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Sub:	Engineering Chemistry			Code:	15CHE12
Date: 8/09/2016	Duration: 90 mins	Marks: 50	Sem: I (J,K,L,M,N,O)	Branch:	ECE/EEE/ME

Internal Assessment Test I – September 2016

Answer any five (5) full set of questions

Q1. a) Derive Nernst equation for a single electrode potential.



The equilibrium constant (K_c) is related to change in free energy by equation

$$\Delta G = \Delta G^{\circ} + RT \ln K_c \text{-----(1)}$$

$$K_c = \frac{[M]}{[M^{n+}]} \text{-----(2)}$$

$$-\Delta G = n \times F \times E$$

$$\Delta G = -n \times F \times E \text{----- (3)}$$

Under standard conditions, when concentrations of all species is unity, standard free energy change is given by equation

$$\Delta G^{\circ} = -n \times F \times E^{\circ} \text{-----(4)}$$

Therefore by substituting values of ΔG , ΔG° and K_c from equation (2), (3) and (4) into equation (1), we get

$$-nFE = -nFE^{\circ} + RT \ln \frac{[M]}{[M^{n+}]}$$

$$-nFE = -nFE^{\circ} + RT \ln [M] - RT \ln [M^{n+}]$$

Dividing whole equation by $-nF$

$$\frac{-nFE}{-nF} = \frac{-nFE^{\circ}}{-nF} + \frac{RT \ln [M]}{-nF} - \frac{RT \ln [M^{n+}]}{-nF}$$

$$E = E^{\circ} - \frac{RT \ln [M]}{nF} + \frac{RT \ln [M^{n+}]}{nF}$$

Assume $[M] = 1$, $\ln 1 = 0$

$$\therefore E = E^\circ + \frac{RT \ln[M^{n+}]}{nF} \text{ ----- (7)}$$

Substituting the values for R ($8.314 \text{ JK}^{-1} \text{ mol}^{-1}$), F (96500 Cmol^{-1}), T (298 K) and converting natural log to base 10 in eqn (7) we get

$$E = E^\circ + \frac{0.0591 \log[M^{n+}]}{n}$$

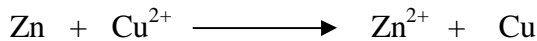
This is the mathematical representation of Nernst equation.

Nernst equation for cell potential

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

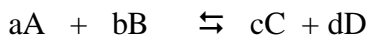
$$\text{Or, } E = E^\circ + \frac{0.0591}{n} \log \frac{[\text{Species at cathode}]}{[\text{Species at anode}]}$$

For example, for Daniel Cell



$$E = E^\circ - \frac{0.0591}{n} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

Consider the cell reaction



$$E = E^\circ - \frac{0.0591}{n} \log \frac{[C^c][D^d]}{[A^a][B^b]}$$

b) Describe the construction and working of Li ion battery.

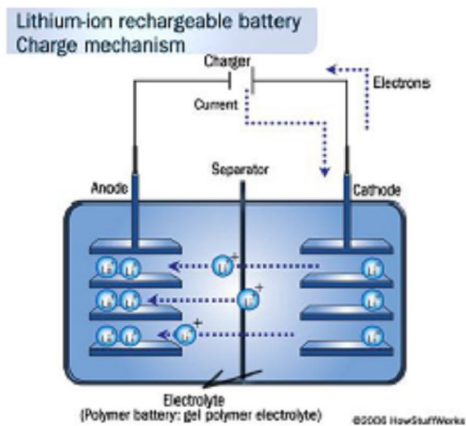
A lithium-ion battery is a member of a family of rechargeable battery types in which lithium ions move from the negative electrode to the positive electrode during discharge and back when charging.

Anode : Li-metal oxide , like lithium cobalt oxide

Cathode: carbon

Electrolyte: lithium salts (LiCl, LiBr) in organic carbonate solvents(ethylene carbonate)

Separator : polypropylene separator

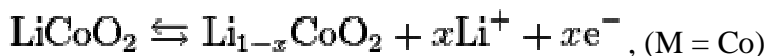


Type and Cell representation:

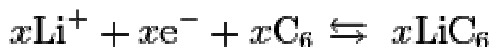


Working:

The positive electrode half-reaction is:



The negative electrode half reaction is:



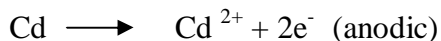
The overall reaction has its limits. Over discharge supersaturates lithium cobalt oxide, leading to the production of lithium oxide, possibly by the following irreversible reaction:



It is used in portable devices like mobile phones and smartphones, laptops and tablets, digital cameras

Q2. a) What are concentration cells? The emf of the cell Cd/CdSO₄ (0.0093 M)//CdSO₄ (xM)/ Cd was found to be 0.086 V at 298K. Calculate the value of x and write cell reaction.

The cell in which both the electrodes are made of same material and dipped into the same electrolytic solution but of different concentration is known as concentration cell.



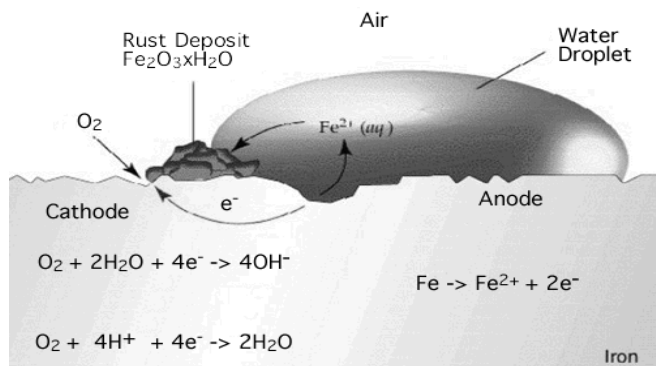
$$\text{Formula : } E_{\text{cell}} = \frac{0.0591}{n} \log \frac{[C_2]}{[C_1]}$$

or, $0.086 = 0.0591 \log [x] / [0.0093]$, since $C_1 = 0.0093 \text{ M}$ and $C_2 = x$

or, $0.086 / 0.0591 = \log [x] / [0.0093]$

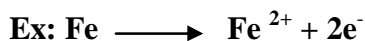
or $x = 7.52 \text{ M}$

b) Explain the electrochemical theory of corrosion by taking Fe as an example.



According to electrochemical theory, corrosion of metals takes place due to the formation of anodic and cathodic regions on the same metal surface or when two metals are in contact with each other in the presence of a conducting medium.

AT ANODE:

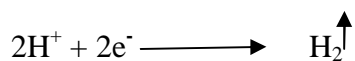


At cathode:

Since metal cannot be reduced further, metal atoms at the cathodic region are not affected. Therefore, cathodic reaction depends on the nature of the electrolyte.

There are three possible ways in which the reduction can take place.

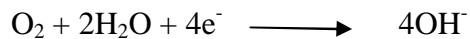
(a) If the solution is deaerated and acidic, the cathodic reaction involves evolution of hydrogen.



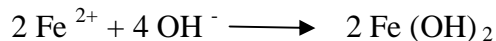
(b) If the solution is deaerated and almost neutral the cathodic reaction involves evolution of hydrogen gas and hydroxyl ions.



(c) If the solution is aerated and almost neutral the alkaline oxygen or water are reduced to OH^- ions.



Corrosion of iron produced Fe^{2+} ions and OH^- ions at the anode and cathode sites respectively. These ions diffuse towards each other. Since small Fe^{2+} ions diffuse more rapidly than OH^- ions. Their combination occurs more commonly near cathodic region.



(Ferrous hydroxide)

In an oxidizing environment, it is oxidized to ferric oxide and the yellow rust is hydrated ferric oxide.



[Rust]

Q3. a) What is metal finishing? Mention the technological importance of metal finishing.

Process of surface modification by way of deposition of another metal or metal alloy or polymer or ceramic or oxide layer to bring about intended better surface characteristics is known as metal finishing.

Technological Importance:

Technological significance of metal finishing refers to imparting following different characteristics:

- (i) Better corrosion resistance,
- (ii) Better hardness, strength, wear / abrasion resistance, etc.
- (iii) Better thermal conductance or resistance or reflectance, etc.
- (iv) Better optical reflectance,
- (v) Better electrical conductance or insulation, etc.
- (vi) Building up material or restoration

b) Describe the effect of the following factors on the rate of corrosion:

i) Temperature

The rate of chemical reaction, in general, increases with rise in temperature. Corrosion process is one such chemical reaction. Therefore the rate of corrosion increase as the temperature increases. Increase in corrosion increases the conduction of the corrosion medium, which also contribute to the increase in the corrosion rate.

ii) Corrosion product

The nature of the oxide layer largely decides the rate of further corrosion. If its composition is stoichiometric, highly insoluble and non porous with low ionic and electrical conductivity, the layer acts

as protective film and prevent further corrosion. For eg. Al, Ti and Cr develops such a layer on their surface and become passive to further corrosion. If the oxide layer is non stoichiometric, highly porous, soluble, unstable, it can not control further corrosion. In such cases the fresh metal surface is continuously exposed to corrosion environment and corrosion takes place continuously. Eg. Fe and Zn

iii) Relative areas of anode and cathode

The rate of corrosion largely depends on the relative size of anode and a cathode.

(a) If the metal has a small anodic and large cathodic area (i.e; the ratio of anode to cathode is small) then the corrosion is more intensive and faster in rate. This is explained as follows

At anode oxidation takes place and electrons are liberated. At the cathode these electrons are consumed. When the anode is smaller and cathode region is large, the electrons liberated at the anode, are rapidly consumed, at the cathode region. This process makes the anodic reaction to take place faster, thus increasing the corrosion rate.

(b) If the cathode is smaller, the consumption of electrons will be slower and the corrosion reaction as a whole will be slower.

Ex: A broken coating of tin on iron surface, tin is cathodic to iron and the small exposed part of iron acts as an anodic region and rest of the large tin coated surface acts as a cathodic region. Because of a small ratio of anodic to cathodic area, the corrosion rate is very high, on the other hand Zn plating on Fe gives an anodic coating to iron (Zn is above Fe in electrochemical series). Thus even if Zn plating peels off at some point, Fe does not get corroded.

Q4. a) Illustrate the following battery characteristics.

(i) Capacity

Capacity is the charge or amount of electricity that could be obtained from a battery and is given in ampere hours (Ah). It depends on the size of the battery and is given by Faraday's relation

$$C = \frac{wnF}{M}$$

w = mass of active material, M = Molar mass of active material

Therefore, the amount of active materials actually consumed during discharge determines the capacity of the battery. Capacity can also be measured by finding the time for a fixed current discharge (i amperes), time

taken for battery to reach minimum voltage, E_{cell}^{min} when cell is said to be dead.

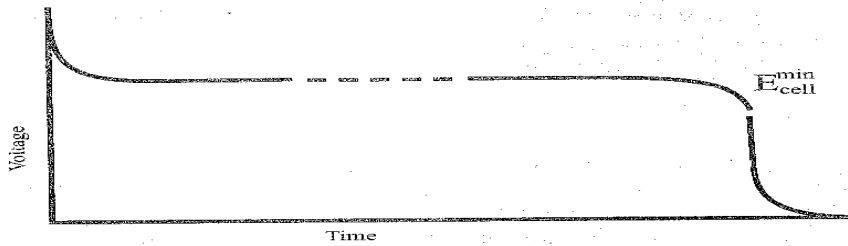


Fig. 2.2 *Battery voltage against time at constant current discharge*

Length of flat portion of curve is a measure of capacity of battery, longer the flat portion, better is the capacity.

(ii) cycle life

An important feature of secondary batteries is the rechargeability. The number of times a battery can be discharged/ recharged before occurrence of failure is called cycle life. Cycle life depends on chemical composition, morphological changes and distribution of active materials in the cell.

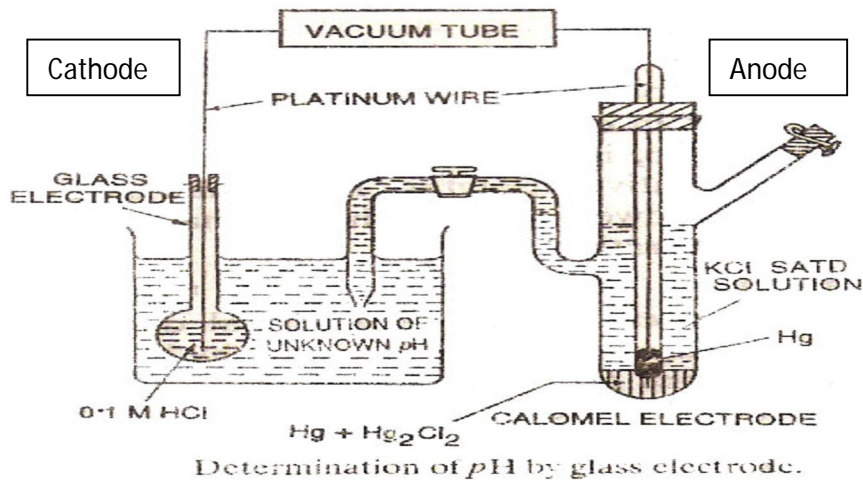
Reasons which lower the cycle life of battery are as listed:

- Corrosion at contact points.
- Shedding of active materials from plates.
- Short circuiting between electrodes due to irregular crystal growth and changes in morphology.

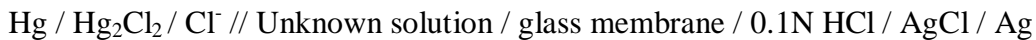
b) What are ion selective electrodes? Explain the determination of pH of a solution using glass electrode.

The electrodes which are selective to a particular ion is known as ion selective electrode.

To determine the pH of given solution, glass electrode is dipped in a solution whose pH has to be determined. It is combined with a saturated calomel electrode through a salt bridge.



Cell assembly representation:



From the emf, the pH of the solution is calculated as below:

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

$$E_{\text{cell}} = E_{\text{cal}} - E_{\text{glass}}$$

$$E_{\text{cell}} = E_{\text{cal}} - (E_G + 0.0591 \text{ pH})$$

$$E_{\text{cell}} = E_{\text{cal}} - E_G - 0.0591 \text{ pH}$$

$$\text{pH} = \frac{E_{\text{cal}} - E_G - E_{\text{cell}}}{0.0591}$$

$$0.0591$$

$$\text{pH} = \frac{K' - E_{\text{cell}}}{0.0591}$$

$$0.0591$$

Q5. a) What is anodic metal coating? Describe Galvanization process.

The metal coating which is anodic to the base metal is called anodic metal coating.

GALVANIZATION: the process of galvanization is carried out as follows,

- (i) The base metal is first treated with organic solvent to remove grease or oil material present on it.
- (ii) It is further treated with dil. H_2SO_4 to remove rust or oxide layer present on it.
- (iii) The metal is then treated with flux of ZnCl_2 and NH_4Cl for best adhesion property.

(iv) Finally the base metal is dipped into the zinc at 430-470°C.

(v) The excess zinc is removed from the surface by rolling or wiping etc.

These steps are diagrammatically shown in Fig below....

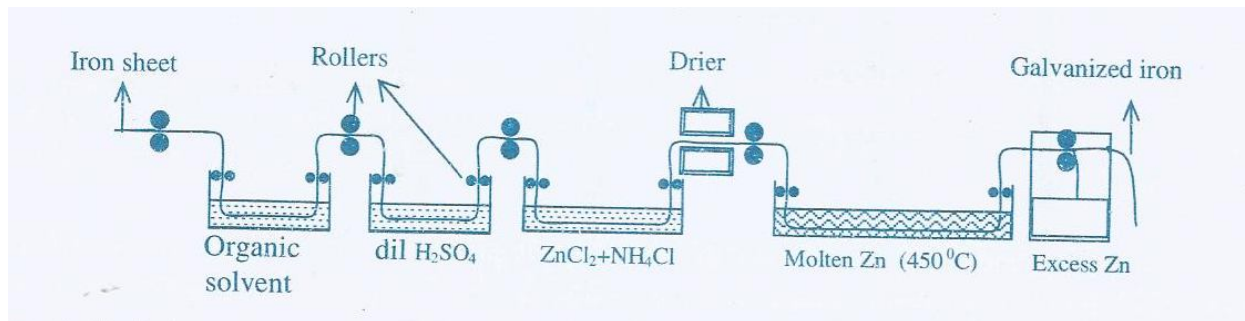


Fig: Galvanisation of Iron

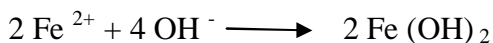
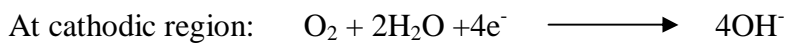
b) What is differential aeration corrosion? Explain Waterline corrosion.

The difference in oxygen or air concentration on the surface of the metal develops a galvanic cell.

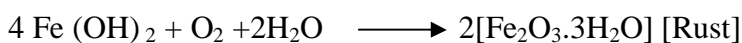
The water line corrosion takes place due to the formation of differential oxygen concentration cells. The part of the metal below the water line is exposed only to dissolved oxygen acts as anode and gets corroded while the part above the water is exposed to higher oxygen concentration of the atmosphere thus part of the metal below the water act as cathode and free from corrosion. A distinct brown line is formed just below the water line due to deposition of rust.

EX: Water storage steel tanks

The part of the metal exposed to higher oxygen concentration acts on the cathodic region since oxygen has a demand for electrons and hence can undergo reduction and the part of the metal exposed to lower oxygen concentration acts as anodic region, consequently the poorly oxygenated region undergoes corrosion.



(Ferrous hydroxide)



Q6. a) What is cathodic protection? Explain sacrificial anodic technique for prevention of corrosion.

Cathodic protection is a method of protecting a metal or alloy from corrosion by converting it completely into cathodic and no part of it is allowed to act as anode. This can be achieved by providing electrons from an external source.

Sacrificial anodic method:

In this method, the base metal structure is converted into a cathode by connected it to a more active [higher up in galvanic series or less noble] metal. This active metal actually acts as an auxiliary anode. Mostly Zn, Mg, Al are the common auxiliary anodes used in this method. These metals being more active, acts as anode and undergo destruction and protect the metal structure.

Since the anode material sacrifice to protect the metal structure, the method is known as sacrificial anode method. After continuous use exhausted sacrificial anodes are replaced by new ones as and when required.

Ex: A Mg block connected to buried oil storage tank.

b) What is fuel cell? Describe construction and working of methanol-oxygen fuel cell and mention one application of this cell.

The cell which can generate electrical energy by combustion reaction of fuel is known as fuel cell.

It is good example for liquid fuel cell

Construction: Methanol – oxygen fuel cell consist of

1. Anode – It is a porous platinum (Pt) electrode.
2. Cathode - It is a porous platinum (Pt) electrode.
3. Electrolyte – Aqueous sulphuric acid (H_2SO_4)
4. Active components: (a) Fuel – Methanol mixed with sulphuric acid supplied at anode. (b) Oxidant – Pure oxygen is supplied at cathode.
5. Adjacent to cathode towards electrolyte side, a semi permeable membrane is inserted to allow the diffusion of H^+ ions, but disallow the diffusion of methanol and its direct oxidation at cathode.

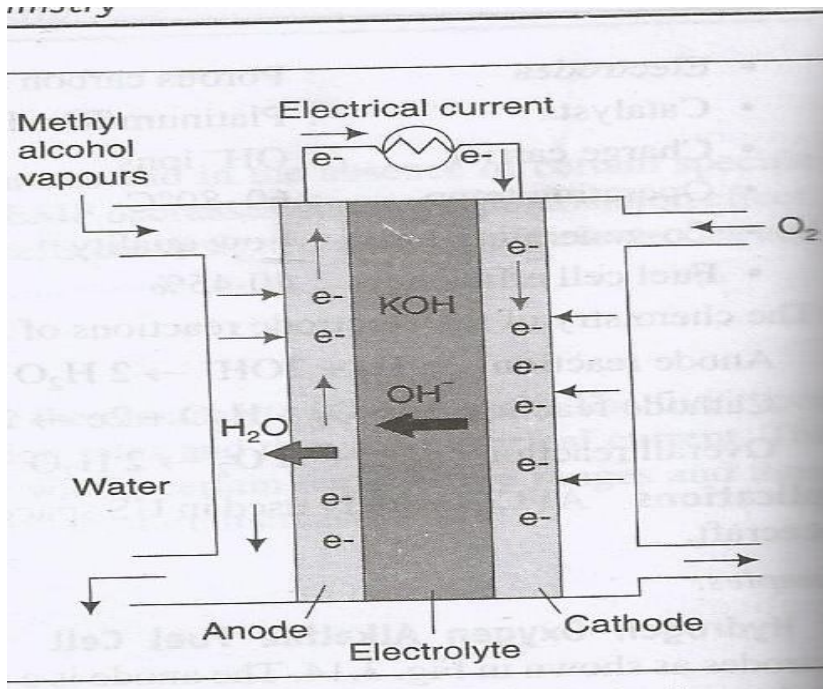
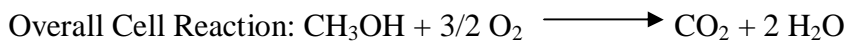
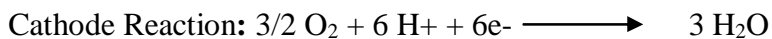
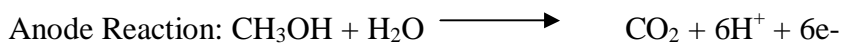


Fig. 2.11 *Methanol - oxygen fuel cell*

Working:

Cell reaction;



H_2O and CO_2 are formed do not harm the cell functioning because they are removed as and when they are formed.

Cell Potential : 1.2 V

Application:

used in automobiles, military applications.

Q7. a) Explain construction, working and application of Nickel metal hydride battery.

It is also good example for secondary battery are also called as rechargeable battery.

Construction:

1. Anodic material - Metal hydride such as VH_2 , ZrH_2 , TiH_2 etc with a hydrogen storage alloy such as LaNi_5

2. Cathodic material – NiO(OH) nickel oxy hydroxide. (Highly porous Ni substrate into which Ni(O)OH is impregnated).
3. Electrode – Porous nickel foil/grid on to which active materials are either coated or pasted.
4. Electrolyte – Aqueous solution of KOH (30%).
5. Separator – Synthetic non – woven polypropylene is used, it serves the purpose of separator as well as electrolyte absorbent.

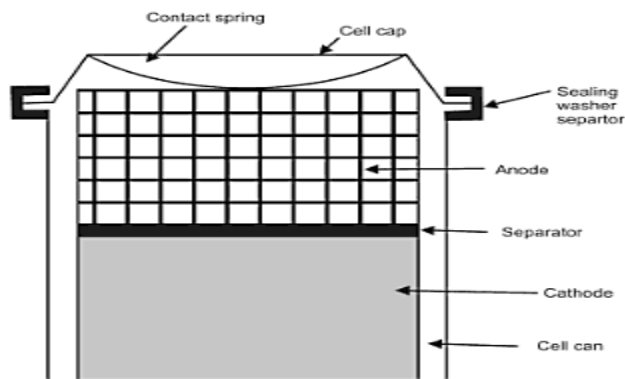


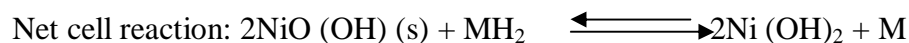
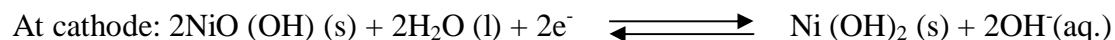
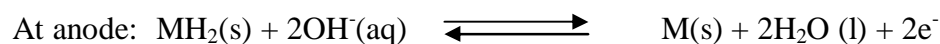
Fig. 2.8 *Nickel – metal hydride battery*

Cell representation

The battery is represented as, $MH_2/KOH (30\%) / Ni(OH)_2, NiO(OH)$

Working:

The cell reactions occurring during discharging (\rightarrow) and recharge (\leftarrow) are,



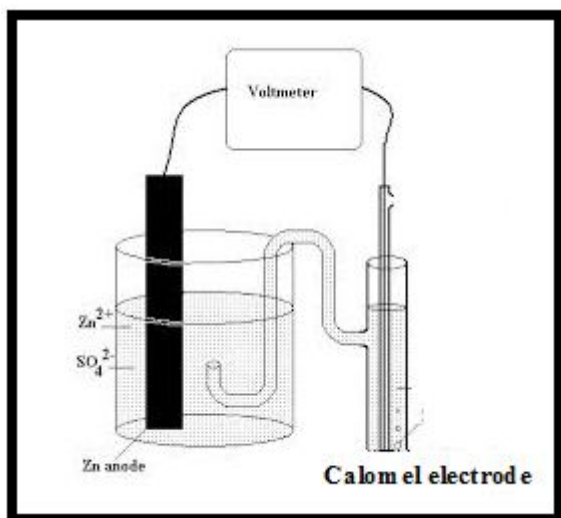
During discharging process, at anode MH_2 reduces to M & at cathode Ni^{3+} reduces to Ni^{2+} . Finally the battery produces a potential of 1.35V.

Ni-MH battery is used in, electric razors, toothbrushes, cameras, pagers, cellular phones and laptop computer

b) What are reference electrodes? Explain the determination of electrode potential of an unknown electrode using calomel electrode.

The electrodes which are used to measure the potential of unknown electrode are known as reference electrodes.

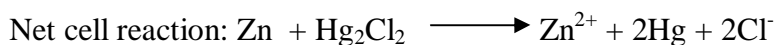
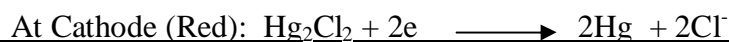
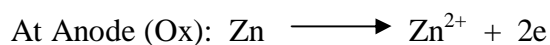
The given electrode, say zinc electrode, is coupled with saturated calomel electrode as in the figure. Since the reduction potential of zinc electrode less than that of calomel electrode, zinc acts as anode and calomel as cathode.



The cell assembly is representation:

The cell assembly is represented as, $Zn / ZnSO_4 (1 M) // KCl (satd) / Hg_2Cl_2 / Hg$

Cell reactions:



The EMF of the cell assembly is,

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

$$= E_{\text{cal}} - E_{Zn/Zn^{2+}}$$

$$\text{Or, } 1.002 = 0.242 - E_{\square} \text{Zn/Zn}^{2+}$$

$$\text{Or, } E_{\square} \text{Zn/Zn}^{2+} = 0.242 - 1.002$$

$$\text{Or, } E_{\square} \text{Zn/Zn}^{2+} = -0.76 \text{ volt.}$$