

**NITTE MEENAKSHI INSTITUTE OF TECHNOLOGY**  
**ATNMS UNDER VTU**  
**DEPT OF CHEMISTRY**  
**SYLLABUS 2017-2018**

**Sub Code: 17CHE12 /17CHE22**  
**Hrs/Week: 04**  
**Total Hrs: 48**

**IA Marks: 50**  
**Exam Hours: 03**  
**End SEM Exam: 50**

**Unit I**

**Chemical energy sources:**

Introduction to energy, Fuels-definition, classification, importance of hydrocarbon fuels, Calorific value-definition, Gross and Net calorific value, (SI units).Determination of calorific value of a solid/liquid fuel using Bomb calorimeter. Determination of calorific value of a gaseous fuel using Bouy's calorimeter Petroleum cracking-Fluidized catalytic cracking, Reformation of petrol. Numericals.

**Conversion and storage of electrochemical energy:**

Single electrode potential- definition, origin, sign convention. Derivation of Nernst equation. Standard electrode potential- definition. Construction of galvanic cell-classification of primary, secondary and concentration cells. EMF of a cell-definition, notation and convention.

**Batteries-** Introduction to batteries, charging and discharging, characteristics of batteries, types, primary and Secondary battery (Li -Ion)construction and working principle.

**Green Chemistry:** An overview of Green chemistry, twelve principles of green chemistry.

**-10 hrs**

**Unit II**

**Corrosion Science:**

**Corrosion-** definition, Chemical Corrosion and electrochemical theory of Corrosion, Types of Corrosion, Differential metal corrosion, Differential aeration corrosion(Pitting and water line corrosion) Stress corrosion, Factors effecting the rate of corrosion. Corrosion control: Design, Metal coatings-Galvanizing and Tinning, Cathodic Protection.

**Environmental Chemistry and waste management:**

**Atmospheric pollution - Gaseous pollutants:** Oxides of carbon, nitrogen and sulphur, hydrocarbons; their sources, harmful effects and prevention; Green house effect and Global warming; Acid rain; Particulate pollutants: Smoke, dust, smog, fumes, mist; their sources, harmful effects and prevention.

**Water pollution** -Impurities in the water, Definition- COD and BOD: Determination of different constituents in water- COD and DO. Numericals. Sewage Treatment, Potable water, Purification of water-, Electrodialysis, and Reverse osmosis. .

**Waste management** –Introduction, various types of waste management , Solid waste management – non-hazardous and municipal. **-10 hrs**

### **Unit III**

#### **Crystal structure**

Introduction to crystal structure. Miller indices, Features of Miller indices, Packing fraction or atomic packing factor (APF) OR relative density of packing, Inter planar spacing, Expression for spacing between lattice planes, Solved Problems, Exercises

#### **Liquid crystals and their application:**

Introduction, Classification thermotropic and Lyotropic with examples Types of Mesophases-Nematic and Chiral nematic (cholesteric) smectic and columnar with example. Application of liquid crystals in display systems .working of L.C.D.

#### **OLED'S :**

Introduction to OLEDs, Types of OLEDs, OLED Structure, Working of OLEDs, current and future OLEDs

**-09 hrs**

### **Unit IV**

#### **Semiconductors :**

**Introduction to Semiconductors**, conductivity equation of pure semiconductors, defects in solids photocopying process.

**Renewable energy sources** -definition, history, importance of **renewable energy sources**, notational and international energy scenario, Main stream renewable technologies- solar energy( PV Cells dye sensitizer ), Wind energy, Tidal energy, Hydro thermal and Applications of solar, Wind, Tidal, Hydro thermal energies.

**-09 hrs**

### **Unit V**

#### **Nanoscience:**

Introduction- Overview of Nanoscience Theory, definitions and history – Properties at nanoscale. . Different classes of Nanomaterials –1D, 2D, 3D and 0D; **Nano Scale materials** – nano rods, nanotubes, Quantum dots, nanomembranes **Synthesis** by “Top-down” approach- Hydro thermal and Photolithography “Bottom up approach” – CVD, PVD, Solgel and precipitation methods.**Characterization** : Introduction, principle, working of Scanning Electron Microscope **Applications** : Nano Solar cells and Bio medical application –diagnosis using sensors and treatment of cancer using Gold nano particles.

#### **Nano composites**

Introduction- Overview of nano composites, classification Properties and Applications- Nanoclay-reinforced composites. Carbon nanotube-reinforced composites. Nanofibre-reinforced composites, and Inorganic particle-reinforced composites. Nanocomposites applications **- 10hrs**

### **TEXT BOOKS :**

1. **F.W. Billmeyer, John Wiley & Sons**, Text book of Polymer Science,1994.
2. **Benny Joseph, Environmental studies**,Mc Graw-Hill publishing company 2004.
3. **M.G. Fontana**, Corrosion Engg, Mc Graw Hill Publication.2005.

### **REFERENCE BOOKS:**

1. **Stanley and Co**,Environmental Chemistry by Mc Graw Hill Publication,2008.
2. **G.L. Hornyak, J.Dutta, H.F. Tibbals, A.K.Rao**, Introduction to Nanoscience, CRC Press, 2008.
3. **A.Nabok**, *Organic and Inorganic Nanostructures*, Artech House 2005.
4. **Hari Singh Nalwa**, *Nanostructured Materials and Nanotechnology*, Academic Press. 2015.
5. **Gordon M Barrow** Physical Chemistry Mc Graw Hill-Kagakusha, 1987.

## UNIT I

### CHEMICAL ENERGY SOURCES

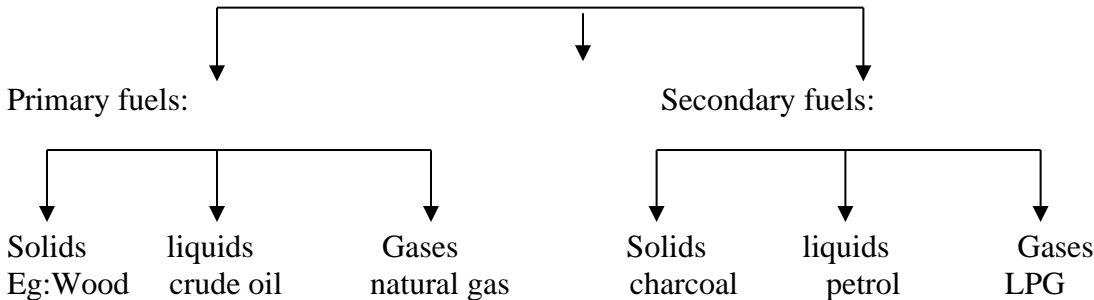
**FUEL:** A fuel is a naturally occurring or artificially manufactured carbonaceous material, which acts as a source of heat and light on combustion with oxygen or air.

#### **CLASSIFICATION OF FUELS:**

On the basis of occurrence, fuels are classified as

1. **Primary fuels** occur in nature and are used without processing.
2. **Secondary fuels** are obtained by chemical processing of primary fuels.

Fuels



**CALORIFIC VALUE:** It is defined as the amount of heat liberated when a unit weight or unit volume of a fuel is completely burnt in excess amount of air or oxygen. Unit of calorific value in CGS = cal/g; SI unit = J/Kg; for a gas = J/m<sup>3</sup>

Fuels generally contain hydrogen in addition to carbon. During combustion, the hydrogen is converted to steam and carbon to carbon dioxide

**GROSS CALORIFIC VALUE: (HIGHER CALORIFIC VALUE)** It is defined as the amount of heat liberated when a unit weight or unit volume of a fuel is completely burnt in excess amount of air or oxygen and the products of combustion are cooled to ambient temperature. Therefore the heat liberated includes the sensible heat and the latent heat of condensation of water produced during combustion.

$$\text{GCV} = \text{NCV} + \text{latent heat of water condensed}$$

**NET CALORIFIC VALUE: (LOWER CALORIFIC VALUE)** It is defined as the amount of heat liberated when a unit weight or unit volume of a fuel is completely burnt in excess amount of air or oxygen and the products of combustion are allowed to escape into the atmosphere. Therefore the heat liberated doesn't include the latent heat of condensation of water. So GCV is always greater than NCV

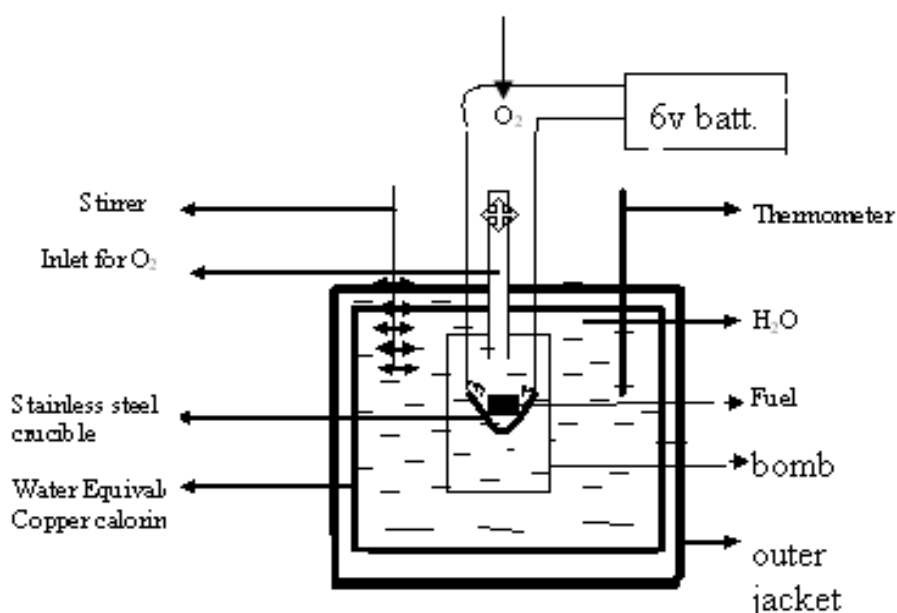
$$\text{NCV} = \text{GCV} - \text{latent heat of water condensed}$$

## **DETERMINATION OF CALORIFIC VALUE OF SOLID AND LIQUID FUELS USING BOMB CALORIMETER:**

The calorific value of solid and liquid fuels can be determined by burning a known mass of the fuel in  $O_2$  under high pressure using bomb calorimeter.

Principle: The heat liberated by the fuel = heat absorbed by the  $H_2O$  surrounding the bomb and water equivalent Copper calorimeter

Construction: The bomb calorimeter consists of a stainless steel airtight cylindrical vessel called Bomb. It has an inlet valve for providing atmospheric  $O_2$  and an electrical ignition coil for the initiation of combustion of fuel. The bomb is placed in a large well-insulated copper calorimeter containing known mass of the water in it. The copper calorimeter is equipped with a mechanical stirrer for dissipation of heat and a thermometer to read the temperature.



Working: A known mass of the fuel is taken in a stainless steel crucible. The crucible containing the fuel is placed inside the bomb. The bomb is sealed air tight by the lid. The sealed bomb containing the sample is next placed in large well-insulated copper calorimeter it is covered by accurately measured quantity of water. The stirrer keeps the water in constant agitation. Initial temperature of the water is carefully measured, the bomb is filled with  $O_2$  and the combustion of the fuel is initiated by passing electric current through the ignition coil.

As the sample burns in the bomb heat is liberated and is absorbed by the surrounding water and copper calorimeter. The temperature of water is noted before and after the experiment.

Observations and calculation:

Mass of the fuel: m kg

Weight of H<sub>2</sub>O taken: W<sub>1</sub> kg

Water equivalent of cooper calorimeter: W<sub>2</sub> kg

Initial temperature of water: t<sub>1</sub> °C

Final temperature of water: t<sub>2</sub> °C

Difference in temperature: Δt °C

Heat liberated by the fuel = heat gained by the H<sub>2</sub>O + Copper calorimeter

$$Q = \text{GCV} = \frac{(W_1 + W_2) \times \Delta t}{m} \text{ cal/g}$$

$$= \frac{(W_1 + W_2) \text{ kg} \times \Delta t \text{ } ^\circ\text{C} \times 4.187 \text{ kJ/kg}}{m \text{ kg}}$$

$$\text{LCV} = \text{GCV} - \text{H}_2 \% \times 0.09 \times \text{latent heat of steam (587 kcal/g or 2454 kJ/kg)}$$

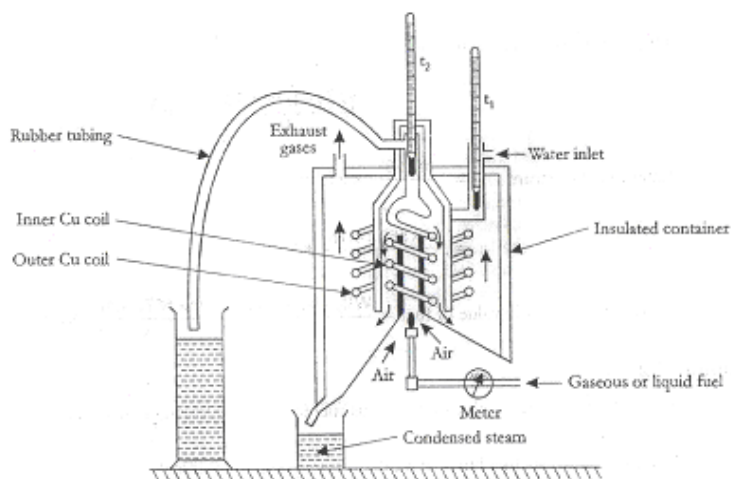
### **DETERMINATION OF CALORIFIC VALUE OF GASEOUS FUELS USING BOUYS CALORIMETER:**

The calorific value of gaseous fuels can be determined by burning a known volume of the fuel using Bouys calorimeter.

Principle: The heat liberated by the fuel = heat absorbed by the H<sub>2</sub>O flowing in the Cu coils

#### Construction:

It consists of a combustion chamber. The outer and inner walls of the chamber are coiled by copper tubing through which the cold water is circulated at constant rate. The water enters the copper tube from the top(as inlet) moves down the bottom of chamber, then goes through the inner coils and finally leaves the combustion chamber as outlet. The water circulated is collected using measuring jar. The gas sample is burnt using burner. Kept inside the combustion chamber. The flow is measured using gas meter. The whole assembly is enclosed in a insulated chamber, the stream produced during combustion is collected as condensed water. The thermometer t<sub>1</sub> & t<sub>2</sub> placed at the inlet and outlet to note the initial & final temp respectively recorded at steady temp.



**Working:** The gas sample is burnt at the burner at constant flow rate of the gas and simultaneously cooling water is circulated at constant rate. The above flow is continued for some time to establish steady conditions. At steady condition following observations are made.

**Observations and calculation:**

Mass of the fuel:  $V \text{ m}^3$

Weight of  $\text{H}_2\text{O}$  taken:  $W \text{ kg}$

Initial temperature of water:  $t_1 ^\circ\text{C}$

Final temperature of water:  $t_2 ^\circ\text{C}$

Difference in temperature:  $\Delta t ^\circ\text{C}$

Mass of condensed water =  $m \text{ kg}$

Heat liberated by the fuel = heat gained by the  $\text{H}_2\text{O}$

$$Q = \text{GCV} = \frac{W \times \Delta t ^\circ\text{C}}{V} \text{ cal / m}^3$$

$$= \frac{W \text{ kg} \times \Delta t ^\circ\text{C} \times 4.2 \text{ kJ / m}^3}{V \text{ m}^3}$$

$$\text{LCV} = \text{GCV} - \frac{m}{V} \times \text{latent heat of steam (587 kcal/g or 2,454 kJ/kg)}$$

**CATALYTIC CRACKING:**

It is a chemical process where high molecular hydrocarbons (high boiling point) are broken into low molecular hydrocarbons (low boiling point)



**FLUIDIZED CATALYTIC CRACKING (MOVING BED CATALYTIC CRACKING)**

In the FCC process, the oil is preheated to  $300^{\circ}\text{C}$  and is sprayed from the bottom into the catalytic chamber, containing the catalyst maintained at  $700^{\circ}\text{C}$  to produce the reaction mixture temp. of  $550^{\circ}\text{C}$ . The oil is allowed to undergo cracking. The cracked vapours are then sent into the fractional column where it gets divided into petrol, diesel etc. The uncracked oil remains at the bottom of fractional column simultaneously, the deactivated catalyst is sent into the regenerating chamber where it gets activated by removing the carbon deposit using hot air. The regenerated catalyst is again introduced back into the cracking chamber by a current of air. The uncracked oil is recycled into the cracking chamber to get high yield.

#### Conditions

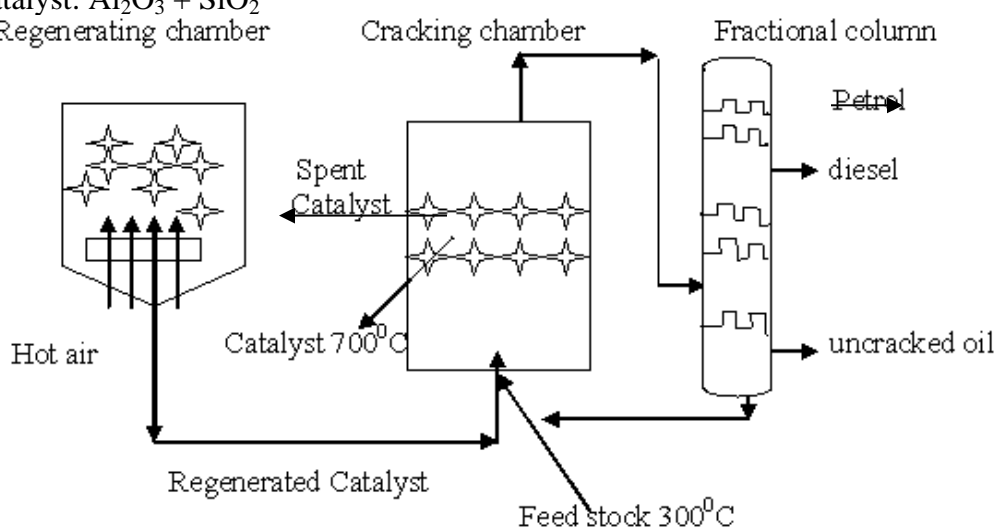
Feed stock: crude oil

Temp:  $550^{\circ}\text{C}$

Pr: 10- 25 atm pr

Catalyst:  $\text{Al}_2\text{O}_3 + \text{SiO}_2$

Regenerating chamber



#### REFORMATION:

It is a process of bringing structural modifications in the straight chain hydrocarbons (with lower octane number) to increase the octane number and thereby improving the anti-knocking characteristics of petrol. It is a process, of upgrading the octane no. of petrol fraction is called as reformation. By reformation high-octane petrol is obtained. If the reformation is done using a catalyst it is called as **catalytic reformation**.

The process involves a molecular rearrangement of hydrocarbons without any change in the no of carbon atoms to form new compounds

#### Conditions:

Feed stock: Low grade petrol

Temp:  $470- 550^{\circ}\text{C}$

Pr: 10- 25 atm pr

Catalyst: Pt

Octane number is defined as the percentage of isooctane present in a standard mixture of isooctane and n-heptane, which knocks at the same compression ratio as the petrol being tested.

Isooctane is the branched chain hydrocarbon has least knocking rate, hence its



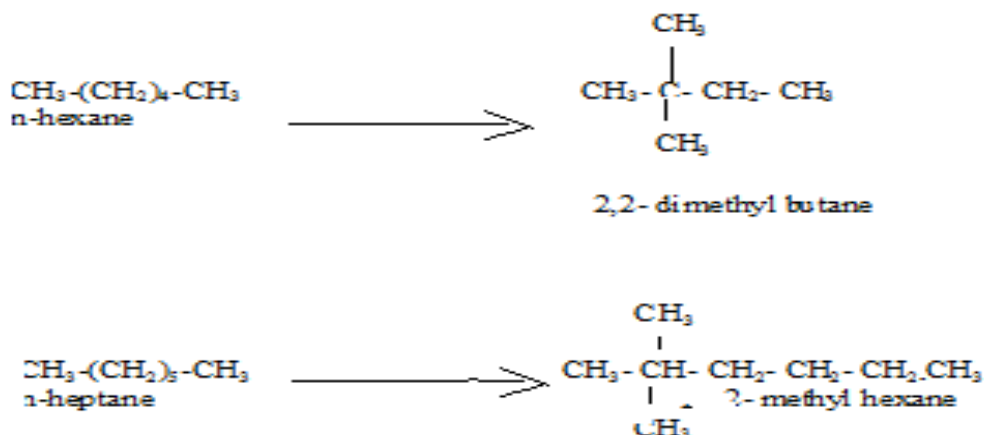
octane number is arbitrarily fixed as 100. N-heptane a straight chain hydrocarbon has highest tendency to knock hence its octane number is fixed as zero. Octane number of petrol is 80 means it contains 80% by volume isooctane and 20% by volume n- heptane.

Reforming is a chemical process, which involves modification of the structure of molecules without much change in the molecular masses. Reformation of petroleum involves the following reforming reactions:

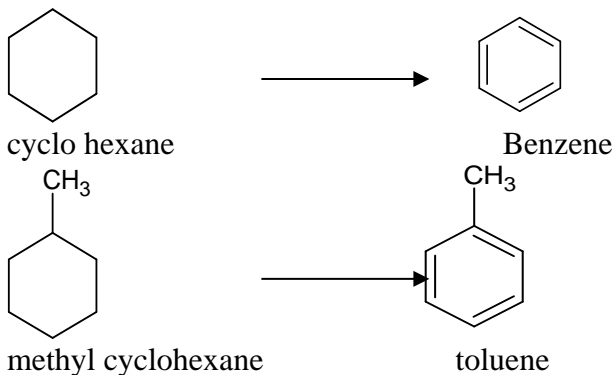
- 1) Isomerisation.
- 2) Dehydrogenation.
- 3) Cyclisation & dehydrogenation and
- 4) Hydro cracking.

### 1) Isomerisation: -

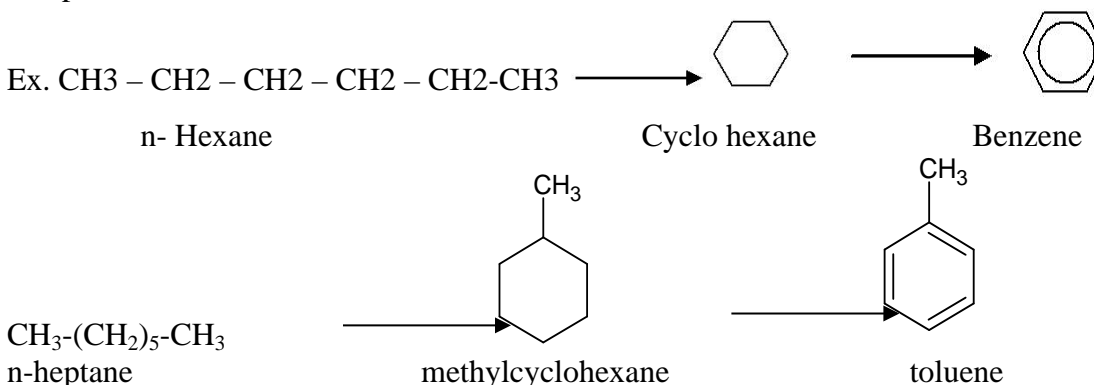
It is a process of converting the straight chain hydrocarbon compound of lower octane number into a branched chain hydrocarbon compound of higher octane number.



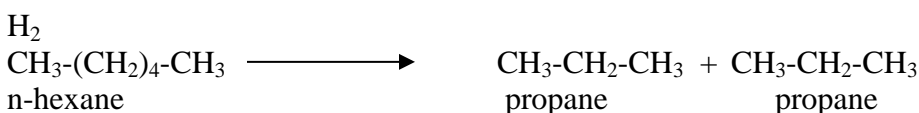
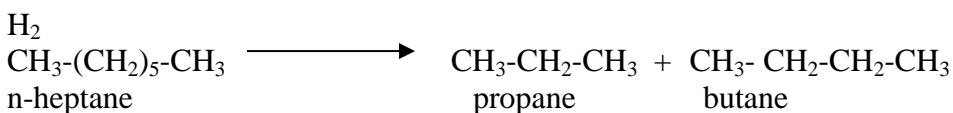
**2)Dehydrogenation:** It is process in which the H<sub>2</sub> is removed producing a aromatic molecule.



**3) Cyclization and dehydrogenation:** Straight chain hydrocarbons undergo cyclisation to form cyclic compounds, which further undergoes dehydrogenation to form aromatic compounds.



**4) Hydro cracking:** -Straight chain hydrocarbons undergo hydro cracking in presence of hydrogen and platinum catalyst producing low molecular weight gaseous fractions which are removed to improve the octane number.



### **PROBLEMS:**

#### **BOMB CALORIMETER**

1) Calculate calorific value coal samples from the following data.

Mass of the coal = 1g.

Water equivalent of calorimeter = 2 Kg.

Specific heat of water = 4.187 J/Kg/c.

Rise of temperature = 4.8°C.

**SOLUTION:** 
$$\text{GCV} = \frac{W \times S \times \Delta t}{M} \text{ J/Kg}$$

$$= \frac{2 \times 4.187 \times 4.8}{0.001}$$

$$= 40195.2 \text{ KJ/Kg.}$$

2) A coal sample with 93% carbon, 5% of Hydrogen and 2% Ash is subjected to combustion in a bomb calorimeter. Calculate GCV and NCV Given that Mass of the coal sample = 0.95g

Mass of water in copper calorimeter = 2000g.

Water equivalent wt of calorimeter = 700g.

Rise in temp = 2.8°C

Latent heat of = 587 cal/g.

Specific heat of water = 1 cal/g/°C

$$\begin{aligned} \text{GCV} &= \frac{(W+w) \times S \times \Delta t}{M} \\ &= \frac{(2000+700) \times 10^{-3} \text{ kg} \times 1 \text{ cal/g/}^\circ\text{C} \times 2.8^\circ\text{C} \times 4.184}{0.95 \times 10^{-3} \text{ kg}} \\ &= 33295.83 \text{ J/kg.} \end{aligned}$$

$$\begin{aligned} \text{NCV} &= \text{GCV} - 0.09 \times \% \text{H}_2 \times 587 \times 4.184 \text{ J/kg.} \\ &= 33295.83 \text{ J/kg} - 0.09 \times 5 \times 587 \times 4.184 \text{ J/kg.} \\ &= \mathbf{32190.62 \text{ J/kg}} \end{aligned}$$

- 3) When 0.84g of coal was burnt completely in Bomb calorimeter the increase in temp of 2655 grams of water was 1.85°C if the water equivalent calorimeter is 156g Calculate GCV.

$$\begin{aligned} \text{GCV} &= \frac{(W+w) \times S \times \Delta t}{M} \\ &= \frac{(2655+156) \times 1.85 \times 10^{-3} \times 4.187}{0.84 \times 10^{-3}} \\ &= 25921.26 \text{ J/Kg} \end{aligned}$$

- 4) Calculate GCV and NCV of a fuel from the following data. Mass of fuel = 0.75g, W = 350g,  $\Delta t = 3.02^\circ\text{C}$ , Mass of water = 1150, % H<sub>2</sub> = 2.8.

$$\begin{aligned} \text{GCV} &= \frac{(W+w) \times \Delta t \times S}{M} \\ &= \frac{(1150+350) \times 10^{-3} \times 3.02 \times 4.184}{0.75 \times 10^{-3}} \end{aligned}$$

$$\text{GCV} = \mathbf{25271.36 \text{ KJ/Kg}}$$

$$\begin{aligned} \text{NCV} &= \text{GCV} - 0.09 \times H \times 587 \times 4.184 \\ &= 25271.36 - 0.09 \times 2.8 \times 587 \times 4.184 \end{aligned}$$

$$\text{NCV} = \mathbf{24652.44 \text{ KJ/Kg}}$$

- 5) Calculate calorific value of a fuel sample of a coal from the following data. Mass of the coal is 0.6g. Water equivalent wt of calorimeter is 2200g. Specific value 4.187 Kg/KJ/°C rise in temperature = 6.52°C.

$$\text{GCV} = \frac{(W_1+W_2) \times S \times \Delta t}{M}$$

$$= \frac{(2200) \times 10^{-3} \times 4.184 \times 6.52}{0.6 \times 10^{-3}}$$

$$= \mathbf{100025.49 \text{ KJ/Kg.}}$$

6) Calculate GCV and NCV of a fuel from the following data. Mass of fuel = 0.83g, W = 3500g, W = 385 g, t<sub>1</sub> = 29.2°C, t<sub>2</sub> = 26.50°C, % H<sub>2</sub> = 0.7 and S = 4.2 kJ/kg/c

$$\begin{aligned} \text{GCV} &= \frac{(W+w) \times \Delta t \times S}{M} \\ &= \frac{(3.5 + 0.385) \times (29.2 - 26.5) \times 4.2}{0.83 \times 10^{-3}} \end{aligned}$$

$$\text{GCV} = 53079.39 \text{ KJ/Kg}$$

$$\text{NCV} = \text{GCV} - 0.09 \times H \times 587 \times 4.184$$

$$= 53079.39 - 0.09 \times 0.7 \times 587 \times 4.2$$

$$\text{NCV} = \mathbf{52924.07 \text{ KJ/Kg}}$$

### BOUYS CALORIMETER

1) Calculate gross and net calorific value of a gaseous fuel from the following data obtained from boys experiment:

i) Volume of gaseous fuel burnt at STP	= 0.09 m <sup>3</sup>
ii) Weight of water used for cooling	= 25.0 kg
iii) Temperature of inlet water	= 25.0° C
iv) Temperature of outlet water	= 40.0° C
v) Weight of water produced by steam condensation	= 0.02 kg
vi) Latent heat of steam	= 587 k cal kg

### Solution:

$$\text{Higher calorific value of the given gaseous sample} = \frac{W \times (t_2 - t_1)}{V} \times 4.187$$

$$= 25 \times (40 - 25) \times 4.187$$

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$$= \frac{0.09}{0.09} \times 17445.8 \text{ kJ m}^3$$

$$0.02 \times 587 \times 4.187$$

$$\text{Heat released in condensing steam} = \frac{0.02 \times 587 \times 4.187}{0.09}$$

Net calorific value

$$= 546.17 \text{ kJ m}^3$$

$$= \text{HCV} - \text{latent heat of steam}$$

$$= 17445.8 - 546.17$$

$$= 16899.63 \text{ kJ m}^3$$

2) Calculate the gross and net calorific value of a gaseous fuel at STP from the following data

$$\text{Volume of gas burnt} = 0.02 \text{ m}^3$$

$$\text{Temperature of the gas} = 293 \text{ K}$$

$$\text{Mass of water passing through calorimeter} = 4.5 \text{ kg}$$

$$\text{Rise in temp} = 18.5 \text{ K}$$

$$\text{Absolute pressure of gas} = 101990 \text{ N/m}^2$$

$$\text{Specific heat of water} = 4.18 \text{ J/g/K}$$

$$\text{Amount of water collected} = 7.5 \text{ cm}^3$$

**Solution:**

i) Heat absorbed by cold water

$$= \text{mass of water} \times \text{specific heat} \times \text{rise in temp} = 4.5 \text{ kg} \times 4.18 \text{ J/g/K} \times 18.5 \text{ K}$$

$$= 4500 \text{ g} \times 4.18 \text{ J/g/K} \times 18.5 \text{ K}$$

$$= 348000 \text{ J or } 348 \text{ KJ}$$

ii) Reduce the volume of the gas to that at STP using combined gas law

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\frac{101990 \text{ N/m}^2 \times 0.02 \text{ m}^3}{293 \text{ K}} = \frac{101325 \text{ N/m}^2 \times V}{273 \text{ K}}$$

$$V = 0.0188 \text{ m}^3$$

iii) Calorific value,  $Q = \frac{\text{Heat absorbed by cold water}}{\text{Volume of gas}}$

Volume of gas

$$= 348 / 0.0188$$

$$= 18510 \text{ kJ/m}^3$$

iv) Net Q:

Water condensed during combustion =  $7.5 \text{ cm}^3 = 7.5 \text{ gram}$  Latent heat of steam at  $288 \text{ K} = 2.454 \text{ kJ/g}$

Therefore heat to be deducted from gross calorific value

$$= \frac{7.5 \text{ g} \times 2.454 \text{ kJ/g}}{0.0188 \text{ m}^3}$$

$$= 979 \text{ kJ/m}^3$$

Therefore Net Q =  $18510 - 979 = 17531 \text{ kJ/m}^3$

1. Calculate the gross calorific value and net calorific value of a sample of coal 0.5g of which when burnt in a bomb calorimeter, raised the temperature of 1000g of water from 293K to 301.6K. The water equivalent of calorimeter is 350 g. The specific heat of water is  $4.187 \text{ kJ kg}^{-1}$ , latent heat of steam is  $2457.2 \text{ kJ kg}^{-1}$ . the coal sample contains 93% carbon, 5% hydrogen and 2% ash.
2. Calculate the gross calorific value and net calorific value of a gaseous fuel,  $0.012 \text{ m}^3$  of which when burnt raised the temperature of 3.5kg of water by 8.2K. Specific heat of water is  $4.2 \text{ kJ kg}^{-1} \text{ K}^{-1}$ . Latent heat of steam is  $2454 \text{ kJ kg}^{-1}$ . The volume of water collected is  $6.5 \text{ cm}^3$ . ( $1 \text{ g} = 1 \text{ cm}^3$ ) Latent heat of steam is  $2457.2 \text{ kJ kg}^{-1}$
3. Calculate the calorific value of coal sample from the following data:  
Mass of coal: 1g, water and water equivalent of calorimeter: 2 Kg  
Specific heat of water:  $4.187 \text{ KJ kg}^{-1} \text{ C}^{-1}$  and rise in temperature:  $4.8^\circ \text{C}$
4. On burning  $0.83 \times 10^{-3} \text{ Kg}$  of a solid fuel in a bomb calorimeter, the temperature of 3.5Kg of water increased from  $26.5^\circ \text{C}$  to  $29.2^\circ \text{C}$ . The water equivalent of calorimeter and latent heat of steam are 0.385Kg and  $4.2 \times 587 \text{ KJ/Kg}$  respectively. If the fuel contains 0.7% hydrogen, calculate its gross and net calorific values.
5. Calculate the gross and net calorific values of a gaseous fuel at STP given  $0.03 \text{ m}^3$  of the gas at STP raised the temperature of 6 Kg of water by 16K and  $13.8 \text{ cm}^3$  of water was collected. Specific heat of water is  $4.18 \text{ KJ kg}^{-1} \text{ C}^{-1}$  and latent heat of steam at STP is  $2.45 \text{ KJ kg}^{-1}$
6. Calculate Gross calorific and Net calorific values of a coal sample from the following data:  

Weight of coal sample taken:	$8.5 \times 10^{-4} \text{ Kg}$
Weight of water taken in the calorimeter:	3.5 Kg
Water equivalent of calorimeter	0.5 Kg
Initial temperature of water	$25^\circ \text{C}$
Final temperature of water	$27.5^\circ \text{C}$
Percentage of $\text{H}_2$ in the coal sample	2.5
Latent of Heat of steam	$2455 \text{ kJ/Kg}$
7. Calculate Gross calorific value of a coal sample from the following data:  

Weight of coal sample taken	$5.5 \times 10^{-3} \text{ Kg}$
Weight of water taken in the calorimeter:	2.5 Kg
Water equivalent of calorimeter	0.5 Kg
Initial temperature of water	$24^\circ \text{C}$

### **CONVERSION AND STORAGE OF ELECTROCHEMICAL ENERGY: ELECTRODE POTENTIAL AND CELLS**

An electrochemical cell is a device, which is used to convert chemical energy into electrical energy and vice versa.

These electrochemical cells are classified into two types as follows.

**1) Galvanic or Voltaic cells:** These are the electrochemical cells, which convert chemical energy into electrical energy.

Ex. Daniel cell, Dry cell, etc.

**2) Electrolytic cell:** These are the electrochemical cells, which are used to convert electrical energy into chemical energy.

Ex: Lead acid battery, Nickel cadmium battery etc.,

#### **Galvanic or Voltaic cells:**

Galvanic or Voltaic cells are again classified into three types as follows

**a) Primary cells:** These are the cells which serve as a source of energy only as long as the active chemical species are present in the cell. The cell reactions are irreversible. These are designed for only single discharge and cannot be charged again.

Ex: Dry Cell, Zn – Hgo cell, Zn-Ag<sub>2</sub>O cell etc.

**b) Secondary cells:** These cells are chargeable and can be used again and again. The cell reactions are reversible and are often called as reversible cells. During discharging the cells act like voltaic cells converting chemical energy into electrical energy. During charging the cell acts like electrolytic cell by converting electrical energy into chemical energy, hence these batteries are called as storage batteries.

**Ex:** Lead acid Battery, Ni-cd cells. Lithium ion cells etc.

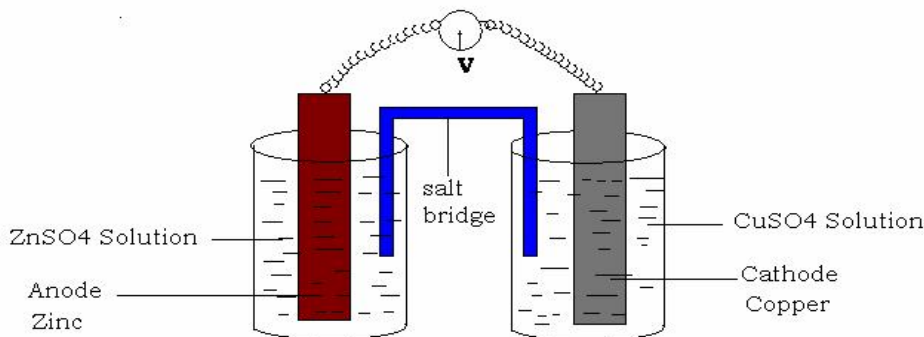
#### **Concentration of cells:**

These are the electrochemical cells consisting of same metal electrodes dipped in

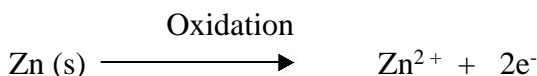
same metal ionic solution in both the half cells but are different in the concentration of the metal ions.

**Ex:** copper concentration cell, Zinc concentration cell

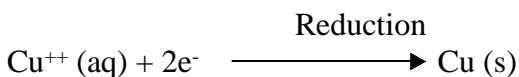
### Construction and working of Daniel cell



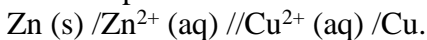
The Daniel cell consisting of two half cells in which zinc and copper electrodes are immersed in zinc Sulphate and copper Sulphate solution respectively. The two half cells are internally connected by a salt bridge and externally by a metallic wire. The zinc electrode undergoes oxidation and loses electron. The electron liberated migrates to another half cell.



In the other half-cell the cupric ions accept the electrons, undergo reduction, and get deposited on copper electrode as copper atoms.



Due to the above simultaneous oxidation and reduction reactions the Daniel cell generates electrical current, which is indicated by voltmeter or ammeter. The Daniel cell can be represented as



### Single electrode potential:

When an electrode is dipped in a solution of its own ions, the metal can undergo oxidation or reduction. As a result, potential is developed at the interface of the metal and the solution called the single electrode potential **OR** it's a measure of the tendency of a given half reaction to occur as reduction when its in equilibrium with its other half cell. Electrode potential is denoted as **E**.

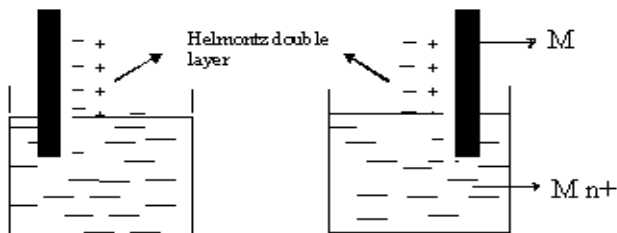
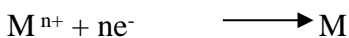
### Origin of Single electrode potential:

When an electrode is contact with a solution of its own ions, two types of reactions are possible. (i) The metal shows a tendency to go into the solution as metal ions by losing electrons.





S<sup>illy</sup> (ii) the metal can get deposited as metal atoms



Depending upon the nature of the metals, either the dissolution of the metal or the deposition of the metal is faster. (i) If the dissolution is faster than the deposition metal atoms dissolve into the solution as +ve metal ions, leaving behind electrons on the electrode surface. This layer of negative charges attracts a layer of positive charges forming a double layer. (ii) If the deposition is faster than the dissolution metal ions get deposited on the electrode as +ve metal ions, this layer of positive charges attracts a layer of negative charges forming a double layer, called as electrical double layer or Helmholtz double layer. The Helmholtz double layer didn't give a fair explanation hence it was modified by Stern.

### Sign convention:

- If a metal is coupled with standard hydrogen electrode (SHE) and if the metal undergoes oxidation, the metal will have a -ve potential

Eg: Zn- SHE then Zn = -0.76v

- If a metal is coupled with standard hydrogen electrode (SHE) and if the metal undergoes reduction, the metal will have a +ve potential

Eg: SHE-Cu then Cu = +0.34v

### **Standard electrode potential.**

It is defined as potential developed at the interface between the metal and the solution. When a metal is dipped in a solution containing its own ions of unit ion concentration and at 298K. [If the electrodes involve gases then it is one atmospheric pressure] It is denoted as  $E^0$

Electrode	$E^0$ (volts)	Electrode	$E^0$ (volts)
Li/Li <sup>+</sup>	-3.04	Fe/Fe <sup>2+</sup>	-0.44
K/K <sup>+</sup>	-2.92	Pt/H <sub>2</sub> / H <sup>+</sup>	0.00
Ca/Ca <sup>2+</sup>	-2.90	Cu/Cu <sup>2+</sup>	+0.34
Na/Na <sup>+</sup>	-2.71	Ag/Ag <sup>+</sup>	+0.80
Mg/Mg <sup>2+</sup>	-2.40	Pt/ Pt <sup>4+</sup>	+0.86
Al/Al <sup>3+</sup>	-1.70	Au/Au	+1.50
Zn/Zn <sup>2+</sup>	-0.76		

Is defined as the potential of an electrode when the electrode is in contact with a solution of unit concentration, at 298 K and 1 atm pr. Standard electrode potential is denoted as  $E^\circ$

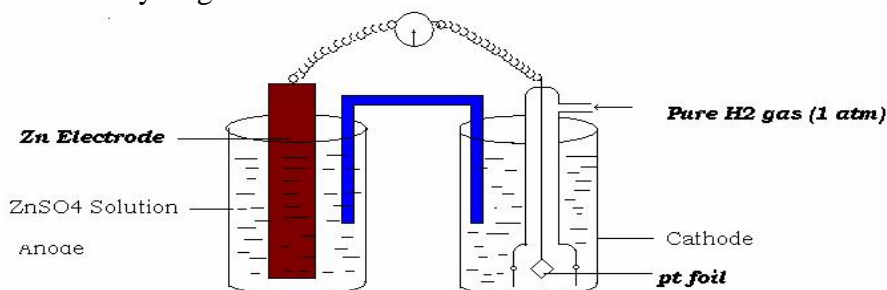
### Measurement of electrode potential

The electrode potentials of any metal electrodes can be determined by using reference electrodes like standard hydrogen electrode. (SHE).

The SHE is coupled with the electrode whose electrode potential is to be determined and the electrode potential of the electrode is determined by fixing the electrode potential and SHE as zero [at all temperatures]

Example: Consider the determination of Single electrode potential of Zinc electrode using Standard Hydrogen electrode.

To determine the Single electrode potential of Zinc electrode it is coupled with Standard Hydrogen electrode as follows



The electrode potential of Zinc electrode can be calculated as

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

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

$$0.76 = 0 - E_{\text{Zn}}$$

$$E_{\text{Zn}} = -0.76 \text{ V}$$

### Electron motive force. (EMF)

It is defined as the potential difference between the two electrodes of a galvanic cell which causes the flow of current from an electrode with higher reduction potential to the electrode with lower reduction potential. It is denoted as  $E_{\text{cell}}$ .

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$$

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

### Standard EMF:

Is defined as the emf of a galvanic cell when the reactants and the products of the cell are in unit concentration, at 298 K and 1 atm pr.

$$E^\circ_{\text{cell}} = E^\circ_{\text{right}} - E^\circ_{\text{left}}$$

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

**Problems:**

- 1) Calculate emf of a cell constructed by combining Cu & Zn electrodes dipping in their respective ionic solutions. The standard electrode potential of Cu and Zn are 0.34 V and 0.76 V respectively at 298K.

$$\begin{aligned}
 E_{\text{cell}} &= E_{\text{cathode}} - E_{\text{anode}} \\
 &= E_{\text{Cu}} - E_{\text{Zn}} \\
 &= 0.34 - (-0.76) = 1.1 \text{ volt}
 \end{aligned}$$

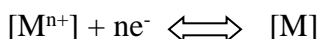
**Sign convention of a cell**

- Convention 1: any electrode undergoing oxidation is anode and is placed on the left hand side. If an electrode undergoes reduction is cathode and is placed on the right hand side.
- Convention 2: If the cell reaction is spontaneous then the EMF of the cell is positive i.e electron flow from left hand side to right hand side to cathode. If the cell reaction is non-spontaneous then the EMF of the cell is negative i.e electron flow from right hand side to left hand side to cathode
- Convention 3: The term electrode potential refers to the reduction potential  $E_{\text{Mn}^{n+}/\text{M}}$

**Nerns't Equation:**

In 1889 Nerns't derived a quantitative relationship between the electrode potential and the concentration of the ions.

Consider an reversible equation



The decrease in the free energy is  $-\Delta G$  represents the maximum work done that can be obtained from a cell

$$-\Delta G = W_{\text{max}}$$

$$\text{Electrical energy} = \text{Volt} \times \text{Total charge}$$

OR

$$\text{Energy available} \times \text{no. of coulombs} = E \times nF$$

Coulomb

$$-\Delta G = nEF \longrightarrow 1$$

Under standard conditions the Eq reduces to

$$-\Delta G^0 = nE^0F \longrightarrow 2 \quad -\Delta G = \text{decrease in free energy}$$

$$-\Delta G^0 = \text{decrease in free energy at std. state}$$

$E$  = potential

For a reversible equation the decrease in free energy is related to the equilibrium constant by a Eq. Vant Hoff equation derived from thermodynamics

$$-\Delta G = -\Delta G^0 - RT \ln K \longrightarrow 3$$

Substitute eq. 1&2 in the eq. 3

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

$[\text{M}^{n+}]$

$$[\text{M}] = 1, \ln = \log \times 2.303 \text{ and divide by } nF$$

$$E = E^0 + \frac{RT}{nF} \log [M^{n+}]$$

R= gas const=8.314 J K<sup>-1</sup> mol<sup>-1</sup>

F=Faraday's constant =96,500 coulombs,

n = no. of moles.

$E = E^0 + \frac{0.0591}{n} \log [M^{n+}]$
for a single electrode

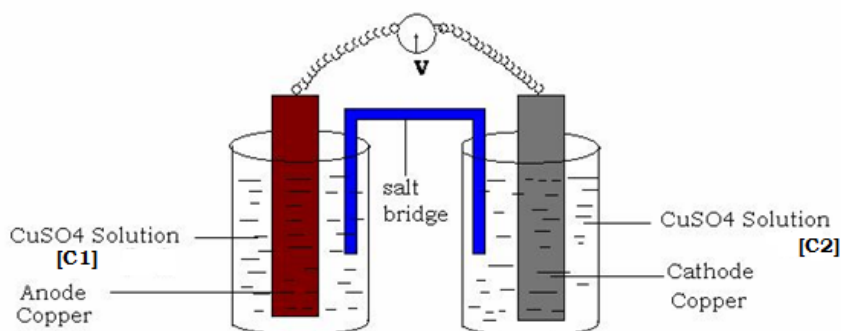
$$E = E^0 - \frac{0.0591}{n} \log \frac{[\text{Products}]}{[\text{Reactants}]}$$

$$E = E^0 - \frac{0.0591}{n} \log \frac{[Zn^{2+}]}{[Cu^{2+}]} \text{ for a Daniel cell}$$

### Concentration cells:

A galvanic cell, consists of two identical electrodes in contact with its salt solution of different concentration. The cell potential is due to difference in the concentrations of the metal ions, hence called concentration cell.

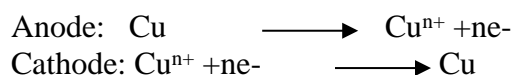
NOTE: The electrode with lesser concentration of metal ions behaves as anode and with higher concentration of metal ions acts as cathode.



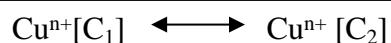
**Concentration Cell**

A cell in which electrodes are made of same materials, electrolytes are also the same but the EMF arises due to the difference in their concentrations are called concentration cells.  
Eg: Cu-Cu cell.

The above concentration cell contains a Cu rod dipped in CuSO<sub>4</sub> of concentration C<sub>1</sub> that is taken as anode half-cell. It also contains a Cu rod dipped in CuSO<sub>4</sub> of concentration C<sub>2</sub> that is taken as cathode half-cell. Both are connected internally by salt bridge and externally through a voltmeter



EMF of a Concentration cell,  
 $\text{EMF} = E_C - E_A$



$$= E^0 + \frac{0.0591}{n} \log [\text{C}_2] - E^0 + \frac{0.0591}{n} \log [\text{C}_1]$$

$$\text{EMF} = \frac{0.0591}{n} \log \frac{[\text{C}_2]}{[\text{C}_1]}$$

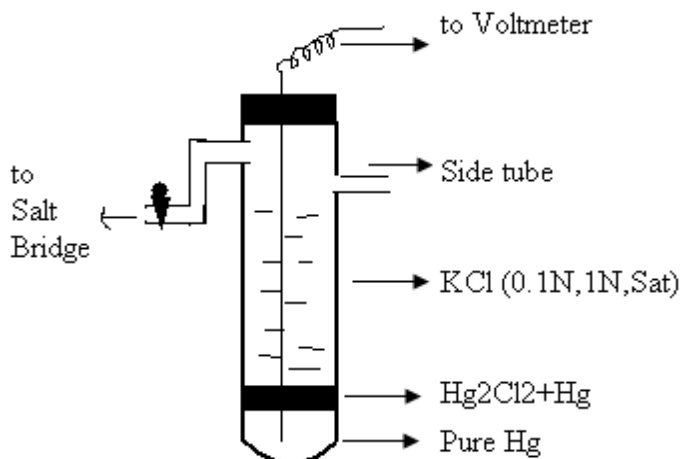
### Reference electrodes

These are the electrodes, which are used to determine the electrode potential of other electrodes and are also called as standard reference electrodes, which mean that the electrodes potential value of these electrodes is known. Reference electrodes are classified as Primary reference electrodes and secondary reference electrodes.

Hydrogen electrodes are primary reference electrodes. But, it has certain limitations. Which includes that construction is difficult because

- 1) hydrogen gas must be very pure free from sulphur otherwise the platinum foil gets poisoned and this will disturb the equilibrium and the potential developed may not be correct and the electrodes containing
- 2) hydrogen must be pure, should not contain any arsenic compound or oxidisable compound if not the platinum foil gets poisoned.
- 3) maintenance of 1 atm pressure and 1M concentration is difficult
- 4) It can not be used in the presence of oxidizing agents.

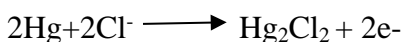
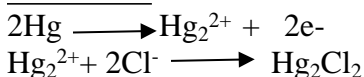
Hence the use of hydrogen electrodes has its own limitations. The limitations of primary electrodes are over by the introduction of secondary reference electrodes. Eg: Calomel electrode



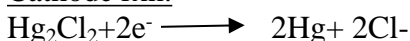
Calomel electrode is constructed by placing a small amount of mercury in a glass vessel and over it a paste made up of solid Mercurous chloride and mercury is placed over it and a saturated solution of potassium chloride is covered above the solid mixture. A glass tube carrying platinum electrodes is introduced in the above arrangement to make electrical connections. Also a salt bridge is immersed in potassium chloride solution to couple calomel electrodes with other electrodes. These electrodes can be used as anode as well as cathode to determine potential of other electrodes.

The electrodes representation is  $\text{Hg}/\text{Hg}_2^{2+}/\text{KCl}(\text{sat})$

Anode rxn:



Cathode rxn.



The potential of a calomel electrode is given

$$E = E^0 - 0.0591/n \log [\text{Cl}^-]^2$$

The potential of calomel electrodes depends on concentration of potassium chloride solution in it, for saturated solution hence the potential is 0.2404V, for one normal solution then potential is 0.2808V and for decinormal solution then potential is 0.334V.

It may be noted that for decinormal solution of potassium chloride the potential is more than that of 1 normal, this is because when calculation are made taking the cell potential for KCl, we get the potential for decinormal solution as 0.334V.

Advantages of Calomel electrodes

- The construction is very simple
- The cell potential is reproducible
- Potential does not vary much for a long time
- temperature invariant

#### PROBLEMS:

1. Given:  $T=298K$ ;  $E^0_{\text{cell}} = 1.5V$ .

$$[Ag^+] = 5.2 \times 10^{-6}M$$

$$[Zn^{+2}] = 1.3 \times 10^{-3}M$$

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

w.k.t

$$E_{\text{cell}} = 1.5 + \frac{0.0591}{2} \log \frac{5.2 \times 10^{-6}}{1.3 \times 10^{-3}} = \frac{5.2 \times 10^{-6}M}{1.3 \times 10^{-3}}$$

$$E_{\text{cell}} = 1.5 - 0.0709$$

$$E_{\text{cell}} = 1.4291 \text{ V.}$$

2. Given:  $T=298K$ ;  $E^0_{\text{Fe}} = -0.44V$ ;  $E^0_{\text{Ag}} = 0.8V$

$$[Fe^{+2}] = 0.1M$$

$$[Ag^+] = 0.05M$$

cell representation:  $Fe_{(s)} | FeSO_4(0.1M) || AgNO_3(0.05M) | Ag_{(s)}$

w.k.t.  $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$

$$E_{\text{cell}} = E^0_{\text{cathode}} + \frac{0.0591}{n} \log [Ag^+] - E^0_{\text{anode}} - \frac{0.0591}{n} \log [Fe^{+2}]$$

$$E_{\text{cell}} = E^0_{\text{cathode}} - E^0_{\text{anode}} + \frac{0.0591}{n} \log \frac{[Ag^+]^2}{[Fe^{+2}]}$$

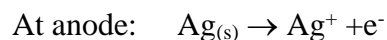
$$E_{\text{cell}} = 1.24 - 0.0089$$

$$E_{\text{cell}} = 1.2311 \text{ V.}$$

3. Given:  $E^0_{\text{Zn}} = -0.76V$ ;  $E^0_{\text{Cu}} = 0.34V$

w.k.t  $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$

$$E_{\text{cell}} = 0.34 - (-0.76) = E_{\text{cell}} = 1.1 \text{ V.}$$



$$w.k.t \quad E_{\text{cell}} = \frac{0.0591}{n} \log \left( \frac{C_2}{C_1} \right) \quad \text{at } 298K$$

$$E_{\text{cell}} = 0.0591 \log \left( \frac{1.2}{0.018} \right) \quad (n=1)$$

$$E_{\text{cell}} = 0.1078 \text{ V.}$$

5. Given:  $E^0_{\text{cell}} = 1.97V$

$$[Mg^{+2}] = 1M$$

$$[Cd^{+2}] = 7 \times 10^{-11}M$$

$$E_{\text{cell}} = E_{\text{cell}}^0 + \frac{0.0591}{n} \log \frac{[Cd^{+2}]}{[Mg^{+2}]}$$

$$E_{\text{cell}} = 1.97 + \frac{0.0591}{2} \log 7 \times 10^{-11}$$

$$E_{\text{cell}} = 1.97 - 0.3001 = E_{\text{cell}} = 1.6699 \text{ V.}$$

6. Given:  $E_{\text{Cd}}^0 = -0.4\text{V}$ ;  $E_{\text{Cu}}^0 = 0.34\text{V}$ ;  $[Cd^{+2}] = 0.01\text{M}$ ;  $[Cu^{+2}] = 0.5\text{M}$

At anode:  $\text{Cd} \rightarrow \text{Cd}^{+2} + 2e^-$

At Cathode:  $\text{Cu}^{+2} + 2e^- \rightarrow \text{Cu}$

Net cell reaction:  $\text{Cd} + \text{Cu}^{+2} \rightarrow \text{Cu} + \text{Cd}^{+2}$

$$E_{\text{cell}} = E_{\text{cathode}}^0 - E_{\text{anode}}^0 + \frac{0.0591}{n} \log \frac{[Cu^{+2}]}{[Cd^{+2}]}$$

$$E_{\text{cell}} = 0.34 - (-0.4) + \frac{0.0591}{2} \log \frac{0.5}{0.01}$$

$$E_{\text{cell}} = 0.74 + 0.0502$$

$$E_{\text{cell}} = 0.7902 \text{ V.}$$

7. **Given:**  $\frac{[Cu^{+2}]_{\text{cathode}}}{[Cu^{+2}]_{\text{anode}}} = \frac{C_2}{C_1} = 10$

w.k.t  $E_{\text{cell}} = \frac{0.0591}{n} \log \left( \frac{C_2}{C_1} \right)$ ; at 298 K

$$E_{\text{cell}} = \frac{0.0591}{2} \log(10)$$

$$E_{\text{cell}} = 0.0296 \text{ V.}$$

8. Given:  $T = 298\text{K}$ ;  $E_{\text{Cu}}^0 = 0.34\text{V}$

$[Cu^{+2}] = 0.1\text{M}$

$$E_{\text{Cu}^{+2}/\text{Cu}} = E^0 + \frac{0.0591}{n} \log [Cu^{+2}] \quad \text{at } 298 \text{ K}$$

$$E_{\text{Cu}^{+2}/\text{Cu}} = 0.34 + \frac{0.0591}{2} \log(0.1)$$

$$E_{\text{Cu}^{+2}/\text{Cu}} = 0.34 - 0.0296$$

$$E_{\text{Cu}^{+2}/\text{Cu}} = 0.3105 \text{ V.}$$

9) Calculate the emf of the cell  $\text{Fe} / \text{Fe}^{++} (0.01) // \text{Ag}^+(0.1) / \text{Ag}$  at 298K if standard electrode potentials of Fe and Ag electrodes are  $-0.42$  and  $0.8 \text{ V}$  respectively.

$$E_{\text{cell}}^0 = E_{\text{cathode}}^0 - E_{\text{anode}}^0$$

$$= E_{\text{Ag}^+/\text{Ag}}^0 - E_{\text{Fe}^{++}/\text{Fe}}^0$$

$$= 0.8 - (-0.42)$$



$$= 1.22 \text{ V.}$$

$$n \quad = E^0_{\text{cell}} + \frac{0.0591}{n} \log_{10} \frac{[\text{Ag}^+]^2}{[\text{Fe}^{++}]}$$

$$= 1.22 + \frac{0.0591}{2} \log_{10} \frac{(0.1)^2}{(0.01)}$$

$$e. 1.22 + 0.02955 \log 1$$

$$f. 1.22 \text{ V.}$$

**10)** A cell is constructed by coupling Zn electrode dipped in 0.5 M ZnSO<sub>4</sub> and

Ni electrode dipped in 0.05 M NiSO<sub>4</sub>. Write the cell representation, cell reaction. Calculate the EMF of cell, given that reduction potentials of Zn and Ni as – 0.76 and – 0.25 volt respectively.

Cell representation: Zn / ZnSO<sub>4</sub>(0.5M ) // NiSO<sub>4</sub> ( 0.05M ) / Ni. Cell reactions: Zn (S) + Ni<sup>++</sup> (aq) → Zn<sup>++</sup> (aq) + Ni (S)

$$E^0_{\text{cell}} = E^0_{\text{cathode}} - E^0_{\text{anode}}$$

$$= E^0_{\text{Ni}^{++}/\text{Ni}} - E^0_{\text{Zn}^{++}/\text{Zn}}$$

$$= -0.25 - (-0.76) = \mathbf{0.51 \text{ V.}}$$

$$\begin{aligned}
&= E^0_{\text{cell}} + \frac{0.0591}{n} \log_{10} \frac{[\text{Ni}^{++}]}{[\text{Zn}^{++}]} \\
&= 0.51 + \frac{0.0591}{2} \log_{10} \frac{(0.05)}{(0.5)} \\
&= 0.51 + 0.02955 \log 0.1 \\
&= \mathbf{0.4805 \text{ V.}}
\end{aligned}$$

11) Calculate the potential of Ag – Zn cell at 298 K if the concentrations of  $\text{Ag}^+$  and  $\text{Zn}^{++}$  are  $5.2 \times 10^{-6} \text{ M}$  and  $1.3 \times 10^{-3} \text{ M}$  respectively.  $E^0$  of the cell at 298K is 1.5 V. Calculate the change in free energy  $\Delta G$  for the reduction of 1 mole  $\text{Ag}^+$ . 1 faraday = 96.5 k J/ V / mole.

Cell reaction:  $2\text{Ag}^+ (\text{aq}) + \text{Zn} (\text{S}) \rightarrow \text{Zn}^{++} (\text{aq}) + 2\text{Ag} (\text{S})$

$$\begin{aligned}
&= E^0_{\text{cell}} + \frac{0.0591}{n} \log_{10} \frac{[\text{Zn}^{++}]}{[\text{Ag}^+]^2} \\
&= 1.5 + \frac{0.0591}{2} \log_{10} \frac{(1.3 \times 10^{-3})}{(5.2 \times 10^{-6})^2} \\
&= 1.5 + 0.02955 \log (20 \times 10^{-9}) \\
&= \mathbf{1.2729 \text{ V.}}
\end{aligned}$$

For the reduction of 2 moles of  $\text{Ag}^+$  ions, 2 electrons are required For the reduction of 1 mole of  $\text{Ag}^+$  ions, 1 electron is required

$$\begin{aligned}
\Delta G &= -n F E_{\text{cell}} \\
&= -1 \times 96.5 \times 1.2729 \\
&= \mathbf{-122.83 \text{ K J / mol}}
\end{aligned}$$

## **BATTERY TECHNOLOGY**

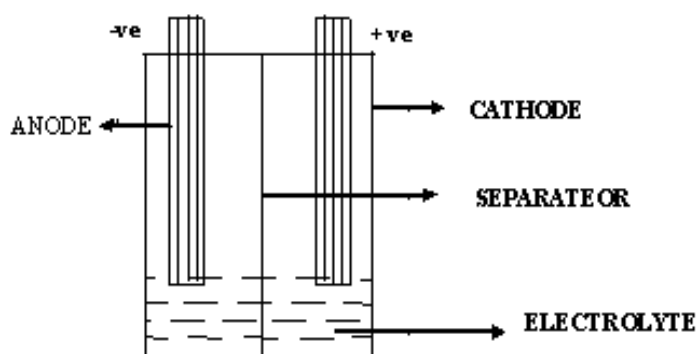
**BATTERY:** Is a device, consisting of two or more galvanic cells connected in series or in parallel or both, that can store chemical energy in the form of active materials and on demand convert chemical energy into electrical energy.

**SIZE:** from cubic centimeter to cubic decimeter.

**USES:** digital watches, cameras, cars, emergency lighting etc.

### **BASIC CONCEPTS:-**

The basic electrochemical unit in a battery is a galvanic cell containing components such as, anode cathode electrolyte & separator.



**Emf of a battery:-** Can be calculated using Nernst equation.

$$E = E_0 - \frac{0.0591}{n} \log \left[ \frac{\text{Products}}{\text{Reactants}} \right]$$

### **CLASSIFICATION OF BATTERY**

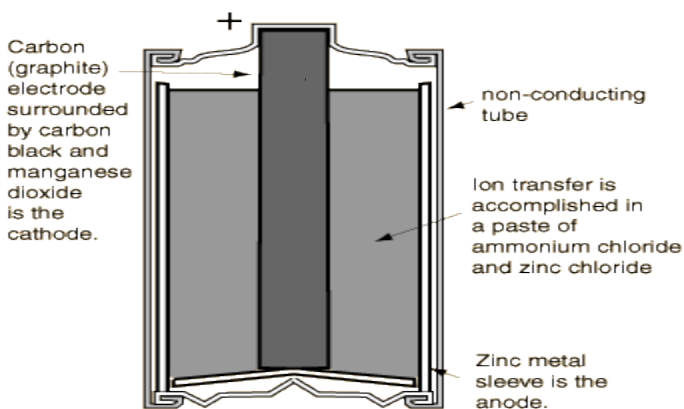
1. Primary Battery:- Eg:- Dry cell.
2. Secondary Battery:- Eg:- Ni – cd Battery /Lead acid battery

#### **1. Primary Battery:**

Eg: Dry cell or Leclanche cell or Zn-MnO<sub>2</sub> cell.

It contains

1. Graphite rod at the centre acts as cathode
2. Surrounding the graphite rod it contains 2 layers. The inner layer of MnO<sub>2</sub> +graphite+ acetylene black MnO<sub>2</sub> has low conductivity so, graphite is added to increase the conductivity & acetylene black helps in retaining moisture.
3. The outer layer is electrolyte in the form of thick paste contains NH<sub>4</sub>Cl+ZnCl<sub>2</sub>
4. The entire assembly is enclosed inside a Zn container.
5. Externally covered by polymer to make the whole cell leak proof

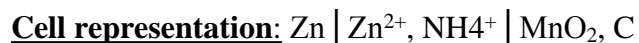
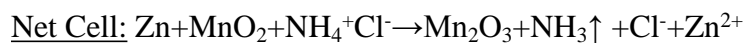
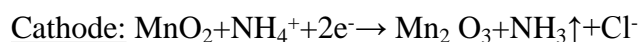
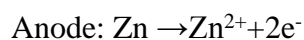


A dry cell is a portable form of a leclanche cell. It consists of a zinc vessel which acts as a negative electrode or anode. The vessel contains a moist paste of saw dusts saturated with a solution of ammonia chloride and zinc chloride.

The ammonium chloride acts as an electrolyte and the purpose of zinc chloride is to maintain the moistness of the paste being highly hygroscopic. The carbon rod covered with a brass cap is placed in the middle of the vessel. It acts as the positive electrode or cathode. It is surrounded by a closely packed mixture of charcoal and manganese dioxide ( $\text{MnO}_2$ ) in a muslin bag. Here  $\text{MnO}_2$  acts as a depolarizer. The zinc vessel is sealed at the top with pitch or shellac. A small hole is provided in it to allow the gases formed by the chemical action to escape. The chemical action inside the cell is the same as in a leclanche cell.

The voltage of a dry cell is 1.5V. If this cell is used continuously, the polarization defect may develop in this cell, but it remains if allowed to rest for a while.

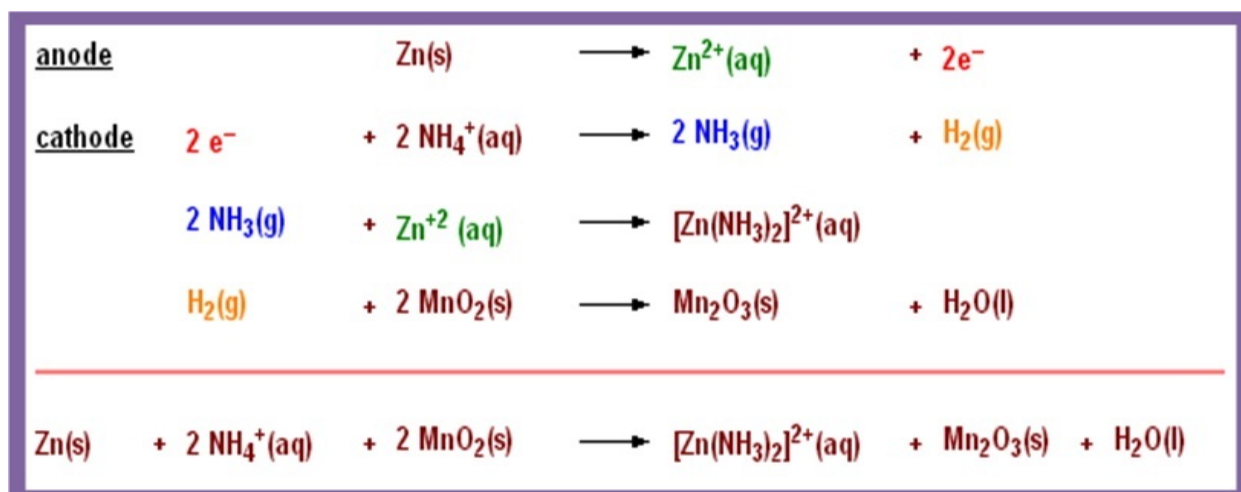
End point voltage of a cell. It is the lowest voltage a cell can tolerate and still be functional. The end point voltage of a dry cell is 0.8V.



Emf: 1.5v

Uses: In cameras, radios, Walkman's etc

Mechanism of dry cell reaction



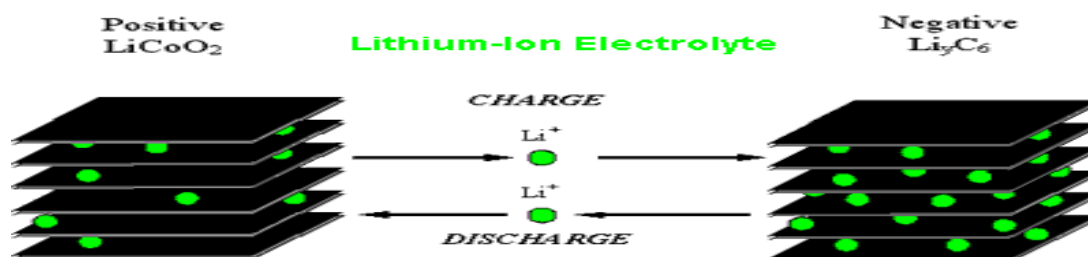
### Lithium-ion battery (Li-ion Battery)

Li-ion batteries are secondary batteries.

- The battery consists of an anode of Lithium, dissolved as ions, into a carbon.
- The cathode material is made up from Lithium liberating compounds, typically the three electro-active oxide materials,
  - Lithium Cobalt-oxide ( $\text{LiCoO}_2$ )
  - Lithium Manganese-oxide ( $\text{LiMn}_2\text{O}_4$ )
  - Lithium Nickel-oxide ( $\text{LiNiO}_2$ )

### Principle

- During the charge and discharge processes, lithium ions are inserted or extracted from interstitial space between atomic layers within the active material of the battery.
- Simply, the Li-ion is transferred between anode and cathode through lithium Electrolyte.
- Since neither the anode nor the cathode materials essentially change, the operation is safer than that of a Lithium metal battery.



### Construction

- Li-ion cell has a four-layer structure.

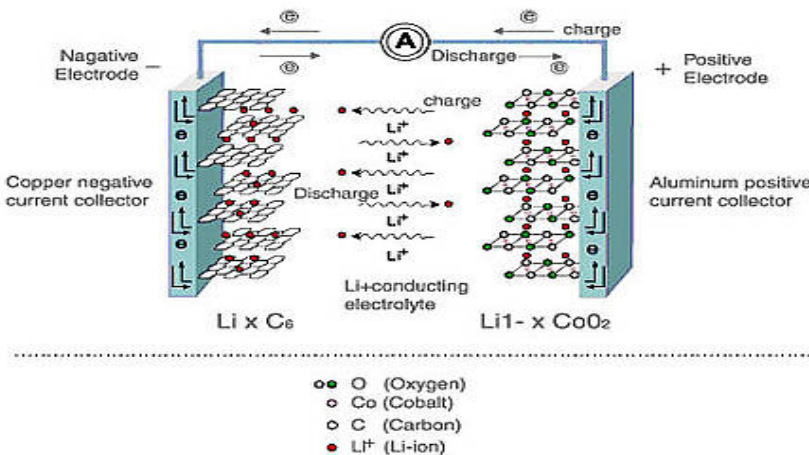
- A positive electrode made with Lithium Cobalt Oxide has a current collector made of thin aluminum foil - **cathode**
- A negative electrode made with specialty carbon has a current collector of thin copper foil – **anode**
- A **separator** is a fine porous polymer film.
- An **electrolyte** made with lithium salt in an organic solvent.

### Working

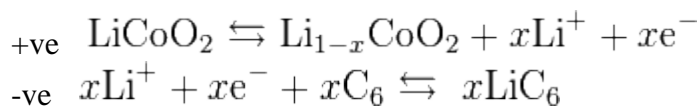
The traditional batteries are based on galvanic action but Lithium ion secondary battery depends on an "intercalation" mechanism.

This involves the insertion of lithium ions into the crystalline lattice of the host electrode without changing its crystal structure.

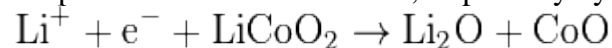
These electrodes have two key properties. One is the open crystal structure, which allow the insertion or extraction of lithium ions and the second is the ability to accept compensating electrons at the same time. Such electrodes are called intercalation hosts.



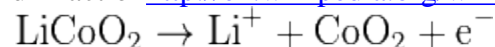
Useful work is performed when electrons flow through a closed external circuit. The following equations show one example of the chemistry, in units of moles, making it possible to use coefficient  $x$ .



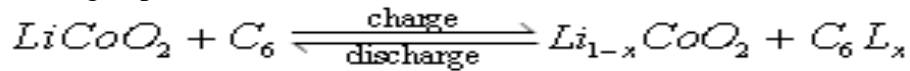
The overall reaction has its limits. Over discharge supersaturates lithium cobalt oxide, leading to the production of lithium oxide,<sup>[45]</sup> possibly by the following irreversible reaction:



Overcharge up to 5.2 volts leads to the synthesis of cobalt(IV) oxide, as evidenced by x-ray diffraction [http://en.wikipedia.org/wiki/Lithium-ion\\_battery\\_-\\_cite\\_note-46](http://en.wikipedia.org/wiki/Lithium-ion_battery_-_cite_note-46)



The chemical reaction that takes place inside the battery is as follows, during charge and discharge operation:



The lithium ion is inserted and exerted into the lattice structure of anode and cathode during charging and discharging

During discharge current flows through external circuit and light glows

During charging, no the electrons flows in the opposite direction

- During charging, lithium ion positive electrode material is ionized and moves from layer to layer and inserted into the negative electrode.
- During discharge Li ions are dissociated from the anode and migrate across the electrolyte and are inserted into the crystal structure of the host compound of cathode.
- At the same time the compensating electrons travel in the external circuit and are accepted by the host to balance the reaction.
- The process is completely reversible. Thus the lithium ions pass back and forth between the electrodes during charging and discharging.
- Because of this reason, the lithium ion batteries are called ‘Rocking chair’, ‘Swing’ cells.
- A typical Li-ion battery can store 150 watt-hours of electricity in 1 kilogram of battery as compared to lead acid batteries can store only 25 watt-hours of electricity in one kilogram
- All rechargeable batteries suffer from self-discharge when stored or not in use.

Normally, there will be a three to five percent of self-discharge in lithium ion batteries for 30 days of storage

#### ***Advantages***

- They have high energy density than other rechargeable batteries
- They are less weight
- They produce high voltage out about 4 V as compared with other batteries.
- They have improved safety, i.e. more resistance to overcharge
- No liquid electrolyte means they are immune from leaking.
- Fast charge and discharge rate

#### ***Disadvantage***

- They are expensive
- They are not available in standard cell types.

#### ***Applications***

- The Li-ion batteries are used in cameras, calculators
- They are used in cardiac pacemakers and other implantable device
- They are used in telecommunication equipment, instruments, portable radios and TVs, pagers
- They are used to operate laptop computers and mobile phones and aerospace application

## FUEL CELLS

These are galvanic cells in which electrical energy is obtained by the combustion of fuels. Here, the fuels are supplied from outside and do not form integral part of the cell. These do not store energy. Electrical energy can be obtained continuously as long as the fuels are supplied and the products are removed simultaneously. In these aspects fuel cells differ from conventional electrochemical cells

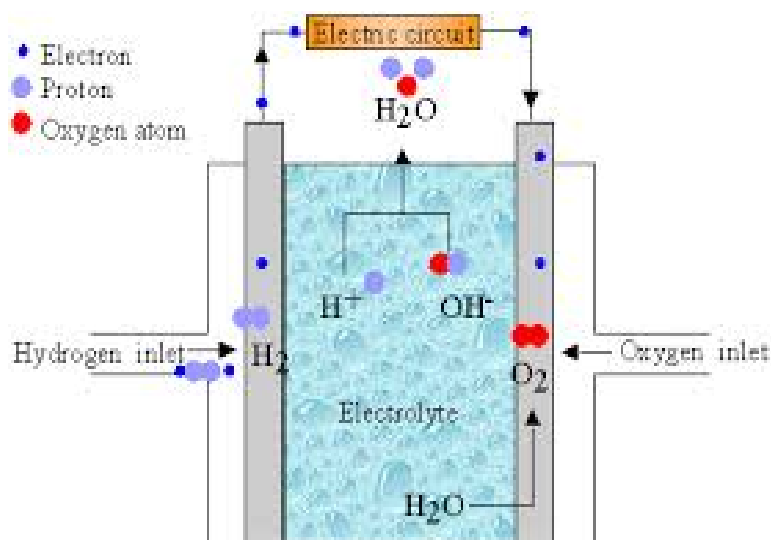
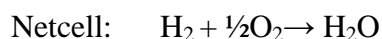
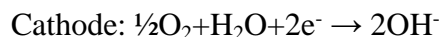
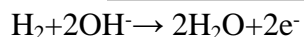
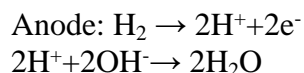
### **Advantages of fuel cells:**

- Power output is high.
- Do not pollute the atmosphere
- Electrical energy can be obtained continuously.

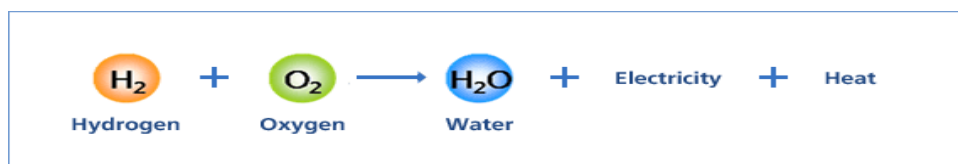
### **Hydrogen – oxygen fuel cell**

It consists of porous Carbon rods impregnated with Catalysts of Pt-Ru-Co. or Pt-Ru-Ni both the rods are placed in a con KOH solution.  $H_2$  &  $O_2$  are bubbled through the anode and cathode compartments respectively. The gases diffuse through the electrodes and bring about the reaction.

$H_2O$  being the product should be removed at the same rate as it is formed. Or else waters will dilute the KOH. So electrolyte is kept hot (temp  $80^0$  C) to evaporate  $H_2O$  and also the cell is provided with a wick, which helps in maintaining the water balance..







Cell representation:  $\text{H}_2 \mid \text{H}^+, \text{KOH} \mid \text{O}_2, \text{C}$

Emf: 1.23 V

Uses:

- Electric power source for space vehicles
- military and mobile power system.

### Advantages and Disadvantages of fuel cells

#### Advantages

Power efficiency is higher

Eco-friendly since products are highly non toxic

They can produce direct current for long periods

No Charging

#### Disadvantages

Moderate output

Costly process as fuel cost is high

Storing the fuel & Oxidants is a problem

Difference b/w a battery and a fuel Cell

#### Battery

Here reactants form the integral Part of the cell

Chemical energy is stored

#### Fuel cell

Here the reactants are fuel fed from outside

Chemical energy not stored