CBCS SCHEME

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1BCHEE102

First Semester B.E./B.Tech. Degree Examination, Dec.2025/Jan.2026
Applied Chemistry for Emerging Electronics and Futuristic Devices (EEE, ECE)

Time: 3 hrs. Max. Marks: 100

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

		Module – 1	M	L	C
Q.1	a.	Distinguish between organic and inorganic semiconductors.	6	L3	CO1
	b.	Discuss construction and working principle of Poly (3-hexylthiophene) (P3HT) as a donor and Phenyl-C61-butyric acid methyl ester (PCBM) as an acceptor.	7	L2	CO1
	c.	Explain working principle and applications of Micro-electromechanical systems (MEMS)-based energy harvesters.	7	L2	CO1
		OR			
Q.2	a.	What is battery? Explain the battery characteristics: capacity, power density, shelf life & cycle life.	6	L2	CO1
	b.	Explain construction and working of ultra-small asymmetric super capacitor and its applications in IoT/wearable devices.	7	L2	CO1
	c.	Discuss construction, working principle and advantages of solar photovoltaic cell (PV cell).	7	L2	CO1
		Module – 2			
Q.3	a.	Explain the size dependent properties: catalytic, optical properties and electrical conductivity.	6	L2	CO2
	b.	Explain synthesis of silicon based Quantum Dots by sol gel method and Cd-Se Quantum Dots by hot injection method.	7	L2	CO2
	c.	Discuss synthesis and properties of chitosan-carbon quantum dots hydrogel and its applications in next-generation flexible and wearable electronics.	7	L2	CO2
		OR			
Q.4	a.	What are Quantum dots (QDs)? Explain optical and electronic properties of quantum dots (QDs).	6	L2	CO2
	b.	Explain synthesis of TiO_2 nano particles by sol-gel method and its uses in sensor applications.	7	L2	CO2
	c.	Discuss synthesis and properties of Graphene Quantum Dots using citric acid method and its applications in emerging electronics.	7	L2	CO2

		Module – 3			
Q.5	**a.**	Explain synthesis and conduction mechanism of polyaniline.	**6**	**L2**	**CO3**
	b.	A sample of polymer contains 20 molecules of molecular mass 3000, 30 molecules of molecular mass 5000 and the remaining molecules of molecular mass 7000.Calculate number average, weight average molecular mass and poly dispersity index.	**7**	**L3**	**CO3**
	c.	Discuss working principle of lithography for micro-patterned copper deposition.	**7**	**L2**	**CO3**
		OR			
Q.6	**a.**	What are polymer composite? Explain synthesis and properties of epoxy resin magnetite (Fe_3O_4) composite from ultra-sonication method.	**6**	**L2**	**CO3**
	b.	Discuss the synthesis and properties of Kevlar Fiber Reinforced Polymer (KFRP) for smart electronic devices applications.	**7**	**L2**	**CO3**
	c.	Explain the synthesis, properties of PDMS (Polydimethylsiloxane) and its uses in e-skin (electronic skin).	**7**	**L2**	**CO3**
		Module – 4			
Q.7	**a.**	Discuss types of electrodes with examples.	**6**	**L2**	**CO4**
	b.	Discuss instrumentation and application of potentiometric sensor for the estimation of iron in steel.	**7**	**L2**	**CO4**
	c.	What is concentration cell? A zinc concentration cell is obtained by combining two zinc electrodes of concentrations 0.2M and 0.4 M immersed in zinc sulphate solution at 298K. Write the cell reactions and calculate EMF of the cell.	**7**	**L3**	**CO4**
		OR			
Q.8	**a.**	Discuss construction and working of glass electrode.	**6**	**L2**	**CO4**
	b.	Describe instrumentation and application of colorimetric sensor in the estimation of copper in PCBs with diagram.	**7**	**L2**	**CO4**
	c.	Explain the principle and instrumentation of conductometric sensor and its application in the estimation of acid mixture.	**7**	**L2**	**CO4**
		Module – 5			
Q.9	**a.**	What is e-waste? explain the need for e-waste management.	**6**	**L2**	**CO4**
	b.	Apply the principles of electroplating to explain the process of chromium plating used for hard and decorative coatings.	**7**	**L2**	**CO4**
	c.	What is CPR? A thick steel sheet of area 80 $inch^2$ is exposed to moist air. After 6 months it was found to experience a weight loss of 340 g due to corrosion, if the density of the steel is 7.9 g/cm^3. Calculate the corrosion penetration rate in mpy and mmpy (Given K = 534 in mpy and 87.6 mmpy).	**7**	**L3**	**CO4**

		OR			
Q.10	**a.**	What is metal finishing? Explain technological importance of metal finishing.	**6**	**L2**	**CO4**
	b.	Discuss electrochemical theory of corrosion taking iron as an example.	**7**	**L2**	**CO4**
	c.	Apply the concept of galvanization to prevent corrosion in steel structures exposed to marine environments. Justify your choice with appropriate chemical reasoning.	**7**	**L3**	**CO4**

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Sub:	Applied Chemistry for Emerging Electronics and Futuristics Device					Sub Code:	1BCHEE102	Branch: ECE
Date:		Duration:	180 min's	Max Marks:	100	Sem / Sec:	I	

Solutions for VTU question paper

Module-1

1 (a). Distinguish between organic and inorganic semiconductors

Feature	Organic Semiconductors	Inorganic Semiconductors
Composition	Made of carbon-based molecules or polymers with conjugated π-bonds.	Made of pure elements or compounds like Si, Ge, GaAs.
Structure & Bonding	Molecular or polymeric, with van der Waals interactions between molecules.	Crystalline lattice, strong covalent or ionic bonding.
Processing & Cost	Can be solution-processed or printed, often low-cost fabrication.	Requires high-temperature, complex crystal growth, expensive fabrication.
Flexibility	Highly flexible, suitable for bendable devices.	Rigid and brittle, not suitable for flexible electronics.
Mobility	Moderate to low charge carrier mobility (10^{-3} – 1 cm²/V·s).	High mobility (100–1500 cm²/V·s), efficient charge transport.
Stability	Lower chemical and thermal stability, sensitive to air/light.	High chemical and thermal stability, durable in ambient conditions.
Applications	Flexible displays, OLEDs, OFETs, organic solar cells.	Traditional electronics: transistors, diodes, solar cells, microchips.
Energy Band Gap	Generally larger band gaps (~1.5–3 eV), tunable via chemical modification.	Typically smaller band gaps (~0.6–1.5 eV), fixed by crystal structure.
Environmental Impact	Often eco-friendly and biodegradable depending on material.	Can be toxic or non-biodegradable, environmental disposal is a concern.

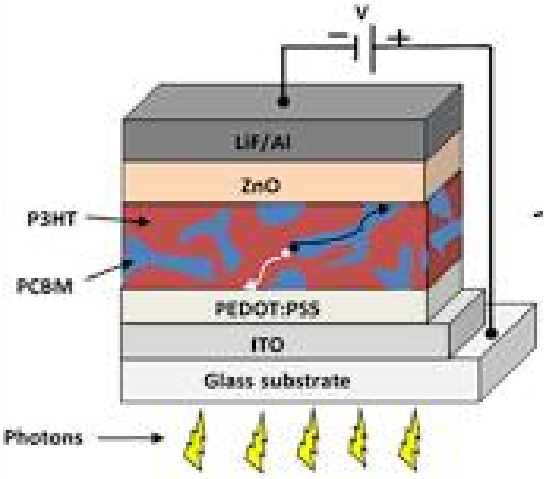
1(b) Discuss construction and working principle of P3HT as donor and PCBM as an acceptor?

Organic photovoltaics (OPVs) are solar cells made from organic semiconducting materials (conjugated polymers and fullerene derivatives). They are lightweight, flexible, low-cost, and can be fabricated using printing/coating techniques. A common bulk heterojunction (BHJ) OPV uses: Donor material: Poly(3-hexylthiophene) (P3HT) – a conjugated polymer. Acceptor material:Phenyl-C61-butyric acid methyl ester (PCBM) – a fullerene derivative. The P3HT:PCBM blend is one of the most studied systems in OPV research.

Construction of P3HT:PCBM Organic Solar Cell

A typical device structure is:

1. Substrate– Glass or flexible plastic.
2. Transparent Electrode (Anode) – Indium Tin Oxide (ITO).
3. Hole Transport Layer (HTL) – PEDOT:PSS (poly(3,4-ethylenedioxythiophene) : polystyrene sulfonate).
4. Active Layer– Blend of P3HT (donor) + PCBM (acceptor) (bulk heterojunction).
5. Electron Transport Layer (ETL) – Often LiF, TiO_2, or ZnO.
6. Cathode– Aluminum (Al) or Silver (Ag).



Working Principle

1. Light Absorption: The donor polymer P3HT absorbs sunlight, generating excitons (bound electron-hole pairs) due to photon energy.
2. Exciton Diffusion: Excitons diffuse to the donor–acceptor interface between P3HT (donor) and PCBM (acceptor) within their diffusion length (~10–20 nm).
3. Charge Separation: At the interface, the electron transfers from P3HT to PCBM, leaving the hole in P3HT. This separation converts excitons into free charge carriers.
4. Charge Transport: Electrons move through PCBM to the cathode, while holes move through P3HT to the anode, driven by built-in electric fields.
5. Charge Collection: Charges are collected at the electrodes, generating a photocurrent, which can be

extracted to power an external circuit.

Applications

1. Flexible Solar Panels: P3HT:PCBM OPVs can be fabricated on flexible substrates, enabling lightweight, bendable solar panels.
2. Building-Integrated Photovoltaics (BIPV): These OPVs can be integrated into windows or facades to generate electricity while maintaining transparency or aesthetic design.

1(c) Explain working principle and applications of Micro-electromechanical systems (MEMS)-based energy harvesters.

Micro Electromechanical Systems (MEMS)-based energy harvesters are miniature devices that convert ambient mechanical energy (such as vibrations, motion, or pressure) into electrical energy using microfabricated components. They are designed to power small electronic devices or sensors without external batteries, making them ideal for IoT and wireless sensor networks.

The three main types of MEMS-based energy harvesters are:

1. Piezoelectric Energy Harvesters – Convert mechanical vibrations or stress into electrical energy using piezoelectric materials (e.g., PZT, ZnO).
2. Electromagnetic Energy Harvesters – Generate electricity through electromagnetic induction when a magnet and coil move relative to each other.
3. Electrostatic (Capacitive) Energy Harvesters – Produce electrical energy by changing the capacitance between moving microelectrode plates during vibrations.

Construction:

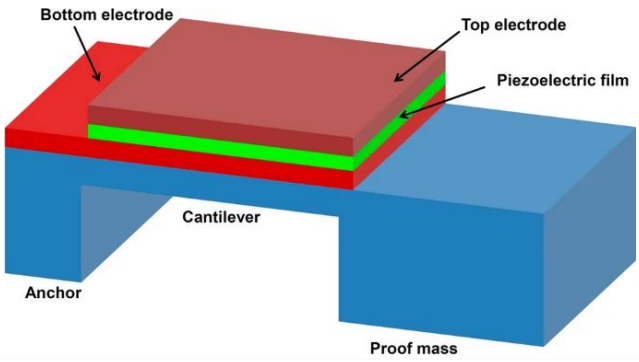
A **piezoelectric energy harvester** consists of:

A **piezoelectric material** (like PZT Lead Zirconate Titanate, with the chemical formula $Pb(Zr_xTi_{1-x})O_3$, ZnO, or PVDF) coated on a **substrate or cantilever beam which is made up off Si or SiO_2**.

A **proof mass** attached at the free end to enhance vibration response.

Electrodes (Pt films about 100 nm) on both sides of the piezoelectric layer to collect generated charge.

It is usually fabricated using **MEMS techniques** for compact size and high sensitivity.



Piezoelectric Energy Harvesters Working Mechanism:

1. When a piezoelectric MEMS device is subjected to mechanical vibration or acceleration, the cantilever structure undergoes bending, which induces mechanical strain in the attached piezoelectric layer.
2. Because of the non-centrosymmetric crystal structure of the piezoelectric material, this strain causes a displacement of positive and negative charge centers within the crystal lattice.
3. Consequently, charges accumulate on the top and bottom electrodes, generating a voltage (potential difference) across them.
4. This voltage can be harnessed by an external circuit, either to store energy in capacitors or batteries or to directly power small electronic devices such as sensors or wearable electronics.
5. Piezoelectric MEMS energy harvesters thus efficiently convert mechanical energy into usable electrical energy at the microscale.

Applications of MEMS-Based Energy Harvesters:

1. Wireless Sensor Networks (WSNs): Powering sensors in structural health monitoring, agriculture, and industrial automation. Eliminates the need for battery replacement in remote locations.
2. Wearable Electronics: Harvesting energy from body movements to power health-monitoring devices. Examples: Fitness trackers, smartwatches, medical implants.
3. Internet of Things (IoT): Self-sustaining sensors and devices in smart homes and cities. Enhances deployment flexibility and reduces maintenance.
4. Biomedical Devices: Powering pacemakers or drug delivery systems using body motion or temperature differences. Reduces or eliminates the need for surgical battery replacement.
5. Industrial Monitoring: Autonomous sensors on rotating machinery, pipelines, or vehicles. Increases safety and system reliability with real-time data.

2(a). What is battery? Explain the battery characteristics: capacity, power density, shelf life and cycle life?

A battery is an electrochemical device that converts chemical energy into electrical energy through redox reactions. It consists of one or more electrochemical cells, each having two electrodes (anode & cathode) and an electrolyte. Batteries are widely used in portable electronics, electric vehicles, renewable energy storage, and military applications.

Characteristics of Batteries

1. **Capacity (Ah or mAh):** Measure of total charge a battery can store. Indicates how long a battery can supply current before depletion.
2. **Power Density (W/kg or W/L):** Indicates how quickly energy can be delivered. High power density is needed in applications like EV acceleration.

3. **Cell Balancing**: In multi-cell packs (e.g., Li-ion in EVs), individual cells may charge/discharge unevenly. Balancing ensures equal voltage across cells to improve performance and safety.

4. **Shelf Life of a Battery:** The shelf life refers to the amount of time a battery can be stored without being used before it begins to degrade. It's the period during which the battery retains a significant portion of its capacity while not in active use.

Typical Shelf Life: Lithium-ion: 2-3 years (with proper storage), Lead-acid: 1-2 years, Nickel-metal hydride (NiMH): 3-5 years, Alkaline (non-rechargeable): 5-10 years

5.Cycle Life of a Battery: The cycle life refers to the number of charge and discharge cycles a battery can go through before its capacity drops to a specified level (usually 80% of its original capacity). A "cycle" is defined as one full discharge followed by one full recharge.

Lithium-ion: 500-1,500 cycles (depending on factors like DoD and charging practices)

Lead-acid: 300-500 cycles (depending on depth of discharge)

Nickel-metal hydride (NiMH): 500-1,000 cycles

Lithium iron phosphate (LiFePO4): 2,000-5,000 cycles (known for a long cycle life)

2(b) Explain the construction and working mechanism of ultra-small asymmetric super capacitors applications in IoT/wearable devices?

Ultra-Small Asymmetric Supercapacitor: An ultra-small asymmetric supercapacitor (ASC) is a miniaturized energy storage device that combines two different types of electrode materials: One behaving like a battery electrode (faradaic, pseudocapacitive, high capacity). The other is like a capacitor electrode (nonfaradiac, electrostatic, high power). This hybrid design allows higher energy density than traditional capacitors and better power & cycle life than batteries. They are particularly suitable for IoT, wearable electronics, flexible sensors, and implantable devices due to their tiny size, fast charging, flexibility, and safety.

Construction

Anode (EDLC Electrode): high surface area, good electrical conductive materials like activated carbon, CNTs, graphene

Cathode (Pseudocapacitive Electrode): metal oxides like MnO_2, RuO_2

Electrolyte: contains positive and negative ions which can freely movable between electrodes like KOH, H_2SO_4 and ionic liquids

Separator: A thin porous polymer film (cellulose paper). Prevents electrical contact between electrodes but allows ion flow.

Current Collectors: Copper foil or aluminum foil (both sides).

Encapsulation: Protective flexible packaging to ensure safety, biocompatibility, and durability.

Working Principle:

During Discharging (energy release):

Activated carbon stores charge via an electric double layer, and during discharge electrons flow out while K^+ ions diffuse back into the electrolyte to maintain neutrality. MnO_2 gets reduced by

accepting electrons from the external circuit, and simultaneously K^+ ions insert into its lattice. Thus, AC releases stored charge electrostatically while MnO_2 undergoes redox with ion insertion to balance charge.

At the anode (Activated Carbon): $C^- . K^+_{(adsorbed)} \rightarrow C + e- + K^+_{(solution)}$

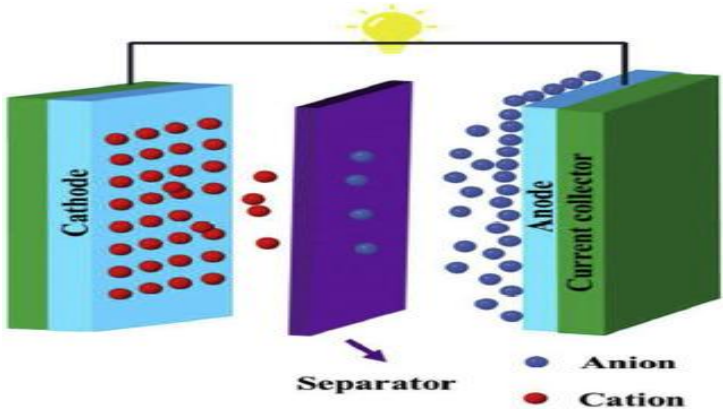
Reduction reaction: $MnO_2 + K^+ + e- \rightarrow KMnO_2$

During Charging (energy storage):

Electrons are withdrawn by the power source, causing $KMnO_2$ to undergo oxidation and release the inserted K^+ ions back into the electrolyte. The AC electrode receives electrons at the negative terminal, and cations from the electrolyte migrate toward its negatively charged surface to maintain charge neutrality and form an electric double layer.

At the cathode: $KMnO_2 \rightarrow MnO_2 + K^+ + e-$

At the anode (Activated Carbon): $C + e- + K^+_{(solution)} \rightarrow C^- . K^+_{(adsorbed)}$



Applications of ultra-small asymmetric supercapacitor in IoT & Wearable Devices

Ultra-small asymmetric supercapacitors (ASCs) are emerging as next-generation energy storage devices for powering IoT and wearable devices due to their high-power density, fast charging, long cycle life, and miniaturized size.

In IoT (Internet of Things):

1. Wireless Sensor Networks (WSNs): Provide stable, rapid power for intermittently operating IoT sensors. Enable energy harvesting from solar, vibration, or RF sources to support continuous IoT node operation.

2. Smart Home Devices: Used in ultra-small sensors (temperature, humidity, motion, gas). Quick recharge allows reliable operation of always-on IoT devices.

Applications in Wearable Devices

1. Smart Wearables: Powering smartwatches, fitness trackers, smart rings, AR/VR glasses. Provide quick charge and discharge to support wireless communication (Bluetooth, Wi-Fi).

2. Electronic Textiles (E-textiles): Embedded into fabrics as flexible energy storage units. Useful for military uniforms, smart clothing, and fashion tech with LEDs or sensors.

2(c) Discuss construction, working principal and advantages of solar photovoltaic cell (PV cell).

A Photovoltaic (PV) cell, also known as a solar cell is a device that converts sunlight (solar energy) directly into electricity using the photovoltaic effect. It is the basic building block of solar panels used in solar energy systems.

Construction

1. Semiconductor Layers:

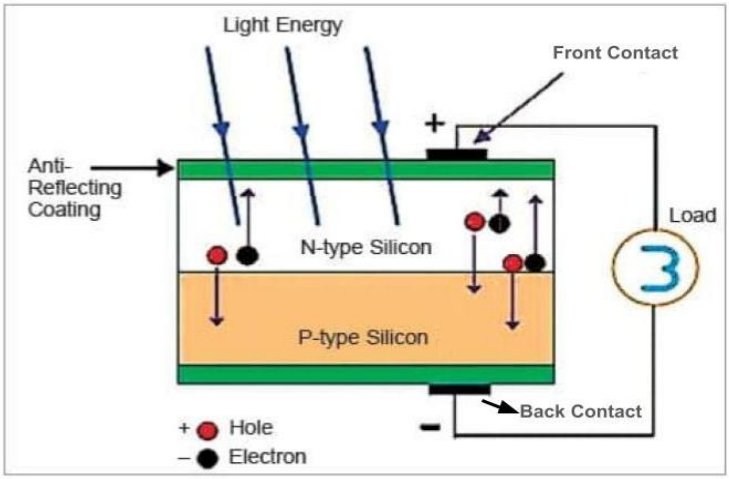
n-type layer: Doped with phosphorus to add extra electrons as upper layer

p-type layer: Doped with boron to create "holes" (positive charge carriers) as bottom layer and these layers form a p-n junction.

2. Front Contact: A thin metal grid on the top surface that allows sunlight to pass through while conducting electricity.

3. Anti-reflective Coating: Reduces reflection and allows more sunlight to be absorbed (TiO_2).

4. Back Contact: A conductive metal layer that completes the electrical circuit.



Working Principle (Photovoltaic Effect):

1. **Diffusion of electrons:** When p-type and n-type silicon layers are joined, electrons from the n-side diffuse into the p-side which initiates the process.

2. **Formation of charge shortage zone and electron–hole pairs:** This diffusion creates a depletion (charge-shortage) region with a built-in electric field. When sunlight (photons) with energy $E=hc/\lambda \geq Eg$ (band gap energy) strikes the junction, electrons in Si are excited from the valence band to the conduction band, generating electron–hole pairs.

3. **Movement of charge carriers and current generation:** The internal electric field drives electrons toward the n-side and holes toward the p-side. When an external load is connected, electrons flow through the circuit to recombine with holes on the p-side, producing electric current.

Advantages

1. Renewable Source: Utilizes abundant solar energy.

2. Environmentally Friendly: No emissions or pollution.

3. Low Operating Cost: Minimal maintenance required.

4. Scalable: Used in small devices to large power plants.

5. Silent Operation: No moving parts, noise-free.

Module–2

3 (a). Explain the size dependant properties: catalytic, optical properties and electrical conductivity?

A. **Catalytic Properties**

Catalysis relies heavily on the number and accessibility of active sites. Nanosized catalysts expose a greater number of surface atoms and often have unsaturated coordination or defect sites that enhance their activity.

Examples: Gold nanoparticles (Au NPs): Bulk gold is inert, but Au nanoparticles (<5 nm) become highly catalytic. For instance, Au NPs supported on TiO_2 catalyze CO oxidation at low temperatures.

B. Optical Properties

Nanomaterials exhibit unique optical properties due to quantum confinement, where reducing particle size alters electronic band gaps. Smaller nanoparticles show blue-shifted absorption and enhanced photoluminescence.

Example: CdSe quantum dots change color from red to blue as size decreases, while gold nanoparticles shift plasmon resonance from red to violet with size reduction.

C. Electrical Properties

At the nanoscale, electrons are confined within extremely small dimensions. This leads to quantum confinement effects that result in discrete energy levels (instead of continuous bands in bulk), size-dependent band gap variation and altered charge transport behavior.

Examples: Single-walled carbon nanotubes (SWCNTs): Depending on their chirality and diameter, they can behave as metallic or semiconducting, making them useful in nanoscale transistors and interconnects.

3 (b) Explain synthesis, properties of silicon based QDs by sol gel method and Cd-Se Quantum Dots by hot injection method.

Synthesis of Silicon Quantum Dots by Sol-Gel Method

The sol–gel method is one of the most versatile bottom-up approaches for synthesizing silicon quantum dots (SiQDs), owing to its ability to provide uniform particle size, high purity, and good control over surface chemistry.

1. **Hydrolysis of TEOS:** TEOS undergoes hydrolysis in the presence of water and an acid/base catalyst (commonly HCl or NH_4 OH), forming silanol (Si–OH) groups:

2. **Condensation Reaction**: Silanol groups condense through dehydration or alcohol elimination, leading to the formation of a Si–O–Si network (silica gel):

3. **Gelation and Aging**: A stable gel is formed, which undergoes aging to strengthen the silica network

and remove residual solvents and byproducts.

4. **Drying and Calcination**: The gel is dried and then annealed at high temperatures (e.g., 800–1100 °C) under an inert or reducing atmosphere (H_2 /Ar, N_2 , or forming gas). This thermal treatment reduces SiO_2 into crystalline SiQDs embedded in a silica matrix.

5. **Etching**: To extract freestanding SiQDs, selective chemical etching (commonly HF treatment) is employed to dissolve the surrounding silica matrix, leaving behind surface-functionalized SiQDs.

Step-by-step procedure for the synthesis of CdSe QDs using hot injection method

1. Preparation of Cadmium Precursor Complex: When CdO is used as precursor, it is dissolved in a fatty acid such as stearic acid (R–COOH) or oleic acid at high temperature to form cadmium stearate/oleate.

2. Formation of Selenium Precursor: Elemental selenium (Se) is insoluble in nonpolar solvents, so it is dissolved in trioctylphosphine (TOP) to make TOPSe under intert gas. This keeps selenium reactive and soluble until injection.

3. Hot Injection (Nucleation Step): At high temperature (≈ 280–320 °C), the selenium precursor (TOPSe) is swiftly injected into the hot cadmium complex solution. The reaction produces cadmium selenide (CdSe) nuclei and this step is very fast and undergoes an intense nucleation event, leading to burst nucleation.

4. Quench, purify and stabilize: Quench by cooling and adding a solvent/ligand (e.g., toluene + oleic acid). Purify by precipitation (ethanol/acetone) and centrifugation; redissolve in nonpolar solvent. Surface ligands ($RCOO^-$) cap QDs, stabilizing them: $CdSe{\cdot}(RCOO)_2$.

3 (c) Explain synthesis and properties of chitosan-carbon quantum dots hydrogel and its applications in next-generation flexible and wearable electronics.

Step-by-step synthesis of a chitosan–carbon-quantum-dot (CQD) hydrogel

1. **Make carbon quantum dots (CQDs):** Dissolve citric acid and urea in water, transfer to a Teflon-lined autoclave, hydrothermal 160–200 °C, 2–6 h. Cool and dialyze/filter to get CQDs (2–8 nm) with surface functionalization of –COOH/–OH/–NH_2

2. Prepare chitosan solution: Disperse chitosan powder in an acetic solution, such as glacial acetic acid to make it soluble and stir the mixture for several hours to obtain a homogenous, viscous solution which forms the basis of the hydrogel.

3. Disperse CQDs in chitosan: Carbon quantum dots (CQDs) can be dispersed in a chitosan solution, followed by adding glutaraldehyde as a crosslinker. The aldehyde groups react with amino groups of chitosan through Schiff-base formation (-C=N-), embedding CQDs within the hydrogel matrix. This yields a stable, fluorescent CQDs–chitosan hydrogel network.

4) Set, wash, and store: Allow gel to set (30–60 min), then wash with water to remove excess small molecules (acetic acid, TPP, by-products). Store hydrated; the gel shows blue/green fluorescence under

UV due to embedded CQDs.

Properties:

1. Biocompatible: Made from natural chitosan and non-toxic carbon dots, making it safe for drug delivery and wound healing.
2. Fluorescent: CQDs give strong blue/green photoluminescence under UV light, useful for imaging and sensing.
3. High Water Absorption: The porous 3D network absorbs large amounts of water, giving good swelling and tissue-like softness.
4. Antibacterial: Chitosan's natural antimicrobial action plus CQDs helps inhibit bacterial growth—ideal for wound dressings.

Applications

1. **Flexible Biosensors**: Used for glucose, lactate, and sweat sensing because the hydrogel absorbs body fluids and CQDs give clear fluorescence/electrochemical signals.
2. **Wearable Health Monitors**: Used in wearable patches to monitor heart rate, hydration, and stress due to their conductivity and skin-friendly nature.
3. **Smart Wound Dressings**: Detect infection (pH/bacteria) and support faster healing with chitosan's natural antibacterial properties.
4. **Stretchable Electrodes**: Work as soft, bendable electrodes for electronic skin and flexible circuits without losing conductivity.

4 (a) What are Quantum dots (QDs)? Explain optical and electronic properties of quantum dots (QDs).

Quantum dots (QDs) are tiny semiconductor nanocrystals that confine electrons in all three dimensions, g optical and electronic properties.

Optical and electronic properties of quantum dots

Quantum dots (QDs) exhibit remarkable optical and electronic properties due to quantum confinement—where charge carriers (electrons and holes) are confined in all three spatial dimensions.

Optical Properties

1. **Size-dependent emission:** The colour of light emitted by QDs changes with their size — smaller QDs emit blue light, and larger QDs emit red light.
2. **Narrow emission spectrum:** QDs emit very sharp and narrow peaks of light, giving pure and bright colours.
3. **Broad absorption spectrum:** They can absorb a wide range of wavelengths, making them good for solar cells and LEDs.
4. **High photoluminescence efficiency:** QDs convert absorbed light into emitted light very efficiently.
5. **Tunable band gap:** By changing the size or composition of QDs, their band gap can be adjusted

easily.

Electronic Properties

1. **Quantum Confinement Effect**: When the size of QDs becomes very small (below ~10 nm), the movement of electrons is restricted, which changes their energy levels.
2. **Discrete Energy Levels (Atom-like States):**
   Because of their tiny size, QDs show **separate (quantized) energy levels** instead of continuous bands, making them behave like artificial atoms.
3. **High Charge Carrier Mobility:** QDs can transfer electrons and holes efficiently due to their tunable surface and band structure, improving their electronic performance.
4. **Tunable Conductivity:** By changing size, shape, or surface ligands, the electrical conductivity of QDs can be increased or decreased as required.

4 (b) Explain synthesis of TiO2 nanoparticles by sol-gel method and its uses in sensor applications

The sol-gel method is a popular technique for synthesizing TiO_2 nanoparticles. It involves a series of chemical reactions, starting with the hydrolysis of a titanium precursor (metal alkoxides), followed by condensation to form a gel, and finally, calcination to obtain the desired TiO_2 nanoparticles. This method allows for the control of particle size, morphology, and crystallinity by adjusting various parameters.

1. Precursor Selection: Titanium tetraisopropoxide (TTIP) $Ti[OCH(CH_3)_2]_4$ or titanium butoxide $Ti(OBu)_4$ are commonly used precursors.

2. Hydrolysis (sol formation): The precursor is dissolved in a solvent (like methanol or isopropanol) and then hydrolyzed by adding water, often with an acid (HNO_3). The alkoxide groups (–OR) are partially or completely replaced by hydroxyl groups (–OH).

For titanium isopropoxide (R = $–CH(CH_3)_2$):

$Ti[OR]_4 + 4H_2O \rightarrow Ti(OH)_4 + 4\ ROH$

3. Gelation: Transfer the sol to a sealed container (parafilm or PTFE-lined cap) and age 12–24 h at room temp (or 40 °C for 4–6 h). The hydrolyzed precursor undergoes condensation reactions, forming Ti-O-Ti bonds and creating an oxide network structure, which leads to the formation of a 3D gel.

(a) Water condensation: $Ti–OH + HO–Ti \rightarrow Ti–O–Ti + H_2O$

(b) Alcohol condensation: $Ti–OR + HO–Ti \rightarrow Ti–O–Ti + ROH$

Together, these condensation reactions build up a polymeric Ti–O–Ti gel network.

4.Drying and Calcination: The wet gel is dried at 60–80 °C overnight (either in air or under vacuum) to resulting in either a xerogel or an aerogel. The dried material is then calcined at a high temperature (e.g., to remove organic residues and further crystallize the TiO_2.

Applications of TiO_2 nanoparticles in sensor development:

- Gas Sensors: TiO_2 NPs detect gases like H_2, CO, NO_2, and O_2 due to their high surface

area and strong surface adsorption properties.

- Biosensors: TiO_2 NPs act as biocompatible platforms for enzyme or DNA immobilization, enabling glucose, cholesterol, and pathogen detection.
- UV/Optical Sensors: Because of their wide bandgap and strong UV absorption, TiO_2 is used in UV photodetectors and optical switches.
- Electrochemical Sensors: TiO_2 nanoparticle-modified electrodes enhance electron transfer for detecting metal ions, pollutants, and biomolecules.

4 (c) Discuss synthesis and properties of Graphene Quantum Dots using citric acid method and its applications in emerging electronics.

Graphene Quantum Dots (GQDs) are nanoscale fragments of graphene with strong quantum confinement and edge effects. They exhibit excellent photoluminescence, high surface area, biocompatibility, and chemical stability. Their tunable optical and electronic properties make them useful in bioimaging, sensors, energy devices, and optoelectronics.

synthesis of GQDs from citric-acid (bottom-up)

1) Nucleation of GQDs by Melt and carbonize the citric acid

When citric acid is heated to about 160 °C for 10 minutes and further heated at 180–200 °C for 15 minutes changes the color from yellow to orange and then to brown. This indicates dehydration and decarboxylation reactions, leading to the formation of tiny sp^2 carbon nuclei that become the cores of graphene quantum dots (GQDs).

2) Quench and neutralize (stop growth; make dots water-dispersible)

After heating citric acid, the solution is cooled and treated with warm NaOH (0.5–1 M) under stirring until the pH reaches 7–8. This step stops further carbonization and prevents the growth of larger particles. The –COOH groups on the carbon dot edges are deprotonated to $–COO^-$, making the graphene quantum dots stable, soluble, and brightly fluorescent.

3) N-doping / surface passivation (brighter PL, different color)

In the synthesis of graphene quantum dots, adding ethylenediamine (EDA) or urea followed by mild heating (80–120 °C) helps in forming amide or imine linkages at the edges. This process introduces nitrogen atoms into the GQDs, known as nitrogen doping. Nitrogen doping improves surface properties and causes a shift in fluorescence emission.

4) Purify

After synthesis, the solution is first filtered (0.22 μm) to remove large particles and then dialyzed for 24–48 hours in water to purify it. This gives a clear solution of graphene quantum dots (GQDs) that glows blue or green under UV light. The GQDs can be stored at room temperature or 4 °C.

Applications of Graphene Quantum Dots (GQDs) in Emerging Electronics

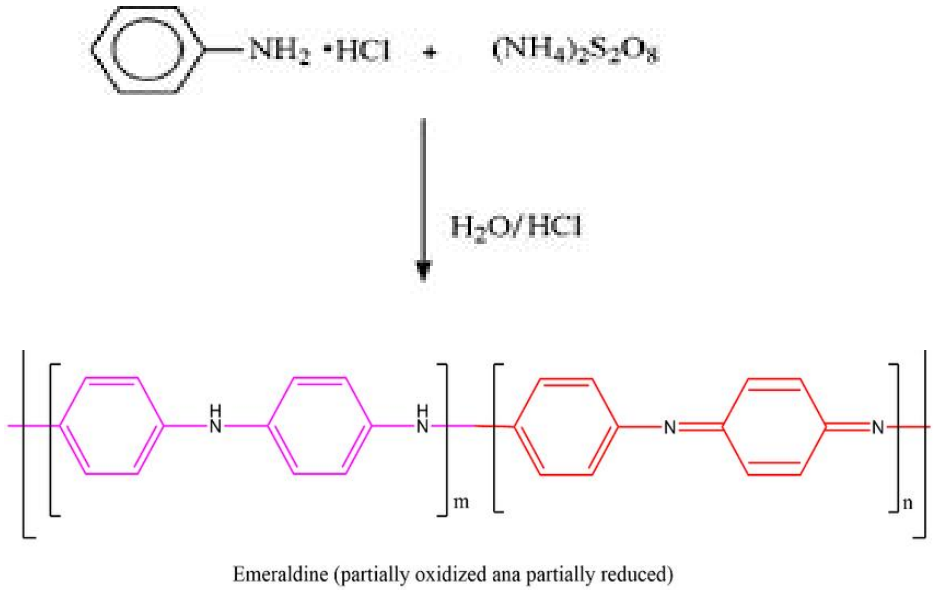
1. **LEDs:** GQDs show strong, tunable fluorescence, making them useful in efficient blue, green, and white LED fabrication.
2. **Solar Cells:** GQDs provide broad light absorption and fast electron transfer, improving photovoltaic efficiency.
3. **Flexible Displays:** High luminescence and nanoscale size allow GQDs to be used in thin, bendable display panels.
4. **Transistors:** GQDs enhance electrical conductivity and charge mobility in thin-film transistor devices.
5. **Sensors:** GQDs show fluorescence changes on analyte interaction, enabling sensitive gas, ion, and biomolecule sensing.
6. **Supercapacitors:** GQDs increase electrode surface area and conductivity, boosting energy storage performance.

Module-3

5 (a) Explain the synthesis, conducting mechanism of Polyaniline.

Polyaniline synthesis, conducting mechanism

Polyaniline is synthesized by the **chemical oxidative polymerization** of aniline in acidic medium using ammonium persulfate as the oxidant. The polymer is then filtered, washed, and dried for use.



Emeraldine (partially oxidized ana partially reduced)

P-Type Conducting Mechanism of Polyaniline

Step 1: Protonation of Emeraldine Base: When emeraldine base (EB) is treated with an acid (H^+ A^-), the imine nitrogens get protonated.

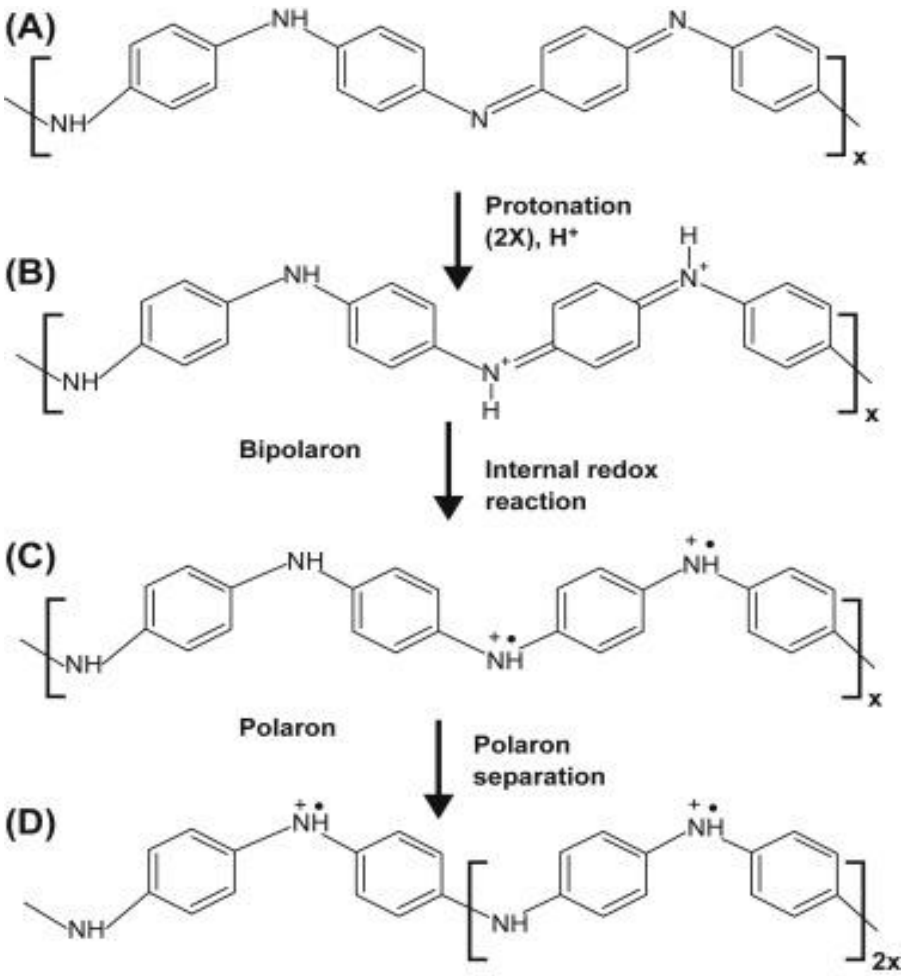
Step 2: Formation of Bipolarons: by losing lone pair of electrons on imine nitrogen results in two polarons and can combine to form a **bipolaron** (dication).

Step 3: Formation of Polarons (Radical Cations): Protonation causes internal electron transfer,

creating a **polaron** (radical cation).

Step 4: Delocalization → Conductivity: Polarons and bipolarons become **delocalized** along the conjugated chain. Delocalized charges move under an electric field → **electrical conductivity**.

Step 5: Formation of Emeraldine Salt (Conducting PANI): Overall, protonation (p-type doping) converts EB into the conducting emeraldine salt (ES).



5 (b) A sample of polymer contain 20 molecules have molecular mass of 3000, 30 molecules have molecular mass of 5000, and remaining molecules have molecular mass of 7000, calculate the number average and weight average molecular weights of the polymer and its PDI.

Polymer Molecular Weight Calculation

Given Data:

20 molecules → 3000

30 molecules → 5000

50 molecules → 7000

Total molecules = 100

Step 1: Number Average Molecular Weight (Mn)

$Mn = \Sigma(NiMi) / \Sigma Ni$

Mn = [(20×3000) + (30×5000) + (50×7000)] / 100

Mn = 560000 / 100

Mn = 5600

Step 2: Weight Average Molecular Weight (Mw)

Mw = Σ(NiMi²) / Σ(NiMi)

Mw = [20(3000²) + 30(5000²) + 50(7000²)] / 560000

Mw = 3.38×10^9 / 560000

Mw ≈ 6036

Step 3: Polydispersity Index (PDI)

PDI = Mw / Mn

PDI = 6036 / 5600

PDI ≈ 1.08

5 (c) Discuss basic principle and working of lithography for micro-patterned copper deposition.

Principle: Lithography is a pattern-transfer technique used to create very small, precise structures on a surface. It is one of the most important processes in microelectronics, semiconductor manufacturing, MEMS, nanotechnology, and material science.

Working / Process Steps

1. Substrate Cleaning: Silicon wafer is thoroughly cleaned using solvents like acetone, IPA, and DI water. Removes dust, grease, and organic contaminants to improve film adhesion.

2. Metal Deposition: A thin **adhesion layer** (Ti or Cr, typically 10–20 nm) is deposited using sputtering or thermal evaporation. A **copper film** (100–500 nm) is deposited over the adhesion layer. Ti/Cr is used because Cu alone does not bond strongly to Si/SiO_2 .

3. Spin-Coating Photoresist: Liquid photoresist is dropped onto the wafer and spun at high speed (2000–4000 rpm) which creates a uniform thin resist layer. Thickness depends on application (1–10 μm).

4. Soft Bake (Pre-bake): Wafer is heated on a hot plate (90–100 °C for ~1–2 min) which removes remaining solvent and improves adhesion.

5. UV Exposure Through Mask: The wafer is aligned under a **photomask** that contains the micropattern design. UV light selectively exposes areas of the photoresist.

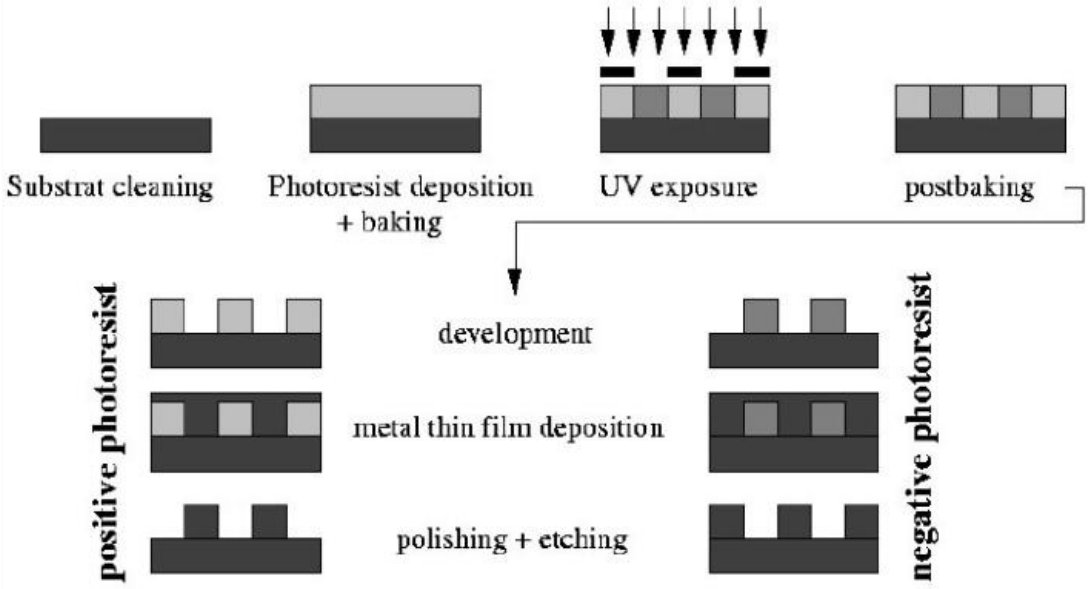
- For **positive resist**: exposed regions become soluble.
- For **negative resist**: exposed regions become cross-linked and insoluble.

6. Development: Wafer is dipped into developer solution to remove the soluble part of the resist, revealing Cu beneath in patterned areas on the wafer.

7. Copper Etching: Wet etchant (e.g., ferric chloride $FeCl_3$ or ammonium persulfate) removes Cu only in exposed regions. Protected Cu under resist remains intact.

8. Photoresist Stripping: Acetone or plasma cleaning removes the remaining resist which results in precise copper micropatterns remain on the substrate.

Lithography-based copper micro-patterning is a key technique in microelectronics for fabricating interconnects, integrated circuits, MEMS devices, sensors, and printed electronic components. It provides high precision, repeatability, and compatibility with large-scale production.



6(a) What is polymer composite? Explain synthesis and properties of epoxy resin magnetite (Fe_3O_4) composite from ultra-sonication method for sensors applications

Polymer composites are materials formed by combining a polymer matrix with reinforcing fillers such as nanoparticles, or flakes to improve mechanical, thermal, and electrical properties.

Synthesis:

1. **Preparation of Fe_3O_4 NPs**: Iron oxide nanoparticles are produced by adding Fe^{2+} /Fe^{3+} salt solution to an alkaline medium, which precipitates Fe_3O_4 instantly. The nanoparticles are then washed, separated, and stabilized to avoid agglomeration.
2. **Prepare nanoparticle dispersion:** Weigh Fe_3O_4 NPs (typical loading 1–20 wt% relative to epoxy) and disperse in small volume of solvent to make a slurry.
3. **Ultrasonication:** Sonicate the Fe_3O_4 slurry using a probe or bath sonicator at moderate power (e.g., 100–300 W probe) for 10–30 minutes with pulse mode (e.g., 10 s on / 5 s off) and cooling (ice bath) to avoid overheating. This breaks agglomerates and yields a uniform dispersion.
4. **Mix with epoxy resin:** Add the sonicated dispersion to the epoxy resin (base) and stir mechanically for 10–20 min to maintain homogeneity.
5. **Degassing:** Place the mixture in a vacuum desiccator (≈10–30 min) to remove entrapped air and solvent.
6. **Casting and curing:** Pour the composite into molds. Cure at room temperature for primary set

(typical 24 h), then post-cure at elevated temperature (e.g., 60–80 °C for 2–4 h) to complete crosslinking.

Properties:

1. **High mechanical strength**: Fe_3O_4 nanoparticles reinforce the epoxy matrix, improving tensile, compressive, and impact strength.
2. **Magnetic responsiveness**: Exhibits strong magnetic properties for smart and controllable device applications.
3. **Improved thermal stability**: Nanoparticles enhance heat resistance and increase thermal conductivity.
4. **Enhanced electrical properties**: Fe_3O_4 provides tunable electrical conductivity for EMI shielding and sensing.
5. **Good chemical resistance**: Stable against solvents, moisture, and corrosion environments.

Applications in sensors:

1. **Magnetic sensors**: Used for detecting magnetic fields due to strong magnetic responsiveness of Fe_3O_4.
2. **Pressure and strain sensors**: Composite changes electrical resistance under mechanical force.
3. **Temperature sensors**: Improved thermal conductivity enables accurate thermal sensing.
4. **Gas sensors**: Surface interaction with gas molecules alters conductivity for gas detection.
5. **Biosensors**: Suitable for immobilizing biomolecules and enabling magnetic-assisted sensing.
6. **EMI shielding sensors**: Used in electromagnetic interference monitoring and protection in electronics.

6(b) Discuss the synthesis and properties of Kevlar Fiber Reinforced Polymer (KFRP) for smart electronic devices applications.

Kevlar Fiber Reinforced Polymer (KFRP) is a composite material made by reinforcing a polymer matrix with Kevlar fibers to improve strength, toughness, and impact resistance.

1. Synthesis of Kevlar Fiber (Poly-para-phenylene Terephthalamide, PPTA)

Kevlar is synthesized through a **step-growth (condensation) polymerization** reaction between **p-phenylenediamine (PPD)** and **terephthaloyl chloride (TPC)** in a cold solvent system (usually concentrated sulfuric acid). The polymer solution is then **wet-spun into fibers**, stretched, and heat-treated to align molecules for high strength.

2. **Preparation of Polymer Matrix:** A thermosetting resin such as epoxy, polyester, or vinyl ester is prepared by mixing resin with a hardener.
3. **Fiber Impregnation/Resin Wetting:** Kevlar fibers are placed in molds and impregnated with polymer resin using resin transfer molding (RTM), or vacuum bagging to ensure complete wetting.
4. **Curing and Solidification:** The composite is compressed and cured at room temperature or under

heat/pressure in an autoclave to form a solid laminate structure.

5. **Finishing:** The cured composite is removed, trimmed, and machined into required shapes for applications.

Properties:

1. **High tensile strength and toughness**: Kevlar fibers provide excellent resistance to stretching and impact forces.
2. **Lightweight with high strength-to-weight ratio**: Stronger than steel by weight, useful for lightweight structural parts.
3. **Excellent thermal stability**: Maintains strength at high temperatures and resists thermal degradation.
4. **Good chemical and corrosion resistance**: Stable against acids, bases, and moisture, increasing durability.

Applications in smart electronic devices:

1. **Flexible and wearable electronics**: Kevlar composites are used as strong, lightweight substrates in flexible circuits and smart textiles.
2. **Protective casings for smartphones, laptops, and tablets**: Provides high impact resistance and durability while reducing weight.
3. **Energy-harvesting devices**: Used in flexible piezoelectric or triboelectric sensors for motion-based power generation.
4. **Structural health monitoring sensors**: Embedded KFRP sensors detect strain, cracks, and vibration in smart infrastructures.

6(c) Explain the synthesis, properties and applications of PDMS (Polydimethylsiloxane) and its uses in e-skin (electronic skin).

Polydimethylsiloxane (PDMS) is a widely used silicon-based organic polymer belonging to the silicone family. It is known for its excellent flexibility, transparency, biocompatibility, and chemical stability. PDMS is commonly used in microfluidics, soft lithography, biomedical devices, and wearable electronics due to its elastic and soft rubber-like behavior.

Synthesis: PDMS is synthesized mainly through two major steps: formation of siloxane monomers and polymerization to form long silicone chains, followed by cross-linking to create an elastomer.

Step 1: Formation of Siloxane Monomers: Dimethyldichlorosilane $Si(CH_3)_2Cl_2$ undergoes hydrolysis with water, it forms dimethylsiloxane units and releases HCl.

$$Si(CH_3)_2Cl_2 + 2H_2O \rightarrow HO–Si(CH_3)_2–OH + 2HCl$$

These hydroxyl-terminated units then undergo condensation reactions, forming siloxane (Si–O–Si) bonds, producing cyclic monomers or linear siloxane chains.

Step 2: Polymerization: The cyclic siloxane monomers undergo ring-opening polymerization using acid or base catalysts, producing long PDMS polymer chains of controlled molecular weight.

Step 3: Cross-linking (Curing): To convert liquid PDMS into solid elastomer, cross-linking is

performed using platinum-catalyzed hydrosilylation curing. This step joins polymer chains into a 3-D network, producing soft, rubber-like PDMS used in microfabrication.

Properties

1. High flexibility and elasticity
2. Optical transparency (UV–visible)
3. Chemical and thermal stability
4. Hydrophobic surface and low surface energy
5. Gas permeability (O_2, CO_2)
6. Biocompatible and non-toxic
7. Electrically insulating and mechanically durable

Applications in Electronic skin (E-skin)

1. Acts as a flexible and stretchable substrate with excellent biocompatibility closely mimicking the softness and elasticity of human skin.
2. Easily micro-patterned using soft lithography, allowing integration of pressure, strain, and temperature sensors.
3. Supports real-time physiological monitoring for healthcare and wearable diagnostics.

Module–4

7 (a) Discuss types of electrodes with examples?

Types of electrodes:

Following are some important types of single electrodes –

(a) **Metal – metal ion electrode:** It consist of a metal dipped in a solution containing its own ions. For eg: Zn/Zn^{2+}, Cu/Cu^{2+}, Ag/Ag^{+} etc.

(b) **Metal – metal salt ion electrode:** It consist of metal in contact with a sparingly soluble salt of the same metal and is dipped in a solution containing same anion as the salt. For eg. Calomel electrode ($Hg/Hg_2Cl_2/Cl^-$), silver – silver chloride electrode ($Ag/AgCl/ Cl^-$).

(c) **Gas electrode:** In this type of electrode, a gas is in contact with an inert metal wire/foildipped in solution containing ions to which gas is reversible. For eg. H_2 electrode($Pt/ H_2/H^+$)

(d) **Amalgam electrode:** It is similar to metal – metal ion electrode. In this metal - amalgam is in contact with a solution containing its own metal ions. For eg. Lead amalgam electrode ($Pb\text{-}Hg/Pb^{2+}$).

(e) **Redox electrode:** In this electrode potential arises from the presence of oxidized and reduced forms of same substance in solution. Potential developed is picked up by an inert electrode like Platinum (Pt). For eg. Pt/Fe^{2+}, Fe^{3+}.

(f) **Ion Selective Electrode:** In this electrode, a membrane is in contact with a solution, with which it can exchange ions. For eg. Glass electrode (exchanges H^+ ions with solutions).

7 (b) Discuss instrumentation and application of of potentiometric sensor for the estimation of iron in steel?

Theory or Principle:

The estimation of concentration of substances in solution by the measurement of emf is known as potentiometric titration. Here, emphasis is laid on the changes in emf of an electrolytic cell as a titrant of known concentration is added.

Thus, the concentration can be calculated, provided Eo of the electrode is known.

Redox titrations can be carried out potentiometrically

For the reaction; Reduced form $\longrightarrow$ Oxidized form + n e-

The potential is given by Nernst equation

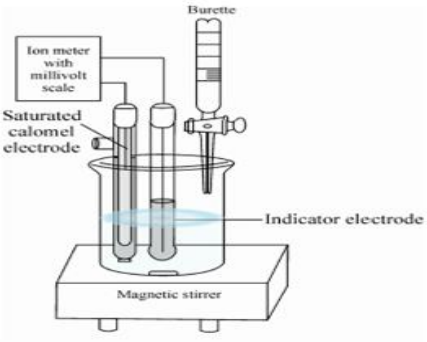
$$E = Eo + \frac{0.0591}{n} \log [\text{oxidized form}]/[\text{Reduced Form}]$$

The potential of the system is controlled by the ratio of concentration of the oxidized to that of the reduced species. A plot of change in potential against volume is characterized by a sudden change of potential at the equivalent point. At the end point, potential is determined by large jump in the potential value.

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
IV. Stirrer to mix the solution

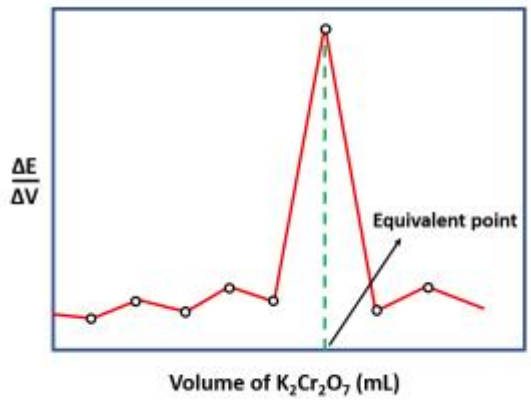


Application in estimation of Fe in steel: **Potentiometric estimation of Fe using standard $K_2Cr_2O_7$**

solution

Pipette out 25ml of iron solution into a beaker. Add 1 t.t dil H2SO4. Immerse calomel electrode + platinum electrode into it. Connect the assembly to a potentiometer and measure the potential by adding K2Cr2O7 in the increments of 0.5ml. Plot graph ΔE/ΔV against volume of K2Cr2O7, and determine the equivalence point. From the normality and volume K2Cr2O7, solutions calculate the normality and the weight of FAS in the given solution.

$Cr_2O_7^{2-} + 14\ H^+ + Fe^{2+} \rightarrow Fe^{3+} + Cr^{3+} + 7H_2O$



Advantages:

(i) They give results more reliable than those obtained from titrations using indicators

(ii) The method is applicable to both coloured and turbid solutions also

7 (c) What is concentration cell? A zinc concentration cell is obtained by combining two zinc electrodes of concentrations 0.2M and 0.4 M immersed in zinc sulphate solution at 298 K. Write the cell reactions and calculate EMF of the cell.

A concentration cell is an electrochemical cell in which both electrodes are made of the same material but are immersed in solutions of different concentrations. The EMF of the cell arises due to the difference in concentration.

Electrode: $Zn \mid Zn^{2+}$ (0.2 M) || Zn^{2+} (0.4 M) | Zn

Temperature = 298 K

Number of electrons (n) = 2

Anode (oxidation, lower concentration 0.2 M):

$Zn(s) \rightarrow Zn^{2+}$ (0.2 M) + $2e^-$

Cathode (reduction, higher concentration 0.4 M):

Zn^{2+} (0.4 M) + $2e^-$ → Zn(s)

Overall Reaction:

Zn^{2+} (0.4 M) → Zn^{2+} (0.2 M)

Using Nernst Equation at 298 K:

$E = (0.0591 / n) \log (C_2 / C_1)$

$E = (0.0591 / 2) \log (0.4 / 0.2)$

$E = 0.02955 \log (2)$

$\log(2) = 0.3010$

$E = 0.02955 \times 0.3010$

$E = 0.0089$ V

EMF of the concentration cell at 298 K = 0.0089 V

8 (a) Discuss construction and working of glass electrode.

These electrodes selectively respond to a specific ion in a solution 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 and Working

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 also placed in the solution for electrical contact.

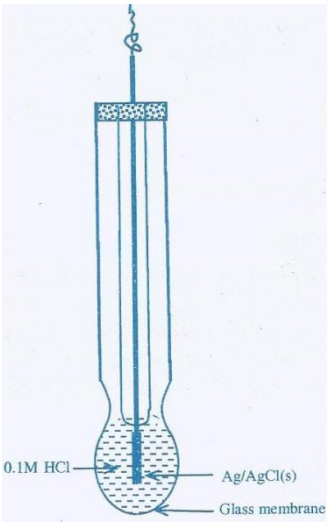


Fig: Glass Electrode

The electrode is represented as,

Ag/AgCl (s)/ 0.1M HCl/ Glass or Glass/0.1M HCl/AgCl(s)/Ag

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.

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

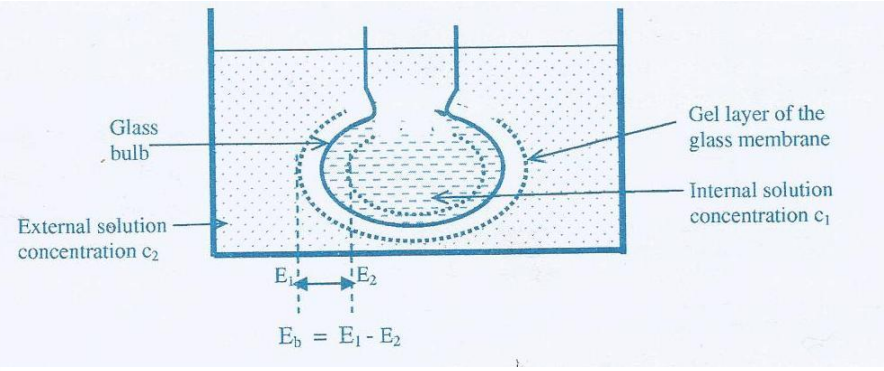


Fig : Boundary Potential

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 (E1-E2) developed across the gel layer of the glass membrane between the two liquid.

Mathematically it is represented as,

$E_b = \mathbf{E_1 - E_2}$

Where, $\mathbf{E_1}$= Potential due to H^+ present in outside solution (Unknown solution)

$\mathbf{E_2}$ = Potential due to H^+ present in inside solution (known solution)

According to Nernst equation

$$E_b = \frac{2.303RT}{nF} \log \frac{C_1}{C2}$$

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

Where, C_1 is the concentration of H^+ ions of the solution into which glass membrane is dipped. The concentration of H^+ ion inside the bulb (C_2) is constant i.e. $C_2 = 0.1$ M.

Thus, $E_b = \frac{0.0591}{n} \log C_1 + \mathbf{K}$ **or**

$$= \mathbf{K} + \frac{0.0591}{n} \log C_1$$

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

Hence $C_1 = \mathbf{H^+}$

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

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

Thus, $E_b = K - 0.0591pH$ ----------(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 C1= C2, Eb Should be 0, however it has been observed practically that even when C1 = C2, 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 Eb from equation (2) in equation (4)

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

$E_G = E^o_G - 0.0591pH$ .....(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.

8(b) Describe instrumentation and application of colorimetric sensor in the estimation of copper in the PCBs with diagram?

Colorimetry or Colorimetric Sensors

Principle: When a monochromatic light of intensity I_0 is incident on a transparent medium, a part I_a of is absorbed, a part I_r is reflected and the remaining part is transmitted I_t.

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

For a glass-air interface I_r is negligible, therefore,

$$\mathbf{I_0 = I_a + I_t}$$

$\mathbf{I_t / I_0 = T}$ called the transmittance, $\mathbf{\log 1/T = \log I_0 / I_t}$ is called the absorbance or optical density.

Colorimetry measurements are based on ***Beer-Lambert's law***. This law gives the relation between absorbance A, concentration c (expressed in mo1/dm^3) and path length t, (expressed in cm).

Beer-Lambert's law: When monochromatic light passes through a transparent medium, the amount of light absorbed is directly proportional to the concentration and path length of the solution.

$$\mathbf{A \propto ct}$$

$$A = \log I_0/I_t = \varepsilon ct$$

Where **ε** is the molar extinction coefficient, **c** is the concentration, **t** is the path length and is a constant for a given substance at a given wavelength. If the length is kept constant (t),

$$A \propto c$$

Hence a plot of absorbance against concentration gives a straight line.

Instrumentation: The instrument used to measure the absorbance of a solution is called photoelectric colorimeter.

It consists of

Tungsten lamp as the light source.

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

A sample cell

A photocell detector

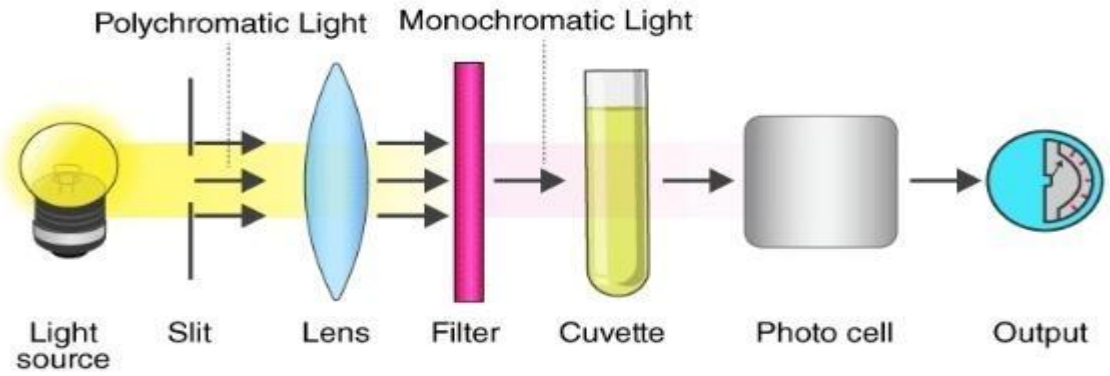
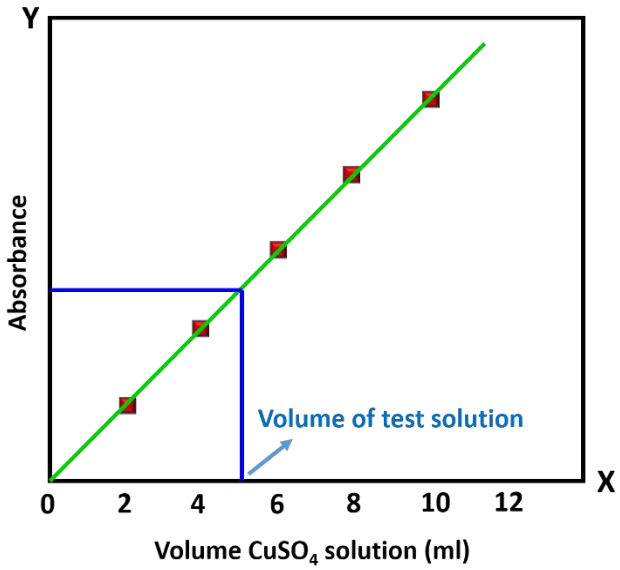


Fig: Schematic layout of colorimeter

Application in estimation of Copper in PCBs:

Transfer the given copper sulphate solution (stock solution) to a burette and draw out **2**, **4**, **6**, **8** and **10** mL of the solution into a 50 mL volumetric flask. Add 5 mL of ammonia solution to each of them and dilute up to the mark with ion exchange water. Stopper the flasks and mix the solutions well. add 5 mL of ammonia solution to the given test solution and then dilute up to the mark with ion exchange water and mix well. Prepare a blank solution by diluting 5 mL of ammonia solution in a 50 mL measuring flask up to the mark with ion exchange water and mixing well. Measure the absorbance of the solutions against the blank at 620 nm using a photoelectric colorimeter. Tabulate the readings as shown. Draw a calibration curve by plotting the absorbance against the volume of copper sulphate solution. Using the calibration curve, find out the volume of copper sulphate solution given i.e., the volume of the test solution and calculate the amount of copper in the given solution.



8 (c) Explain the instrumentation and application of conductometric sensor and its application in the estimation of acid mixture?

Conductometry (Its principle, instrumentation and application in estimation of weak acid)

Principle : Conductometry is based **on Ohm's law.**

Ohm's law states that the current i (amperes) flowing in a conductor is directly proportional to the applied electromotive force, E (volts), and inversely proportional to the resistance R (ohms) of the conductor.

$$i = \frac{E}{R}$$

Conductivity (specific conductance) is defined as the conductance of a solution present between two parallel electrodes having unit area and are placed unit distance apart.

$k = c\ l\ /a$

The principle underlying conductometric titrations is the substitution of ions with a specific mobility by ions of another specific mobility. Therefore, the conductance of solution depends on the number of mobility of ions. The equivalence point is determined graphically by plotting conductance against titer values.

Instrumentation : Conductometric assembly consists of

Conductivity cell : It has two platinum electrodes, which have unit area of cross section and are placed unit distance apart.

A conductance measuring device known as conductivity meter.

Stirrer : To mix the solution

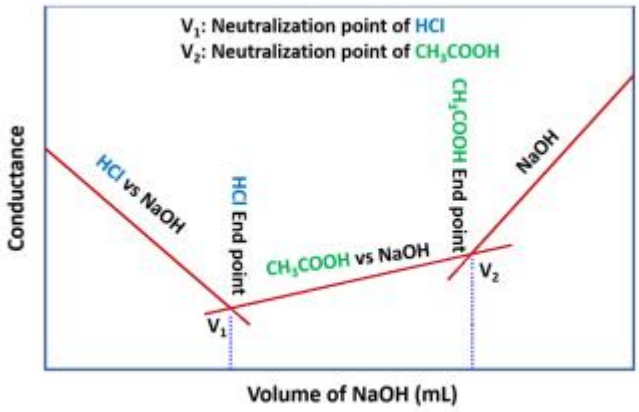
A simple arrangement of conductometric titration is depicted in figure. The solution to be titrated is taken in the beaker.

Application in the estimation of acid mixture:

Pipette out 50ml of acid mixture into a beaker. Immerse the conductivity cell into it. Connect the conductivity cell to a conductivity meter and measure the conductance by adding NaOH from the burette by increment of 1 ml. Plot a graph of conductance against volume of NaOH. Determine the neutralization points from the graph as shown below**.**

In the titration of a mixture of week acid (CH3COOH) and strong acid (HCl) with a strong base (NaOH), the conductance decreases upon adding NaOH to acid mixture owing to the substitution of highly mobile H^+ ions by the less mobile Na^+ ions. This trend continues till all the H^+ ions of HCl are replaced i.e., the strong acid is neutralized. Continued addition of NaOH raises the conductance moderately, as the weak acid (CH_3COOH) is converted into its salt (CH_3COONa).

Further addition of NaOH raises the conductance steeply due to the presence of OHions.



Module -5

9 (a) What is e-waste? Explain the need for e-waste management?

Introduction: 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. E-waste management is defined as a holistic method of cutting down E-waste from the earth to prevent its harmful toxic to deteriorate earth. It recycles and reuses the e-waste that is no longer needed.

Need of E- Waste Management:

- E-waste management is necessary because it helps to address several environmental, health, and resource-related concerns, including:
- Protecting the environment: E-waste contains toxic substances, such as lead, mercury,and cadmium that can have harmful effects on the environment and human health if not properly managed.
- Conserving resources: E-waste contains valuable resources, such as metals, that can be recovered and reused through proper recycling.
- Reducing greenhouse gas emissions: The production of new electronic products releases greenhouse gases, such as carbon dioxide, into the atmosphere. Proper recycling and disposal of e-waste can

reduce the environmental impact of electronic products.

- Reducing land filling: land filling of electronic waste can result in the release of toxic materials into the environment and contribute to soil and water pollution.
- Protecting public health: Improper handling and disposal of e-waste can expose workers and the general public to hazardous materials and cause serious health problems.
- E-waste can be toxic, is not biodegradable and accumulates in the environment, in the soil, air, water and living things.
- It causes air pollution, Soil pollution and water pollution.
- Electronic Recycling Promotes Soil Fertility and Maintain Nutrient.
- E-waste management programs aim to promote responsible recycling and disposal of electronic waste and minimize the release of hazardous materials into the environment. This helps to protect the environment, conserve resources, and promote public health and safety.

9 (b) Apply the principles of electroplating to explain the process of Cr plating used for hard and decorative coatings.

Electroplating is the process of depositing a thin layer of one metal onto the surface of another metal by passing an electric current through an electrolytic solution.

Electroplating of Chromium: Chromium is employed for either decorative purposes (as a thinner coat) or engineering purposes (as a thicker hard coat).

Mentioned below are coating specifications.

Chromium plating	**Decorative Chromium**	**Hard Chromium**
Bath composition	CrO3: H2SO4 = 100: 1 ratio	CrO3: H2SO4 = 100: 1 ratio
Temperature	45-55 ^{o}C	45 -66 ^{o}C
pH	2-4	2-4
Current density	100 – 200 mA/cm^2	215 – 430 mA/cm^2
Anode	Insoluble lead- Pb-Sb alloy or Pb-Sn alloy (with lead oxide coating)	Insoluble lead- Pb-Sb alloy or Pb-Sn alloy (with lead oxide coating)
Cathode	Surface cleaned object metal to be plated	Surface cleaned object metal to be plated
Application	Provide durable and good decorative finish on automobiles, surgical instrument etc.	Extensively used in industrial and engineering applications.

There is a complex sequence of reactions which control the concentration of Cr^{3+} in the plating bath. The plating bath contains CrO3 in which Cr is in +6 oxidation state. This is reduced to Cr^{3+} by

a series of complex reactions in the presence of $SO4^{--}$ furnished by H2SO4. Cr^{3+} ions are reduced to elemental Cr which gets deposit on the substrate.

$$CrO_3 + H_2O \longrightarrow H_2CrO_4$$

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

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

$$Cr^{3+} + 3e \longrightarrow Cr$$

The amount of Cr^{3+} ions should be restricted in order to obtain good deposits**.**

<u>Insoluble anodes covered with PbO2</u> which oxidizes Cr^{3+} to Cr^{6+} and thus control the Cr^{3+} ion concentration.

$$2Cr^{3+} + 3O2 \longrightarrow 2CrO3 + 6e^-$$

<u>Active chromium anode is not used because</u>

(i) Cr metal passivate strongly in acid sulphate medium.

(ii) Further the anode efficiency is nearly 100% and that of the cathode is only around 20% at the best, thus there will be increase in concentration of Cr^{3+} ions which results in poor quality electrodeposits (black deposits).

Applications :

Decorative chromium provides a durable finish on cycles, automobiles, furniture, household fittings, aircraft, surgical and dental instruments.

Hard chromium is mostly used in industries in the making of gauzes, dies, cutting tools, piston rings, cyli crankshafts of marine and aero engines, bearings, hydraulic rams and in printing industry.

9 (c) What is CPR? A steel sheet of area 80 in^2 is exposed to moist air placed near the ocean. After 6 months it was found to experience a weight loss of 340 gr due to corrosion. Calculate the CPR in mmy and mpy if the density is 7.9 g/cm^3 and K = 87.6 and 534)

Corrosion Penetration Rate (CPR) is defined as the rate at which the thickness of a metal decreases due to corrosion over a period of time. It is commonly expressed in millimeters per year (mm/y) or mils per year (mpy).

Area of steel sheet (A) = 80 in²

Weight loss (W) = 340 g

Exposure time (T) = 6 months

Density of steel (D) = 7.9 g/cm³

K constant = 87.6 (for mm/y), 534 (for mpy)

Area in cm² = 80 × 6.4516 = 516.13 cm²

Weight loss in mg = 340 × 1000 = 340000 mg

Time in hours = 6 × 30 × 24 = 4320 hours

Formula Used: CPR = (K × W) / (D × A × T)

Calculation of CPR in mm/year

CPR (mm/y) = (87.6 × 340000) / (7.9 × 516.13 × 4320)

CPR (mm/y) = 1.691 mm/year

Calculation of CPR in mils/year (mpy)

CPR (mpy) = (534 × 340000) / (7.9 × 516.13 × 4320)

CPR (mpy) = 10.31 mils/year

Final Answer

Corrosion Penetration Rate = 1.691 mm/year

Corrosion Penetration Rate = 10.31 mpy

10 (a) What is metal finishing and give the technological importance of metal finishing?

Process of **surface modification** by way of deposition of another metal or metal alloy or polymer or ceramic or oxide layer to bring about better surface characteristics is known as **metal finishing.**

Technological Importance:

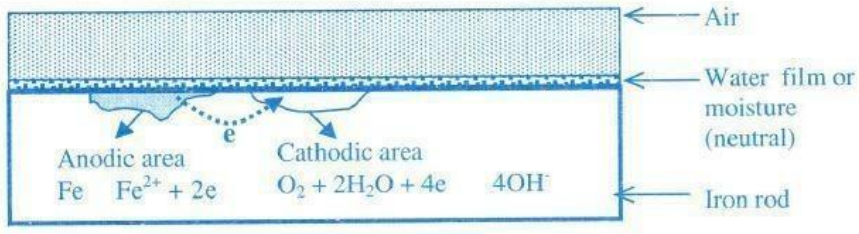
Technological significance of metal finishing refers to imparting following different characteristics:

- Better corrosion resistance,
- Better hardness, strength, wear / abrasion resistance, etc.
- Better thermal conductance or resistance or reflectance, etc.
- Better optical reflectance,
- Better electrical conductance or insulation, etc.
- Building up material or restoration
- Manufacturing printed circuit boards, capacitors, contacts, etc.
- Electrotyping (e.g., gramophone records)
- Electroforming or reforming of articles,
- Electrochemical machining, electropolishing and electrochemical etching, etc.

10 (b) Discuss electrochemical theory of corrosion taking iron as an example?

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:

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

If the solution is aerated and acidic:

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

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

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

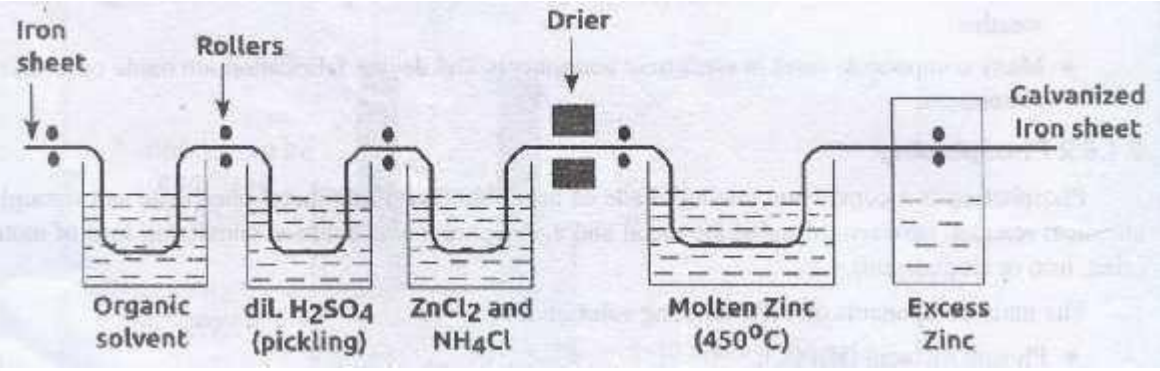
In an oxidizing environment, it is oxidized to ferric oxide and the rust is hydrated ferric oxide.

$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3 \rightarrow 2[Fe_2O_3.3H_2O]$

[Rust]

10(c) Apply the concept of galvanization to prevent corrosion in steel structures exposed to marine environments. Justify your choice with appropriate chemical reasoning?

Galvanisation: It is a process of coating a base metal surface with Zinc metal by hot dipping method.



The galvanization process involves the following steps.

1. The steel or iron surface is first cleaned to remove oil, grease, dirt, and rust using alkali or solvent cleaning. This ensures good adhesion of zinc.
2. The cleaned metal is dipped in a dilute acid solution (usually **10–15% H_2SO_4 or HCl**) to remove oxide scales and rust from the surface.
3. After pickling, the metal is passed through water bath to remove any acid and later treated with a flux solution (commonly **zinc ammonium chloride**) to prevent oxidation before and after dipping into molten zinc and to promote proper bonding.
4. The prepared metal is then immersed in a bath of **molten zinc** at about **450°C**. A thin, uniform layer of zinc is formed on the surface by metallurgical bonding.
5. The coated metal is slowly withdrawn from the molten zinc, excess zinc is drained off by passing through a pair of hot rollers, followed by annealing process to make more adherence between two layers and finally article is cooled in air or water to solidify the zinc coating.

Applications:

Galvanization is used to protect roofing sheets, water pipes, barbed wire, buckets etc.

Galvanised articles are not used for preparing and storing foodstuffs, since Zinc dissolves in dilute acids producing toxic Zinc compounds.

Justification: Galvanization is justified because zinc has a more negative electrode potential than iron, so it acts as a sacrificial anode and oxidizes preferentially. This cathodically protects steel even if the coating is damaged. Additionally, zinc forms stable oxide and carbonate layers, providing barrier protection in chloride-rich marine environments.