MODULE -1

1 What are reference electrodes? Describe the construction and working of Calomel electrode.

Reference electrodes are those whose potentials are known.

Construction and working of CALOMEL ELECTRODE

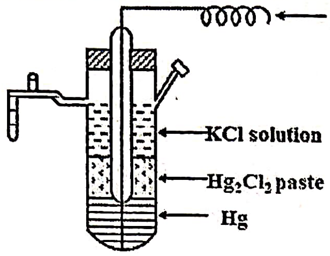


Fig: 3.13 CalomelElectrode

The calomel electrode consists of a glass vessel containing a layer of Hg over which is placed a paste of an Hg, Hg_2Cl_2 and KCl. Above this there is a solution of KCl saturated with the Mercurous salt. A platinum wire is fused in the glass tube for electrical connection Fig: 3.13. A salt bridge is used to couple with other half-cell.

The half-cell is represented as Net reversible electrode: $Hg / Hg_2Cl_{2\,(sat)} / KCl_{\,(sat)}$

Net reversible electrode reaction is

$$Hg_2Cl_2 + 2e^- \rightleftharpoons 2Hg + 2Cl^-$$

Electrode potential is calculated using Nernst equation,

Electrode potential is calculated using Nernst equation,

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

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

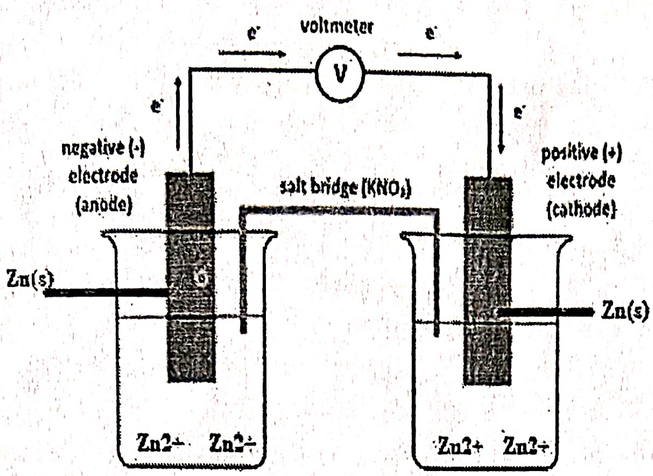
$$= E^\circ - 0.0591 \log [Cl^-] \text{ at } 298\text{ K}$$

2 Define concentration cell .Explain the construction and working of concentration cell.

Concentration cell consists of two half cells having two identical electrodes and identical electrolytes but with different concentration. EMF of this cell depends upon the difference of concentration.

Construction:

A typical example of Zinc concentration cell is shown above. It consists of two zinc electrodes are immersed in two different concentrations of ZnSO4 solutions. These two electrodes are externally connected by metallic wire and internally by a salt bridge as shown in Fig;. The cell can be represented as,



The cell can be represented as,

$$Zn_{(s)} | Zn^{2+} (C_1) \| Zn^{2+} (C_2) | Zn_{(s)}$$

By convention left hand electrode is the anode and right hand electrode is cathode.

At anode : $Zn_{(s)} \rightarrow Zn^{2+} + 2e^-$

At cathode: $Zn^{2+}(C_2) + 2e^- \rightarrow Zn_{(s)}$

Net cell reaction: $Zn^{2+}(C_2) \rightleftharpoons Zn^{2+}(C_1)$

$$E_{cell} = E_{cathode} - E_{anode} \quad \text{... (1)}$$

$$E_{cell} = \frac{0.0591}{n}\log[C_2] - \frac{0.0591}{n}\log[C_1] \quad \text{... (2)}$$

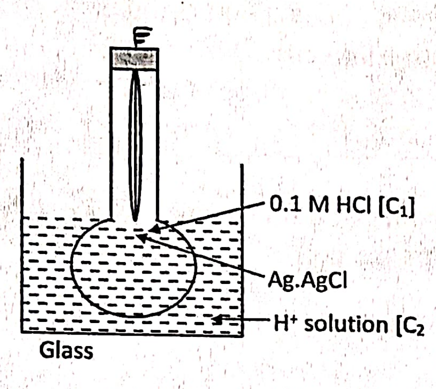
$$E_{cell} = \frac{0.0591}{n}\log\frac{[C_2]}{[C_1]} \text{ at 298 K} \quad \text{... (3)}$$

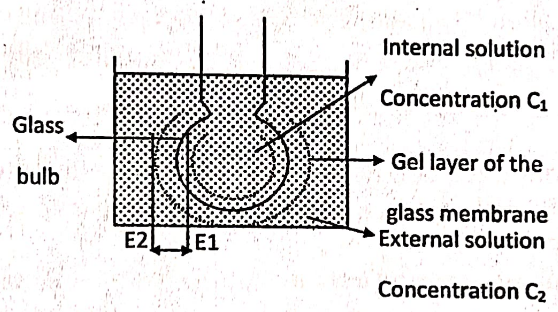
3. **What is ion selective electrode? Explain the construction and working principle of glass electrode. Mention the advantages and disadvantages of glass electrode.**

Ion selective electrode is one which selectively responds to a specific ion in a mixture and the potential developed at the electrode is a function of the concentration of that ion in the solution.

Construction:

A glass electrode is an ion selective electrode where potential depends upon the pH of the medium. The glass electrode consists of a glass bulb made up of special type of glass which consisting of 72% of SiO_2, 22% Na_2O and 6% CaO, has low melting point and relatively high electrical conductivity. (Fig:1.3) The glass bulb is filled with a solution of constant pH (0.1 M HCl) and insert with a Ag-AgCl electrode, which is the Internal reference electrode and also serves for the external electrical contact. The electrode dipped in a solution containing H^+ ions (Fig:)





The electrode representation is, **Ag-AgCl | 0.1 M HCl | Glass.**

Working Principle:

If a thin walled glass bulb containing an acid is immersed in another solution containing H^+ ions, a potential is developed across the glass membrane. This is due the ion exchange reaction taking place at the gel layers of glass membrane. This is called boundary potential E_b.

$$Na^+Gl^- + H^+ \rightleftharpoons H^+Gl^- + Na^+$$

The boundary potential is due to the difference in potential (E_1-E_2) developed across the gel layer of the membrane between the two liquids.

The electrode representation is, **Ag-AgCl | 0.1 M HCl | Glass**

Consider, $C_1 > C_2$

The boundary potential is given by Nernst equation at membrane $E_b = E_1 - E_2$

$$E_b = \frac{2.303RT}{nF}\log C_1 - \frac{2.303RT}{nF}\log C_2$$

Therefore $E_b = 0.0591 \log C_1 - 0.0591 \log C_2$

$E_b = K + 0.0591 \log C1$ where $K = -0.0591 \log C2$

OR

$E_b = K - 0.0591pH$

Since $pH = -\log [H^+]$

The glass electrode E_G has three components

Therefore $E_G = E_b + E_{Ag|AgCl} + E_{asy}$

$E_G = K - 0.0591\,pH + E_{Ag|AgCl} + E_{asy}$

$\boxed{E_G = E_G^0 - 0.0591pH}$

where, $E_G^0 = K + E_{Ag|AgCl} + E_{asy}$

Advantages

1. This electrode can be used to determine pH in the range 0 – 9, with special type of glass even up to 12 can be calculated.
2. It can be used even in the case of strong oxidizing agents.

Disadvantages

1. The glass membrane though it is very thin, it offers high resistance. Therefore ordinary potentiometers cannot be used; hence it is necessary to use electronic potentiometers.
2. This electrode cannot be used to determine the pH above 12

4 A concentration cell was constructed by immersing two silver electrodes in 0.05 M and 1 M $AgNO_3$ solution. Write the cell representation, cell reactions and calculate the EMF of the cell.

Solution

Cell representation: Ag(s) | $AgNO_3$ (0.05 M) || $AgNO_3$ (1 M) | Ag(s)

At anode : Ag (0.05 M) $\rightarrow$ Ag^+ (0.05 M) + e^-

At cathode: Ag^+ (1 M) + e^- $\rightarrow$ Ag (1 M)

Net cell reaction: Ag (0.05 M) + Ag^+ $\rightarrow$ Ag^+ (0.05 M) + Ag

$$E_{cell} = \frac{0.0591}{n}\log\left(\frac{C_2}{C_1}\right)$$

$$E_{cell} = \frac{0.0591}{n}\log\left(\frac{1}{0.05}\right)$$

$E_{cell} = 0.0768$ V

5 The emf of a cell Ag/$AgNO_3$ (0.02M)//$AgNO_3$(X)/Ag found to be 0.084V at 298 K. Write the cell reactions and calculate the value of X.

Solution:

$$E_{cell} = \frac{0.0591}{n}\log\left(\frac{C_2}{C_1}\right)$$

$$E_{cell} = \frac{0.0591}{1}\log\left(\frac{X}{0.02}\right)$$

$$\text{Log}\left[\frac{X}{0.02}\right] = \frac{E_{Cell}\ X\ n}{0.0591}$$

$$\frac{X}{0.02} = Antilog\ \frac{E_{Cell}\ X\ n}{0.0591}$$

$$\frac{X}{0.02} = Antilog\ \frac{0.084\ X\ 1}{0.0591}$$

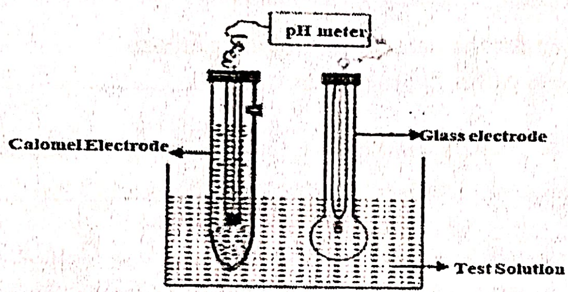
$$\frac{X}{0.02} = Antilog\ (1.421)$$

$$\frac{X}{0.02} = 26.36$$

$$X = 0.5272M$$

6.	Explain how the pH of the given solution is determined using glass electrode.

When a thin glass membrane is placed between two solutions of different pH values, a potential difference arises across the membrane. The potential difference varies as the pH of these solutions varies. In practice, pH of one of these solutions is kept constant and therefore the electrode potential depends on pH of the other solution i.e .experimental solution.



3.15 Determination of pH

$Hg_{(l)}|\ Hg_2Cl_2|Cl^-||$Solution of unknown pH|glass|0.1M HCl|AgCl $|Ag_{(s)}$

The emf of the above cell, E_{cell} is measured using an electronic voltmeter with a pH meter.

The emf of the cell is given by

$$E_{cell} = E_{cathode} - E_{anode} \quad ....1$$

$$E_{cell} = E_G - E_{SCE}$$

$$E_G = E^0_G - 0.0591pH$$

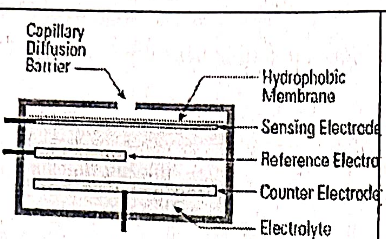
$$E_{cell} = E^0_G - 0.0591\ pH - E_{SCE}$$

$$pH = \boxed{\frac{E^0_G - E_{SCE} - E_{cell}}{0.0591}}$$

7 Discuss the construction and working of Electrochemical sensors. Mention any four applications.

Sensors which convert the effect of electrochemical reaction between analyte and electrode surface into a useful signal are known as electrochemical sensors.

Construction of electrochemical sensor: It consists of two or three electrodes.



Electrochemical sensor consists of a sensing electrode (or working electrode) and a counter electrode and is separated by a thin layer of electrolyte and reference electrode.

Working:
Electrochemical sensor consists of a transducer element covered by a recognition element.

The recognition element interacts with target analyte and signal is generated. Electrochemical transducers transform the chemical changes into electrical signals. The electric signals are related to the concentration of analyte.

Applications

1. Electrochemical sensors used for the detection of blood glucose
2. Electrochemical sensors are used for pH measurements
3. Used to detect pesticides
4. Used in the detection of hydrocarbon pollutants

8 Analysis of Dissolved oxygen in Industrially used boilers is a compulsory criterion, which sensor is preferred to analyze dissolved oxygen and discuss the construction and working of this sensor.

Amount of Oxygen present in water is called dissolved oxygen.
DO sensor is used to measure DO in

1. Lake ware
2. Raw water
3. Boiler feed water etc

Construction and working of DO sensor

Components:
Cathode : Working electrode- Ag
Anode : Zn, Pb or any other active metal
Electrolyte: KOH, NaOH or any other inert electrolyte
Membrane: Teflon
Working:
The difference in potential between the anode and the cathode should be at least 0.5V. DO sensor is immersed in water sample. Oxygen

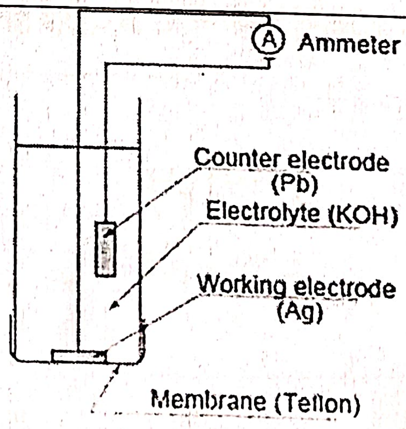
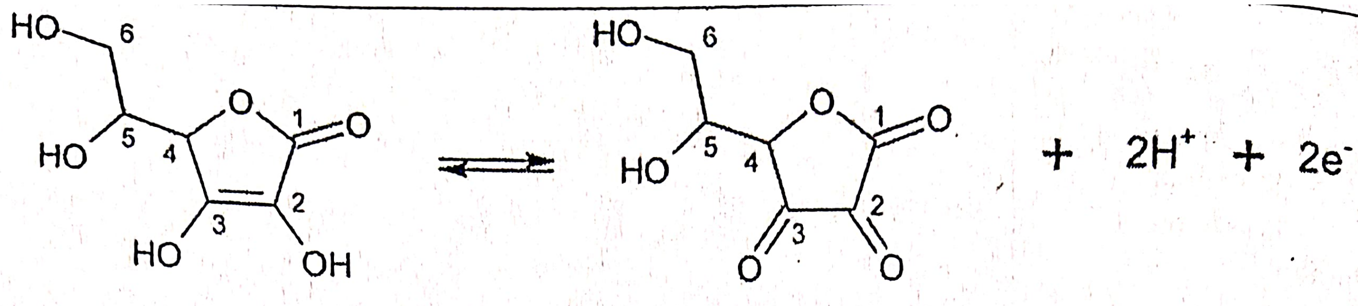


Fig:1.9 Galvanic Sensor for DO measurement

	molecule diffuses across the oxygen-permeable membrane (Teflon) and the rate of diffusion is proportional to the pressure of oxygen in the water. Molecular Oxygen reduces to OH^- at cathode.	
	This reaction produces an electrical current that is directly related to the oxygen concentration. This current is carried by the ions in the electrolyte and runs from the cathode to the anode.	
	Reactions: **Anode(Pb):** **Oxidation** $2Pb \longrightarrow 2Pb^{2+} + 4e^-$ **Cathode(Ag):** **Reduction** $O_2 + 4e^- + 2H_2O \longrightarrow 4OH^-$ **Overall:** $2Pb + O_2 + 2H_2O \longrightarrow 2Pb(OH)_2$	
9.	Ascorbic acid is an essential amino acid and deficiency or excess quantity is not good, elaborately discuss the construction of working of a sensor used for the ascorbic acid detection.	
	It is comprising three disposable electrodes: one working electrode, one auxiliary or counter electrode, and one reference electrode. Each one includes a contact or terminal, a section and an active area. All electrodes have been manufactured by silkscreen printing with conductive material ink on a **plastic polyester (PET) sheet.** The active surfaces of the **counter electrode** and **working electrode** have been printed with a **conductive ink of C** (MWCNT) and modified with **gold nanoparticles.** Active surface of the **reference electrode** has been printed with an **Ag/AgCl ink.** The electrochemical sensor can catalyze the **two-electron electro catalytic oxidation** and **hydrogen dissociation of AA** to L-dehydroascorbic acid in the presence of oxygen in solution. The amount of volage or current produced is direct measure of concentration of ascorbic acid. Electrooxidation reactions:	



Ascorbic acid

Dehydroascorbic acid

Fig: 1.18 Oxidation of Ascorbic acid

10 **Define disposable sensor. Disposable sensors are advantageous over reusable sensors. Justify your answ**

Disposable sensors are low-cost and easy-to-use sensing devices designed for short-term or rapid single point measurements.

Advantages of disposable sensors:

1. They transduce physical, chemical, or biological changes in their environment to an analytical signal.
2. Disposable sensors are biodegradable and sustainable
3. They have a short duration of analysis and fast response times.
4. It provide digitized chemical and biological information.
5. Prevents the contamination of samples.

MODULE 2

1 **Identify the p-type and n-type organic semiconductor material used in making organic memory devices and discuss the switching behavior of these materials in transistors.**

Pentacene is a linear aromatic hydrocarbon and possess holes as major charge carrier is called p-type semiconductor.

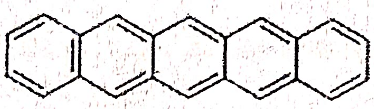
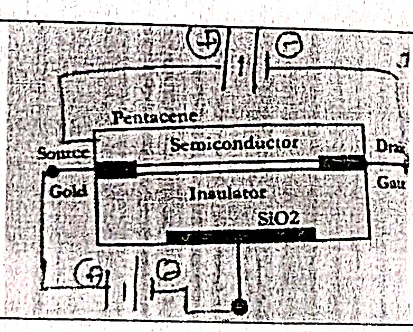
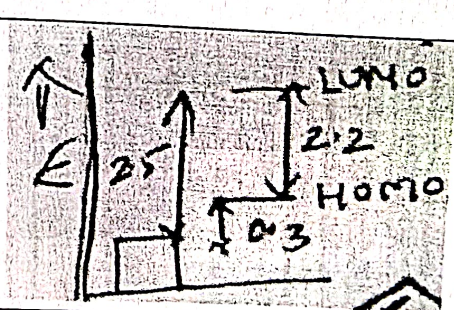


Fig: 2.6 Pentacene





NOTE: refer class notes for simplified diagram

Pentacene is used as a switching layer in the fabrication of Optical thin film transistors.

Source and drain are made using gold, gate is made of SiO_2 with Al metal contact. Pentacene is placed above insulator and sandwiched between source and drain.
Working: Switching property of Pentacene is controlled by changing the gate-source potential. Application of negative potential between gate and source induces positive holes in the source. Positive charges are accumulated at the interface of SiO_2 and Pentacene layer. Now, application of secondary voltage between source and drain drives positive holes to drain and create a conducting channel because the energy gap between Fermi energy level of gold and HOMO of pentacene is 0.3eV and memory is stored as one bit. Just by reversing gate source voltage conduction is inhibited, this is read as zero bit.

Perfluoropentacene is obtained by fluorination of Pentacene and possess negatively charged electrons as major charge carriers and therefore called as n-type semiconductor.

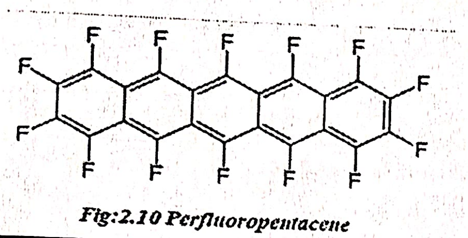
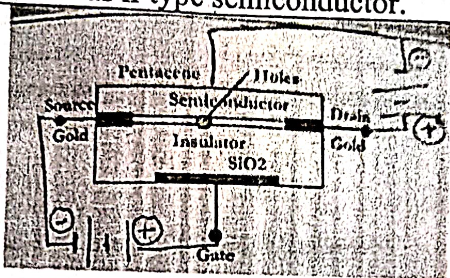
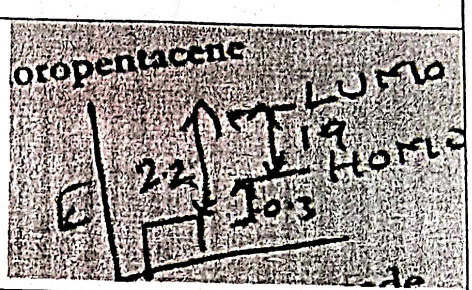


Fig:2.10 Perfluoropentacene



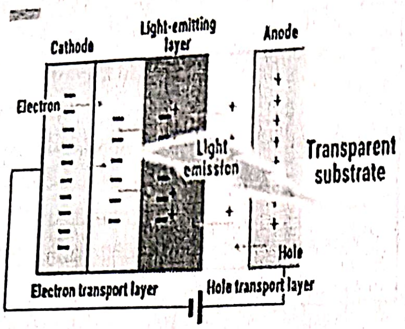


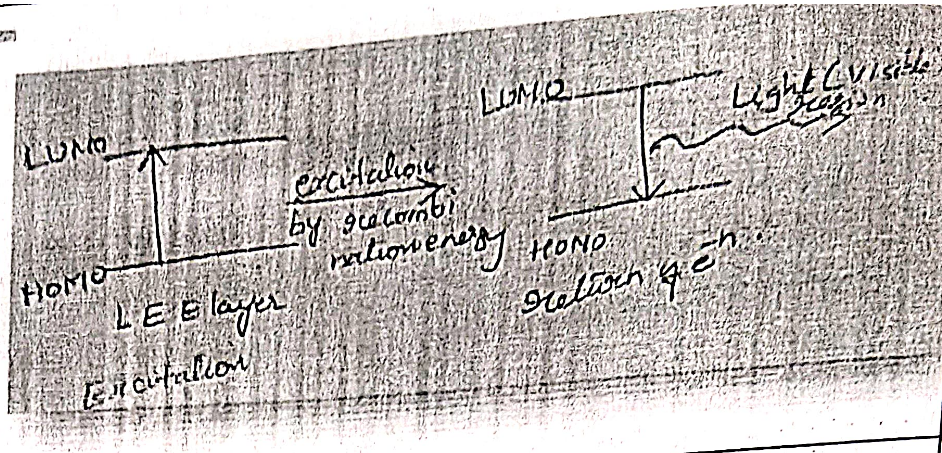
Switching behaviour of perfluoropentace is controlled by changing the gate source potential. Perfluoropentace is used as a switching layer in the fabrication of OTFT. Application of positive potential between the gate and source injects negative electrons in the source and accumulated at the interface of perfluoropentacene layer and silicon. Application of secondary voltage drives the electrons to drain and create a conducting channel because the energy gap between fermi level and LUMO of semiconductor is 1.9eV and memory is stored as one bit. Reversing of gate source potential conduction is inhibited, this is read as zero bit.

2. Analyse the working principle of photoactive and electroactive materials used in the fabrication of optoelectronic devices.

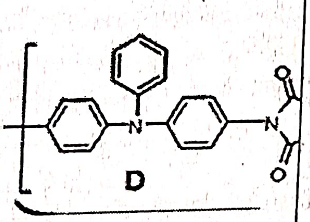
Organic semiconductors used in electronic and optoelectronic devices , which convert light energy into electrical energy and vice-versa are called as electro active and Photoactive materials.

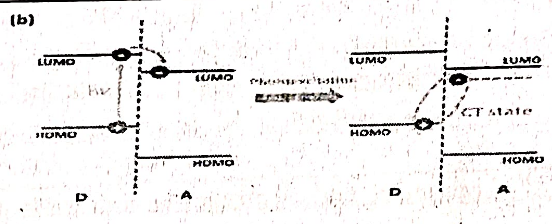
Working Principle:
LEL layer of made using Photoactive and electroactive material. Application of external voltage permit recombination of electron-hole pair in the LEL and Release additional energy, this energy is being used by LEL for transion of electron from HOMO tO LUMO. Light energy is released in the visible regeion when the excited electron return to ground state. This light is extracted by a transparent substrate placed adjacent to either of the electrode.





3.	Discuss the importance of structure property relation responsible storing data using Polymer material.
	The relationship between the chemical structure and memory properties is a subject of utmost importance in the development of polymer memory materials. Example: Polyimide used for making DRAM The device uses the transfer of charge carriers with in the material to store and retrieve data. It is based on charge transfer complexes.





Polyimide consists of
Donor: Triphenyl Amine group (TPA)
Acceptor: Phthalimide group
Hexafluoroisopropylidene (6F): Increases the solubility of PI
The donors and acceptors of PIs contribute to the electronic transition based on an induced charge transfer (CT) effect under an applied electric field.When an electric field more than threshold energy is applied, the electrons of the HOMO (TPA unit) is excited to LUMO.After excitation the electron transferred to LUMO(acceptor), generating a CT state.This permits the generation of holes in the HOMO, which produces the open channel for the charge carriers to migrate through.

4	Write the properties and applications of Silicon Nano Crystals that are suitable for making optoelectronic devices.
	Any substance in which at least one dimension is less than 100nm is called nanomaterials. The properties of nanomaterials are different from bulk materials due to: 1. Quantum Confinement effect 2. Increased surface area to volume ratio

Properties of Silicon Nano Crystal:

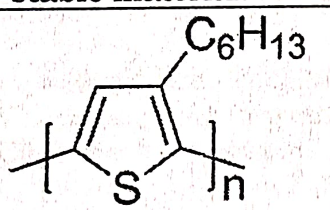
- Si NCs are actually crystalline Si nanoparticles or Si quantum dots
- Si quantum dots are very small in size ie smaller than ~10 nm.
- After the manipulation of the size, surface and doping of Si NCs shows higher light emission property.
- Si NCs exhibit quantum yield of more than 60%.

Applications:

- Si NCs are used in neuromorphic computing and down-shifting in photovoltaics
- Si NCs are used in the construction of novel solar cells, photodetectors and optoelectronic synaptic devices.
- optoelectronic synaptic devices.
- Medical application: Imaging devices

5 Write the properties and applications of Polythiophenes (P3HT) that are suitable for making optoelectronic devices.

Polythiophenes are an important class of conjugated polymers, environmentally and thermally stable material. It is used as a light absorbing material in optoelectronic devices.



Properties:

1. P3HT is a semiconducting polymer with high stability and exhibits conductivity due to holes therefore considered as p-type semiconductor.
2. Poly-3-hexylthiophene (P3HT) have great capability as light-absorbing materials in organic electronic devices.
3. P3HT has a crystalline structure and good charge-transport properties required for Optoelectronics.
4. P3HT has a direct-allowed optical transition with a fundamental energy gap of 2.14 eV.
5. Fundamental bandgap of P3HT is 490nm visible region, corresponding to $\pi \rightarrow \pi^*$ transition, giving electron-hole pair.
6. P3HT indicate that an increase in the conductivity is associated with an increase in the degree of Crystallinity.

Applications:

- P3HT-ITO forms a p-n junction permit the charge carriers to move in opposite direction and hence, used in Photovoltaic devices.
- It can be used as a positive electrode in Lithium batteries.
- Used in the construction of Organic Solar Cells.
- Manufacture of smart windows.

6. Write the properties and applications of **Poly[9-vinylcarbazole] (PVK)]** that are suitable for making optoelectronic devices.

Light emitting material - Poly[9-vinylcarbazole] (PVK)]

Poly (N-vinyl carbazole) (PVK) is one of the highly processable polymers as hole conducting material and therefore used as an efficient hole transport material to prepare highly efficient and stable planar heterojunction perovskite solar cells.

Structure of poly(9-vinylcarbazole) (PVK)

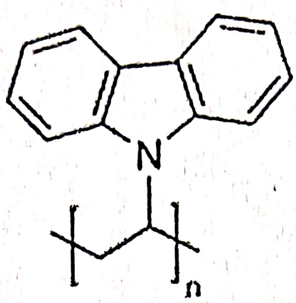


Fig: 2.15 Structure of Poly[9-vinylcarbazole] (PVK)]

Properties of PVK relevant for optoelectronics

- It is a semiconducting polymer and an electron acceptor converts ultra-violet (UV) light into electricity.
- PVK has a band gap of 3.4 eV, which corresponds to an optical absorption edge stating at 350 nm capable of absorbing Ultra-Violet light.
- The PVK film is hydrophobic, thermally stable with a relatively high glass transition temperature (T_g) of 200 °C
- The PVK solution also showed good wettability, and can easily form smooth and uniform thin films on glass/ITO substrates without receiving any UV/Ozone or thermal treatments

Applications

- PVK has been commonly used in OLEDs , light harvesting applications , photorefractive polymer composites and memory devices
- Used in the fabrication of light-emitting diodes and laser printers.
- Used in the fabrication of organic solar cells when combined with TIO on glass substrate.
- Used in the fabrication of solar cells when combined with Perovskite materials.
  - PVK-Perovskite junction is used in Light-Emitting Diodes with Enhanced Efficiency and Stability

7 Briefly discuss the classification of Liquid crystals and give one example each.

The liquid crystals are a unique state of matter between solid (crystalline) and liquid (isotropic) phases.

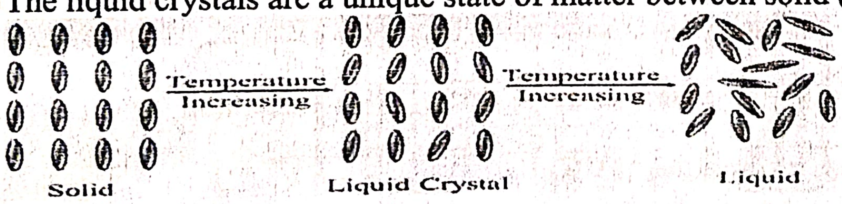


Fig: 2.14 Alignment of molecules in different phases

Classification of liquid crystals

A. Thermotropic liquid crystals
B. Lyotropic liquid crystals

Thermotropic liquid crystals have been classified into the following types:

1) Nematic liquid crystals
2) Smectic liquid crystals
3) Cholesteric liquid crystals
4) Discotic

Nematic (or thread-like liquid crystals)

- The molecules move either sideways or up and down. Each molecule can also twist or rotate around its axis giving rise to a twisted nematic.

The alignment of molecules is ***temperature sensitive*** – as the temperature is increased, the degree of orientation of the nematic crystals decreases and they change into isotropic liquids.

Examples: p-azoxyphenetole, anisaldazine.

Smectic (or soap-like liquid crystals)

The molecules in smectic crystals are oriented parallel to each other as in the nematic phase but in layers.

These layers can slide pass each other because the force between the layers is weak.

They are denoted by alphabet letter A, B, C, etc. Some common types of smectic liquid crystals are given below.

(a) Smectic A In smectic A, the molecules are aligned perpendicular to the layer planes.

(b) Smectic C The arrangement of molecules is similar to smectic A except that the molecules are slightly tilted.

They have high viscosity and are not suitable for devices

Cholesteric liquid crystals

This type of mesophase is formed by derivatives of cholesterol such as cholesteryl esters.

Like the nematic phase, the molecules in this type of crystal are also parallel to each other but arranged in layers.

The molecules in successive layers are slightly twisted or rotated with respect to the layers above and below so as to form a continuous helical or spiral pattern.

Cholesteryl benzoate, the first known liquid crystal, is of cholesteric type. Its transition temperature is 146 °C and melting point is 178.5 °C.

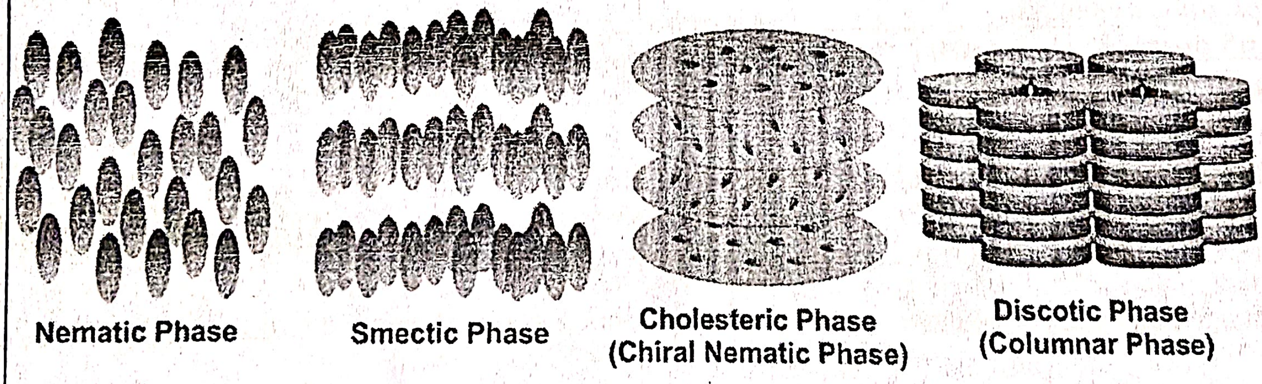
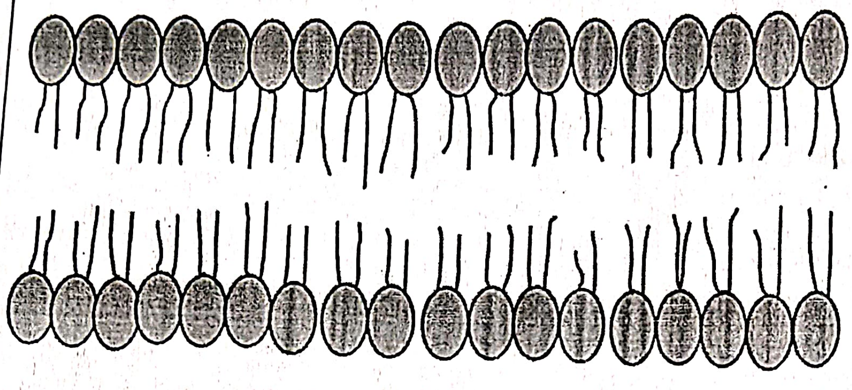


Fig:2.18 Structures of different types of liquid crystals

Lyotropic liquid crystals

The orientational behaviour of lyotropic crystals is a function of concentration and solvent. These molecules are amphiphilic – they have both hydrophilic and hydrophobic ends in their molecules. At low concentrations, these molecules are randomly oriented but as the concentration increases, the molecules start arranging themselves.



2.19 Arrangement of molecules in Lyotropic Liquid Crystals

10 Define corrosion. Mention any four implications of corrosion.

Destruction of a metal by chemical or electrochemical reaction when a metal is in contact with corrosive medium is called corrosion.

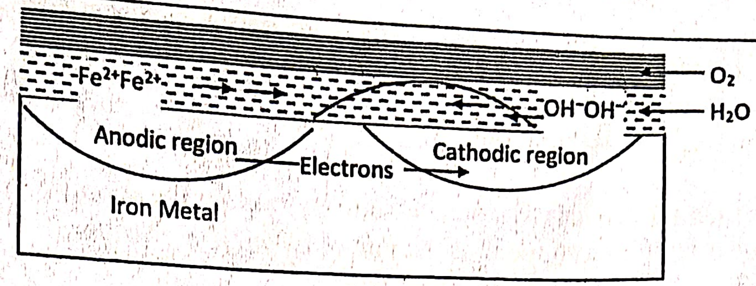
Implications or ill effects or disadvantages of corrosion:

1. It is estimated that 20% of Iron ore produced by mining is used to replace damaged Iron objects.
2. Corrosion causes poor appearance of the object.
3. Increases the maintenance and operating cost of metallic structure.
4. Severe corrosion of machinery and tools leads to shutdown of production plants
5. Loss of valuable products due to leakage.
6. Effects on safety and reliability in handling hazardous materials.

11 Define corrosion. Describe electrochemical theory of corrosion. OR Explain electrochemical theory of corrosion with iron as example.

Definition of corrosion: Corrosion is defined as the destruction of metals or alloys by the surrounding environment through chemical or electrochemical reactions.

Electrochemical theory of corrosion: According to electrochemical theory, when a metal such as iron is exposed to corrosive environment, following changes occur. A large number of tiny galvanic cells with anodic and cathodic regions are formed.



Reactions:

Reaction at anodic region: As mentioned above, oxidation of metal takes place at anode.

e.g. $Fe \rightarrow Fe^{2+} + 2e^-$

The Fe^{2+} ions dissolve, so corrosion takes place at the anodic region.The electrons travel through the metal from the anodic region to cathodic region.

Reactions at cathodic region: The metal is unaffected at the cathodic region. At cathode, the reaction is either a) liberation of hydrogen or b) absorption of oxygen.

a) Liberation of hydrogen (in the absence of oxygen)

In acidic medium the reaction is

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

In neutral or alkaline medium, the reaction is

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2\uparrow$$

b) Absorption of oxygen (in the presence of oxygen)

In acidic medium, the reaction is

$$4H^+ + O_2 + 4e^- \rightarrow 2H_2O$$

In neutral or alkaline medium, the reaction is

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

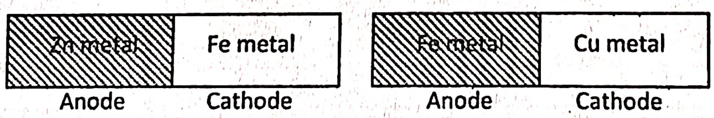
Overall reaction:

$$Fe + \tfrac{1}{2}O_2 + H_2O \rightarrow Fe(OH)_2\downarrow$$

$$2\ Fe(OH)_2 + \tfrac{1}{2}O_2 + H_2O \rightarrow Fe_2O_3 . 3H_2O$$

12 ***Discuss galvanic corrosion with a neat labeled diagram and reactions.***

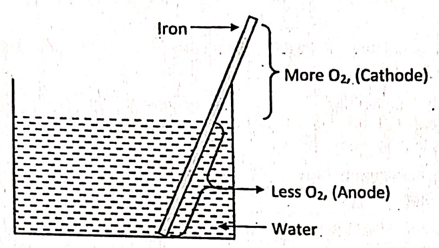
Differential metal corrosion OR Galvanic corrosion



This type of corrosion occurs when two dissimilar metals are in contact with each other and are exposed to a corrosive environment. The two metals differ in their electrode potentials. The metal with lower electrode potential acts as anode and the other metal with higher electrode potential acts as cathode. The anodic metal undergoes oxidation and gets corroded. A reduction reaction occurs at the cathodic metal. The cathodic metal does not undergo corrosion.

The reactions may be represented as follows:

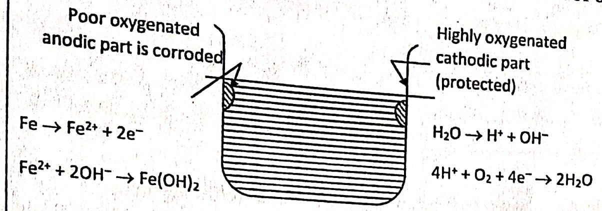
At anode: $M \rightarrow M^{n+} + ne^-$

	At cathode: $2H_2O + O_2 + 4e^- \rightarrow 4OH^-$ Factors affecting rate of galvanic corrosion: • **Higher the potential difference between the anodic and cathodic metals, higher is the rate of corrosion.** • **Smaller anodic area and larger cathodic area increases the rate of galvanic corrosion.**
13	*Explain differential aeration corrosion OR Write a note on differential aeration corrosion.*  This type of corrosion occurs when two different parts of the same metal are exposed to different oxygen concentrations. (e.g. An iron rod partially dipped in water.) The part of the metal which is exposed to less oxygen concentration acts as anode as shown in Fig. The part which is exposed to more oxygen concentration acts as cathode. The anodic region undergoes corrosion and the cathodic region is unaffected. The reactions may be represented as follows: **At anode:** $M \rightarrow M^{n+} + ne^-$ (Oxidation of M) **At cathode:** $2H_2O + O_2 + 4e^- \rightarrow 4OH^-$ (Reduction of O_2)
14	Explain waterline corrosion OR Discuss the waterline corrosion with a labeled diagram. <u>Water line corrosion</u>: This is an example of differential aeration corrosion. When a steel tank is partially filled with water for a long time, the inner portion of the tank below the water line is exposed only to dissolved oxygen, whereas, the portion above the water line is exposed to more oxygen. Thus the portion below the water line acts as anode and undergoes corrosion. The upper portion acts as cathode and is unaffected. A distinct brown line is formed just below the water line due to the deposition of rust.

The reactions may be represented as follows:

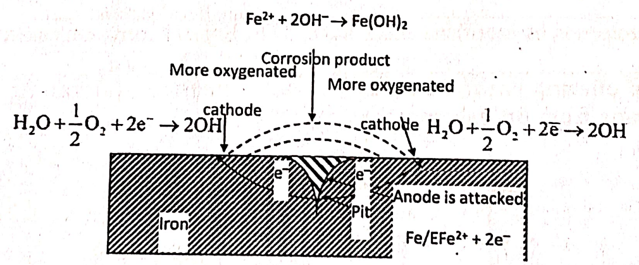
At anode: $M \rightarrow M^{n+} + n\,e^-$ (Oxidation of metal, M)

At cathode: $2\,H_2O + O_2 + 4\,e^- \rightarrow 4\,OH^-$ (Reduction of oxygen)



15	**Discuss pitting corrosion with reactions.**

<u>Pitting corrosion</u>: This is an example of differential aeration corrosion. When a small dust particle gets deposited on a steel surface, the region below the dust particle is exposed to less oxygen compared to the remaining part. As a result, the region below the dust particle acts as anode undergoes corrosion and forms a pit. The remaining region of the metal acts as cathode and is unaffected. The pit is filled with highly unstable, porous, highly conducting corrosion product, which enhances the rate of reaction at localized place.



The reactions may be represented as follows:

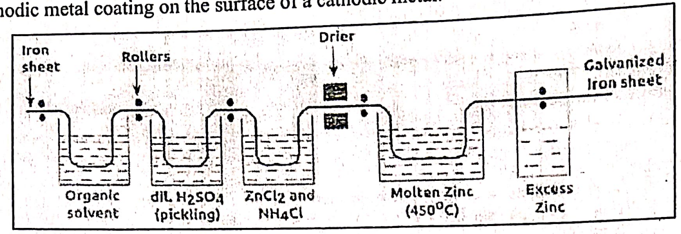
At anode: $M \rightarrow M^{n+} + n\,e^-$

At cathode: $2\,H_2O + O_2 + 4\,e^- \rightarrow 4\,OH^-$

Formation of a small anodic area and a large cathodic area results in <u>intense</u> corrosion below the dust particle.

16	What is galvanizing? Describe galvanizing of iron.

Galvanizing is the process of coating a metal surface such as iron with zinc metal. Galvanizing of iron is an example of anodic metal coating on the surface of a cathodic metal.



Galvanization is carried out by hot dipping method as shown in Fig.2.6. It involves the following steps

1. Solvent Cleaning: The metal surface is washed with organic solvents to remove organic impurities on the surface.
2. Alkali Cleaning: Residual organic impurities are removed by treating the object with alkali such as NaOH.
3. Picking: Rust and Scale is removed by washing the object with dilute sulphuric acid H_2SO_4
4. Finally, the article is washed with water and air-dried.
5. The article is then dipped in a bath of molten zinc at 430°C to 470°C (Molten zinc is covered with a flux of ammonium chloride to prevent the oxidation of molten zinc.)
6. The excess zinc on the surface is removed by passing through a pair of hot rollers.

Application

Galvanization of iron is carried out to produce roofing sheets, fencing wire, buckets, bolts, nuts, pipes etc.

18 Explain cathodic protection by sacrificial anode method OR Explain corrosion control by sacrificial anode method.

It is a method of offering cathodic protection to a specimen (metal) against corrosion by providing electrons from an external source.

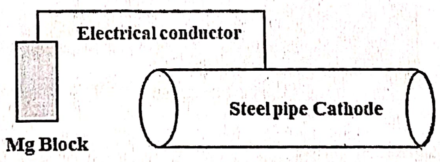


Fig: 3.10 Sacrificial anode technique

In sacrificial anode method, the metal to be protected is electrically connected to a more active metal using insulated copper wire. For example, when steel is to be protected, it may be connected to a block of Mg or Zn. In such a situation, steel acts as **cathode** (high electrode potential) and is unaffected as shown Fig.3.10. Mg and Zn act as anode (low electrode potential) and undergo sacrificial corrosion. When the sacrificial anode gets exhausted, it is replaced with new ones.

Advantages: (i) The method is simple.

(i) Low installation cost and low maintenance.
(ii) Does not require power supply.

Disadvantage: Replacement of consumed anodes

9 **Define corrosion penetration rate.** A sheet of carbon steel one meter wide by three meters long has lost 40g to corrosion over the past six months. Convert that mass loss to a penetration rate of the steel in mm units and mpy units. What would be the corrosion rate? (Carbon steel density=7.8g/ cm3) To calculate CPR in mmpy.

	Given	CPR mm/yr
K		87.6
W	40g	40X1000 mg
ρ	7.8g/cc	7.8 g/cc
A	1mx3m=3m^2	3x100X100 cm^2
t	6 months	6x30X24 hrs

$$CPR=\frac{KW}{\rho XAXt}$$

$$CPR=\frac{87.6\ X\ 40\ X\ 1000mg}{7.8\frac{g}{cc}\ X3x100X100\ cm^2\ X\ 6x30X24\ hrs} = 3.466\ X10^{-3}\ mm/yr.$$

CPR= 0.003466mm/yr

To calculate CPR in mpy

	Given	CPR in mpy
K		534
W	40g	40 x 1000 mg
ρ	7.8g/cc	7.8 g/cc
A	1mx3m=3m^2	3 x1550 inch^2
t	6 months	6 x 30 x 24 hrs

1 sq mt= 1550 sq inch

$$CPR=\frac{KW}{\rho XAXt} \qquad CPR=\frac{534\ X\ 40\ X\ 1000mg}{7.8\frac{g}{cc}\ X3x1550\ in^2\ X\ 6x30X24\ hrs}= 0.1363mpy$$

20 A piece of corroded steel plate was found in a submerged ocean vessel, it was estimated that the original area was 10inch^2 that approximately 2.6kg had corroded away during the submersion. Assuming a corrosion penetration rate of 200mpy for this alloy in sea water, estimate the time in years, density of steel 7.9g/cc.

	Given	CPR in mpy
K		534
W	2.6kg	2.6 x 1000 x1000 mg
P	7.9g/cc	7.9 g/cc
A	10 inch^2	10 inch^2
T	X	X hrs

$CPR = \frac{KW}{\rho X A X t}$ and $t = \frac{KW}{\rho X A X cpr}$

$t = \frac{534 X 2.6 X 10^6\ mg}{7.9\ g/cc X 10 in^2 X 200 mpy}$ $t = 87873.41 hrs$

$$\boxed{t = \frac{87873.41}{365 X 24} = 10.03 yrs}$$

Calculate the CPR in both mpy and mm/yr for a thick steel sheet of area 100 in^2 which experiences a weight loss of 485g after one year. (density of steel=7.9g/cm^3).

	Given	CPR in mpy
K		534
W	485g	485 x1000 mg
P	7.9g/cc	7.9 g/cc
A	100 in^2	100 $inch^2$
T	1 yr	365 X 24 hrs

$CPR = \frac{KW}{\rho X A X t}$ $CPR = \frac{534 X 485 X 1000 mg}{7.9 \frac{g}{cc} X 100\ in^2\ X 365 X 24\ hrs}$

CPR=37.424mpy

	Given	CPR in mm/y
K		87.6
W	485g	485 x1000 mg
P	7.9g/cc	7.9 g/cc
A	100 in^2	100 x 6.45cm^2
T	1 yr	365 x 24 hrs

1 in^2 = 6.45cm^2

1 cm^2= 0.155 in^2

$CPR = \frac{KW}{\rho X A X t}$ $CPR = \frac{87.6 X 485 X 1000 mg}{7.9 \frac{g}{cc} X 100 X 6.45\ cm^2\ X 365 X 24\ hrs} = 0.9518 mm/y$