Solution for BCHEE102 VTU 2022-23 1st Semester Examination held in April-May 2023

CBCS SCHEME

USN ☐☐☐☐☐☐☐☐☐☐ BCHEE102

First Semester B.E./B.Tech. Degree Examination, Jan./Feb. 2023
Chemistry for EEE Stream

Time: 3 hrs. Max. Marks: 100

Note: 1. Answer any FIVE full questions, choosing ONE full question from each module.
2. VTU Formula Hand Book is permitted.
3. M : Marks , L: Bloom's level , C: Course outcomes.

		Module – 1	M	L	C
Q.1	a.	Explain the classification of materials as conductors, insulators and semiconductors along with a suitable example with the help of band theory.	7	L2	CO1
	b.	Define the following with respect to polymers : i) Conducting polymers ii) Number average molecular weight iii) Weight average molecular weight.	6	L1	CO1
	c.	Describe eletroless plating of copper with bath composition and reaction in the manufacture of double-sided printed circuit board (PCB).	7	L2	CO1
		OR			
Q.2	a.	Discuss the production of electronic grade silicon by Czochralski(CZ) process.	6	L2	CO1
	b.	What are Polymers? In a sample of a polymer, 100 molecular have molecular mass 10^3g/mol, 200 molecular have molecular mass 10^4g/mol and 250 molecular have molecular mass 10^5g/mol. Calculate number average macular mass weight average molecular mass and polydisperisty index.	7	L3	CO1
	c.	What is grapheme? Describe the preparation and properties of graphene oxide.	7	L2	CO1
		Module – 2			
Q.3	a.	What are batteries? Explain the construction with a diagram and working of sodium-ion battery.	7	L2	CO2
	b.	What are fuel cells? Explain the construction with a diagram and working of methanol- oxygen fuel cell.	7	L2	CO2
	c.	List out a minimum three advantages and disadvantages of solar photovoltaic cells.	6	L1	CO2

		OR			
Q.4	**a.**	Describe the construction, and working of Vanadium redox flow battery. Mention its applications.	7	L2	CO2
	b.	Explain the construction, working and applications of Polymer Electrolyte Membrane (PEM) fuel cell.	7	L2	CO2
	c.	Discuss the construction and working of photovoltaic cell.	6	L2	CO2
		Module – 3			
Q.5	**a.**	What is corrosion? Explain the electrochemical theory of corrosion taking iron as an example.	7	L2	CO3
	b.	Define corrosion penetration rate (CPR). Calculate the CPR in both mpy and mmpy for steel sheet of area 150 inch^2 which experienced a weight loss of 490g after one year. Given density of steel = 7.9g/cc.	6	L3	CO3
	c.	Discuss sources, types and effects of e-waste on environment and human health.	7	L2	CO3
		OR			
Q.6	**a.**	Demonstrate the type of corrosion taking place in the following cases : i) A steel screw in copper sheet for a long time ii) Partially buried pipeline in soil.	6	L3	CO3
	b.	What is e-waste? Explain the methods of e-waste disposal.	7	L2	CO3
	c.	Describe the extraction of copper from e-work. Mention any two advantages of recycling.	7	L2	CO3
		Module – 4			
Q.7	**a.**	What are nanomaterials? Explain the following size dependent properties of nanomaterials : i) Surface area ii) Catalytic property iii) Conducting property.	7	L2	CO4
	b.	Describe the synthesis of nanomaterials by sol – gel method with a suitable example.	6	L2	CO4
	c.	What are liquid crystals? Explain the classification, properties and applications of liquid crystals in display systems.	7	L2	CO4
		OR			
Q.8	**a.**	Explain the properties and applications of nanofibers and nanosensors.	6	L2	CO4
	b.	Mention the properties and applications of : i) Organic Light Emitting Diode (OLED) ii) Quantum Light Emitting Diode (QLED).	7	L2	CO4
	c.	What are perovskite materials? Give the properties and applications of perovskite materials in optoelectronic devices.	7	L2	CO4

		Module – 5			
Q.9	a.	What is reference electrode? Describe the construction and working of calomel electrode.	7	L2	CO5
	b.	What are concentration cells? Explain the construction and working of electrolyte concentration cell with a suitable example.	6	L2	CO5
	c.	What are optical sensors? Explain the principle and instrumentation of colorimetric sensor.	7	L2	CO5
		OR			
Q.10	a.	What are ion-selective electrode? Discuss the construction and working of glass electrode.	7	L2	CO5
	b.	What are potentiometric sensors? Explain working principle instrumentation and applications of potentiometric sensor.	7	L2	CO5
	c.	A concentration cell is constructed by combining two lithium electrodes immersed in lithium sulphate solution of concentration 0.1m and 0.4m at 298K. Write the cell representation, cell reaction and calculate the EMF of the cell.	6	L3	CO5

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Module 1

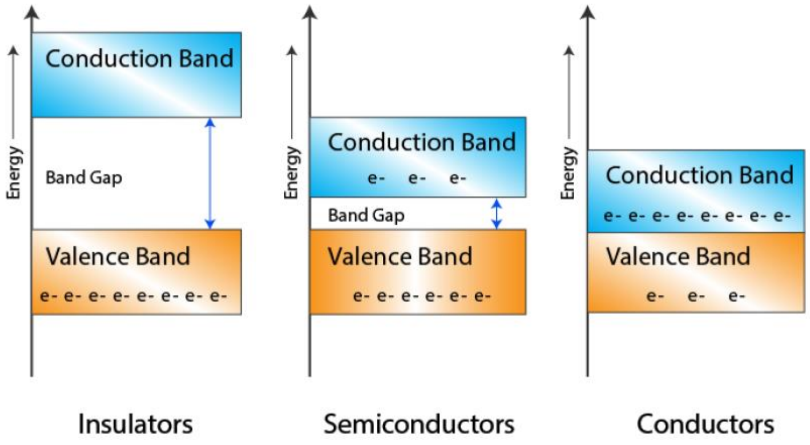
Answer 1a) Band theory describes the possible energies of electrons in a solid and provides insight into electrical conductivity. The band theory states that conduction occurs only when some electrons are present in the conduction band. In solids, the conduction band is the outermost energy band.

Band Theory of conduction:

Conductors: According to band theory, a conductor is essentially a substance with its conduction bands and valence bands overlapping, permitting electrons to move freely between the valence band and the conduction band. In conductors, conduction band is only partially filled. This means there are spaces for electrons to move into conduction band and hence thee materials acts as conductors. Example: Copper, Brass, Steel, Gold, and Aluminium

Semiconductors: In a semiconductor, the gap between the valence band and conduction band is smaller. The completely occupied valence band and the unoccupied conduction band classify semiconductors. As per band theory semiconductors will operate as insulators at absolute zero. Above this temperature there is sufficient energy available to move some electrons from the valence band into the conduction band and hence material acts as semiconductor. An increase in temperature increases the conductivity of a semiconductor because more electrons will have enough energy to move into the conduction band. Example: Silicon.

Insulators: An insulator has a large gap between the valence band and the conduction band. The valence band is full and no electrons can move up to the conduction band, hence these material can't conduct. Example: Glass, Plastic, Rubber.



Answer 1b)

Conducting polymers: These are the organic polymers with highly delocalized π-electron systems having conductance of the order of conductors.

Number average molecular weight is the ratio of total weight of all the molecules to the total number of molecules.

$$\overline{M}_n = \frac{N_1M_1 + N_2M_2 + N_3M_3 + \ldots\ldots\ldots + NiMi}{N_1 + N_2 + N_3 + \ldots\ldots Ni}$$

$$\boxed{\overline{M}_n = \frac{\Sigma NiMi}{\Sigma Ni}}$$

Weight average molecular weight is the ratio of molecular mass of all of all the molecules to the total weight of the polymer.

$$\overline{M}_w = \frac{N_1M_1^2 + N_2M_2^2 + N_3\,M_3^2 + \ldots\ldots\ldots\ldots\ldots\ldots\ldots + N_iM_i^2}{M_1N_1 + M_2N_2 + M_3N_3 + \ldots\ldots\ldots\ldots M_iN_i}$$

$$\boxed{\overline{M}_w = \frac{\Sigma \mathbf{N_iM_i^2}}{\Sigma \mathbf{M_iN_i}}}$$

Answer 1(c) Electroless plating is the controlled deposition of a continuous film of a metal from its salt solution on a catalytically active surface of the substrate by a suitable reducing agent, without the use of electrical energy.

Electroless-plating of Copper on PCB

Activation of surface: The base of a printed circuit board is a plastic material such as epoxy or phenolic polymer or a glass fiber reinforced polymer composite. It is activated by treatment with acidified $SnCl_2$ and then with acidified $PdCl_2$ leads to deposition of Pd.

$SnCl_2 + PdCl_2 \rightarrow Pd + SnCl_4$

In the manufacture of double sided PCB, the board is clad on either side with thin electroformed copper foils. Then both sides of the copper clad board are printed with etch-resistant circuit patterns. Rest of the unprotected copper foil is etched (formation of tracks) away by using an acid. This leaves only the circuit patterns on both sides of the board. Electrical connection between the two sides of PCB is made by drilling a hole through the board. The hole is then activated & electroless plated with copper, as it can't be electroplated. The composition of the electroless plating bath & the procedure given below.

Constituents	**Purpose**
$CuSO_4$	Provides metal ions
HCHO	Reducing reagent
Rochelle salt	Complexing agent
NaOH	Provides alkaline medium
EDTA	Exaltant & complexing agent
pH	11.0
Temperature	25°C

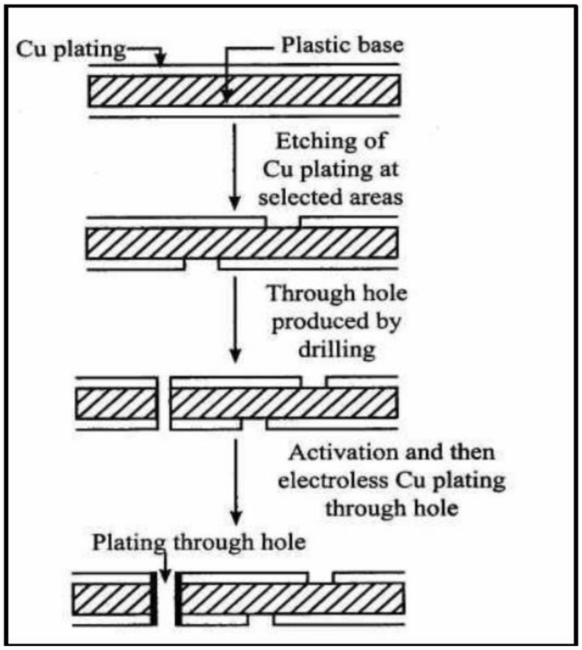
Following reactions takes place during the process:

Reactions:

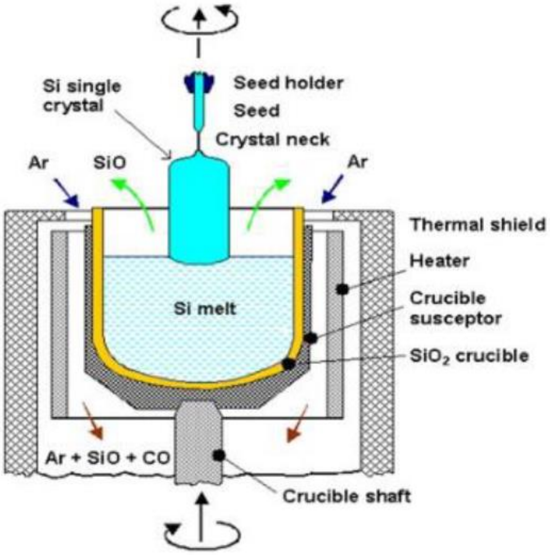
Oxidation of reducing reagent : $2HCHO + 4OH^- \longrightarrow 2HCOO^- + 2H_2O + H_2 + 2e^-$

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

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



Answer 2(a): Production of electronic grade silicon: A silicon wafer is a thin piece of semiconductor which is used in fabrication process in integrated circuits. There are two different method to grow a single crystal.



1. Czochralski process (CZ)

The Czochralski process, is a method of crystal growth used to obtain single crystals of semiconductors (e.g. silicon, germanium and gallium arsenide), metals (e.g. palladium, platinum, silver, gold), salts and synthetic gemstones. In this process high-purity polycrystalline silicon is placed in the quartz crucible and melted using a RF coil in an atmosphere of argon. The temperature is maintained at the melting point of the silicon (around 1,412 °C). Dopant impurity atoms such as boron or phosphorus can be added to the molten silicon in precise amounts to dope the silicon, thus changing it into p-type or n-type silicon, with different electronic properties. A rotating puller rod with a seed crystal at the bottom is lowered such that the seed crystal just touches the surface of molten silicon. A slight temperature drop initiates the crystallization of silicon on the seed crystal. The puller rod is pulled out at the rate of 1.5-5 cm/hour and simultaneously rotated at a speed of 100 rpm. As the rod is pulled away from the surface, silicon solidifies and a single crystal of silicon having the same crystal structure as that of the seed crystal is obtained. By precisely controlling the temperature gradients, rate of pulling and speed of rotation, it is possible to extract a large, single-crystal, cylindrical ingot from the melt.

Answer 2(b) Polymers are the macromolecules formed by the repeated unit of simple molecules called monomers

Calculation of number average molecular weight

$$\overline{M}_n = \frac{N_1M_1 + N_2M_2 + N_3\,M_3 + \ldots\ldots\ldots\ldots\ldots\ldots\ldots + NiMi}{N_1 + N_2 + N_3 + \ldots\ldots\ldots\ldots Ni}$$

$$\boxed{\overline{M}_n = \frac{\mathbf{\Sigma NiMi}}{\mathbf{\Sigma Ni}}}$$

$$\overline{\text{Mn}} = \frac{(100\times10^3) + (200\times10^4) + (250\times10^5)}{100 + 200 + 250}$$

$$\overline{\text{Mn}} = 49272.7 \text{ g/mol}$$

Calculation of weight average molecular weight

$$\overline{M}_w = \frac{N_1M_1^2 + N_2M_2^2 + N_3\,M_3^2 + \ldots\ldots\ldots\ldots\ldots\ldots\ldots + NiMi^2}{M_1N_1 + M_2N_2 + M_3N_3 + \ldots\ldots\ldots\ldots MiNi}$$

$$\boxed{\overline{M}_w = \frac{\mathbf{\Sigma NiMi^2}}{\mathbf{\Sigma MiNi}}}$$

$$\overline{\text{Mw}} = \frac{[100\times(10^3)^2] + [200\times(10^4)^2] + [250\times(10^5)^2]}{(100\times10^3) + (200\times10^4) + (250\times10^5)}$$

$$\overline{\text{Mw}} = 92992.6 \text{ g/mol}$$

$$\text{PDI} = \frac{\overline{\text{Mw}}}{\overline{\text{Mn}}} = \frac{92992.6 \text{ g/mol}}{49272.7} = 1.88$$

Answer 2(c): Graphene a form of carbon consisting of planar sheets which are one atom thick, with the atoms arranged in a honeycomb-shaped lattice.

Graphene oxide (GO): It is a layered carbon structure with oxygen-containing functional groups (=O, -OH, -O-, -COOH) attached to both sides of the layer as well as the edges of the plane. As with any 2D carbon material, GO can also have either single layer or multilayer structure. A structure with one layer is graphene oxide; two layers of graphene oxide are referred to as a two-layered GO, GO with five to ten layers is called multi layered GO, and material with eleven or more layers is called graphite oxide. In contrary to graphene, GO is hydrophilic, and it is hence relatively simple to prepare a water- or organic solvent-based suspensions. Highly oxidized forms of GO are electric insulators with a bandgap of approximately 2.2 eV. Simplistically, GO is a monolayer sheet of graphite containing hydroxyl, carboxyl, and epoxy oxygen groups on its basal plane and edges, resulting in a mixture of sp^2 and sp^3 hybridized carbon atoms.

Properties of Graphene Oxide:

- The properties of graphene can be changed by the functionalization of graphene oxide. The chemically-altered graphene's could possibly be used in several applications.
- Graphene Oxide has a high surface area, and so it can be fit for use as electrode material for batteries, capacitors and solar cells.
- Graphene Oxide is cheaper and easier to manufacture than graphene, and so may enter mass production and use sooner.
- GO can easily be mixed with different polymers and other materials, and enhance properties of composite materials like tensile strength, elasticity, conductivity and more.

Synthesis of Graphene Oxide:

Synthesis of Graphene Oxide

The synthesis of graphene oxide (GO) involves the oxidation of graphene, typically using strong oxidizing agents.

Hummers' method.

- In a fume hood, mix graphite powder, sodium nitrate ($NaNO_3$), potassium permanganate (KMnO4), and concentrated sulfuric acid (H2SO4) in a round-bottom flask.
- Stir the mixture at a low temperature (around 0-5°C) for few hours.
- Slowly add deionized water or ice to the reaction mixture to quench the reaction and obtain graphite oxide suspension.
- Wash the resulting graphite oxide suspension with acid and water to remove impurities and unreacted chemicals.

Applications of Graphene Oxide:

- Air pollution caused by the industrial release of harmful gases such as CO_2, CO, NO_2, and NH_3.
- GO can be employed in catalysis for converting polluting gases during industrial processing.
- The approach of GO application in this area can be divided into two paths: pollutant adsorption and conversion.
- The functional groups of few-layered GO composites exhibit unique adsorption behaviour towards different gases like acetone, formaldehyde, H2S, SO2 , and NOx can be adsorbed by GO-based composites.
- GO exhibits high adsorption ability towards Cd(II), Co(II), Au(III), Pd(II), Ga(III), and Pt(IV).
- Adsorption ability mainly depends on the synthesizing method. Multilayered graphene oxide nanosheets show a very high affinity towards Pb(II) ions, with a sorption capacity of about 842 mg g^{-1} at 293 K.
- Small-molecule drug delivery seems to be another promising medical application of GO. Small molecules of drugs can be attached to a GO surface using pH-sensitive linkers.
- More over cancer targeting was successfully manifested as a codelivery of camptothecin (CPT) using folic acid conjugated nano GO (FANGO).

Module 2

Answer(3a) "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: Non-graphitic anodes, which consist largely of various carbonaceous materials (such as carbon black, pitch-based carbon-fibers, hard carbons etc)

Cathode: layer and tunnel type transition metal oxides, transition metal sulfides and fluorides etc

Electrolyte: The most common electrolyte formulations for SIBs are $NaClO_4$ or $NaPF_6$ salts in carbonate ester solvents (particularly propylene carbonate).

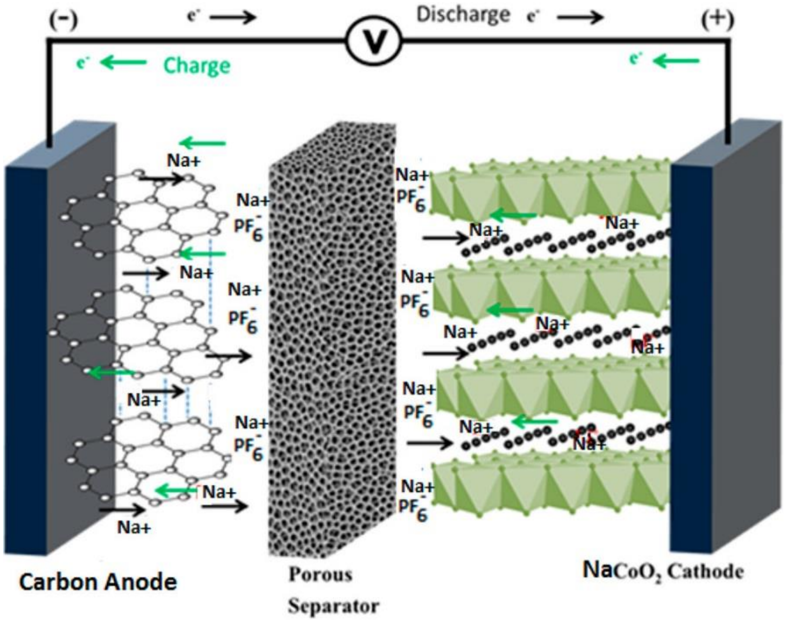


Figure. Na-ion Battery (SIB)

Working principles of SIBs

When the battery is being charged, Na atoms in the cathode release electrons to the external circuit and become ions which migrate through the electrolyte toward the anode, where they combine with electrons from the external circuit while reacting with the layered anode material. This process is reversed during discharge.

At anode: $$Na_xC_6 \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftarrows}} xNa^+ + xe^- + C_6$$

At cathode: $$NaMO_2 + xNa^+ + xe^- \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftarrows}} Na_{1+x}MO_2 + C_6$$

Overall cell reaction: $$Na_xC_6 + NaMO_2 \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftarrows}} Na_{1+x}MO_2 + C_6$$

Applications: Sodium-ion batteries can be used for a broad range of battery applications, including renewable energy storage for homes and businesses, grid storage, and backup power for data and telecom companies.

Answer (3b) 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 (H_2SO_4), 3.7 M.
4. Active components: (a) Fuel – Methanol mixed with sulphuric acid supplied at anode. (b) Oxidant – Pure oxygen is supplied at cathode.

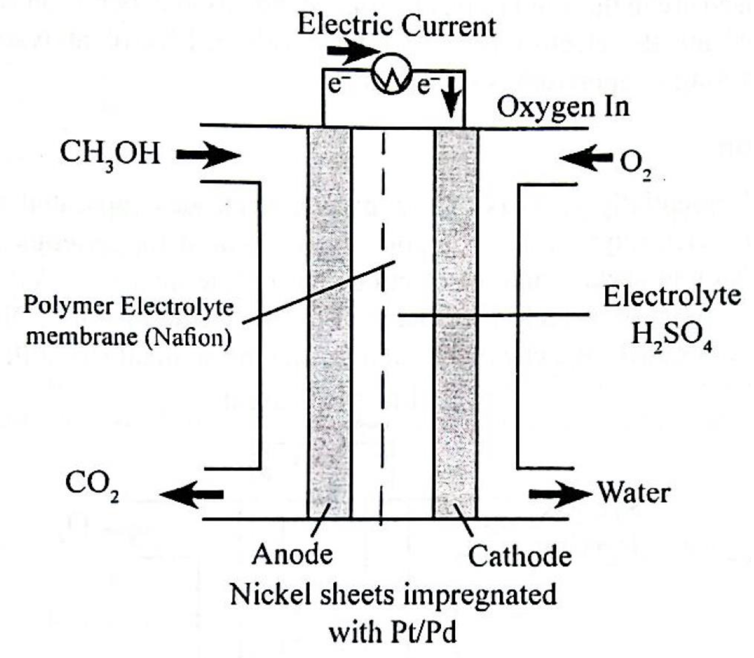


Figure: Methanol – oxygen fuel cell

Working:

Cell reaction;

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

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

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 (3c) 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 4a.

Flow battery: A flow battery, or redox flow battery, is a type of electrochemical cell where chemical energy is provided by two chemical components dissolved in liquids that are pumped through the system on separate sides of a membrane. Example: **Vanadium redox flow battery**

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).

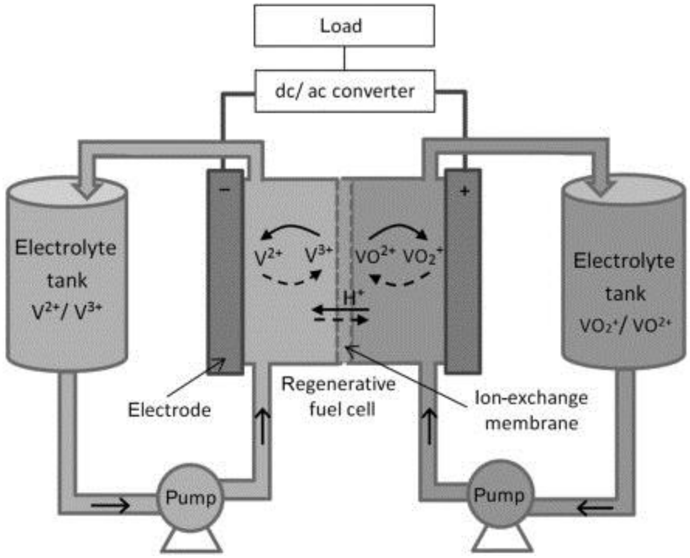


Figure. A diagram of a vanadium redox flow battery

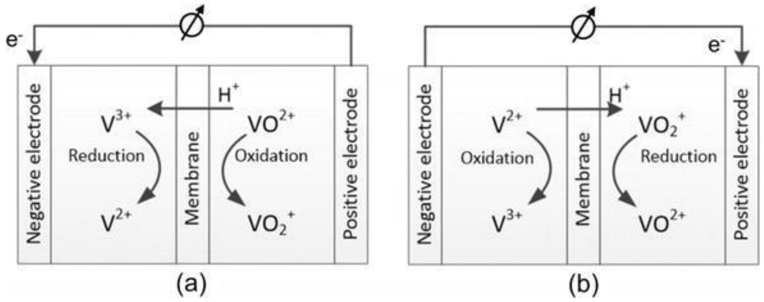


Figure. Vanadium redox flow battery: (a) charge reaction and (b) discharge reaction.

Working:

Negative electrode: $$V^{2+} \underset{\text{Charge}}{\overset{\text{Discharge}}{\longleftrightarrow}} V^{3+} + e^-$$

Positive electrode: $$VO_2^+ + e^- + 2H^+ \underset{\text{Charge}}{\overset{\text{Discharge}}{\longleftrightarrow}} VO^{2+} + H_2O$$

Overall reaction: $$VO_2^+ + V^{2+} + 2H^+ \underset{\text{Charge}}{\overset{\text{Discharge}}{\longleftrightarrow}} VO^{2+} + V^{3+} + H_2O \qquad (E^0 = 1.26\ V)$$

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

Answer 4b

Fuel cells are the galvanic cells which convert chemical energy of a fuel- oxidant system directly into electrical energy by oxidation of fuel at anode and reduction of oxidant at cathode".

Construction: A PEFC comprising a proton-conductive solid polymer electrolyte membrane of thickness 50–180 μm and porous carbon electrodes containing a platinum or platinum alloy catalyst (Figure). The most typical polymer electrolyte membrane is the perfluorosulfonic-acid-type ion exchange membrane such as Nafion®, which has a molecular structure based on a main polytetrafluoroethylene chain with side chains containing sulfonic acid. Pure hydrogen or hydrogen reformed from methanol or natural gas is used as fuel.

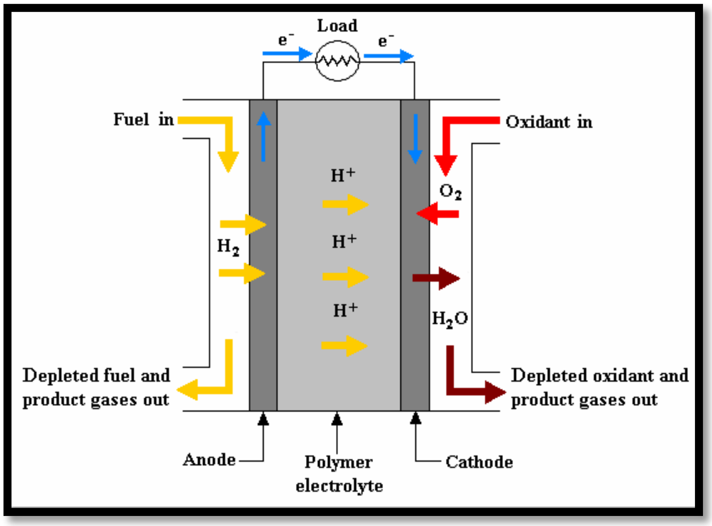


Figure: Polymer electrolyte fuel cell

Working:

Hydrogen supplied to the anode side is oxidized, and produced H^+ moves through the membrane to the cathode side. This H^+ is used in the reaction in which water is formed by the reduction of oxygen supplied to the cathode side. As the electrons generated at the anode flow through the external circuit to arrive at the cathode, an electric current can be retrieved. The reactions at the anode and cathode, and the overall reaction, are given as follows.

Anode: $H_2 \rightarrow 2H^+ + 2e^-$

Cathode: $\frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O$

Overall reaction: $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$

Applications: Polymer electrolyte fuel cells (PEFCs) are of interest as power sources in vehicles and portable applications because of their high energy efficiency and environmentally friendly qualities.

Answer 4c.

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.

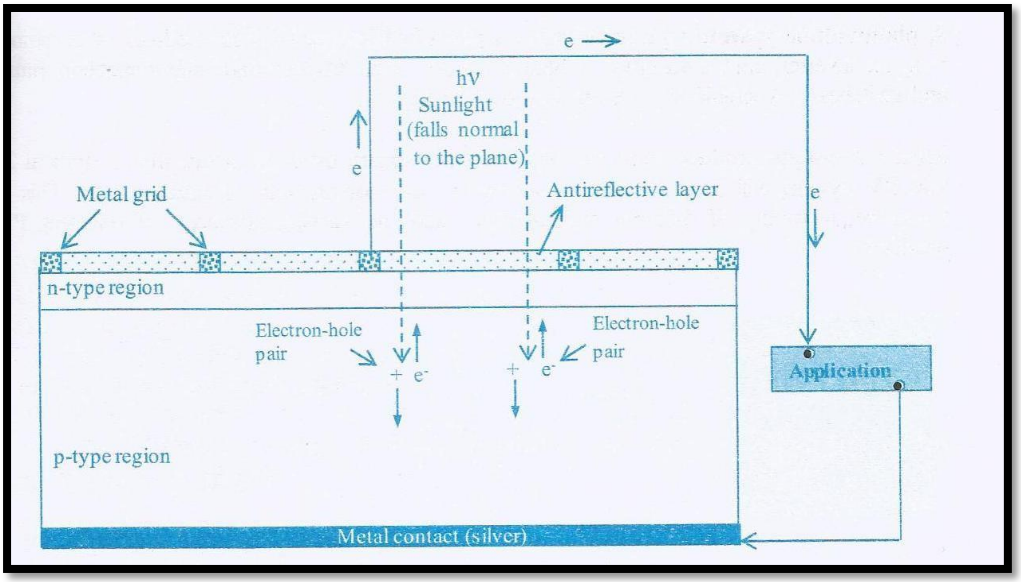


Figure Photovoltaic cells

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 mettalic 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 TiO_2

Working:

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

$$\mathbf{E = hc/\lambda}$$

Where, h = Planck's constant, c = velocity of light, λ = 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 electron-hole 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.

Module 3

Answer (5 a)

Definition: Metal when exposed to the atmosphere undergoes gradual destruction. Such destruction of metal is known as Corrosion. It's defined as the "destruction of metal or alloys from its surface by the surrounding environment through chemical or electrochemical changes".

Eg. Rusting of Fe- A reddish brown scale formation on iron. It is due to the formation of hydrated ferric oxide, Green scale formed on Cu vessel- It is due to the formation of basic cupric carbonate ($CuCO_3+Cu(OH)_2$)

Electrochemical theory of corrosion:

According to electrochemical theory, corrosion of the metal take place due to the formation of anodic and cathodic regions on the same metal surface in the presence of a conducting medium. At the anodic region oxidation reaction takes place and the metal gets corroded into ions liberating the electrons. Consequently metals undergo corrosion at the anodic region. At the cathodic region reduction reaction takes place. Metal ions in the cathodic region are unaffected by the cathodic reaction.

The electrons liberated at the anodic region migrate towards the cathodic region constituting corrosion current. The metal ions liberated at the anode and some anions formed at the cathode region diffuse towards each other through the conducting medium and form a corrosion product somewhere between the anode and the cathode. Corrosion of metal continues as long as both the anodic and cathodic reactions take place simultaneously.

Corrosion reactions:

At the anodic region: At anodic region, iron is liberating Fe2+ ions and electrons,

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

At the cathodic region:

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.

If the solution is aerated and almost neutral,

$$1/2O_2 + H_2O + 2e^- \rightarrow 2OH^-$$

If the solution is deaerated and almost neutral:

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

If the solution is deaerated and acidic:

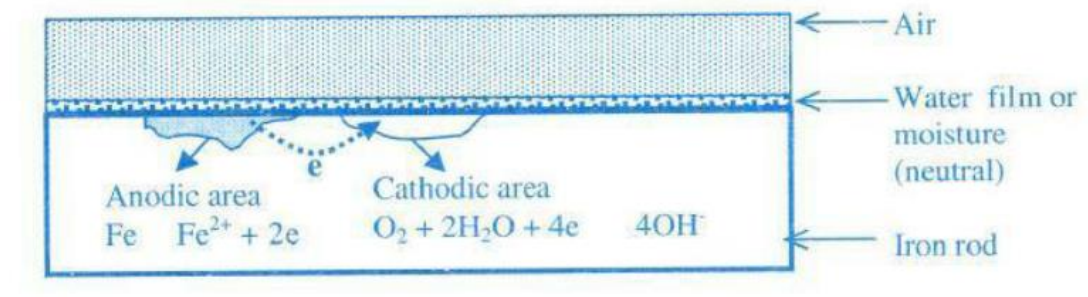
$$2H^+ + 2e^- \rightarrow H_2$$

The electrons liberated at the anodic region migrates to the cathodic region. 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

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

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

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



Answer 5b:

The corrosion penetration rate (CPR) is defined the speed at which any metal in a specific environment deteriorates due to a chemical reaction in the metal when it is exposed to a corrosive environment. or The amount of corrosion loss per year in thickness.

CPR = KW/DAT = (534×490×1000)/(7.9×150×365×24) = 25.2066 mpy

CPR = KW/DAT = (87.6×490×1000)/(7.9×150×6.45×365×24) = 0.6410 mmy

Answer 5c. E-waste or electronic waste means discarded electrical or electronic devices or components.

Sources of e-waste: The common sources of e-waste are as follows.

- Large household appliances like refrigerators/freezers, washing machines, dishwashers, televisions.
- Small household appliances which include toasters, coffee makers, irons, hairdryers.
- Information Technology (IT) and Telecommunications equipment namely personal computers, telephones, mobile phones, laptops, printers, scanners, photocopiers etc.
- Lighting equipment such as fluorescent lamps.
- Electronic or Electrical tools i.e. handheld drills, saws, screwdrivers etc.
- Toys, leisure and sports equipment.
- Monitoring and control instruments.
- Automatic dispensers.

Types of e-waste:

It is categorized into 21 types under two broad categories:

- Information technology and communication equipment.
- Consumer electrical and electronics.

Due to rapid technology changes large amount of electronic or electrical devices are turning into waste. Some of the common e-waste elements are mobile phones, computers, laptops, hard drives, fans, microwaves, DVD, printers, lamps, etc.

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

The consequences of improper e-waste disposal in landfills or other non-dumping sites pose serious threats to current public health and can pollute ecosystems for generations to come. When electronics are improperly disposed of and end up in landfills, toxic chemicals are released, impacting the earth's air, soil, water, and ultimately, human health.

Effects on Air quality: 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.

Effects on Soil: 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.

Effects on Water: 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.

Effects on Humans: 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 6a:

The corrosion occurring is differential metal Corrosion. When two dissimilar metals are in contact with each other a potential difference is set up resulting in a galvanic current. The two metals differ in their tendencies to undergo oxidation, the one with lower electrode potential or the more active metal acts as anode and the one with higher electrode potential acts as cathode. The anodic metal undergoes corrosion and the cathodic metal is generally unattacked. The steel screw acts as anode and undergoes corrosion. The copper sheet acts as cathode.

At the anode, $Fe \rightarrow Fe^{2+} + 2e^-$

At the cathode, $H_2O + \frac{1}{2} O_2 + 2e^- \rightarrow 2OH^-$

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

$2Fe(OH)_2 + 1/2O_2 + H_2O \rightarrow [Fe_2O_3 . 3H_2O]$ (rust)

The corrosion occurring is differential aeration corrosion: Differential aeration corrosion occurs when a metal surface is exposed to differential air concentrations of Oxygen concentrations. The part of the metal exposed to higher oxygen concentration acts as a cathodic region and the part of the metal exposed to lower oxygen concentration acts as anodic region. Corrosion of metal arising as a result of the formation of an oxygen concentration cell due to uneven supply of air on the metal surface is known as differential aeration corrosion. The buried portion acts as anode and undergoes corrosion. The exposed portion acts as cathode.

At the anode (less O_2 concentration), $Fe \rightarrow Fe^{2+} + 2e^-$

At the cathode (more O2 concentration), $H_2O + \frac{1}{2} O_2 + 2e^- \rightarrow 2OH^-$

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

$2Fe(OH)_2 + 1/2O_2 + H_2O \rightarrow [Fe_2O_3 . 3H_2O]$ (rust)

Answer 6b: E-waste or electronic waste means discarded electrical or electronic devices or components. This includes working and broken items that are thrown in the garbage or donated to a charity reseller, their components, consumables, parts, and spares.

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.

Answer 6c: Extraction of Copper from e-waste

E-waste contains 10mtimes more excessive concentration of gold compared to ores. Concentration of copper in PCB is 20-40 times more than that is present in the ore. Hence, e-waste can act as a vital source of precious metal and can satisfy their demand in various industries.

There are three stages in metal recovery by hydrothermal method

1) Pretreatment stage
2) Chemical treatment stage
3) Metal recovery stage

Pretreatment stage

In the pretreatment stage, e-waste is manually dismantled to separate various fractions like metals, ceramics, plastics, wood and paper. Technics such as gravity separation, electrostatic separation, Magnetic separation and eddy current separations are used to separate metals from other fractions.

Chemical treatment stage

In the chemical treatment step, targeted metals are leached into solution by treating with appropriate chemical reagents.

Acid leaching is the most common method used to extract copper. H_2SO_4 / HNO_3 in the presence of oxidizing agent H_2O_2 is used in the process.

$Cu + ½\ O_2 + 2H^+\ Cu^{2+} + H_2O$

Metal recovery stage

In this step, metal is recovered from leach solutions. Copper metal can be recovered by electrodeposition. Pure copper metal taken as cathode and inert anode are dipped in leaching solution. When current is applied, copper is electrodeposited on cathode.

Advantages of Recycling E-Waste

The top 5 benefits of recycling e-waste include the following:

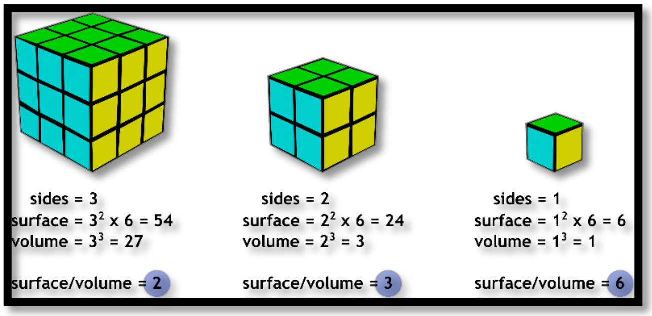
- Reduces Landfill Sites
- Preserves Natural Resources
- Prevents Toxic Chemicals from Polluting the Ecosystem
- Creates New Business & Employment Opportunities
- Promotes Mindful Consumerism.

Module 4

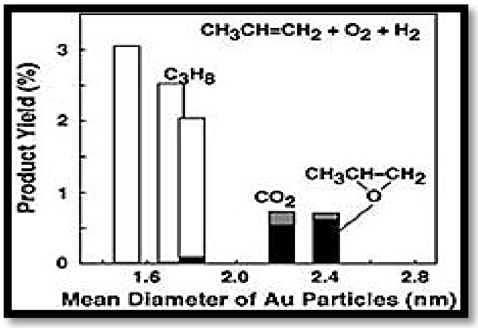
Answer 7a: Size-dependent properties

1). Surface area: In chemical reactions, this surface-to-volume ratio plays an important role. There is an enormous change in the properties of materials due to the increased surface area-to-volume ratio. The nanomaterials have a relatively larger surface area when compared to the same volume of the material produced in a larger form. So we know that material has high surface energy if it is small in size and vice versa. Therefore, nanoparticles have a large surface area to volume ratio and they possess large surface energy. Due to high surface energy materials are more reactive and also nanoparticles show enhanced stability and a broader scope of applications. In some cases, materials that are inert in their larger form are reactive when produced in their nanoscale form. This affects their strength or electrical properties.

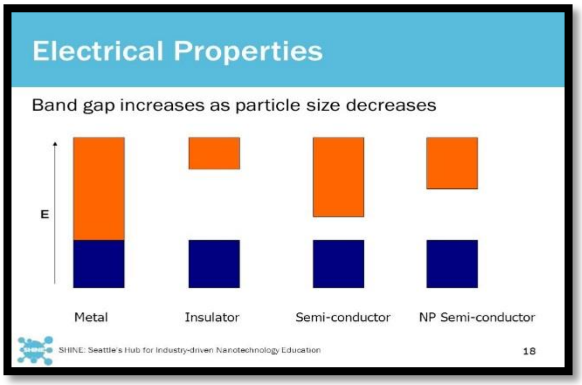
The ratio of surface area to volume of a material is given by $area/volume = 4\pi r^2 / 4/3\ \pi r^3 = 3/r$



2) Catalytic properties: The factors such as very small size, very high surface-to-volume ratio, and the increasing number of atoms on the surface are the most important reasons for the emergence of catalytic properties in nanomaterials. Basically, when particles become very small (nanoscale), due to the very high curvature they find, they have many atoms on their surface, which are very weakly bonded to the lattice atoms of the lattice. Therefore, these particles have very high surface energy and are highly active, and it is said that surface atoms are in a state of physical instability and are chemically active, and are prone to perform many chemical reactions. It can be said that the main and determining reason for the emergence of catalytic properties in nanomaterials is their very high surface-to-volume ratio. The higher this ratio, the higher the catalytic properties in nanomaterials due to the increase in surface energy. In principle, the reason for these changes is due to changes in the electronic structure of materials, which can be justified by quantum mechanics.The effect of gold nanoparticle size on catalytic activity in the propene epoxidation reaction has been investigated, which shows that by reducing the size of gold nanoparticles, the yield of the product increases.



3) Conducting properties: In bulk metals, the valence and conduction bands overlap, while in metal nanoparticles there is a gap between these bands. The gap observed in metal nanoparticles can be similar in size to that seen in semiconductors (< 2 eV) or even insulators (> 2 eV). This results in a metal becoming a semiconductor. For example, carbon nanotubes can be either conductors or semiconductors depending on their nanostructure. Another example is supercapacitors which have effectively no resistance and disobey ohm’s law.


Electrical Properties

Band gap increases as particle size decreases

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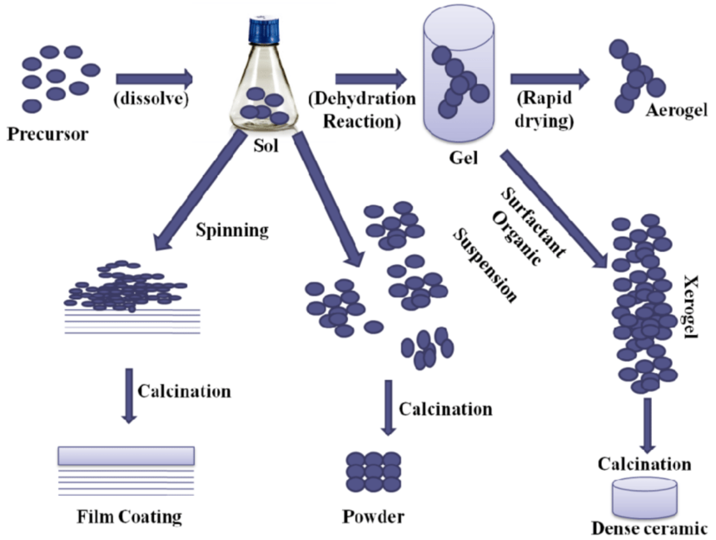
Answer 7(b) Nanotechnology can be defined as the manipulation of atoms and molecules (one billionth) scale (1-100 nm) to produce devices, structures, or systems with at least one novel or superior property. Materials having at least one dimension in the nanoscale are called **nanomaterials**.

The sol-gel process, involves the evolution of inorganic networks through the formation of a colloidal suspension (sol) and gelation of the sol to form a network in a continuous liquid phase (gel). The precursors for synthesizing these colloids consist usually of a metal or metalloid element surrounded by various reactive ligands. The starting material is processed to form a dispersible oxide and forms a sol in contact with water or dilute acid. Removal of the liquid from the sol yields the gel, and the sol/gel transition controls the particle size and shape. Calcination of the gel produces the oxide.



Step1: Formation of different stable solutions of the alkoxide or solvated metal precursor (the sol).

M-OR + H_2O----------------- ► M-OH + HOR

Step 2: Gelation resulting from the formation of an oxide or alcohol bridged network (the gel) by polycondensation or poly esterification reaction. This results in a dramatic increase in the viscosity of the solution.

M-OH + M-OR------------------► M-O-M + HOR
M-OH + M-OH----------------- ► M-O-M + HOR

Step 3: Aging of the gel(synthesis), during which the polycondensation reactions continue until the gel transforms into a solid mass. This is accompanied by the contraction of the gel network and the expulsion of solvent from gel pores.

Step 4: Drying of the gel, when water and other volatile liquids are removed from the gel network. If isolated by thermal evaporation, the resulting is termed a xerosal. If the solvent (such as water) is extracted under supercritical or near supercritical conditions, the product is an aerogel.

Step 5: Dehydration, during which surface-bound M-OH groups are removed. This is normally achieved by calcination of the monolith at temperatures up to 800 0 C.

Step 6: Densification and decomposition of the gels at high temperature ($T>800^0$ C). The pores of the gel network collapse and the remaining organic species are volatilized.

The typical steps that are involved in sol gel processing are shown in fig. By different processes, one can get either nano film coating or nanopowder or dense ceramic with nanograins.

Example: Sol-Gel synthesis process ZnO NPs First of all, in a 100ml beaker 30 ml of water was added with 35 ml of triethanolamine(TEA) and drop wise ethanol was added with continuous stirring to get a homogeneous solution. After addition of 100 drops ethanol that was about 3 ml and continuous stirring results a homogeneous solution. Keeping the stoichiometry in mind a 2.0 gm batch of zinc oxide was prepared. Firstly, 30ml of water was mixed with 20 ml of TEA with constant stirring and drop wise addition of ethanol. The obtained homogeneous solution was kept at rest for 3.0 hours. For 2.0 gm batch of zinc oxide 5.49gm of zinc acetate dihydrate was mixed with 50ml water and 0.5M of solution was prepared which was subjected to continuous stirring to get a homogeneous solution. After that the two solutions were mixed together in 500ml beaker and drop wise ammonium hydroxide was added with continuous heating and stirring for 20minutesvia hot plate. Nearly 10ml of distil water was added during stirring. Then the solution was left for half an hour which results in the formation of white bulky solution. The obtained solution was then washed 10-12 times with distil water and filtered in a filter paper. The residue obtained waskept for drying in an oven at a temperature of about 95°C for 6 hours. The yellowish white powder obtained was then subjected to calcinations at a temperature of600°C for 5 hours

Answer 7(c) Liquid crystals (LCs) are a state of matter that has properties between those of a conventional liquid and a solid crystal.

2.1. Types of Liquid Crystals:

This classification is based on breaking order of the solid state and has two types:

1. Thermotropic liquid crystals 2. Lyotropic liquid crystals

2.1.1 Thermotropic liquid crystals Thermotropic phases are those that occur in a certain temperature range.

a) Smectic liquid crystals

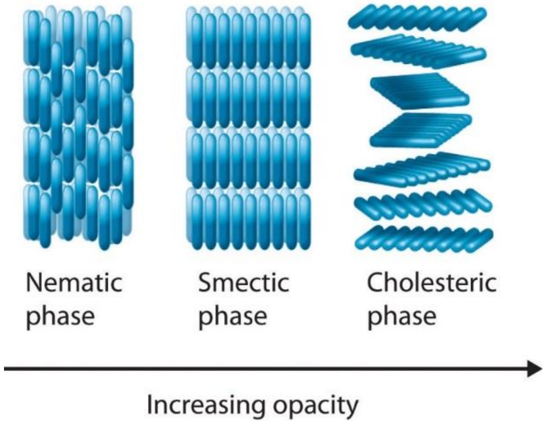
b) Nematic liquid crystals

c) Cholesteric liquid crystals

a) Nematic or thread-like liquid crystals: These are less ordered. These on heating lose their planar structure but retain a parallel alignment. Thus, they retain orientation but lose periodicity. The molecules tie parallel to each other but can move up or down or sideways or can rotate along their axes. N-paramethoxy benzylidene – p – butyl aniline changes to nematic liquid at 240 C and this state persists up to 430C, after which it melts into an isotropic liquid. Nematic liquid crystals do not conduct electricity when they are in pure form. They flow like liquids, but their mechanical (like viscosity, elasticity) electrical (like dielectric constant) , optical properties and diamagnetism etc., depending upon the direction along which they are measured..

b) Smectic (or) soap-like liquid crystals: Smectic is the name given by G. Friedel for certain mesophases with mechanical properties similar to soaps. All smectic LCs have layered structures, with definite interlayer spacing. This can be measured by X-ray diffraction. Smectic liquid crystals on heating retain long-range order, yielding a smectic phase. They lose the periodicity within the planes but retain the orientation and arrangement in equispaced planes. Example: para-n-octyloxybenzoicacid

c) Cholesteric liquid crystals: These are optically active and possess the arrangement of molecules similar to those in the nematic type. Such liquid crystals are characterized by very high optical rotation, probably a thousand times greater than that of their crystalline variety. Moreover, on raising the temperature, the pitch decreases. This results in a corresponding change in the wavelength of reflection. They are named so because the skeleton of these substances pass through a state similar to that of cholesterol, a steroid present in blood. Example: Cholesteryl benzoate



2. Lyotropic liquid crystals

Some compounds are transformed to an LC phase, when mixed with other substances (solvent) or when the concentration of one of the components is increased. Such compounds are called lyotropic LCs. A lyotropic liquid crystal exhibits liquid-crystalline properties in certain concentration ranges. Many amphiphilic molecules show a lyotropic liquid-crystalline phase. Examples are: Sodium laureate in water and Dhosphatidly choline in water.

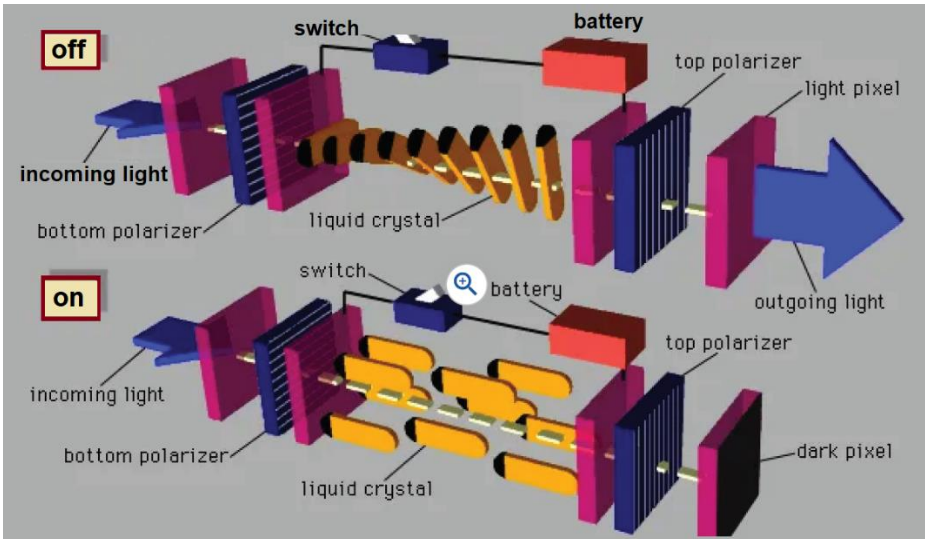
Properties of liquid crystals:

- These compounds display properties of both solid and liquid.
- Anisotropic: possess some orientational or positional order but with a lower degree of organisation compared with a crystalline solid.
- liquid crystal possesses liquid-like flowing behaviour,
- compounds are often more viscous.
- Liquid crystals are attributed to their sensitivity to various stimuli, such as temperature, electric and magnetic fields.
- Exhibit birefringence. That is, light that enters the crystal is broken up into two oppositely-polarized rays that travel at different velocities. Observation of a birefringent material between crossed polarizing filters reveals striking patterns and color effects.

Applications of LCs

(1) Working principles of LCD: The properties of liquid crystals which make them suitable for use in displays are; their ability to affect the path of plane polarized light and their reaction to changes of temperature. Thermotropic liquid crystals are a type of liquid crystal which reacts to changes in temperature. This class of liquid crystals is subdivided into isotropic, where molecules have a random order and nematic liquid crystals where all the axes through the centre of the molecules are aligned. The nematic phase of liquid crystals is the one most often used in LCD displays. The molecules are rod-shaped and can move with respect to each other but with their molecular long axes, n, remaining aligned . Changes in this alignment of the nematic phase are seen when an external electric field is applied. Twisted versions of these nematic phases are used in the formation of pixels. A twisted nematic liquid crystal is trapped between two parallel glass sheets with polarizers at 90° to each other placed on either side of this sandwich. The nature of the liquid crystal is such that the orientation of a beam of polarized light will be turned through 90° allowing

it to pass, unchanged, through the pixel as it will now be at the correct angle to pass through the second polariser. This causes the device to be in an on state and glowing. On application of an external electric field the liquid crystal molecule will realign so that polarized light is not transmitted by the molecule and as such does not pass through the second polarizer turning that pixel off. A series of transistors is used to turn on and off pixels in order to make up an image.



2) When a beam of light strikes a film of a smectic liquid crystal, the properties of the reflected light depending on this characteristic distance. Since this distance is temperature sensitive, the reflected light changes with changing temperature. This phenomenon is the basis of liquid crystal temperature sensing devices, which can detect temperature changes as small as $0.01^{O}C$ with ordinary light.

3) Liquid crystals are used in gas-liquid chromatography because their mechanical and electrical properties lie in between crystalline solids and isotropic liquids.

4) Liquid crystals are employed as solvents during the spectroscopic study of the structure of anisotropic molecules.

5) Cholesteric liquid crystals are used in thermography a method employed for detecting tumors in the body.

Answer 8(a) **Nano-fibers** are slender, elongated, threadlike material with a diameter between 50 and 300 nanometers.

Properties of Carbon Nanofibers:

- Nanofibers have diameter 1000 times smaller than that of human hair
- high surface area with tunable porosity,
- 3D topography
- flexible surface functionalities
- and better mechanical properties (i.e., stiffness and tensile strength).
- Carbon nanofiber has a low density.

- The thermal conductivity ranges between 1950 – 6000 W/m K and electrical resistivity from 1×10^{-3} to 1×10^{-4}.
- Activated CNFs have a specific surface area with high adsorption capacity.

Applications of Carbon nanofibers:

- **Biosensors:** High sensitivity towards the target molecules, good electron transferability, a larger surface area for adsorption and being highly electrocatalytic towards the oxidation of small molecules like viruses, proteins and nucleic acids, glucose, hydrogen peroxide, dopamine, and cortisol they can be used efficiently in various clinical biosensing applications.
- **Wound dressing materials:** carbon-based nanofibers have been seeking more attention because of their excellent mechanical strength and biocompatibility. They are being used in the biomedical sector especially wound dressing, biomedicine and bioengineering.
- **Carbon nanofibers as supercapacitors:** PAN/polymethylmethacrylate (PMMA)/carbon composite nanofiber mats used as electrode material in a supercapacitor, characterized by a low loss after 10,000 charge-discharge cycles.
- **Carbon nanofibers for electrocatalytic applications**
- **Carbon nanofibers for CO_2 adsorption:**
- **Carbon nanofibers as cathode and anode material in advanced batteries.**
-

Nanosensors are sensors that make use of the unique properties of nanomaterials and nanoparticles to detect and measure materials and components on the nanoscale. The signals can be biomedical, optical, electronic, electrical, physical or mechanical.

Properties of Nanosensors:

- Available in small sizes
- Requires less power to operate
- Less weight
- Works as data storage systems
- Great sensitivity, accuracy, scalability, efficiency, precision, and specificity
- Easy to execute.
- Provides a high-volume ratio.
- Response time is low.

Nanosensor Applications

They are used:

- To detect various chemicals in gases for pollution monitoring.
- Nanosensors have potential applications in the food sector, in food processing monitoring, food quality assessment, food packaging, food storage, shelf-life monitoring, and viability, as indicators of food safety and microbial contamination.
- For medical diagnostic purposes either as bloodborne sensors or in lab-on-a-chip type devices. The nanosensors provide an understanding of a person's health status through noninvasive detection of clinically relevant biomarkers in several biofluids such as tears, saliva, and sweat without sampling, complex manipulation, and treatment steps.
- To monitor physical parameters such as temperature, displacement and flow
- To monitor plant signaling and metabolism to understand plant biology

- To study neurotransmitters in the brain for understanding neurophysiology

Answer 8(b) Organic Light Emitting Diodes (OLED's) operates on the principle of converting electrical energy into light, a phenomenon known as electroluminescence. OLED is a semiconductor device, in which the emissive electroluminescent layer is a film of organic compound which emit light in response to an electric current.

Properties of OLED's

- Very thin solid-state device.
- Lightweight: the substrates are shatter resistant unlike glass displays of LCD devices.
- High luminous power efficiency: an inactive OLED element does not generate light or consumes power, hence allowing true blacks.
- Fast response time making entertaining animations- LCDs reach as low as 1ms response time for their fastest colour transition.
- Wide-viewing angle: OLEDs enable wider viewing angle in comparison to LCDs because pixels in OLEDs emit light directly. The colours appear correct.
- Self-emitting hence, removing requirement of a backlight source.
- Colour tuning for full colour displays
- Flexibility- OLED displays are fabricated on flexible plastic substrates producing flexible organic LEDs.
- Cost advantages over inorganic devices- OLEDs are cheaper in comparison to LCD or plasma displays.
- Low power consumption

Applications of OLEDs

1. To build digital displays in TV screens, cell phones, PDAs, monitors, car radios, digital cameras.
2. OLEDs have wide applications in lightning
3. It is used in watches.
4. OLEDs have replaced CRTs (Cathode Ray Tubes) or LCDs (Liquid Crystal Display).

Quantum dot light-emitting diode (QLED) use quantum dots for emission and attracted much attention for the next generation of display

Properties:

- high color saturation
- tunable color emission
- high stability.
- QLED display has advantages in flexible and robust application, which makes wearable and stretchable display possible in the future.
- energy efficient, thin-film display and solid-state lighting applications.
- facile scale-up capability
- Wide-viewing angle

Applications of QLED

- quantum dot light-emitting diodes (QLED) are cost-effective electroluminescence devices ideal for large-area display and lighting applications.
- For photomedical applications: facilitate widespread clinical applications of photodynamic therapy (PDT) or photobiomodulation (PBM).
- Consumer electronics: Used in smart phones, tablets, laptops, and televisions.
- Lighting: Used in lighting applications
- Wearable devices:Used in smart watches and fitness trackers.
- Automotive displays:Used in automotive displays

- Medical devices: OLEDs are used in medical devices
-

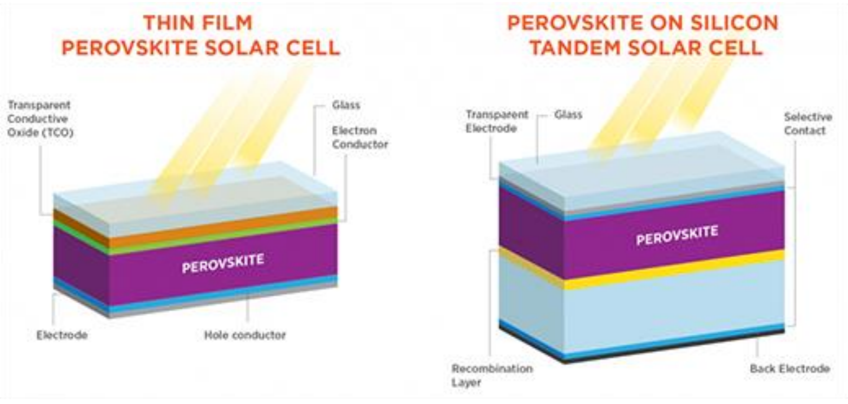
Answer (8c) Perovskite Materials is a material that has the same crystal structure as the mineral calcium titanium oxide (Perovskite).

Properties of Perovskite Materials:

- Generally, perovskite compounds have a chemical formula of ABO_3, where B is a transition metal ion with a small radius, a larger A ion is alkali earth metals or lanthanides with a larger radius, and O is the oxygen ion with a ratio of 1:1:3. In the cubic unit cell of ABO_3 perovskite, atom A is located at the body center, atom B is located at the cube corner position, and oxygen atoms are located at face-centered positions.
- Optical Properties: As one of the unique properties of metal-organic halide perovskites, the optical properties of photo-generated charge carriers have been researched. The specific excitonic absorption peaks of the metal-organic halide perovskite could be transited to various absorption spectra, and it changed significantly in visible light through the adjustment of metal atoms and halogens
- Electroneutrality; the perovskite formula must have a neutral balanced charge therefore the product of the addition of the charges of A and B ions should be equivalent to the whole charge of the oxygen ions.
- Dielectric properties: There are some properties inherent to dielectric materials like ferroelectricity, piezoelectricity, electrostriction, and pyroelectricity. One of the important characteristics of perovskites is ferroelectric behavior.
- Electrical conductivity: Some perovskites exhibited great electronic conductivity
- Superconductivity: One of the obvious properties of perovskites is superconductivity.
- Catalytic Activity: Perovskites exhibited high catalytic activity.
- Piezoelectric property: Piezoelectric Effect is the ability of certain materials to generate an electric charge in response to applied mechanical stress. Various applications such as capacitors, piezoelectric devices, and ferroelectric devices have been designed by using traditional inorganic perovskite materials.

Applications in Optoelectronic devices 1. Solar cells: A perovskite solar cell is a type of solar cell, which includes a perovskite structured compound, most commonly a hybrid organic-inorganic lead or tin halide-based material, as the light-harvesting active layer.

Perovskite materials are usually cheap to produce and relatively simple to manufacture. They possess intrinsic properties like broad absorption spectrum, fast charge separation, long transport distance of electrons and holes, long carrier separation lifetime, which make them very promising materials for solid-state solar cells.



2. Photodetectors: Lead halide perovskites have also been used to fabricate high-performance photodetectors.

3. Apart from these perovskite materials can be used in Light-emitting devices, Lasers, Water splitting applications such as Oxygen reduction and oxygen evolution reactions, Hydrogen evolution reactions and solid oxide fuel cells.

4. Nanoperovskites are recently utilized in electrochemical sensing of alcohols, gases, amino acids, acetone, glucose, H_2O_2, and neurotransmitters exhibiting good selectivity, sensitivity, unique long-term stability, excellent reproducibility, and anti-interference ability.

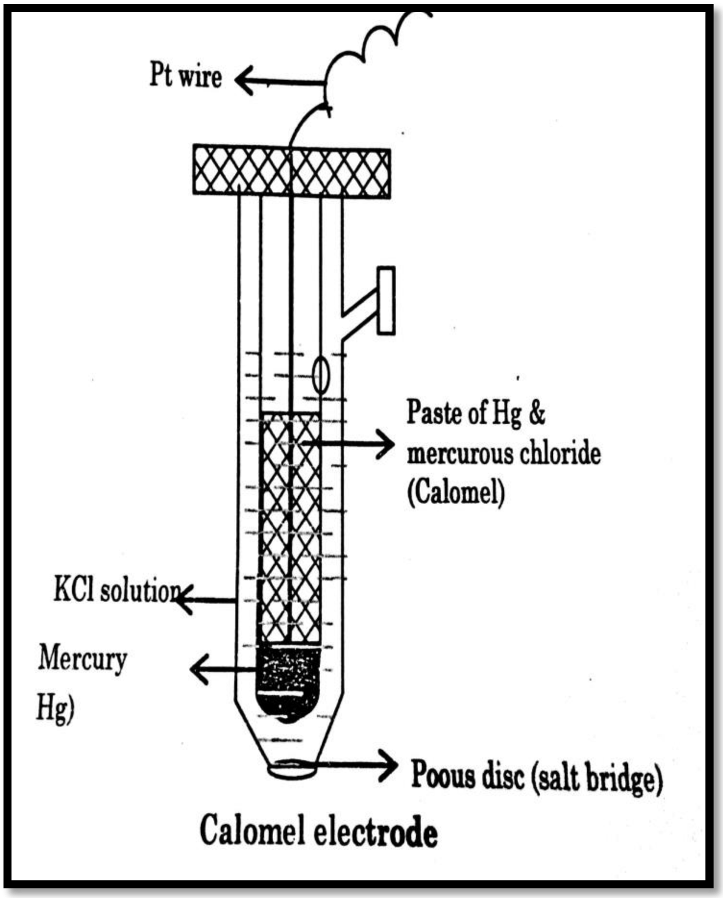
Module 5

Answer 9 a **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 ($HgCl_2$) 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

$$2Hg \longrightarrow Hg_2^{2+} + 2\,e^-$$

$$\underline{Hg_2^{2+} + 2Cl^- \longrightarrow Hg_2Cl_2}$$

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

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

$$Hg_2^{2+} + 2\,e^- \longrightarrow 2Hg$$

$$\underline{Hg_2Cl_2 \longrightarrow Hg_2^{2+} + 2Cl^-}$$

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

Thus, Net reversible electrode reaction is

$$\boxed{Hg_2Cl_2 + 2e^- \rightleftharpoons 2Hg + 2Cl^-}$$

Electrode potential is calculated using Nernst equation,

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

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.

Answer 9 (b) Concentration Cells

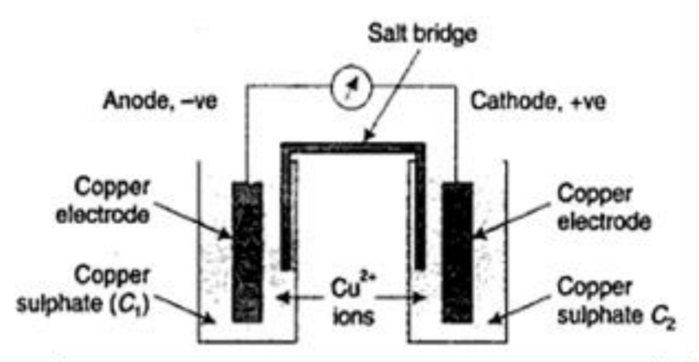
The concentration cell is an electrochemical cell in which both anode and cathode are made up of same elements (identical electrodes) and immersed in same ionic solution (electrolyte) but of different concentration.

Electrolyte concentration cell: In these cells, the two electrodes of same element is in contact with solution of same metal ion (electrolyte) but of different concentration.

Eg. Two copper electrodes immersed in copper sulphate solutions of different concentrations C_1 and C_2. Cell is represented as

$Cu / Cu^{2+}(C_1) // Cu^{2+}(C_2) / Cu$

Construction:



Electrolyte Concentration cell

The Electrode reactions are as follows:

At anode Cu $\rightarrow$ $Cu^{2+}(C_1)$ + $2e^-$

At cathode $Cu^{2+}(C_2)$ + $2e^-$ $\rightarrow$ Cu

EMF of cell is given by

$$E_{cell} = E_{cathode} - E_{anode}$$

$$= \left[E^{\circ} + \frac{2.303\ RT}{nF}\log C_2\right] - \left[E^{\circ} + \frac{2.303\ RT}{nF}\log C_1\right]$$

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

Where C_2 is the concentration at cathode while C_1 is the concentration at anode.

The following conclusions are drawn from the above eq.

1. When two solutions are of the same concentration i.e. C2 = C1, no current flows. The cell reaction is a change in concentration as a result of which current flows. Therefore cell can operate only as long as concentration terms are different.

2. For above cell to be operative, E_{cell} should be positive which is possible only if $C_2 > C_1$. Thus the direction of spontaneous reaction is from the more concentrated one to the less concentrated one.

3. In a concentration cell, electrode with lower electrolyte concentration acts as anode and the one with higher electrolyte concentration acts as cathode. Higher the ratio $\left[\frac{C_2}{C_1}\right]$, higher is the emf.

Answer 9c. Optical Sensors

The method of sensing light rays is known as optical sensing. The sensor type used for optical sensing is known as optical sensor. Optical Sensor converts light rays into electrical signal. The purpose of an optical sensor is to measure a physical quantity of light and, depending on the type of sensor, then translates it into a form that is readable by an integrated measuring device.

Working principle:

The operating principle is the transmitting and receiving of light in an optical sensor, the object to be detected reflects or interrupts a light beam sent out by an emitting diode. Depending on the type of device, the interruption or reflection of the light beam is evaluated. This makes it possible to detect objects independently of the material they are constructed from (wood, metal, plastic or other). Special devices even allow for a detection of transparent objects or those with different colors or variations in contrast.

Optical sensors use visible or ultraviolet light to interrogate sensors for analysis. Optical sensors can be represented in general terms as a wavelength-selectable light source, the sensor material itself interacting with analytes, and a light detector (Fig.). What the detector monitors varies by technique (e.g., refractive index, scattering, diffraction, absorbance, reflectance, photoluminescence, chemiluminescence, etc.), can cover different regions of the electromagnetic spectrum, and can allow measurement of multiple properties (e.g., intensity of light, lifetime, polarization, etc.).

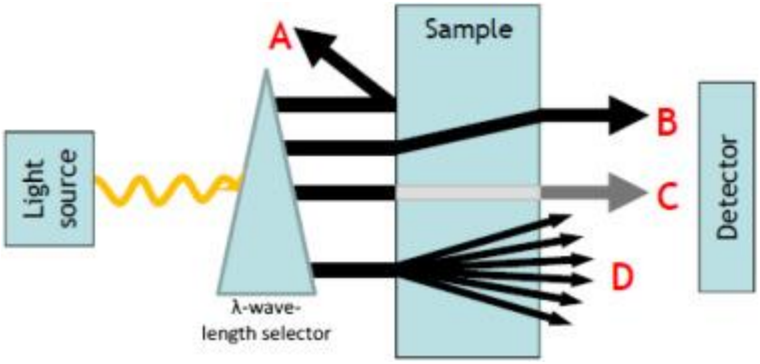


Figure: Working operation of optical sensing. General arrangement of spectroscopic measurements: (A) light reflection; (B) light refraction; (C) light absorption; (D) fluorescent emission.

Principle: Colorimetry is a scientific technique that is used to determine the concentration of colored compounds in solutions.

When a beam of incident light of intensity $\mathbf{I_0}$ passes through a solution, a part of the incident light is relected ($\mathbf{I_r}$), a part is absorbed ($\mathbf{I_a}$) and rest of the light is transmitted ($\mathbf{I_t}$)

Thus, $\mathbf{I_0 = I_r + I_a + I_t}$

In colorimeter, $\mathbf{I_r}$ is eliminated. For this purpose, the amount of light relected ($\mathbf{I_r}$) is kept constant by using cells that have identical properties. **(I_0)** & **(I_t)** is then measured. Colorimetry measurements are based on Beer-Lambert's law which states that when a monochromatic light passes through a transparent medium, the amount of light absorbed is directly proportional to the concentration and path length of the solution.

$A = \varepsilon ct$

Where A is absorbance, ε is the molar extinction coefficient, c is the concentration, t is the path length. If t, the path length is kept constant, then, $A \propto c$. Hence a plot of absorbance against concentration gives a straight line.

Instrumentation: Photoelectric colorimeter consists of

(i) Tungsten lamp as the light source.

(ii) A filter which provides the desired wavelength range wherein the solution gives the maximum absorbance.

(iii) A sample cell

(iv) A photocell detector: Detector are photosensitive elements which converts light energy into electrical energy

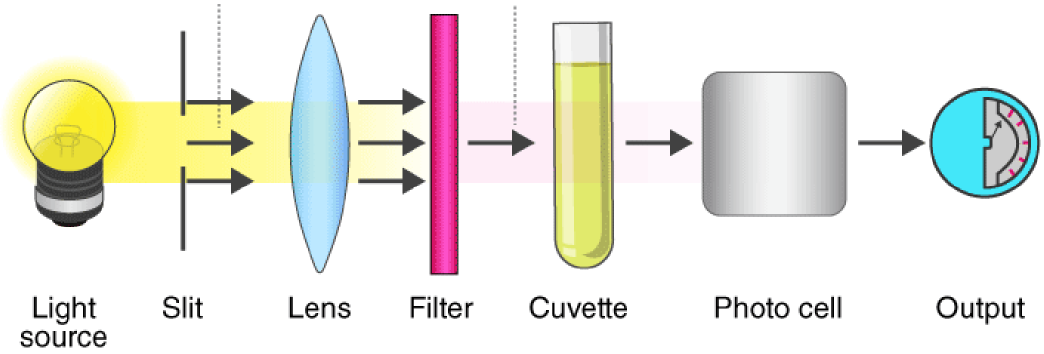
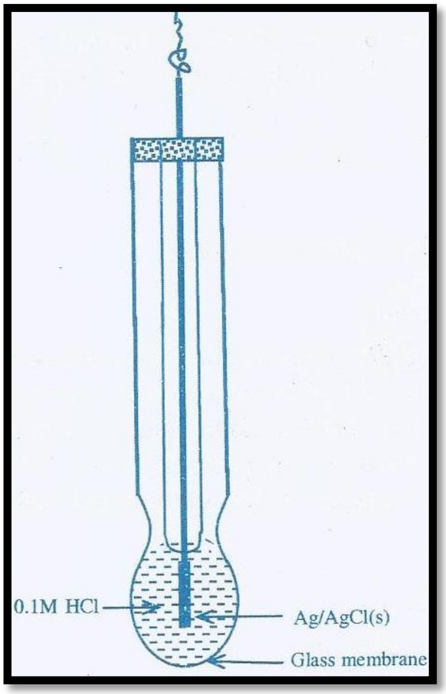


Fig: Schematic layout of colorimeter

Answer 10a. **Ion Selective electrodes** 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 C_2). An Ag/AgCl electrode (internal reference electrode) is placed in the solution and connected by a pt wire for electrical contact. Fig: Glass Electrode



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.

$$H^+ + Na^+ GI^- \longrightarrow Na^+ + H^+GI^-$$

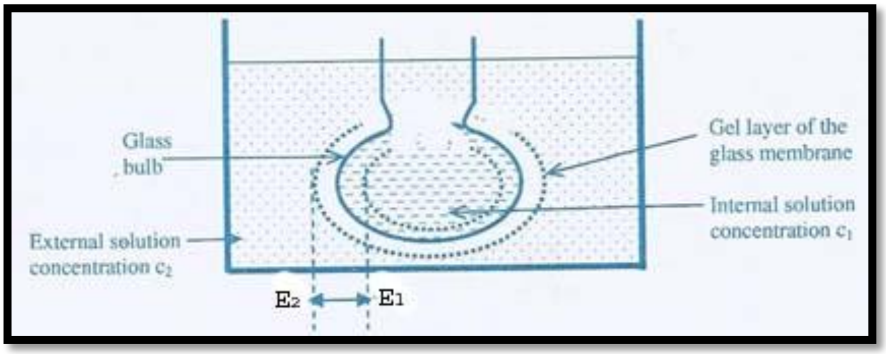


Fig : Boundary Potential (E_b = E_2-E_1)

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,

$$E_b = E_2-E_1$$

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

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

$$E_b = \frac{0.0591}{n} \log C_2 - \frac{0.0591}{n} \log C_1 \text{..................(1)}$$

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 (C_1) is constant i.e. $C_1 = 0.1$ M.

Thus, $E_b = \frac{0.0591}{n} \log C_2 + K$ or

$= K + \frac{0.0591}{n} \log C_2$

Glass electrode selects only H^+ ions ignoring other ions.

Hence $C_2 = H^+$

$E_b = K + 0.0591 \log [H^+]$

Where, $\log [H^+] = -pH$

$$\boxed{\text{Thus, } E_b = K - 0.0591pH \text{ ---------------------}\mathbf{(2)}}$$

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

$E_G = E_b + E_{Ag\text{-}AgCl}$ ………………………(3)

From equation 1, theoretically if $C_1 = C_2$, E_b should be 0, however it has been observed practically that even when $C_1 = C_2$, a small potential is developed which is called as asymmetric potential (E_{asym}). Hence equation 3 can be rewritten as

$E_G = E_b + E_{Ag\text{-}AgCl} + E_{asym}$ ………………………(4)

Substituting the value of E_b from equation (2) in equation (4)

$E_G = K - 0.0591pH + E_{Ag/AgCl} + E_{assy}$

$\boxed{E_G = E^o_G - 0.0591pH}$ **………………(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.

Advantages of Glass electrode:

1. It can be used in presence of strong oxidizing /reducing substances and metal ions.
2. It does not get poisoned easily.

3. Equilibrium is easily attained.
4. Portable and compact.

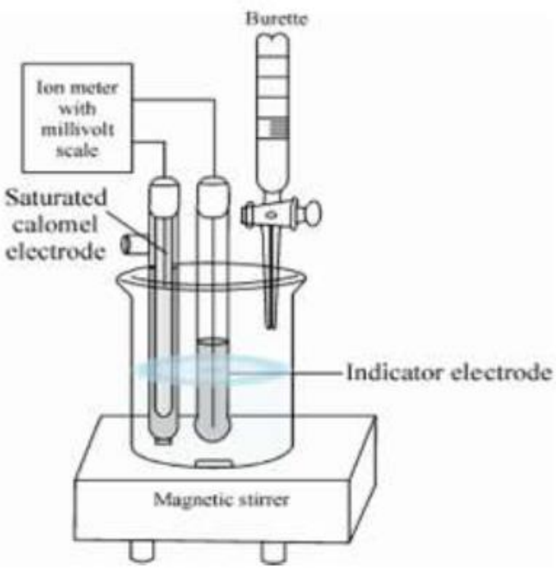
Limitation of glass electrode:

1. It can be used up to pH 13 but becomes sensitive to Na^+ ions above pH 9 resulting in an alkaline error.
2. It does not function satisfactorily in pure alcohol.
3. It has to be handled with care because of glass electrode, and is very fragile.

Answer 10b **Principle:** The procedure of using measurement of emf to determine the concentration of ionic species in solution is called as potentiometry also known as potentiometric titration. When a metal M is immersed in a solution containing its own ions M_{n+}, the electrode potential is
given by Nernst equation.

$$E = E^{o} + \frac{0.0591}{n} \log\left[M^{n+}\right]$$

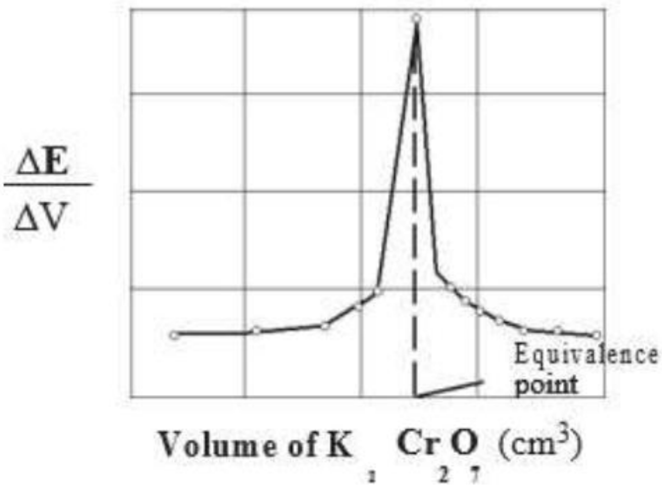
Thus, the concentration can be calculated, provided E^{o} of the electrode is known. The principle involved in potentiometric titration is the measurement of emf between two electrodes, an indicator electrode, (the potential of which is function of the concentration of the ion to be determined) and a reference electrode of constant potential. In this method, the measurement of emf is made while the titration is in progress. The equivalence point of the reaction is revealed by a sudden change in potential in the plot of emf readings against the volume of titrant.



Instrumentation: A potentiometer consists of: (i) Calomel electrode as a reference electrode, (ii) Platinum electrode as an indicator electrode, (iii) a device for measuring the potential and (iv) Magnetic stirrer.

Application: Potentiometric estimation of FAS using standard $K_2Cr_2O_7$ solution: Pipette out 25ml of FAS into a beaker. Add 1 t.t dil H_2SO_4, immerse calomel electrode + platinum electrode into it. Connect the assembly to a potentiometer and measure the potential by adding

$K_2Cr_2O_7$ in the increments of 0.5ml. Plot graph ΔE/ ΔV against volume of $K_2Cr_2O_7$, and determine the equivalence point. From the normality and volume $K_2Cr_2O_7$, solutions calculate the normality and the weight of FAS in the given solution.



Answer 10 c

$$E_{cell} = \frac{0.0591}{n} \log (C2/C1) \text{ at } 298K$$

Cell representation: $Li(s)/Li_2SO_4(0.1M)//Li_2SO_4(0.4M)/Li(s)$

Anodic reaction: $Li(s) \rightarrow Li^+ (aq)$ (C1 = 0.1M) + e^-
Cathodic reaction: $Li^+(aq)$ (C2= 0.4M) + $e^- \rightarrow Li(s)$
Substitution of C1, C2 and n moles

$$E_{cell} = \frac{0.0591}{1} \log (0.4/0.1) \text{ at } 298K$$

$$= 0.0591 \log 4$$

$$= 0.0591 \times 0.6020$$

$$E_{cell} = 0.0355 \text{ V}$$

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