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Internal Assessment Test 1 – Nov 2024											
Sub:	Chemistry for EEE stream					Sub Code:	BCHEE102	Branch:	ECE	2	
Date:	20-11-2024	Duration:	90 min's	Max Marks:	50	Sem / Sec:	I / M, N, O &	Р			OBE
Question no. 1 is COMPULSORY and answer any THREE FULL Questions from the rest. MARKS									RBT		
1 (a)	What are photovoltaic cells? Explain construction and working of PV cells and mention its[7]advantages.						CO2	L3			
(b)	Define corrosion. Explain the electrochemical theory of corrosion taking rusting of iron as example.						ple.	[7]	CO3	L3	
2 (a)	Discuss classification of batteries with suitable examples.							[6]	CO2	L1	
(b)	Define battery. Describe construction, working and applications of Li polymer battery.							[6]	CO2	L2	
3 (a)	Explain the construction and working of vanadium redox flow battery and mention its applications. [6]					CO2	L2				
(b)	What are fuel cells? Explain construction and working of methanol-oxygen fuel cell.							[6]	CO2	L2	
4 (a)	Identify and explain the type of corrosion taking place in following cases[6](i) A steel screw fitted in the copper sheet for long time(ii) Half filled steel water tank						[6]	CO3	L3		
(b)	What is cathodic protection? Explain sacrificial anode method of corrosion control.							[6]	CO3	L2	
5(a)	Discuss the methods of disposal of e-waste.							[6]	CO3	L2	

	Define corrosion penetration rate (CPR). A thick steel sheet of area 540 cm ² is exposed to air near the ocean. After 3 years it was found to experience a weight loss of 585 gm due to corrosion. Calculate CPR in mpy and mm/y. [Density of the metal is 7.9 gm/cm ³ , $K(mpy) = 534$ and $K(mm/y) = 87.6$].
6 (a)	What is e-waste ? Discuss effects of e-waste on environment and human health.
(b)	What is galvanisation? Discuss the process of galvanisation and mention its applications.

7 (a) Describe the extraction of Cu and gold from E-waste.(b) What are reference electrodes? Describe the construction and working of calomel electrode.

8 (a) What are ion selective electrodes? Explain construction and working of glass electrode.

(b) The EMF of concentration cell, constructed by combining two silver rods immersed in silver nitrate solution is 0.195 V at 25 °C. If concentration of anodic compartment is 0.005 M. Calculate the concentration of cathodic compartment. Represent the cell and write the cell reaction.

Answer 1(a) :

Photovoltaic Cells:

Photovoltaic cells or solar cells are semiconductor device that converts sunlight into direct current (DC) electricity. As long as light is shining on the solar cell, it generates electrical power. When light stops, electricity stops.

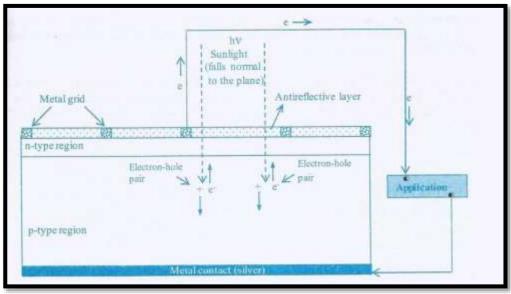


Figure Photovoltaic cells

Construction & Working of Photovoltaic Cells Construction:

- Photovoltaic Cells consist of a semiconductor diode (p-n junction) made of a silicon.
- Silicon wafer or very thin silicon slices are made by silicon blocks and they are doped by p-type and n-type dopents to make p-n junction.
- It has two electrical contact, on one of its sides, a metallic grid is used and on the other side a layer of noble metal (such as Ag) is used.
- The metal grid permits the light to fall on the diode between the grid lines.
- The part between the metallic grid is coated with antireflective compound. eg TiO₂

Working:

• Electromagnetic radiation consists of particle called photon (hv). They carry a certain amount of energy given by the Plank quantum equation.

$$E = hc/\lambda$$

Where, h = Planck's constant, c = velocity of light, $\lambda = wavelength$ of the radiation

- The electromagnetic radiation (sunlight) falls normal to the plane of the solar cell, the photons which possess energy sufficient to overcome the barrier potential are absorbed, electrons are ejected and electronhole pairs are formed.
- The electrons move towards the n-region (as it is positively charged). The electrons are driven into the external circuit and used for various applications or appliances.

Advantage of Photovoltaic cells -

- 1. It is unlimited, inexhaustible and renewable source of energy.
- 2. The solar cell operates reliably for a long period of time with no maintenance.

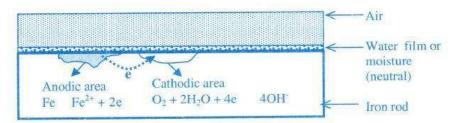
- 3. A photovoltaic system can be constructed to any size based on energy requirement.
- 4. Easy to operate
- 5. Quick installation.
- 6. Can be integrated into new or existing building structure.
- 7. Completely pollution free during its use.

Disadvantage of Photovoltaic cells -

- 1. High installation cost.
- 2. Energy can be produced only during the day-time.
- 3. The efficiency of solar cells depends on the seasonal variations, latitude and climate.
- 4. Space required to generate unit power output is relatively more.
- 5. Solar cell generates DC current. It needs to be converted to AC for use.

Answer 1(b) : Corrosion is defined as the destruction of metal or alloys from its surface by the surrounding environment through chemical or electrochemical changes. Eg. 1. Rusting of Iron

Electrochemical theory of corrosion: Most of the corrosion problems are best explained on the basis of electrochemical theory.



(i) According to electrochemical theory, corrosion of metals takes place due to the formation of minute galvanic cells over the surface of metal. Thus anodic and cathodic regions are formed on the same metal surface or when two metals are in contact with each other in the presence of a conducting medium.

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

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

Ex: Fe \longrightarrow Fe $^{2+}$ + 2e⁻

(iii) The electrons flow from the anodic to cathodic area and 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. There are three possible ways in which the reduction can take place.

(i) If the solution is aerated and almost neutral, oxygen is reduced in presence of water to OH- ions according to the equation.

 $\frac{1}{2}O_2 + H_2O + 2e^- \longrightarrow 2OH^-$

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

 $2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$

(iii) If the solution is deaerated and acidic, the H⁺ ions are reduced to H₂

 $2H^+ + 2e^- - H_2 \uparrow$

(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 each other through the conducting medium-range and form a corrosion products.

Corrosion of iron produced Fe $^{2+}$ ions and OH⁻ ions at the anode and cathode sites respectively. These ions diffuse towards each other and produce insoluble Fe (OH)₂.

Fe²⁺ + 2 OH - Fe (OH)2 (Ferrous hydroxide)

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

2Fe (OH) $_2 + \frac{1}{2}O_2 + (n-2)H_2O \longrightarrow [Fe_2O_3.nH_2O] [Rust]$

Corrosion of metal continues as long as both anodic and cathodic reactions take place simultaneously.

Answer 2a. Classification of Batterie: Batteries are classified under the following categories:

• **Primary battery:** In primary batteries, chemical energy stored in the battery is converted to electrical energy spontaneously as long as active materials are present. This battery cannot be recharged, because cell reaction is irreversible. *Example:* Zn-MnO₂ battery, Li-MnO₂ battery.

• Secondary battery: This battery can be recharged by passing electric current, because cell reactions are reversible. The redox reaction is reversed during recharing. Electrical energy is stored in the form of chemical energy in these batteries and used when needed. *Example:* Lead acid battery, Ni-MH battery, Li-ion battery. Primary cells act only as galvanic cell, whereas, a secondary cell can act both as galvanic cell and electrolytic cell. During discharging it acts as galvanic cell converting chemical energy to electrical energy and during charging process it acts as electrolytic cell converting electrical energy to chemical energy

• **Reserve battery:** In this battery, one of the key component is stored separately, and is incorporated into battery when required. When long storage is required, reserve batteries are often used, since the active component of the cell is separated until needed, thus reducing self-discharge.

Example: Mg-AgCl battery. They are activated by adding sea water. These batteries have high reliability and long shelf life, hence they find applications in missiles and submarines. Another example is zinc-air batteries where the cell is sealed until use, the seal is removed to admit air and activate the cell when needed.

Answer 2b: Battery is a device consisting of two or more galvanic cells arranged in series or parallel or both, that can generate electrical energy.

Construction:

Anode: Lithium intercalated Carbon or graphite

Cathode: lithium transition metal oxides (such as lithium-cobalt oxide (LiCoO₂)),

Electrolyte & Separator: High conductivity semisolid (gel) polymers electrolyte polymer electrolytes and include poly(methyl methacrylate) (PMMA), poly(acrylonitrile) (PAN)

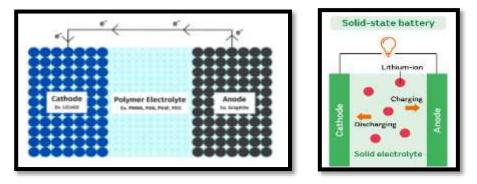


Figure: LiPo Battery

Working:

0						
	Discharge					
At anode: Li _x C ₆	\leftarrow xLi ⁺ +	$xe^{-} + C_6$				
	Charge					
	Discharge					
At cathode: $LiCoO_2 + xLi^+ + xe^- \longrightarrow Li_{1+x}CoO_2$						
Charge						
		Discharge				
Overall cell reaction:	xLiC ₆ + Li CoO ₂	$\checkmark Li_{1+x} CoO_2 + xC_6$				
		Charge				

Applications: These batteries provide higher specific energy than other lithium battery types and are used in applications where weight is a critical feature, such as mobile devices, radio-controlled aircraft and some electric vehicles.

<u>Answer 3a.</u> Vanadium redox flow battery: The vanadium redox battery (VRB), also known as the vanadium flow battery (VFB) or vanadium redox flow battery (VRFB), is a type of rechargeable flow battery. It employs vanadium ions as charge carriers.

Construction: A vanadium redox battery consists of an assembly of power cells in which two electrolytes are separated by a proton exchange membrane.

Electrodes: The electrodes in a VRB cell are carbon based. The most common types are carbon felt, carbon paper, carbon cloth, and graphite felt. Recently, carbon nanotube-based electrodes have attracted interest from the scientific community.

Electrolytes: Both electrolytes are vanadium-based. The electrolyte in the positive half-cells contains VO_2^+ and VO^{2+} ions, while the electrolyte in the negative half-cells consists of V^{3+} and V^{2+} ions. The electrolytes can be

prepared by several processes, including electrolytically dissolving vanadium pentoxide (V_2O_5) in sulfuric acid (H_2SO_4). The solution remains strongly acidic in use.

Membrane: The most common membrane material is perfluorinated sulfonic acid (PFSA) (Nafion). polytetrafluoroethylene (Teflon).

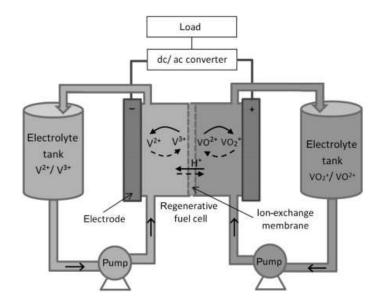


Figure. A diagram of a vanadium redox flow battery

 V^{2+}

Working:

 \leftrightarrow

Discharge

Charge

Discharge

 $V^{3+} + e^{-}$

Positive electrode: $VO_2^+ + e^- + 2H^+$

Charge Discharge

Overall reaction: $VO_2^+ + V^{2+} + 2H^+ \iff VO^{2+} + V^{3+} + H_2O$ (E⁰=1.26 V) Charge

Application: Vanadium batteries are typically used for grid energy storage, i.e., attached to power plants/electrical grids.

 $VO^{2+} + H_2O$

Answer 3b.

Definition: A fuel cell is a device that converts the chemical energy of a fuel (hydrogen, natural gas, methanol, gasoline, etc.) and an oxidant (air or oxygen) into electricity.

Construction, working and applications of methanol-oxygen fuel cell.

It is good example for liquid fuel cell. They use either acidic or alkaline medium. The preferred electrolyte is the acidic. Methanol is an efficient active organic fuel at low temperature.

Construction: Methanol – oxygen fuel cell consist of

1. Anode – It is a porous Nickel (Ni) electrode impregnated with Pt/Pd catalyst.

- 2. Cathode It is a porous Nickel (Ni) electrode coated with silver (Ag) catalyst.
- 3. Electrolyte Aqueous sulphuric acid (H₂SO₄), 3.7 M.

4. Active components: (a) Fuel – Methanol mixed with sulphuric acid supplied at anode. (b) Oxidant – Pure oxygen is supplied at cathode.

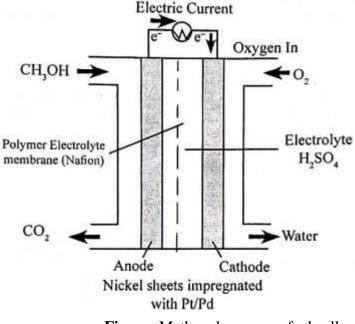


Figure: Methanol – oxygen fuel cell

Working:

Cell reaction;

Anode Reaction: $CH_3OH + H_2O \longrightarrow CO_2 + 6H^+ + 6e^-$

Cathode Reaction: $3/2 O_2 + 6 H^+ + 6e^- 3 H_2O$

Overall Cell Reaction: $CH_3OH + 3/2 O_2 \longrightarrow CO_2 + 2 H_2O$

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

Cell Potential : 1.2 V

Applications:

- 1. used in automobiles, military applications.
- 2. Power backup and portable instruments.
- 3. In large scale power production.

Answer 4a.

(i) The type of corrosion which takes place when steel screw is in contact with Cu sheet is <u>Differential metal</u> <u>corrosion (Galvanic corrosion)</u>

- Differential metal corrosion arises when two dissimilar metals are in contact with each other. Under this condition a potential difference is set up resulting in a galvanic current.
- A metal placed high in the electrochemical series is said to be anodic to the one placed below it.
- In this case steel screw (Fe) acts as anode and Cu acts as cathode.
- A galvanic cell forms in this cell, and electrons flow from steel screw (Fe) to Cu sheet, indicating that Fe is the anode and Cu is the cathode. The reaction that take place as follows-

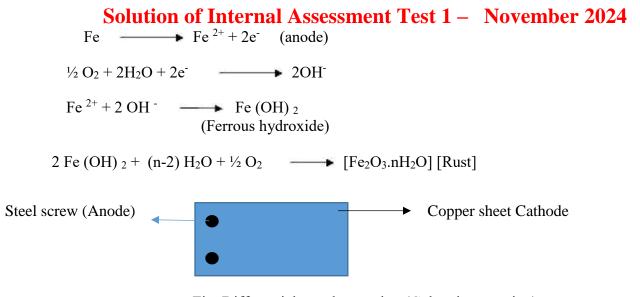
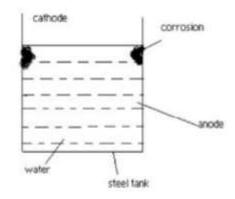


Fig. Differential metal corrosion (Galvanic corrosion)

(ii) The type of corrosion occurring is *Water line corrosion:*

Water line corrosion takes place due to the formation of differential oxygen concentration cells. The part of the metal below water is exposed to lower oxygen concentaration and acts as anode, and undergoes corrosion. The part above water is exposed to higher oxygen concentration and act as cathode.

At anode : $Fe \rightarrow Fe^{2+} + 2e^{-}$ At cathode : $\frac{1}{2}O_2 + H_2O + 2e^{-} \rightarrow 2OH^{-}$ **Rust formation:** $Fe^{2+} + 2OH^{-} \rightarrow Fe(OH)_2$ (Ferrous hydroxide) Further oxidation leads to rust formation. $2Fe(OH)_2 + \frac{1}{2}O_2 + H_2O \rightarrow [Fe_2O_3.3H_2O] \dots [Rust]$

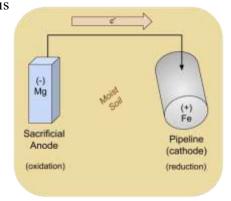


<u>Answer: 4b. CATHODIC PROTECTION:</u> Cathodic protection is a method of protecting a metal or alloy from corrosion by converting it completely into cathodic and no part of it is allowed to act as anode.

<u>Sacrificial anodic method:</u> 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. Eg: A Mg/ Zn block connected to buried oil storage tank, Mg/Zn base areas fixed to the side of ocean going ships, Mg/ Zn blocks area connected to the buried pipe lines.

Fig: Cathodic Protection by sacrificial anode

Advantage: (i)The method is simple.



(ii) low installation cost.

(iii) minimum maintenance cost.

(iv) Doesn't require power supply.

Disadvantages: Involves recurring expenditure for Replacement of consumed anodes.

Answer 5a Methods of disposal of E-waste:

To avoid the toxic effects of e-waste, it is crucial to dispose them in proper manner, so that items can be recycled, refurbished, resold, or reused.

Following methods are used to dispose e-waste:

Landfills: This is the most commonly used method of disposing e-waste. In this method, large trenches are made in the soil to bury e-waste. But this is not a good method to dispose e-waste because e-waste contains toxic substances like lead, mercury, etc., that leak into the earth and harm the underground water and soil. Incineration: It is also the most commonly used method to dispose of e-waste. In this method, the e-waste is burned at high temperatures in specially designed incinerators. Due to which the volume of e-waste is reduced and the energy produced by this method is also utilized separately. But this is also not a good method because when the e-waste burns, it releases harmful gases which harm our environment.

Acid Bath: In this method, the e-waste is soaked in powerful sulphuric, hydrochloric, nitric acid solutions that remove the metal from the e-waste. The recovered metal is further reused to create other products. This method also has drawbacks, like the acid solutions sometimes dumped into the water resources which is harmful for living things.

Recycling: This is the most efficient method and also environmentally friendly. Recycling involves dismantling, processing and end processing. In this method, separation is done to recover used circuit boards, ICs, motherboard, etc from the e-waste and recycle them. Precious metals like copper, lead, etc., are separated from the e-waste using a PCB recycling machine without harming the environment.

Re-use: It includes direct second hand use or use after slight modifications to the original functioning equipment like Inkjet cartridge is used after refilling. Old working computers can be donated to schools or organization working in the field of education. Computers beyond repairs can be returned back to the manufacturers. This can considerably reduce the volume of E-Waste generation converted into less hazardous compounds.

<u>Answer 5b</u> Corrosion Penetration Rate (CPR) is defined as: CPR is the thickness loss of material/metal per unit time when it is exposed to a corrosive environment The CPR is calculated as follows: $CPR = (k \times W) / (D \times A \times T)$

where k = a constant depends on unit used. when K = 534 the mpy will be used. when K = 87.6, mm/yr will be used. W = total weight lost (m_o – m) m = weight after corroded m_o = weight before corroded T = time taken for the loss of metal A = the surface area of the exposed metal D = the metal density in g/cm³ Corrosion penetrating rate in mpy CPR = KW/DAT Weight loss, W= 585g = 585 × 10³ mg Density, D = 7.9g/cm³; Time, T = 3×24×365 hours = 26280 hours Area A = 540 cm² = (540/6.45) in² = 83.72 in² CPR = $\frac{534 \times 585 \times 10^3}{7.9 \times 83.72 \times 26280}$ CPR = 14.90 mpy

Corrosion penetrating rate mm/y CPR = KW/DAT Weight loss, W= 585g = 585 × 10³ mg Density, D = 7.9g/cm3; Time, T = 3×24×365 hours = 26280 hours Area A = 540 cm² CPR = $\frac{87.6 \times 585 \times 10^3}{7.9 \times 540 \times 26280}$

CPR = 0.457 mm/y

<u>Answer 6a</u> Definition: E-waste or electronic waste means discarded electrical or electronic devices or components.

Effects of e-waste on environment and human health: E-waste is a serious issue for our environment because it releases harmful toxic chemicals from the metals due to chemical reactions and these toxic chemicals harm our environment, therefore they must be handled with care when no longer wanted or needed.

Electronic scrap components, such as CPUs, contain potentially harmful materials such as lead, cadmium, beryllium, or brominated flame retardants. Improper disposal of e-waste is highly dangerous to the global environment involving significant risk to the health of workers and their communities

<u>Effects on Air quality:</u> Contamination in the air occurs when e-waste is informally disposed of by dismantling, shredding, or melting the materials, releasing dust particles or toxins, such as dioxins, into the environment that cause air pollution and damage respiratory health. Chronic diseases and cancers are at a higher risk to occur when burning e-waste because it also releases fine particles, which can travel thousands of miles, creating numerous negative health risks to humans and animals. The air pollution caused by e-waste impacts some animal species more than others, which may be endangering these species and the biodiversity of certain regions that are chronically polluted. Over time, air pollution can hurt water quality, soil, and plant species, creating irreversible damage to ecosystems.

<u>Effects on Soil:</u> When the improper disposal of e-waste in regular landfills or in places where it is dumped illegally, both heavy metals and flame retardants can seep directly from the e-waste into the soil, causing contamination of underlying groundwater or contamination of crops that may be planted nearby or in the area in the future. When the soil is contaminated by heavy metals, the crops become vulnerable to absorbing these toxins, which can cause many illnesses and doesn't allow the farmland to be as productive as possible.

<u>Effects on Water:</u> After soil contamination, heavy metals from e-waste, such as mercury, lithium, lead, and barium, then leak through the earth even further to reach groundwater. When these heavy metals reach groundwater, they eventually make their way into ponds, streams, rivers, and lakes. Through these pathways, acidification and toxicity are created in the water, which is unsafe for animals, plants, and communities even if they are miles away from a recycling site. Clean drinking water becomes problematic to find.

<u>Effects on Humans</u>: Electronic waste contains toxic components that are dangerous to human health, such as mercury, lead, cadmium, polybrominated flame retardants, barium, and lithium. The negative health effects of these toxins on humans include brain, heart, liver, kidney, and skeletal system damage. It can also considerably affect the nervous and reproductive systems of the human body, leading to disease and birth defects.

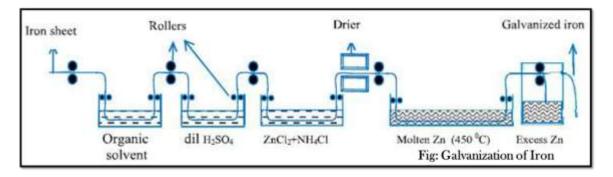
Answer 6b The process of coating Zn on iron is called galvanizing/galvanization.

Process of galvanization:

- I. Iron sheet is cleaned with organic solvent to remove grease/oil.
- II. It is treated with dil. H₂SO₄ to remove rust.
- III. It is treated with ZnCl₂ and NH₄Cl.
- IV. Finally it is dipped in zinc at ~450 °C.

V. Excess zinc is removed from the surface by rolling.

Application: Galvanization of fencing wire, bolts, nuts and pipes and construction materials.



Answer 7a:) Extraction of copper and gold from e-waste: The electronic waste also contains fair percentage of precious metals like Cu, Ag, Au, Pd, Rh etc. These metals can be recovered from E-waste at cheaper cost than from the usual ores. The recycling of metals such as gold and copper from discarded e-waste is an important aspect to develop the environmental friendly manufacturing processes. Techniques such as Pyrometallurgy, Hydrometallurgy and Biohydrometallurgy are used to recover precious metals like copper, silver and gold.

The extraction of copper and gold from e-waste using hydrometallurgical route comprises the liberation of the metallic fractions from downsized PCBs, a two-stage acid leaching process to provide a bulk separation of copper and gold from the other metals present, and subsequent purification of the copper and gold-containing solutions by solvent extraction using highly selective phenolic oxime and amide extractants, respectively.

Following steps are involved in the process.

1. Pre-processing: After collection of e-waste, it is segregated, delaminated, cleaned with water and acetone and treated with N,N-dimethylacetamind (DMA) to remove the orgamic components (epoxy resins) present in the e-waste. This pretreated e-waste is shredded into small pieces and powdered, further it is subjected to recovery of precious metals. The metals were dissolved in acid and non-metallic component such as plastic and ceramic is separated by filtration.

2. Leaching: The liberated metallic fraction collected from the pre-processing step was leached in two stages to provide a bulk separation of copper and gold from the other metals present.

(i) First stage leaching process involves the selective dissolution of copper over gold. The samples were dissolved in dilute nitric acid, which almost exclusively leached the copper.

(ii) The filtered residue was then subjected to a second stage leaching process using sulfuric acid and halide salts (NaCl, NaBr) to selectively dissolve, silver and tin.

3. Solvent extraction:

(i) Recovery of Cu: Distilled water and ammonia solution was added to the leach solutions obtained after stageone leaching process. To selectively recover the copper, the phenolic oxime dissolved in kerosene was used as the extractant. The Cu metal loaded organic phase was separated from the acidic aqueous leach liquor and washed with either sulfuric acid or nitric acid.

(ii) Recovery of Au: In the second-stage solvent extraction, an organic amide diluted in toluene was used as the extractant. The gold-loaded organic phase was then separated from the aqueous phase and stripped of the metal using either water or sodium hydroxide.

Answer 7b: Reference Electrodes

Reference electrodes are the electrodes whose potentials are known and they are used for the determination of potentials of other electrodes.

Calomel electrode: It is a metal – metal salt ion electrodes and also a secondary reference electrode.

Construction: It consists of mercury, mercurous chloride and a solution of KCl. It is made up of glass tube, Hg is placed at the bottom of the glass tube. It is covered with a paste of calomel (HgCl₂) and KCl solution. A solution of KCl is introduced above the paste through the side tube. Electrical contact is made through Pt wire (dipped in Hg). This glass tube is taken into another glass tube, which has a side tube and a porous plug at the bottom. This porous plug act as salt bridge. The conc of KCl solution used is either decinormal, normal or saturated. Correspondingly, the electrode is known as decinormal, normal or saturated calomel electrode. This constitutes one half cell. Calomel electrode can act as either anode or cathode. It is connected to the other half cell through salt bridge.

Half cell representation

The calomel electrode is represented as,

 Hg/Hg_2Cl_2 (s)/ Cl^- (anode) Or Cl^{-}/Hg_2Cl_2 (s)/ Hg (Cathode)

Working: Depending on the potential of electrode with which the calomel electrode is connected, calomel electrode acts as anode or cathode. (a). When it acts as anode, electrode reaction is

> 2Hg \longrightarrow Hg₂²⁺ + 2 e⁻ $Hg_2^{2+} + 2Cl^- \longrightarrow Hg_2Cl_2$ $2Hg + 2Cl^{-} \longrightarrow Hg_2Cl_2 + 2e^{-}$

(b) When it acts as cathode, electrode reaction is

$$Hg_{2}^{2+} + 2 e^{-} \longrightarrow 2Hg$$

$$Hg_{2}Cl_{2} \longrightarrow Hg_{2}^{2+} + 2Cl^{-}$$

$$Hg_{2}Cl_{2} + 2e^{-} \longrightarrow 2Hg + 2Cl^{-}$$

Thus, Net reversible electrode reaction is

 $Hg_2Cl_2 + 2e^ 2Hg + 2Cl^{-}$

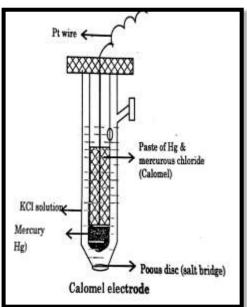
Electrode potential is calculated using Nernst equation,

$$\frac{E_{cal} = E^{\circ} - 2.303RT}{2F} \log [Cl^{-}]^{2}$$

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.



<u>Answer 8a: Ion Selective electrodes</u> These electrodes selectively respond to a specific ion in a mixture and potential developed is a function of concentration of that ion in the solution. These electrodes consist of a membrane which is capable of exchanging specific ions with solution with which it is in contact. These are also called as membrane electrodes. Eg. Glass electrode.

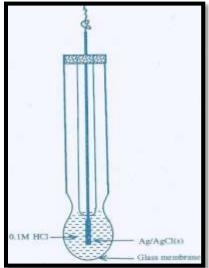
Glass Electrode

Construction: The glass electrode consist of glass tube, the bottom of the glass tube is glass bulb made up of very thin glass membrane. The thickness of glass membrane varies from 0.03 mm to 0.1 mm. The membrane is made up of special glass of low melting point and high electrical conductivity. Its composition is $SiO_2 - 72\%$, Na_2O - 22%, CaO- 6%. It can sense H⁺ ions up to a pH of about 9. Glass bulb contains 0.1 N HCl (Assume concentration is C₂). An Ag/AgCl electrode (internal reference electrode) is placed in the solution and connected by a pt wire for electrical contact.

The electrode is represented as, Ag/AgCl (s)/ 0.1N HCl/ Glass

Working of glass electrode: When the glass electrode is dipped into any solution containing H^+ ions, the Na+ ions of the glass membrane are exchanged for H+ ions of the test solution.





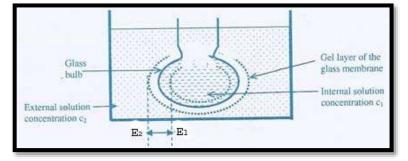


Fig : Boundary Potential (E_b = **E**₂-**E**₁)

If a thin walled bulb containing an acid is immersed in another solution containing H^+ ions (fig), a potential is developed across the glass membrane. This is called the boundary potential E_b . It is a potential developed across the glass membrane when concentration of the solution inside and outside the glass membrane are different. The E_b is due to the difference in potential (E_2 - E_1) developed across the gel layer of the glass membrane between the two liquid.

Mathematically it is represented as,

 $\mathbf{E}_{\mathbf{b}} = \mathbf{E}_2 \mathbf{-} \mathbf{E}_1$

Where, E_2 = Potential due to H⁺ present in outside solution (Unknown solution)

 E_1 = Potential due to H⁺ present in inside solution (known solution)

According to Nernst equation

$$E_{b} = \underbrace{2.303RT}_{nF} \quad \log C_{2} \\ E_{b} = \underbrace{0.0591}_{n} \log C_{2} - \underbrace{0.0591}_{n} \log C_{1}....(1)$$

Where, C_2 is the concentration of H⁺ ions of the solution into which glass membrane is dipped. The concentration of H⁺ ion inside the bulb (C₁) is constant i.e. $C_1 = 0.1$ M. Thus, $E_b = 0.0591 \log C_2 + K$ or $R = K + 0.0591 \log C_2$

Glass electrode selects only H^+ ions ignoring other ions. Hence $C_2 = H^+$ $E_b = K + 0.0591 \log [H^+]$ Where, $\log [H^+] = -pH$

Thus, $E_b = K - 0.0591 pH$ -----(2)

The combined glass electrode is dipped into acidic solution, then the potential of the glass electrode is given by....

$$\begin{split} E_G &= E_b + E_{Ag-AgCl} \qquad \dots \qquad (3) \\ \text{From equation 1, theoretically if } C_1 &= C_2, E_b \text{ should be 0, however it has been observed practically that even} \\ \text{when } C_1 &= C_2, \text{ a small potential is developed which is called as asymmetric potential (} E_{asym}\text{)}. \text{ Hence equation 3} \\ \text{can be rewritten as} \\ E_G &= E_b + E_{Ag-AgCl} + E_{asym} \dots \qquad (4) \\ \text{Substituting the value of } E_b \text{ from equation (2) in equation (4)} \\ E_G &= K - 0.0591 pH + E_{Ag/AgCl} + E_{assym} \\ \end{split}$$

 $E_G = E^o_G - 0.0591 pH$ (5)

Where $(E^{o}_{G} = K + E_{Ag/AgCl} + E_{assy})$

The above expression (eq 5) indicate that the potential of glass electrode, E_G varies with the pH of the acidic solution.

Answer 8(b) Concentration Cells:

Cell representation: $Ag(s) / Ag^+(C_1 = 0.005 \text{ M}) // Ag^+(C_2 = X \text{ M}) / Ag(s)$

The Electrode reactions are as follows:

At anode Ag \rightarrow Ag⁺ (C₁=0.005 M) + e⁻

At cathode $Ag^+(C_2 = XM) + e^- \rightarrow Ag$

EMF of cell is given by

$$E_{cell} = \frac{2.303RT}{nF} \log \frac{C_2}{C_1}$$

 $\begin{array}{c} 0.195 = 2.\underline{303 \times 8.314 \times 298} & \log \underline{X} \\ 1 \times 96500 & 0.005 \end{array}$

X = 9.95 M