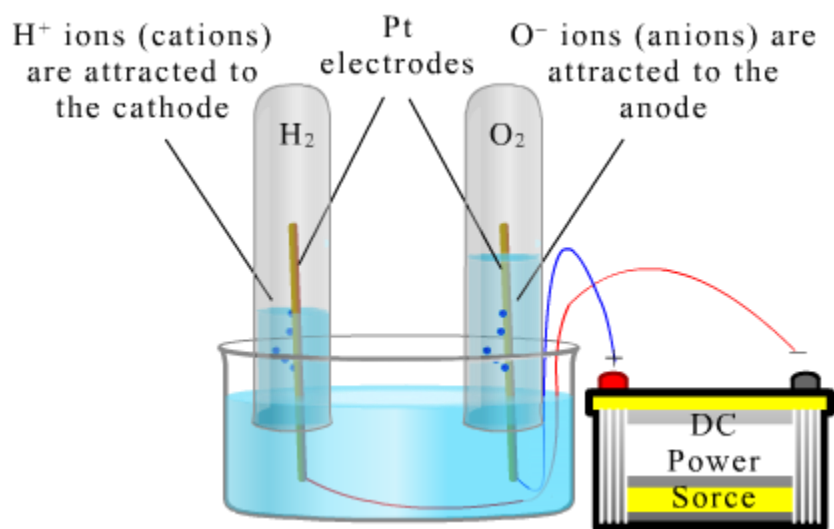
Mechanism of electrolysis

It was put forward by Avante Arrhenius, a Swedish chemist. Following are the points given in his theory of electrolytic dissociation.

- An electrolyte is a substance which in an aqueous solution breaks into positively charged cations and negatively charged anions.
- The movement of ions within the electrolyte is responsible for the flow of electric current.
- The degree of dissociation refers to the extent to which electrolyte dissociates into ions.
- Cations and anions unite to form neutral ion, setting up equilibrium.
- An electrolyte is electrically neutral.

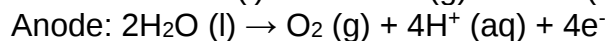
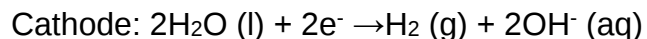
Electrolysis of water:

Add a small amount of salt to water and pour this solution into a beaker. Connect two electrical wires to the terminal of the battery as shown in the figure. The two ends of the wires will serve as electrodes when the insulating cladding is removed from them. Take two test tubes and fill them with the solution of salt and water. Invert these test tubes on the electrodes and restrict the formation of air bubbles. Switch on the power supply.



Observe the two test tubes when the electric current is passed through it. The volume of the gas formed in one test tube is double than that of the gas formed in the other test tube.

The gas formed at the cathode is hydrogen while the gas formed at the anode is oxygen.



Characteristics of electrolysis

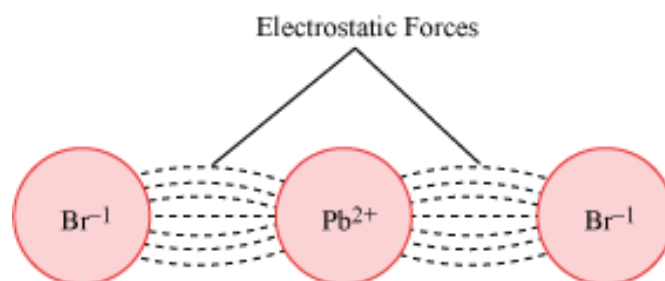
- On passing the electric current, cations migrate towards cathode while the anions migrate towards the anode.
- The number of electrons accepted by an anode is equal to the number of electrons donated by the cathode.
- The products of electrolysis are formed on the surface of the cathode where the exchange of electrons occurs.
- The preferential discharge of ions depends upon their position in electrochemical series and the concentration of ions.
- Neutral atoms of metals and hydrogen are liberated at the cathode. Therefore, they are called electropositive elements. Neutral atoms of non-metals are liberated at the anode. Therefore, they are called electronegative elements.
- According to Faraday's law of electrolysis, the mass of a substance discharged at an electrode is directly proportional to the quantity of electricity passing through the electrolyte.
- Direct current is suitable to carry out electrolysis.
- Electrolysis is a redox reaction, where reduction occurs at cathode and oxidation occurs at anode.

Do you know solid ionic compounds do not conduct electricity while fused ionic compound and aqueous solution do?

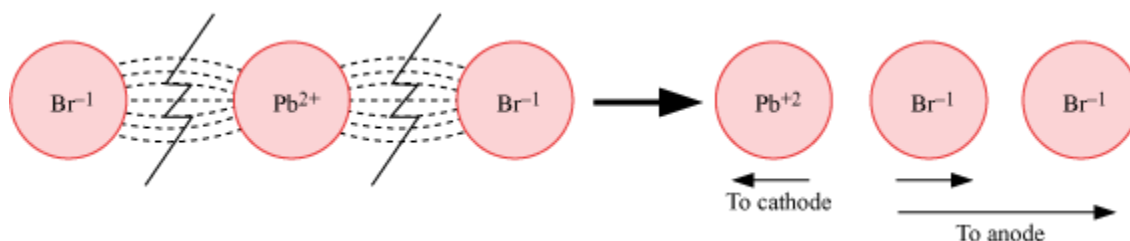
This happens because the electric current passes through an ionic compound only if it has free ions for migration. In a solid ionic compound, ions are held together by strong electrostatic forces. Hence, the ions are not free to migrate. Therefore, solid ionic compounds do not conduct electricity. But fused ionic compound and an aqueous solution of a compound have free ions produced by electrolytic dissociation of the ionic compound. These ions are free to conduct electricity.

Let us study it with the help of some examples.

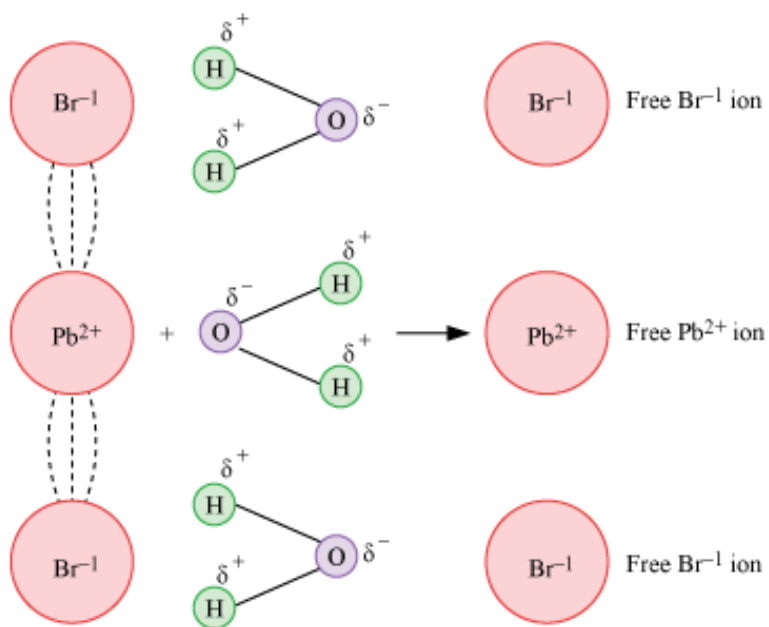
Example- Solid ionic lead bromide does not conduct electricity as lead ions and bromide ions are not free to migrate. This is because they are held together by strong electrostatic forces.



But when lead bromide is heated, ions gain kinetic energy. At one point, ions have more kinetic energy than the electrostatic bonds holding them and they start moving freely. Hence, the fused compound conducts electricity.



In an aqueous solution of compounds, say lead bromide, the slight positive charge on hydrogen atom pulls the bromine ions and slight negative charge on oxygen atom pulls the lead ions. This weakens the electrostatic attraction between lead and bromide ions. Thus, free ions are migrated towards cathode and anode and thus, it conducts electricity.

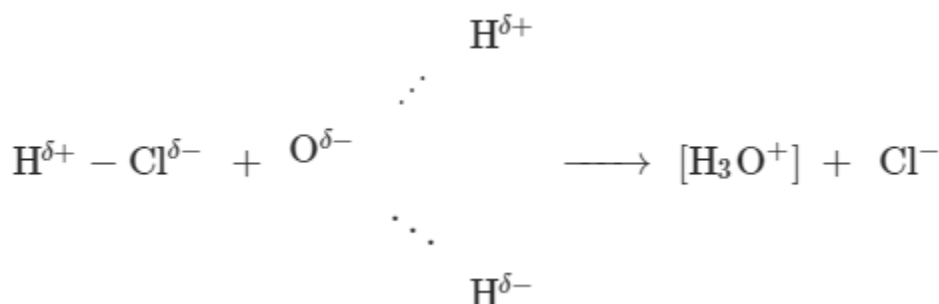


Also, covalent compounds such as molten wax or kerosene oil do not conduct electricity as they do not produce free ions even on heating or in solution form. However, there are

certain covalent compounds that form ions when dissolved in water and thus conduct electricity.

The process of conversion of polar covalent compounds into ions in aqueous solution is known as **ionisation**. For example, pure hydrogen chloride does not contain any ion. It does not conduct electricity.

However, due to the difference in the electronegativities of H and Cl, there exists a small charge distribution, making it a polar covalent compound. Addition of this pure hydrogen chloride to water helps in charge separation causing the formation of ions in the solution.



Electrochemical Series

Depending on the ease with which metals lose or gain electrons to form ions, they are arranged in a vertical column called electrochemical series.

Electropositive series

Depending on the ease with which metals lose electrons to form ions, they are arranged in a vertical column called electropositive series.

Metals, which ionise very easily such as potassium, are placed at **the top of electropositive series**. The cations formed are not discharged easily during electrolysis.

Metals, which do not ionise easily such as silver ion, are placed **at the bottom of electropositive series**. The cations formed are discharged very easily during electrolysis.

Electronegative series

Depending on the ease with which non-metals or group of non-metals gain electrons to form ions, they are arranged in a vertical column called electronegative series.

Non-metals or group of non-metals, which accept electrons very easily such as fluorine, are placed at **the top of electronegative series**. The anions formed are not discharged easily during electrolysis.

Non-metals or group of non-metals, which do not accept electrons easily such as hydroxyl ion, are placed at **the bottom of electronegative series**. The cations formed are discharged with very difficulty during electrolysis.

Electropositive series			Electronegative series	
Metal	Cation	Notes	Anion	Notes
K	K^{1+}	Increasing ease of reduction Discharge with maximum difficulty Cations are discharged at cathode by the gain of electrons Discharge with maximum ease	SO_4^{1-}	Increasing ease of oxidation Discharge with maximum difficulty Anions are discharged at anode by the loss of electrons Discharge with maximum ease
Ca	Ca^{2+}		NO_3^{1-}	
Na	Na^{1+}		F^{1-}	
Mg	Mg^{2+}		Cl^{1-}	
Al	Al^{3+}		Br^{1-}	
Zn	Zn^{2+}		I^{1-}	
Fe	Fe^{2+}			
Pb	Pb^{2+}			
[H]	H^{1+}			
Cu	Cu^{2+}			
Hg	Hg^{2+}			
Ag	Ag^{1+}		OH^{1-}	

Selective discharge of ions

It refers to the preferential discharge of one particular cation at cathode and one particular anion at anode when an electrolyte contains two or more anions or cations.

Let us study the factors which influence selective discharge of ions.

- Relative positions of cations and anions in electrochemical series**

Ions which are present at lower position in the electrochemical series have greater tendency of their discharge at respective electrode to form an element.

For example, in an electrolyte containing silver ion and hydrogen ion, both will migrate to cathode, but silver ions are discharged preferentially due to its lower position in electrochemical series.

In an electrolyte containing chloride ion and hydroxyl ion, both will migrate to cathode, but hydroxyl ions are discharged preferentially due to its lower position in electrochemical series.

- **Concentration of ions**

Higher the concentration, greater are the chances of their discharge on respective electrodes.

- **Nature of anode**

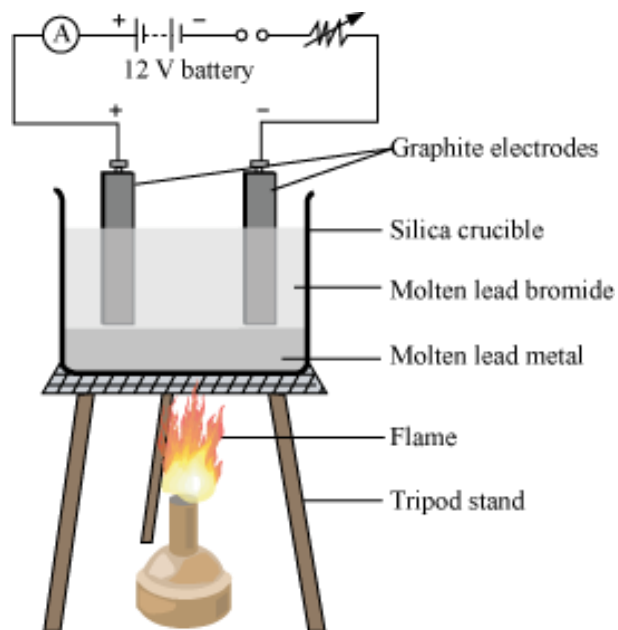
The selective discharge of anions migrating towards anode depends of the nature of anode. The anode can be chemically inert such as iron, graphite, etc. or chemically attackable such as nickel, silver, etc.

Electrolysis of some Common Electrolytes

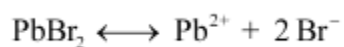
Electrolysis of lead bromide

It is carried out under following conditions:

- **Electrolytic cell-** Silica crucible, containing fused lead bromide and graphite electrodes, is used as it is non-reactive and a bad conductor of electricity.
- **Electrolyte-** Molten fused lead bromide is used as solid lead bromide is a bad conductor of electricity while molten fused lead bromide is a good conductor of electricity.
- **Electrodes-** Inert electrodes are used because they do not react with the products formed. Graphite is used as cathode and anode in preference to platinum because bromine evolved at anode can react with platinum.
- **Temperature-** A temperature of 380°C or above is maintained by external heating, which is the melting point of lead bromide.



- Dissociation of electrolyte**

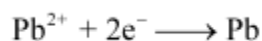


Lead ions and bromide ions are formed in the process.

On passage of electric current, lead ions are attracted towards cathode while bromide ions migrate towards anode.

At cathode

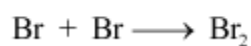
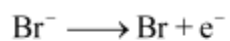
Cathode acts as electron donor. Therefore, the following reaction takes place.



Lead metal is formed at cathode, which settles down at the base of crucible.

At anode

Anode acts as electron acceptor. Therefore, the following reaction takes place.

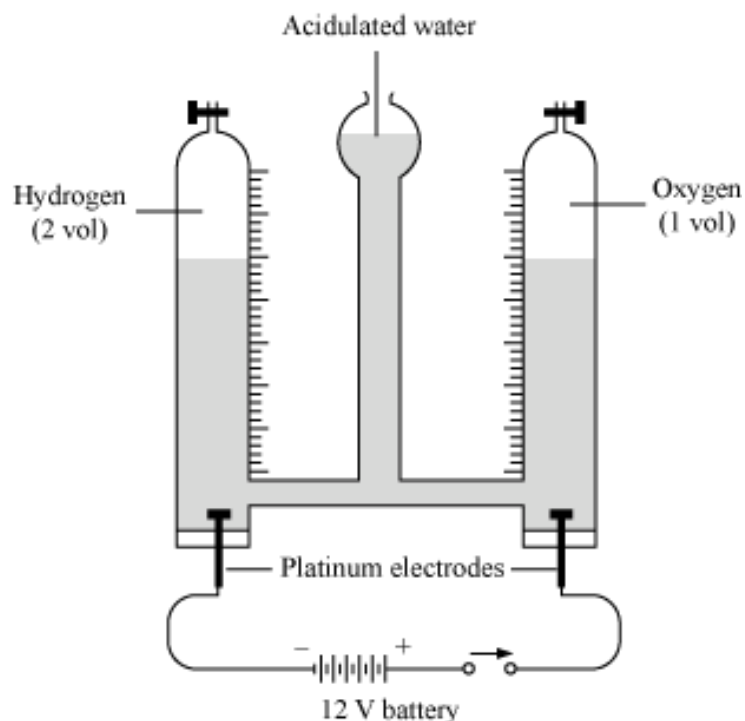


Therefore, bromine vapours are formed at anode.

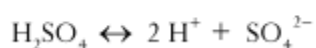
Electrolysis of acidulated water

It is carried out under the following conditions:

- **Electrolytic cell**- Hofmann's voltameter is used. It consists of three interconnected glass tubes. The central tube is used for pouring acidulated water while products are collected from side tubes.
- **Electrolyte** – Distilled water containing 2% sulphuric acid is used. Sulphuric acid is used because it helps in dissociation of water.
- **Electrodes**- Inert electrodes are used because they do not react with the products formed. Platinum strip is used as cathode and anode because the products formed at anode do not react with platinum.
- **Temperature**- The electrolysis is carried out at room temperature.



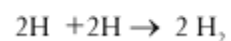
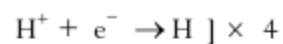
- **Dissociation of electrolyte**



On passage of electric current, H^+ ions are attracted towards cathode while OH^- and SO_4^{2-} ions migrate towards anode.

At cathode

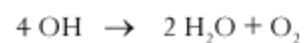
Cathode acts as electron donor. Therefore, the following reaction takes place.



Hydrogen atoms are formed at cathode.

At anode

Anode acts as an electron acceptor. Therefore, the following reaction takes place.

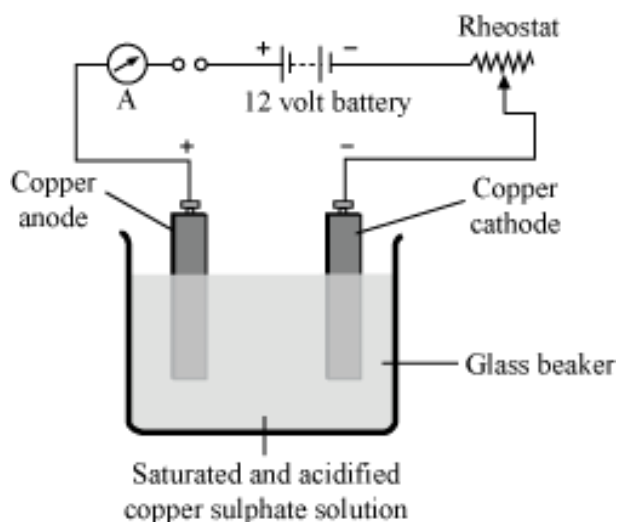


Hence, oxygen gas is liberated at anode.

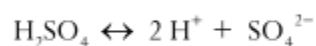
Electrolysis of aqueous acidulated copper sulphate solution using copper sulphate-

It is carried out under the following conditions:

- **Electrolytic cell-** A glass container is used as it is a bad conductor of electricity. It contains saturated copper sulphate solution and two copper electrodes.
- **Electrolyte** – Saturated aqueous copper sulphate solution acidified with sulphuric acid is used. It is acidified to prevent hydrolysis of copper sulphate.
- **Electrodes-** Inert electrodes are used because they do not react with the products formed. Copper plate or copper rod is used as cathode and anode.
- **Temperature-** The electrolysis is carried out at room temperature.



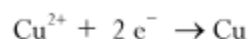
- Dissociation of electrolyte**



On the passage of electric current, H^+ and Cu^{2+} ions are attracted towards cathode while OH^- and SO_4^{2-} ions migrate towards anode.

At cathode

Cathode acts as electron donor. Therefore, the following reaction takes place.



Copper metal is formed at cathode.

At anode

Anode acts as an electron acceptor. Therefore, the following reaction takes place.



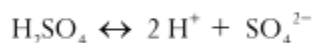
The concentration of Cu^{2+} ions does not change. It is because the number of ions deposited at the cathode is equal to the number of copper atoms, which ionise at the

anode.

Electrolysis of aqueous acidulated copper sulphate solution using platinum anode and copper or platinum cathode

It is carried out under the following conditions:

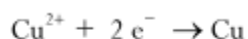
- **Electrolytic cell**- A glass container is used as it is a bad conductor of electricity. It contains saturated copper sulphate solution and platinum or copper electrodes.
- **Electrolyte** – Saturated aqueous copper sulphate solution acidified with sulphuric acid is used. It is acidified to prevent hydrolysis of copper sulphate.
- **Electrodes**- Inert electrodes are used because they do not react with the products formed. Copper plate or copper/platinum rod is used as cathode and platinum anode.
- **Temperature**- The electrolysis is carried out at room temperature.
- **Dissociation of electrolyte**



On passage of electric current, H^+ and Cu^{2+} ions are attracted towards cathode while OH^- and SO_4^{2-} ions migrate towards anode.

At cathode

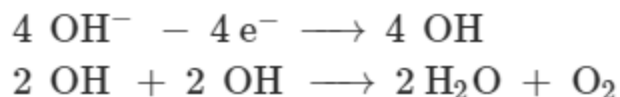
Cathode acts as electron donor. Therefore, the following reaction takes place.



Copper metal is formed at cathode.

At anode

Anode acts as electron acceptor. Since OH^- ions are low in electrochemical series than SO_4^{2-} ions, hence they will be discharged at anode to give off oxygen gas as shown below:



Note: Once the electrolysis of copper sulphate is complete, then the electrolysis of water starts in and hydrogen gas is liberated at cathode, while oxygen is liberated at anode. Also, in this electrolysis the blue colour of the electrolyte fades away due to decrease in the concentration of Cu^{2+} ions.

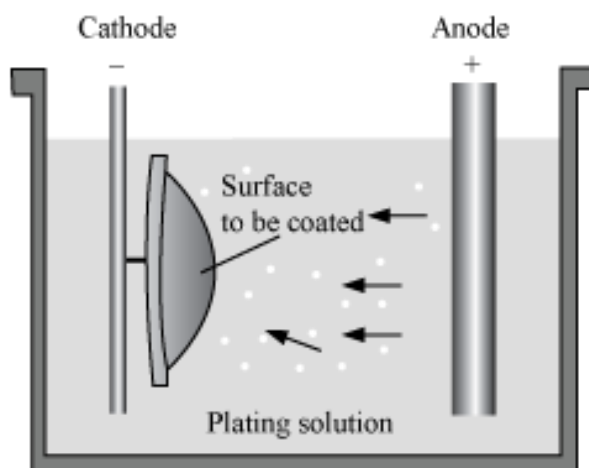
Application of Electrolysis

Electrolysis is used for the following purposes:

- Electroplating
- Electro-refining
- Extraction of metals by electrolysis

Electroplating

The process of depositing a thin and compact layer of superior metal over the inferior metal by the process of electrolysis is called **electroplating**. It can be of many types such as silver plating and nickel plating.



It is done for the following reasons:

- To prevent metallic articles from rusting

For example, articles made of iron are electroplated with nickel so as to prevent them from rusting.

Do You Know?

Ships are made of iron and a part of them remains under water. Seawater contains many salts dissolved in it and salt water makes the process of rusting faster. Therefore, ships suffer a lot of damage. As a result, a fraction of the ship's iron has to be replaced every year. Hence, a large amount of money is spent to replace the damaged iron and steel.

- To improve appearance of articles

For example, decoration articles made from copper or brass are electroplated with silver to improve their appearance.



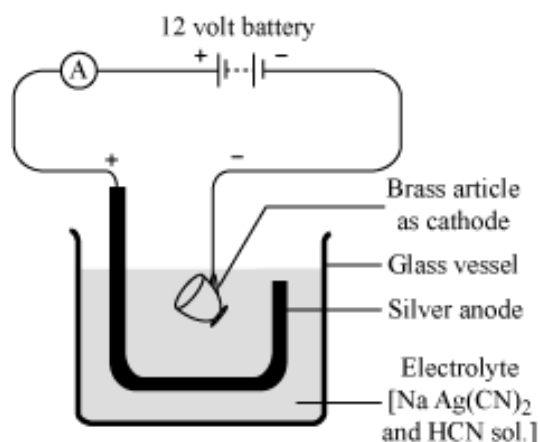
Conditions of electroplating

- Articles to be electroplated must be very clean.
- Articles to be electroplated are made cathode while the metal to be electroplated is made anode.
- The metal to be electroplated is to be replaced periodically as it is consumed.
- The electrolyte must be in the form of an aqueous saturated solution and it must contain ions of metals to be electroplated.

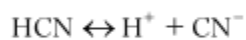
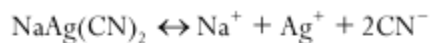
- The electrolyte must be acidulated with some acid containing negative ions so as to prevent hydrolysis.
- Low and direct current should be used so that the electrolyte is not heated up.

Let us study silver plating now.

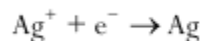
The electrolyte used is the saturated aqueous solution of sodium argento cyanide acidified with hydrocyanic acid. A highly cleaned article is used as a cathode while a hollow cylinder of silver surrounding cathode is used as an anode.



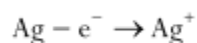
Electrolyte dissociates as follows:



At the cathode, silver ions discharge because of their low reduction potential.

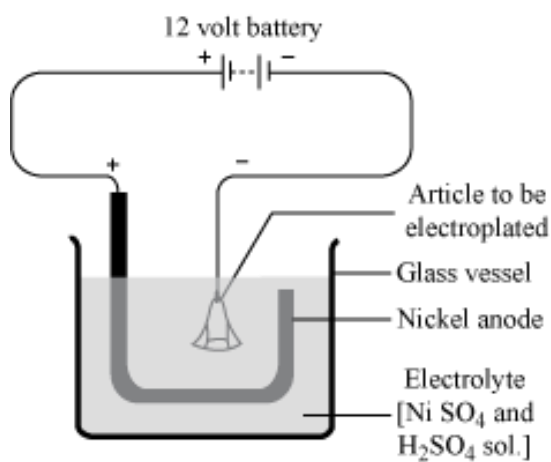


At the anode, silver atoms discharge to form silver ions because of their low reduction potential.



Let us study nickel plating now.

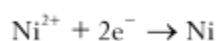
The electrolyte used is the saturated aqueous solution of nickel sulphate acidified with sulphuric acid. A highly cleaned article is used as a cathode while a hollow cylinder of nickel surrounding cathode is used as an anode.



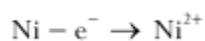
Electrolyte dissociates as follows:



At the cathode, nickel ions discharge because of their low reduction potential.



At the anode, nickel atoms discharge to form nickel ions because of their low reduction potential.



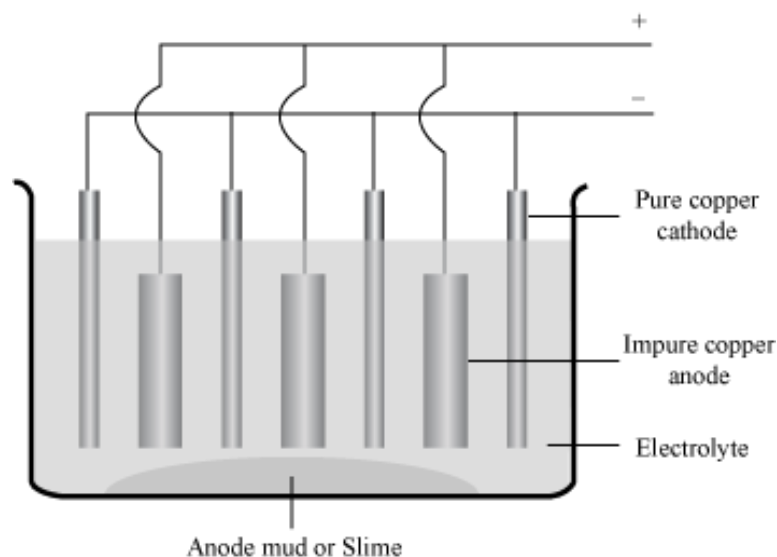
Electro-refining

Electro-refining is the process by which impurities are removed from an impure metal.

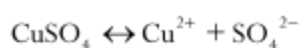
Metals such as silver and copper are refined using electro-refining.

Let us study electro-refining of copper.

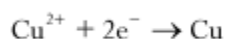
The electrolyte used is the saturated aqueous solution of copper sulphate acidified with sulphuric acid. Pure copper thin sheets connected in parallel are used as a cathode while impure copper thin sheets connected in parallel are used as an anode.



Electrolyte dissociates as follows:



At the cathode, copper ions discharge because of their low reduction potential.



At the anode, copper atoms discharge to form copper ions because of their low reduction potential.



Let us watch an animation to understand better.

Electro-metallurgy

It refers to the process of extraction of metals from their fused ores by the process of electrolysis. This method is useful for extraction of reactive metals like potassium (K), sodium (Na), magnesium (Mg), etc. Halides of reactive metals are used as electrolytes and the electrodes are iron (as a cathode) and graphite (as an anode). The aqueous solution of reactive metals is not employed for the extraction process, as it contains H^+ ions will be preferentially discharged on the cathode instead of metal ions.

The table given below explains the extraction of these reactive metals by electrolysis.

Metal to be extracted	Potassium (K)	Sodium (Na)	Magnesium (Mg)
Electrolyte	Fused KBr	Fused NaCl	Fused MgCl ₂
Reaction at cathode	$K^+ + e^- \rightarrow K$	$Na^+ + e^- \rightarrow Na$	$Mg^{2+} + 2 e^- \rightarrow Mg$
Reaction at anode	$Br^- \rightarrow Br + e^-$ $Br + Br \rightarrow Br_2$	$Cl^- \rightarrow Cl + e^-$ $Cl + Cl \rightarrow Cl_2$	$Cl^- \rightarrow Cl + e^-$ $Cl + Cl \rightarrow Cl_2$
Element discharged at cathode	K	Na	Mg

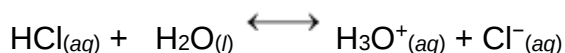
Ionisation of Acids and Bases

Arrhenius Concept

- Strong acids are those which completely dissociate in aqueous solutions to give H⁺ ions which form H₃O⁺ ions.
- Examples: Perchloric acid (HClO₄), hydrochloric acid (HCl), hydrobromic acid (HBr), hydroiodic acid (HI), sulphuric acid (H₂SO₄), nitric acid (HNO₃)
- Strong bases are those which completely dissociate in aqueous solutions to give OH⁻ ions.
- Examples: Lithium hydroxide (LiOH), sodium hydroxide (NaOH), potassium hydroxide (KOH), barium hydroxide (Ba(OH)₂)

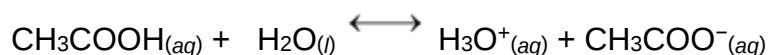
Bronsted-Lowry Concept

- The conjugate base of a strong acid is a weak base.



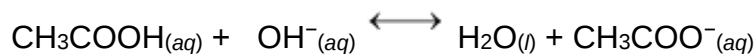
Strong acid Weak base

- The conjugate base of a weak acid is a strong base.



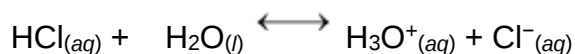
Weak acid Strong base

- The conjugate acid of a strong base is a weak acid.



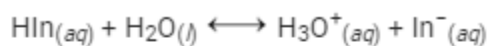
Strong base Weak acid

- The conjugate acid of a weak base is a strong acid.



Weak base Strong acid

- Weaker the conjugate base, stronger is the acid. Similarly, weaker the conjugate acid, stronger is the base.
- Phenolphthalein and bromothymol blue
- Weak acids
- Exhibit different colours in their acid (HIn) and conjugate base (In⁻) forms.



Acid	base	Conjugate acid	Conjugate base
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colour (A)	colour (B)
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- Used as indicators in acid-base titration

Strong and Weak Electrolyte

1. Strong electrolyte: Electrolytes which ionise in water completely are termed as strong electrolytes such as NaCl, MgCl₂ etc. Strong acids, strong bases, and soluble salts are strong electrolytes.

2. Weak electrolyte: Electrolytes which do not ionise completely in water are termed as weak electrolytes such as acetic acid. Weak acids, weak bases, and sparingly soluble salts are weak electrolytes.

Degree of Dissociation

When an electrolyte is dissolved in water or any solvent it may either completely dissociate or partially dissociate. Their solubility in a solvent such as water is expressed by the degree of dissociation.

It is defined as the extent to which an electrolyte dissociates into ions in a solvent. It is represented by the symbol α . It is calculated as follows

$$\alpha = \frac{\text{Number of moles dissociated}}{\text{Initial number of moles}}$$

The value of α is 1 for strong electrolytes as they are completely dissociated and less than 1 for weak electrolytes since they are not completely dissociated.

The value of α for an electrolyte depends on

- (i) Nature of solvent: Solvent having a high dielectric constant will favour the dissociation.
- (ii) Nature of electrolytes: Strong electrolytes dissociate completely while weak electrolyte dissociates partially.
- (iii) Dilution: Increasing dilution will increase the degree of dissociation of weak electrolytes.
- (iv) Temperature: Increase in temperature generally favours the dissociation.