Roll No.				

Internal Assessment Test 2 – Jan 2025

Sub:	Chemistry					Sub Code:	BCHEE102	Branch:	ECE
Date:	17-01-2025	Duration:	90 min's	Max Marks:	50	Sem / Sec:	I / M, N, O & P		OBE

Question no. 1 is COMPULSORY and answer any THREE FULL Questions from the rest.

			MARKS	CO	RBT
1	(a)	Define electroless plating. Illustrate the electroless plating of copper in the manufacture of double-sided PCB with suitable reactions.	[7]	CO3	L3
	(b)	What are electrochemical sensors? Explain their working principle and mention any 4 applications.	[7]	CO4	L2
2	(a)	Explain the principle, instrumentation and applications of potentiometric sensor by taking estimation of iron as an example.	[6]	CO4	L2
	(b)	What is thermometric sensors? Describe its working principle and mention any 4 applications.	[6]	CO4	L2
3	(a)	Define liquid crystals? Describe the classification of liquid crystals with examples.	[6]	CO1	L2
	(b)	What are OLED's. Discuss their properties along with applications	[6]	CO1	L2
4	(a)	What are conducting polymers? Explain the conduction mechanism in polyacetylene. Mention its commercial applications.	[6]	CO1	L3
	(b)	Discuss the preparation, properties and commercial applications of graphene oxide.	[6]	CO1	L2
5	(a)	Explain the applications of Liquid crystals in LCD's (Display) with the help of suitable diagram.	[6]	CO1	L3
	(b)	Discuss the properties and applications of nanosensor and nanofibre.	[6]	CO1	L1
6	(a)	Explain the terms conductors, semiconductors and insulators on the basis of band theory.	[6]	CO1	L1
	(b)	In a sample of polymer 100 molecules have molecular mass 10^3 g/mol, 200 molecules have molecular mass 10^4 g/mol and 250 molecules have molecular mass 10^5 g/mol. Calculate number average molecular mass, wt average molecular mass and PDI.	[6]	CO1	L3
7	(a)	What are nanomaterials? Describe any 3 size dependent properties of nanomaterials.	[6]	CO1	L2
	(b)	Explain the synthesis of nanomaterials by sol-gel method with suitable example.	[6]	CO1	L2
8	(a)	Describe the production of electronic grade silicon by Czochralski (CZ) process.	[6]	CO1	L2
	(b)	Explain the principle and instrumentation of colorimetric sensors and its applications in the estimation of copper.	[6]	CO4	L2

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Solution of IAT 2 –Jan2025 for the course code BCHEE102

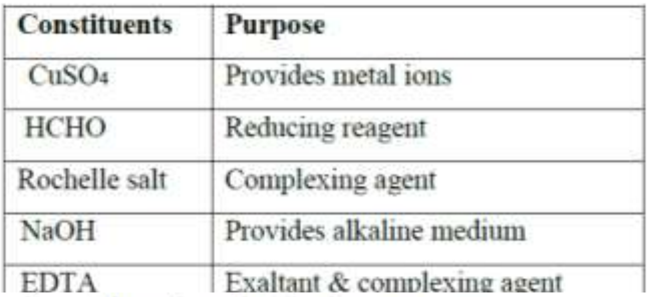
Answer 1a. Electroless plating is the controlled deposition of a continuous film of a metal from its salt solution on a catalytically active surface of the substrate by a suitable reducing agent, without the use of electrical energy.

Electroless-plating of Copper on PCB

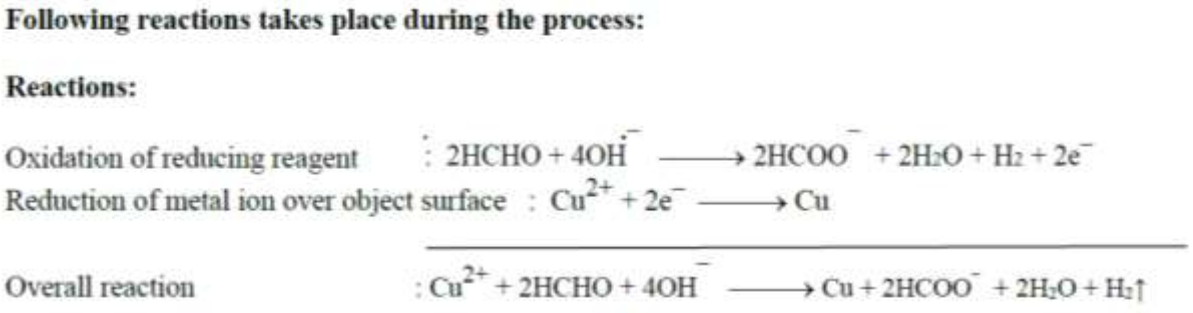
Activation of surface: The base of a printed circuit board is a plastic material such as epoxy or phenolic polymer or a glass fiber reinforced polymer composite. It is activated by treatment with acidified $SnCl_2$ and then with acidified $PdCl_2$ leads to deposition of Pd.

$SnCl_2 + PdCl_2 \rightarrow Pd + SnCl_4$

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



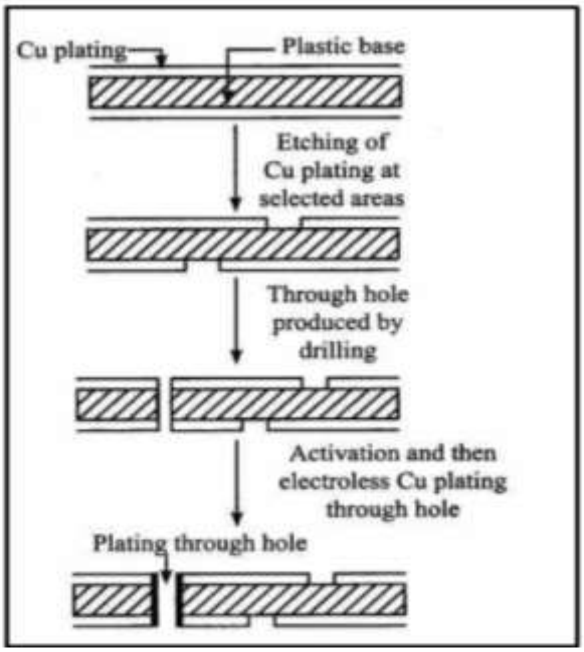
Following reactions takes place during the process:

Reactions:

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

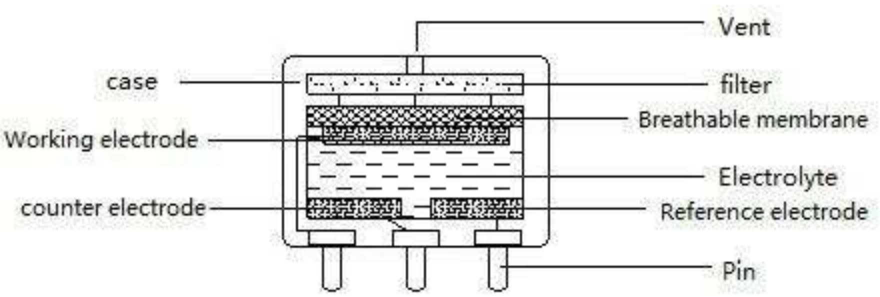
Reduction of metal ion over object surface : $Cu^{2+} + 2e^- \longrightarrow Cu$

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



Answer 1b. Electrochemical sensors are devices that give information about the composition of a system in real time by coupling a chemically selective layer (the recognition element) to an electrochemical transducer. **Electrochemical sensors** are made on the basis of ion conduction. According to the formation of their electrical characteristics, electrochemical sensors can be divided into potential sensors, conductivity sensors, electricity sensors, polarographic sensors, and electrolytic sensors. Electrochemical sensors are mainly used to analyze gas, liquid, or solid components dissolved in liquids, the measurement of liquid pH, conductivity, and oxidation-reduction potential.

Working Principle: The electrochemical sensor works by reacting with the measured gas and generating an electric signal proportional to the gas concentration. A typical electrochemical sensor consists of a sensing electrode and a counter electrode and is separated by a thin electrolytic layer.



The gas first reacts with the sensor through the tiny capillary-shaped opening, then the hydrophobic barrier layer, and finally reaches the electrode surface. Using this method can allow an appropriate amount of gas to react with the sensing electrode to form a sufficient electrical signal while preventing electrolytes from leaking out of the sensor. The electrochemical sensor contains the following main components:

a) **Breathable membrane** (also called hydrophobic membrane): The breathable membrane is used to cover the sensing (catalytic) electrode, and in some cases, it is used to control the molecular weight of the gas reaching the electrode surface.

b) **Electrode**: The electrode material should be a catalytic material that can perform semi-electrolytic reactions over a long period of time. Generally, electrodes are made of precious metals, such as platinum or gold, which react effectively with gas molecules after catalysis.

c) **Electrolyte**: The electrolyte must be able to carry out the electrolysis reaction and effectively transfer the ionic charge to the electrode.

d) **Filter**: Sometimes a scrubber filter is installed in front of the sensor to filter out unwanted gas. The most commonly used filter material is activated carbon.

Application of electrochemical sensors

i. Humidity sensor - The sensor used to measure relative humidity is coated with piezoelectric quartz crystal, which is made of small quartz crystal by photolithography and chemical etching technology.

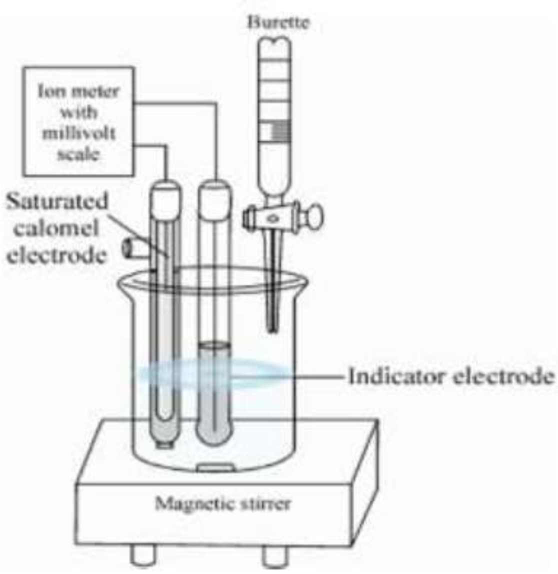
(ii) Detection of toxic gases like nitrogen oxide, hydrogen sulfide and sulfur dioxide with high selectivity and sensitivity

Answer 2a **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.

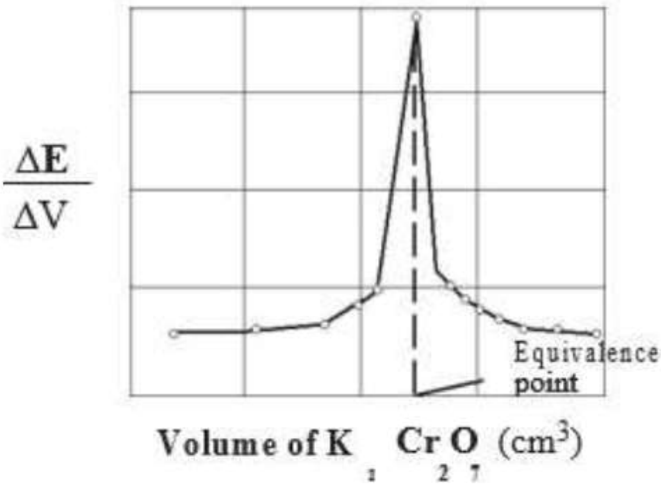
$$E = E^{o} + \frac{0.0591}{n} \log \left[M^{n+}\right]$$

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 $\Delta E / \Delta V$ 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 2b **Thermometric sensor** quantify the quantity of heat energy or even coldness produced by an item or system, allowing us to “sense” or detect any physical change in that temperature, generating an analog or digital output.

Classification:

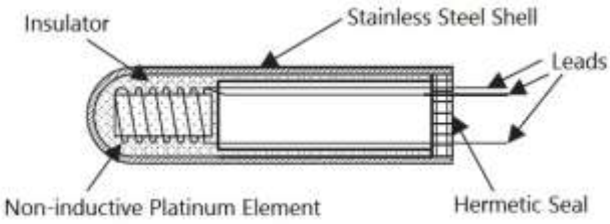
The temperature sensor is one of the most frequently used sensors, which is widely used in computers, automobiles, kitchen appliances, air conditioners, and household thermostats. The five common types of temperature sensors include,

i. Thermocouples,
ii. Thermistors,
iii. RTDs (Resistance Temperature Detectors),
iv. Analog thermometer IC, and
v. Digital thermometer IC.

Working principle:

Different types of temperature sensors have different working principles:

Resistance temperature detectors (RTD) measures the temperature according to the rule that the resistance of the conductor changes with temperature. The temperature-sensing element of resistance thermometers are commonly made of metal wires as platinum and copper, and at low temperatures, carbon, germanium, and rhodium iron are often used for the element. Because they are almost made of platinum, we often call them platinum resistance thermometers.



As the temperature changes, the resistance value of the metal also changes. And for different metals, the resistance value changes differently with the temperature, which can be directly used as the output signal.

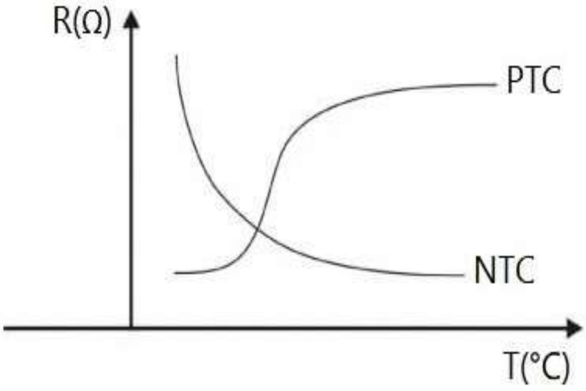
Resistance changes in 2 different ways:

Positive temperature coefficient

- temperature increases & resistance increases
- Temperature decreases & resistance decreases

Negative temperature coefficient

- temperature increases &resistance decreases
- Temperature decreases &resistance increases



Application:

1. Sensing Application - The thermal conversion method of temperature sensors is often used to measure physical quantities, such as flow rate, radiation, gas pressure and type, humidity, thermochemical reaction, etc.
2. Biomedical Domain - Special temperature sensors are often applied for biomedical applications. These temperature sensors have low power consumption, long-term stability, and high reliability, with an accuracy of less than 0.1℃ between 32℃ C and 44℃
3. Industrial Application - Integrated temperature sensors can be applied in automation and microbe thermal detection.
4. Consumer Products - Many low-cost integrated temperature sensors and transmitters have been used in consumer products such as washing machines, refrigerators, and air conditioners

Answer 3a 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

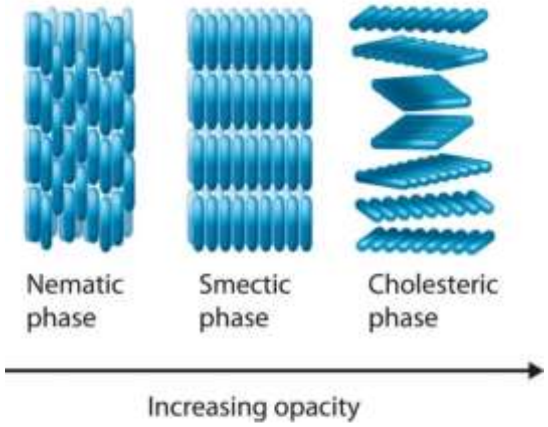
Thermotropic phases are those that occur in a certain temperature range. If the temperature is too high, the thermal motion may destroy the ordering in the LC phase and an isotropic liquid phase will occur. Ex: Cholesteryl benzoate, p-azoxy anisole etc. These have been classified into the following types.

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 240C 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.

Answer 3b. 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

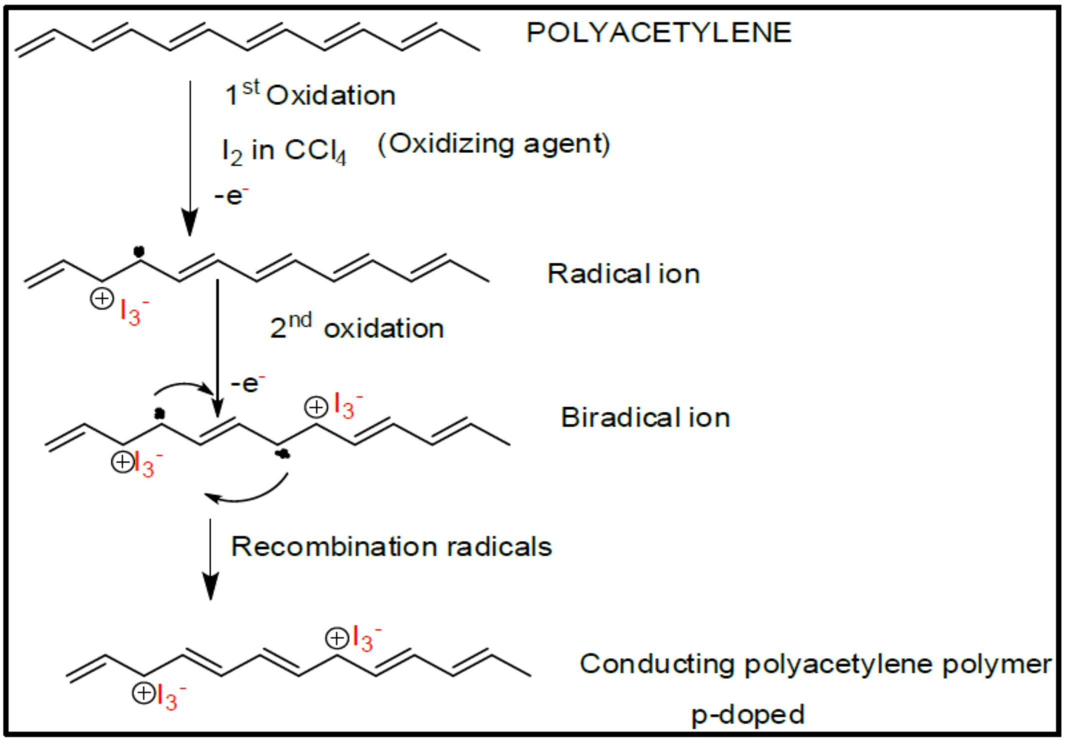
1. To build digital displays in TV screens, cell phones, PDAs, monitors, car radios, digital cameras.
2. OLEDs have wide applications in lightning
3. It is used in watches.
4. OLEDs have replaced CRTs (Cathode Ray Tubes) or LCDs (Liquid Crystal Display).

Answer 4a. Polymers which can conduct electricity are called conducting polymers.

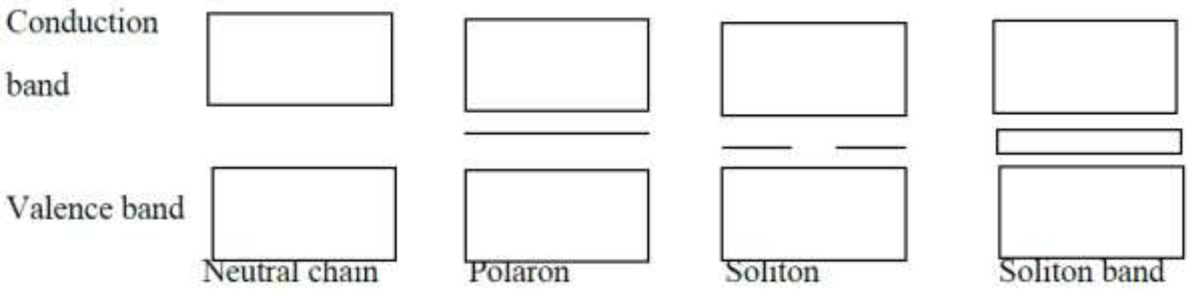
Mechanism of conduction in polyacetylene:

(i) By Oxidative doping (p-doping): In this process, π-back bone of polymer is partially oxidized using a suitable oxidizing agent such as I_2 in CCl_4. The removal of an electron from the polymer π-back bone leads to the formation of delocalized radical ion called polaron. A second oxidation of chain containing polaron produces bipolaron which on radical recombination yields two charge carries on each chain. The positive charge sites on the polymer chain are compensated by anion I_3^- formed by the oxidizing agent during doping. The delocalized positive charges on the polymer chain are mobile, not the dopant anions. Thus these delocalized positive charges are current carriers for conduction. These charges must move from chain to chain as well as along the chain for bulk conduction .

(v) On doping polyacetylene using I_2 in CCl_4, the conductivity increases from 10^{-5} S cm^{-1} to 10^{3}-10^{5} S cm^{-1}.



If polyacetylene is heavily doped, polarons form pairs called solitons. In polyacetylenes the solitons are delocalized over 12 carbon atoms. Due to the formation of soliton, a new localized electronic state appears in the middle of the energy gap. When the doping is high, several charged solitons form soliton band. This band can later merge with edges of valence and conduction bands thus exhibiting conductivity.



Application of polyacetylene: .
The most extensively studied and is widely investigated computationally and experimentally for use in electronic devices such as light-emitting diodes, water purification devices, hydrogen storage, and biosensors.

Answer 4b. Graphene Oxide

- Graphene oxide (GO) 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 sp2 and sp3 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:

Graphene oxide (GO) is synthesized using the Hummers' method by oxidizing graphite with sulfuric acid (H_2SO_4) and potassium permanganate ($KMnO_4$). The process involves several steps, including:

1. Dissolving sodium nitrate: Dissolve sodium nitrate ($NaNO_3$) in sulfuric acid
2. Adding graphite: Add graphite to the sulfuric acid and sodium nitrate solution
3. Adding potassium permanganate: Add potassium permanganate to the solution
4. Heating: Heat the solution to a higher temperature
5. Adding water and hydrogen peroxide: Add water and hydrogen peroxide to the solution
6. Adding hydrochloric acid: Add hydrochloric acid to the solution
7. Washing and filtering: Wash and filter the solution to obtain graphene oxide powder

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.

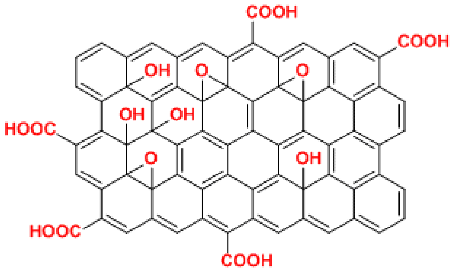
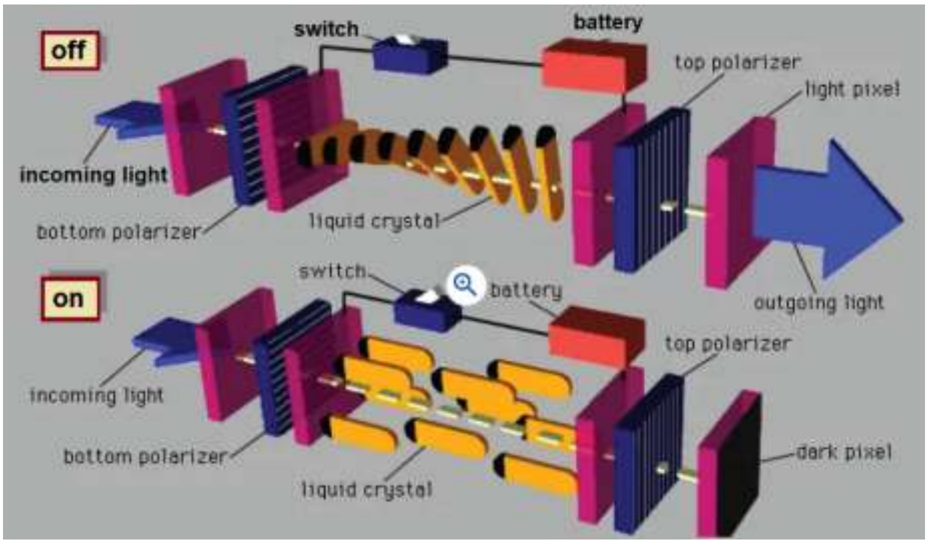


Figure: **Graphene Oxide**

Answer 5a (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 5b. 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

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:

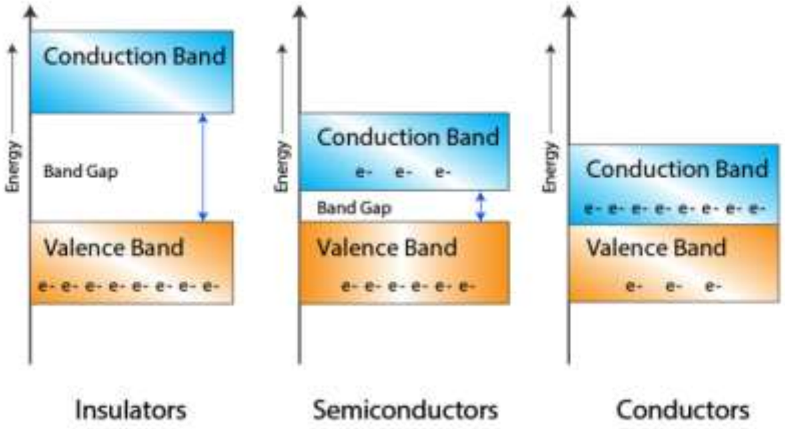
- **Biosensors:** High sensitivity towards the target molecules, good electron transferability, a larger surface area for adsorption and being highly electrocatalytic towards the oxidation of small molecules like viruses, proteins and nucleic acids, glucose, hydrogen peroxide, dopamine, and cortisol 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**

Answer 6a. **Conductors** are the materials or substances which allow electricity to flow through them. They conduct electricity because they allow electrons to flow easily inside them from atom to atom. Also, conductors allow the transmission of heat or light from one source to another. Example: metals (Fe, Cu etc)

A **semiconductor** is a material which has an electrical conductivity value falling between that of a conductor, such as copper, and an insulator, such as glass. Its resistivity falls as its temperature rises; metals behave in the opposite way. Its conducting properties may be altered in useful ways by introducing impurities ("doping") into the crystal structure. Example Silicon, Germanium

Insulators are the materials or substances which resist or don’t allow the current to flow through them. In general, they are solid in nature. Also, insulators are finding use in a variety of systems. As they do not allow the flow of heat. The property which makes insulators different from conductors is its resistivity. Example: Dry wood, glass, rubber, ceramic, dry cotton, etc



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.

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.

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.

Answer 6b. Solution:

Number average molecular weight Mn = $\frac{N_1M_1 + N_2M_2 + N_3M_3}{N_1 + N_2 + N_3}$

= $\frac{(100 \text{ x } 1000) + (200 \text{ x } 10000) + (250 \text{ x } 100000)}{100+200+250}$

= 49272.7 g/mol

Weight average molecular weight = $\frac{N_1M_1^2 + N_2M_2^2 + N_3M_3^2}{N_1M_1 + N_2M_2 + N_3M_3}$

= $\frac{(100 \text{ x } 1000 \text{ x } 1000) + (200 \text{ x } 10000 \text{ x } 10000) + (250 \text{ x } 100000 \text{ x } 100000)}{(100 \times 1000) + (200 \times 10000) + (250 \times 100000)}$

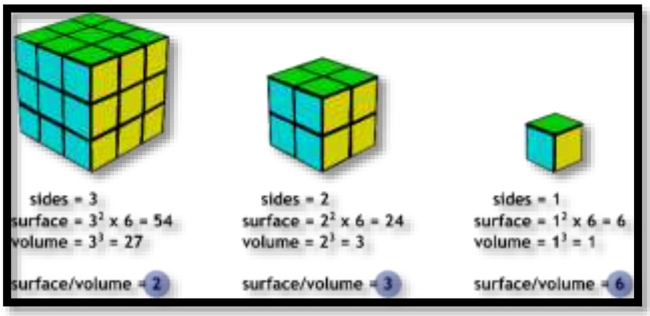
= 92992.61 g/mol

PDI: Mw/Mn = 92992.61/49272.7 = 1.88

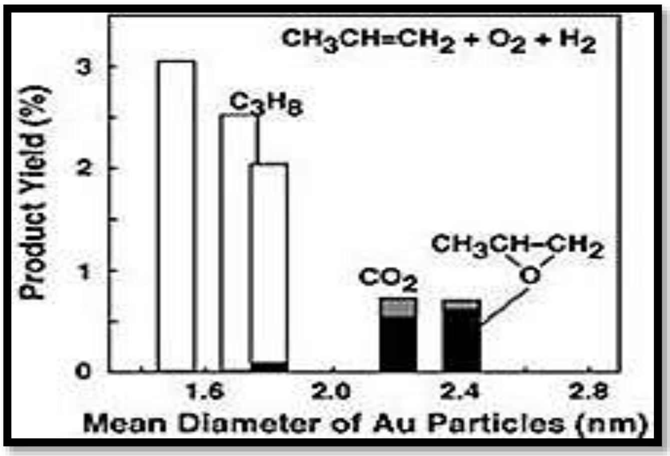
Answer 7a. Size-dependent properties

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.

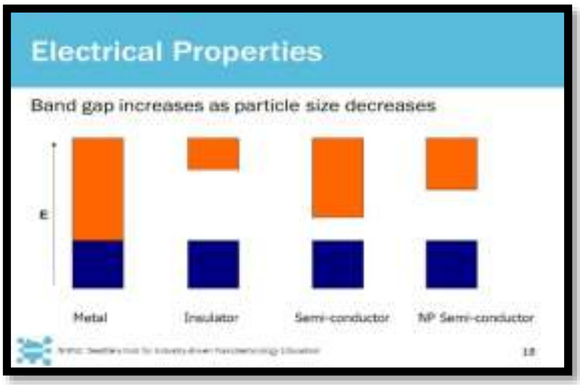
The ratio of surface area to volume of a material is given by *area*/*volume* = 4πr2/ 4/3 πr3 = 3/r



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.



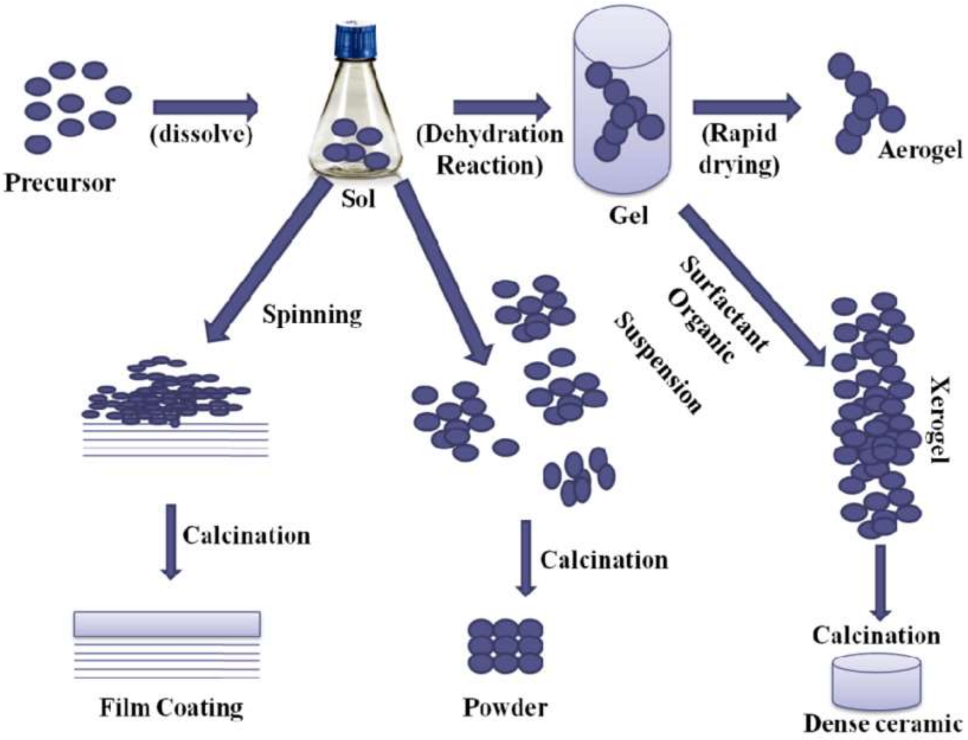
3) Conducting properties: In bulk metals, the valence and conduction bands overlap, while in metal nanoparticles there is a gap between these bands. The gap observed in metal nanoparticles can be similar in size to that seen in semiconductors (< 2 eV) or even insulators (> 2 eV). This results in a metal 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

Answer 7b: Nanomaterials are materials with at least one dimension measuring 100 nanometers or less. They can be made from a variety of elements, including carbon, silver, and titanium. Nanomaterials can be found in nature, or they can be engineered.

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 + H2O ----------------- ► 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.

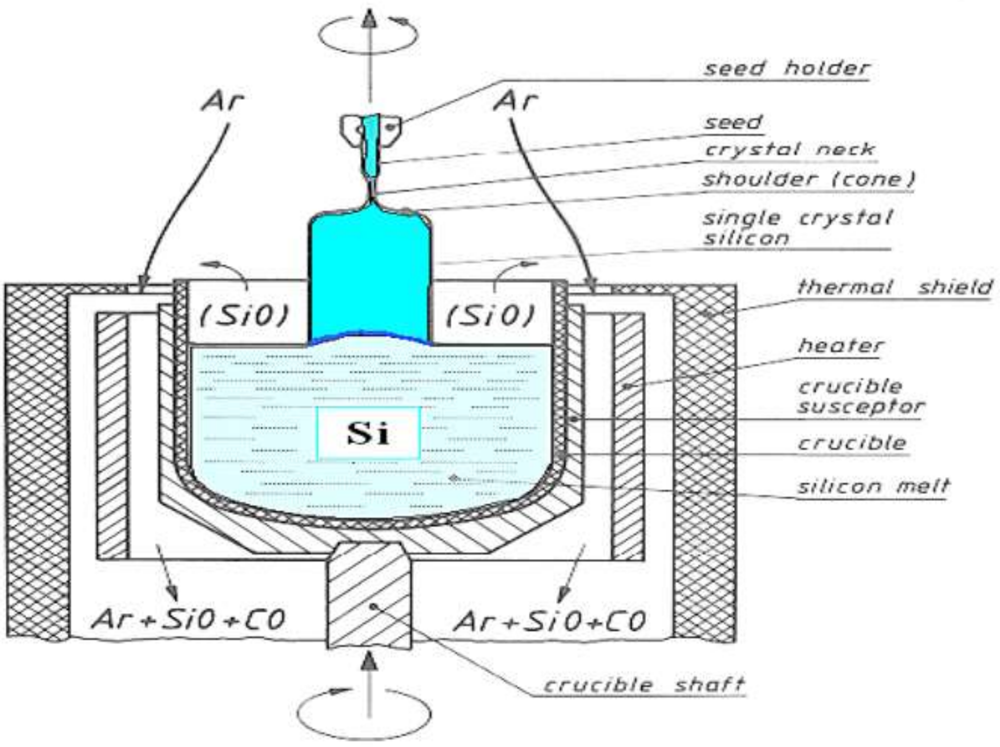
Step 5: Dehydration, during which surface-bound M-OH groups are removed. This is normally achieved by calcination of the monolith at temperatures up to 800 0 C.

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: 8a



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 8b

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 **I_0** passes through a solution, a part of the incident light is relected (**I_r**), a part is absorbed (**I_a**) and rest of the light is transmitted (**I_t**)

Thus, **$I_0 = I_r + I_a + I_t$**

In colorimeter, **I_r** is eliminated. For this purpose, the amount of light relected (**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.

$A = \varepsilon c t$

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

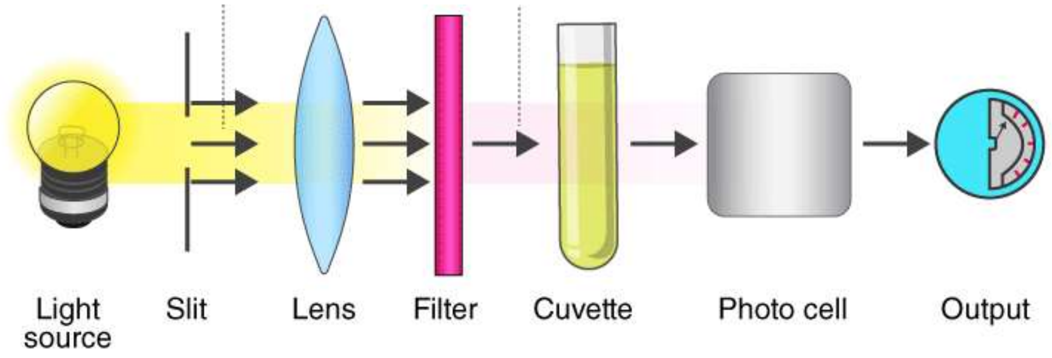
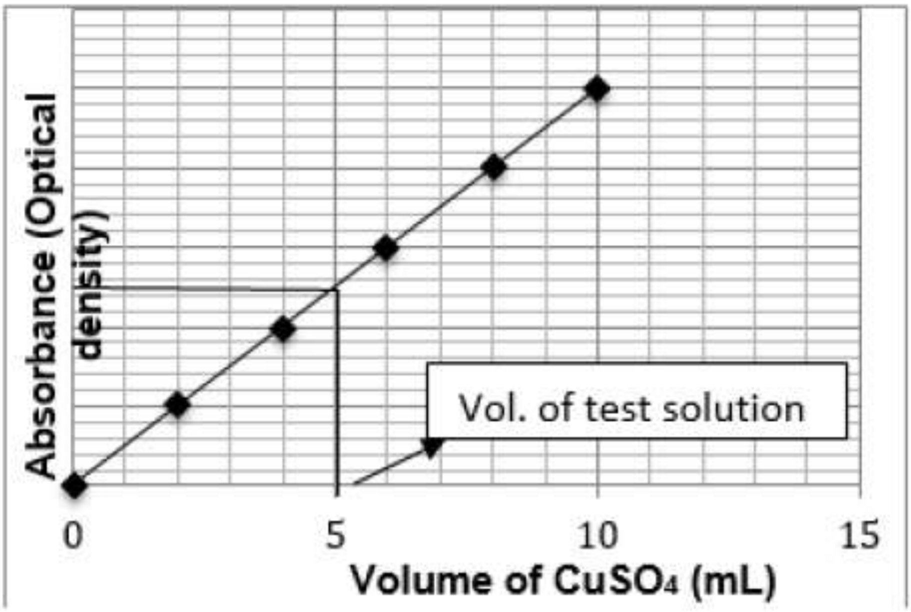


Fig: Schematic layout of colorimeter

Application: Colorimetric estimation of Cu in $CuSO_4$. Draw out 2, 4, 6, 8, and 10 ml cm$_3$ of the Copper sulphate solution into 50cm$_3$ volumetric flask. Add 5cm$_3$ of ammonia solution to each of them and dilute upto the mark with distilled water and mix well. Prepare a blank solution by diluting 5cm^3 of ammonia solution in 50cm^3 volumetric flasks. For test solution add 5ml of NH_3 and make up to the mark. Measure the absorbance of each of these against blank solution at 620 nm. Plot a graph of absorbance (OD) against volume of copper sulphate solution and determine the volume of copper sulphate solution in the test sample as shown in the figure and find the amount of copper present in it.


Absorbance (Optical density)
Vol. of test solution
0
5
10
15
Volume of CuSO4 (mL)

……………………….………..**END**……………………………………..……………