

SYLLABUS :

- (i) Electrolytes and non-electrolytes.

Definitions and examples.

- (ii) Substances containing molecules only, ions only, both molecules and ions.

Substances containing molecules only, ions only, both molecules and ions. Examples: relating their composition with their behaviour as electrolyte (strong and weak), non-electrolyte.

Definition and explanation of electrolysis, electrolyte, electrode, anode, cathode, anion, cation, oxidation and reduction (on the basis of loss and gain of electrons).

- (iii) An elementary study of the migration of ions, with reference to the factors influencing selective discharge of ions, illustrated by the electrolysis of: molten lead bromide; acidified water with platinum electrodes and aqueous copper (II) sulphate with copper electrodes; electron transfer at the electrodes.

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

- (iv) Application of electrolysis: electroplating with nickel and silver; purification of copper; choice of electrolyte for electroplating.

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

- (v) Acids, bases and salts as electrolytes: reference should be made to the activity series as indicating the tendency of metals, e.g., Na, Mg, Fe, Cu, to form ions.

6.1 INTRODUCTION

This chapter deals with a process called "Electrolysis" which establishes a relationship between electrical energy and chemical change.

The word electrolysis is made up of two words '**electro**' meaning flow of electrons or electricity and '**lysis**' meaning separating, i.e., bringing about a (chemical) change in a substance by passage of electricity.

Many substances allow electricity to pass through them and many do not. It has also been found that all the substances allowing passage of electricity do not undergo chemical change.

Most metallic **elements** like copper, aluminium, iron and all alloys, whether in solid state or in molten state, allow an electric current to pass through them without undergoing any chemical change. Non-metals (except graphite) like sulphur, phosphorus, etc., do not conduct electricity. Therefore, metals and alloys are called **conductors** and non-metals are called **non-conductors** (insulators) of electricity.

The conduction of a current by a conductor is due to the flow of electrons. Insulators do not possess mobile electrons.

Chemical **compounds** behave differently when an electric current is passed through them. Some compounds conduct electric current in aqueous state or in molten state but not in solid state and are decomposed by the passage of electric current. *For example*, the passage of electric current through copper chloride solution decomposes it to metallic copper and chlorine. Such chemical compounds which conduct electric current in molten or aqueous state are called **electrolytes**. Some compounds do not conduct electric current at all whether in solid state or in aqueous state. They are called **non-electrolytes**, e.g., sugar solution.

Chemical decomposition of a chemical compound can be brought about by using electric current. Such a chemical process is called **electrolysis**.

Table 6.1 Differences between metallic conductors and electrolytic conductors

Metallic conductors e.g. Cu wire	Electrolytic conductors e.g. CuSO_4 solution
1. Flow of current consists of a single stream of electrons flowing from the negative pole to the positive pole.	1. Flow of current consists of two streams, one of the positive cations flowing towards the negative cathode and the other of negative anions flowing towards the positive anode.
2. Metals, both in solid and liquid state are good conductors of electricity.	2. Electrolytes are good conductors only in aqueous solution or in molten state.
3. No change of form or in composition occurs during conduction of electricity. This is only a physical process.	3. New products are formed at the electrodes. This involves chemical changes.

Table 6.2 Differences between strong and weak electrolytes

Strong electrolytes	Weak electrolytes
<p>1. Electrolytes which allow a large amount of electricity to flow through them.</p> <p>2. These are <i>good conductors of electricity</i>.</p> <p>3. These are almost, <i>completely dissociated in fused or aqueous solution state</i>.</p> <p>4. These solutions contain (<i>almost</i>) <i>only free mobile ions</i>.</p> <p>5. Strong electrolyte allows a bulb to glow brightly.</p> <p><i>Examples</i></p> <p>Acids – Hydrogen chloride, Sulphuric acid, Nitric acid, etc.</p> <p>Bases – NaOH, KOH (aqueous or molten state)</p> <p>Salts – NaCl (molten or aqueous) PbBr_2 (molten), CuCl_2 (aq.) CuSO_4 (aq.)</p>	<p>1. Electrolytes which allow small amounts of electricity to flow through them.</p> <p>2. These are <i>poor conductors of electricity</i>.</p> <p>3. These are <i>partially dissociated in fused or aqueous solution state</i>.</p> <p>4. These solutions <i>contain ions as well as molecules</i>.</p> <p>5. Weak electrolyte allows a bulb to glow dimly.</p> <p><i>Examples</i></p> <p>Acids – Carbonic acid, acetic acid, oxalic acid, etc.</p> <p>Bases – Calcium hydroxide, ammonium hydroxide. (aqueous or molten state)</p> <p>Salts – Sodium carbonate and bicarbonate.</p>

6.2 SOME IMPORTANT TERMS

(i) **Electrolysis** : *It is the process of decomposition of a chemical compound in aqueous solutions or in molten state accompanied by a chemical change by using direct electric current.*

(ii) **Electrolytes** are compounds which either in aqueous solution or in molten state allow electric current to pass through them. Electrolytes can be **electrovalent compounds**, composed of metals and non-metals, or **polar covalent compounds**, that form ions in water.

Examples of electrolytes

Acids – H_2SO_4 , HNO_3 , H_3PO_4 , HCl ;

Bases – NaOH , KOH , NH_4OH , $\text{Ca}(\text{OH})_2$;

Salts – NaCl , CuSO_4 , PbBr_2 ;

Electrolytes are of *two* types, based on their conductivity and ability to dissociate into ions.

1. Strong electrolyte
2. Weak electrolyte

(iii) **Non-electrolyte** : *It is a compound which neither in solution nor in the molten state allows an electric current to pass through it.*

It also does not decompose at the electrodes.

Non-electrolytes do not have ions even in solution. They contain only **molecules**.

Examples of non-electrolytes

Distilled water, alcohol, kerosene, carbon disulphide, cane sugar, benzene, glucose and urea.

(iv) **Electrolytic cell** : A non-conducting vessel in which electrolysis is carried out, is called an **electrolytic cell** or **voltameter**. It converts electrical energy into chemical energy (Fig. 6.1).

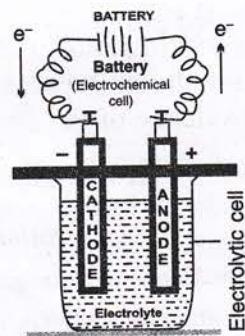


Fig. 6.1 A simple electrolytic cell or voltameter.

(v) **Electrochemical cell** : It is a device used to convert chemical energy into electrical energy.

Examples : Simple voltaic cell, Daniel cell, etc.

(vi) **Electrodes** : Two metal plates or wires or graphite rods or gas carbon rods immersed in the electrolyte through which the current enters and leaves the electrolytic cell are called electrodes.

Anode : The electrode connected to the positive terminal of the battery is called anode.

Cathode : The electrode connected to the negative terminal of the battery is called cathode.

Note : When the current is turned on, the cathode becomes the negative electrode by which electrons enter the electrolyte and the anode becomes the positive electrode by which electrons leave the electrolyte.

The electrodes Which is which ?

How to remember :

Anode → ADD = + i.e. positive

The anode (positive) hence cathode (negative)

Anion (negative) goes to Anode

Cation (positive) goes to Cathode

A to A and C to C

Table 6.3 Differences between anode and cathode.

Anode	Cathode
1. It is the electrode connected to positive terminal of the battery.	1. It is the electrode connected to negative terminal of the battery.
2. Anions migrate to anode.	2. Cations migrate to cathode.
3. It is an oxidising electrode. Oxidation takes place at anode.	3. It is a reducing electrode. Reduction take place at cathode.

(vii) **Ions** : The atoms or groups of atoms which carry a positive or a negative charge are known as ions.

Atoms which carry positive charge are called **cations** and the atoms which carry negative charge are called **anions**.

The charge on an ion, positive or negative is equal to the valency of the atom or the ion.

Table 6.4 Differences between cations and anions

Cations	Anions
1. Are positively charged ions.	1. Are negatively charged ions.
2. Migrate to the cathode during electrolysis.	2. Migrate to the anode during electrolysis.
3. Gain electron(s) from the cathode and get reduced to become a neutral atom.	3. Lose electrons to the anode and get oxidised to become a neutral atom.

Examples :

Cations : Na^+ , Ca^{2+} , Al^{3+}

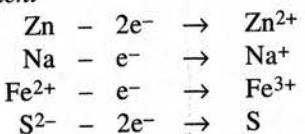
Examples :

Anions: PO_4^{3-} , Cl^- , SO_4^{2-} , OH^-

Oxidation

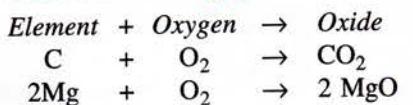
In the electronic concept, **oxidation** is defined as a **process in which an atom or an ion loses electron(s)**.

Element



Oxidation is also defined as a **chemical process which involves addition of oxygen or removal of hydrogen**.

(a) Addition of oxygen :



In the above reactions, carbon and magnesium get oxidised to carbon dioxide and magnesium oxide respectively by the gain of oxygen.

(b) Removal of hydrogen :



Hydrogen sulphide is oxidised to sulphur due to the loss of hydrogen.

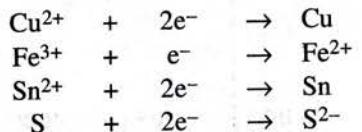
Oxidising Agents : An oxidising agent is one that oxidises other substances by either accepting electrons or by providing oxygen or an electronegative ion [or by removing hydrogen or an electropositive ion]. Thus, in the above examples, oxygen and chlorine are the oxidising agents.

Some examples of oxidising agents.

- Solids** : Manganese dioxide, red lead, lead dioxide, etc.
- Liquids** : Hydrogen peroxide, conc. nitric acid, conc. sulphuric acid, bromine, etc.
- Gaseous** : Oxygen, ozone, chlorine, sulphur dioxide, etc.

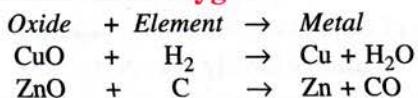
(ix) Reduction

In the electronic concept, **reduction** is defined as a **process in which an atom or an ion gains electron(s)**.



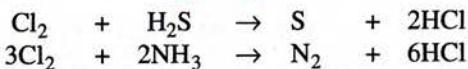
Reduction is also defined as a **chemical process which involves removal of oxygen or addition of hydrogen**.

(a) Removal of oxygen:



Copper (II) oxide and zinc (II) oxide are reduced to copper and zinc respectively by the loss of oxygen.

(b) Addition of Hydrogen :



In the above reactions, chlorine is reduced to hydrogen chloride due to the gain of hydrogen.

Reducing agents : A reducing agent is one that reduces other substances by providing electrons, or by providing hydrogen or an electropositive ion, (or by removing oxygen or an electronegative ion). Thus, in the above examples, hydrogen, carbon, hydrogen sulphide and ammonia are the reducing agents.

Some examples of reducing agents.

1. **Solids** : Carbon, metals like Zn, Al, Cu and Na, stannous chloride, glucose, etc.
2. **Liquids** : Hydrogen peroxide, hydrogen iodide, hydrogen bromide, etc.
3. **Gaseous** : Hydrogen sulphide, carbon monoxide, sulphur dioxide, etc.

6.3 THEORY OF ELECTROLYTIC DISSOCIATION

Svante Arrhenius, in 1887, gave an ionic theory.

According to him :

1. An electrolyte on dissolving in water dissociates into free mobile ions i.e. cations [+ve ions] and anions [-ve ions] and allows the flow of an electric current through it.
2. All ions carry an electric charge and are responsible for the flow of current through the solution.
3. The conductivity of the electrolyte depends upon the concentration of the ions in the solution.
4. The number of positive charges equals the number of negative charges in the solution and thus the solution is in electrolytic equilibrium.
The equilibrium is also established between the unionized molecules and the ions produced.
5. In non-electrolytes, such as sugar solution, benzene, etc., there is no ionisation and therefore, only molecules are present in solution.

6. The degree of dissociation is the extent to which an electrolyte dissociates or breaks up into ions.

The difference between Arrhenius and Modern concept

Arrhenius considered that water ionises electrolytes but Modern concept consider that electrolytes are ionic even in solid state and their ions are held by strong electrostatic forces which make them immobile.

Water renders these ions mobility by breaking the electrostatic forces.

6.4 CONDUCTION IN COMPOUNDS

The electrovalent compounds consist of aggregate of oppositely charged ions held in their positions by the strong electrostatic forces of attraction. Hence, in the solid state, an electrovalent compound like sodium chloride cannot conduct electricity despite the presence of ions.

When the electrovalent compounds are melted or dissolved in water, the forces of attraction between their ions are broken and the ions then move about and conduct electricity.

Covalent compounds which are polar in nature also ionise in aqueous solution and conduct electricity e.g. HCl, NH₃, H₂O.

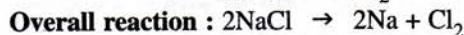
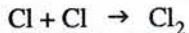
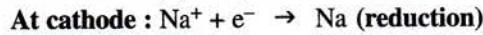
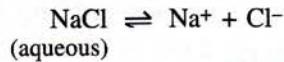
6.5 CHARACTERISTICS OF ELECTROLYSIS

1. The passage of electricity through an electrolyte causes the positive ions i.e., cations to migrate towards the cathode and negative ions i.e., anions to migrate towards the anode.
2. The number of electrons gained by the anode is equal to the number of electrons given by the cathode.
3. 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.
4. Only hydrogen gas and metals are liberated at the cathode and hence are called *electro-positive elements*.
5. Only non-metals are liberated at the anode and are called *electronegative elements*.
6. The mass of a substance produced at an electrode during electrolysis is proportional to the quantity of electricity passing through the electrolyte (Faraday's Law of electrolysis).

7. The process of electrolysis is a redox reaction.

The reaction at the cathode involves reduction of cations as they gain electrons to become neutral atoms while that at anode involves oxidation of anions as they lose electrons to become neutral.

Example : Dissociation of sodium chloride during electrolysis.



8. The alternating current (A.C.) does not cause any chemical change when passed through an electrolyte and therefore does not help electrolysis to occur. *Electrolysis is caused by direct current.*

6.5.1 Electrolytic Dissociation

The process due to which an ionic compound dissociates into ions in the fused state or in aqueous solution is called **electrolytic dissociation**.

Electrolytic dissociation of sodium chloride

1. Solid sodium chloride is an electrovalent compound and its crystal structure contains sodium ions $[\text{Na}^+]$ and chloride ions $[\text{Cl}^-]$. In solid state sodium chloride ions are not free but are held together by an electrostatic force of attraction hence it does not conduct electricity (due to the absence of free ions). [Fig 6.2].

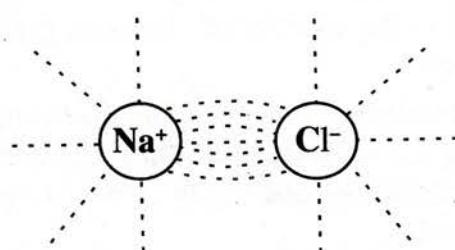


Fig. 6.2 In solid state, ions are held by electrostatic attraction.

When electrovalent compounds like NaCl are fused or dissolved in water, the oppositely charged ions become mobile and conduct electricity.

2. When solid sodium chloride is dissolved in water (**aqueous solution**) or melted (**fused state**), it conducts electricity.

(a) **In the aqueous state**, the slightly negatively charged oxygen atoms of the polar water molecule exerts a pull on the positively charged sodium ions. A similar pull is exerted by the slightly positively charged hydrogen atoms of the water on the negatively charged chloride ions. Thus the ions becomes free in solution. These free ions conduct electricity.

(b) **In the molten state**, the high temperatures required to melt the solid weakens the bond between the particles and the ions are set free. [Fig. 6.3].

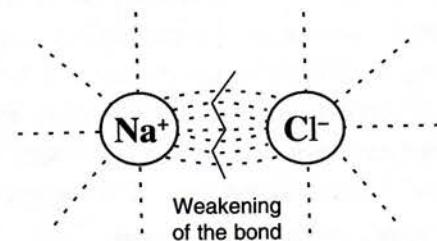


Fig. 6.3 In water solution or in molten state, the attraction is lost and ions are free to move about.

6.5.2 Ionisation

There are *certain* covalent molecules which are not made up of ions but form ions when dissolved in water. These solutions conduct an electric current.

The process by which polar covalent compounds are converted into ions, in water solution, is called **ionisation**.

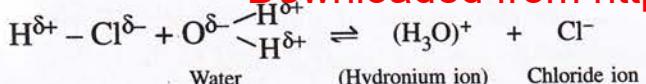
For example, hydrogen chloride.

1. In the gaseous state or in the pure liquid state, **HCl** is unionized and does not conduct an electric current.
2. It is, however, polar covalent in nature, i.e. shows charge distribution in its molecule such that the hydrogen atom has a slight positive charge and the chlorine atom has a slight negative charge.



3. When hydrogen chloride is added to water [a polar solvent], the slightly negatively charged oxygen atom of the water exerts an electrostatic pull on the slightly positively charged hydrogen ions present in the molecule of **HCl**.

* The quantity of electricity is often expressed in unit of Faraday. 1 Faraday is equal to 96,500 coulombs of electricity.



Thus, H⁺ ions combine with water to form hydronium ions [H₃O]⁺.

- (d) a positively charged non-metallic ion,
(e) the electrode at which reduction occurs,
(f) a non-metallic element which is a conductor of electricity.

Electrolysis is a redox process. Explain.

6.5.3 Comparison of ionisation and dissociation

Ionisation	Dissociation
<p>1. Formation of positively or negatively charged ions from molecules which are not initially in the ionic state.</p> <p>2. Polar covalent compounds show ionisation e.g., HCl, H_2CO_3, NH_4OH, etc.</p>	<p>1. Separation of ions which are already present in an ionic compound.</p> <p>2. Electrovalent compounds show dissociation e.g., potassium chloride, lead bromide, etc.</p>

Intext Questions

- 1.** Fill in the blanks.

 - Powdered sodium chloride (common salt) does not conduct an electric current, but it does so when or when
 - Molten lead bromide conducts electricity. It is called an It is composed of lead and bromide The lead ions are charged and are called The bromide are charged and are called
 - Substances which conduct electricity in the solid state are generally.....
 - The electron releasing tendency of zinc is than that of copper.
 - A solution of HCl gas in water conducts electricity because, but a solution of HCl gas in toluene does not conduct an electric current because

2. Define the following terms :

 - Electrolysis, (b) Non-electrolyte,
 - Cation and anion, (d) Weak electrolytes.

3. What is the difference between :

 - Modern explanation and Arrhenius explanation for the theory of electrolysis,
 - Electrolytic dissociation and ionisation,
 - A cation and an anion,
 - Electrolytic dissociation and thermal dissociation.

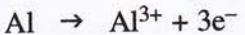
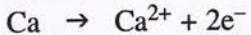
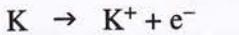
4. Name :

 - a salt which is a weak electrolyte,
 - a base which is a weak electrolyte,
 - an inert electrode and an active electrode.

6.6 ELECTROCHEMICAL (EC) SERIES

Metal elements lose electrons from the outermost shell of their atoms, forming positive metallic ions.

i.e. forming cations :



However, the tendency to lose these valence electrons varies from metal to metal. Consequently, the metallic elements can be arranged in decreasing order of their tendency to lose valence electrons.

6.6.1 Electrochemical Series of metals :

Sodium gets converted to Na^+ much more easily than copper to Cu^{2+} , Zn becomes Zn^{2+} more easily than Ag to Ag^+ .

Based on the ease with which atoms of metals lose electrons to form positively charged ions, the metals are arranged in a series known as the electrochemical series.

Table 6.5 : Electrochemical Series of Metals

Metals		Cations	
K		K^+	
Ca		Ca^{2+}	
Na		Na^+	
Mg		Mg^{2+}	
Al		Al^{3+}	
Zn		Zn^{2+}	
Fe	Cations are discharged at cathode by gain of electron(s)	Fe^{3+}	
Ni		Ni^{2+}	
Sn		Sn^{4+}	
Pb		Pb^{2+}	
H		H^+	
Cu		Cu^{2+}	
Hg		Hg^{2+}	
Ag		Ag^+	
Au		Au^{3+}	
Pt		Pt^{4+}	

↔

Increasing ease of discharge at cathode

About Electrochemical Series of Metals

1. A metal with a higher position in the series displaces the one with a lower position.
2. Metals below hydrogen cannot displace hydrogen from acids while those above it can.
3. Elements lower in the series get discharged more easily at the cathode during electrolysis because their cations can easily gain electrons.
4. Metal atoms which form their ions most easily, will accept the electrons back to form the atoms with greatest difficulty.
5. Hydrogen has some properties of a metal, e.g. formation of a positive ion. Thus, its position amongst metals confirms its identity with metals. Therefore, it has been placed along with metals in the series.

Electrochemical series of the anions

Anions are negatively charged ions. On electrolysis, they move towards the anode. They lose their extra electrons or the negative charge at the anode and are discharged there. But all anions do not have identical tendency to lose electrons.

Based on their tendency to lose electrons and get discharged at the anode, the anions have been arranged in the increasing order.

ELECTROCHEMICAL SERIES OF ANIONS

SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Br ⁻	I ⁻	OH ⁻
Increasing ease of discharge					

ABOUT ELECTROCHEMICAL SERIES OF ANIONS

1. Lower the position of an anion in the series, more easily it gets discharged at anode.
2. Higher the position of an anion in the series, more difficult for it to lose electrons or get oxidised.

SOME SOLVED PROBLEMS

1. Can we store CuSO₄ solution in an iron vessel?

Ans. Iron is above copper in the electrochemical series and is thus more electropositive than copper. So, iron displaces copper from copper sulphate solution. This liberated copper appears in the form of a red precipitate. Hence CuSO₄ solution cannot be stored in an iron vessel.



2. On electrolysis of dilute copper (II) sulphate solution, copper is deposited at the cathode but no hydrogen gas evolves there. Explain why ?

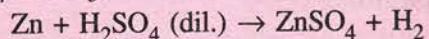
Ans. Copper is below hydrogen in the electrochemical series. So, Cu²⁺ gets easily reduced to metallic copper than does H⁺ to hydrogen gas.

3. When a dilute aqueous solution of sodium chloride is electrolysed between platinum electrodes, hydrogen gas is evolved at the cathode but metallic sodium is not deposited. Why ?

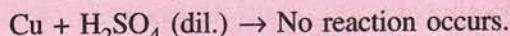
Ans. Position of hydrogen is much below that of sodium in the electrochemical series. So, hydrogen is preferentially discharged at the cathode.

4. Zinc can produce hydrogen on reacting with acids but copper cannot. Explain.

Ans. Since zinc is above hydrogen in the electrochemical series, it is more electropositive and can displace hydrogen from acids like HCl, H₂SO₄, HNO₃.



Whereas Cu is below hydrogen and is less electropositive than hydrogen. Therefore, it cannot displace hydrogen from acids.

**6.7 PREFERENTIAL OR SELECTIVE DISCHARGE OF IONS AT ELECTRODES**

When two or more ions of the same charge are present in a solution of an electrolyte, under identical conditions, and are competing for discharge at the same electrode, one of them gets preferentially discharged. This is known as *selective discharge* of ions.

Selective discharge of ions depends on three factors :

- (a) *The relative position of ions in the electrochemical (activity) series.*
- (b) *The relative concentration of ions.*
- (c) *The nature of the electrodes.*

- (a) **The relative position of ions in the electrochemical series**

If all other factors are constant, any ion lower in the electrochemical series gets discharged at the relevant electrode in preference to those above it (Refer Table 6.5). The table given ahead makes the point clear.

Electrolyte	Dissociation of electrolytes	Ions migrating to cathode	Ion discharged at cathode	Ions migrating to anode	Ion discharged at anode
1. Dilute CuSO ₄ solution	CuSO ₄ → Cu ²⁺ + SO ₄ ²⁻ H ₂ O ⇌ H ⁺ + OH ⁻	Cu ²⁺ , H ⁺	Cu ²⁺	SO ₄ ²⁻ , OH ⁻	OH ⁻
2. Dilute H ₂ SO ₄ solution	H ₂ SO ₄ ⇌ 2H ⁺ + SO ₄ ²⁻ H ₂ O ⇌ H ⁺ + OH ⁻	Only H ⁺	H ⁺	SO ₄ ²⁻ , OH ⁻	OH ⁻
3. Dilute NaCl solution	NaCl → Na ⁺ + Cl ⁻ H ₂ O ⇌ H ⁺ + OH ⁻	Na ⁺ , H ⁺	H ⁺	Cl ⁻ , OH ⁻	OH ⁻

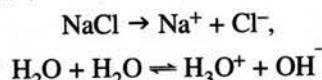
(b) Concentration of ions in the electrolyte

If an electrolyte has a much higher concentration of a particular ion, then that ion will be discharged at the relevant electrode in preference to those ions which are lower in the electrochemical series but are present alongwith.

Examples :

Electrolysis of concentrated NaCl solution.

Ionic equation :



At cathode :

Both Na⁺ and H₃O⁺ migrate to cathode. But concentration of Na⁺ in this case is much higher than that of H₃O⁺ in a highly concentrated solution of NaCl.

So, Na⁺ ions discharge in preference to H₃O⁺ irrespective of its higher position than H₃O⁺ in electrochemical series.

At anode :

Both Cl⁻ and OH⁻ migrate to the anode. But the concentration of Cl⁻ is much higher than that of OH⁻, hence Cl⁻ is discharged, although OH⁻ has lower position in the electrochemical series.

(c) Nature of the electrodes used

Electrodes used in the process of electrolysis are either inert or active.

The electrodes used determine the ion preferred for discharge. If **inert electrodes** like graphite and platinum are used, they will not take part in the electrolytic reaction. The electrolysis will thus depend only on the above two factors i.e. position in the electrochemical series and the concentration of ions.

The **active electrodes** like Cu, Ni, Ag, if used

take part in the electrolytic reaction and the product formed is different.

Example :

In the electrolysis of copper (II) sulphate solution, copper atom is deposited at the cathode and copper ions are formed at the anode if copper cathode and copper anode are used. Oxygen is formed at the anode if the platinum anode is used. (Section 6.8 III and IV).

6.8 EXAMPLES OF ELECTROLYSIS

I. Electrolysis of molten lead bromide

- (i) **Electrolyte :** Molten lead bromide (PbBr₂).
- (ii) **Temperature :** Above 380°C, the melting point of PbBr₂ is maintained by continuous heating by a burner.

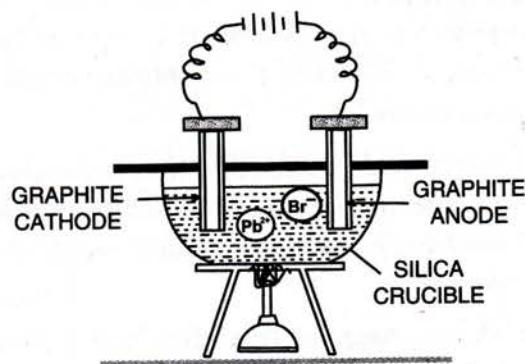


Fig. 6.4 Electrolysis of molten lead bromide.

- (iii) **Electrolytic cell :** Crucible is made of **silica** because silica is non-reactive, withstands high temperature and is almost a non-conductor of electricity.
- (iv) **Electrodes :** The cathode and anode are both made of graphite plates which are inert. They are connected by copper wires to the two ends of a battery.

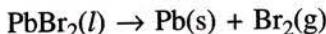
(v) **Current :** 3 amperes.

(vi) **Ions present :** Pb^{2+} and Br^- , i.e., lead ions and bromide ions.

(vii) Electrode reactions :



The overall reaction is :



The process is shown in Fig. 6.4.

(viii) Observations :

- (a) Dark reddish brown fumes of **bromine** evolve at the **anode**.
- (b) *Greyish* white metal lead is formed on the **cathode**.

Explanation : When the current is turned on, the positive lead ions (Pb^{2+}) migrate towards the cathode. They take 2 electrons each and become neutral lead atoms. The negative bromide ions (Br^-) come in contact with the anode, give an electron each and become bromine atoms. These two atoms combine to form bromine molecule (Br_2).

Note :

1. Since silica is non-reactive, hence an electrolytic cell is made of silica. *It can withstand high temperature and is almost a non-conductor of electricity. The silica crucible is heated slowly from outside.*

(a) 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.*

(b) The ions become free when lead bromide is in the fused or molten state. *Hence the crucible is heated from outside to keep lead bromide in the molten state.*

2. Graphite anode is preferred to other inert electrodes such as platinum since *graphite is unaffected by the reactive bromine vapours.*

II. Electrolysis of acidified water using platinum electrodes (Fig. 6.5) :

Electrolytic Cell : Hoffman's Voltameter

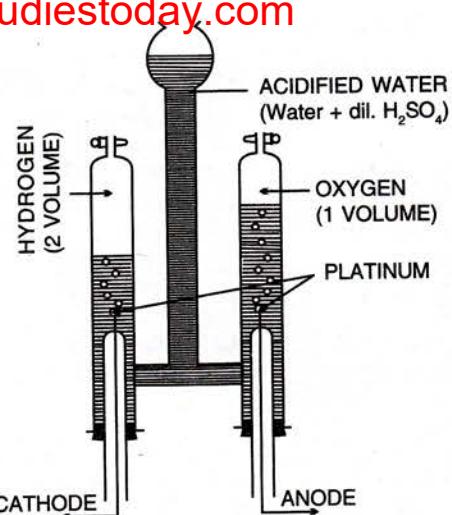


Fig. 6.5 Electrolysis of acidified water using platinum electrodes.

Electrolyte : Acidified water

(Water + dilute H_2SO_4)

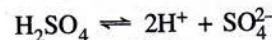
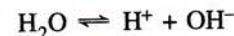
Note : Dilute sulphuric acid is preferred because it is non-volatile while dilute nitric acid or hydrochloric acid are volatile acids.

Electrodes : Platinum foils, which are inert, connected by copper wires to the two terminals of a battery.

Current : 3 amperes.

Dissociation of water : Water is a non-conductor of electricity. It consists almost entirely of molecules. It is a polar covalent compound and can form ions, when traces of dilute Sulphuric acid is added. *As dilute sulphuric acid catalyse this dissociation, hence electrolysis of acidified water is considered as an example of catalysis.*

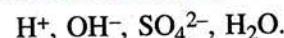
Ionisation of acidified water :



Ions present solution :



Particles present in solution :

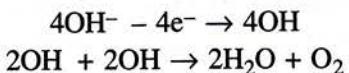


Reaction at Cathode :

Hydrogen ions, H^+ , being the only positively charged ions, migrate to the cathode. Since the cathode is a reservoir of electrons, H^+ gains an electron and becomes a neutral hydrogen atom.



Reaction at anode : The SO_4^{2-} and OH^- ions both migrate to the anode. The OH^- ions, being lower in electrochemical series as compared to SO_4^{2-} ions, discharge to form neutral (OH) radical. The neutral (OH) radicals reunite to form water and oxygen.



Product at anode : Oxygen.

Product at cathode : Reddish brown copper is deposited.

When the deposition of Cu ions is completed, then electrolysis of water takes place. Hydrogen gas is liberated at the cathode and oxygen gas is liberated at the anode.

Note : The blue colour of Cu^{2+} ions in the electrolyte solution fades due to decrease in Cu^{2+} ions and finally the solution becomes colourless as soon as Cu^{2+} ions are finished.

IV. Electrolysis of aqueous copper sulphate — using copper electrodes

- | | | |
|-----------------------------|---|------------------------------------|
| 1. Electrolytic cell | : | Iron crucible or glass voltameter |
| 2. Electrolyte | : | Aqueous copper sulphate |
| 3. Electrode | : | Cathode : Copper
Anode : Copper |
| 4. Temperature | : | Ordinary temperature |
| 5. Current | : | Current : 3 ampere |

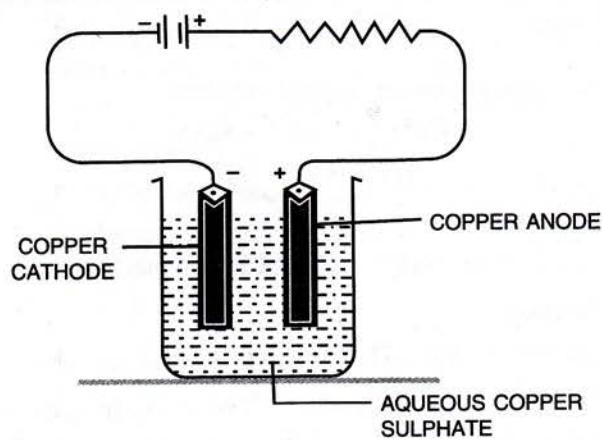


Fig. 6.7 Electrolysis of aqueous copper sulphate

- | | | |
|---|---|--|
| 6. Dissociation of Copper sulphate (aq.) | : | $\text{CuSO}_4 \rightleftharpoons \text{Cu}^{2+} + \text{SO}_4^{2-}$ |
| <i>Ions present</i> | : | $\text{Cu}^{2+}, \text{H}^+, \text{SO}_4^{2-}, \text{OH}^-$ [copper ions, hydrogen ions, sulphate ions, hydroxyl ions] |
| Reaction at cathode | : | $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$ |

cathode, Cu^{2+} ions discharged as neutral copper atoms, by accepting electrons (as it is lower in the series).

Reaction at anode

- | | | |
|---------------------------|---|---|
| Product at anode | : | $\text{Cu} - 2e^- \rightarrow \text{Cu}^{2+}$
SO_4^{2-} and OH^- ions migrate to anode but neither of them are discharged due to the nature of the anode, (copper loses electrons more easily than SO_4^{2-} and OH^-) because copper anode itself ionises to give Cu^{2+} ions. |
| Product at cathode | : | Nil because copper anode keep dissolving during the reaction, as Cu^{2+} ions are formed. |
| Note : | : | Reddish brown Cu is deposited. |

Note :

1. The electrolyte aqueous copper [II] sulphate may be acidified with traces of dilute sulphuric acid. This enhances the conductivity of the electrolyte and may prevent its hydrolysis.
2. **The blue colour of aq. copper [II] sulphate solution remains unchanged during its electrolysis due to the copper electrodes.**

Reason : For every copper ion $[\text{Cu}^{2+}]$ discharged at the cathode as neutral copper atom, a copper ion $[\text{Cu}^{2+}]$ is released or added to the solution by the anode and hence total number of Cu^{2+} ions remains the same. *Therefore, the blue colour does not fade.*

H^+ ions, SO_4^{2-} ions and OH^- ions do not take part in the electrolytic reaction and are known as spectator ions.

Intext Questions

1. Name two substances in each case :
 - (a) Contain only molecules,
 - (b) Contain only ions,
 - (c) Contain ions as well as molecules.
2. Explain the following :
 - (a) A solution of cane sugar does not conduct electricity, but a solution of sodium chloride is a good conductor,
 - (b) Hydrochloric acid is a good conductor of electricity,
 - (c) During the electrolysis of an aqueous solution of NaCl, hydrogen ion is reduced at the cathode and not the sodium ion though both Na^+ and H^+ ions are present in the solution.
3. (a) Among Zn and Cu, which would occur more readily in nature as metal and which as ion?
 (b) Why cannot we store AgNO_3 solution in copper vessel ?
 (c) Out of Cu and Ag, which is more active ?

6.9.1 Electroplating

4. (a) How would you change a metal like Cu into its ions?
(b) How would you change Cu^{2+} ion to Cu?
5. A solution of caustic soda (NaOH) in water or when fused, conducts an electric current. What is the similarity in these two cases?
6. During electrolysis of an aqueous solution of sulphuric acid between platinum electrodes, two types of anions migrate towards the anode but only one of them is discharged:
(a) Name the two anions,
(b) Name the main product of the discharge of anion at the anode and write the anode reaction,
(c) Name the product at the cathode and write the reaction.
(d) Do you notice any change in colour. State why?
(e) Why this electrolysis, is considered as an example of catalysis?
7. An electrolytic cell is set up using two platinum electrodes and an aqueous solution of copper (II) sulphate,
(a) Draw a labelled diagram of the electrolytic cell,
(b) Name the ions present in the cell,
(c) Name the ions migrating towards the anode,
(d) Name the ions migrating towards the cathode,
(e) Name the ions which will not be discharged at electrodes during electrolysis,
(f) Write the reaction at the cathode,
(g) Write the reaction at the anode,
(h) Name the spectator ion in the solution.
8. State the electrode reaction at the anode during electrolysis of:
(a) Very dilute sulphuric acid,
(b) Aqueous copper sulphate solution,
(c) Sodium chloride solution,
(d) Fused lead bromide,
(e) Magnesium chloride (molten).
9. Choosing only words from the following list, write down the appropriate words to fill in the blanks (a) to (e) below: anions, anode, cathode, cations, electrode, electrolyte, nickel, voltameter.

The electroplating of an article with nickel requires an
(a) _____ which must be a solution containing
(b) _____ ions. The article to be plated is placed as the (c) _____ of the cell in which the plating is carried out. The (d) _____ of the cell is made from pure nickel. The ions that are attracted to the negative electrode and discharged are called (e) _____

6.9 APPLICATIONS OF ELECTROLYSIS

Electrolysis has several technical and commercial applications. These are as follows :

1. Electroplating with metals,
2. Electrorefining of metals,
3. Extraction of metals (Electrometallurgy).

Electroplating is a process in which a thin film of a metal like gold, silver, nickel, chromium, etc. gets deposited on another metallic article with the help of electricity.

Reasons for electroplating :

- (i) *Decoration purposes* : For example, brass objects are frequently plated with silver to give them the shining appearance and beauty of a silver article.
- (ii) *To protect from rusting and corrosion* : Iron tools and instruments are often electroplated with nickel or chromium or zinc to protect against rusting.

Conditions for electroplating

Condition	Reason
1. The article to be electroplated is always placed at the cathode.	During electrolytic reaction, the metal is always deposited at the cathode by gain of electrons.
2. The metal to be plated on the article is always made the <i>anode</i> and has to be periodically replaced.	The metal anode continuously dissolves as ions in solution and is replaced periodically.
3. The electrolyte must contain ions of the metal which is to be plated on the article [i.e. be a suitable salt of the plating metal].	The electrolyte dissociates into ions of the metal which migrate towards the cathode and are deposited as neutral metallic atoms on the cathode.
4. A low current for a longer time should be used.	Higher current causes uneven deposition of the metal. Longer time and low current initiates a thicker uniform deposition.
5. A direct current 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.

I. Electroplating an article with silver

In order to get a perfect deposit of silver on an article, say brass spoon. The spoon is first cleaned and then it is washed in a hot solution of caustic soda followed by dilute hydrochloric acid and water. It is now thoroughly washed with detergent and several times with distilled water.

The spoon is then dried and made the cathode.

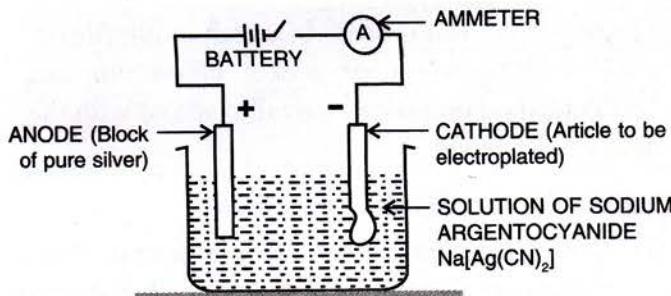
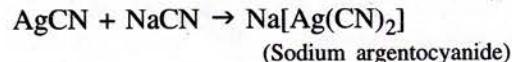
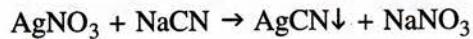


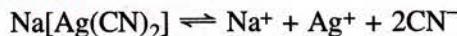
Fig. 6.8 Electroplating of a brass spoon with silver

Electrolyte : Sodium argentocyanide $\text{Na}[\text{Ag}(\text{CN})_2]$ or Potassium argentocyanide $\text{K}[\text{Ag}(\text{CN})_2]$.

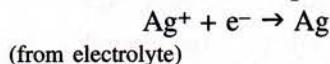
Sodium silver cyanide is prepared by adding sodium cyanide to a solution of silver nitrate until the precipitate formed just dissolves.



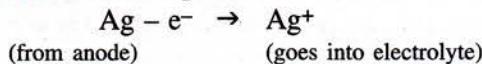
Dissociation :



Cathode : Article to be electroplated is duly cleaned.



Anode : Plate of pure clean silver.



The negative ions (anions) CN^- and OH^- ions migrate to the anode but none of them are discharged. Instead, the atoms of anode (silver) lose electrons and pass into solution as silver ions (Ag^+) due to the nature of the anode. Silver ions are attracted to the brass spoon (cathode). Here, they gain electrons and become atoms of silver which deposit on the spoon as a firm coating.

The thickness of the coating will depend on the duration of the current passed.

The spoon is taken out of the bath repeatedly, washed several times with water, dried and polished.

Note : If silver nitrate solution is used directly instead of double cyanide of sodium and silver, the deposition of silver will be very fast and hence not very smooth and uniform.

II. Electroplating with nickel :

Iron gets easily rusted when exposed to air. If iron articles are coated with a metal like nickel, tin or zinc, rusting can be prevented.

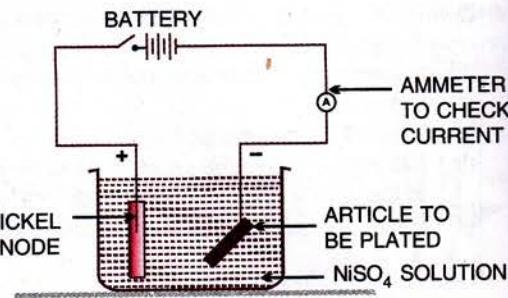
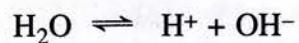
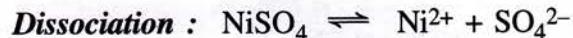


Fig. 6.9. Electroplating of an article with nickel

If nickel plating is to be done, the iron article to be coated is made the cathode, nickel plate is made the anode, and a solution of nickel sulphate containing a small amount of dilute sulphuric acid is used as an electrolyte.

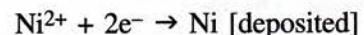
Electrolyte : Aqueous solution of nickel sulphate $[\text{NiSO}_4]$.



Cathode : Article to be electroplated is duly cleaned.

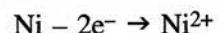
Anode : Block of pure nickel metal.

Reaction at cathode :



Nickel ions are discharged at the cathode as neutral nickel atoms by gain of electrons [in preference to H^+ ions].

Reaction at anode :



SO_4^{2-} and OH^- ions both migrate to the anode but neither are discharged due to the nature of electrode. Instead, the nickel anode loses electrons to give Ni^{2+} ions in solution.

Note : Article to be plated is always kept at the cathode.

6.9.2 Electrolytic refining of metals

Electrolytic refining is a process by which metals containing impurities are purified electrolytically to give a pure metal.

Refining of Copper :

The most important use of copper is in the form of wire for electric transmission. For this, *copper must be absolutely pure because very small amounts of impurities reduce its conductivity to a great extent.*

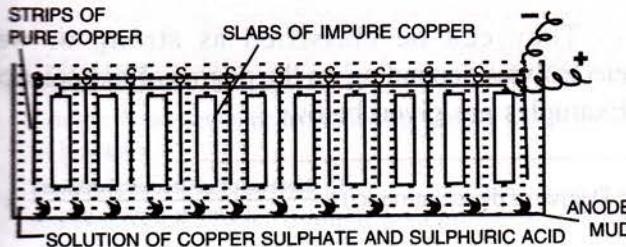


Fig. 6.10 Refining of copper

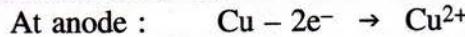
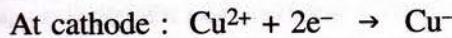
Electrolyte : A solution of copper sulphate and dilute sulphuric acid. (Fig. 6.10).

Cathode : Thin strip of pure copper.

Anode : Impure copper.

When the current is passed through the electrolyte, the copper ions of the copper sulphate solution are attracted to the cathode where they gain electrons and get deposited on the pure copper strips. The impure copper loses electrons and passes into solution as soluble copper ions.

Reaction :



These copper ions migrate to the cathode in the form of a procession and after gaining electrons from it, get deposited on the cathode. *The net result is that, gradually the impure slabs of copper get finished and thin strips of pure copper become thicker and thicker.* The copper deposited on the cathode is 99.9% pure. After the electrolysis is over, these strips are melted and transformed into the desired shapes.

Some impurities get dissolved in the acid while others, namely silver and gold which are insoluble get collected near the anode (*anode mud*) and are recovered.

Metals like zinc, lead, mercury, silver and copper are refined (purified) by electrolysis.

Metals which are higher in the activity series are generally extracted by electrolysis.

Activity series

K

Na

Ca

Mg

Al

Zn

Fe

Pb

[H]

Cu

Hg

Ag

Pt

Au

They are extracted by electrolysis of their fused salts.

These metals have strong affinity for oxygen.

They are generally extracted by reducing agents like carbon, carbon monoxide and hydrogen as their oxides are less stable.

Metals extracted by thermal decomposition.

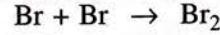
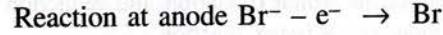
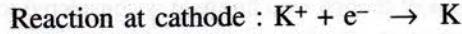
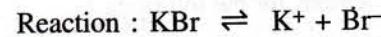
Reactive metals are extracted from their halides (chlorides, bromides, etc.) by electrolysis using inert electrodes. Cathode is usually made of iron and anode of graphite.

Reactive metals : They are not extracted from their aqueous salt solutions by electrolysis as they can react with water.

For example :

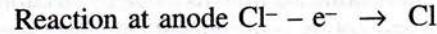
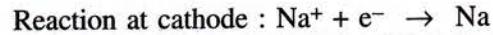
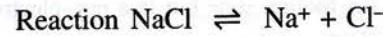
Potassium

Electrolyte : Fused potassium bromide



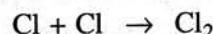
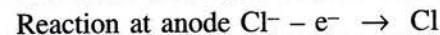
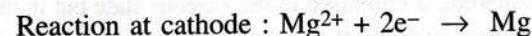
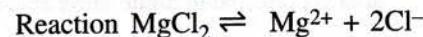
Sodium

Electrolyte : Fused Sodium chloride



Magnesium

Electrolyte : Fused Magnesium chloride

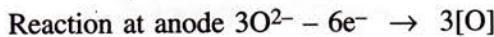
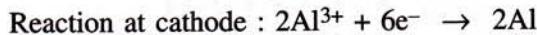
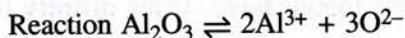


6.9.3 Electrometallurgy

Electrometallurgy is the process of extraction of metals by electrolysis.

Aluminium* is obtained by electrolysis of its oxide, i.e., Alumina (Al_2O_3), where **gas carbon lining of electrolytic cell act as cathode, and graphite rod act as anode.**

Electrolyte : Pure Alumina (Al_2O_3), cryolite (Na_3AlF_6) and Fluorspar (CaF_2).



* Refer 7.12

6.10 ACIDS, BASES AND SALTS AS ELECTROLYTES

Acids and alkalis ionise when dissolved in water, whereas bases and salts dissociate in fused (molten) state or in their aqueous solutions into free mobile ions.

They can be classified as strong or weak electrolytes depending on the degree of dissociation#. Examples are given below.

$$\# \text{Degree of dissociation } (\alpha) = \frac{\text{Number of molecules dissociated}}{\text{Total number of molecules}} \times 100$$

Examples of ionisation or electrolytic dissociation of acids, bases and salts.

ACIDS	BASES	SALTS
(A) STRONG ELECTROLYTES Hydrochloric acid $\text{HCl} \rightleftharpoons \text{H}^+ + \text{Cl}^-$ [aq] Nitric acid $\text{HNO}_3 \rightleftharpoons \text{H}^+ + \text{NO}_3^-$ [aq] Sulphuric acid $\text{H}_2\text{SO}_4 \rightleftharpoons 2\text{H}^+ + \text{SO}_4^{2-}$	STRONG ELECTROLYTES Potassium hydroxide $\text{KOH} \rightleftharpoons \text{K}^+ + \text{OH}^-$ [aq] Sodium hydroxide $\text{NaOH} \rightleftharpoons \text{Na}^+ + \text{OH}^-$ [aq] Lithium hydroxide $\text{LiOH} \rightleftharpoons \text{Li}^+ + \text{OH}^-$	STRONG ELECTROLYTES Lead bromide $\text{PbBr}_2 \rightleftharpoons \text{Pb}^{2+} + 2\text{Br}^-$ [molten] Copper chloride $\text{CuCl}_2 \rightleftharpoons \text{Cu}^+ + 2\text{Cl}^-$ [aq] Silver nitrate $\text{AgNO}_3 \rightleftharpoons \text{Ag}^+ + \text{NO}_3^-$
(B) WEAK ELECTROLYTES Acetic acid $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$ [aq] Formic acid $\text{HCOOH} \rightleftharpoons \text{HCQO}^- + \text{H}^+$ [aq] Carbonic acid $\text{H}_2\text{CO}_3 \rightleftharpoons 2\text{H}^+ + \text{CO}_3^{2-}$ [aq]	WEAK ELECTROLYTES Calcium hydroxide $\text{Ca}(\text{OH})_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{OH}^-$ [aq] Magnesium hydroxide $\text{Mg}(\text{OH})_2 \rightleftharpoons \text{Mg}^{2+} + 2\text{OH}^-$ [aq] Ammonium hydroxide $\text{NH}_4\text{OH} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$ [aq]	WEAK ELECTROLYTES Sodium carbonate $\text{Na}_2\text{CO}_3 \rightleftharpoons 2\text{Na}^+ + \text{CO}_3^{2-}$ [aq] Potassium bicarbonate $\text{KHCO}_3 \rightleftharpoons \text{K}^+ + \text{HCO}_3^-$ [aq] Lead acetate $(\text{CH}_3\text{COO})_2\text{Pb} \rightleftharpoons 2\text{CH}_3\text{COO}^- + \text{Pb}^{2+}$ [aq]

EXERCISE

- Give reasons for the following :
 - Electrolysis of molten lead bromide is considered to be a reaction in which oxidation and reduction go side by side, i.e., a redox reaction.
 - The blue colour of aqueous copper sulphate fades when it is electrolysed using platinum electrodes.
 - Lead bromide undergoes electrolytic dissociation in the molten state but is a non-electrolyte in the solid state.
 - Aluminium is extracted from its oxide by electrolytic reduction and not by conventional reducing agents.
 - The ratio of hydrogen and oxygen formed at the cathode and anode is 2 : 1 by volume.
 - In the electrolysis of acidified water, dilute sulphuric acid is preferred to dilute nitric acid for acidification.
 - Ammonia is unionised in the gaseous state but in the aqueous solution, it is a weak electrolyte.
 - A graphite anode is preferred to other inert electrodes during electrolysis of fused lead bromide.
- For electroplating with silver, silver nitrate is not used as electrolyte.
- Carbon tetrachloride is a liquid but does not conduct electricity.
- Classify the following substances under three headings :
(a) strong electrolytes (b) weak electrolytes (c) non-electrolytes.
Acetic acid, ammonium chloride, ammonium hydroxide, carbon tetrachloride, dilute hydrochloric acid, sodium acetate, dilute sulphuric acid.
- Write down the words or phrases from the brackets that will correctly fill in the blanks in the following sentences:
(a) Pure water consists entirely of _____ (ions/molecules).
(b) We can expect that pure water _____ (will/will not) normally conduct electricity.
- To carry out the so-called “electrolysis of water”, sulphuric acid is added to water.
How does the addition of sulphuric acid produce a conducting solution ?

5. Copy and complete the following table which refers to two practical applications of electrolysis

	Anode	Electrolyte	Cathode
Silver plating of a spoon		Solution of potassium argentocyanide	
Purification of copper			

6. Complete the sentence by choosing correct words given in brackets.

Electrolysis is the passage of _____ (electricity/electrons) through a liquid or a solution accompanied by a ___ (physical/chemical) change.

004

1. Element X is a metal with a valency 2. Element Y is a non-metal with a valency 3.

- (a) Write equations to show how X and Y form ions ?
- (b) If Y is a diatomic gas, write the equation for the direct combination of X and Y to form a compound,
- (c) Write two applications of electrolysis in which the anode diminishes in mass,
- (d) If the compound formed between X and Y is melted and an electric current passed through the molten compound, the element X will be obtained at the and Y at the of the electrolytic cell. (Provide the missing words)

2. (a) What kind of particles will be found in a liquid compound which is a non-electrolyte?

- (b) If HX is a weak acid, what particles will be present in its dilute solution apart from those of water ?

- (c) Cations are formed by (loss/gain) of electrons and anions are formed by (loss/gain) of electrons. (Choose the correct word to fill in the blanks).

- (d) What ions must be present in a solution used for electroplating a particular metal ?

- (e) Explain how electrolysis is an example of *redox reaction*.

005

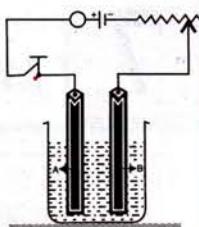
1. Explain why :

- (a) Cu, though a good conductor of electricity is a non electrolyte,
- (b) Solid sodium chloride does not allow electricity to pass through ?

2. Name the gas released at cathode when acidulated water is electrolysed.

1. Copper sulphate solution is electrolysed using a platinum anode.

- (a) Study the diagram given alongside and answer the following questions :
- (i) Give the names of the electrodes A and B.



- (ii) Which electrode is the oxidizing electrode ?
- (b) A strip of copper is placed in four different colourless salt solutions. They are KNO_3 , AgNO_3 , $\text{Zn}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_2$. Which one of the solutions will finally turn blue ?

2007

1. Choose A, B, C or D to match the descriptions (i) to (v) below. Some alphabets may be repeated.

- | | |
|---------------------|-----------------------|
| A. non-electrolyte | B. strong electrolyte |
| C. weak electrolyte | D. metallic conductor |

- (i) Molten ionic compound,

- (ii) Carbon tetrachloride,

- (iii) An aluminium wire,

- (iv) A solution containing solvent molecules, solute molecules and ions formed by the dissociation of solute molecules.

- (v) A sugar solution with sugar molecules and water molecules.

2008

1. (a) Here is an electrode reaction :



At which electrode (anode or cathode) would such a reaction take place? Is this an example of oxidation or reduction ?

- (b) A solution contains magnesium ions (Mg^{2+}), iron (II) ions (Fe^{2+}) and copper ions (Cu^{2+}). On passing an electric current through this solution, which ions will be the first to be discharged at the cathode? Write the equation for the cathode reaction.

- (c) Why is carbon tetrachloride, which is a liquid, a non-electrolyte ?

2. During the electrolysis of molten lead bromide, which of the following takes place?

- A. Bromine is released at the cathode,
- B. Lead is deposited at the anode,
- C. Bromine ions gain electrons,
- D. Lead is deposited at the cathode.