

School of excellence Secondary school: Chemistry handout for Grade 12th

UNIT THREE ELECTROCHEMISTRY

After completing this unit, you will be able to:

- Understand the difference b/n electrolytic cells and galvanic (voltaic) cells.
- Develop skill in writing the oxidation half-reaction, reduction half-reaction and cell reaction for the electrolysis of molten electrolytes that occur in electrolytic cells.
- Understand the differences b/n metallic conduction and electrolytic conduction.

Electrochemistry

- It is a field of chemistry that deals with the relationship b/n electrical energy and chemical energy.
- A process that bring about chemical reaction using electricity or generating electrical energy using from chemical reactions.

Electrical conductivity

- It is the power of substances to conduct electricity is called Electrical conductivity.
- The substances that transmit electricity are called electrical conductors.
- There are two types of conduction. Those are metallic and electrolytic conductions

1. Metallic conductors

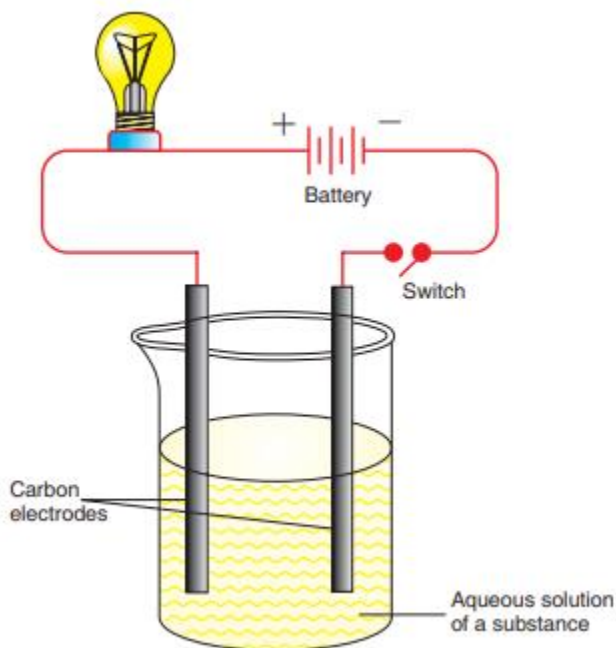
- A metallic conductor is the conduction of electric current by the flow of electrons. Are also called electronic conductions b/c the charge carries are free electrons.
 - Transmitted electricity without undergoing chemical changes.
 - *The transmission of electric current through metals. Caused by the flow of mobile electrons due to repulsion exerted on them from the electron entering the metal from the source of electricity*

2. Electrolytic conductors, or electrolytes

- Are distinguished by the fact that passage of an electric current through them results in an actual transfer of matter; this transfer is manifested by changes of concentration and frequently. A substance that transmitted electricity in a molten state or in aqueous solution.
- Based on degree of ionization, electrolyte can be classified as strong electrolytes and weak electrolytes. Strong electrolytes ionized almost completely and weak electrolytes ionize only slightly.
- Example of strong electrolyte include strong acid such as H_2SO_4 , HCl , HNO_3 e.t.c, strong base like KOH , NaOH e.t.c. weak electrolyte are weak acid such as CH_3COOH , H_2CO_3 e.t.c

School of excellence Secondary school: Chemistry handout for Grade 12th

Figures-1.

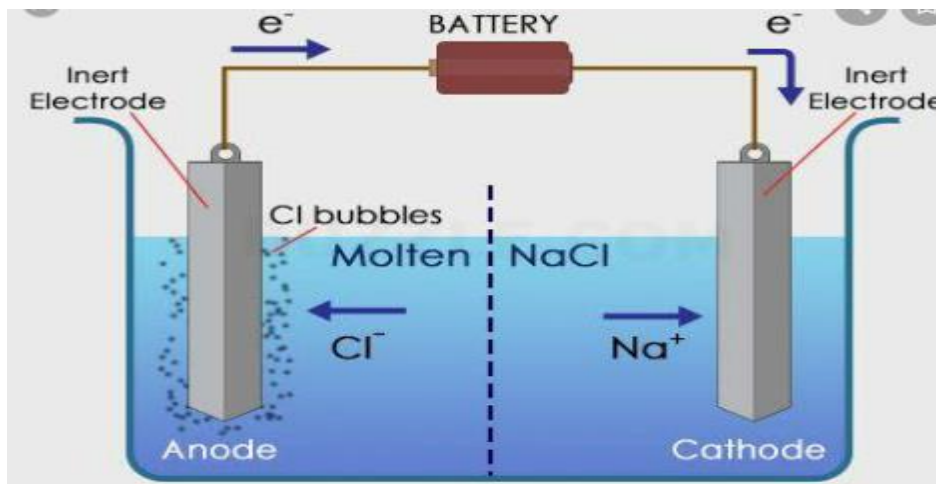


Electrochemical Cell

- Electrochemical cell is divided into two types.
 - (a) Electrolytic Cell
 - (b) Galvanic Cell or Voltaic Cell

Electrolytic Cell:

- It is a device in which electrolysis (chemical reaction involving oxidation and reduction) is carried out by using electricity or in which conversion of electrical energy into chemical energy is done. figures-2

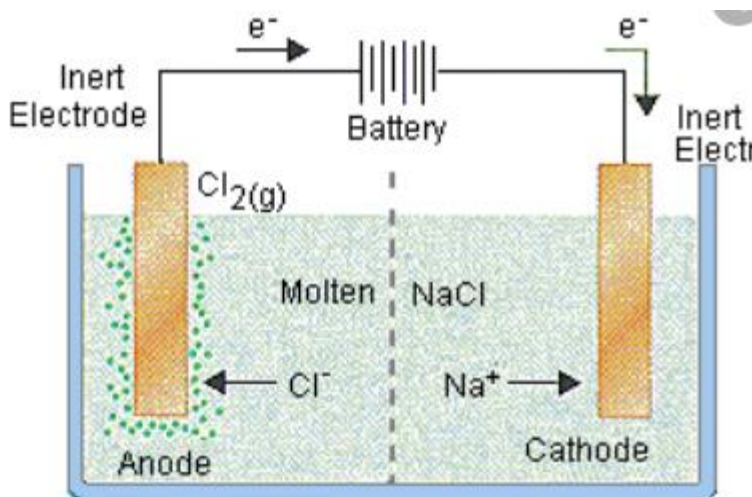


- To explain what happens in an electrolytic cell let us examine the decomposition of molten sodium chloride into sodium metal and chlorine gas. The reaction is written below.

School of excellence Secondary school: Chemistry handout for Grade 12th

-----> Non spontaneous (electrolytic cell)				
2 Na Cl (l)		2 Na (s)	+	Cl ₂ (g)
<----- Spontaneous (electrochemical cell)				

Figures-3



- Electrons from the negative terminal travel to the cathode and are used to reduce sodium ions into sodium atoms. The sodium will plate onto the cathode as it forms. The sodium ions are migrating towards the cathode
- The negative Chlorine ions migrate towards the anode and release electrons as they oxidize to form chlorine atoms. The chlorine atoms will combine together to form chlorine gas which will bubble away
- Note that the site of oxidation is still the anode and the site of reduction is still the cathode, but the charge on these two electrodes is reversed. Anode is now + charged and the cathode has a negative charge.

Major component of electrolytic cells

- Connective wire
- Electrodes
- Direct current source
- Electrolyte

Electrodes

- Are strips of metal or graphite that allow electrons to leave or enter the electrolytes
- They can be chemically active or inert.

School of excellence Secondary school: Chemistry handout for Grade 12th

- Active electrodes directly take a part in reaction i.e. it reacts with electrolyte or product of electrolysis.
- Inert electrodes do not directly take a part in chemical reactions i.e. it does not affect the result of electrolysis.

Galvanic (Voltaic) Cell:

- The device used to convert the chemical energy produced on a red-ox reaction into electrical energy is called an electrochemical cell or simply a chemical cell. In those cells electron flow is produced due to spontaneous oxidation-reduction reactions,
- Voltaic (Galvanic) Cells are electrochemical cells which contain a spontaneous reaction, and always have a positive voltage.
- The electrical energy released during the reaction can be used to do work.
- The Electrons in voltaic cells flow from the negative electrode to the positive electrode, which flows from anode to cathode
- **Reduction** occurs at the **Cathode** and **Oxidation** occurs at the anode.
- In order for oxidation-reduction reaction to occur, the two substances in each respective half-cell are connected by closed circuit so that electrons can flow from the reducing agent to the oxidizing agent.
- It also needs a salt bridge so that reaction can keep proceeding

A voltaic cell consists of two compartments called half-cells.

1. The half-cell where oxidation occurs is called anode.
2. The other half-cell where reduction occurs is called cathode..

Daniel Cell:

- It consists of two half-cells. The left hand half-cell contains a zinc metal electrode dipped in ZnSO_4 solution. The half-cell on the right hand side consists of Cu metal electrode in a solution of CuSO_4 .
- A salt bridge that prevents the mechanical mixing of the solution joins the half-cells.

When the zinc and copper electrodes are joined by a wire the following observation are made.

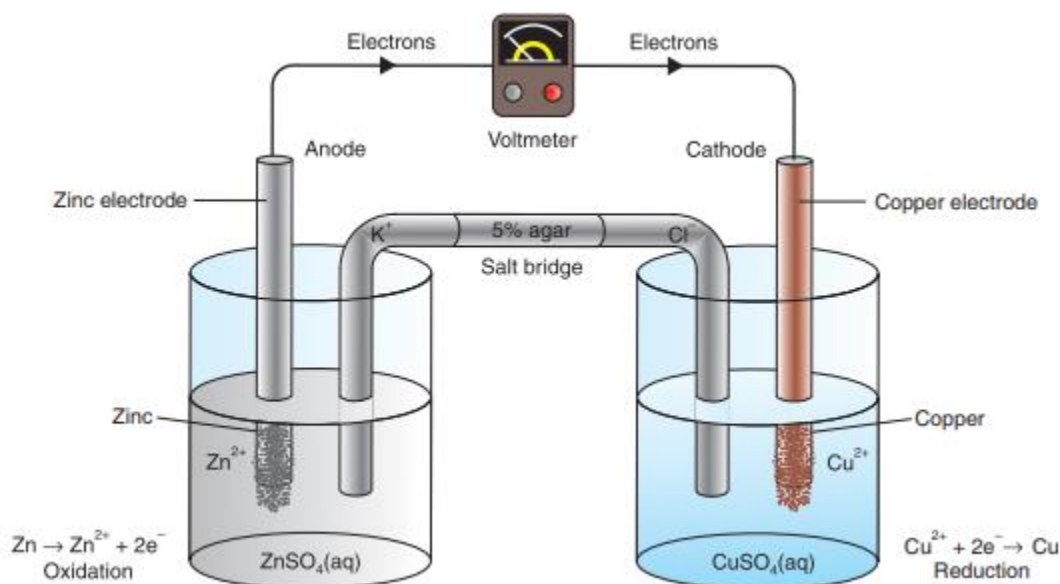
- There is flow of electric current through the external circuit
- The zinc atoms from the zinc electrode lose two electrons each and become zinc ions, Zn^{+2} ions. The ions enter into the solution while the electrons remain on the electrode and flow the external circuit to the copper electrode. This condition make zinc electrode negative and the solution to have an over positive charge due to increasing the concentration of Zn^{+2} ions entering into the solution from the anode. So the solution in this compartment will contain more Zn^{+2} ions than SO_4^{-2} ions.
- On the other hand, in the compartment containing the copper electrode, copper ions, Cu^{+2} ions from the solution move to copper electrode, gain two electrons each, become copper atoms and are deposited on the surface of copper electrode. The solution in which it placed to have negative charge. This because as Cu^{+2} ions are

School of excellence Secondary school: Chemistry handout for Grade 12th

discharged at the cathode, the amount of Cu^{+2} ions in the solution will decrease so there will be more SO_4^{-2} ions to cause the solution have a slightly negative charge.

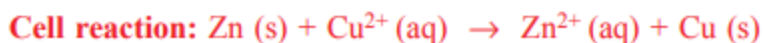
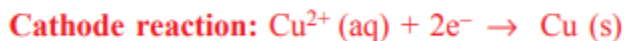
- The solutions in both the compartments remain electrically neutral.

Figures-4



Electrode Sign : The sign of the anode and cathode in the voltaic or galvanic cells are opposite to those in the electrolytic cells.

The half-cell reactions and the cell reaction in **Daniell cells** are represented as



In anodic half-cell,

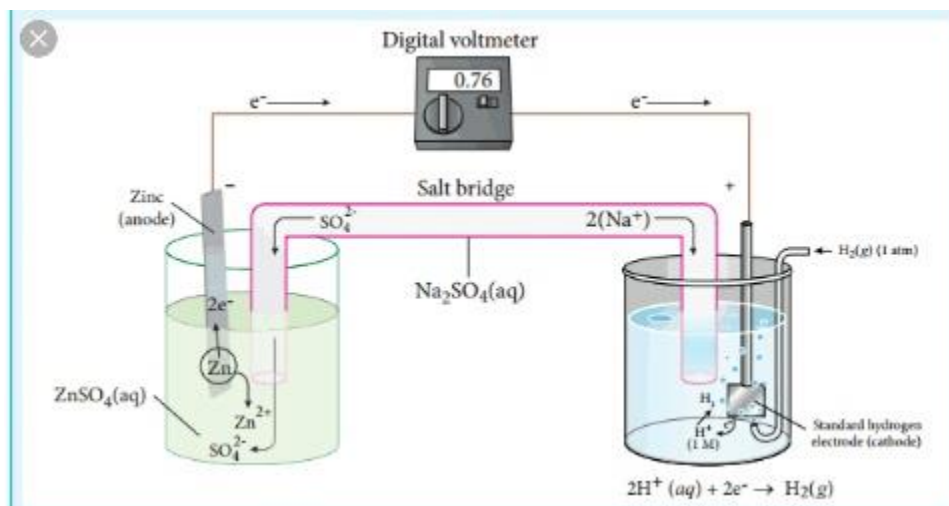
- Positive ions pass into solution and there shall be accumulation of extra positive charge in the solution around the anode, which will prevent flow of electrons from anode.

In the cathode half cell

- Accumulate around cathode due to deposition of positive ions by reduction. To neutralize these ions, sufficient numbers of positive and negative ions are provided by salt bridge. Thus salt bridge maintains electrical neutrality of the solution.

School of excellence Secondary school: Chemistry handout for Grade 12th

Figures-5



Salt bridge and its function:

- Salt bridge is usually an inverted U-tube filled with concentrated solution of inert electrolytes.
- An inert electrolyte is one whose ions neither involved in any electrochemical change nor do they react chemically with the electrolytes in two half-cells.
- Generally salts like KCl, KNO₃, and K₂SO₄ etc. are used.
- For the preparation of salt bridge, gelatin or agar-agar is dissolved in a hot concentrated aqueous solution of an inert electrolyte and solution thus formed is filled in the U-tube.
- On cooling the solution set in the form of a gel in the U-tube.
- The ends of the U-tube are plugged with cotton wool as to minimize diffusion effects.

Function of salt bridge:

- It connects the solutions of two half cells and complete the cell circuit.
- It prevents transference or diffusion of the solutions from one half cell to the other
- It keeps the solutions in the two half-cells, electrically neutral.
- It prevents liquid-liquid junction potential i.e. the potential difference which arises between two solutions when contact with each other.

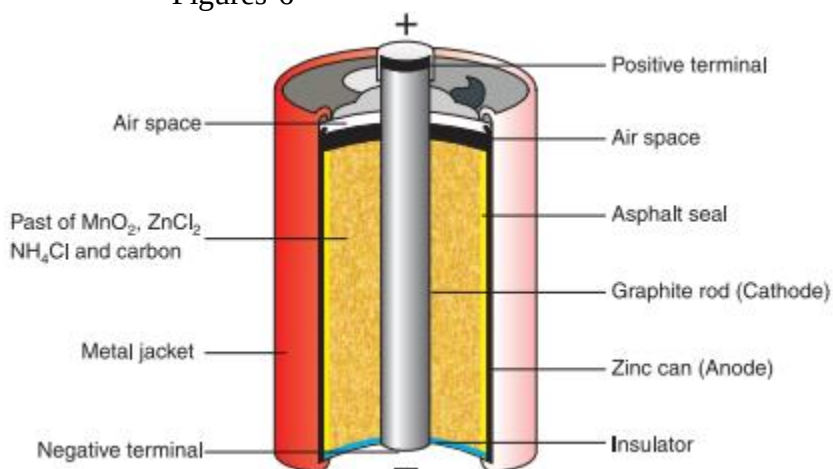
There are three types of galvanic cells.

1. Primary galvanic cells

- They are non-rechargeable cells b/s it is not possible to recover them by changing the cells.
- The entire cell reaction cannot be reversed on charging
- Example of primarily cells includes Daniel cell, zinc-carbon (leclanche cell) dry cell, alkaline battery and silver oxide cell.

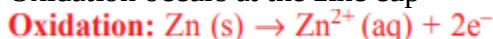
School of excellence Secondary school: Chemistry handout for Grade 12th

Figures-6

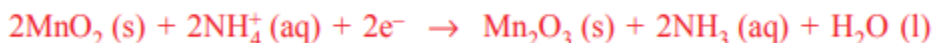


Zinc-carbon dry cell (Leclanche cell)

- A zinc-carbon dry cell produces electricity as a result of a spontaneous redox reaction.
- Oxidation occurs at the zinc cup



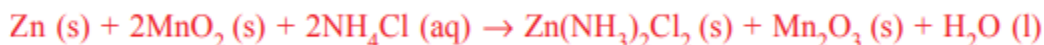
- Reduction takes place at the graphite (carbon) electrode.



- A build up of ammonia gas around the cathode may disrupt the current. However, this is prevented by the reaction between Zn^{2+} and NH_3 to form a complex ion, $[\text{Zn}(\text{NH}_3)_2]^{2+}$ which crystallizes as a chloride salt



The overall reaction occurring in a Leclanche cell is:



- There are other examples of dry cells, such as the alkaline dry cell, silver oxide cell, and copper oxide cell.

Exercise 3.3

1. In a Daniell cell, copper and zinc are used as electrodes. Which metal serves as an anode and which one as a cathode? Is the anode the positive or the negative terminal in this cell?
2. Which electrode is negative and which one is positive in the Leclanche cell? Is the polarity of the electrodes in Galvanic cells similar to that of the electrodes in electrolytic cells?
3. Why do we refer to the redox reactions in electrolytic and voltaic cells as non-spontaneous and spontaneous, respectively?

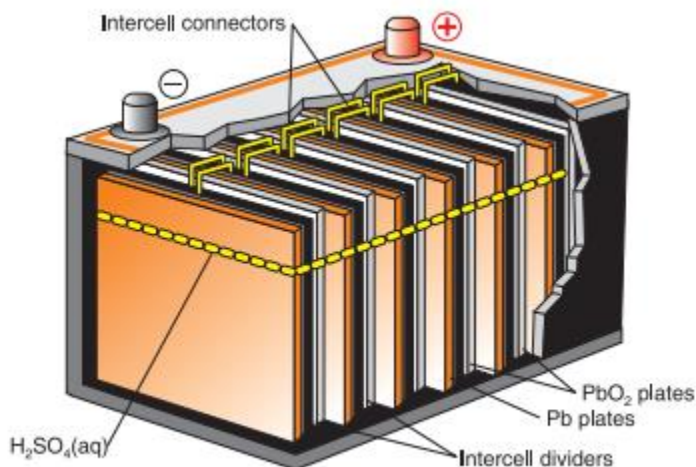
School of excellence Secondary school: Chemistry handout for Grade 12th

2. Secondary galvanic cell.

- Secondary batteries convert chemical energy to electrical energy (on discharge) and electrical energy to chemical energy (on charging).
- They are rechargeable galvanic cells
- Reactants are generated by the reverse reaction by passing direct current through the cell in the direction opposite to the discharge current flow.
- A lead storage battery is an example of a secondary cell.

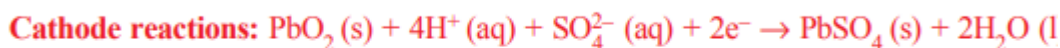
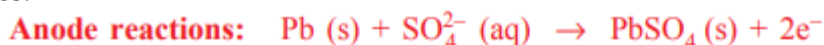
A lead Storage

- Battery is the common automobile battery that usually delivers either 6 or 12 volts, depending on the number of cells used in its construction. The inside of the battery consists of galvanic cells connected in series.
- A fully-charged lead-acid cell is made up of a stack of alternating lead and lead (IV) oxide plates isolated from each other by porous separators.
- The individual cells contain a number of lead anodes connected together, plus a number of cathodes composed of PbO_2 , also joined together. These electrodes are immersed in 35% sulphuric acid, which serves as an electrolyte.
- A single lead-storage cell delivers 2 volts. Therefore, a 12 V battery contains six cells connected in series.



Lead - Storage Battery (figures-7).

When a lead-storage battery is in operation (on discharge), the following reactions occur at the electrodes:



and the overall reaction is:



- From the electrode reactions it can be noticed that PbSO_4 is produced at both electrodes. Unlike primary cells a lead-storage battery is rechargeable when the battery runs down.
- The electrode reactions can be reversed by placing a potential across the electrodes that is slightly larger than that which the battery can deliver.

School of excellence Secondary school: Chemistry handout for Grade 12th

The reaction that takes place on recharging a lead storage battery is given by the following equation



3. Fuel cells

- Requires continuous supply of reactants to keep function.
- Do not store chemical energy like batteries
e.g hydrogen-oxygen fuel cells.

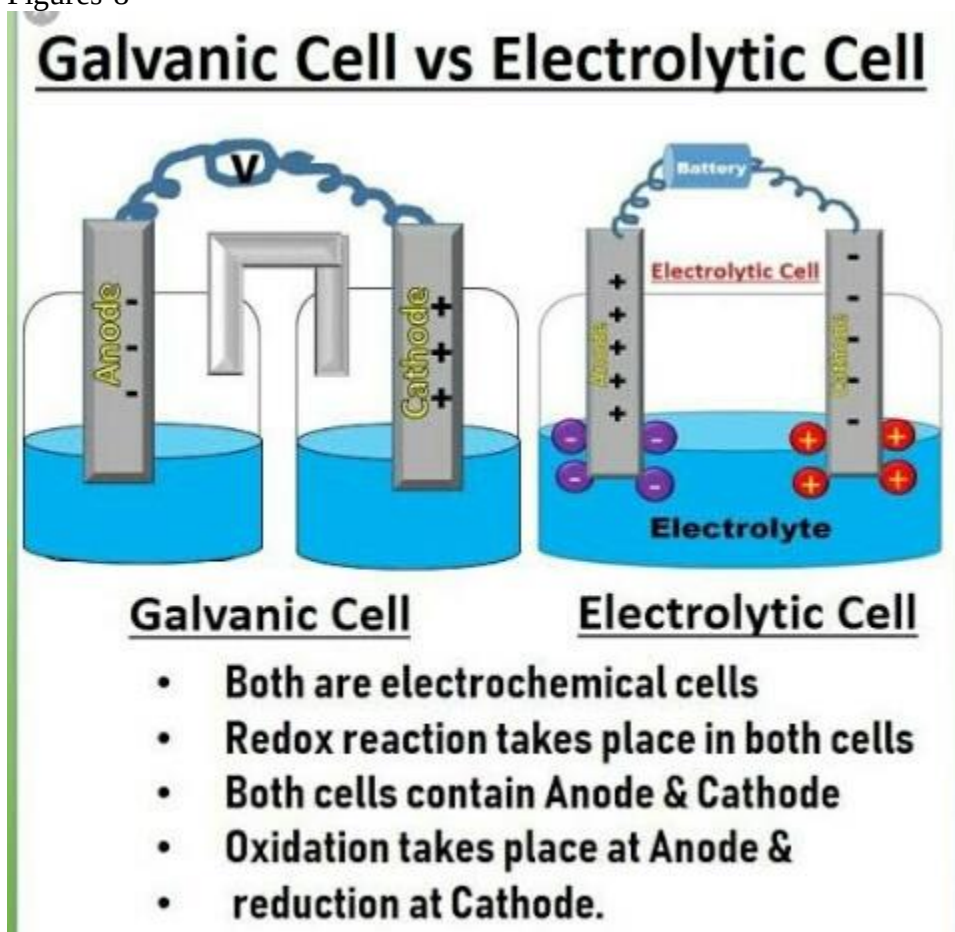
Electrochemical cell (Galvanic Cell)

- A Galvanic cell converts chemical energy into electrical energy.
- Here, the redox reaction is spontaneous and is responsible for the production of electrical energy.
- The two half-cells are set up in different containers, being connected through the salt bridge or porous partition.
- Here the anode is negative and cathode is the positive electrode.
- The reaction at the anode is oxidation and that at the cathode is reduction.
- The electrons are supplied by the species getting oxidized. They move from anode to the cathode in the external circuit.

Electrolytic cell

- An electrolytic cell converts electrical energy into chemical energy.
- The redox reaction is not spontaneous and electrical energy has to be supplied to initiate the reaction.
- Both the electrodes are placed in a same container in the solution of molten electrolyte.
- Here, the anode is positive and cathode is the negative electrode. The reaction at the anode is oxidation and that at the cathode is reduction.
- The external battery supplies the electrons. They enter through the cathode and come out through the anode.

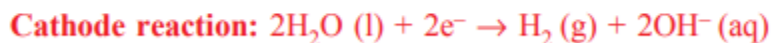
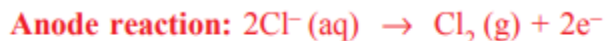
Figures-8



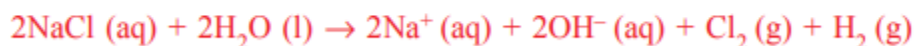
School of excellence Secondary school: Chemistry handout for Grade 12th

INDUSTRIAL APPLICATIONS OF ELECTROLYSIS

1. The production of chemicals like sodium hydroxide, from electrolysis of brine (concentrated NaCl solution), using inert electrodes.

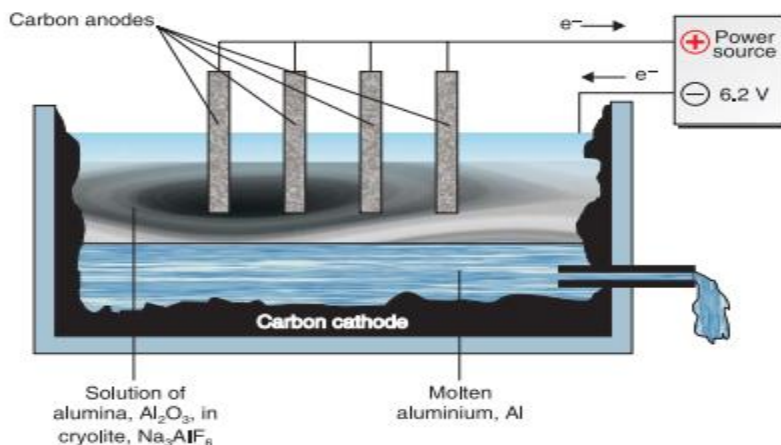
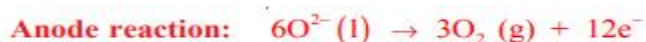


The overall cell reaction is:



2. For the production of metals and non-metals

- The non-metals like H_2 , Cl_2 , F_2 etc are manufactured on an industrial scale by the process called electrolysis. The metal aluminum is extracted industrially by the Hall Process.
- This process involves the electrolysis of molten alumina (Al_2O_3) mixed with some amount of cryolite, Na_3AlF_6 .
- The role of cryolite is to reduce the melting point of alumina from 2000°C to 1000°C .
- The vessel holding the molten mixture (Figure 3.8) is made up of iron lined with carbon, which serves as the cathode. Carbon (graphite) rods that serve as the anode are inserted into the melt.
- When the molten mixture is electrolyzed, pure aluminum is produced. The reactions at the electrodes are:

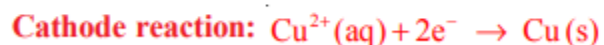
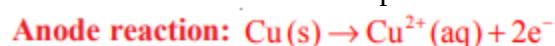


School of excellence Secondary school: Chemistry handout for Grade 12th

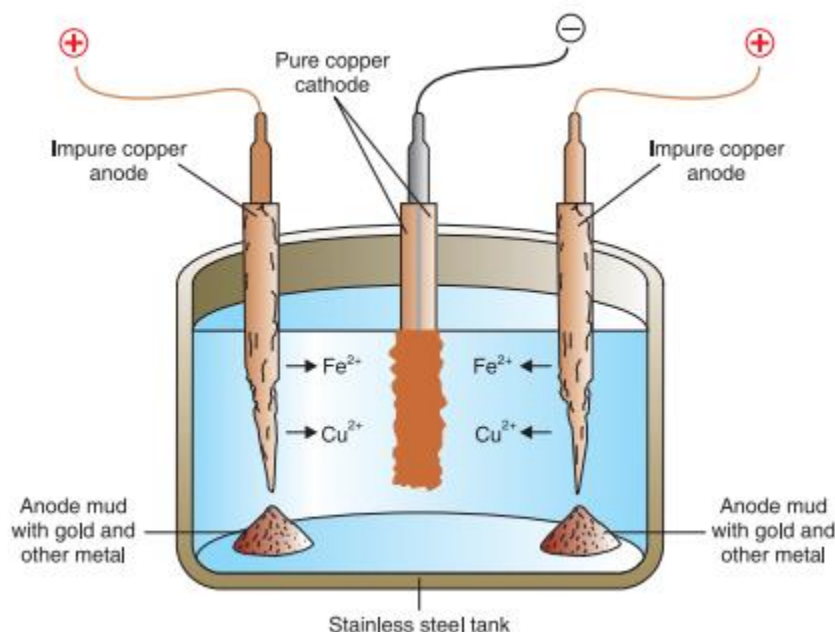
3. For the Purification of Metals.

- Another important application of electrolysis is the purification of metals like copper. When first separated from its ore, copper metal is about 99% pure with nickel, silver, gold and platinum as major impurities.
- In the refining process, the impure copper is used as the anode, copper metal of high purity used as cathode, and copper sulphate, CuSO_4 solution and aqueous H_2SO_4 as the electrolyte.
- When electrolysis is carried out, copper and impurities that are more easily oxidized than copper, such as nickel, will go into the solution. Copper passes through the solution and deposits on the cathode, while the impurities remain in solution.
- Impurities like silver and gold are less easily oxidized and do not dissolve but fall away from the anode as 'sludge'.

The electrode reaction in the purification of copper is the following



During the process, the size of the impure copper anode decreases and that of the pure copper cathode increases (figures-9).



Always remember that, in the purification of metals by electrolysis, the impure metal should be used as the anode, the pure form of the metal as the cathode and an electrolyte should contain soluble salt (ions) of the metal to be purified. The process of purifying metals by electrolysis is called electrorefining.

School of excellence Secondary school: Chemistry handout for Grade 12th

4. For Electroplating

Electroplating: - is a process of covering the surface of a metal (metal article) with a thin layer of another metal. Using this process, metals that easily corrode can be protected by a thin coating of another metal that resists corrosion.

- For example, tin cans are steel cans with a thin coating of tin, and chrome-plated bumpers are used for automobiles. Thus, the main objective of electroplating is to protect an article from corrosion and to give articles a beautiful appearance.
- In the process of electroplating, the pure plating metal should be used as the anode, the article (metal) to be plated as the cathode and a solution containing ions of the plating metal as the electrolyte. For example, to produce a silver-plated copper article, say, a medal, one should use silver as the anode, the copper medal as the cathode and silver nitrate solution as the electrolyte (Figure 10)

