

Thermodynamic Functions

It is a branch of science that deals with the relationships between heat and other forms of energy (such as mechanical, electrical and chemical energy).

The first law states that the amount of energy added to a system is equal to sum of its increase in heat energy and work done on the system.

$$U = q + W$$

Here, U is the change in internal energy, U of the system. q is the net heat transferred into the system. w is the net work done on the system. The first law is an example of principle of conservation of energy.

The second law states that heat flows spontaneously from a hot body to a cold body, but the reverse process is not spontaneous.

All refrigerators, air- conditioning systems, heat pumps, etc work on the basis of this law of thermodynamics.

Use of Free Energy in Chemical Equilibria

Free Energy (G): The spontaneity of a process can't be predicted on the basis of enthalpy or entropy alone. For this purpose a new function called Gibbs free energy is defined. It is defined as *the maximum amount of energy available to a system to perform useful work*. It is a thermodynamic state function, which is related to enthalpy and entropy as;

Energy available as useful work = Total energy available – Non available form of energy

$$G = H - TS$$

Where, G is Gibbs free energy, H is enthalpy, S is entropy and T is temperature.

At constant temperature, the change in Gibbs free energy is given by,

$$G = H - T S$$

Free energy and spontaneity of a process:

Spontaneity of any process can be predicted in terms of Gibbs free energy as follows;

1. If G is negative, i.e., if free energy decreases, the process is spontaneous.
2. If G is equal to zero, the process is in equilibrium.
3. If G is positive, i.e., if the free energy increases, the process is non-spontaneous.

As G is a combination of H and S , the value of both enthalpy change and entropy change in combination, decides the spontaneity of a process.

Entropy (S): It has been regarded as a measure of disorder or randomness of a system. During a process entropy change is mathematically defined as, $\Delta S = q/T$, where q is the heat exchanged (evolved or

absorbed) during the process. It is expressed in Joules per Kelvin (JK^{-1}). This is known as entropy unit e.u. Entropy is an extensive property depends upon amount of substance present. Therefore it is necessary to mention the quantity of substance involved. Thus entropy is given per moles.

Thus when a system goes from a more orderly to less orderly state, there is an increase in randomness hence, entropy of the system increases. In an irreversible (spontaneous) process the entropy of a system and its surroundings taken together increases, but it remains constant in a thermodynamically reversible process. Since all the processes in nature are spontaneous and irreversible, so the entropy of the universe increases continuously.

But these are the processes which are not accompanied by increase in randomness or entropy and yet spontaneous.

Ex: $\text{H}_2\text{O}_{(\text{g})} \rightarrow \text{H}_2\text{O}_{(\text{l})}$ (rain)

$\text{H}_2\text{O}_{(\text{g})} \rightarrow \text{H}_2\text{O}_{(\text{s})}$ (snow)

Therefore, randomness or entropy alone is not the criterion for spontaneity.

EMF of a Cell: (E cell)

Definition: The potential difference between the two electrodes of a galvanic cell which causes the flow of current from one electrode (higher potential) to the other (lower potential) is called the electromotive force (emf) of the cell or the *cell potential*.

Nernst Equation:

Consider a general red-ox reaction: $\text{Mn}^{n+} + \text{ne}^- \rightleftharpoons \text{M}$. ----- (1)

The decrease in free energy change for a reversible reaction is given by

$$-\Delta G = -\Delta G^0 - RT \ln Q \quad \text{----- (2)}$$

Where, ΔG = free energy change, ΔG^0 = standard free energy change

Q is the reaction quotient of the concentration of the products and reactants i.e.

$$Q = \left[\frac{\text{products}}{\text{reactants}} \right] = \frac{a_{\text{M}}}{a_{\text{M}^{n+}}} \quad \text{----- (3)}$$

Where a_{M} is the activities of the product $a_{\text{M}^{n+}}$ is the activities of the reactants

By substituting Eqs.(3) in Eq.(2)

$$-\Delta G = -\Delta G^0 - RT \ln \frac{a_{\text{M}}}{a_{\text{M}^{n+}}}$$

As an approximation, substituting molar concentration for activities

$$-\Delta G = -\Delta G^0 - RT \ln \frac{[\text{M}]}{[\text{M}^{n+}]} \quad \text{----- (4)}$$

For a reversible reaction the electrical energy is produced by decreasing the free energy of the system i.e.,

$$-\Delta G = nEF \quad \text{and} \quad -\Delta G^0 = nE^0F \quad \text{----- (5)}$$

Where E =electrode potential; E^0 =standard reduction potential n =number of electrons change;
 F is Faraday = 96,500C mol⁻¹

By substituting eq.(5) in (4) ;

$$nEF = nE^0F - RT \ln \frac{[M]}{[M^{n+}]}$$

Dividing by nF ,

$$E = E^0 - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]} \quad \text{----- (6)}$$

$$E = E^0 - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]} \quad \text{----- (7) (since [M] =1)}$$

$$E = E^0 + \frac{2.303RT}{nF} \log [M^{n+}] \quad \text{----- (8)}$$

Eq. (8) is called Nernst Equation.

The electrode potentials vary with temperature and the concentration of metal ions.

$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$; $T = 298\text{K}$; $F = 96500 \text{ coulomb}$

$$E = E^0 - \frac{0.0591}{n} \log [M^{n+}] \quad \text{at } 298 \text{ K} \quad \text{----- (9)}$$

The Nernst equation can also be applied for the calculation of emf of a cell.

Consider a cell reaction,



The Nernst equation for the emf of the cell is,

$$E_{\text{cell}} = E^0_{\text{cell}} - \frac{2.303RT}{nF} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$E_{\text{cell}} = E^0_{\text{cell}} - \frac{0.0591}{nF} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Where n = number of electrons transferred during the cell reaction and E^0_{cell} is the standard emf of the cell.

Electrochemical Systems:

Reference electrode:

The absolute value of single electrode potential cannot be measured since the metal and its ions are in equilibrium. We can only measure the potential difference between two electrodes. This can be done by choosing a reference electrode whose electrode potential is arbitrarily fixed or known. This reference electrode can be combined with other electrodes to form a galvanic cell. From the measured cell potential we can calculate the electrode potential of any particular electrode, with reference to the reference electrode.

Definition: Reference electrode is an electrode whose electrode potential is arbitrarily fixed or known and is reliable.

This can be used to measure the electrode potentials of other electrodes by constructing a galvanic cell using the electrode and the reference electrode.

Two types of reference electrodes:

1. Primary reference electrode, Example: Hydrogen gas electrode
2. Secondary reference electrode, Example: Calomel electrode and silver-silver electrode

Limitations of Primary Reference Electrode (Standard hydrogen electrode):

1. The equilibrium between the two processes is not reached quickly.
2. It is difficult to control the pressure of hydrogen gas at 1 atm.
3. The electrode cannot be easily setup.
4. The electrode gets poisoned by impurities

Secondary Reference Electrodes:

For the sake of simplicity and to overcome the above difficulties, there was a need for the development of secondary reference electrodes. The potentials of these electrodes are known on the hydrogen scale and are used in place of hydrogen electrode. These electrodes can be easily set up.

Calomel electrode:

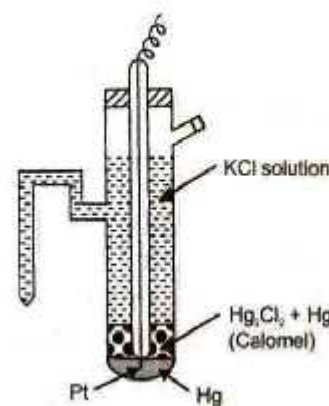
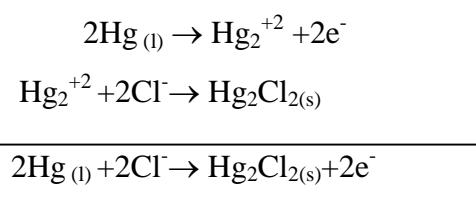
Construction and working:

It is a metal-insoluble salt electrode, where metal is in contact with its insoluble salt and the solution contains the anion of the salt.

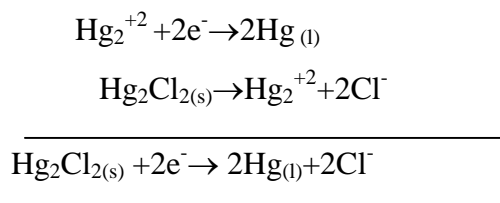
Electrode representation: $\text{Hg}_{(s)} | \text{Hg}_2\text{Cl}_2 (\text{paste}); \text{Cl}^-$

Mercury is placed at the bottom of the glass tube above which a paste of mercury and mercurous chloride are present. It is filled on the top with the saturated solution of KCl. A platinum wire sealed into a glass tube is dipped into mercury and used to provide the external electrical contact. Depending on the nature of the other electrode it can either act as an anode or cathode.

If the electrode behaves as an anode, the electrode reaction is:



If the electrode behaves as cathode, the electrode reaction is:



The electrode potential may be represented by the Nernst equation as

$$\begin{aligned}
 E &= E^0 - \frac{2.303RT}{nF} \log[\text{Cl}^-]^2 \\
 E &= E^0 - \frac{2.303RT}{nF} 2\log[\text{Cl}^-] \\
 E &= E^0 - \frac{0.0591}{2} 2\log[\text{Cl}^-] \text{ at } 298\text{K} \\
 E &= E^0 - 0.0591 \log[\text{Cl}^-] \text{ at } 298\text{K}
 \end{aligned}$$

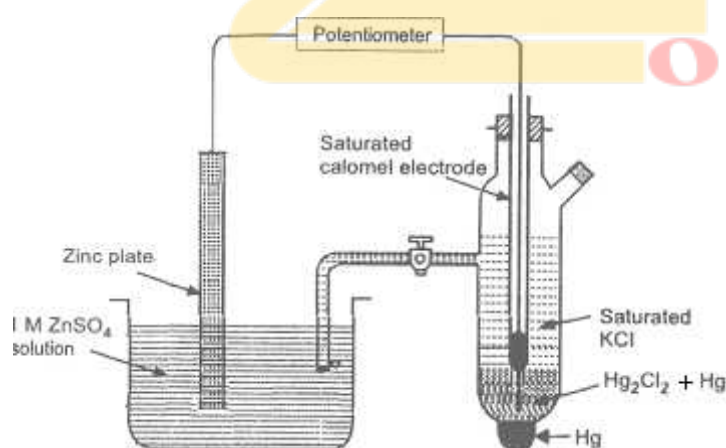
The electrode potential decreases with increase in the concentration of chloride ions.

The potential values depend on the concentration of the solution used in the construction of the electrode:

For 0.1N KCl	E=0.3335V (called Decinormal calomel electrode)
For 1N KCl	E=0.2810V (called Normal calomel electrode)
For saturated KCl	E=0.2422V (called Saturated calomel electrode)

Uses: It is used as a secondary reference electrode in the measurement of single electrode potential. It is the most commonly used reference electrode in all potentiometric determination.

Measurement of Single Electrode Potential.



Measurement of single electrode potential is not possible, only difference in the potentials between the two electrodes can be measured using potentiometer. By knowing the potential of one of the electrode, the potential of the other can be calculated.

To determine the single electrode potential (for e.g. Zinc electrode), it is coupled with the reference electrode (say Saturated Calomel Electrode) through a salt bridge. If experimental electrode acts as anode,

the cell is represented as: $\text{Zn} \mid \text{Zn}^{2+} (1\text{M}) \parallel \text{Cl}^{-}(\text{aq}) \mid \text{Hg}_2\text{Cl}_2 (\text{paste}) \mid \text{Hg}(\text{s})$

The emf of the above cell can be measured by means of a potentiometer (i.e. Null deflection method). The single electrode potential is calculated by substituting the potential values in the relation:

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

$$\text{OR } E_{\text{cell}} = E_{\text{SCE}} - E_{\text{Zn}}$$

$$E_{\text{cell}} = 0.242 - E_{\text{Zn}}$$

Ion Selective Electrode:

Definition: Ion-selective electrode is one, which selectively responds to a specific ion in a mixture of ions in solutions ignoring all other ions and develops a potential. The potential developed is a function of the concentration of that particular ion.

The electrode generally consists of a membrane which is capable of exchanging the specific ions with the solution with which it is in contact. Therefore these electrodes are also referred to as membrane electrodes.

Glass Electrode:

Principle:

When two solutions of different hydrogen ion concentrations, i.e. different pH values are separated by a thin glass membrane, there develops a potential difference between the two surfaces of the glass membrane.

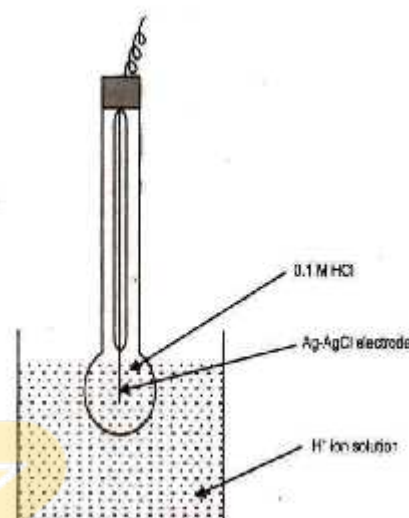
The potential developed is proportional to the difference in the pH values of the two solutions. If the pH of the one solution is kept constant, the potential becomes proportional only to the pH of the other solution. This is the basis of the glass electrode.

Construction:

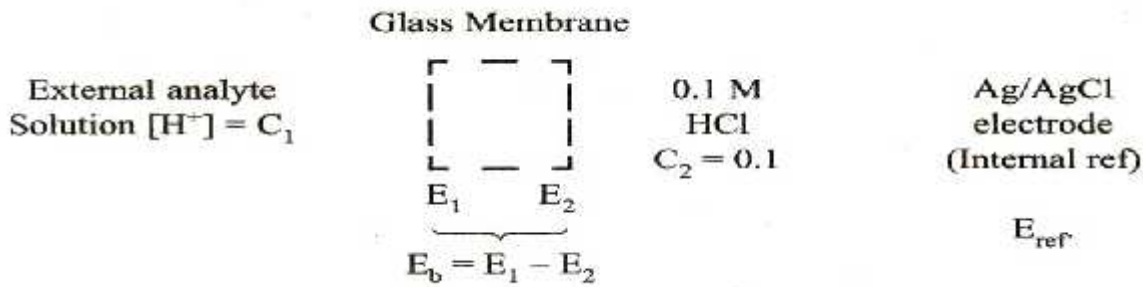
The glass electrode consists of a glass bulb made up of a special type of glass with high electrical conductivity. The composition of the glass membrane is approximately 22% Na_2O , 6% CaO , and 72% SiO_2 . The glass bulb is filled with a solution of known pH (0.1M HCl) and is inserted with an Ag-AgCl electrode, which is the internal reference electrode and also serves for the external electrical contact. The electrode is dipped in a solution whose pH is to be determined (containing H^+ ions).

The glass electrode system can be represented as follows:

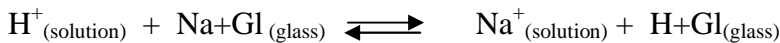
$\text{Ag/AgCl}_{(\text{s})}/0.1\text{MHCl/glass}$



When dipped in a solution of unknown pH, it can be represented as,



The glass membrane exchanges ions with the solution



The exchange of ions by the inner and outer membrane gives rise to a boundary potential. This boundary potential consists of two potential E_1 and E_2 , which are associated with the outer and inner membrane respectively.

$$\text{Therefore, } E_b = E_1 - E_2$$

From thermodynamic consideration it has been shown that E_1 and E_2 are related to the hydrogen ion activities at each face, by Nernst like equation,

$$E_1 = j_1 - \frac{(0.0591)}{n} \log \frac{a_1^1}{a_1}$$

$$E_2 = j_2 - \frac{(0.0591)}{n} \log \frac{a_2^1}{a_2}$$

Where j_1 and j_2 are constants and a_1 and a_2 are activities of H^+ in the outer and inner solution respectively, a_1^1 and a_2^1 are the activities of H^+ ions at the external and internal surface of the glass membrane.

Since the glass at the inner solution and outer membrane are identical, $j_1 = j_2$ and also $a_1^1 = a_2^1$

$$\text{Then } E_b = E_1 - E_2 = 0.0591 \log \frac{a_1}{a_2} \quad (n = 1 \text{ for } \text{H}^+ \text{ ions})$$

Thus the boundary potential E_b depends only upon the hydrogen ion activities of the solutions. Since the concentration of the inner solution is constant, a_2 is constant. The above equation simplifies to,

$$E_b = L^1 + 0.0591 \log a_1$$

$$E_b = L^1 + 0.0591 \log C_1$$

$$E_b = L^1 - 0.0591 \text{ pH}$$

Where $L_1 = -0.0591$, $\log a_2 = -0.0591 \log C_2$

The total potential of the glass electrode E_G has three components

- (i) The boundary potential
- (ii) The potential of the internal Ag/AgCl reference electrode and
- (iii) A small asymmetry potential

$$E_G = E_b + E_{ref} + E_{asy}$$

$$E_G = L_1 + 0.0591 \log C_1 + E_{ref} + E_{asy}$$

$$E_G = E_G^0 + 0.0591 \log C_1$$

$$E_G = E_G^0 - 0.0591 pH$$

Where E_G^0 is a combination of three constant terms.

$$E_G^0 = L_1 + E_{ref} + E_{asy}$$

Asymmetric potential arises due to the difference in response of the inner and outer surface of the glass bulb to changes in H^+ ion activity. This may originate as a result of differing conditions of strain in the two glass surfaces (due to difference in curvature). This asymmetric potential varies with time and therefore, glass electrode must be standardized frequently by placing a solution of known H^+ activity (pH).

Advantages:

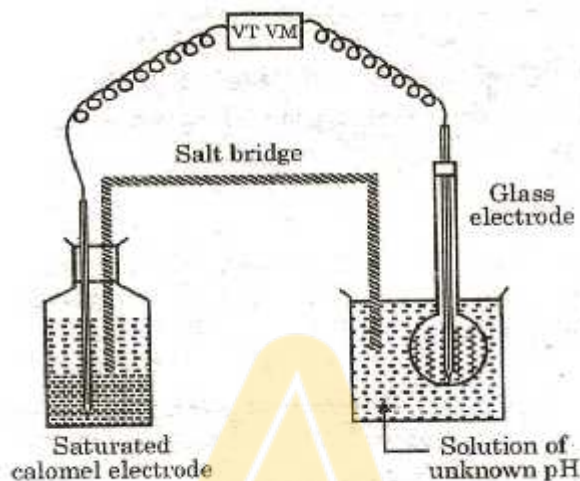
1. This electrode can be used to determine P^H in the range 0-9, with special type of glass even up to 12 can be calculated.
2. It can be used even in the case of strong oxidising agents.
3. The equilibrium is reached quickly.
4. It is simple to operate, hence extensively used in various laboratories.

Limitations

1. The glass membrane though it is very thin, it offers high resistance. Therefore ordinary potentiometers cannot be used, hence it is necessary to use electronic potentiometers.
2. This electrode cannot be used to determine the P^H above 12.

Determination of pH using Glass Electrode:

- The given glass electrode is dipped in the unknown solution containing hydrogen ions, constitutes a half cell.
- It is coupled with reference electrode (ex: saturated calomel electrode) through a salt bridge, where calomel electrode forms an outer reference electrode.



- The above cell may be represented as:



- In the above cell, the glass electrode behaves as cathode and calomel electrode as anode.
- The cell potential may be determined using electronic potentiometer.
- The E_G^0 is obtained by repeating the experiment using the solution of known pH.
- The pH value of the experimental solution can be calculated by substituting the values of E_{cell} , E_{calomel} and E_G^0 in the following relation:

$$E_{\text{cell}} = E_G - E_{\text{SCE}}$$

$$E_{\text{cell}} = (E_G^0 - 0.0591\text{pH}) - E_{\text{SCE}}$$

$$0.0591\text{pH} = E_G^0 - E_{\text{SCE}} - E_{\text{cell}}$$

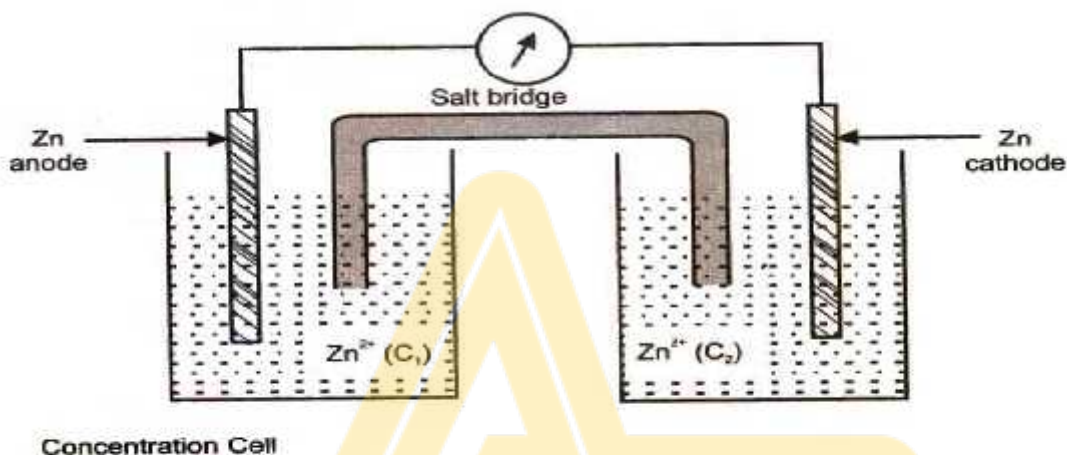
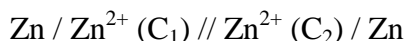
$$\text{pH} = \frac{E_G^0 - E_{\text{SCE}} - E_{\text{cell}}}{0.0591}$$

Concentration cells:

Electrolyte concentration cell:

Definition: Concentration cells are those in which both the anode and the cathode are made up of the same element (metal or nonmetal) in contact with the solutions of the same electrolyte, but of different concentrations.

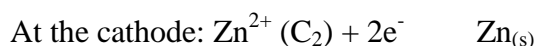
Eg: A cell in which the electrodes are made up of zinc metal dipped in ZnSO_4 solutions of different concentrations C_1 and C_2 . The cell is represented as:



At the anode zinc gets converted into Zn^{2+} ions and goes into the solution liberating two electrons.



At the cathode Zn^{2+} ions are deposited as zinc metal.



There is no net cell reaction. At one electrode zinc atoms go into the solution and at the equal number of zinc atoms are deposited. The emf of the cell is given by,

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

$$E_{\text{cell}} = E^0 + \frac{2.303RT}{nF} \log[C_2]_{\text{cathode}} - E^0 - \frac{2.303RT}{nF} \log[C_1]_{\text{anode}}$$

$$E_{\text{cell}} \approx \frac{2.303RT}{nF} \log(C_2) - \frac{2.303RT}{nF} \log(C_1)$$

$$E_{\text{cell}} \approx \frac{2.303RT}{nF} \log \frac{C_2}{C_1} \quad (\text{or}) \quad E_{\text{cell}} \approx \frac{0.0591}{n} \log \frac{C_2}{C_1} ; \quad \text{at } 298 \text{ K}$$

It is evident from the above expression that E_{cell} can be positive only if $C_2 > C_1$.

Thus in a concentration cell, the electrode with lower electrolyte concentration acts as the anode and the one with higher electrolyte concentration acts as the cathode. The concentration of ions increases at the anode and decreases at the cathode when cell is in operation. The emf of the cell is dependent on the ratio of electrolyte concentrations at two electrodes. Higher the ratio (C_2/C_1), higher is the emf. Therefore, the cell can operate only as long as the concentration terms are different. When the current is drawn from the cell, C_1 increases and C_2 decreases and as a result the emf of the cell goes on decreasing and becomes zero when the two becomes equal.

Energy Storage Systems

Cell:

Definition: It is an electrochemical cell or Galvanic cell, which converts chemical energy into electrical energy making use of an electro – chemical redox reaction. The decrease in free energy in the reaction appears as electrical energy.

Battery:

Definition: Battery is a device consisting of two or more Galvanic (Voltaic) cells connected in series that can generate power and can act as a portable source of electrical energy.

Examples: Lead acid storage battery, Ni - Cd battery.

Classification of Batteries :

(1) Primary Batteries :

A primary cell is one in which electrical energy can be obtained at the expense of chemical energy only as long as the active materials are still present. Once these have been consumed, the cell cannot be profitably or readily recharged and must be discarded. Eg.: Dry cell, HgO – Zn cell, Ag₂O – Zinc cell

(2) Secondary cells: (Storage cells)

A secondary cell, once used can be recharged by passing current through it. It can be used over and over again. The redox reaction gets reversed during recharging. The electrical energy is stored in the form of chemical energy and utilized for supplying the current when needed. Secondary cells are also known as storage cells.

Primary cell acts as only galvanic cell. But secondary cell acts both as galvanic cell and electrolytic cell. During discharging it acts as a galvanic cell (C.E. to E.E.) while recharging Electrolytic cell (E.E. to C.E.) E.g.: Lead storage battery

(3) Reserve Batteries :

The batteries which may be stored in an inactive state and made ready for use by activating them prior to the application are referred to as the reserve batteries. In this type, a key component is separated from the rest of the battery prior to activation. Usually the electrolyte is the component that is isolated. Batteries, which use highly active component material, are designed in this form to withstand deterioration in storage and to eliminate self-discharge prior to use. The reserve design is also used for batteries required to meet extremely long or environmentally severe storage requirements.

In most of the batteries the key component separated from the battery is the electrolyte, thus preventing the chemical reaction in the battery. In lead storage battery by adding 5M H_2SO_4 acid, it can be charged. There are some commercial batteries, which can be activated by adding water or allowing air to enter. E.g.: Mg – H_2O activated batteries

Zn - Ag_2O reserve batteries etc.

Thermal batteries are reserve batteries that use inorganic salt electrolytes, which are non-conductive solids. The battery is activated by melting the electrolyte. Commercial batteries are used as convenient sources of energy when a small amount of energy is required for short durations.

Nickel-metal hydride battery:

Nickel-metal hydride battery is rechargeable:

Construction and working:

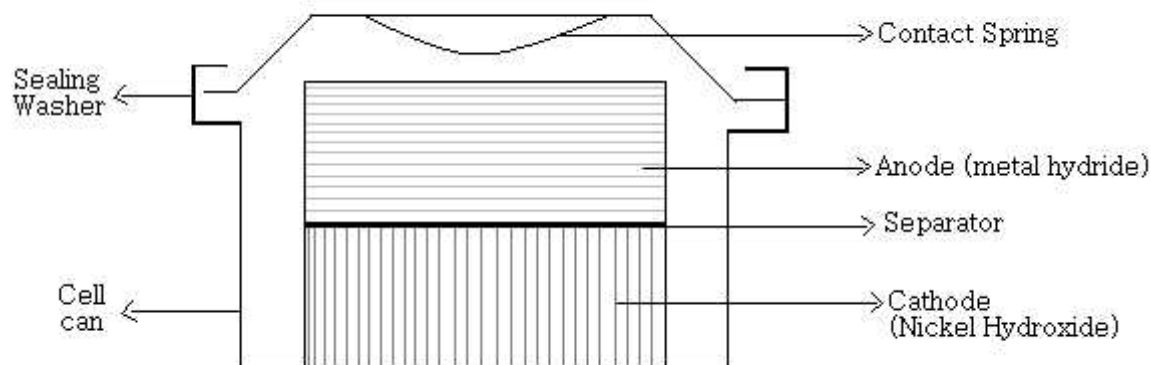
Anode material : A metal hydride such as VH_2 , ZrH_2 or TiH_2 containing hydrogen storage metal alloys such as LaNi_5 or TiNi

Cathode material: It is Nickel Oxy hydroxide, $\text{NiO}(\text{OH})$. The electrode materials are coated or pasted on Nickel wire gauze grids.

Electrolyte: Aqueous KOH solution.

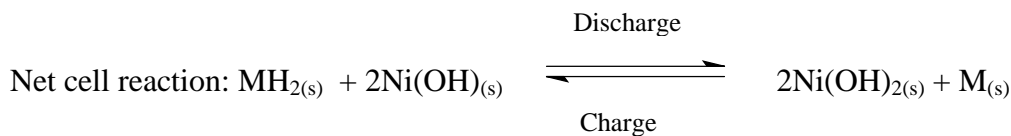
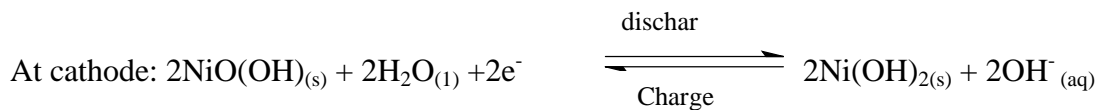
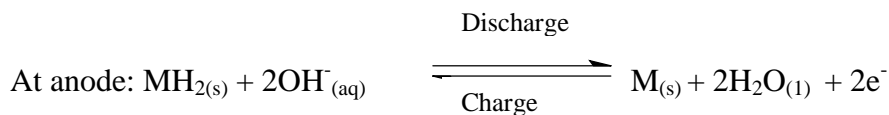
The electrodes are separated by a porous separator soaked in KOH solution.

The button type of cell is shown below:



Cell representation; $\text{MH}_2 \mid \text{KOH (5.35 M)} \parallel \text{Ni(OH)}_2 \mid \text{NiO(OH)}$

Half cell reactions during discharge and charge;



The cell has a cell potential of 1.25 to 1.35 V. During charging the reactions at the electrodes are reversed.

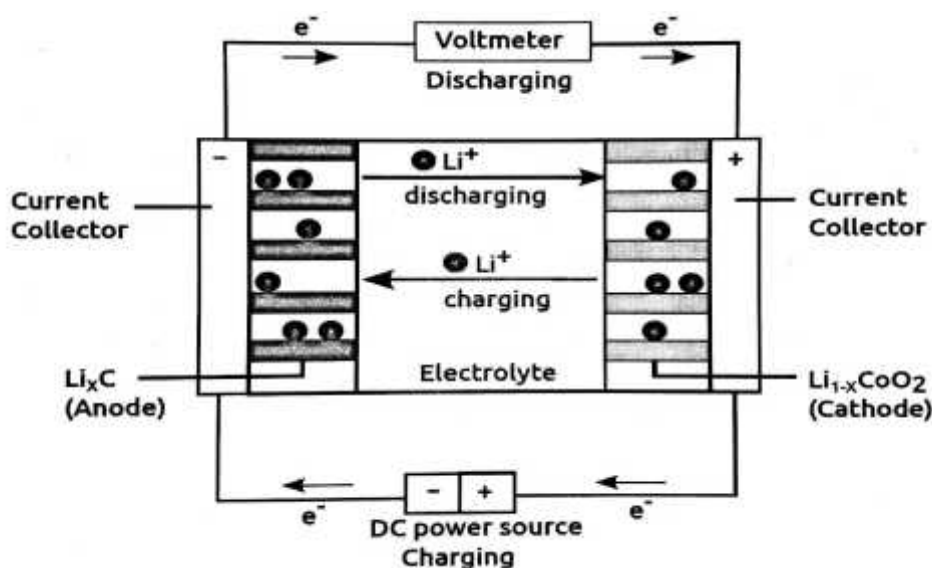
Advantages:

- 1) The battery has a large capacity
- 2) Since it is a sealed battery, no maintenance is required
- 3) It is Cadmium free and therefore does not cause pollution
- 4) It can be recharged rapidly
- 5) It has a long life and shelf life

Applications:

- 1) Used in space craft since it can be used directly with pressurized hydrogen
- 2) Used in cellular phones, computers and other portable gadgets
- 3) Used in electrical vehicles.

Lithium-ion battery:



Anode: Lithium intercalated Carbon or graphite, metal matrix composite or polymer.

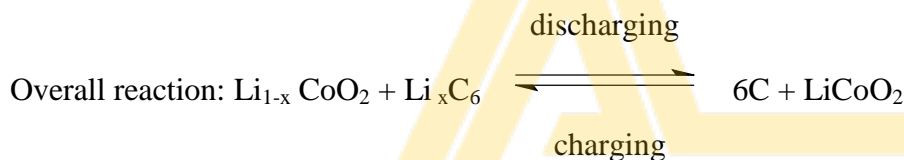
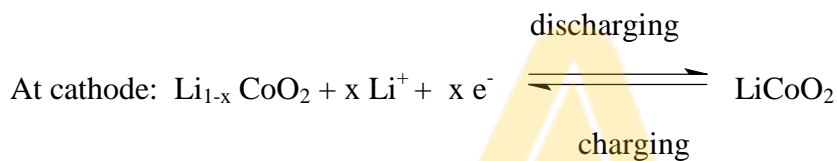
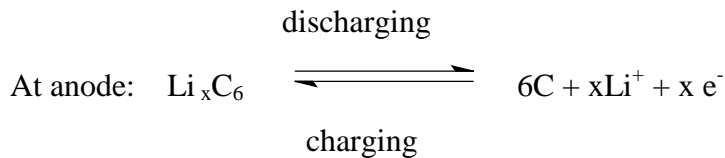
Anode current collector: Copper foil.

Cathode: Partially Lithiated transition metal oxides of nickel, cobalt, and manganese: Li_yNiO_2 , Li_yCoO_2 & $\text{Li}_y\text{Mn}_2\text{O}_4$.

Cathode current collector: Aluminium foil.

Electrolyte: LiPF_6 in a mixture of organic solvents like propylene carbonate.

Cell reactions:



The unit cells are cylindrical, and of jelly-roll design, usually of the same size as nicad (Ni-Cd) cells. The open circuit voltage is about 4.1V. Self discharge rate is about 10% per month.

Applications:

For portable telephones, computers, camcorders, etc.