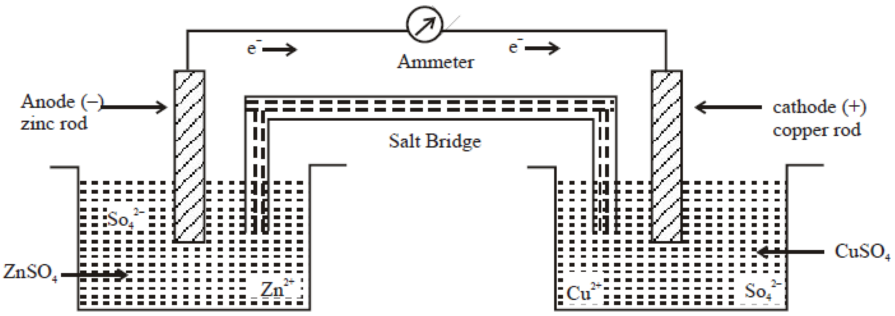
UNIT-2

ELECTRO CHEMICAL ENERGY SYSTEMS

Galvanic Cell: It is one in which electrical current is generated by a spontaneous redox reaction.

A bar of zinc metal (anode) is placed in $ZnSO_4$ solution in the left container. A bar of copper (cathode) is immersed in $CuSO_4$ solution in the right container. The zinc and the copper electrodes are joined by a copper wire. A salt bridge containing potassium sulphate solution connects the solutions in the anode compartment and the cathode compartment.



The oxidation half reaction occurs in anode compartment is

$$Zn \rightarrow Zn^{++} + 2e^-$$

And reduction half reaction takes place in cathode compartment as

$$Cu^{++} + 2e^- \rightarrow Cu$$

When the cell is setup, electrons flow from zinc electrode through the wire to the copper cathode. Zinc dissolves in the anode solution to form Zn^{2+} ions. The Cu^{2+} ions in the anode half-cell pick up electrons and are converted into atoms at cathode. At the same time SO_4^{2-} ions from cathode half-cell migrates to the anode half-cell through the salt bridge. Zn^{2+} ions from the anode half-cell move into cathode half-cell. This is the flow of ions from one h-half- cell to other complete the electrical circuits which insures continuous supply of current.

Definition:

From the above example it follows that “An arrangement for producing an electric current through the agency of an oxidation-reduction is known as an electro chemical cell, chemical cell, galvanic cell or a voltaic cell”.

Electrochemical conventions:

Certain conventions and notations are followed regarding the electrochemical cells which are as follows:

1. A half-cell, such as strip of Zinc immersed in a solution of Zn^{2+} ion of concentration m is indicated as:

$$Zn/Zn^{2+}\ (m)$$

The vertical line denotes a solid phase in contact with a liquid phase.

2. A galvanic cell may be represented as

$$Zn/Zn^{2+}\ (m)\ ||\ Cu^{2+}\ (m)/Cu$$

The two vertical lines in between two half cells represent the salt bridge.

3. The electrode potential is given a positive sign if the electrode reaction involves reduction and a negative sign if the electrode reaction involves oxidation.

Reduction: $Zn^{2+} + 2e^{-} \rightarrow Zn$

Oxidation: $Zn \rightarrow Zn^{2+} + 2e^{-}$

4. The E.MF of a cell is the algebraic sum of the potential of the two half cells. For example, in a general cell

$$A\ |\ A^{+}\ ||\ B^{+}\ |\ B$$

The E.M.F of the cell is given by the potential difference of two electrode i.e.

E_{cell} = $E_{(right)}$– $E_{(left)}$

= {Reduction potential of right hand electrode} – {Reduction potential of left hand electrode}

= $E_{cathode}$ – E_{anode}

Other convention used is

i) E_{cell} = oxidation potential of anode – oxidation potential of cathode

In short, $E_{cell} = E_{anode} - E_{cathode}$

ii) E_{cell} = Oxidation potential of anode + Reduction potential of cathode.

If cell potential (E_{cell} is positive, the reaction is spontaneous.

Further, the more positive the value of E_{cell} is, the more faster the reaction is. In case the value of cell potential is negative, the reaction will not take place spontaneously as written. However, the reaction will take place.

Electro Chemical series: Arrangement of metals in the order of decreasing tendency of their atoms to give electrons (i.e. undergo oxidation) is known as electro chemical series. Table 1.1 .is also the arrangement of metals when arranged in the order of their electrode potentials.

Electrode	Half Cell Reaction	Standard Oxidation E^0 Volts	Potential at 25^0C
Li/Li^+	$Li \rightarrow Li^+ + e^-$	+3.045	Active Anodic
K/K^+	$K \rightarrow K^+ + e^-$	+2.925	
Ca/Ca^{2+}	$Ca \rightarrow Ca^{2+} + 2e^-$	+2.870	
Na/Na^+	$Na \rightarrow Na^+ + e^-$	+2.714	
Mg^{2+}/Mg	$Mg \rightarrow Mg^{2+} + 2e^-$	+2.370	
Zn/Zn^{2+}	$Zn \rightarrow Zn^{2+} + 2e^-$	+0.763	
Fe/Fe^{2+}	$Fe \rightarrow Fe^{2+} + 2e^-$	+0.440	
Cd/Cd^{2+}	$Cd \rightarrow Cd^{2+} + 2e^-$	+0.403	

Pb/Pb^{2+}	$Pb \rightarrow Pb^{2+} + 2e^-$	+0.126	
$Pt/H_2/2H^+$	H_2(1 atm) $\rightarrow 2H^+ + 2e^-$	+0.000	
Cu/Cu^{2+}	$Cu \rightarrow Cu^{2+} + 2e^-$	-0.337	Noble Cathode
Ag/Ag^+	$Ag \rightarrow Ag^+ + e^-$	-0.799	
$Pt/Cl^-/Cl_2$	$2Cl^- \rightarrow Cl_2 + 2e^-$	-1.36	
Au/Au^{3+}	$Au \rightarrow Au^{3+} + 3e^-$	-1.50	

Applications of Electromotive Series:

i) The electrochemical series offers a means of predicting the chemical behaviour of different elements. Thus the alkali metals which occupy the top positions of the list are the most reactive of all metals. They can decompose even in cold water, with the evolution of hydrogen.

ii) The electrochemical series offers method of studying the displacement reactions. Thus a metal which is placed higher up in the series will displace all metals which are kept below it from solutions of their salts. For example, Zinc can displace Copper and Silver from their salts.

iii) From the values of standard electrode potentials as seen from the electrochemical series, E.M.F of the cell can be calculated.

iv) The relative corrosion tendencies of the metals and alloys can be explained by the means of the series.

Single electrode potential

Each cell is made up of two electrodes, at one electrode oxidation takes place i.e. electrons are evolved. At the other electrode reduction takes place i.e. electrons are taken up. Each electrode is regarded as a half cell. The tendency of an electrode to lose or gain electrons when it is in contact with its own ions in solution is called electrode potential.

It is not possible to determine experimentally the potential of a single electrode (i.e. of a half cell). It is only the difference of potentials between two electrodes that we can measure by combining them to give a complete cell. By arbitrarily fixing potential of one electrode zero, it is possible to assign numerical values to potentials of the various other electrodes. Since the potential of the reference electrode is known, that of the other electrode can be easily obtained.

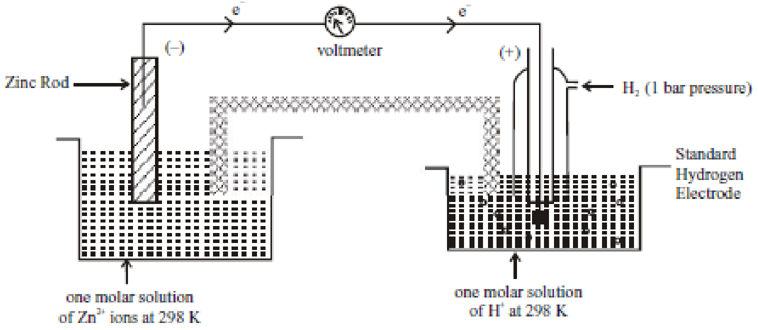


Fig. 15.9 : *Measurement of standard electrode potential of Zn/Zn^{2+} electrode*

The two commonly reference electrodes are the standard hydrogen electrode and calomel electrode.

Standard hydrogen electrode (Normal Hydrogen electrode):

By convention, the potential of this electrode (standard or normal hydrogen electrode) when hydrogen is passed at one atmospheric pressure through a solution of hydrogen ions of unit concentration is arbitrarily fixed as zero.

It consists of a platinum foil coated with platinum black which [consists of a platinum foil] absorbs hydrogen gas. A platinum wire welded to the electrode surrounded by an glass tube is placed in 1M solution of the Hcl, Pure H_2 gas, is passed at 1 atmospheric pressure through the inlet of the glass tube. Small amount of the gas is absorbed by the electrode while the remaining escapes.

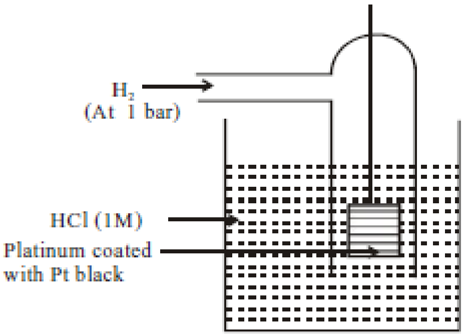


Fig. 15.8 : *Standard Hydrogen electrode*

When it acts at anode oxidation occurs.

$$H_2 \rightarrow 2H^+ + 2e^-$$

When it acts as cathode, reduction occurs.

$$2H^+ + 2e^- \rightarrow H_2$$

The electrode is represented as

$$Pt, H_2\ (1\ atm)/H^+\ (1M)$$

The only practical difficulty in setting this electrode is the maintenance of the pressure of the gas uniformly at one atmosphere and the activity of the hydrogen ions at one gram ion per litre.

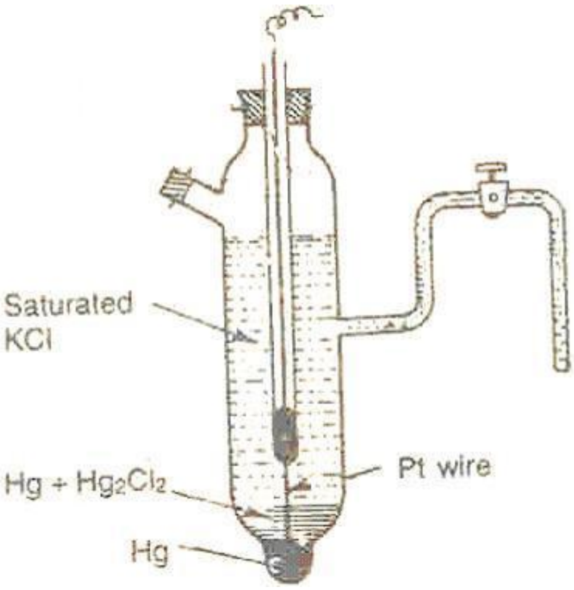
2. Calomel Electrode:

Mercury of high degree of purity is placed at the bottom of a glass tube with a side tube on both the sides. It is connected to the outer circuit by means of a platinum wire sealed in a glass tube. The surface of mercury is covered with a paste of mercurous chloride (calomel). A saturated, normal or decinormal Potassium chloride solution is introduced through the side tube present in the right side.

If this electrode acts as anode i.e., when oxidation takes place at the electrode, the electrode gives mercurous ions (Hg_2^{2+}) into solution with the liberation of electrons. These Hg_2^{2+} ions combine with chloride ions (from KCl) to form sparingly soluble mercurous chloride with the result the concentration of chloride ions falls in the solution.

$$2Hg(l) \rightleftarrows Hg_2^{2+} + 2e^-$$

On the other hand, when the electrode acts as cathode i.e. when reduction occurs, the mercurous ions given by Hg_2Cl_2 would be discharged at the electrode. Hence more and more of the mercurous chloride (calomel) pass into solution which results in an increase in the concentration of chloride ions.



$$Hg_2Cl_2(s) \rightleftarrows Hg_2^{2+} + 2Cl^-$$

This electrode is connected with the help of the side tube on the left through a salt bridge with the other electrode, the potential of which is to be determined.

The potential of the calomel electrode depends upon the concentration of the Potassium Chloride solution. It has been accurately determined by connecting it to a standard hydrogen electrode and the results obtained for the reduction potential of this electrode (Hg/Hg_2Cl_2) for different concentrations of potassium chloride at 25^0C is

for saturated KCl solution electrode potential is 0.2415 Volts

for 1N KCl standard reduction potential is 0.28 Volts for 0.1N KCl solution the reduction potential is 0.3338 Volts.

Nernst equation:

Electrode potential depends on the concentration of metallic ions in solution, the variation of electrode potential with concentration of metallic ion solution is given by Nernst equation.

The reduction reaction for an electrode in a general way can be written as

$$M^{n+} + ne^{-} \rightarrow M$$

According to Nernst equation

$$\mathrm{E} = \mathrm{E}^{0} - \frac{2.303\ \mathrm{RT}}{\mathrm{nF}} \log \frac{[\mathrm{M}]}{[\mathrm{Mn}+]}$$

Where, E = Electrode potential of the metal

E^0 = Standard electrode potential

R = Gas constant (8.314 Joules per mole per degree abs.)

T = Absolute temperature

n = No. of electrons involved in the half cell reaction

F = One faraday (96500 Columbs)

[M] = Activity of metal in the metal phase and is taken as unity for pure metals.

$[M^{n+}]$ = Activity of metal ions in the solution and is taken equal to their molarities

At 298K, $\mathrm{E} = \mathrm{E}^{0} - \frac{0.059}{\mathrm{n}} \log \frac{[\mathrm{M}]}{[\mathrm{M}]}$

$$= \mathrm{E}^0 - \frac{0.059}{\mathrm{n}} \log \frac{[\mathrm{Products}]}{[\mathrm{Reactants}]}$$

Concentration Cells:

A cell in which electrical energy is produced by the transference of a substance from a system of high concentration to one at low concentration is known as concentration cell.

Concentration cells may be divided into two main types.

(a) **Electrode concentration cell:** These are the cells in which the two electrodes are of different concentrations and are dipped in the same solution of their salt i.e. the electrolyte of only one concentration.

(b) **Electrolyte concentration cells:** These are the cells in which the two electrodes are of the same material which are dipped into two solutions of same electrolyte through of different concentrations.

Electrode concentration cell:

This is a cell in which two hydrogen electrodes at partial pressures P_1 and P_2 are dipped in the same solution of hydrogen ions. The potential of such type of cells depends upon the pressure of the gases and the concentration of their ions in solution.

When the cell operates, the oxidation will take place at the left hand electrode

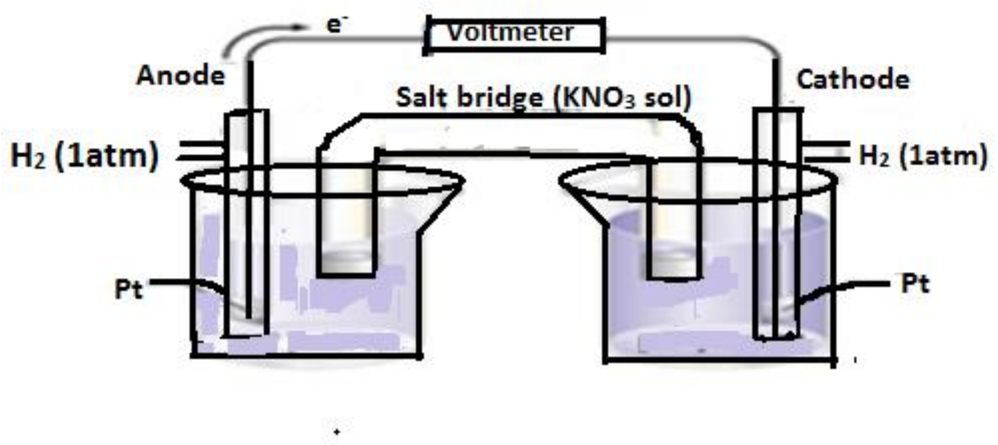
$$H_2\ (P_1) \rightleftarrows 2H^+ + 2e^- \text{ (Oxidation reaction)}$$

Similarly, the cell reaction taking place on right hand electrode is reduction is represented as

$$2H^+ + 2e^- \rightleftarrows H_2\ (P_2) \text{ (Reduction reaction)}$$

There is only transfer of hydrogen gas from electrode with pressure (P_1) to the electrode with pressure (P_2). The E.M.F of electrode depends only on the two pressures and independent of concentration of hydrogen ions in which electrodes are immersed

$$E_{cell} = \frac{RT}{2F}\log\left(\frac{P_1}{P_2}\right)$$



Electrolyte concentration cell:

It consists of two identical electrodes dipped into two electrolytes having different concentrations. It consists of two silver electrodes, one immersed in 0.1M Silver nitrate solution and the other in 1M solution of the same electrolyte. The two solutions are in contact through a salt bridge.

Electrons flow from the electrode in dilute solution (0.1M) to that in more concentrated (1M) solution and transfer of material takes place from high concentration to low concentration.

Cell can be represented as $Ag/Ag^+ (c_1) \| Ag^+ (c_2)/Ag$

When the cell operates at the left hand side electrode, oxidation takes place and electrons are given

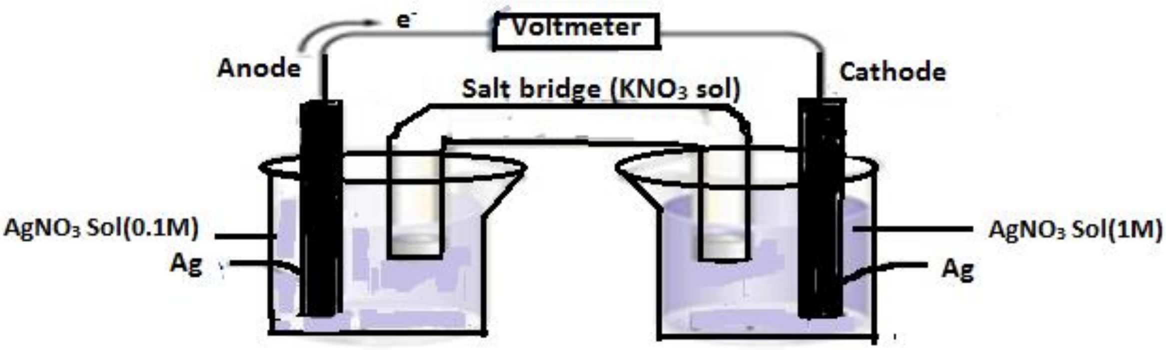
$Ag \rightarrow Ag^+ + e^-$ (Oxidation) Anode

Similarly the cell reaction taking place on right hand electrode is reduction taking of electrons is represented as

$Ag^+ + e^- \rightarrow$ Ag (Reduction) Cathode

Eventually the solution in the two compartments will have equal Ag^+ ion concentration and there will be no E.M.F recorded. Therefore the E.M.F of the cell is given as

$$E = E^0 + \frac{0.0591}{n} \log_{10} \frac{c_1}{c_2}$$



Glass **Electrode:**

It is the most useful and versatile electrode used for P^H measurement.

Principle: When two solutions of different hydrogen ion concentrations are separated by a glass membrane, a potential difference develops across the glass membrane. The magnitude of the potential difference depends upon the difference in the concentration of the hydrogen ions in the two solutions.

A glass electrode consists of a thin walled bulb of p^H sensitive glass (special type of membrane having approximate composition of 72% SiO_2 , 22% Na_2O and 6% CaO) sealed to a stem of non- pH sensitive high resistance glass. Inside the glass electrode is a silver-

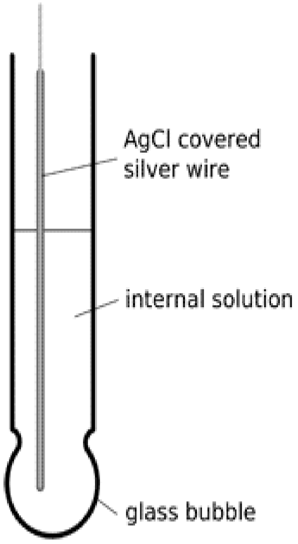
silver chloride electrode or calomel electrode or simply a Pt wire dipped in 0.1 N HCl solution.

This glass electrode is dipped in a solution of varying hydrogen ion concentration (unknown pH) and is connected to an external reference electrode ,usually a calomel electrode with the help of a salt bridge.

The cell may be represented as

Ag, AgCl, 0.1N HCl / Glass / Experimental solution / KCl, $Hg_2Cl_2(s)$, Hg

Pt, 0.1N HCl / Glass / Experimental solution / KCl, $Hg_2Cl_2(s)$, Hg



Batteries:

Battery is basically a galvanic cell where the chemical energy of a redox reaction is converted into electrical energy. This energy is stored in the cell and can be used when required. There are mainly two types of batteries. These are

i) Primary Batteries

ii) Secondary Batteries

i) **Primary Batteries (or Primary Cells):** In these batteries, the cell reaction is irreversible. Once the cell reaction has taken place and the reactants have been converted into products, the cell gets discharged and cannot be used again.

ii) **Secondary Batteries (or Secondary Cells):** In these batteries, the cell reaction is reversible. Once the forward reaction occurs and the cell is discharged, it can be charged again by applying external potential.

Primary Batteries:

1. **Dry Battery (Leclanche Cell):**

The cell consists of a zinc container and acts as the anode. The cathode is a carbon (graphite) rod surrounded by powdered manganese dioxide and carbon. The space between the electrodes is filled by ammonium chloride (NH_4Cl), zinc chloride ($ZnCl_2$) to which starch is added to make a thick paste.

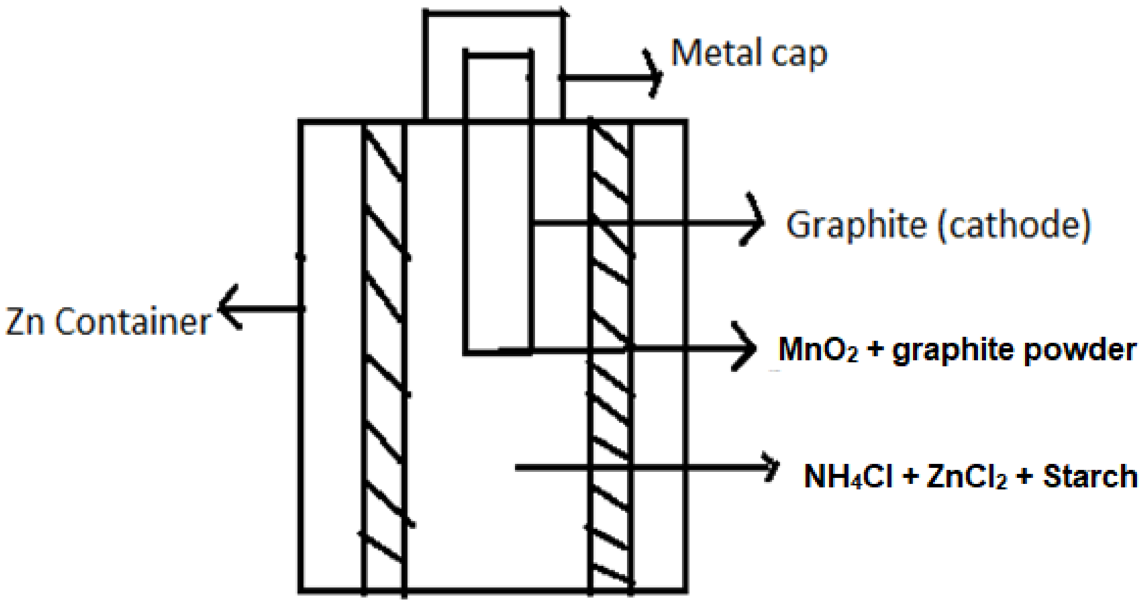
Cell reactions are

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

Cathode: $2Mno_2(s) + 2NH_4^+ (aq) + 2e^- \rightarrow 2NH_3 (aq) + Mn_2O_3 (s) + H_2O (l)$

Net cell reaction: $Zn(s) + 2NH_4^+ + 2Mno_2(s) \rightarrow Zn^{2+} (aq) + 2NH_3 + Mn_2O_3 (s) + H_2O$

Ammonia liberated reacts with Zn^{2+} to form a complex $[Zn (NH_3)_2]^{2+}$. The cell is a primary cell and gives a voltage of 1.5V. Gradually, the products are formed and the cell voltage drops.



Uses:

1. These are used in transistors, radios, watches, tap recorders, toys, portable electronic gadgets.

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LITHIUM BATTERIES:

In lithium cells ,lithium metal acts as the anode due to its light weight ,lower electrode potential and good conductivity ,lithium cells are safer ,cheaper and non - toxic that exhibit high performance .

Lithium cells are primary batteries that use lithium metal or lithium compounds as anode. Lithium-ion batteries are Rechargeable batteries in which lithium ions move between the anode and the cathode .It can produce voltage from 1.5V to 3.7V.

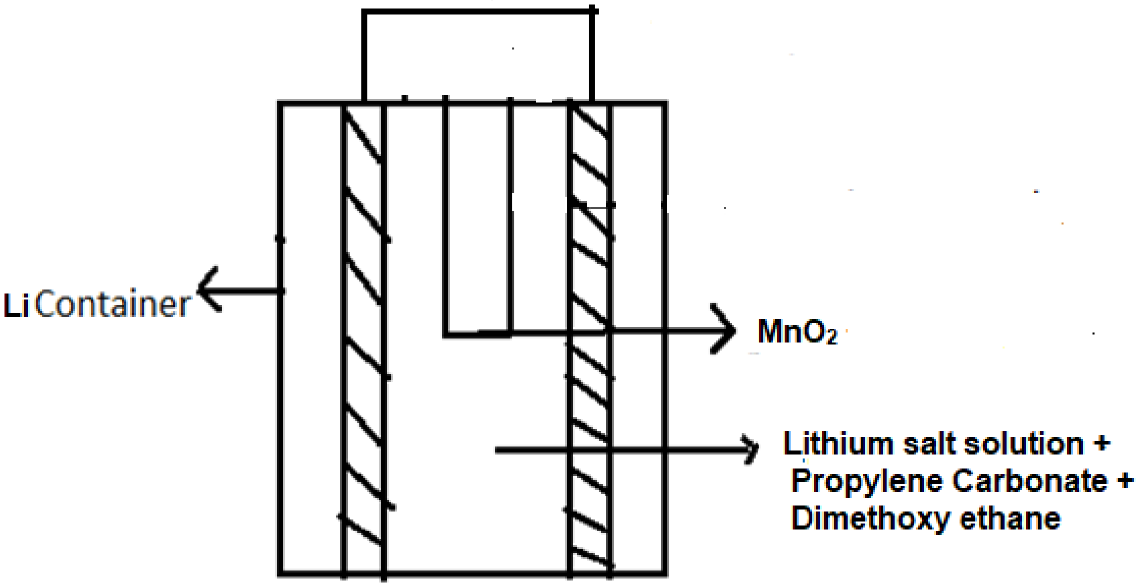
a. **Lithium Cells:** These are primary batteries that cannot be recharged. In these batteries lithium metal or lithium compounds are used as anode. The cathode is made of specially treated MnO_2 crystals obtained by special heat treatment. Since lithium is highly reactive with water hence these solvents cannot be used as electrolyte. Hence lithium salt solution in propylene carbonate and Dimethoxy salts is used as the electrolyte. Solvents like thionyl chloride containing lithium compounds ($LiCl$, $LiClO_4$) can also be used.

Cell reactions are

At anode: $Li \rightarrow Li^+ + e^-$

At cathode: $MnO_2 + Li^+ + e^- \rightarrow LiMnO_2$

Net cell reaction: $Li + MnO_2 \rightarrow LiMnO_2$



Uses

1) Used in clocks, calculators, toys, digital cameras, watches.

2) Medical equipments like artificial pacemakers, thermometers, etc.

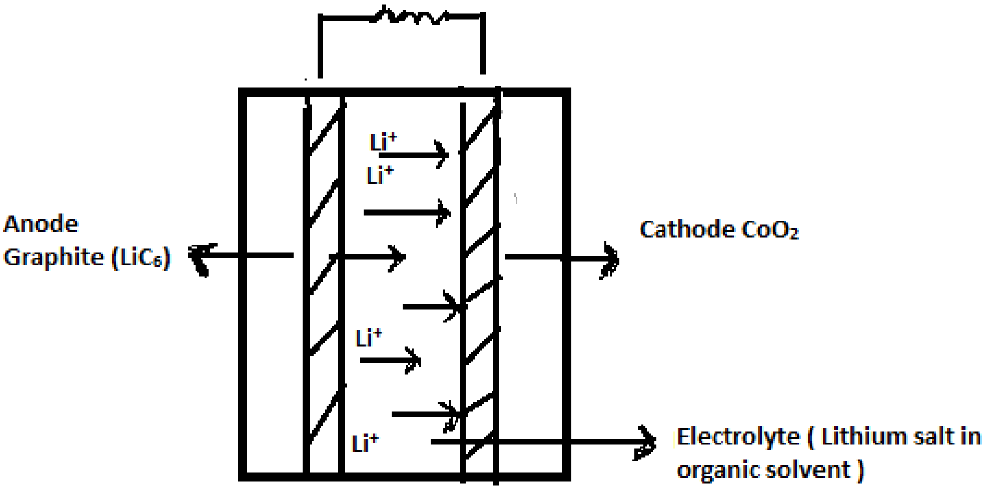
Lithium Ion Cell:

These are secondary rechargeable batteries where lithium acts as cathode and graphite acts as anode. These is migration of only lithium ions between the two electrodes through a lithium-based salt as an electrolyte ($LiPF_6$ or $LiBF_4$ dissolved in ethylene carbonate).Both the electrodes allow lithium ions to migrate towards and away from them. When a lithium-ion cell discharges, the positive ion is extracted from the negative electrode, i.e Graphite and inserted into the positive electrode,i.e intercalated lithium compound . During charging the reverse occurs

Anode: At Anode: $LiC_6 \rightarrow C_6 + Li^+ + e^-$

Cathode: $CoO_2 + Li^+ + e^- \rightarrow LiCoO_2$

Net reaction: $LiC_6 + CoO_2 \rightarrow C_6 + LiCoO_2$



Secondary Cells:

Most of the commercial batteries are not able to meet the performance requirements of many applications. Thus, a continual need exists for both the conventional battery technology with improved performance and advance battery technologies with characteristics such as high energy level, long life, low cost, no maintenance and safety. Chemical reactions in secondary cells are reversible. They can be recharged.

Eg: Zn – air battery, Nickel – metal hydride cell

1) Zinc air battery:

In Zinc air battery, the anode is made of Zinc plates a perforated carbon plate treated with water repellent acts as a cathode. Sodium hydroxide or Potassium hydroxide is used as an electrolyte. The anode, cathode and the electrolyte are contained in an ebonite or polymeric case. At the anode, Zinc reacts with electrolyte to form Zincate ions which decay into Zinc oxide and water. The electrons released at the anode travel to the cathode where oxygen of the air accepts the electrons to form hydroxide ions.

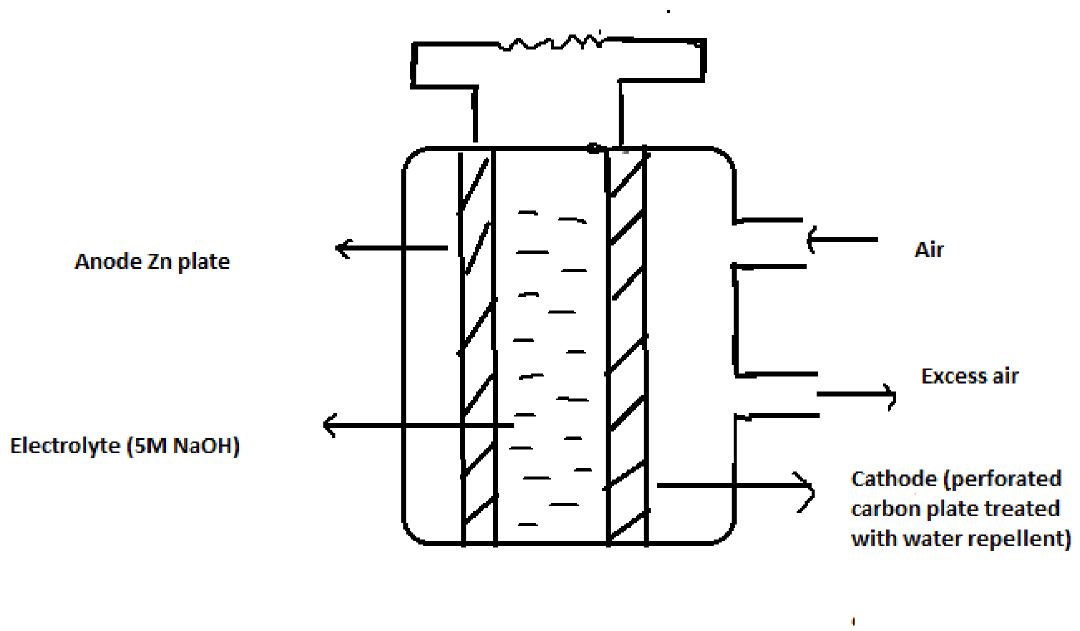
Cell reactions are

At Anode: $2Zn(s) + 4OH^-_{(aq)} \rightarrow 2Zno(s) + 2H_2O(l) + 4e^-$

At Cathode: $O_2\,(g) + 2H_2O\,(l) + 4e^- \rightarrow 4OH^-_{(aq)}$

Net cell reaction $2Zn(s) + O_2\,(g) \rightarrow 2Zno\,(s)$

They produce 1.65 Volts. Zinc air batteries have the properties of both fuel cell and batteries. They are electrically non-rechargeable,however they can be recharged mechanically by converting the Zinc oxide produced in the battery back into Zinc metal.



Uses:

1) They are very cheap
2) Small button size cells are used in watches and in hearing aids.
3) Large batteries are used in cameras and also for the electric propulsion of vehicles.

Challenges of battery technology:

The technology that is most important is battery that can be used as power source that can lead to the electric vehicle revolution.

The sources of sustainable energy for electricity production requires the availability of suitable technology for energy storage namely batteries. Hence the development of batteries that can store sustainable energy with long term stability, very prolonged cycle life and meeting environmental constrains is an important challenge for modern batteries.

Lithium ion batteries are one of the most advanced rechargeable batteries. They are currently the dominant mobile power sources for portable electronic devices exclusively used in cell phones, computers ,laptops. The Li-ion batteries increases rapidly especially with the demand from electric powered vehicle. Li-ion batteries will also be employed to buffer the intermittent and fluctuating green energy supply from renewable resources such as solar and wind another important aspect of Li-ion battery is related to battery safety .

Li-ion batteries will still be dominated in the rechargeable battery market, at least for the next decade, for the advantages they offer.

1. They can be formed into a wide variety of shapes and sizes so as to efficiently fit the available space in the device they power.

2. They don't suffer from the problem of effect.

3. They have a voltage nearly three times the values of typical Ni based batteries.

4. The self-discharge rate is very low

It is also sometimes dangerous if something goes away with the separator , and electrodes come in contact with one another the battery starts to heated up .And liquid electrolytes are highly flammable this leads to explosion in batteries .Some of the solutions being worked to introduce alternative materials that increase the efficiency and thermal stability of batteries

FUEL CELLS

A fuel cell is a device that converts the chemical energy of a fuel (hydrogen, natural gas, methanol etc) and an oxidant (air or oxygen) into electricity. A fuel cell also has two electrodes and an electrolyte. The fuel and oxidising agent are continuously and separately fed into their respective electrodes, at which they undergo redox reactions generating electrical energy.

Fuel + Oxidant → Oxidation products + electricity

A fuel cell may be represented as

Fuel / electrode / electrolyte / electrode / oxidant.

Fuel cells are basically divided into five types on the basis of electrolyte used:

1) Alkaline fuel cell – An aqueous solution of KOH.
2) Phosphoric Acid fuel cell – phosphoric acid.
3) Polymer Electrolytic membrane fuel cell – Polymer perfluoro sulfonated acid.
4) Molten carbonate fuel cell – A solution of lithium, sodium and potassium carbonates.
5) Solid oxide fuel cell – Yettria stabilized zirconia.

Based on their operating temperatures, Fuel cells are of three types :

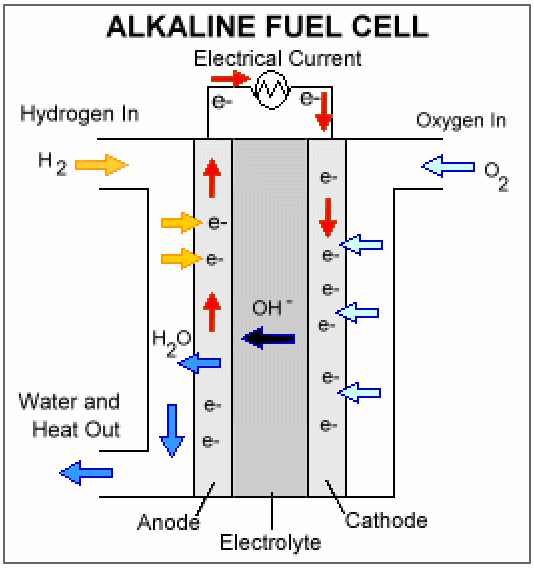
1) Low temperature fuel cells: These operate at temperatures of about 75^0C with water - based electrolytes.
2) Moderate -Temperature fuel cells : These operate at temperatures of about 600^0C ,with salt-based electrolytes.
3) High -Temperature fuel cells: These operate at temperatures ranging 600^0C -1000^0C with solid or ceramic -based electrolytes.

1) **Hydrogen – Oxygen fuel cell**: It consists of two porous carbon electrodes. The electrodes are placed in the aqueous solution of NaOH or KOH which acts as an electrolyte. Hydrogen and oxygen are supplied at anode and cathode. The gases diffuse at respective electrodes. Anode is a porous carbon electrode coated with a nickel/platinum catalyst and cathode is porous carbon impregnated with Ag catalyst.

At anode: $2H_2 \rightarrow 4H^+ + 4e^-$ (Oxidation)

At cathode: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ (Reduction)

Net reaction is $2H_2\,(g) + O_2\,(g) \rightarrow 2H_2O\,(l)$



Applications:

1) The cell gives a voltage of nearly 1.2 volts.

2) It is used in space craft and military for uninterrupted power supply

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propane and Oxygen Fuel Cell :

The fuel cell consists of an anode made up of Nickel acts as anode .The cathode is made up of silver. Nickel electrode acts as electro catalyst which provides the necessary surface for the initial decomposition of the molecules into atomic species. In this cell, the electrolyte consists of a layer of solid polymer which allow the transmission of proton from one electrode to another. A stream of propane is allowed to enter the anode side. At the anode side, it is catalytically split into protons and electrons. The newly formed protons permeate through the polymer electrolyte membrane to the cathode side. The electrons travel along an external circuit having load to the cathode side, thus generating current. Simultaneously a stream of oxygen is delivered to the cathode which react with .protons permeating through the polymer electrolyte membrane and electrons arriving in the external circuit to form water molecules.

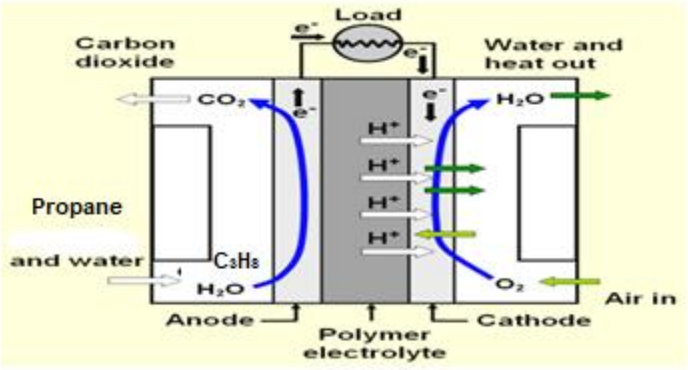
Anode : $C_3H_8 (g) + 6H_2O (l) \rightarrow 3CO_2(g) +20 H^+ (aq) +20 e^-$

Cathode : $5 O_2 (g) + 2 OH^+ (aq) +20 e- \rightarrow 10 H_2O (l)$

Net reaction : $C_3H_8 (g) + 5 O_2 (g) \rightarrow 3CO_2 (g) + 4 H_2O (l)$

Applications:

1. Propane-oxygen fuel cells are easy to transport.
2. These are stable at all environmental conditions.



Merits Of Fuel Cell :

1) The energy conversion is highly efficient (75 to 82.8 %) by fuel cells;
2) Fuel cell produces drinking water of potable quality;
3) Noise and thermal pollution are low;

4) They offer excellent method for efficient use of fossil fuels and thus save fossil fuels.

5) They have low maintenance costs.

6) Fuel cells are regenerative used as energy storage system for space applications.

Limitations of Fuel cells:

1) Life time of fuel cell is not known accurately.

2) Their initial cost is high.

3) There is lack of infrastructure for the distribution of hydrogen.

Solved Examples

1) Calculate the standard EMF of a cell which involves the following cell reaction $Zn + 2Ag^+ \rightarrow Zn^{2+} + 2Ag$

Given that E^0 (Zn^{2+}, Zn) = -0.76 Volt

E^0 (Ag^+, Ag) = 0.80 Volt

Ans: At Anode (left hand side) $Zn \rightarrow Zn^{2+} + 2e^-$

At Cathode (Right hand side) $2Ag^+ + 2e^- \rightarrow 2Ag$

$E^0 = E^0_{right} – E^0_{left}$

$= 0.80 – (–0.76)$

$= 1.56$ Volts

2) Can a solution of 1M $CuSo_4$ be stored in a vessel made of nickel metal? Give thatE^0 (Ni^{2+}, Ni) = -0.25 Volt

E^0 (Cu^{2+}, Cu) = +0.34 Volt

Sol: $E^0 = E^0_{right} – E^0_{left}$

$= 0.34 – (–0.25)$

$= 0.59$ Volt

Thus EMF of the cell is positive hence $CuSo_4$ reacts with nickel. Hence $CuSo_4$ cannot be stored in nickel vessel.

3) Calculate the EMF of a Daniel cell, when the concentration of $ZnSo_4$ and $CuSo_4$ are 0.001M and 0.1M respectively. The standard potential of the cell is 1.2 Volts.

Sol: cell is $Zn(s)/Zn^{2+}$ (0.001 M) || Cu^{2+} (0.1M) | Cu(s)

$$E_{cell} = E^0_{cell} - \frac{0.0591}{n}\log\frac{[Cu^{2+}]}{[Zn^{2+}]}$$

$$E_{cell} = 1.2 - \frac{0.0591}{2}\log\frac{0.1}{0.001}$$

$$= 1.2 + \frac{0.0591}{2} \times 2$$

$$= 1.2 + 0.0591$$

$$= 1.2591 \text{ Volts}$$

4) Calculate the equilibrium constant for the reaction

$Zn + Cd^{2+} \rightleftarrows Zn^{2+} + Cd$ [$E^0_{cell} = 0.36V$]

Sol: $E^0_{cell} = \frac{0.0591}{2}\log K_{eq}$

$$0.36 = \frac{0.0591}{2}\log K_{eq}$$

$$= \log K_{eq} = \frac{0.36 \times 2}{0.0591}$$

$$K_{eq} = \text{Antilog } (12.1827)$$

$$K_{eq} = 1.52 \text{ X } 10^{12}$$

5) Calculate the emf of a concentration cell at 25^0C consisting of two Zn electrodes immersed in solutions of Zn^{2+} ions of 0.1M and 0.01M concentration.

Sol: EMF of concentration Cell at 25^0C is given by

$$E_{cell} = \frac{0.0591}{n}\log\frac{c_2}{c_1}\ (c_2 > c_1)$$

$$= \frac{0.0591}{2}\log\frac{0.1}{0.01}$$

$$= \frac{0.0591}{2}\log 10$$

$= 0.0296 \times 1$

$E_{cell} = 0.0296$ Volt

THEORETICAL QUESTIONS

1. Discuss the working of calomel electrode.

2. What is concentration cell? Explain with example. Derive the equation for EMF of concentration cell.

3. What is electrochemical series? Explain its uses.

4. Describe the construction of standard hydrogen electrode.

5. What is a primary battery? Discuss the working and construction of a dry cell.

6. Write an account of Zinc air cell.

7. Explain an of electrolyte concentration cell.

8. Explain the working of Lithium cells.

9. What is a single electrode potential?

10. What is an electro chemical cell . Explain the working of galvanic cell.

11. Why does a dry cell become dead after sometime even though it is not used.

12. Calculate the EMF f a cell if the oxidation and reduction potentials of the cell are 0.763V and -- 0.337V.

13. Explain the working of Glass electrode.

14. Write about the working of propane oxygen fuel cell ? Write its merits.

15. What is an electrochemical series? Explain the various applications of electrochemical series.

16. Derive Nernst equation. How can you determine the equilibrium constant of a reaction using Nernst equation.

17. What is a primary cell? Explain the working of Dry or Leclanche cell.

18. What are the challenges of modern batteries?

MULTIPLE CHOICE QUESTIONS

1. Which of the following constitutes Daniel cell?

   (a) Zn-Ag cell (b) Cu-Ag cell

   (c) Zn-Cu Cell (d) none

2. The EMF of a cell is

   (a) Sum of the two oxidation potentials

   (b) Sum of the two reduction potentials

   (c) Difference of two electrode potentials

   (d) None

3. An electrochemical cell stops working after sometime because

   (a) Electrode potentials of both the electrodes become equal in magnitude but opposite in sign

   (b) Electrode potentials of both the electrodes go on decreasing

   (c) Electrode potentials of both the electrodes go on increasing

4. Four metals A, B, C and D are having standard electrode potentials as -3.05 V, -1.66 V, –0.40 V and 0.80 V, respectively. Which one will be the most reducing?

   (a) A (b) B (c) C (d) D

5. The standard EMF for the cell reaction

$$Zn + Cu^{++} + Cu$$

is 1.1 V at 25°C.

The EMF of the cell reaction when 0.1 M Cu^{++} and 0.1 M Zn^{++} solutions are used at 25°C is

(a) 1.10 V (b) 0.10 V c) -1.10 V (d) -0.110 V

6. In an electrochemical cell,

(a) potential energy decreases

(b) kinetic energy decreases

(c) potential energy changes into electrical energy

(d) chemical energy changes into electrical energy

7. Glass electrode is an example of

(a) Fuel cell (b) ion selective electrode (c) Galvanic cell (d) Daniel cell

8. The electrode potential of SHE is

(a) 1 (b) 2 (c) 1.018 (d) Zero

9. In the concentration cells, the electrical energy is due to

(a) Oxidation of fuel (b) Heat energy

(c) Chemical reaction (d) Transfer of substance from one solution to another

10. The galvanic cells are used to convert

(a) Chemical energy to electrical energy

(b) Electrical energy to chemical energy

(c) Kinetic energy to potential energy

(d) Potential energy to kinetic energy

11. If a salt bridge is removed between the half cells, the voltage

(a) Decreases to zero. (b) Increases rapidly

(c) Increases (d) Do not change

12. In an electrochemical cell, the electrons flow

(a) From cathode to anode (b) From anode to cathode

(c) From anode to the solution (d) From the solution to cathode

13. For a galvanic cell, which one is wrong?

(a) Anode is negatively charged (b) Cathode is positively charged

(b) Reduction takes place at anode (d) Reduction takes place at cathode

14. In the cell Zn | Zn^{++} || Cu^{++} | Cu,

(a) Copper gets reduced (b) Zinc gets oxidised

(c) Zinc gets oxidised and copper gets reduced

(d) Copper gets oxidised

15. The EMF of a galvanic cell can be calculated from

(a) The size of the electrode (b) The pH of the solution

(c) The amount of metal in the anode (d) The E^0 values of the half cells

16. The difference of potentials of two electrodes of a galvanic cell is called

(a) Potential difference (b) Ionic difference

(c) EMF (d) Electrode difference

17. In the standard notation for a galvanic cell, a vertical double line (||) represents

(a) A phase boundary (b) A gas electrode

(c) A metal connection (d) Salt bridge

18. In the salt bridge, KCl is used because

(a) KC1 is an electrolyte (b) K+ and C1 ions are isoelectronic

(c) K+ and C1 have the same mobility

19. A, B, C and D are four elements whose standard oxidation potentials are +2.82 V, +2.17 V, +1.67 V and -2.87 V. The strongest reducing agent is

(a) A (b) B (c) C (d) D

20. The reactions that take place at anode and cathode are, respectively

(a) Reduction, oxidation (b) Oxidation, reduction

(c) Reduction, hydrolysis (d) Oxidation, hydrolysis

21. A battery is a device that can operate

(a) As electrical cell (b) As voltaic cell

(c) Both as voltaic cell and electrical cell (d) None of the above

22. The cell whose reaction is reversible is called

(a) Fuel cell (b) Primary cell

(c) Secondary cell (d) All the above

23. Ionisation of an electrolyte in an aqueous solution is due to

(a) Hydrolysis electrolyte

(b) Instability of the compound in aqueous medium

(c) Increase on the electrostatic forces of attraction between the ions

(d) Decrease in the electrostatic forces of attraction between oppositely charged ions.

24. _________________ is a secondary cell or battery.

(a) Ni - Cd cell (b) Daniel cell (c) Voltaic cell (d) Leclanche cell

25 When copper turnings are added to silver nitrate solution, a blue-coloured solution is formed after some time. It is because copper ______________

(a) Is oxidised to Cu^{+2} (b) Displaces silver from the solution

(c) Is reduced to Cu^{+2} (d) Forms a blue complex with $AgNO_3$

26. Which of the following is a primary cell?

(a) Mercury battery (b) Lithium battery

(c) Daniel cell (d) Ni-Cd cell

Answers:

1. c 2. c 3. a 4. d 5. a 6. d 7.b 8. d 9. d 10. a

11. a 12. b 13. c 14. c 15. b 16. c 17. d 18. c 19. a 20. b

21. b 22. c 23. d 24. a 25. b 26. c