ELECTROCHEMISTRY

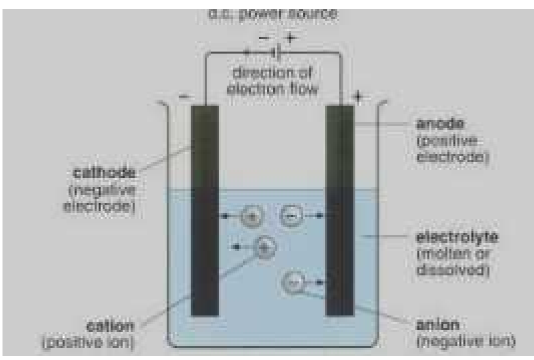
This is a branch of chemistry which deals with changes in electrical energy caused by chemical reactions. It is subdivided into three sections, electrolysis, applications of electrolysis and electrochemical cells.

ELECTROLYSIS

Definition:

This is the decomposition of a substance when in solution or molten state by passing an electric current through it.

Terms used in electrolysis



1. **Electrolyte**

This is an ionic compound which when in solution or molten state allows a current to go through it and becomes decomposed.

Types of electrolytes

a. **Strong electrolytes**

   These are electrolytes which completely dissociate or ionize in dilute solutions examples include

   i) All strong mineral acids when dilute e.g. dilute sulphuric acid, dilute nitric acid and dilute hydrochloric acid.

   ii) All aqueous solutions of soluble salts e.g. NaCl, $CuSO_4$, $Al_2(SO_4)_3$ etc

   iii) All strong alkalis while in solution i.e. NaOH and KOH

b. Weak electrolytes

These are electrolytes which partially ionize in aqueous solution producing few free mobile ions. These allow small current to pass through them.

i) All weak acids e.g. carbonic acid, organic acids like ethanoic acid

ii) All weak alkalis i.e. aqueous ammonia

2. Non electrolytes

This is a substance which when in solution or molten state does not allow current to pass through it and no decomposition occurs. e.g. covalent compounds like sugar, organic solvents e.g. benzene and alcohol.

NB: electrolytes conduct electricity because of presence of mobile ions which they produce while in solution or in molten state.

3. Conductor

This is a solid substance which allows an electric current to go through it e.g. all metals and graphite. These conduct electricity because they have delocalized electrons which transmit the electric current.

4. Non conductor

This is a solid substance which does not allow electric current to pass through it e.g. rubber and other non metals like sulphur. These do not conduct electricity because they have localized electron which are not free to move and thus cannot transmit an electric current. They are used as insulators.

Differences between a conductor and an electrolyte

Electrolyte	Conductor
Conducts electricity while in molten or in solution state	Conduct electricity while in solid state
Conduct electricity because of presence of mobile ions	Conduct electricity because of delocalized electrons
Gets decomposed when an electric current passes through it	Does not get decomposed when an electric current goes through it

5. Electrodes

These are terminals through current enters or leaves the electrolyte or terminals of conductors through which electrons enter or leave the electrolyte.

Types of electrodes

Cathode

This is the negative terminal through which current leaves the electrolyte or the negative terminal through which electrons enter the electrolyte. It is connected to the negative terminal of the battery. Positively charged ions are attracted to this electrode.

Anode

This is the positive terminal through which current enters the electrolyte or the positive terminal through which electrons leave the electrolyte. It is connected to the positive terminal of the battery. Negatively charged ions are attracted to this terminal.

6. **Ion**

This is a charged atom which has either gained or lost an electron i.e.

$Na \longrightarrow Na^+ + e$

$Cl + e \longrightarrow Cl^-$

An ion can either be negatively charged e.g. OH^-, O^{2-} and Cl^- etc or positively charged e.g.Mg^{2+}, Na^+ and Al^{3+} etc.

Types of ions

Cations

These are positively charged ions which migrate to the cathode e.g. Mg^{2+}, Na^+ and Al^{3+} etc.

Anions

These are negatively charged ions which migrate to the anode e.g. $SO4^{2-}$, Br^- and OH^- etc.

7. **Discharge**

This is the process of ions losing their charges and turn into free atoms by either losing or gaining electrons.

Cations are discharged at the cathode by gaining electrons and are deposited there e.g.

$Cu^{2+}(aq) + 2e \longrightarrow Cu(s)$

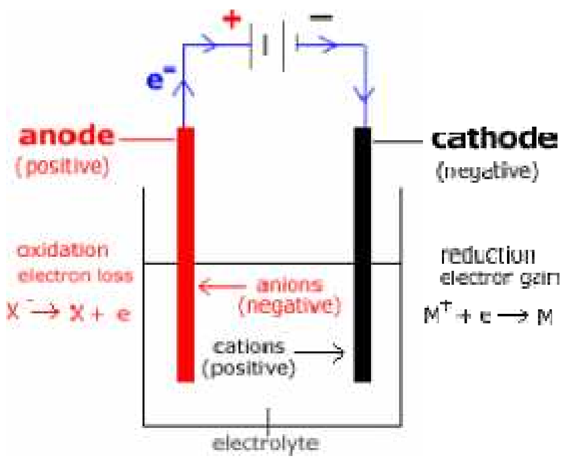
$Na^+(aq) + e \longrightarrow Na(s)$

Anions are discharged at the anode by losing electrons and are liberated there e.g.

$2\ Cl^-(aq) \longrightarrow Cl_2\ (g)$

Flow of current and electrons during electrolysis

Current flows through the electrolyte from the positive terminal through the electrolyte then to the negative terminal. Electrons flow from the negative terminal through the electrolyte then to the positive terminal. When the circuit is complete the bulb gives light.



Ionic theory

The theory states that electrolytes consist of ions which are positively and negatively charged atoms and radicals. Anions move to the anode while cations migrate to the cathode.

The properties of an ion differ from those of the element or radical. Ions are inert and stable because they have electronic configuration of noble gases.

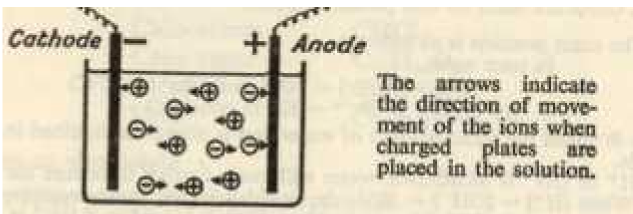
Metals and hydrogen form positive ions and migrate to the cathode, they are electropositive while nonmetals and acid radicals form negative ions and migrate to the anode, and they are electronegative.

The charge of an ion is the same as the valency of its atom or radical. Monovalent elements loose or gain one electron to form ions e.g. Na, OH^-, Cl etc, divalent elements or loose or gain two electrons to form ions e.g. Cu, $SO4^{2-}$, Mg etc.

A solution or molten compound is neutral, and the total charge of the positive ions equals that of negative ions.

Migration of ions during electrolysis

Positively charged ions migrate to the cathode while negatively charged ions migrate to the anode. The anions transfer electrons to the anode. The electrons then move to the cathode through the d.c source to the cathode where they are picked up by the cations.

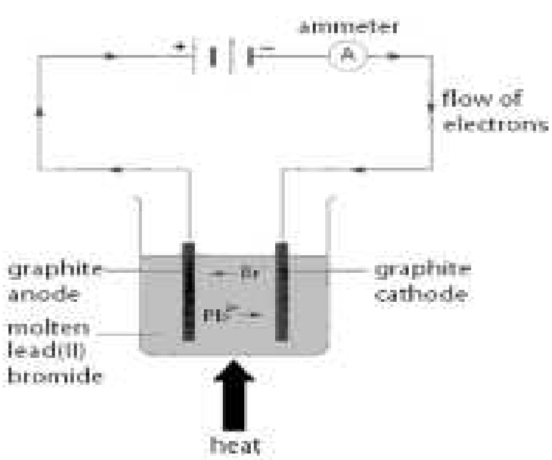


Electrolysis of molten ionic compounds

Solid Ionic compounds do not conduct an electric current in solid state. This is because the ions are held in a fixed position within the crystal lattice by strong electrostatic forces of attraction. When theses ionic solids are headed, they melt to a molten state. Heating breaks down the strong electrostatic forces of attraction making the ions mobile and hence conduct an electric current. When molten binary ionic compounds are electrolysed, metal is deposited at the cathode and the nonmetal formed at the anode.

Example: electrolysis of molten lead ii bromide

Lead ii bromide is heat until it melts and then electrolysed using carbon electrodes.



Ions present

Lead ii bromide dissociates to form lead (ii) ions and bromide ions

$PbBr_2(s) \longrightarrow Pb^{2+}(l) + 2Br^{-}(l)$

At the cathode

Pb^{2+} ions migrate to the cathode where they are discharged by picking up 2 electrons to form lead atoms.

$Pb^{2+}(l) + 2e^{-} \longrightarrow Pb(l)$

Observation

Liquid lead is formed at the cathode which solidifies to form a silver grey solid.

At the anode

Br^{-} ions migrate to the anode where they lose an electron to form bromine atoms. The bromine atoms combine in pairs to form brown bromine fumes.

$Br^{-}(l) \longrightarrow Br(g)$

$Br(g) + Br(g) \longrightarrow Br_2(g)$

Or

$2Br^{-}(l) \longrightarrow Br_2(g)$

Observation

Brown fumes formed at the anode

Overall equation for the electrolytic process

Overall Equation

$$PbBr_2(l) \rightarrow Pb(l) + Br_2(g)$$

Example of other electrolytes that can be electrolysed like molten lead ii bromide include

Molten electrolyte	Cathode product	Anode product
Calcium chloride ($CaCl_2$)	Calcium, Ca	Chlorine, Cl_2
Sodium chloride (NaCl)	Sodium, Na	Chlorine, Cl_2
Aluminium(III) oxide (Al_2O_3)	Aluminium, Al	Oxygen, O_2
Sodium Iodide (NaI)	Sodium, Na	Iodine, I_2

Electrolysis of aqueous solutions

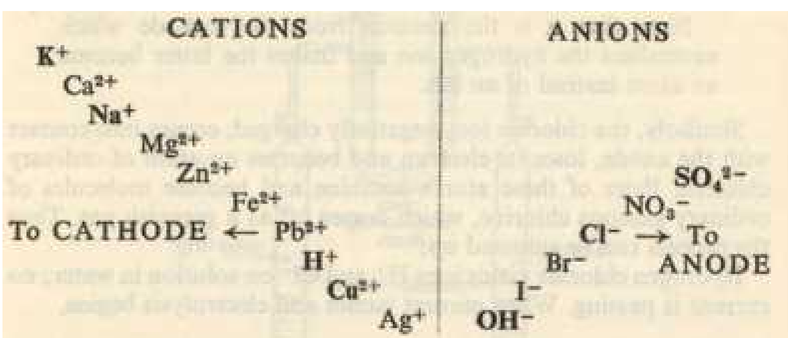
Aqueous solutions of electrolytes contain additional two ions from water i.e. hydrogen ions (H^+) and hydroxyl ions (OH^-) totaling to four ions, two from the electrolytes and the two from water. Electrolysis of aqueous solutions use the theory of selective discharge because more than one ion migrates to each electrode

Selective or preferential discharge of ions at the electrodes

When two or more ions of similar charge are present in solution under similar conditions e.g. OH^- and Cl^- or H^+ and Na^+, one is preferentially selected for discharge depending on the following factors

1. **Position in the electrochemical series**

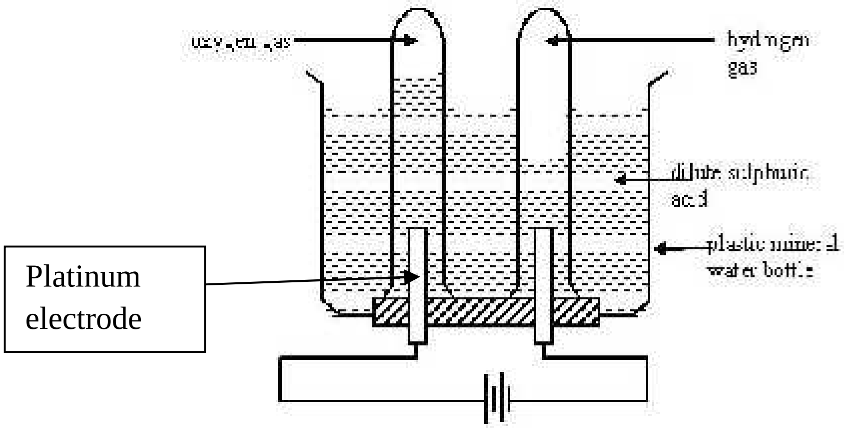
   An electrochemical series is an arrangement of ions in the order of decreasing reactivity.

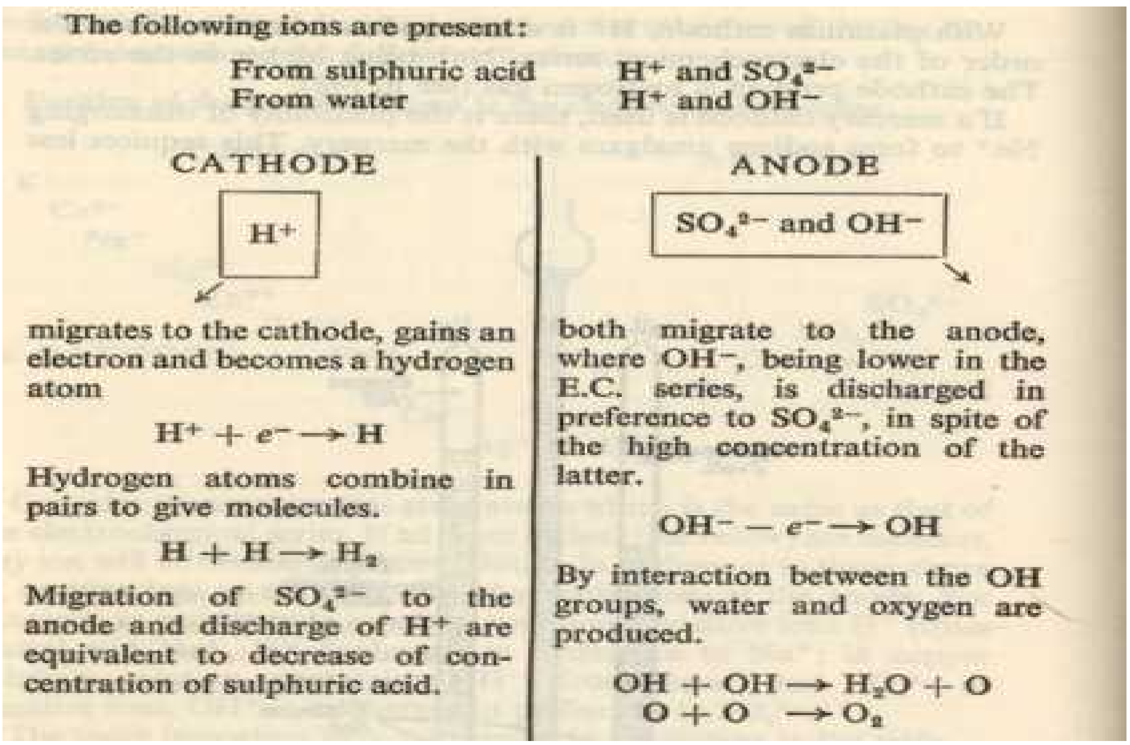


   If all other factors below are constant, any ion will be discharged from the solution in preference to those above it. Lower cations are preferentially selected at the cathode and lower anions are preferentially selected at the anode.

   Examples

Electrolysis of acidified water or dilute sulphuric acid using graphite or platinum electrodes





The following ions are present:

From sulphuric acid	H^+ and SO_4^{2-}
From water	H^+ and OH^-

CATHODE

H^+

migrates to the cathode, gains an electron and becomes a hydrogen atom

$$H^+ + e^- \rightarrow H$$

Hydrogen atoms combine in pairs to give molecules.

$$H + H \rightarrow H_2$$

Migration of SO_4^{2-} to the anode and discharge of H^+ are equivalent to decrease of concentration of sulphuric acid.

ANODE

SO_4^{2-} and OH^-

both migrate to the anode, where OH^-, being lower in the E.C. series, is discharged in preference to SO_4^{2-}, in spite of the high concentration of the latter.

$$OH^- - e^- \rightarrow OH$$

By interaction between the OH groups, water and oxygen are produced.

$$OH + OH \rightarrow H_2O + O$$
$$O + O \rightarrow O_2$$

Overall equations

At the anode

$4OH^-$ (aq) $\longrightarrow$ $2H_2O$ (l) + O_2 (g) + $4e^-$

Observation

Bubbles of a colorless gas that relights a glowing splint

At the cathode

$2H^+ (aq) + 2e^- \longrightarrow H_2 (g)$

Observation

Bubbles of a colorless had that burns with a pop sound

Overall equation for the electrolysis process

$4H^+(aq) + 4OH^+(aq) \rightarrow 2H_2(g) + O_2(g) + 2H_2O(l)$

Note:

- One volume of oxygen is produced at the anode and 2 volumes of hydrogen are produced at the cathode
- The total acidity of the electrolyte remains the same because the products are elements from water.
- The process is referred to as electrolysis of water because the products are in the same ratio as they are in water i.e. H : O is 2 : 1
- To liberate 1 mole of hydrogen gas $2e^-$s are required while for 1 mole of oxygen gas $4e^-$s are required

The same procedure can be followed for the electrolysis of very dilute hydrochloric acid, dilute nitric acid and dilute sodium hydroxide to form similar products i.e.

Electrolyte	Ions present	Cathode	Anode
Dilute HCl	H^+, Cl^- and OH^-	H^+ (aq) migrate here, H_2 (g) liberated	Cl^- and OH^- migrate here and OH^- selected for discharge , O_2 (g) liberated
Dilute Nitric acid	H^+, NO_3^- and OH^-	H^+ (aq) migrate here , H_2 (g) liberated	NO_3^- and OH^- migrate here and OH^- selected for discharge , O_2 (g) liberated

Dilute NaOH	Na^+, H^+ and OH^-	Na^+ and H^+ migrate here were H^+ are selected for discharge, H_2 (g) liberated	OH- migrate here where they are discharged, O_2 (g) liberated

Electrolysis of dilute sodium chloride solution using graphite or platinum electrodes

Ions present Na^+ and Cl^- from NaCl and OH^- and H^+ from H_2O

At the cathode

Both Na^+ and H^+ migrate to this electrode where H+ are selected for discharge because they are lower than Na+ in the electrochemical series.

$$2H^+ (aq) + 2e^- \longrightarrow H_2 (g)$$

Observation

Bubbles of a colorless had that burns with a pop sound

At the anode

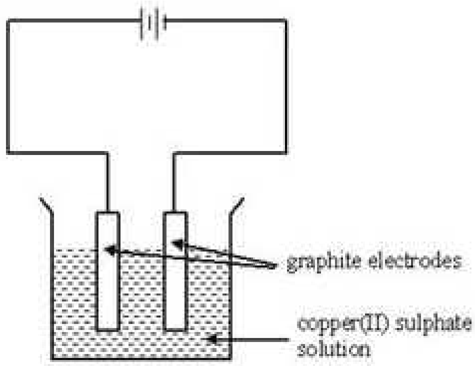
Both OH^- and Cl^- migrate here but OH^- ions are selected for discharge because they are lower in the electrochemical series

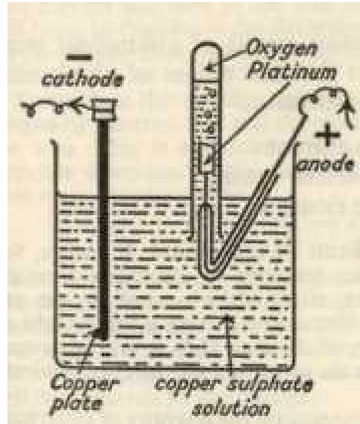
$$4OH^- (aq) \longrightarrow 2H_2O (l) + O_2 (g) + 4e^-$$

Observation

Bubbles of a colorless gas that relights a glowing splint

Electrolysis of copper ii sulphate solution using platinum or graphite electrodes





Ions present: Cu^{2+} and SO_4^{2-} from $CUSO_4$ and H^+ and OH^- from H_2O

At the cathode

Both Cu^{2+} and H^+ migrate to this electrode where Cu^{2+} ions are selected for discharge because they are lower than H^+ in the ECS. The Cu^{2+} picks up 2 electrons to form copper atom

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$

Observation

Brown solid is deposited at the cathode

At the anode

Both SO_4^{2-} and OH^- migrate to this electrode where the OH^- ions are selected for discharge because they are lower in the ECS.

$$4OH^- (aq) \longrightarrow 2H_2O (l) + O_2 (g) + 4e^-$$

Observation

Bubbles of a colorless gas that relights a glowing splint

Note

- The blue color of the solution is due to the Cu^{2+} ions in solution. As the more Cu2+ ions get discharged, the blue color of the solution fades away. If the electrolysis is done for a long time and all the Cu^{2+} ions get discharged, the solution becomes colorless.
- The resultant solution becomes acidic because of the formation of sulphuric acid in solution when the undischarged ions combine.

$$2H^{+}(aq) + SO_4^{2-}(aq) \longrightarrow H_2SO_4(aq)$$

2. Concentration of the ion in solution

Irrespective of the position of the ions in the electrochemical series, there is a tendency to promote the discharge of the most concentrated ion present in solution.

Example

Electrolysis of brine (concentrated sodium chloride solution) using graphite electrodes

Brine is a saturated solution of sodium chloride.

The ions present are:

From sodium chloride Na^{+} Cl^{-}
From water H^{+} OH^{-}

CATHODE

Na^{+}
H^{+}

both migrate to cathode. H^{+}, being lower in the E.C. series, discharges in preference to Na^{+}.

$$H^{+} + e^{-} \rightarrow H$$

Hydrogen molecules are then formed by combination of the atoms in pairs.

$$H + H \rightarrow H_2$$

ANODE

Cl^{-}
OH^{-}

both migrate to the anode. Cl^{-} is discharged because present in much greater concentration than OH^{-} (see p. 144).

$$Cl^{-} - e^{-} \rightarrow Cl$$

The atoms then combine in pairs to give molecules.

$$Cl + Cl \rightarrow Cl_2$$

Overall equations at the electrodes

At the cathode

$$2H^{+}(aq) + 2e^{-} \longrightarrow H_2(g)$$

Observation

Bubbles of a colorless had that burns with a pop sound

At the anode

$$2Cl^{-}(aq) \rightarrow Cl_2(g) + 2e^{-}$$

Observation

Bubbles of a greenish yellow gas evolved

Note

- The cathode may be graphite or platinum but the anode must be graphite to resist attack by chlorine which is very reactive
- The resultant solution is alkaline due to the formation of sodium hydroxide therefore the remaining solution turns red litmus paper blue.

  Na^{+} (aq) + OH^{-} (aq) $\longrightarrow$ NaOH (aq)
- The volume of hydrogen gas liberated is approximately equal to the volume of chlorine gas liberated
- The product of electrolysis of brine are similar to the products of electrolysis of concentrated hydrochloric acid

Electrolysis of concentrated copper ii chloride solution using graphite electrodes

Ions present Cu2+ and Cl- from CuCl2 and H+ and OH- from water

At the cathode

Both Cu^{2+} and H^{+} migrate to this electrode where Cu^{2+} ions are selected for discharge because they are lower than H^{+} in the ECS. The Cu^{2+} picks up 2 electrons to form copper atom

$$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$$

Observation

Brown solid is deposited at the cathode

At the anode

Both OH- and Cl- migrate to this electrode where Cl- ions are preferentially selected for discharge although they are higher in the ECS because they are present in a higher concentration.

$$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$$

Observation

Bubbles of a greenish yellow gas evolved

Note

- The blue color of the solution is due to the Cu^{2+} ions in solution. As the more Cu2+ ions get discharged, the blue color of the solution fades away. If the electrolysis is done for a long time and all the Cu^{2+} ions get discharged, the solution becomes colorless.
- The resultant solution becomes neutral because of the formation of water from the undischarged ions.

  $H^+ (aq) + OH^- (aq) \longrightarrow H_2O (l)$

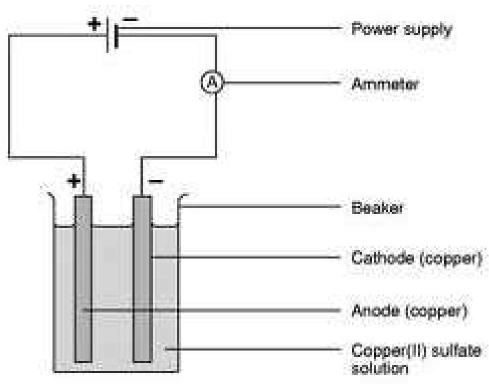
3. **Nature of electrodes**

   Some electrodes are reactive while others are inert.

   Inert electrodes: These are electrodes which do not react with electrolyte or products during electrolysis. Examples include platinum and graphite/

   Active electrodes: These are electrodes which react with products of electrolysis, affecting the course of electrolysis and the products of electrolysis. Examples include mercury and copper.

   Electrolysis of copper (ii) sulphate solution using copper anode (the cathode may remain graphite)



Ions present cu^{2+} and SO_4^{2-} from $CuSO_4$ and H^+ and OH^- from water

At the anode

Both SO_4^{2-} and OH^- migrate to the anode but neither is discharged, instead the copper anode ionizes and dissolves away to form Cu^{2+} ions in solution.

$$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$$

Observations

The mass of the anode decreases

At the cathode

The Cu^{2+} and H^+ both move to this electrode where Cu^{2+} ions are preferentially discharged because they are lower in the ECS.

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$

Observation

Brown solid is deposited at the cathode and the cathode gains weight.

Note

- The anode looses mass while the cathode gains an equal mass
- The concentration of the copper ii sulphate solution does not change and the blue colour does not fade since the process only involves the transfer of Cu^{2+} from the anode to the cathode i.e. the copper from the anode dissolves into solution to replace the lost Cu^{2+} ions at the cathode.
- No gas is evolved at the electrode.

Electrolysis of sodium chloride solution using mercury cathode

Ions present Na^+, Cl^- from sodium chloride and H^+ and OH^- from H_2O.

At the anode

Both Cl^- and OH^- migrate to the anode where OH^- ions are selectively discharged because they are lower in the ECS

$$4OH^-(aq) \longrightarrow 2H_2O(l) + O_2(g) + 4e^-$$

Observation

Bubbles of a colorless gas that relights a glowing splint

At the cathode

Both Na^+ and H^+ migrate to the cathode where the Na^+ are discharged despite them being higher in the ECS because the mercury cathode reacts with sodium to form sodium amalgam. This process is preferred because it requires less energy than discharging H^+.

$$Na^+(aq) + e \longrightarrow Na(s)$$

Applications of electrolysis

Major applications of electrolysis include

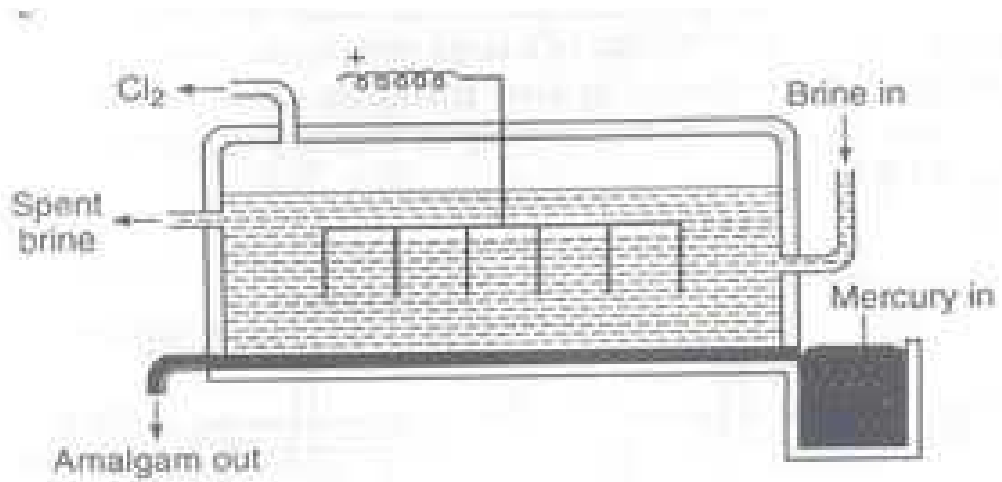
1. Purification of metals
2. Manufacture of sodium hydroxide and chlorine
3. Electro plating
4. Extraction of reactive metals
5. Anodisation

Electrorefining or Purification or refining of metals

Electrorefining is process of using electrolysis for the purification of metals. Metals such as copper and zinc are refined by electrolysis. The impure metal/ ore form the anode while the pure metal forms the cathode. The electrolyte is an acidified solution of the metal to be refined. The metal dissolves away from the anode and gets deposited as pure metal at the cathode. The impurities collect at the anode.

Manufacture of sodium hydroxide and chlorine using a mercury cathode cell

Sodium hydroxide and chlorine are obtained on large scale by electrolysis of brine using the mercury cathode cell. In the mercury cathode cell, a set of graphite rods dipping into brine serve as the anode. Graphite is suitable because is not reactive and is not attacked by chlorine evolved at the anode. The cathode is a stream of mercury which flows slowly across the bottom of the cell. The sodium amalgam formed drops into water and forms sodium hydroxide, hydrogen and mercury, which is used again. The sodium hydroxide is evaporated to dryness to form pellets, the chlorine is dried, liquefied and stored, the hydrogen is collected or converted to synthetic hydrogen chloride by burning it with chlorine.



At the cathode

$Na^+ (aq) + e \longrightarrow Na (s)$

Then

$Na (s) + Hg (l) \longrightarrow NaHg (s)$ sodium amalgam

The sodium amalgam reacts with water to form sodium hydroxide

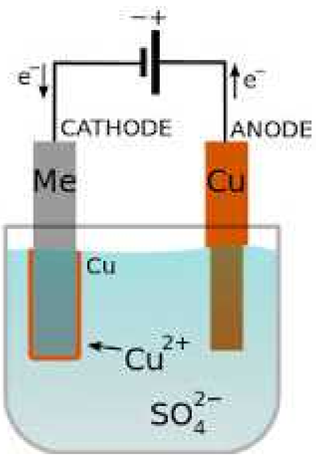
$2Na Hg (s) + 2H_2O (l) \longrightarrow 2NaOH (aq) + H_2 (g) + 2Hg (l)$

At the anode

$$2Cl^- (aq) \rightarrow Cl_2(g) + 2e^-$$

Electroplating

Electroplating is the process of coating the surface of one metal with a thin layer of another metal using electrolysis. The applied metal is usually more expensive than the base metal that is coated. Electroplating is used for the protection of the metal which is coated from rusting, or to give a shining surface. In the process the object to be coated is cleaned and made the cathode while the coating metal is made the anode. The electrolyte is a solution of a metal salt of the metal used to coat the object. The anode dissolves away and the coating metal ions migrate to the cathode where they are deposited. Examples include copper plating, nickel plating, chromium plating and silver plating.



Successful electroplating involves

- Clean cathode (object to be plated
- Steady very low current
- Steady temperature
- Steady concentration of the electrolyte.

Extraction of reactive metals

Metals high in the reactivity series are extracted by electrolysis of their molten salts example potassium, sodium, calcium, magnesium and aluminium.

Anodisation

Aluminium objects may be coated with aluminium oxide using electricity a process known as anodisation. In this process the aluminium object is made the anode and the electrolyte is dilute sulphuric acid. The oxygen evolved reacts with the aluminium object to form the aluminium oxide coating which prevents corrosion.

ELECTROCHEMICAL CELLS

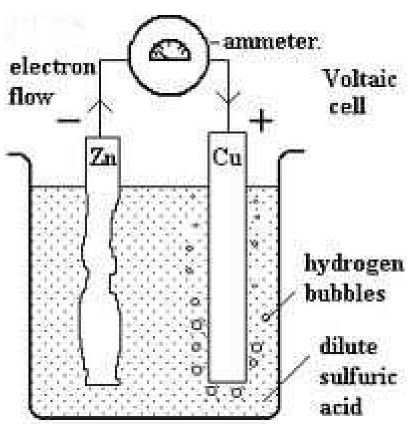
Electrochemical cells convert chemical energy into electrical energy. They produce electricity from chemical reactions.
There are two main types of electrochemical cells.

Primary cells – these cannot be recharged after use e.g. dry cells

Secondary cells- these can be recharged after use and are commonly called accumulators e.g. storage battery.

SIMPLE GALVANIC / VOLTAIC CELL

The electric cell consists of 2 electrodes made of 2 metals of different reactivity. For the galvanic cell the cathode is made of more reactive metal, because they have more tendency of losing electrons and the anode is made of less reactive metal. The further apart the metals in reactivity series, the higher voltage is created.



When zinc and copper strips or plate are dipped in dilute sulphuric acid then connected to an ammeter and bulb by a wire, the ammeter indicates that current is flowing.

Explanation

Zinc is more reactive (more electropositive) than copper therefore it goes in solution by loosing two electrons to form Zn^{2+} ions. This is oxidation.

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$

The two electrons move through the wire to the copper plate completing the circuit. The zinc metal acts as the cathode because it is where oxidation takes place and from where the electrons leave the electrolyte.

The H^+ ions in solution (from the acid) are attracted to the copper plate the positive electrode where electrons from the zinc enter the electrode. The hydrogen ions pick up electrons to form hydrogen gas at the copper plate. This is reduction.

$$2H^+(aq) + 2e^- \rightarrow H_2(g)$$

The overall equation for the simple cell is

$$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$$

Note

After a while, the hydrogen liberated cuts off the copper electrode from the acid and the voltage drops. This is called polarisation of the copper electrode. This polarisation effect can be removed by adding an oxidising agent e.g. potassium permanganate which oxidises the hydrogen gas to water and prevents the formation of hydrogen around the copper strip.

DANIEL CELL

This is constructed by dipping the metal strips in solutions of their own salts. The two salt solutions with their corresponding electrodes from separtate half cells. The half cells are connected by the salt bridge containing a saturated solution of the salt e.g. potassium nitrate or potassium chloride. The bridge makes the elecrtical contact between the cells while keeping them separate from each other.

Importance of the salt brigde

- Complete the circuit by allowing elecrtons flow from one cell to another.
- Prevents mixing of the electrolytes by keeping them separated
- Provides cations and anions which replace the ones consumed at the electrodes

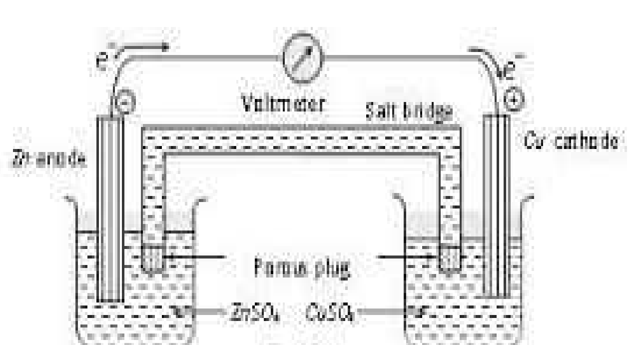
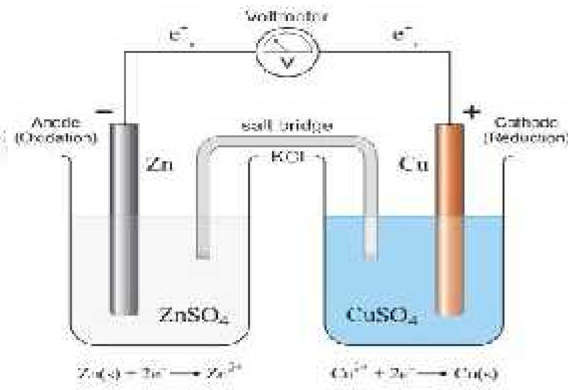


Fig.12.1



Half cell reactions

The zinc half cell acts as the negative electrode because it is more electropositive than copper. The zinc metal goes in solution and looses electrons. This is oxidation.

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$$

The electrons move to the copper electrode through the external wire

At the copper electrode, the copper ions already in solution pick up the incoming electrons from zinc metal and copper metal is deposited on the electrode. This is reduction. The copper electrode acts the positive electrode.

$$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$$

Note that the naming of the electrodes in the Daniel cell is the reverse of conventional electrolysis.

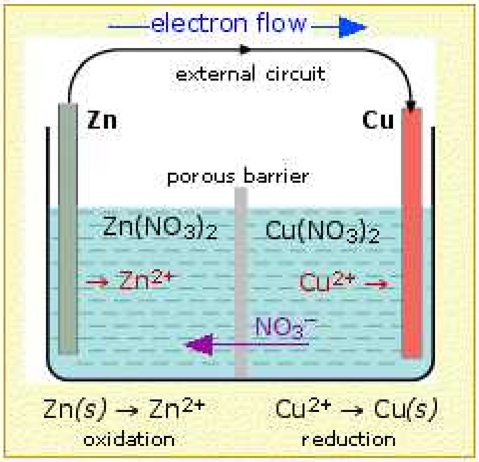
Overall equation

$$Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$$

Other formats of the Daniel cell

In some cases the salt bridge is replaces by a porous partition or porous pot.

a) With porous partition



b) With porous pot

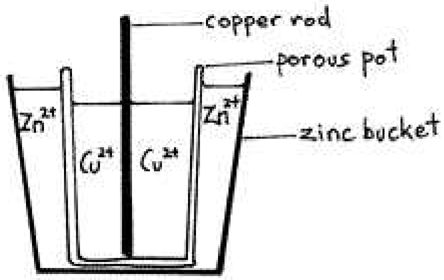


Figure 6 - Daniell's Cell, porous vase version