

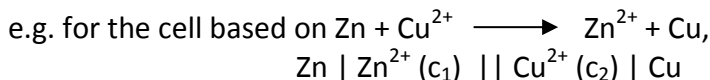
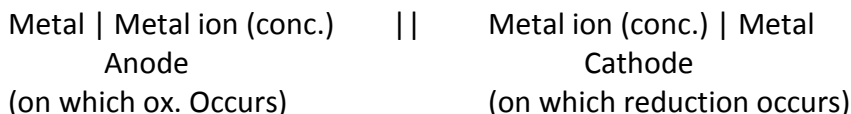
Electrochemistry

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Electrochemistry is defined as that branch of chemistry which deals with the relationship between electrical energy and chemical changes taking place in redox reactions i.e. how chemical energy produced in a redox reaction can be converted into electrical energy or how electrical energy can be used to bring about a redox reaction which is otherwise non-spontaneous.

Difference between Electrochemical and Electrolytic cell is that the former is used to convert chemical energy produced in the redox reaction into electrical energy whereas in the later, electrical energy is passed to bring about the redox reaction (electrolysis) which is otherwise non-spontaneous.

An electrochemical cell is represented as follows:

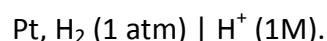


Difference in electrolytic cell and galvanic cell	
S.No. Electrolytic cell	Galvanic cell
(i) Electrical energy is converted into chemical energy.	Chemical energy is converted into electrical energy.
(ii) Anode positive electrode. Cathode negative electrode.	Anode negative electrode. Cathode positive electrode.
(iii) Ions are discharged on both the electrodes	Ions are discharged only on the cathode.
(iv) If the electrodes are inert, concentration of the electrolyte decreases when the electric current is circulated.	Concentration of the anodic half-cell increases while that of cathodic half-cell decreases when the two electrodes are joined by a wire.
(v) Both the electrodes can be fitted in the same compartment.	The electrodes are fitted in different compartments.

Electrode potential is the tendency of an electrode to lose or gain electrons when it is in contact with the solution of its own ions. The tendency to lose electrons is called oxidation potential whereas the tendency to gain electrons is called reduction potential. Further, if standard conditions are used i.e. temp = 298 K, conc. = 1 M and pressure = 1 atm, the electrode potential is called **standard electrode potential**.

Absolute value of electrode potential cannot be determined because oxidation or reduction half reaction cannot occur alone. Moreover, a reference electrode is required.

The reference electrode used is Normal Hydrogen Electrode (N.H.E). Its standard electrode potential is taken as 0.0. It is represented as



EMF or Cell potential or Cell voltage is the difference between the electrode potentials of the two half cells.

EMF is the potential difference when no current is flowing in the circuit. It can be measured by potentiometric method only.

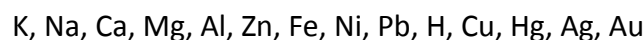
Electrochemical series is the arrangement of electrodes in order of increasing standard electrode potentials (reduction potentials).

Applications of Electrochemical series

- (i) To predict the relative oxidizing and reducing powers. Greater the reduction potential, more easily the substance is reduced and hence is a stronger oxidizing agent e.g. oxidizing powers of halogens are in the order: $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$
- (ii) To predict whether a metal will react with acid to give H_2 gas.
- (iii) To calculate the standard EMF of the cell

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{electrode (R.H.S)}} - E^\circ_{\text{electrode (L.H.S)}} \\ &= E^\circ_{\text{Cathode}} - E^\circ_{\text{Anode}} \end{aligned}$$

- (iv) To compare the relative activities of metals. Greater the oxidation potential of a metal, greater is its activity. As a result, a more active metal can displace a less active metal from its salt solution. Some common elements in order of their decreasing activity are

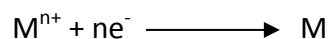


- (v) To predict the spontaneity of any redox reaction. If EMF of the cell is positive, it is spontaneous, otherwise not.
- (vi) To calculate the standard free energy change of the reaction. The relation is $\Delta G^\circ = - nFE^\circ_{\text{cell}}$ where n is the no. of electrons involved in redox reaction and F is faraday (1F=96500 coulomb)..

Nernst Equation:-

The 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



A/c to Nernst Equation,

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{2.303 RT}{nF} \log \frac{[M]}{[M^{n+}]}$$

Where, E = Reduction electrode potential

E^0 = Standard reduction electrode potential

n = Number of electrons involved in the balanced equation of the half reaction.

[M] = Molar concentration or activity of the metal. It is always unity (1)

$[M^{n+}]$ = Molar conc. or activity of the ions.

R = Gas constant, $8.314 \text{ JK}^{-1}\text{Mol}^{-1}$

T = Temperature in Kelvin

F = Faraday constant = 96500 Coulmb.

$$\text{At } 298 \text{ K, } \frac{2.303 RT}{F} = 0.059$$

$$\therefore E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.059}{n} \log \frac{[M]}{[M^{n+}]} \quad [E_{\text{cell}}^0 = E_{\text{cathode}}^0 - E_{\text{anode}}^0]$$

$$= E_{\text{cell}}^0 - \frac{0.059}{n} \log \frac{[\text{Products}]}{[\text{Reactants}]}$$

$$E_{\text{oxi}} \propto \frac{1}{\text{conc. of electrolyte}}$$

$$E_{\text{red}} \propto \text{conc. of electrolyte.}$$

Cell Potential (EMF) from Electrode Potentials.

The difference in potential of the two half cells of a cell is known as electromotive force (emf) of the cell or cell potentials. It is measured in volts.

Cell potential (or EMF) can be determined from electrode potential in the following three ways:

- (i) Cell Potentials (E_{cell}) = Reduction Potential of cathode – Reduction Potential of anode.

In short,

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} \text{ or } E_{\text{cell}} = E_{\text{R}} - E_{\text{L}}$$

- (ii) E_{cell} = Oxidation potentials of anode – oxidation potentials of cathode.

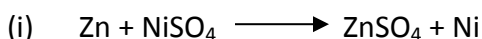
In short,

$$E_{\text{cell}} = E_{\text{anode}} - E_{\text{cathode}}$$

- (iii) E_{cell} = oxidation potential of anode + Reduction Potential of cathode

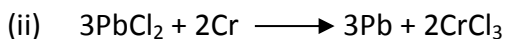
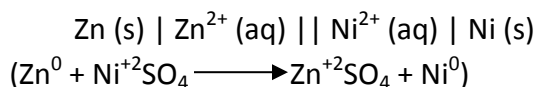
If potential (E_{cell}) is +ve, the reaction is spontaneous. Further the more +ve of the E_{cell} , i.e., the more faster than the reaction. In case the value of cell potential is negative the reaction will not take place spontaneously as written. However, the reaction is possible in opposite direction.

Construct the following cells involving following reactions according to IUPAC convention.



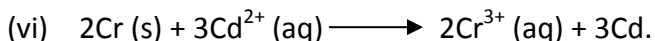
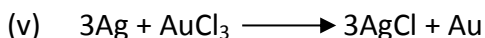
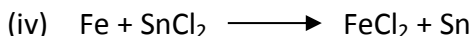
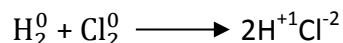
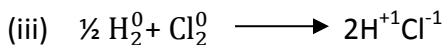
In this reaction Zn is being oxidised and thus will act as anode.

Hence, the cell would be

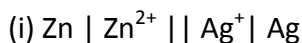


In this reaction Cr is being oxidised and thus will act as anode.

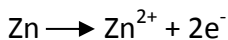
Hence, the cell would be



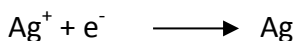
Q. Write the cell reaction and emf equation for the following cell.



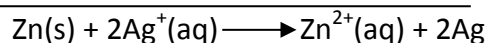
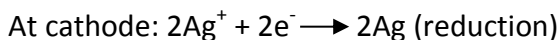
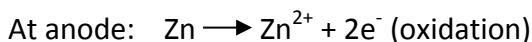
Sol. :- The reaction of oxidation half-cell is



The reaction of reduction half-cell is:



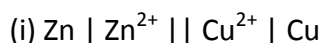
Now, the cell reaction:



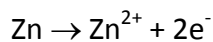
$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{2.303RT}{nF} \log \frac{[\text{Zn}^{2+}][\text{Ag(s)}]^2}{[\text{Ag}^+]^2[\text{Zn(s)}]}$$

$$= E_{\text{Ag}^+/\text{Ag}}^0 - E_{\text{Zn}^{2+}/\text{Zn}}^0 - \frac{2.303RT}{nF} \log \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2}$$

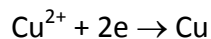
Q. Write the cell reaction and emf equation for the following cells.



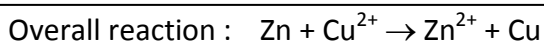
Sol.:- The reaction of oxidation half-cell is:



The reaction of reduction half-cell is:



Now, the cell reaction:



$$E = E^0 - \frac{2.303}{nF} RT \log \frac{[\text{Products}]}{[\text{Reactants}]}$$

$$= (E_R - E_L) - \frac{0.059}{n} \log \frac{[\text{Products}]}{[\text{Reactants}]}$$

$$E = E_{\text{Cu}}^0 - E_{\text{Zn}}^0 - \frac{0.059}{2} \log \frac{[\text{Cu}][\text{Zn}^{2+}]}{[\text{Zn}][\text{Cu}^{2+}]}$$

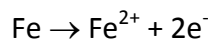
$\therefore [\text{Cu}] = 1$ as they are solids.

$$[\text{Zn}] = 1$$

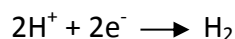
$$\therefore E = E_{\text{Cu}}^0 - E_{\text{Zn}}^0 - \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$



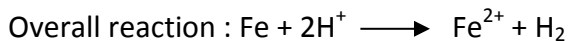
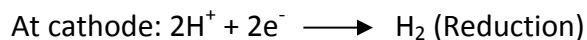
The reaction of oxidation half cell is



The reaction of reduction half cell is



Now cell reaction of reduction:-



A/C to Nernst equation.

$$E = E_R - E_L - \frac{0.059}{n} \log \frac{[\text{Products}]}{[\text{Reactants}]}$$

$$= E_R - E_L - \frac{0.059}{2} \log \frac{[\text{Products}]}{[\text{Reactants}]}$$

$$= E_{\text{H}_2}^0 - E_{\text{Fe}}^0 - \frac{0.059}{2} \log \frac{[\text{Fe}^{2+}][\text{H}_2]}{[\text{H}^+]^2}$$

Free Energy And Electrical Work Done In A Cell:

In the case of electrochemical cells, free energy change, ΔG is related to the electrical work done in the cell. If E is the e.m.f. of the cell and n mole of electrons are involved, the electrical work done will be

$$\Delta G = -nFE_{\text{cell}}$$

Where F is Faraday constant = 96500 C

If reactants and products are in their standard states, then

$$\Delta G^0 = -nFE^0$$

Where E^0 is the standard cell potential.

$$W = -\Delta G = nFE_{\text{cell}}$$

For spontaneous cell reaction ΔG be negative.

If $\Delta G = 0$ then cell reaction at equilibrium.

$$-nFE_{\text{cell}} = 0 \quad \therefore E_{\text{cell}} = 0$$

At equilibrium, $\frac{[P]}{[R]} = K$ (equilibrium constant)

$$E_{\text{cell}}^0 = \frac{0.0591}{n} \log_{10} K$$

$$E_{\text{cell}}^0 = \frac{RT}{nF} \log_e K$$

$$\Delta G^0 = -nFE_{\text{cell}}^0$$

$$\Delta G^0 = -nF \left(\frac{RT}{nF} \log_e K \right)$$

$$\Delta G^0 = -2.303 RT \log_{10} K$$

SOME COMMERCIAL CELLS:

The various commercial cells may be classified mainly into the following three types:

(A) Primary cells

(B) Secondary cells

(C) Fuel cells

Primary cells are those in which the redox reaction occurs only once and the cell becomes dead after some time, and cannot be used again. Two common examples of this type are dry cell and mercury cell.

Secondary cells are those which can be recharged by passing an electric current through them and hence can be used over and over again. Two well known examples of this type are lead storage battery and nickel-cadmium storage cell.

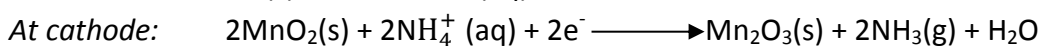
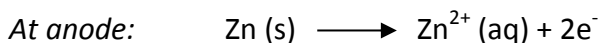
Fuel cells are those in which the energy produced from the combustion of fuels such as H_2 , CO , CH_4 , etc. is directly converted into electrical energy. Such a conversion is possible because combustion reactions are also redox reactions.

A brief description of the examples of each type is given below:

(A) Primary cells.

(1) Dry cell. The dry cell, commonly used in transistors and clocks, is a compact form of the Leclanche cell. It consists of a cylindrical zinc container which acts as the anode. A graphite rod placed in the centre (but not touching the base) acts as the cathode. The space between the anode and the cathode is so packed that zinc container is in touch with the paste of NH_4Cl and ZnCl_2 and the graphite rod is surrounded by powdered MnO_2 and carbon. The graphite rod is fitted with a metal cap and the cylinder is sealed at the top with pitch. The zinc container is covered with cardboard to protect it from the atmosphere.

The reactions taking place at the electrodes are quite complex. However, they can be represented approximately as follows:-

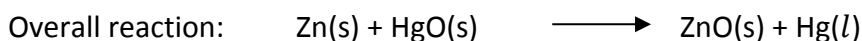
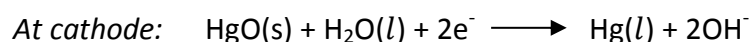


(i.e., Mn has been reduced from oxidation state + 4 to + 3).

The NH_3 formed is not liberated as gas but combines immediately with the Zn^{2+} ions and the Cl^- ions to form complex salt, $[\text{Zn}(\text{NH}_3)_2\text{Cl}_2]$ (diamminedichlorido zinc). These cells have voltage in the range 1.25 V to 1.50 V. However, they do not have a long life because the acidic NH_4Cl corrodes the zinc container even when the cell is not in use.

(2) Mercury cell (Ruben-Mallory cell) This is a newer type of dry cell which has found use in low current devices such as hearing aids and watches. It consists of zinc container as the anode, a carbon rod as the cathode and a paste of mercuric oxide mixed with KOH as the electrolyte. A lining of porous paper keeps the electrolyte separated from the zinc anode.

The cell produces electrical energy by the following reactions:



As the overall cell reaction does not involve any ion whose concentration may change, therefore, this cell gives a constant potential of 1.35 V throughout its life. However, the spent cells should be reprocessed for mercury or mercury compounds from entering the atmosphere and causing pollution.

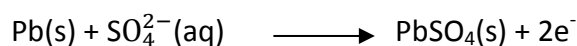
(B) Secondary cells.

(1) Lead storage battery. This is one of the most common batteries used in the automobiles and invertors. A 12 V lead storage battery is generally used which consists of 6 cells each producing 2 V. Each cell consists of a lead anode (or a grid of lead filled with finely divided spongy lead as the anode) and a grid of lead packed with lead dioxide as the cathode. These electrodes are arranged alternately, separated by thin wooden or fibre glass sheets and suspended in dilute sulphuric acid (38% by mass or having a density of 1.30 g cm^{-3}) which acts as the electrolyte.

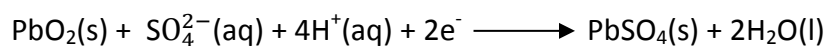
To increase the current output of each cell, the cathode plates are joined together (keeping them in the alternate positions of course) i.e. the cells are connected in parallel (anode to anode and cathode to cathode). To have an output voltage of 12 V, six cells are connected in series.

The electrode reactions that occur during discharge (i.e when the battery is in use) are as follows:-

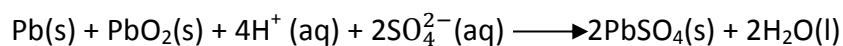
At anode:



At cathode:

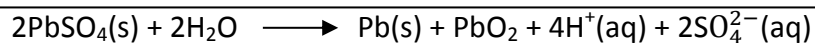
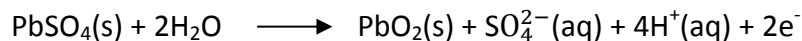
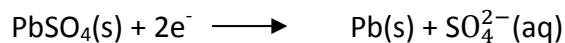


Overall reaction:



From the above equations, it is obvious that H_2SO_4 is used up during the discharge. As a result, the density of H_2SO_4 falls. When it falls below 1.20 g cm^{-3} , the battery needs recharging.

During recharging, the cell is operated like an electrolytic cell, i.e., now electrical energy is supplied to it from an external source. The electrode reactions are the reverse of those that occur during discharge:

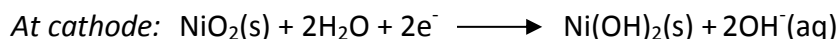
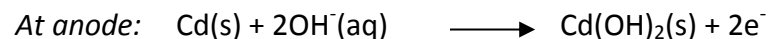


Such an operation is possible because the PbSO_4 formed during discharge is a solid and sticks to the electrodes. It is, therefore, in a position to either receive or give up electrons during electrolysis.

Note. (i) In an automobile, when it is running, electrical energy is produced in the alternator which keeps on charging the battery.

(ii) During discharge, electrolysis of water also takes place. Hence, some water is lost due to electrolysis of water into H_2 and O_2 . Hence, water has to be added periodically into the acid of the battery to have desired concentration. Now days, in the maintenance free batteries, no water needs to be added as they use electrodes of Ca/Pb alloy which prevents electrolysis of water.

(2) Nickel-Cadmium storage cell (or Nicad Cell) This is another rechargeable cell which is becoming more and more popular especially in the calculators. It has a longer life than lead storage cell but is more expensive. It consists of a cadmium electrode (as anode) and a metal grid containing nickel (IV) oxide (as cathode) immersed in KOH solution. The electrode reactions occurring during discharge are as follows:-

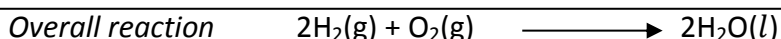
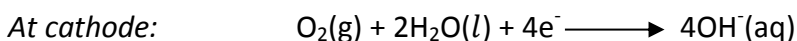


As in the lead storage cell, the reaction products adhere to the electrodes. Hence, the reactions can be reversed during charging. Further, as no gases are produced during discharging or recharging, the battery can be sealed.

The potential of each Ni – Cd cell is approximately 1.4 V.

(c) Fuel Cells. As already explained, fuel cells are the devices which convert the energy produced during the combustion of fuels like hydrogen, methane, methanol etc. directly into electrical energy. One such cell which has been very successful is the hydrogen-oxygen fuel cell. This cell was used as the primary source of electrical energy on the Appolo moon flights. The weight of the fuel sufficient for 11 days in space was approximately 200 kg. This may be compared with the several tons that would have been required for the engine-generator set. Moreover, the product of combustion, namely, water, was used for drinking by the astronauts.

The following electrode reactions take place:

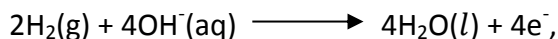


Thus, in these cells, the reactants are fed continuously to the electrodes and the products are removed continuously from the electrolyte compartment.

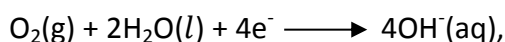
Advantages of fuel cells. The three main advantages of fuel cells are as under:

(i) Because of the continuous supply, such cells never become dead. Such a cell is usually operated at a temperature of 70 - 140°C and gives a potential of about 0.9 V.

The theoretical voltage of the cell may be calculated from half-cell reactions as follows:



$$E^\circ = + 0.40 \text{ V}$$



$$E^\circ = + 0.40 \text{ V} - (- 0.83 \text{ V}) = 1.23 \text{ V}$$

(ii) Theoretically, the fuel cells are expected to have an efficiency of 100%. However practically they give an efficiency of 60 – 70%. Still they are much superior to the thermal power plants in which fuels are burnt to produce heat which then changes water into steam to run the turbine. Such a power plant does not have efficiency of more than 40%.

(iii) They do not cause any pollution problem unlike thermal plants which burn fossil fuels like coal, gas, oil etc.

Efficiency of the fuel cell. As ΔH is the heat of combustion and ΔG is the useful work done, i.e., electrical energy produced therefore, the thermodynamic efficiency (η) of a fuel cell = $\frac{\Delta G}{\Delta H} \times 100$. Thus, for the $\text{H}_2 - \text{O}_2$ fuel cell, the theoretically value can be calculated as follows:

$$\begin{aligned} \Delta G &= -n F E^\circ_{\text{cell}} = - (2) (96500 \text{ C mol}^{-1}) (1.23 \text{ V}) \\ &= - 237390 \text{ CV mol}^{-1} = - 237390 \text{ J mol}^{-1} \end{aligned}$$

$$\Delta H = -285.8 \text{ kJ mol}^{-1}$$

$$\therefore \eta = \frac{\Delta G}{\Delta H} \times 100$$

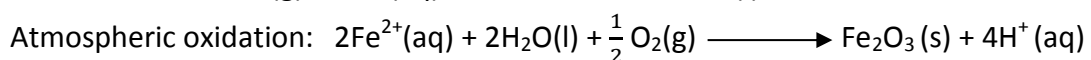
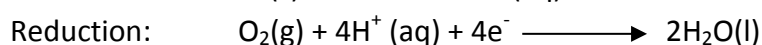
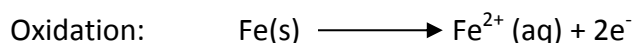
$$= \frac{-237.39 \text{ kJmol}^{-1}}{-285.8 \text{ kJmol}^{-1}} \times 100 = 83\%$$

Difficulties in the construction of fuel cell.

The construction of fuel cells is, however, faced with certain technical, economic and practical difficulties. A few of these are as follows:-

- (i) Providing of contact between the three phases needed in a fuel cell, i.e., the gaseous fuel, the liquid electrolyte and the solid catalyst.
- (ii) The corrosiveness of the electrolytes used.
- (iii) High cost of the catalysts needed for the electrode reactions (e.g., Pt, Pd, Ag, etc.)
- (iv) Problem of handling gaseous fuels at low temperatures or high pressures.

CORROSION: It is a process in which a metal is oxidized by losing electrons to other electronegative elements such as oxygen, sulphur etc., to yield metal oxide and metal sulphide, respectively. For example iron is corroded (rusted) in the presence of moisture and oxygen.

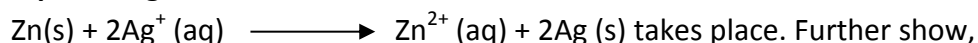


It is basically an electrochemical phenomenon.

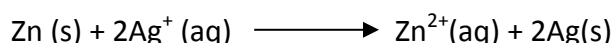
Factors which promote corrosion

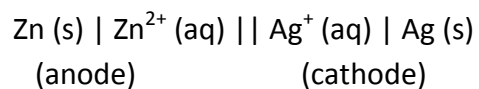
- (i) **Reactivity of the metal:** More active metals are readily corroded.
- (ii) **Presence of impurities:** Presence of impurities in metals enhances the of corrosion. Pure metals do not corrode e.g. pure iron does not rust.
- (iii) **Presence of air and moisture:** Air and moisture accelerate corrosion. Presence of gases like SO_2 and CO_2 in air catalyse the process of corrosion. Iron when placed in vacuum does not rust.
- (iv) **Strains in metals:** Corrosion (e.g. rusting of iron) takes place rapidly at bends, scratches, nicks and cuts in the metal.
- (v) **Presence of electrolytes:** Electrolytes, if present, also increase the rate of corrosion.

Q. Depict the galvanic cell in which reaction



- (i) Which of the electrode is negatively charged?
- (ii) The carriers of the current in cell.
- (iii) Individual reaction in each electrode.





Ans: draw the diagram yourself

∴ (i) Since the negatively charged electrode is anode, hence Zn is the negatively charged electrode.

(ii) Ions are the carriers of the current in the cell, i.e., Zn^{2+} and Ag^+

(iii) At anode : $\text{Zn} \longrightarrow \text{Zn}^{2+} + 2\text{e}^-$ (oxidation)

At cathode : $2\text{Ag}^+ + 2\text{e}^- \longrightarrow 2\text{Ag}$ (reduction)