CMR INSTITUTE OF TECHNOLOGY

Sub:	**Engineering Chemistry**				Code:	18CHE22
Date: 15/04/2019	Duration:	90 mins	Max Marks: 50	Sem: II	Branch:	All

Internal Assessment Test I

1. (a) Define electrolyte concentration cell. The emf of cell Ag/AgNO3(0.001M)//AgNO3(XM)/Ag is 0.059V at 25°C. Find the value of X. **(05 Marks) (CO1, L3)**

Solution: Under standard condition (T=25C=298K)**,**

$$E_{cell} = \frac{0.0591}{n} \log C_2/C_1$$

Where C_2 = Concentration of electrolyte at cathodic compartment = x M

C_1 = Concentration of electrolyte at anodic compartment = 0.002M

E = 0.0751V

n = 1

Substituting the above values in above formula,

0.0751= 0.0591/1 log x/0.002

0.0751= 0.0591 [log x-log 0.002]

0.0751=0.0591 [log x- (-2.69)]

1.12=logx+2.69

logx= -1.57

x= 0.0269M

Thus, the value of x=0.0269M.

(b) Explain the construction and working of Li-ion battery. Mention its applications. **(05 Marks) (CO1, L4)**

Solution: A lithium-ion battery is a secondary battery 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 (LiCl, LiBr) in organic carbonate solvents (ethylene carbonate)
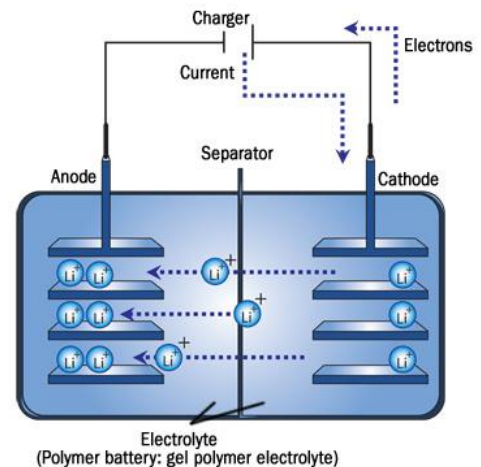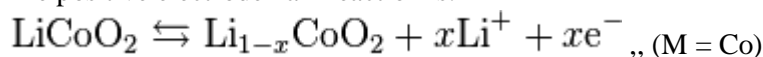
Separator: Polypropylene separator

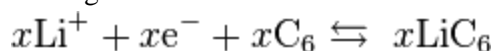Fig. : Lithium Ion battery

Cell representation

The battery is represented as, LiMO2 / electrolyte (lithium salt in an organic solvent) / C (graphite)
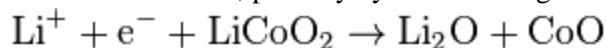
Working:

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:

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

Applications: Li-ion battery is used in

1. Portable devices like mobile phones and smartphones, laptops and tablets, digital cameras and camcorders, electronic cigarettes, handheld game consoles and torches (flashlights).

2. Li-ion batteries are used in tools such as cordless drills, sanders, saws

3. Electric vehicles.

4. Li-ion batteries are used in telecommunications applications.

2. (a) What is single electrode potential? Derive the Nernst equation for single electrode potential.

(06 Marks) (CO1, L3)

Solution: Single Electrode Potential: Electrode potential is defined as the potential developed at the interface between metal and solution, when it is in contact with solutions of its ions.

Or

It is a measure of the tendency of the metal electrode to lose or gain electrons, when it is in contact with its own ionic solution. It is represented as **E**.

Nernst Equation:

The potential of an electrode depends on concentration and temperature. In 1889, W. H. Nernst derived a quantitative relationship between electrode potential and concentration of electrolyte species.

Consider an electrode assembly undergoing a spontaneous reaction.

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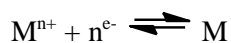
The equilibrium constant (Kc) is related to change in free energy by Vant Hoff equation as follows

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

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

According to thermodynamics, decrease in free energy ($-\Delta G$) 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 × 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

$\Delta G^o = - n \times F \times E^\circ$-----------------------------(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, ΔG^o and Kc from equation (2), (5) and (6) into equation (1), we get

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

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

Dividing whole equation by $-nF$

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

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

Under standard condition [M] = 1,

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

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

$E = E^\circ + 2.303RT\log[M^{n+}]/nF$ ----------------------------------- (8)

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

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

This is the mathematical representation of Nernst equation.

(b) Define secondary and reserve batteries with example. (04 Marks) (CO1, L2)
Solution:
Secondary batteries: In secondary batteries, the net cell reaction is completely reversible and hence these are rechargeable. For example: Lead storage battery, Ni – Cd battery etc.
Reserve batteries: One of the key components i.e. electrolyte, in reserve batteries is incorporated into the battery when required. When one of the key components is separated from remainder, chemical reaction between cell components (self discharge) is prevented and battery can be stored for a long period of time. For example: Mg-AgCl, Mg-CuCl, Zinc – Silver oxide reserve batteries, etc.

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

Solution:

Ion Selective electrodes: 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.

Cell assembly representation:

Hg / Hg2Cl2 / Cl- // Unknown solution / glass membrane / 0.1N HCl / AgCl / Ag

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

Ecell = Eright – Eleft

Ecell = Eglass- Ecal

Ecell = (E G- 0.0591 pH) - Ecal

Ecell = E G- 0.0591 pH- Ecal

pH = (EoG- Ecal – Ecell)/0.0591

pH = (K – Ecell)/0.0591 $\quad$ K= (E^o_G- E_{cal})
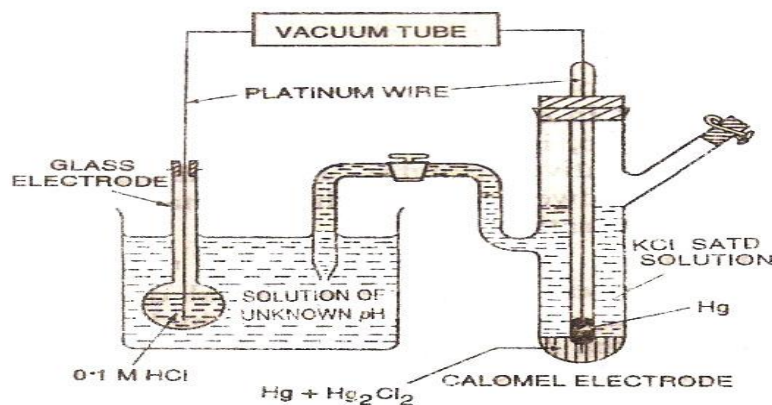
Determination of pH by glass electrode.

(b) Describe the construction and working of Ni-MH battery. Mention it applications. (05 Marks) (CO1, L2)

Solution: Nickel – Metal Hydride Battery: It is a good example for secondary battery which is also called as rechargeable battery.

Construction:

1. Anodic material - Metal hydride such as VH2, ZrH2, TiH2 etc with a hydrogen storage alloy such as $LaNi_5$, $TiZr_2$ etc. Anodic material permits reversible electrochemical storage and release of hydrogen (H_2) during charging and discharging of battery and is corrosion resistant.
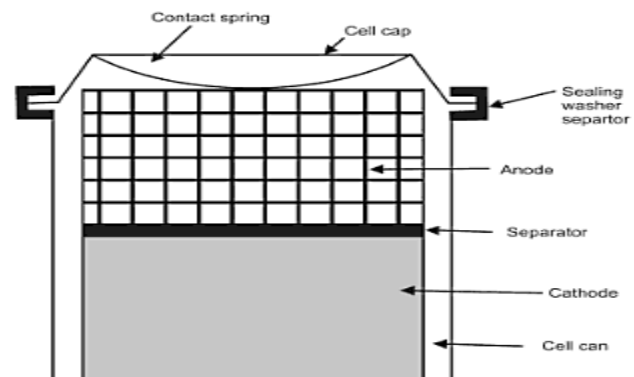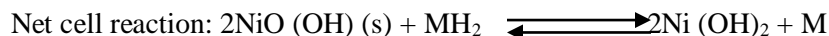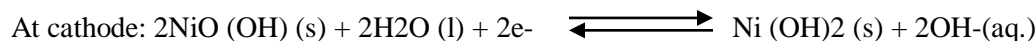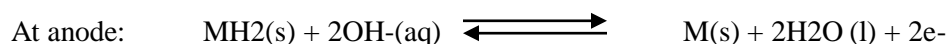
2. Cathodic material – NiO(OH) nickel oxy hydroxide. (Highly porous Ni substrate into which Ni(O)OH is impregnated.

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.

Cell Representation

The battery is represented as, MH2 /KOH (30%) / Ni (OH)2, NiO(OH)

Working:

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

At anode: $MH_2(s) + 2OH^-(aq)$ ⇌ $M(s) + 2H_2O (l) + 2e^-$

At cathode: $2NiO (OH) (s) + 2H_2O (l) + 2e^-$ ⇌ $Ni (OH)_2 (s) + 2OH^-(aq.)$

Net cell reaction: $2NiO (OH) (s) + MH_2$ ⇌ $2Ni (OH)_2 + M$

During discharging process, at anode MH2 reduces to M & at cathode Ni^{3+} reduces to Ni^{2+}. Finally the battery produces a potential of 1.35V.

4. (a) What are reference electrodes? Describe the construction and working of calomel electrode. (05 Marks) (CO1, L2)

Solution: Reference Electrodes: These are the electrodes, used to determine the potentials of unknown electrodes. They are of two types;

I. Primary Reference Electrodes: These are the electrodes whose potentials are known from the method of construction. Eg. Standard hydrogen electrode (SHE).
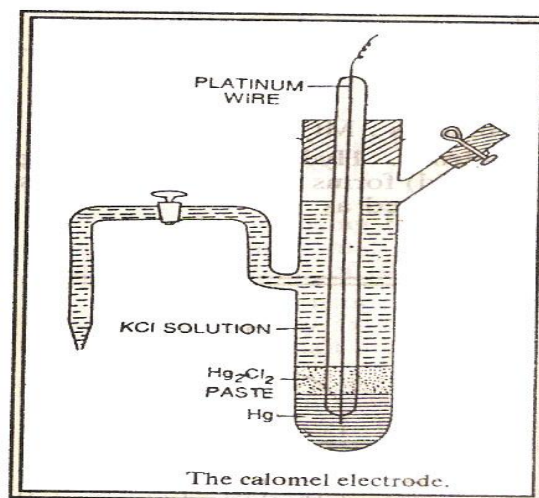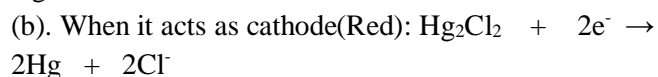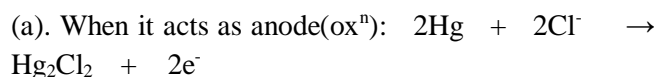
II. Secondary Reference Electrodes: These are the electrode whose potential is known or constant and stable does not vary with temperature.   E.g.: Calomel electrode

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 + Hg_2Cl_2) 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 /$HgCl_2$, Hg

Half cell reactions:

(a). When it acts as anode(ox^n): $2Hg + 2Cl^- \rightarrow Hg_2Cl_2 + 2e^-$

(b). When it acts as cathode(Red): $Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$


The calomel electrode.

The electrode potential of the calomel electrode is mainly depends on the concentration of KCl used, Electrode potential is calculated using Nernst equation,

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

For,   0.344V   for   [KCl] = 0.1N
        0.281V   for   [KCl] = 1.0N
        0.2422V   for   [KCl] = saturated KCl

(b) For the cell, Fe/Fe(NO₃)₂(0.001M)//AgNO₃(0.01M)/Ag, write the cell reaction and calculate the emf of cell at 298K, if standard potentials of Fe and Ag electrodes are -0.44V and +0.8V respectively. (05 Marks) (CO1, L3)

Solution: Fe/Fe(NO₃)₂(0.001M)//AgNO₃(0.01M)/Ag

Fe→ Fe²⁺ (0.01M) + 2e-

[Ag+ (0.1M) + e- →Ag(s)]*2

Overall: Fe + 2Ag⁺ (0.01M)→ Fe²⁺ (0.001M) +2Ag
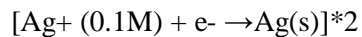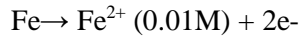
The Nernst equation is: Ecell = E°cell + 0.0592/2 log [Ag⁺]²/[Fe²⁺]

E°cell = E°Cathode - E°Anode

E°cell = 0.80- (-0.44)

E°cell = 1.24V

Ecell = 1.24 + 0.0295 log (0.01)²/0.001

Ecell= 1.24 + 0.0295log (0.0001)/(0.001)

Ecell = 1.21V

5. (a) Define corrosion? Explain the Electro-chemical theory of corrosion by taking the iron as an example. (06 Marks) (CO2, L4)

Solution: Corrosion: It's defined as the destruction of metal or alloys by the surrounding environment through chemical or electrochemical changes.

Electrochemical theory of corrosion;

(i) 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.

(ii)At the anode region oxidation reaction takes place and the metal gets converted into its ions by liberating electrons. Consequently, metal undergoes corrosion at the anodic region.

(iii) At the cathodic region, reduction takes place. Since metal cannot be reduced further, metal atoms at the cathodic region are unaffected by the cathodic reaction. Some constitutions of the corrosion medium take part in the cathodic reaction.

(iv)the electrons liberated at the anodic region migrates to the cathodic region constituting corrosion current, the metal ions liberated at the anode and some anions liberated at the cathode diffuse towards eachother through the conducting medium-range and form a corrosion products some where between anode and cathode.
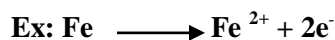
This can be explained by taking Fe metal as an example.

(v) Due to the following regions, formation of anodic and cathodic region of metal may arise

(a) crackness in surface film (b)presence of impurities in the bulk of the metal.

(c) Difference in oxygen concentration along the metal surface.

CORROSION:

AT ANODE:

$$M \longrightarrow M^+ + ne^-$$

**Ex: 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.

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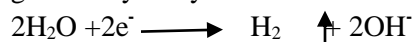
(c) If the solution is aerated and almost neutral the alkaline oxygen or water are reduced to OH$^-$ ions.

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$$
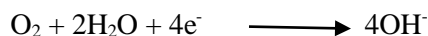
Corrosion of iron produced Fe^{2+} ions and OH$^-$ ions at the anode and cathode sites respectively. These ions diffuse towards each other. Since small Fe^{2+} ions diffuse more rapidly than OH$^-$ ions; their combination occurs more commonly near cathodic region.

$$2\,Fe^{2+} + 4\,OH^- \longrightarrow 2\,Fe(OH)_2$$
$$\text{(Ferrous hydroxide)}$$
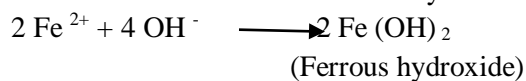
In an oxidizing environment, it is oxidized to ferric oxide and the yellow rust is hydrated ferric oxide.

$$4\,Fe(OH)_2 + O_2 + 2H_2O \longrightarrow 2[Fe_2O_3.3H_2O]\ \text{[Rust]}$$
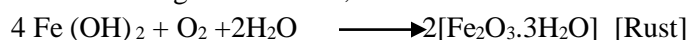
(b) Explain the following concepts in context with electrolysis. (04Marks) (CO2, L4)

(i) Polarization, and (ii) Decomposition potential or Overvoltage

Solution: 1. Polarization: A process of variation in electrode potential due to change in concentration of ionic species at electrode surface by

(i) slow diffusion of ions from the bulk of the electrolyte to the electrode or from the electrode towards the bulk (known as concentration polarization)

(ii) one or more of elementary steps of discharge (or evolution) of gases being slow at electrode surface (known as overvoltage polarization).

Electrode potential is a function of active mass or molar concentration of ionic species in the solution given by the Nernst equation:

$$E = E^\circ + \frac{2.303\,RT}{nF} \log [M^{n+}]$$

For a reduction reaction at the cathodic surface, there is depletion in concentration of M^{n+} ions in the vicinity of cathodic surface. Until that time, ions diffuse from the bulk and re-establish the equilibrium, lower concentration of ionic species alters the electrode potential. Similar such phenomena can be seen at the anodic surface. This effect is known as concentration polarization. Polarization of electrodes depends upon

    (i) current densities applied

    (ii) nature of the electrode (i.e., composition, size, shape, etc.)

    (iii) nature of electrolyte, its concentration and conductivity

    (iv) agitation / temperature of the electrolyte

    (v) nature of the products formed at the electrode surfaces.

Concentration polarization can be minimized by

    (i) having larger electrode surfaces

    (ii) by optimized current densities

(iii) lower concentrations of highly conducting electrolyte

(iv) better agitation / higher temperature of the electrolyte

Knowledge of polarization helps one to realize the importance of agitation of electrolyte in order to minimize concentration polarization and thus, the expenses of electroplating. However, overvoltage cannot be eliminated.

2. Decomposition Potential: (or Decomposition Voltage)

Decomposition potential is the experimentally determined minimum external potential that needs to be applied in order to have continuous decomposition of the electrolyte.

For example, in the decomposition of water, a dilute solution of either an acid or alkali is electrolyzed using smooth platinum electrodes. For the applied potential less than 1.68 V, there is initial surge of current which will drop to zero in a while. When the applied potential is 1.68 V or more, there is continuous decomposition of water with the liberation of hydrogen at cathode and oxygen at the anode. Thus, 1.68 V is the decomposition potential of water.

A knowledge of discharge potentials of different electrodes helps in

(i) Knowing the potential to be externally applied for electrolysis of any electrolyte.

(ii) Predicting the order in which the different substances discharge or deposit at respective electrodes. For example, by the electrolysis of a solution containing C^{u2+} ions, Z^{n2+} ions and C^{d2+} ions, Ag ions, Hg ions the discharge or deposition of metals happens to be in the order: Ag, Hg, Cu, then Cd and later, Zn.

Decomposition potential can be determined by the measurements of current for varying potentials (or voltages) applied across the electrodes immersed in electrolyte under investigation. The set up used for measurement is shown in the figure.

A plot of current against potential (or voltage) helps in knowing the decomposition potential. For lower voltages, there is no significant rise in current till the reach of decomposition potential. Beyond this potential, it starts rising abruptly. Laws of electrolysis are applicable only in this region. Decomposition potential is obtained by the intersection of the two tangents drawn as shown in the figure.

OR

Overvoltage:

Overvoltage can be defined as excess voltage over the theoretical voltage (or reversible discharge potential) required to be applied for the continuous discharge / deposition of a substance at the electrode surface.

For example, decomposition potential of water over smooth platinum surfaces is 1.68 V. However, the theoretically calculated voltage (or reversible cell potential) is 1.23 V. Therefore, overvoltage is 1.68 – 1.23 = 0.45 V.

Explanation:

Evolution of hydrogen gas from a plating bath at cathodic surfaces involves

(i) Diffusion of hydronium ion, H_3O^+.
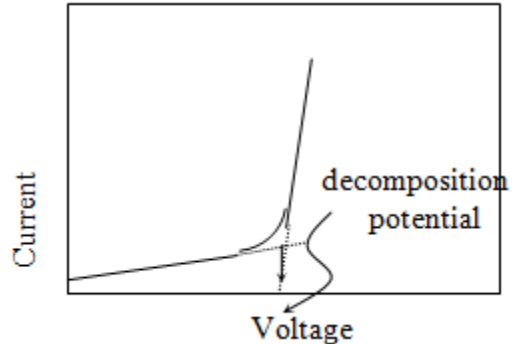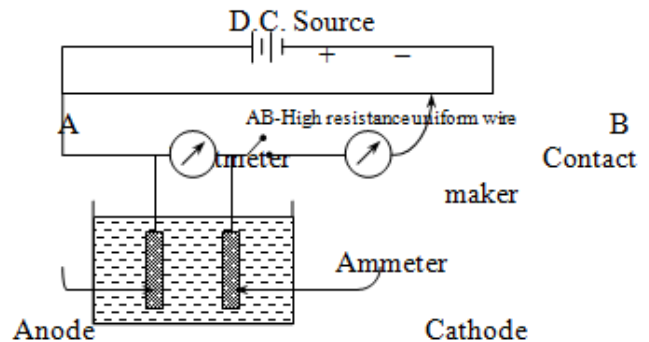
(ii) its becoming H^+ ion and reduction to atomic hydrogen

$$H_3O^+ \longrightarrow H^+ + H_2O$$
$$H^+ + e^- \longrightarrow H$$

(iii) Diffusion of hydrogen atoms towards one another, their union to form molecules, few molecules forming the bubble and escape of hydrogen gas from the surface.

$$H + H \longrightarrow H_2 \uparrow$$
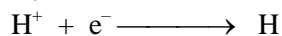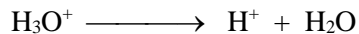
When any one or more of these processes is slow, there is variation of ionic concentrations near electrode surfaces and a change in the potential. As a fact, the third step, diffusion of atomic hydrogen and their union happens to be slow with energy consumption attributing to overvoltage.

Overvoltage depends upon:

(i) Nature and physical state of the electrode: Metals with smooth surfaces have relatively higher overvoltages. Mercury has highest overvoltage. Smooth-Pt has higher overvoltage than platinised Pt.

(ii) Nature of the substance getting deposited: Overvoltages of different substances are different. For example, overvoltages of H_2 and O_2 over same smooth-Pt surface are different, say, 0.024 V and 0.721 V with a current density of 0.001 A/cm^2 at 25°C.

(iii) Current density at the electrode surface: Generally, increase in current density increases overvoltage.

(iv) Temperature of the electrolytic bath: Generally, increase in temperature decreases overvoltage.

6. (a) Explain the following factors affecting corrosion. (04 marks) (CO2, L4)

(i) Nature of corrosion product   (ii) Ratio of anodic to cathodic areas

Solution: 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

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.

(b) Describe the process of electroplating of chromium (Hard or Decorative). (06 marks) (CO2, L2)
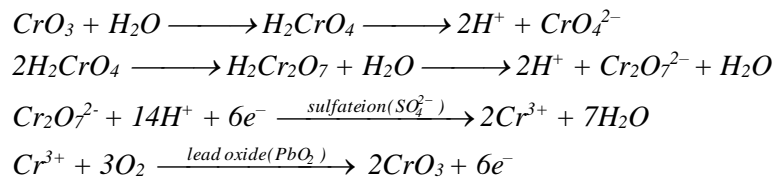
Solution: *Electroplating of Chromium:*

Chromium is employed for either decorative purposes (as a thinner coat) or engineering purposes (as a thicker hard coat). Mentioned below are coating specifications.

- Active chromium anode is not used because, the anode efficiency is nearly 100% and that of the cathode is only around 20% at the best. There will be increase in concentration of Cr^{3+} ions which results in poor quality electrodeposits (black deposits).
- A thin coating of chromium is porous and thicker coating leads to cracking. Therefore, Cr-plating over steel is applied with an undercoat of copper and nickel. Copper is known to offer better finishing. Coverage of nickel and hence chromium is better with copper below. Also, lower thickness of nickel can be opted with an undercoat of copper. Chromium gives decorative & pleasing finish, nickel offers corrosion resistance and copper extends good coverage and better adhesion.

Bath composition	CrO_3 (chromic acid) : H_2SO_4 = 100: 1 ratio
Temperature	$45 - 60\,^{\circ}C$
Current density	$100 - 200$ mA/cm^2
Current efficiency	$17 - 21$ %
Anode material	Insoluble lead- Pb-Sb alloy or Pb-Sn alloy (with lead oxide coating)
Cathode material	Surface cleaned object metal
Reaction at anode	$H_2O \longrightarrow \frac{1}{2} O_2 \uparrow + 2H^+ + 2e^-$
Reaction at cathode	$Cr^{3+} + 3e^- \longrightarrow Cr$

- There is a complex sequence of reactions which control the concentration of Cr^{3+} in the plating bath. Sulfate ion is said to catalyse the conversion of Cr^{6+} into Cr^{3+} and PbO_2 catalyses the conversion of Cr^{3+} into Cr^{6+}.

$$CrO_3 + H_2O \longrightarrow H_2CrO_4 \longrightarrow 2H^+ + CrO_4^{2-}$$

$$2H_2CrO_4 \longrightarrow H_2Cr_2O_7 + H_2O \longrightarrow 2H^+ + Cr_2O_7^{2-} + H_2O$$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \xrightarrow{\text{sulfate ion}(SO_4^{2-})} 2Cr^{3+} + 7H_2O$$

$$Cr^{3+} + 3O_2 \xrightarrow{\text{lead oxide}(PbO_2)} 2CrO_3 + 6e^-$$

Chromium plating is a hard, attractive coating, with low coefficient of friction exhibiting wear resistance, abrasion resistance and also good corrosion resistance (with an undercoat of nickel and copper).

Applications :

- Decorative chromium provides a durable finish on cycles, automobiles, furniture, household fittings, aircraft, surgical and dental instruments.
- Hard chromium is mostly used in industries in the making of gauzes, dies, cutting tools, piston rings, cylinder liners, crankshafts of marine and aero engines, bearings, hydraulic rams and in printing industry.
- Black chromium is used in optical instruments, machine tools and electronic parts. It is also used in non-glare finishes on automobiles, and as an efficient coating for solar energy collectors.

7. (a) What is cathodic protection? Explain impressed current technique for prevention of corrosion. (04 Marks) (CO2, L4).

Solution: CATHODIC PROTECTION: 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.

In this method, by applying a direct current larger than the corrosion current, the base metal is made cathodic by connecting it to the cathode of the external source of current and the anode of the source is connected to an inert electrode (lead or graphite). The cathode is the str to be protected and anode is resin bonded graphite rod, high silicon-iron alloy or platinisedTi connected to the positive terminal.

The metal structure being cathode, doesn't undergo corrosion. Anode being inert, remains unaffected [electrons for protection are supplied by a source of direct current].
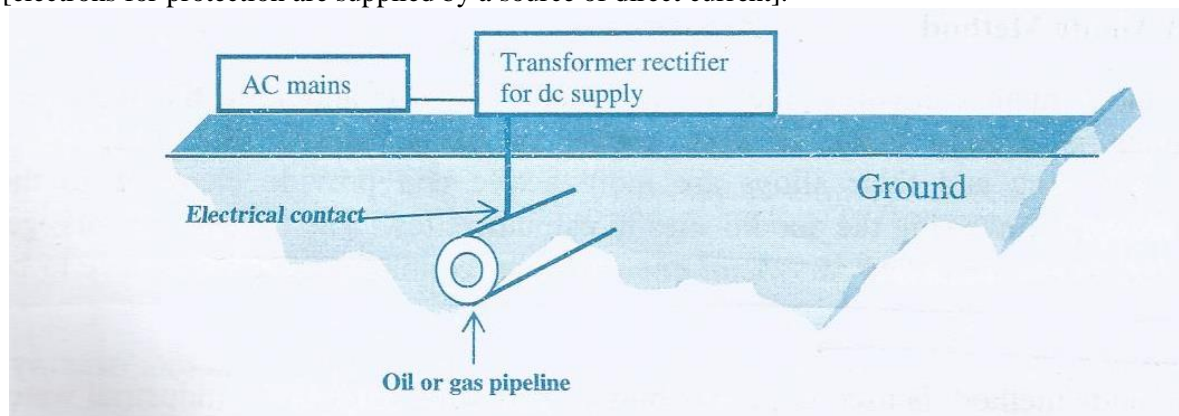

Fig: Protection using an impressed voltage

Advantages:

(i) One installation can protect larger area of metal.

(iii) low maintenance cost.

Disadvantages:

(i)It is very expensive, because it needs continues current.

(ii)If the impressed current is not uniform on the entire surface of the protected structure, localized corrosion takes place on the protected metal.

(b) What is electroless plating? Describe the process of electrolessplating of copper.   (06 marks) (CO2, L2)

Solution: *Electroless-plating:* Deposition of metal or alloy over a conducting or non-conducting substrate surface by **chemical reduction of the metal ions by use of reducing reagent** and without the use of electrical energy is called electroless-plating.

Electroless-plating is generally autocatalytic in nature. Schematically, it can be represented as,
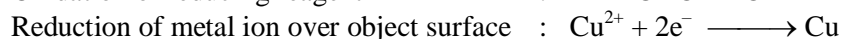
Metal ions + Reducing agent $\xrightarrow{\text{catalyticlly activesurface}}$ Metal atom + Oxidized product
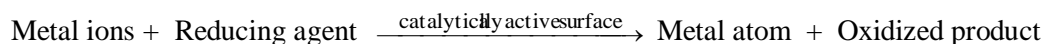
Electroless-plating of Copper:

Substrate surface needs to be cleaned by suitable cleansing methods (solvent degreasing, acid pickling, alkali pickling, mechanical polishing, etc.). However, when the object is non-conducting or insulator material such as, plastics, PCBs, glass, etc. it needs to be activated by treatment with acidified $SnCl_2$ and then with acidified $PdCl_2$. Following bath compositions are used for plating.

Constituents	Amount	Purpose
$CuSO_4$	12 g/L	Provides metal ions
H-CHO	8 g/L	Reducing reagent
Rochelle salt	14 g/L	Complexing agent
NaOH	15 g/L	Provides alkaline medium
EDTA	20 g/L	Exaltant & complexing agent
pH	11.0	
Temperature	25°C	

Reactions:

Oxidation of reducing reagent   : $2HCHO + 4OH^- \longrightarrow 2HCOO^- + 2H_2O + H_2 + 2e^-$

Reduction of metal ion over object surface   : $Cu^{2+} + 2e^- \longrightarrow Cu$

Overall reaction : $Cu^{2+} + 2HCHO + 4OH^- \longrightarrow Cu + 2HCOO^- + 2H_2O + H_2\uparrow$

Applications:
- Metalising PCBs.
- Producing through-hole connections.
- For plating on non-conductors.
- As a base before electroplating.

8. (a) What is differential aeration corrosion? Explain waterline and pitting corrosion with suitable reactions. (06 Marks) (CO2, L4)

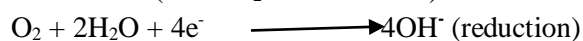**Solution: Differential aeration corrosion:**

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

The part of the metal exposed to higher oxygen concentration acts as 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.

At anode: (less oxygen concentration)

$M \longrightarrow M^{n+} + ne^-$ (oxidation)
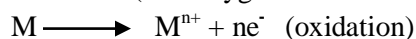
At cathode: (more O_2 concentration)

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

(ii) Corrosion of metals occurs due to the formation of oxygen concentration cell due to uneven supply of air on the metal surface is known as differential aeration corrosion.

Ex: 1. partially buried pipe line in soil or submerged in water undergoes corrosion below the soil or water whereas the exposed part remains free from corrosion

2. Metal under dust, dirt or water undergoes corrosion

Water line corrosion:

(i)The water line corrosion takes place due to the formation of differential oxygen concentration cells.

(ii)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

Ex: Ocean going ship

EX: Water lifting pipes under water.

Though ocean going ships undergo differential aeration corrosion, ships sunk under water are free from corrosion as the difference in oxygen concentration between top and bottom of the ship is negligibly small as ship is exposed to almost uniform concentration of air and hence doesn't undergo differential aeration corrosion.

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

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

_____

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

Pitting corrosion:

(i) Pitting corrosion results when small particles of dust get deposited on a steel surface (fig). The portion covered by the dust will not be well aerated compared to the exposed surface.

(ii) 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.

Ex: Crack developed in tin coating on iron gives rise to a small anodic area and large cathodic area

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

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

_____

$2Fe + O_2 + 2H_2O \longrightarrow 2Fe^{2+} + 4OH^-$
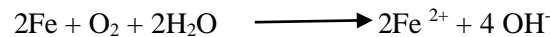
(b) What is meant by metal finishing? Mention (any four) technological importance of metal finishing. (04 Marks) (CO2, L2)

Solution: Definition: 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.