

Chapter 10

Electrochemistry



Definition

“Electrochemistry is concerned with the conversion of electrical energy into chemical energy in electrolytic cells as well as conversion of chemical energy into electrical energy in galvanic or voltaic cell”

Electronic Conduction	Electrolytic Conduction
1. This type of conduction is present in metals	1. This type of conduction is present in molten salts or their aqueous solutions
2. This conduction is due to the movement of free electrons present in metals	2. This conduction is due to the movement of positive and negative ions
3. No physical or chemical change take place in conductor during electronic conduction	3. Ions undergo oxidation and reduction reactions at respective electrodes
4. Example: copper, iron etc	4. Example: Electrolysis of molten NaCl to Cl ₂ and Na

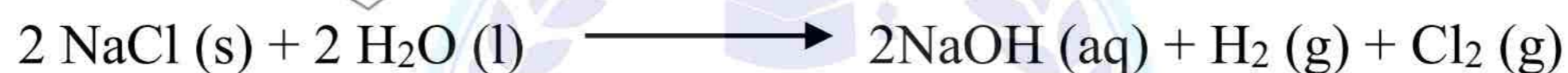
Ionization

When some electrolyte is dissolved in water the process is called ionization.



Electrolysis

A chemical change caused by passage of electricity through molten compound or through its aqueous solution is called electrolysis.



Electrochemical Cells

Definition

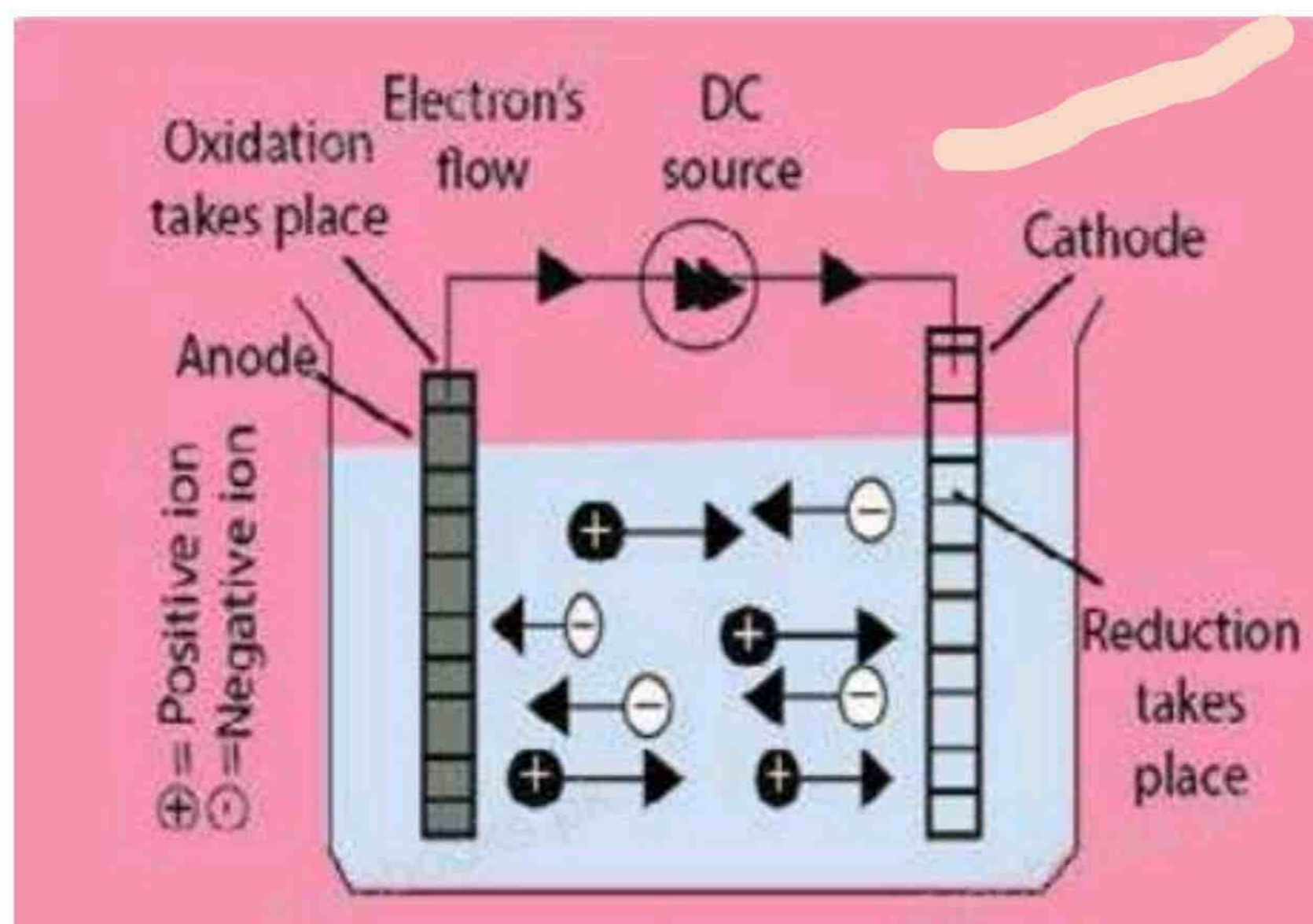
“The cell in which a chemical reaction utilizes electrical energy or produces electrical energy is called electrochemical cell”

There are two types of electrochemical cells:

1. Electrolytic cells

Definition

“An electrochemical cell in which electric current is used to drive a non-spontaneous reaction is called electrolytic cell”



Electrolytic cell consists of two electrodes i.e. cathode and anode dipped in an electrolyte and connected through an external DC source of electricity.

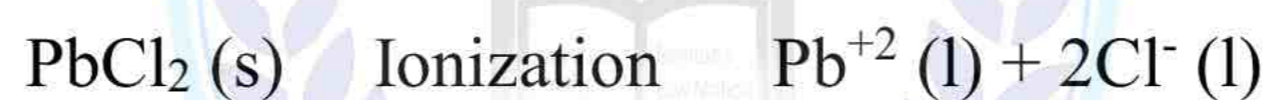
Working

When electricity is passed through the solution, positive ions move towards negative electrode i.e. cathode. They pick up electrons from cathode and are reduced.

On the other hand, negative ions move towards positive electrode i.e. anode where they give up their electrons and are oxidized.

Oxidation takes place at anode while reduction takes place at cathode. The whole process is known as electrolysis.

Electrolysis of Fused Salts



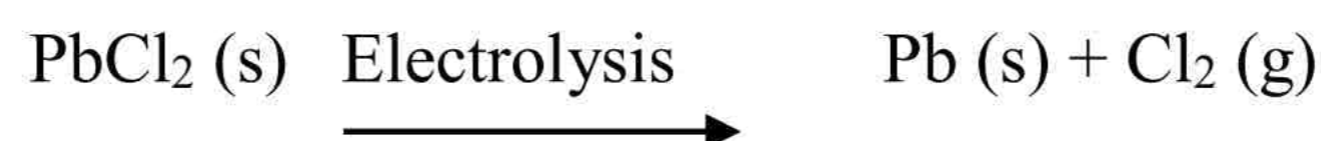
At cathode:



At anode:

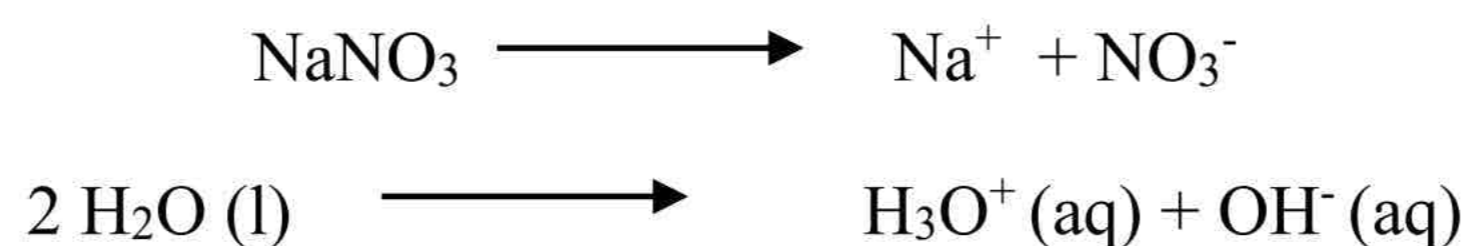


Net Cell Reaction

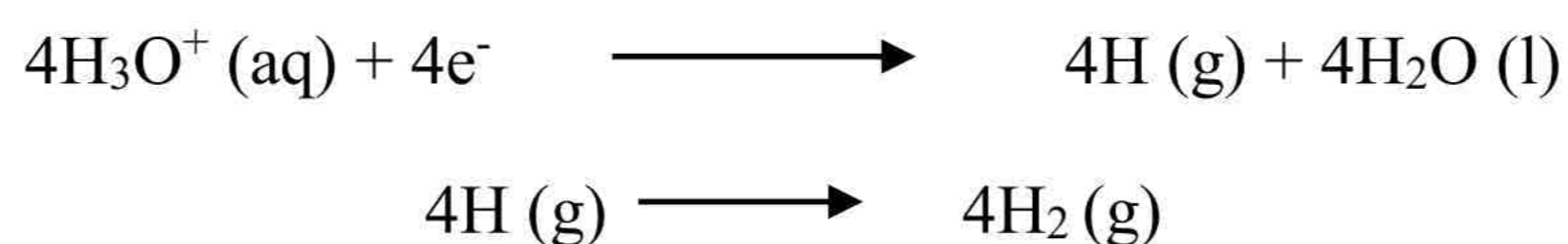


Electrolysis of aqueous solution of salts (using inert electrodes)

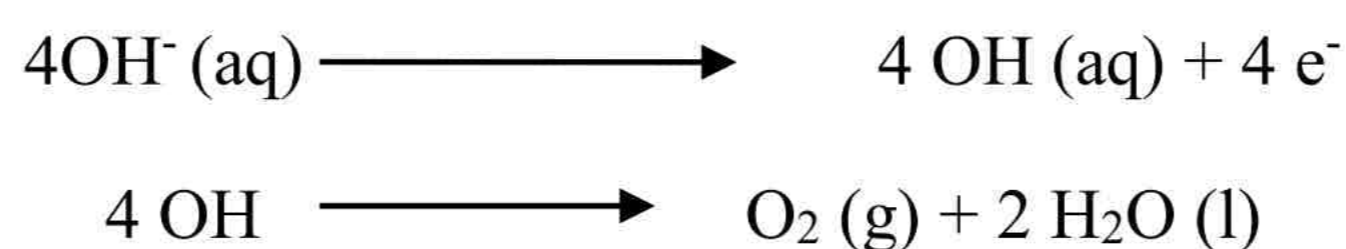
1. Electrolysis of aqueous solution of NaNO_3



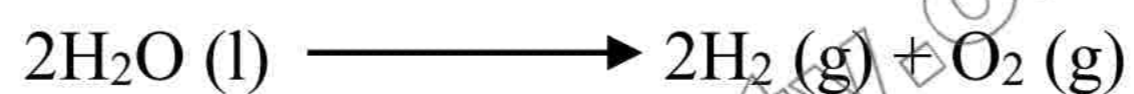
At cathode



At anode



Net cell reaction



Examples of electrolysis

(When electrodes take part in reaction)

a. Electrolysis of CuSO_4 using Cu electrode

Electrolyte: aqueous CuSO_4

Cathode: pure copper

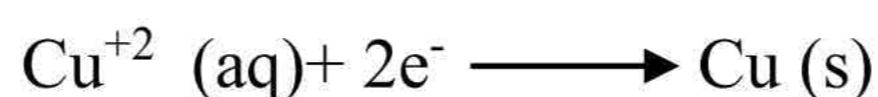
Anode: impure copper



At anode:



At cathode:



b. Electrolysis of AgNO_3 using Ag electrodes

Cathode: pure Ag

Anode: Impure Ag

Electrolyte: AgNO_3



At anode:



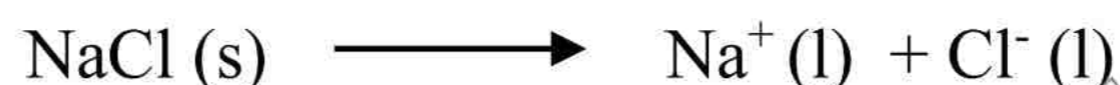
At cathode:



Electrolytic processes of Industrial Importance

a. Electrolysis of Molten NaCl

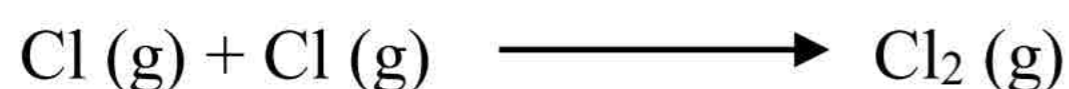
Sodium metal and Cl_2 is prepared in Down's cell using iron cathode and graphite anode.



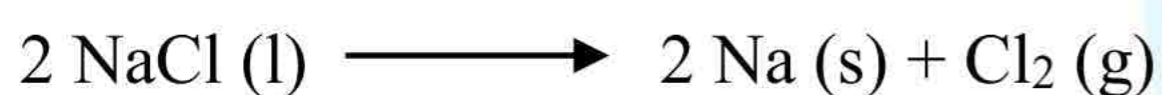
At cathode:



At anode:



Net cell reaction:



b. Electrolysis of conc. aqueous solution of NaCl

Caustic soda is obtained on industrial scale by the electrolysis of concentrated aqueous solution of NaCl using titanium anode and mercury or steel cathode in Nelson's cell. Saturated aqueous solution of NaCl is called brine.



At anode:



At cathode:

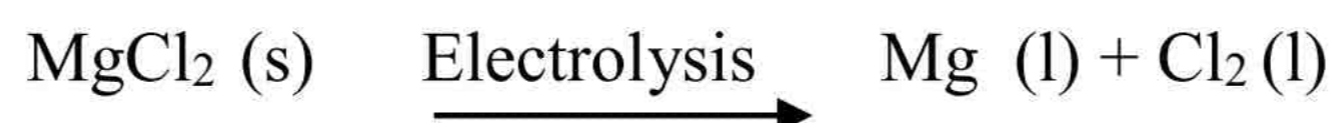


Overall reaction:



c. Extraction of magnesium and calcium

Magnesium and calcium metals are extracted by the electrolysis of their fused chlorides.



d. Extraction of aluminium

Aluminium is extracted by electrolyzing fused bauxite ($\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$) in the presence of fused cryolite (Na_3AlF_6). Cryolite decreases the melting point of aluminium oxide.

e. Preparation of anodized aluminium

Anodized aluminium is prepared by making it an anode in an electrolytic cell containing sulphuric acid or chromic acid which coats a thin layer of oxide on it. The aluminium oxide layer resists attack by corrosive agents. The freshly anodized aluminium is hydrated and can absorb dyes.

f. Extraction of copper

Electrolytic cell can also be used for purification of copper using CuSO_4 as electrolyte. Impure copper as anode and pure copper as cathode. Cu atoms from impure copper are converted to Cu^{+2} and pure copper is deposited on anode. Impurities are left at anode.

At anode:



At cathode:



g. Electroplating

Copper, silver, nickel or chromium plating is done by various types of electrolytic cells.

Voltaic or Galvanic Cell

Definition

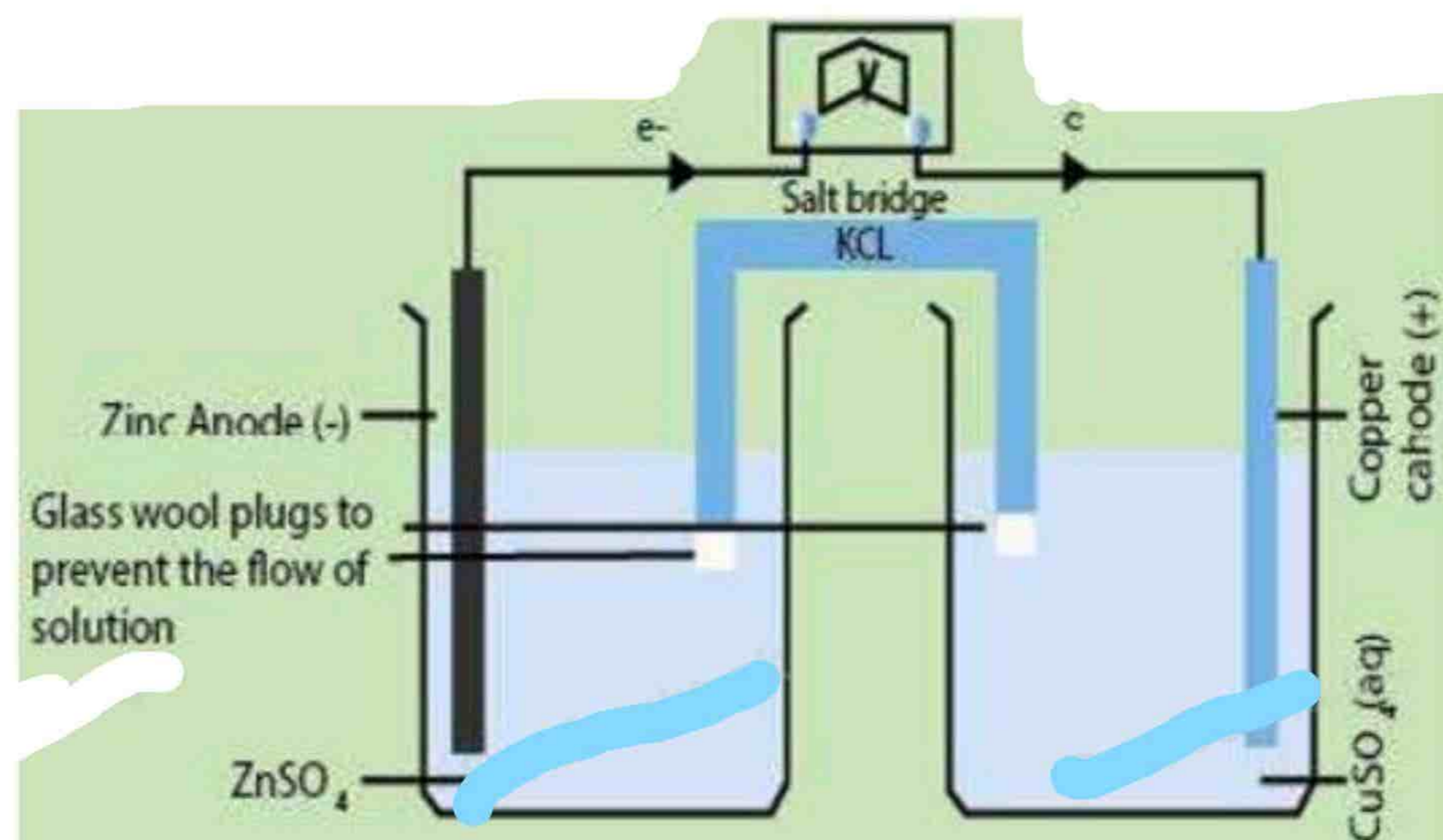
The electrochemical cell in which a spontaneous oxidation-reduction reaction taking place in solution produces electricity is known as voltaic or galvanic cell.

OR

The electrochemical cell in which chemical energy is converted to electrical energy is known as voltaic or galvanic cell.

Construction

- Two half cells are electrically connected
- Each half cell is a portion of total cell in which half reaction takes place



A galvanic cell consisting of Zn and Cu electrodes at 25 °C and 1 M electrolyte solution.

Half Cells

Left half cell consists of Zn strip dipped in 1.0 M solution of ZnSO₄ giving following equilibrium.



Right half cell consists of Cu strip dipped in 1.0 M solution of CuSO₄ giving following equilibrium.



Working

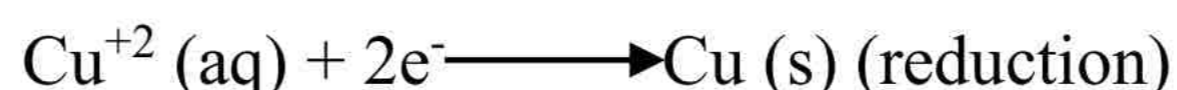
- The half cells are connected electrically by a salt bridge
- Zn tends to lose electrons more rapidly than Cu
- If the external circuit is closed by connecting the two electrodes electrons flow from zinc through external circuit to copper electrode

Half Cell reactions

At anode



At cathode



Overall voltaic cell reaction



Representation of voltaic cell reaction:



Sign || shows salt bridge

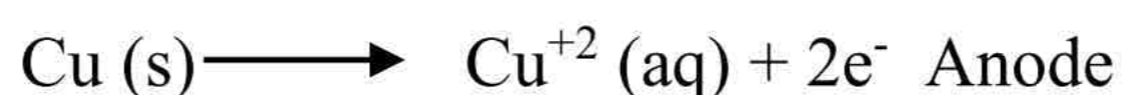
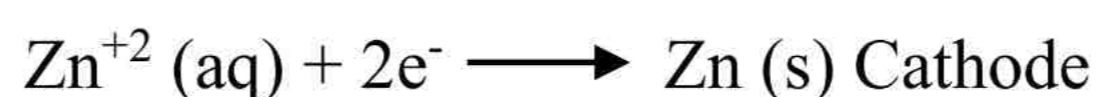
Function of salt bridge

The purpose of the salt bridge is to prevent any net charge accumulation by allowing negative ions to leave the right beaker, diffuse through the bridge, and enter the left beaker. Otherwise, the net charge accumulating in the beakers would immediately stop the flow of electrons through the external circuit and the oxidation-reduction reaction would stop.

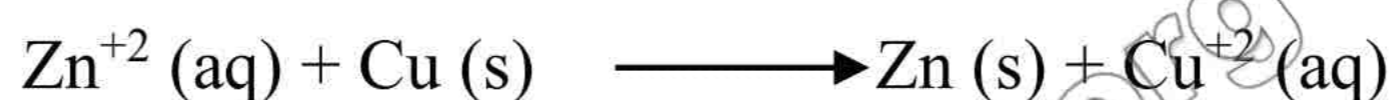
Voltaic Cell is Reversible Cell

If the external source of electricity is applied to voltaic cell then electrode reactions can be reversed. Reverse non-spontaneous reactions occur and cell is called reversible cell.

For Zn-Cu cell



Overall Reaction



Electrode Potential



Definition

The potential set up when an electrode is in contact with one molar solution of its own ions at 298 K is known as standard electrode potential or standard reduction potential of the element. It is represented as E° .

Method of determination

When a metal strip is placed in a solution of its own ions, there are two tendencies.

1. The metal atoms may dissolve as positive ions. The electrons are deposited on the metal electrode.
2. The metal ions present in solution may take up electrons from the metal and get discharged as atoms. It imparts a positive charge to the metal.

Outcome

In both cases, a potential difference is set up between the metal and the solution which is called single electrode potential.

Determination of electrode potential with reference hydrogen electrode

1. Arbitrary scale

Standard electrode potential of hydrogen has arbitrarily been chosen as zero.

2. Comparison with hydrogen electrode

The standard electrode potentials of other elements are found by comparing them with standard hydrogen electrode potential.

3. Equilibrium between atoms and ions

The electrode potential set up when a metal piece is placed in a solution containing its own ions can be explained in terms of equilibrium between the atoms of the metal and its ions in solution.

4. Formation of positive ions

When a metal is placed in a solution, some of its atoms tend to give electrons to the piece of metal and pass into the solution as positively charged ions.

5. Formation of neutral atoms

The metallic ions already present in solution tend to take up electrons from the piece of metal and deposit themselves as neutral atoms.

6. Factor deciding charge

Whichever tendency is greater determines whether the metal becomes negatively or positively charged.

7. No potential difference change

When equilibrium is attained the two opposing processes continue at the same rate and there is no further change in the potential difference.

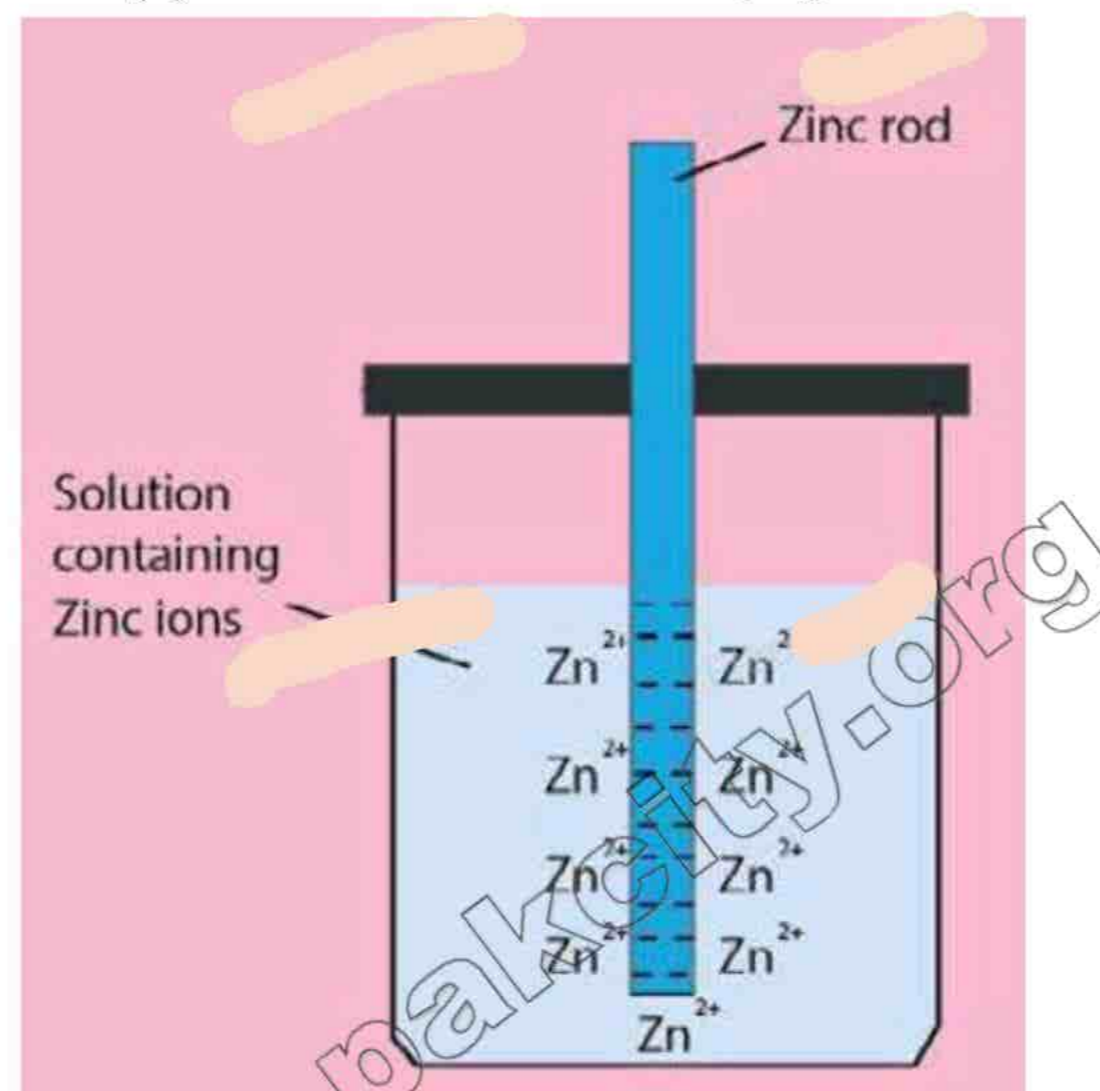
Example

A rod of zinc will bear an accumulation of negative charges. This is due to the net ionization of some of its atoms.

Electrical double layer

The negative charge on the Zn-rod will attract an atmosphere of positively charged zinc ions around the rod to form an electrical double layer.

Equation



Standard Hydrogen Electrode

Construction

It consists of a piece of platinum foil which is coated electrolytically with finely divided platinum black to give it a large surface area and suspended in one molar solution of HCl.

Working

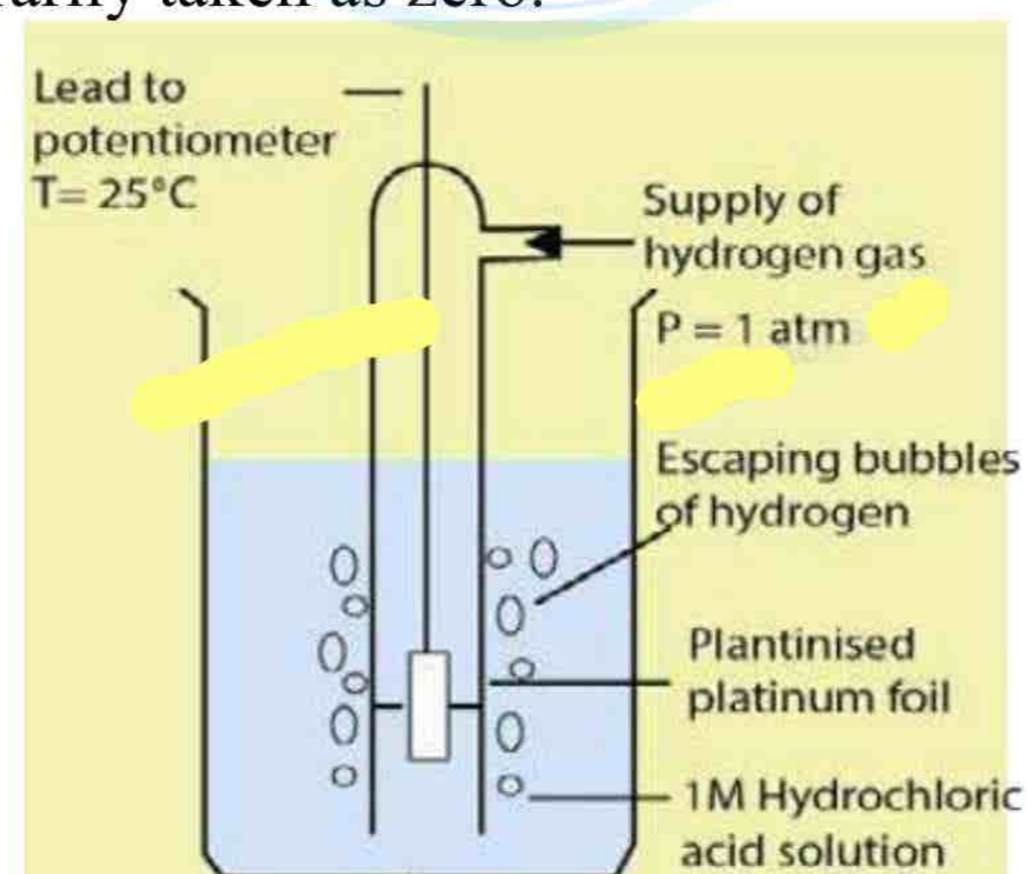
Pure hydrogen gas at one atmosphere pressure is continuously bubbled into 1M HCl solution.

Electrical conductor

The platinum acts as an electrical conductor and also facilitates the attainment of equilibrium between the gas and its ions in solution.

Electrode potential

The potential of this electrode is arbitrarily taken as zero.



Measurement of Electrode Potential

Establishment of galvanic cell

In any measurement of electrode potential, the concerned electrode is joined electrolytically with the standard hydrogen electrode (SHE) and a galvanic cell is established.

Salt bridge

The two solutions are separated by a porous partition or a salt bridge containing a concentrated solution of potassium chloride. The salt bridge is used to provide a highly conducting path between the two electrolytic solutions.

Voltmeter

The potential difference is measured by a voltmeter which gives the potential of the electrode as the potential of SHE is zero.

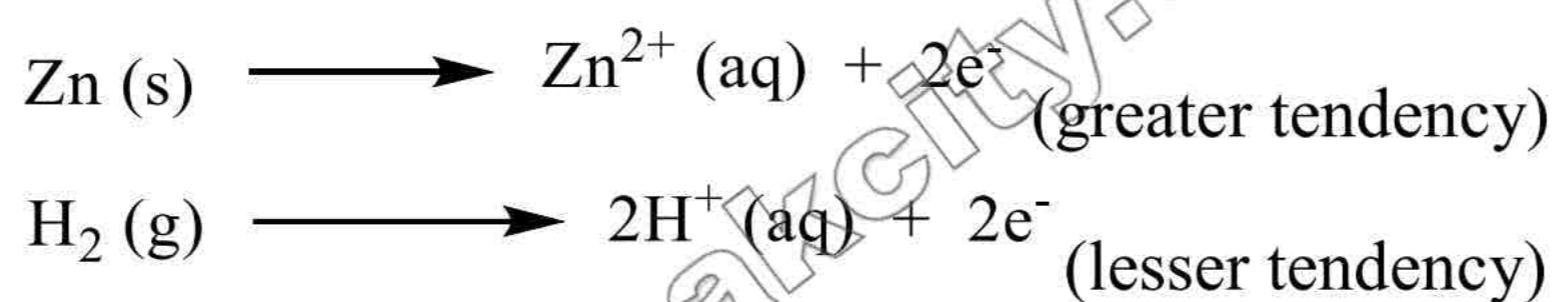
Reaction at SHE

An oxidation or reduction may take place at SHE depending upon the nature of the electrode which is coupled with it.

Example of galvanic cell between zinc and hydrogen

To measure the electrode potential of zinc a galvanic cell is established between zinc electrode dipped in 1 M solution of its ions and standard hydrogen electrode at 25 °C. Under the standard conditions, the voltmeter reads 0.76 volts and the deflection is in such a direction as to indicate that zinc has a greater tendency to give off electrons than hydrogen has.

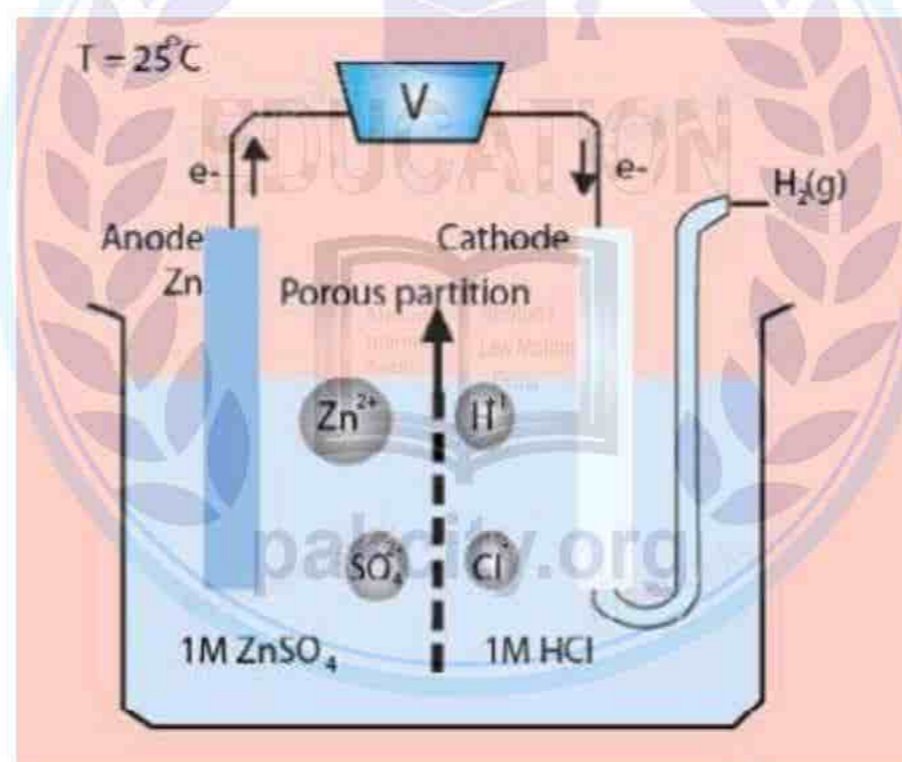
The half reaction:



by 0.76 volts.

Oxidation potential of zinc

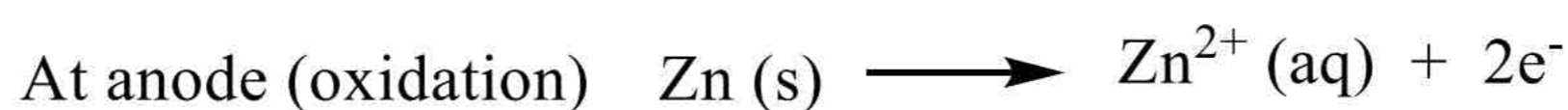
The standard electrode potential of zinc is 0.76 volts. It is called oxidation potential of Zn and is given the positive sign.



The reduction potential Zn-electrode is -0.76 volt.

Electrode Reactions

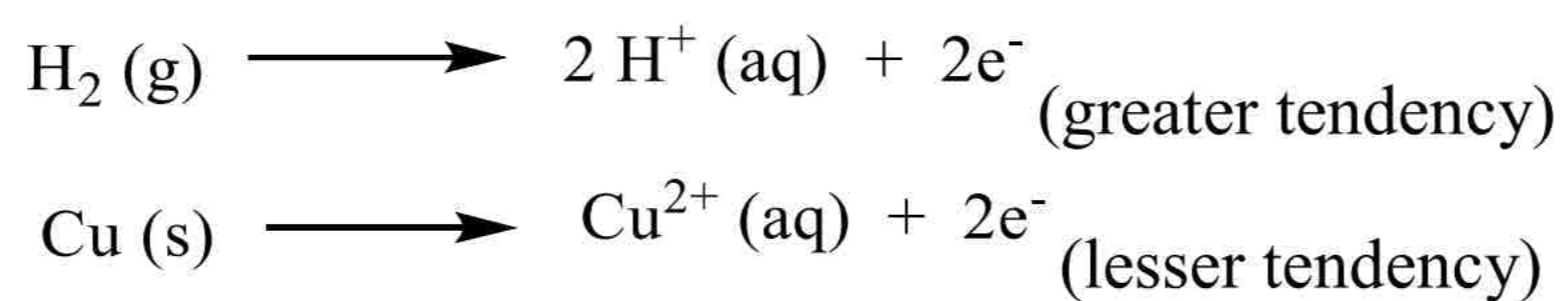
The electrode reactions are as follows.



Example of galvanic cell between copper and hydrogen

The electrode potential of copper can also be measured using galvanic cell in which copper is an electrode dipped in 1 M solution of its ions and connected with SHE. Under standard conditions, the voltmeter reads 0.34

volts and the deflection is in such a direction as to indicate that hydrogen has a greater tendency to give of electrons than copper has.



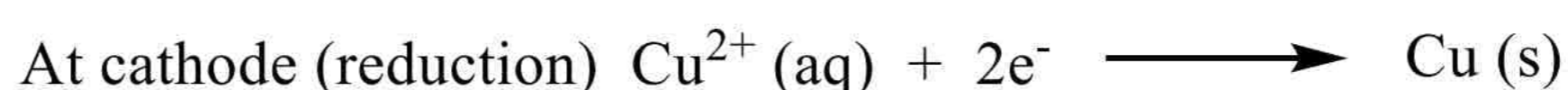
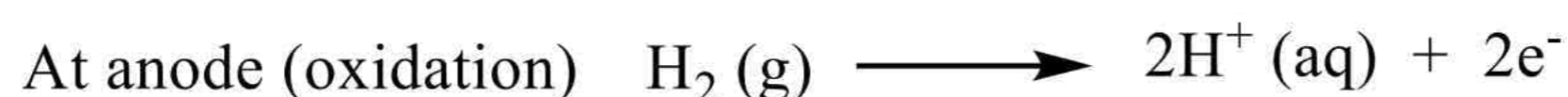
by 0.34 volts.

So the standard electrode potential of Cu is 0.34 volts. It is called reduction potential of Cu.

-0.34 V is called oxidation potential of Cu electrode.

Electrode Reactions

The reactions taking place at two electrodes will be shown as follows.



The Electrochemical Series

Definition

When elements are arranged in the order of their standard electrode potentials on the hydrogen scale the resulting list is known as electrochemical series.

Applications of Electrochemical Series

Following are the applications of electrochemical series:

1. Prediction of the Feasibility of a Chemical Reaction

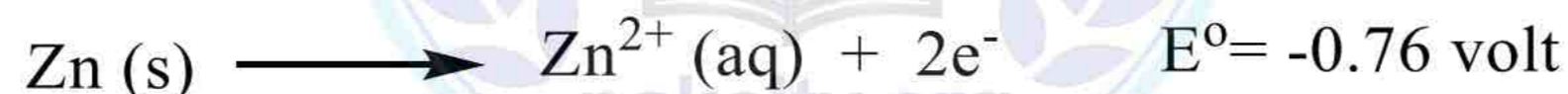
When we look at the electrochemical series it is easy to predict whether a particular reaction will take place or not.

Example

$\text{Cu}^{2+} (\text{aq})$ can oxidize solid zinc but $\text{Zn}^{2+} (\text{aq})$ cannot oxidize solid copper. Standard reduction potential values of copper and zinc can explain this



Zinc is oxidized



Overall Reaction



$$E^{\circ}_{\text{cell}} = 1.10 \text{ volts}$$

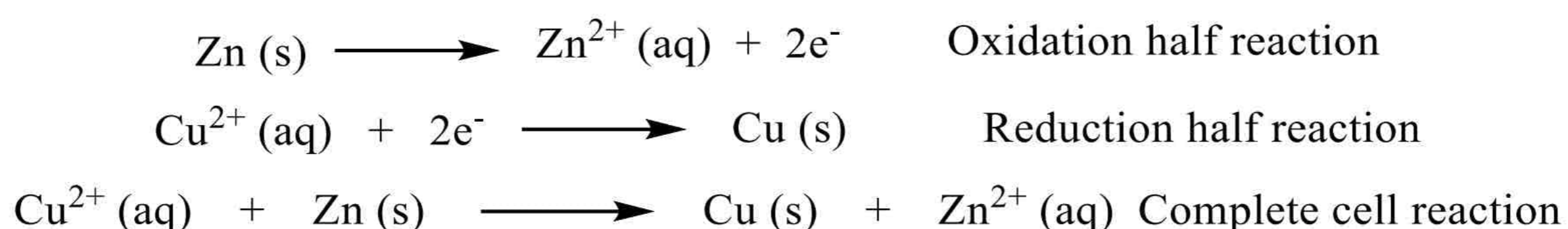
The overall positive value for the reaction potential suggests that the process is energetically feasible.

2. Calculation of the Voltage or Electromotive Force (EMF) of Cells

In a galvanic cell, the electrode occupying a higher position in the electrochemical series, will act as anode and oxidation takes place on it. The electrode occupying the lower position in the series will act as a cathode and reduction will take place.

Example

Let us find out a cell potential or the EMF of the cell. The half cell reactions are:



Calculation of EMF

$$\begin{aligned} E^{\circ}_{\text{cell}} &= E^{\circ}_{\text{oxi}} + E^{\circ}_{\text{red}} \\ E^{\circ}_{\text{cell}} &= 0.76 + 0.34 \\ &= 1.10 \text{ volts} \end{aligned}$$

The cell voltage or emf measures the force with which electrons move in the external circuit and therefore measures the tendency of the cell reaction to take place.

3. Comparison of Relative Tendency of Metals and Non-Metals to Get Oxidized and Reduced Reduction Potential Value

Reducing agent

The value of the reduction potential of a metal or a nonmetal tells us the tendency to lose electrons and act as a reducing agent.

Oxidizing agent

It also gives the information about the tendency of a species to gain electrons and act as an oxidizing agent. Greater the value of standard reduction potential of a given species greater is its tendency to accept electrons to undergo reduction and to act as an oxidizing agent.

Example

1. Ions like Au^{3+} , Pt^{2+} , Hg^{2+} , Ag^{+} , Cu^{2+} and the nonmetal elements like F_2 , Cl_2 , Br_2 and I_2 which lie below the SHE have a strong tendency to gain electrons and undergo reduction.
2. Strong oxidizing agents like F_2 , Cl_2 , Br_2 , etc. have a large positive value of standard reduction potentials
3. Strong reducing agents have large negative values like Li, K, Ca, Na which lie above SHE.

4. Relative Chemical Reactivity of Metals

Greater the value of standard reduction potential of a metal, smaller is its tendency to lose electrons to change into a positive ion and hence lower will be its reactivity.

Examples

1. Metals like Li, Na, K and Rb are highly reactive.
2. Coinage metals, Cu, Ag, and Au are the least reactive because they have positive reduction potentials.
3. Metals like Pb, Sn, Ni, Co and Cd which are very close to SHE react very slowly with steam to liberate hydrogen gas.
4. Metals like Fe, Cr, Zn, Mn, Al and Mg which have more negative reduction potentials react with steam to produce the metallic oxides and hydrogen gas.

5. Reaction of Metals with Dilute Acids

Greater the value of standard reduction potential of a metal, lesser is its tendency to lose electrons to form metal ions and so weaker is its tendency to displace H^{+} ions from acids as H_2 gas.

Examples

1. Metals like Au, Pt, Ag and Cu which have sufficiently high positive values of reduction potentials do not liberate hydrogen gas from acids.
2. Metals like Zn, Mg and Ca which are close to the top of the series and have very low reduction potentials liberate hydrogen gas when they react with acids.

6. Displacement of One Metal by Another from its Solution

One metal will displace another metal from the aqueous solution of its salt if it lies above in the electrochemical series.

Examples

Fe can displace Cu from CuSO_4

Zn does not displace Mg from MgSO_4

Modern Batteries and Fuel Cells

Lead Accumulator or Lead-Acid Battery

It is commonly used as a car battery. It is secondary or a storage cell.

Principle of working and battery design

Passing a direct current through it must charge it. The charged cell can then produce electric current when required. When the two electrodes are connected through an external circuit, it produces electricity by discharge. A single cell provides around 2 volts. For 12 volts, 6 cells are connected in series. Each cell contains two lead grids packed with the electrode materials. The grid is immersed in an electrolytic solution of $\approx 3.2\text{M}$ H_2SO_4 (30%). Fibre glass sheets between the grids prevent shorting by accidental physical contact.

Cathode

The cathode of a fully charged lead accumulator is lead oxide, PbO_2

Anode

Anode is metallic lead.

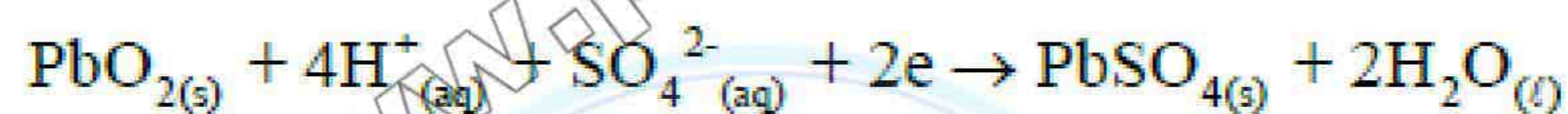
Electrolyte

The electrolyte is 30% sulphuric acid solution (density 1.25 g cm^{-3}).

Discharging

At the anode the lead atoms release two electrons each to be oxidized to Pb^{2+} ions, which combine with SO_4^{2-} ions present in the electrolyte and get deposited on the anode as PbSO_4 .

Cathode (reduction)



Anode (oxidation)



Overall reaction



Explanation of discharging

The electrons released pass round an external circuit as an electric current to be used for starting the engine of a vehicle, for lighting up of car lights and so on. At the cathode the electrons from the anode are accepted by PbO_2 and hydrogen ions from the electrolyte then undergo a redox reaction to produce lead ions and water. The Pb^{2+} ions then combine with the SO_4^{2-} ions and they both deposit at the cathode as PbSO_4 . When both electrodes are completely covered with PbSO_4 deposits the cell will cease to discharge any more current until it is recharged. When the cell is discharged, it generates electrical energy as a voltaic cell.

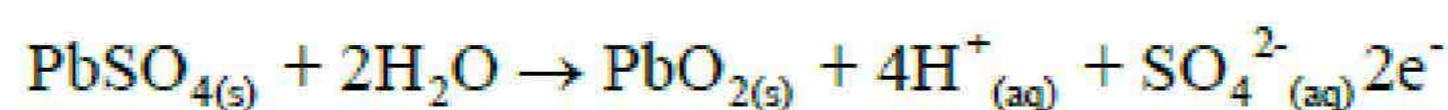
Recharging

During the process of recharging, the anode and the cathode of the external electrical source are connected to the anode and the cathode of the cell respectively. The redox reactions at the respective electrodes are then reversed.

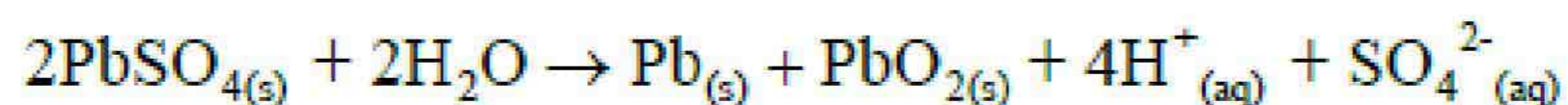
Anode (reduction)



Cathode (oxidation)



Overall reaction



Explanation of recharging

During the process of discharging the concentration of the acid falls decreasing its density to 1.15g cm^3 . After recharging the acid is concentrated again bringing its density to its initial value of 1.25g cm^3 . The voltage of the battery returns to around 12 volts.

Fuel Cells

Definition

Fuel cells are other means by which chemical energy may be converted into electrical energy. The cell runs continuously till the reactants are supplied. Fuel cells are light, portable and sources of electricity. Many fuel cells do not produce pollutants. Fuel cells are very efficient. They convert about 75% of fuels bond energy into electricity.

Principle of working

When gaseous fuels, such as hydrogen and oxygen are allowed to undergo a reaction, electrical energy can be obtained. This cell finds importance in space vehicles. The electrodes are hollow tubes made of porous compressed carbon impregnated with platinum, which acts as a catalyst. The electrolyte is KOH. At the electrodes, hydrogen is oxidized to water and oxygen is reduced to hydroxide ions.

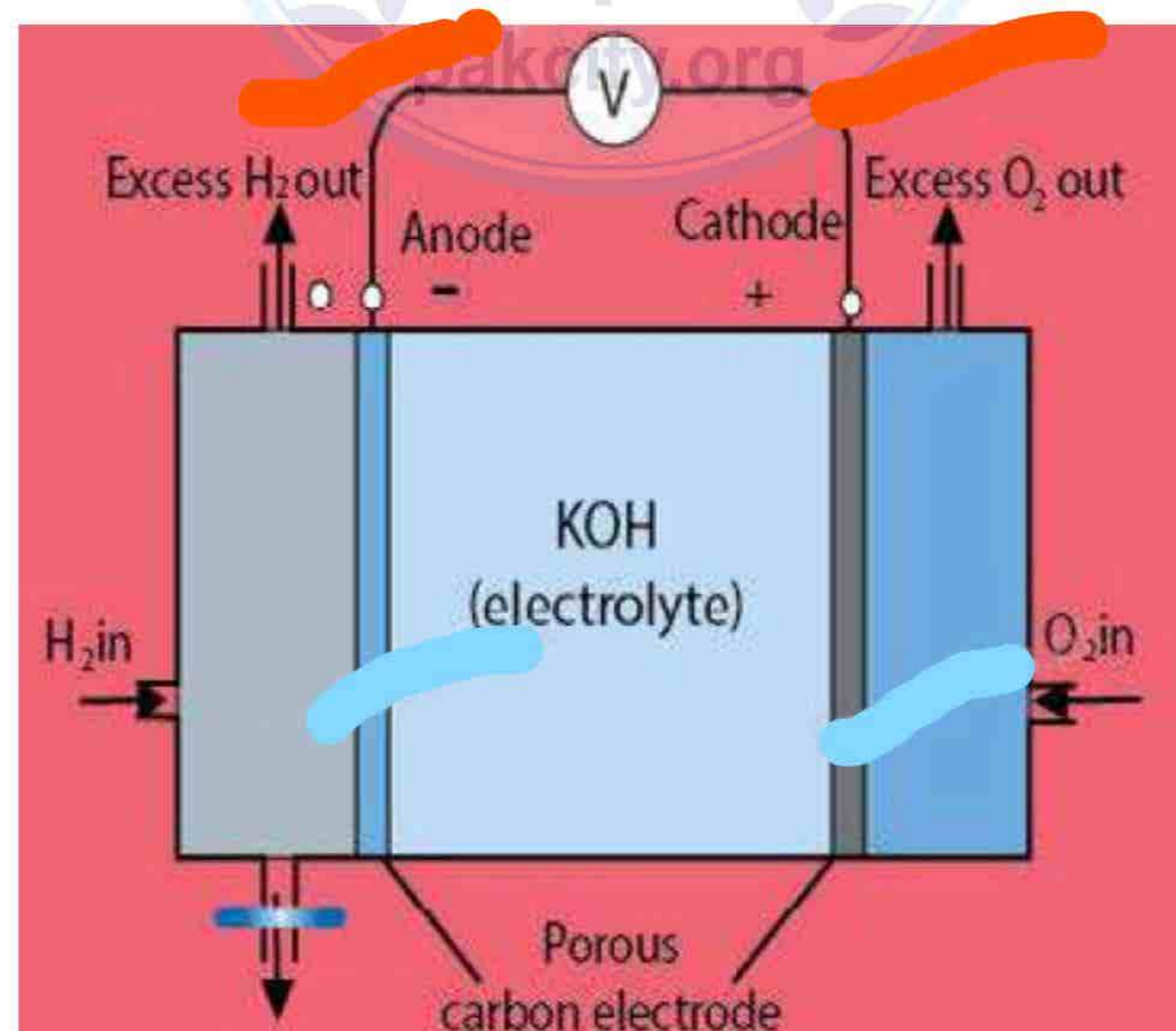
Anode



Cathode



Overall reaction



Water for drinking purpose

This fuel cell is operated at a high temperature so that the water formed as a product of the cell reaction evaporates and may be condensed and used as drinking water for an astronaut.

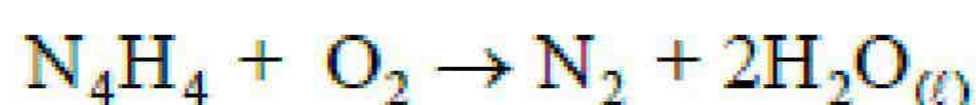
Power generation

A number of these cells are usually connected together so that several kilowatts of power can be generated.

The fuel cells produce electricity and pure water during space flights.

Other fuel cell reactions

Some other cell reactions in fuel cell are:



Important long questions from past papers

33. Define electrochemical series? Explain its any three applications.
34. Explain the structure and function of voltaic or galvanic cell.
35. How can you measure electrode potential of an element using standard hydrogen electrode (SHE)?
36. Describe the construction and working of standard hydrogen electrode?
37. What is standard hydrogen electrode (SHE)? How it is used to measure the electrode potential of Zinc.
38. Describe the electrolysis of molten sodium chloride and a concentrated aqueous solution of sodium chloride.
39. Explain the construction and working of fuel cell.
40. Write a note on fuel cells.
41. Give explanation of discharging and recharging of lead accumulator along with reactions occurring at electrodes.

