CMR INSTITUTE OF TECHNOLOGY





Sub:	Engineering Chemistry			Sub Code:	21CHE22		Branch:		CSE, ISE, CIVIL & ME	
Date:	27/ 08/ 2022 Duration:		90 mins	Max Marks:	50	Sem:	п	Section:	A to G	

Q1a. With a neat diagram explain the hydrogen production by photo electrocatalytic water splitting method. Mention its advantage. (CO4, L4, 7 marks)

Answer: Photo electro catalytic water splitting:

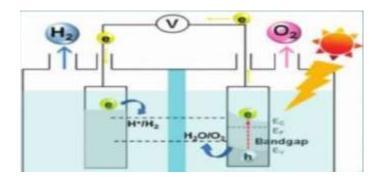
Two electrodes are dipped in aqueous electrolyte and one of the electrode is semiconductor photocatalyst. The system is irradiated with the sunlight and charge carriers are produced. The charges oxides and reduces the water to produce oxygen at anode and hydrogen at cathode.

Input: Semiconductor photocatalyst (anode), Sunlight and water

Output: Hydrogen and Oxygen

At Photoanode
$$2H_2O + 4h \longrightarrow O_2 + 4H^+$$

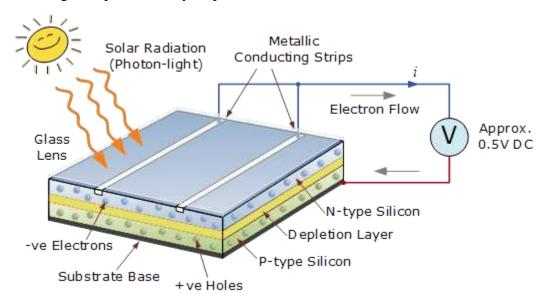
Cathode
$$4H^+ + 4e^- \longrightarrow 2H_2$$



Advantage: Photoelectrocatalytic water splitting is more useful because it permits separation of gases and prevents reverse reaction. It is a clean and renewable resource of energy with a lower adverse impact on climate change

Q1b. Define Photovoltaic cell. Explain the construction, working and applications of PV cells. (CO4, L3, 7 marks)

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



Construction:

Photovoltaic cells consist of a semiconductor diode (p-n junction) made of a silicon. Silicon wafer or very thin silicon slices are made by silicon blocks and they are doped by p-type and n-type dopants to make p-n junction. It has two electrical contacts, on one of its sides, a metallic grid is used and on the other side a layer of noble metal (such as Ag) is used. The metal grid permits the light to fall on the diode between the grid lines. The part between the metallic grid is coated with antireflective compound. eg TiO_2

Working:

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

$$E = hc/\lambda$$

Where, h = Planck's constant, c = velocity of light, $\lambda = wavelength$ of the radiation. The electromagnetic radiation (sunlight) falls normal to the plane of the solar cell, the photons which possess energy sufficient to overcome the barrier potential are absorbed, electrons are ejected and electron-hole pairs are formed. The electrons move towards the n-region (as it is positively charged). The electrons are driven into the external circuit and used for various applications or appliances.

Applications of PV cells: For producing electricity

- (i) In space stations and artificial satellites.
- (ii) In Street light in rural and remote areas.

- (iii). Solar Cell for Transportation: used in electric vehicles
- iv. For Operating water pumps for domestic and agricultural purpose.
- (v) For toys, watches, calculators solar water heaters etc.

Q2a. Define green chemistry. Describe any 6 basic principles of green chemistry. (CO4, L2, 6 marks)

Answer: The term Green Chemistry is defined as -"The invention, design and application of chemical products and processes to reduce or to eliminate the use and generation of hazardous substances"

Basic principles of green chemistry

- 1) **Prevention of waste:** preventing the formation of waste products is always preferable to the clean-up of the waste once it is generated.
- 2) **Atom economy:** the synthetic processes and methods that are devices through green chemistry must always try to maximize the consumption and incorporation of all the raw materials into the final product. This must strictly be followed in order to minimize the waste generated by any process.
- 3) **Avoiding the generation of hazardous chemicals**: reactions and processes that involve the synthesis of certain toxic substances that pose hazards to human health must be optimized in order to prevent the generation of such substances.
- 4) **The design of safe chemicals:** during the design of chemical products that accomplish a specific function, care must be taken to make the chemical as non-toxic to humans and the environment as possible.
- 5) **Design of safe auxiliaries and solvents:** the use of auxiliaries in processes must be avoided to the largest possible extent. Even in the circumstances where they absolutely need to be employed, they must be optimized to be as non-hazardous as possible.
- 6) **Energy efficiency:** The amount of energy consumed by the process must be minimized to the maximum possible extent.
- 7) **Incorporation of renewable feedstock:** the use of renewable feedstock and renewable raw materials must be preferred over the use of non-renewable ones.
- 8) **Reduction in the generation of derivatives:** the unnecessary use of derivatives must be minimalized since they tend to require the use of additional reagents and chemicals, resulting in the generation of excess waste.
- 9) **Incorporation of Catalysis:** in order to reduce the energy requirements of the chemical reactions in the process, the use of chemical catalysts and catalytic reagents must be advocated.

Q2b Define fuel cell? Illustrate the construction, working mechanism and applications of methanol-oxygen fuel cell with a neat sketch. (CO4, L4, 6 marks)

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

Construction: Methanol – oxygen fuel cell consist of

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

Cathode - It is a porous Nickel (Ni) electrode coated with Pt/Pd catalyst.

Electrolyte – Aqueous sulphuric acid (H₂SO₄), 3.7 M.

Fuel – Methanol mixed with sulphuric acid supplied at

Oxidant – Pure oxygen is supplied at cathode.

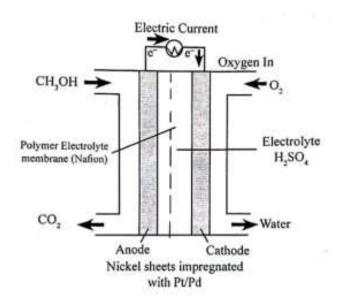


Figure. Methanol – oxygen fuel cell

Working: Cell reaction;

Anode reaction: $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$

Cathode reaction: $3/2 \text{ O}_2 + 6 \text{ H}^+ + 6e^- \rightarrow 3 \text{ H}_2\text{O}$

Overall Cell reaction: $CH_3OH + 3/2 O_2 \rightarrow CO_2 + 2 H_2O$

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

Cell Potential : 1.2 V

Applications:

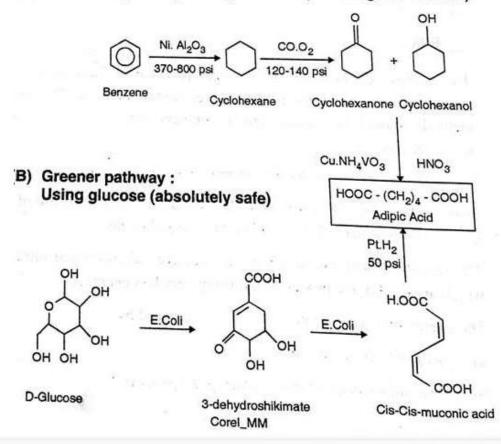
- (1) used in automobiles, military applications.
- (2) Power backup and portable instruments.
- (3) in large scale power production.

Q3a. Explain the synthesis of adipic acid by conventional route from benzene and green route

from glucose. (CO4, L3, 6 marks)

Answer:

(A) Traditional pathway: Using Benzene (Carcinogenic solvent)



Q3b Describe the synthesis, properties and applications of Polyurethanes. (CO3, L2, 6 marks)

Answer: Polyurethanes, along with phenolics, epoxies, and unsaturated polyesters, can be classified as reaction polymers. They can be prepared via the chemical reactions between isocyanates (that contain at least two isocyanate groups per molecule) and polyols (that contain at least two hydroxide groups per molecule). These reactions usually require the presence of a catalyst or some ultraviolet light in order to overcome the activation energy barrier.

Properties of polyurethane

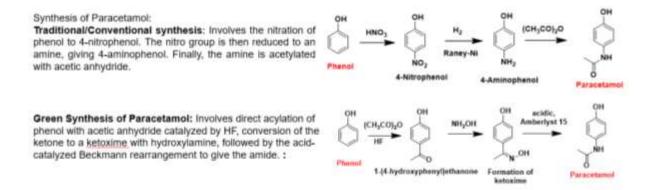
- 1. If polyol chain is long and flexible, the polyurethane will be soft and elastic.
- 2. If cross-linking is very high, the polyurethane will be tough and rigid.
- 3. The cross-linked three-dimensional networks of polyurethane attribute very high molecular weights and has in thermosetting nature.
- 4. Polyurethanes have the ability to make foams.
- 5. resistance to organic solvents but attacked by strong acids & alkalies.

Applications of polyurethanes

- The primary application of polyurethane is in the production of foams. These foams are
 used in a variety of materials such as upholstery fabrics, domestic furniture, and refrigerator
 sheets.
- Polyurethane is also used in some garments.
- Polyurethane mouldings are also used in columns and door frames. In fact, it is not uncommon for such mouldings to be employed in window headers and balusters.
- The low-density foams of polyurethane which exhibit flexibility are widely used in mattresses and other forms of bedding. They are also used in automobile seats and upholstery.
- Flexible polyurethane is also used in the manufacture of partially elastic straps and bands.
- The low-density elastomers of polyurethane are widely used in the footwear industry.
- Another notable application of polyurethane is in the manufacture of bathroom and kitchen sponges. It is also used in seat cushions and couches.

Q4a. Explain the synthesis of paracetamol by conventional and green route from phenol. (CO4, L2, 4 marks)

Answer



Q4b. What are biodegradable polymers? Explain synthesis, properties and applications of polylactic acid. (CO3, L3, 6 marks)

Answer: Biodegradable polymers are defined as materials whose chemical and physical characteristics undergo deterioration and completely degrade when exposed to microorganisms, aerobic, and anaerobic processes.

Polylactic Acid (PLA)

Polylactic acid is a biodegradable aliphatic thermoplastic polymer. It is derived from renewable sources such as starch, sugarcane etc.,

Preparation

It is prepared by the catalytic dimerization of lactic acid resulting in the formation of lactide monomer.

Polymerisation of lactide monomer in presence pf stannous octate to give polylactic acid as a final product.

Properties

- 1. PLA possess good biocompatibility, process ability and high strength.
- 2. D-isomer of PLA is crystalline and L-isomer is amorphous
- 3. Biodegradation of D-isomer is slower than L-isomer.

Applications:

- 1. PLA is used for making medical implants like screws, pins and anchors etc.,
- 2. It is used in a number of biomedical applications like drug delivery devices and dialysis media
- 3. It is used in the preparation of bioplastic for packaging food and disposable tableware.
- 4. It is also used for making compostable packaging materials and food packaging items etc.,

Q5a. Illustrate the hydrogen production by photo catalytic water splitting method with a neat sketch. (CO4, L4, 6 marks)

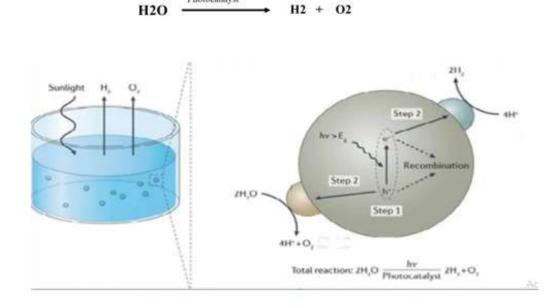
Answer: **Production of hydrogen:** Hydrogen is the future green fuel and does not cause environmental pollution.

Photocatalytic reaction

Input: Photocatalyst particles, sunlight and water

Output: Oxygen and hydrogen

Photocatalyst in the form of particles is immersed in water based electrolyte and it produces charge carriers holes and electrons after absorbing sunlight. Charges are moved to surface of the photocatalyst to start the chemical reaction. Holes are oxidizing the water and electrons reduces hydrogen ions to Hydrogen gas.



Q5b Explain synthesis, properties and applications of Kevlar. (CO3, L3, 6 marks)

Answer: Synthesis of Kevlar: Kevlar is made by a condensation reaction of an amine (1, 4-phenylene-diamine) and acid chloride (terephthaloyl chloride). The Kevlar chains are relatively rigid and tend to form mostly planar sheets, similar to those of silk. This is due to the Paraorientation of the benzene rings. When Kevlar is spun the chains lock together via H-bonds to form a sheet that has a very high tensile strength. The sheets also stack radically, like the spokes on a wheel, allowing additional interactions between the face-to-face aromatic groups on neighbouring sheets to help to increase the strength of the overall fibre.

Properties of Kevlar

- 1. It is strong but light in weight; 2. It is crystalline and non-flammable; 3. It has good impact and abrasion resistance
- 4. It is thermally stable and withstand high temperatures; Not affected by very low temperatures.
- 3. Long exposure to ultraviolet light causes discoloration & degradation of the fibres.
- 4. It can resist chemical attacks, however long exposure to strong acids/bases causes degradation.
- 5. Kevlar remains unaffected by hot water & moisture.
- 6. Kevlar fibre is five times stronger than steel and have high tensile strength

Applications

- **1. Military Body Armor & Jackets:** Kevlar fibre is five times stronger than steel on an equal weight basis, offering superior protection in military body armour and flak jackets.
- **2. Protection Vests:** From higher-level bullets to knives, needles and explosions, protection vests made with Kevlar
- **3. Military Helmets:** Kevlar meet demanding requirements for protection against a wide range of threats, including bullets, shrapnel and fragmentation.
- **4. Automotive Uses:** It is not uncommon for a new vehicle to have several crucial parts that employ products Belts, Brake pads, Clutches, Gaskets, Hoses made of Kevlar brand fibre.

- **5. Kevlar as a Composite:** Formula 1 cars and HANS Device uses Kevlar straps to supports the driver's head and neck— Kevlar absorbs impact forces that are strong enough to pulverize neck vertebrae.
- **6. Kevlar in Fiber Optics:** Kevlar is used to safeguard against mechanical stresses in optical fibre cables.
- **7. Ropes and Cables:** Its resistance to chemicals and temperature extremes make it an ideal component for ropes and cables under severe loads in harsh environments.

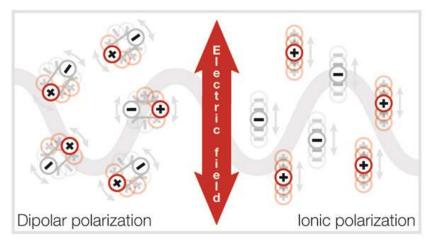
Q6a Describe microwave synthesis with neat sketch and suitable examples. Also mention its advantages. (CO4, L2, 6 marks)

Answer: Microwave synthesis:

Microwave chemistry is based on the efficient heating of materials (in most cases solvents) by dielectric heating effects. Dielectric heating works by two major mechanisms:

i) Dipolar polarization

For a substance to be able to generate heat when irradiated with microwaves it must be a dipole, since, the microwave field is oscillating, the dipoles in the field align to the oscillating field. This alignment causes rotation, which results in friction and ultimately in heat energy.



ii) Ionic Conduction:

During ionic conduction, dissolved (completely) charged particles (usually ions) oscillate back and forth under the influence of microwave irradiation. This oscillation causes collisions of the charged particles with neighboring molecules or atoms, which are ultimately responsible for creating heat energy

Microwave dielectric heating uses the ability of some liquids and solids to transform electromagnetic radiation into heat to drive chemical reactions.

General applications of Microwave Chemistry are,

- 1. Microwave assisted synthesis using Water.
- 2. Microwave assisted synthesis using Organic Solvents.
- 3. Solvent free Reactions.

Hydrolysis of Benzyl Chloride:

Hydrolysis of Benzyl Chloride with water in Microwave oven gives 97% yield of Benzyl alcohol in 3 min. Whereas conventional method takes about 35 min.

Oxidation

Oxidation of toluene by conventional method takes 10 - 12 hr. but by Microwave irradiation the reaction completed in 7 min. with 40% yield.

Advantages; Reaction rate acceleration, Short reaction time, Higher yields, Selective heating, Easy handling, Excellent reproducibility; **Disadvantages:** Expensive equipment, Unsuitable for scale-up, Unfeasible for reaction monitoring

Q6b Discuss the source, effects and control of carbon monoxide and oxides of sulfur (SOx). (CO4, L2, 6 marks)

Answer

Carbon monoxide: Carbon monoxide is one of the most serious air pollutants. It is a colorless and odorless gas, highly poisonous to living beings.

Sources: (a) Carbon monoxide is mainly released into the air by automobile exhaust.

- (b) Incomplete combustion of carbonaceous matter (natural gas, coal or wood) and fossil fuels
- (c) Dissociation of carbon dioxide.

$$2C + O_2 \rightarrow 2CO$$

$$CO_2 + C \rightarrow 2CO$$

Effects: (a) Carbon monoxide is poisonous as it binds with hemoglobin forming *carboxy-haemoglobin*, which reduces O₂ transport in the body. At high concentrations it is very toxic, causing headaches, nausea, and reduced ability to think, and even death.

- (b) Carbon monoxide also binds to the hemeprotein myoglobin
- (c) When carbon monoxide is emitted into the atmosphere it effects the amount of greenhouse gases, which are linked to climate change and global warming.

Control: (a) Modification of engine design for efficient fuel combustion (b) Modern automobiles *use catalytic exhaust reactors* to cut down on carbon monoxide emissions (c) *Fuel modification* and development of substitute fuels (d) *Treatment of exhaust gases*.

Oxides of Sulphur: Sulphur oxides (SO_x) are a group of compounds made up of sulphur and oxygen molecules. The most common sulphur oxide is sulphur dioxide (SO_2) , which is a colourless gas with a burnt match type smell. It includes SO_2 and SO_3

Sources: (a) Emissions from *volcanic eruptions* (b) Most of the Sulphur dioxide in our air is caused by the *burning of coal and oil* for energy generation and industrial activities.

- (c) Pulp and paper manufacture: The sulphite process for wood pulping emits SO₂ in air. The kraft pulping process produces H₂S, which is then burned to produce SO₂
- (d) Oil refining: H_2S is released as a gas during catalytic cracking and it is burned to produce SO_2 . $2SO_2 + O_2 \rightarrow SO_3$

$$SO_2 + O_3 \rightarrow SO_3 + O_2$$

Effects: (a) Sulphur dioxide can cause *breathing difficulties* if inhaled into the body. Even a low concentration of sulphur dioxide causes respiratory diseases e.g., asthma and bronchitis in human beings

- (b) Sulphur dioxide causes irritation to the eyes, resulting in tears and redness
- (c) It is also toxic to plants and can cause acid rain when it reacts with moisture in the air.
- (d) Damage to limestone and marble, damage to leather, increased rate of corrosion of iron, steel, zinc and aluminium.

Control: (a) SO₂ emissions are controlled using a spray dryer absorber (SDA) flue gas desulfurization system.

- (b) Use of *alternative source of energy* such as nuclear, hydro power, low Sulphur CNG, Natural gas
- (c) Build tall smoke stacks.

Q7a Discuss the following. (a) Biocatalysis (b) Solvent free reaction (CO4, L2, 6 marks)

Answer: Bio-catalysis: Bio-Catalyst is an enzyme which alters the rate of chemical or bio-chemical reaction. Enzymes are biocatalyst. These biocatalysts (enzymes) are used in the industrial preparation of ethanol. Ethanol is prepared by the fermentation of molasses -a dark brown

coloured syrup left after crystallization of sugar which still contains about 40% of sugar. The process of fermentation actually involves breaking down of large molecules into simple ones in the presence of enzymes. The source of these enzymes is yeast.

The various reaction taking place during fermentation of carbohydrates are

Sucrose

INVERTASE

$$C_{12}H_{22}O_{11}$$
Sucrose

 $C_{6}H_{12}O_{6} + C_{6}H_{12}O_{6}$
glucose fructose

$$ZYMASE$$

$$C_{6}H_{12}O_{6} \longrightarrow 2 C_{2}H_{5}OH + 2 CO_{2}$$

Solvent free reaction: A solvent free reaction is a chemical reaction in the **absence of a solvent**.

Condition for solvent free reactions

A solvent-free or solid state reaction may be carried out using the reactants alone or incorporating them in clays, zeolites, silica, alumina or other matrices to achieve high degree of stereo-selectivity in the products, to reduce byproducts, to maximize rate of reaction.

Its advantages include: Economic (save money on solvent), Not required to remove a solvent after reaction, Purification step is avoided, Environment friendly because solvent is not required, Reaction rate is high due more availability of reactants

Major Drawback: Unsuitable for solvent assisted chemical reactions

Q7b What are conducting polymers? Explain the synthesis of polyaniline. Mention any 3 factors influencing conduction in organic polymers. (**CO3**, **L4**, **6** marks)

Ans: Conducting polymers are organic polymers that conduct electricity. Example: polyaniline (PANI)

Preparation of Polyaniline: Polyaniline (PANI) is synthesized by polymerization of distilled aniline dissolved in precooled 1M HCl at 0-5 °C(HCl) in the presence of ammonium persulfate (APS) as initiator. The reaction is exothermic and the polymer formed is a mixture of different polyanilines

Factors influencing the conductivity of organic polymers:

- (i) Conjugation and chain length: In general conductivity of a polymer increases with increase in polymer chain length and conjugation.
- (ii) Doping level: The conductivity of a polymer increases with the increase in doping level till the saturation point is reached.
- (iii) Temperature: In general the conductivity decreases when the temperature is lowered.