**CMR
INSTITUTE OF
TECHNOLOGY**

Sub:	**Engineering Chemistry**					Code:	15CHE12
Date: 18/09/2017 Duration:	90 mins	Max Marks:	50	Sem:	I	Branch:	All

Internal Assessment Test I – September 2017

1. (a) Derive Nernst equation for a single electrode potential in a galvanic cell. (05 Marks) (CO1, L3)

Solution: Consider an electrode assembly undergoing a spontaneous reaction.

$M^{n+} + n e^- \rightleftharpoons M$
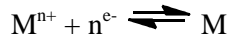
The equilibrium constant (Kc) is related to change in free energy by Vant Hoff equation as follows

$\Delta G = \Delta G^\circ + RT \ln Kc$ ------------------------------------(1)

For above reaction $Kc = \dfrac{[M]}{[M^{n+}]}$ --------------------------------------(2)

According to thermodynamics, decrease in free energy (-ΔG) represents maximum amount of work that can be obtained from a chemical reaction.

$-\Delta G = W_{max}$--- (3)

Work done in electrochemical reaction depends on

(i) Number of coulombs of electricity that flow and (ii) Energy available per coulomb.

Number of coulombs = $n \times F$ (Where n = number of electrons involved in the cell reaction and F = Faraday constant)

Energy available per coulomb = E_{cell} (V) or JC^{-1}

When E_{cell} = maximum, work derived from cell is maximum.

Thus, $W_{max} = n \times F \times E$ --------------------------------------- (4)

n = moles of electrons, F = $Cmol^{-1}$, E = JC^{-1}

Equating equations (3) & (4)

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

$\Delta G = -n \times F \times E$ ------------------------------ (5)

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

$\Delta G^\circ = -n \times F \times E^\circ$------------------------------(6)

Where E° is a constant called **standard electrode potential**. E° is the potential when a metal is dipped in 1M solution of its ions or when an inert electrode is in contact with a gas at a pressure of 1 atm at 298 K.

Therefore by substituting values of ΔG, $\Delta G°$ and Kc from equation (2), (5) and (6) into equation (1), we get

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

$$-nFE = -nF\,E° + RT \ln [M] - RT \ln [M^{n+}]$$

Dividing whole equation by $-nF$

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

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

Under standard condition $[M] = 1$,

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

Converting natural log to base 10 in eqn (7) we get

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

Substituting the values for R (8.314 JK^{-1}mol^{-1}), F (96500Cmol^{-1}) and T (298K) in eqn (8) we get

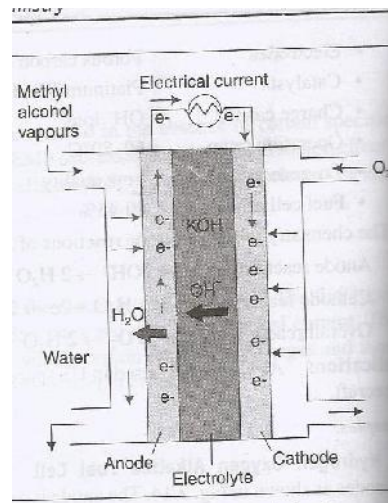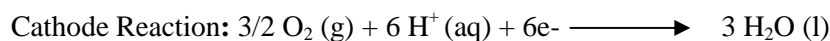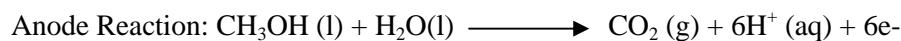$$\boxed{E = E° + \frac{0.0591\log[M^{n+}]}{n}}$$

(b) Explain the construction and working of methanol-oxygen fuel cell. List any two applications. (05 Marks) (CO1, L4)

Solution: Construction: Methanol – oxygen fuel cell consist of

1. Anode – It is a porous platinium (Pt) electrode.
2. Cathode - It is a porous platinium (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.

Working:

Anode Reaction: CH_3OH (l) + H_2O(l) $\longrightarrow$ CO_2 (g) + 6H$^+$ (aq) + 6e-

Cathode Reaction: 3/2 O_2 (g) + 6 H$^+$ (aq) + 6e- $\longrightarrow$ 3 H_2O (l)

Overall Cell Reaction: CH_3OH (l) + 3/2 O_2 (g) $\longrightarrow$ CO_2 (g) + 2 H_2O (l)

Applications: 1. Used in military applications. 2. Used in large scale power production.

2. (a) What is concentration cell? EMF of the concentration cell Ag(s)/AgNO$_3$ (C1)// AgNO$_3$ (C2=1.2M)/Ag(s) is 0.1078 V at 30C. Calculate C1 of the cell and also write cell reaction. (06 Marks) (CO1, L3)

Solution: Concentration Cell: It is an electrochemical cell in which two identical electrodes immersed in same ionic solution but of different concentration.   Ex: Copper concentration cell

Cell Reaction: Ag $\longrightarrow$ Ag$^+$ (C1) + e$^-$ (ANODE)

Ag$^+$ (C2=1.2M) + e$^-$ $\longrightarrow$ Ag   (CATHODE)

n=1, E$_{cell}$= 0.1078V, T=30C=30+273= 303K, C2=1.2M, C1=?

Formula: E$_{cell}$ = 2.303RT/nF log [C$_2$]/[C$_1$]

Substitution: 0.1078 = 2.303×8.314×303/1×96500 log [1.2]/[C$_1$]

Or, 0.1078= 0.06012{log [1.2] – log [C$_1$]}

Or, 0.1078= 0.06012{0.0792 – log [C$_1$]}

Or 1.793= 0.0792 – log [C$_1$]

Or, log [C$_1$] = -1.7138

Or, C$_{1 =}$ 0.019M

(b) What is cathodic protection? Explain how a metal article is protected by sacrificial anodic method.   (04 Marks) (CO2,L4)

Solution: 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. There are two methods of cathodic protection.

(i) Sacrificial anodic method.

(ii) Impressed current method.

(i) Sacrificial anodic method:

In this method, the base metal structure is converted into a cathode by connecting 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: 1. A Mg block connected to buried oil storage tank.

2. Mg base areas fixed to the side of ocean going ships.

3. Mg blocks area connected to the buried pipe lines.

Advantages: (i)The method is simple. (ii) Low installation cost. (iii) Minimum maintenance cost.

(iv) Doesn't require power supply.

Disadvantage (i) Involves recurring expenditure for replacement of consumed anodes.
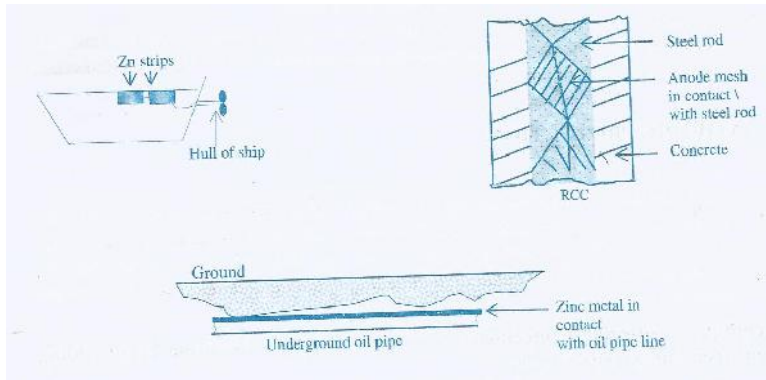

Fig: Cathodic Protection by sacrificial anode

3. (a) Explain with relevant reactions, how electrochemical theory of corrosion can explain rusting of iron. (06 Marks) (CO2, L4)

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 pressure of a conducting medium.

AT ANODE: $Fe \longrightarrow Fe^{2+} + 2e^-$
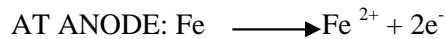
At CATHODE: Since metal cannot be reduced further, metal atoms at the cathodic region are not affected. Therefore, cathodic reaction depends on the nature of the electrolyte. There are three possible ways in which the reduction can take place.
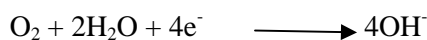
(a) If the solution is deaerated and acidic, the cathodic reaction involves evolution of hydrogen.

$$2H^+ + 2e^- \longrightarrow H_2 \uparrow$$
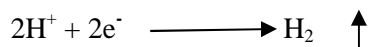
(b) If the solution is deaerated and almost neutral the cathodic reaction involves evolution of hydrogen gas and hydroxyl ions.

$$2H_2O + 2e^- \longrightarrow H_2 \uparrow + 2OH^-$$
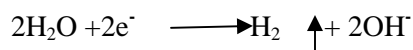
(c) If the solution is aerated and almost neutral the alkaline oxygen or water are reduced to OH$^-$ ions.

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$$

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.

$2\ Fe^{2+} + 4\ OH^- \longrightarrow 2\ Fe(OH)_2$

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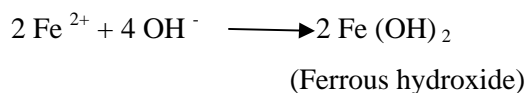
In an oxidizing environment, it is oxidized to ferric oxide and the yellow rust is hydrated ferric oxide.

$4\ Fe(OH)_2 + O_2 + 2H_2O \longrightarrow 2[Fe_2O_3.3H_2O]$

[Rust]
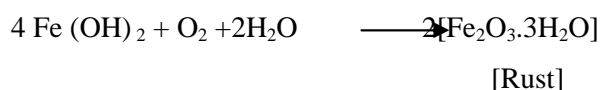
(b) Explain the following characteristics of a battery: (i) Voltage (ii) Energy Efficiency. (04 Marks) (CO1, L4)

Solution: **(i) Voltage:** The voltage of a battery is given by the equation,

$$E_{cell} = (E_c - E_A) - |\eta_A| - |\eta_C| - i\ R_{cell}$$

Where, E_c and E_a are the electrode (reduction) potential of cathode and the anode respectively, η_A, η_C are the over-potentials at the anode and the cathode respectively and iR_{cell} is the internal resistance.

To derive maximum voltage from a battery

    (a)   The difference in the electrode potentials must be high.

    (b)   The electrode reactions must be fast so as to minimize the overpotential.

    (c)   The internal resistance of cell must be low.

The electrode system should be such that the active mass at the positive electrode depletes readily and that at the negative electrode increase easily. This minimize the overpotential at the cathode and anode. The cell should be appropriately designed so as to minimize internal resistance. This can be achieved by keeping the electrodes close to each other and also by using an electrolyte of high conductivity.

(ii) Energy efficiency: Amount of energy released on discharge per unit energy input is referred to as energy efficiency.

$$\% \text{ Energy efficiency} = \frac{\text{amount of energy released during discharge}}{\text{amount of energy required for recharge}} \times 100$$

    Batteries should have high energy efficiency.

It depends on rate of reaction, electron transfer, self discharge, capacity.

4. (a) Define reference electrode? Explain the construction and working of calomel electrode. (05 Marks) (CO1, L4)

Solution: These are the electrodes which have stable electrode potential that does not change with time and is used to determine the potentials of unknown electrodes.

They are of two types;

I. Primary Reference Electrodes: Ex. Standard hydrogen electrode (SHE).

II. Secondary Reference Electrodes: Ex: Calomel electrode

Calomel electrode

It is a metal -metal insoluble salt electrode is also called as secondary reference electrode.

Construction: Electrode consists of glass tube. The bottom of the glass tube is filled with pure mercury (Hg) on which a calomel paste (Hg + Hg2Cl2) is placed. The remaining part of the glass tube is filled with sat. or std KCl Solution. It also contains side tube serves as salt bridge and a platinum wire is dipped into the mercury so that it serves as electrical contact.

Half cell representation: The calomel electrode is represented as, KCl /HgCl2, Hg

Half cell reactions:

(a). When it acts as anode(oxn): 2Hg + 2Cl-   Hg2Cl2   +   2e-

(b). When it acts as cathode(Red): Hg2Cl2   +   2e-   2Hg + 2Cl-

The electrode potential of the calomel electrode is mainly depends on the concentration of KCl used,

Electrode potential is calculated using Nernst equation,

$$E = E° - \frac{2.303RT \log[Cl^-]}{F}$$

The potential of calomel electrode is 0.344V for   [KCl] = 0.1N
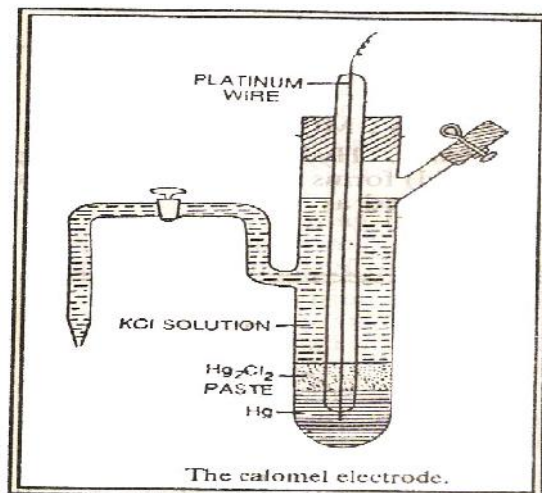
The potential of calomel electrode is 0.281V for   [KCl] = 1.0N

The potential of calomel electrode is 0.2422V for [KCl] = saturated KCl

Advantages:

1. It is simple to construct. 2. The cell potential is stable and reproducible does not vary with temperature.

The calomel electrode.

Applications:

1. It is used as secondary reference electrode in all potentiometric determinations.

2. Used in glass or combined electrode to determine the pH of the unknown solution.

Limitations:

1. Calomel electrode cannot be used beyond a temperature of 60°C.

2. Hg employed in construction poses pollution problem.

(b) Describe construction and working of Li-ion battery. Mention its applications.   (05 Marks) (CO1, L2)

Solution: 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 (graphite)

Electrolyte: lithium salts ($LiClO_4$, $LiBF_4$) in organic carbonate solvents (ethylene carbonate)
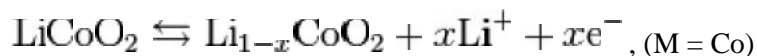
Separator : polypropylene separator

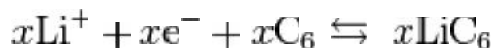Type and Cell representation: Li-ion battery is a secondary battery.

$LiCoO_2$ / electrolyte (lithium salt in an organic solvent) / C(graphite)

Working:

The positive electrode half-reaction is:

$$LiCoO_2 \leftrightarrows Li_{1-x}CoO_2 + xLi^+ + xe^-$$, (M = Co)

The negative electrode half reaction is:

$$xLi^+ + xe^- + xC_6 \leftrightarrows xLiC_6$$

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:

$$Li^+ + e^- + LiCoO_2 \rightarrow Li_2O + CoO$$

Use : It is used in mobile phones and smartphones, laptops and tablets, digital cameras and camcorders, electronic cigarettes, handheld game consoles and torches (flashlights). Li-ion batteries are used in tools such as cordless drills, sanders, saws. Electric vehicles, in telecommunications applications.
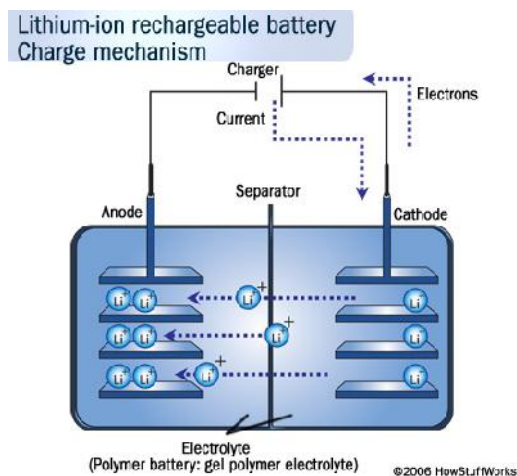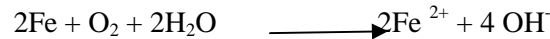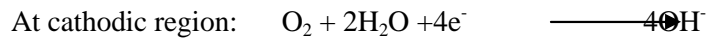
5. (a) Explain in detail the type of corrosion occurring in the following cases.

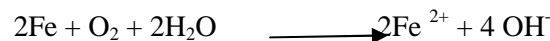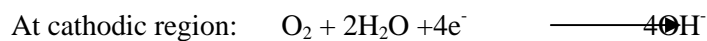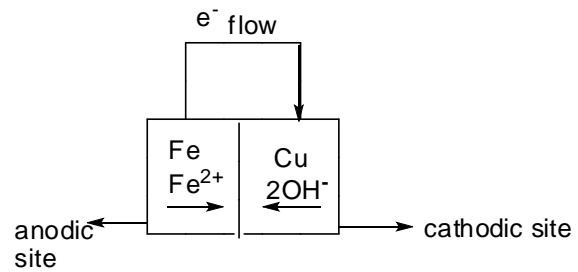**i. Presence of small dust particles on iron surface.**

ii. Copper nut in contact with iron bolt.   **(04 Marks) (CO2, L4)**

Solution: (i) In this case, Pitting corrosion will occur. The part where small particles of dust get deposited on iron surface, will not be well aerated as compared to the exposed surface. The covered portion thus becomes anodic with respect to the surface exposed. In the presence of electrolyte and moisture corrosion takes place in the form of pits thereby increasing the rate of corrosion because of formation of small anodic area.

At anodic region: $Fe \longrightarrow Fe^{2+}$

At cathodic region: $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$

$$2Fe + O_2 + 2H_2O \longrightarrow 2Fe^{2+} + 4\ OH^-$$

(ii) In this case, Differential metal corrosion will occur. When two dissimilar metals are in contact with each other, a potential difference is setup resulting in a galvanic current. The metal with lower reduction potential, in this case Fe is anodic with respect to the Cu that has higher reduction potential and behaves as cathode. Thus, Fe bolt will corrode when it is in contact with Cu nut.

At anodic region: $Fe \longrightarrow Fe^{2+}$

At cathodic region: $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$

$$2Fe + O_2 + 2H_2O \longrightarrow 2Fe^{2+} + 4\ OH^-$$

(b) Describe the effect of the following factors on the rate of corrosion: (i) pH of the medium (ii) Nature of corrosion product (iii) Relative area of anode and cathode. (06 Marks) (CO2, L2)

Solution: (i) **pH** : In general, the rate of corrosion is high when the nature of the environment is acidic.

(a) If the pH<3, severe corrosion occurs even in the absence of air due to the continues evolution of hydrogen at the cathodic region.

(b) If the pH>10, corrosion of the metal practically ceases, due to the formation of a protecting coating of hydrogen oxide of iron.

(ii)**Nature of the corrosion product:** The nature of the corrosion product largely decides the rate of further corrosion. The corrosion product formed on the surface of the metal may or may not act as a protective layer.

(a) The nature of the oxide layer largely decides the rate of further corrosion. If its compositin is stoichiometric, highly insoluble and non poroes 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. Stainless steel (18% Cr, 8% Ni) builds up a thin but a highly protective film of Cr_2O_3 which resist attack in a highly corrosive environment. Metals such as Zr and Mo not only form such protective layer but are also capable of self repairing the oxide films when it is damaged. Hence these metals are extremely resistant to corrosion.

(b) 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

iv) The ratio of anodic and cathodic areas: 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 areas liberated. At the cathode these electrons 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 anodic region and rest of the large tin coated surface acts as cathodic region. Because of 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.

6. (a) What are ion selective electrodes? Explain the determination of pH of unknown solution using glass electrode.   (05 Marks) (CO1, L4).

Solution: These are the electrodes, which responds to specific ions only and develops a potential against that ions while ignoring the other ions present in the solution.

Determination of   pH using glass electrode or calomel 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.

Determination of pH by glass electrode.
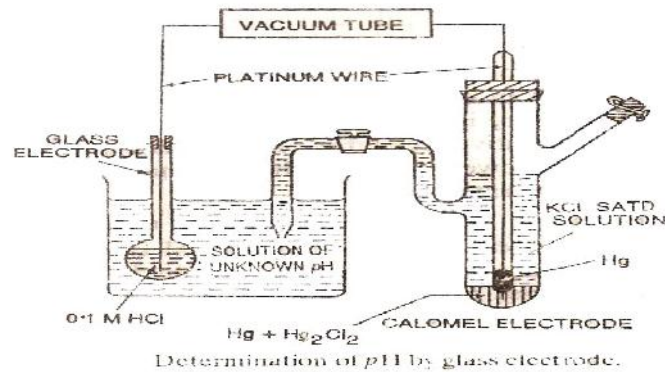
Cell assembly representation:

Hg / Hg_2Cl_2 / Cl- // Unknown solution / glass membrane / 0.1N HCl / AgCl / Ag
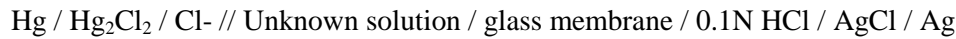
From the emf, the pH of the solution is calculated as below:

$Ecell = E_{right} - E_{left}$

$Ecell = E_{glass} - E_{cal}$

$Ecell = (E_G^o + 0.0591\ pH) - E_{cal}$

$Ecell = E_G^o - E_{cal} - 0.0591\ pH$

$pH = (E_G^o - E_{cal} - Ecell)/0.0591$

$pH = (K' - Ecell)/0.0591$

(**b**) **With a neat sketch, detail the construction, working and applications of Zn-Air battery. (05 Marks) (CO1, L2)**

Solution: This is a type of metal-air batteries which use oxygen directly from the atmosphere to produce electrochemical energy. O_2 diffuses into the cell and is used as the cathode reactant. The air cathode catalytically promotes the reaction of O_2 with an alkaline electrolyte and is not consumed during discharge.

Construction:

1. Anodic material – Loose granulated zinc powder mixed with aqueous alkaline electrolyte (20% NaOH) and a gelling agent (to immobilize the composite).

2. Cathodic material – Carbon, catalyst mixture (oxides of Mn, La) with a wet proofing agent. Beneath Carbon electrode, oxygen permeable membrane Teflon is used. Oxygen is allowed into cell through air access holes to the cathode can.

3. Electrolyte – 20% NaOH absorbed in a porous separator is placed in between anodic zinc and cathodic carbon.
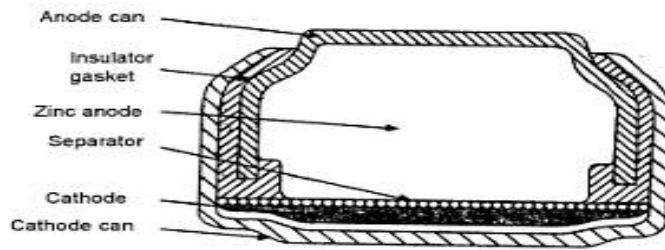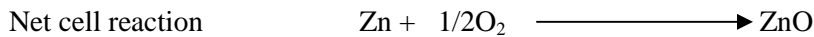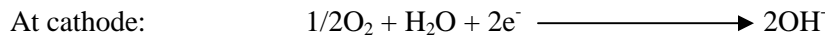
Fig. 2.6   **Zinc – Air** *Battery*

Cell representation;

The battery is representation as, Zn / NaOH (aq, 20%) / air (O$_2$),

Working:

Electrode reactions (discharging and charging) are:

At anode: Zn + 2OH$^-$ $\longrightarrow$ ZnO + H$_2$O + 2e$^-$

At cathode: 1/2O$_2$ + H$_2$O + 2e$^-$ $\longrightarrow$ 2OH$^-$

Net cell reaction   Zn + 1/2O$_2$ $\longrightarrow$ ZnO

During discharging process at, anode Zn oxidizes to Zn^{2+} in ZnO$_2$.similarly, at cathode O$_2$ reduces to O^{2-} forming OH$^-$. Finally the battery produces a potential of 1.7V

Advantages:

1. High energy density as cathodic compartment is not there in cell.

2. Low cost with long shelf life in sealed condition.

Applications:

1. Used in hearing aids and medical devices.

2. Used in telecommunication devices such as pagers and wireless headsets.

3. Zinc-air batteries are often used to power a number of medical devices, such as patient monitors and recorders, nerve and muscle stimulators, and drug infusion pumps.

7. (a) What is surface conversion coating? Describe the process of anodizing of aluminum in detail. (05 Marks) (CO2, L2)

Solution: Surface layer of the metal is converted into a compound, by chemical or electrochemical reactions, which forms a barrier between underlying metal surface and the corrosion environment.

The chemical conversion coating is different from other types of coating in the sense that, they are integral part of the metal itself. Apart from corrosion resistance, thin type of coatings also provides

increased electrical insulation and enhanced adherence for Paints and other similar organic coatings. There are two types of surface conversion coating methods: (i) Anodizing   (ii) Phosphating

Anodizing:

(i) Some metals like Al, Mg, Ni etc and their alloy due to "passivation effect" exhibits much higher corrosion resistance than expected from its position in the galvanic series.

Anodizing is a process in which a protective passive oxide film is artificially (chemically or electrochemically) produced on certain metals. It is also called as anodic oxidation process.

Process:

In this method base metal is made as anode, in an electrolytic bath of suitable composition and passing direct electric current. The most commonly used baths are chromic acid, sulfuric acid, phosphoric acid, oxalic acid etc and lead in general used as a cathode.

When we apply external EMF, at anode oxidation takes place (Al $\longrightarrow$ Al^{3+} + 3e^{-}). The Al^{3+} gets combined with the oxygen and formed Al$_2$O$_3$ on the anode. This oxide layer is a porous. The strength and corrosion resistance of the anodized film can be increased by sealing, which involves dipping the metal in boiling water or steam or metal salt solution. This treatment changes porous alumina at the surface of the coating into monohydrate (Al$_2$O$_3$.H$_2$O), which occupies more volume thereby the pores are sealed. This coating provides good adherence for paints and dyes.

This process is carried out as follows:

The article is degreased, polished and connected to the anode. Steel or copper is made the cathode. The electrolyte consist of 5-10% chromic acid. the temperature of the bath is maintained at 35 ^{o}C. A potential is applied and gradually increased from 0-40 V during first 10 min. Anodizing is continued for 20 min at 40 V. After 20 min, the potential is increased to 50 V and held at this temp for 5 min. An opaque oxide layer is obtained. For higher thickness, 10% sulphuric acid is used as the electrolyte at 22 ^{o}C and a potential of 24 V. The article is dyed by immersing for abt 20 min in a sol of the dye at 50-60 ^{o}C. Finally the article is treated with Ni acetate followed by boiling water. Because of its attractive finish and environmentally safe nature anodized aluminum is one of the most widely used industrial, commercial and domestic materials. It is used in providing attractive, minimum maintenance, highly durable exteriors. It is also used in computer hardware, exhibit displays, and scientific instruments and in a range of home appliances.

(b) What is metal finishing? Mention the technological importance of metal finishing. (05 Marks) (CO3, L1)

Solution: 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

(vii)   Manufacturing printed circuit boards, capacitors, contacts, etc.

(viii)   Electrotyping (e.g., gramophone records)

(ix)   Electroforming or reforming of articles,

(x)   Electrochemical machining, electropolishing and electrochemical etching, etc.