

**GAYATRI VIDYA PARISHAD COLLEGE OF ENGINEERING FOR WOMEN
(AUTONOMOUS)**

(Affiliated to Andhra University, Visakhapatnam)

I-B.Tech.- I Semester Regular Examinations, December / January – 2025

GREEN CHEMISTRY

1.a) With a neat sketch explain the ion-exchange process for the softening of water?

Ans : The process of removing hardness producing salts from water is known as softening of water

ION EXCHANGE OR DEIONISATION:

Ion exchange resins are insoluble, cross-linked, long chain polymers with a micro porous structures and the 'functional groups' attached to the chains are responsible for ion -exchanging properties. Resins containing acidic functional groups(-COOH,-SO₃H,etc) are capable of exchanging their H⁺ ions with their other cations which comes in their contact. Resins containing basic functional groups(-NH₂=NH as hydrochloride) are capable of exchanging their anions with other anions which comes in their contact.

This may be classified as:

1. **Cation exchange Resin(RH⁺)** are mainly "*styrene-divinyl benzene copolymers*" which on sulphonation or carboxylation, become capable to exchange their hydrogen ions with the cations in the water.

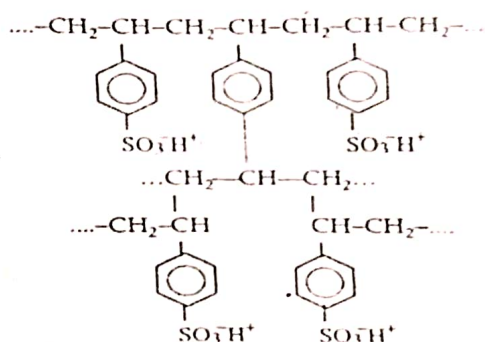
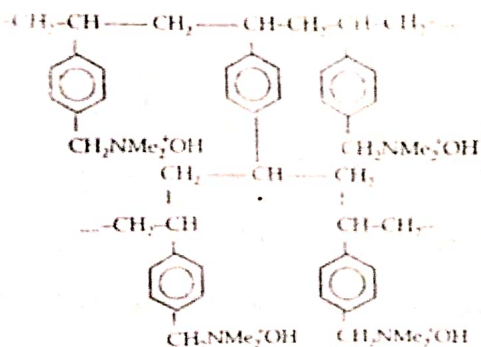


Fig. 6. Acidic or cation exchange resin (sulphonate form)

Fig. Acidic or cation exchange resin(sulphonate form)

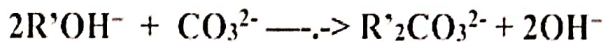
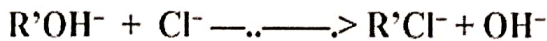
2. **Anion exchange Resin(R'⁺OH⁻)** are "*styrene-divinyl benzene copolymers* or *amine-formaldehyde copolymer*" which contain amino or quaternary ammonium groups as an integral part of the resin matrix. These, after treatment with dil. NaOH solution, become capable to exchange their OH⁻ anions with their in water.



❖ **Process:** The hard water is passed first through cation exchange column, which removes all the cations like (Ca²⁺, Mg²⁺, etc) and equivalent amount of H⁺ ions are released from this column to water. Thus:



After cation exchange column, the hard water is passed through anion exchange column, which removes all the anions (like SO₄²⁻, Cl⁻, etc) and equivalent amount of OH⁻ ions are released from this column to water. Thus:



H⁺ and OH⁻ ions (released from cations exchange and anion exchange columns respectively) get combined to produce water molecule.



Thus, the water coming out from the exchanger is free from cations as well as anions. This water is known as *deionized or demineralized water*.

Regeneration: When capacity of cation and anion exchangers to exchange H⁺ and OH⁻ ions are lost, they are said to be exhausted.

The exhausted cation exchange column is regenerated by passing a solution of dil. HCl or dil. H₂SO₄. The regeneration can be represented as:

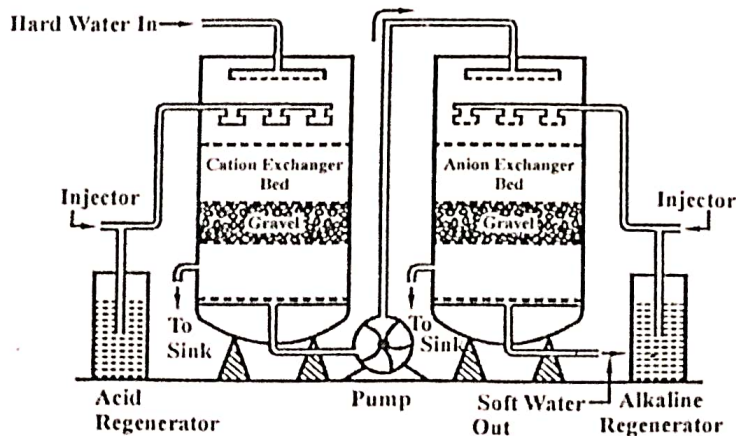
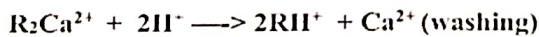


Fig. Demineralization of Water

The column is washed with deionized water and washing (which contains Ca²⁺, Mg²⁺, etc. and Cl⁻ or SO₄²⁻ ions) is passed to sink or drain.

The exhausted anion exchange column is regenerated by passing a solution of dil. NaOH. The regeneration can be represented as:



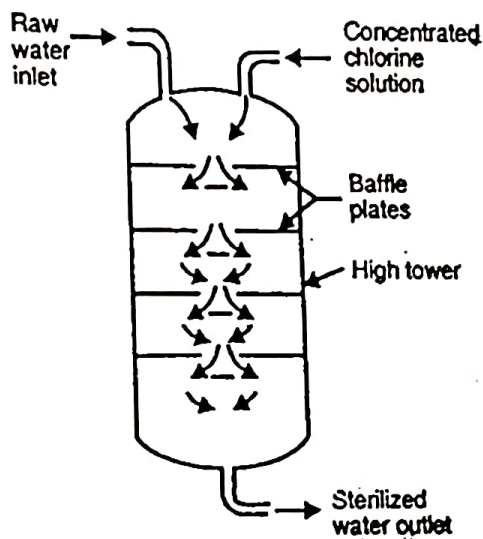
The column is washed with deionized water and washing (which contains Na⁺ and SO₄²⁻ or Cl⁻ ions) is passed to sink or drain.

The regeneration ion exchange resins are then used again.

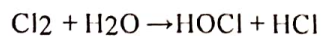
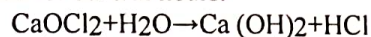
1.b) What is chlorination ? Outline the break-point chlorination process for the disinfection of water?

Ans:

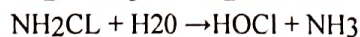
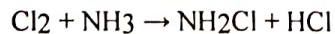
Chlorination: It is the process of adding chlorine to drinking water to kill bacteria and parasites. It can be done in three ways.



- **By adding bleaching powder:** 1kg of bleaching powder is added to 1000 kilolitres of water and water is kept undisturbed for several hours.

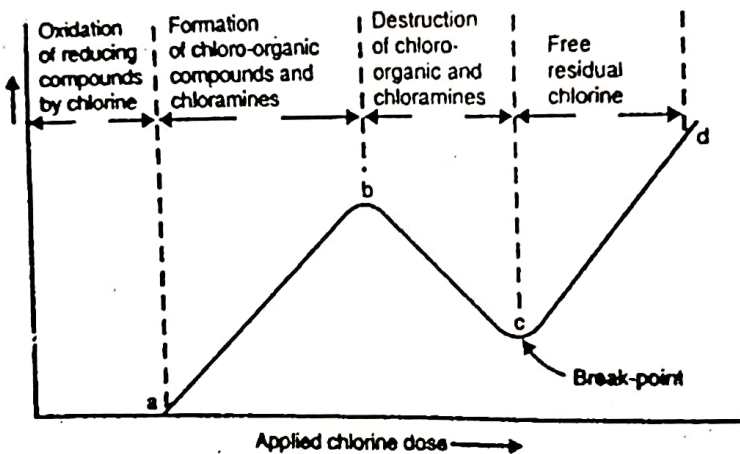
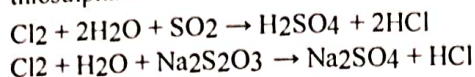


- **By adding chlorine and ammonia:** chlorine and ammonia are mixed together to form chloramine which is used for disinfection of water.



- **Break-point chlorination:** When we add chlorine to the water came from filtration it oxidises the impurities and increases the percentage of derivatives of chlorine and ammonia. Then we add some more amount of chlorine to water which decreases derivative percentage and pathogenic bacteria. When sufficient amount of chlorine is added then it gives residual chlorine. The point where residual chlorine is obtained called as break-point chlorination.

Over-chlorination can be removed by sulphur dioxide and sodium thiosulphate.

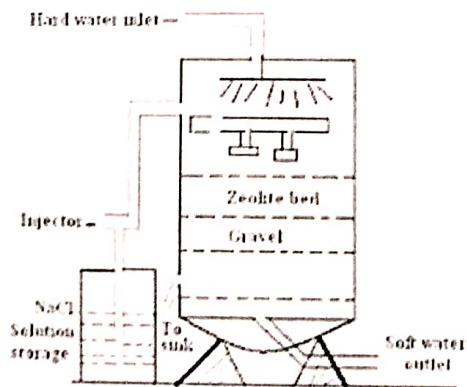


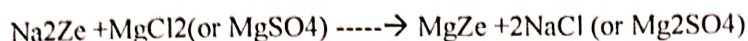
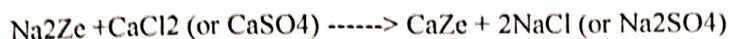
2.a) Explain zeolite process for the softening of water? Write its advantages and disadvantages?

Ans : **Zeolite or permutit process** :Chemical structure of sodium zeolite is may be represented as: $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y \cdot \text{H}_2\text{O}$ where $x=2 - 10$ and $y = 2 - 6$. Zeolite is hydrated sodium alumino silicate capable of exchanging reversibly its sodium ions for hardness-producing ions in water .Zeolites are also known as permutits .Zeolites are of two types :

- (i)**Natural zeolites**:are non –porous. For example, natrolite, $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$.
- (ii)**Synthetic zeolites**:are porous and possess gel structure They are prepared by heating together china clay,feldspar and soda ash.

Process: For softening of water by zeolite process ,hard water is percolated at a specified rate through a bed of zeolite, kept in the cylinder.The hardness causing ions ($\text{Ca}^{+2}, \text{Mg}^{+2}$ etc..)are retained by zeolites as CaZe and MgZe ;while the outgoing water contains sodium salts .Reactions taking place during the softening process are:





Regeneration : During the course of prolong purification , zeolite bed is completely converted to calcium and magnesium zeolites, and no purification of raw water takes place i.e zeolite bed was completely exhausted. Again it can be regenerated by using 10% brine solution



Limitations: The raw water should be free from

- Turbidity** (clogs the pores on zeolite bed)
- Colored ions** like Manganese and ferrous ions ,because they are having high affinity towards the surface of zeolite , Once they have adhered difficult to remove from the surface
- Acid** (Destroys the zeolite bed)

Advantages :

- Removes hardness and results water having hardness around 10 ppm
- Doesn't produce any precipitate(therefore disposal of sludge won't be a problem)
- Equipment is compact

Disadvantages:

- Replaces cations only and leaves less acidic ions
- Treated water contains more amount of sodium ions
- Due to the presence of sodium carbonate in treated water, it may leads to caustic embrittlement

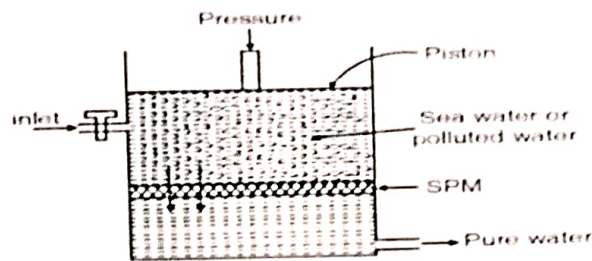
2.b) Discuss the Reverse Osmosis process for the desalination of sea water? Mention its advantages and disadvantages?

Ans: **Desalination of brackish water**

Water containing high concentration of dissolved salts with the peculiar salty or brackish taste is called brackish water. Sea water is an example, which can't be used for domestic and industrial applications unless the dissolved salts are removed by desalination

Reverse Osmosis:- Osmosis can be defined as flow of solvent from low concentration to high concentration solution through semi permeable membrane.

- When we apply an excess and opposite hydro-static pressure to over come the osmotic pressure, then flow of solvent from high concentration to low concentration of solution. This is known as Reverse Osmosis.
- During the reverse osmosis , only the water flows across the membrane and it prevents the salt migration.



Advantages:-

- Simple operational procedure.
- Low capital cost.
- Maximum hardness can be removed and the resultant water can be used for high pressure boilers

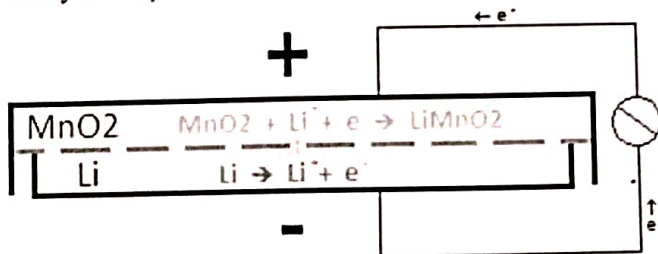
Disadvantages:

- It requires routine filter changes and maintenance..
- The process does not help in disinfecting the water. You will require a separate process to disinfect the water.
- Hard water can damage the system

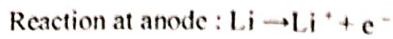
3.a) Demonstrate the construction and functioning of Li- MnO₂ Cell with the chemical reactions involved?

Ans : Lithium solid cathode battery(Li-MnO₂) :

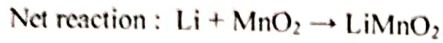
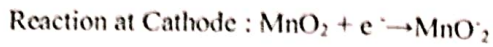
Construction Lithium-Manganese Dioxide cells comprises of a metallic lithium anode and a hard solid manganese delivers the voltage of 3.0V and are cylindrical in shape. Lithium is used as an ideal negative electrode as it offers lowest potential amongst other chemical elements therefore it is offering the highest cell voltage. These cells use solid cathode materials such as MnO₂, CuO, V₂O₅ and carbon monofluoride, (CF)_n. They have the advantage of not being pressurized, although they cannot be discharged as rapidly as liquid cathode cells. They are available in button and cylindrical forms. About 80% (by number) of all lithium batteries in use are of the Li/MnO₂ type. The electrolyte is Propylene carbonate and 1,2- dimethoxy ethane .A main disadvantage of this batteries are it offers lower energy density which means it is most favorable for memory backups.



Working mechanism of the battery: The energy density is similar to that of the Li/SO₂ cells when discharged slowly and their slow self-discharge characteristic make them suitable for memory backup, watches, calculators, cameras, mines and munitions, etc. During the discharge process , the anode (Li) undergoes oxidation to release electrons and Lithium ions, and it can be represented as follows



While at cathode (MnO_2), Reduction reaction taking place and it gains electrons from anode through external circuit and it can be represented as follows

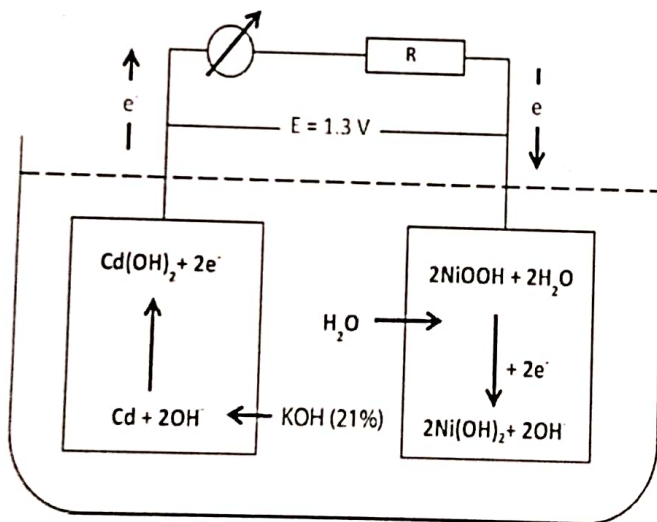


3.b) Outline the construction working and chemical reactions involved in Nickel-Cadmium battery. Give its advantages and disadvantages?

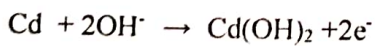
Ans: **Ni-Cd battery (Secondary battery)**

The electrolyte in NiCd is an alkaline electrolyte (potassium hydroxide). Most NiCd batteries are cylindrical in which several layers of positive and negative materials are wound into a jelly-roll. The flooded version of NiCd is used as the ship-battery in commercial aircrafts and in UPS systems operating in hot and cold climates requiring frequent cycling. NiCd is more expensive than lead acid but lasts longer.

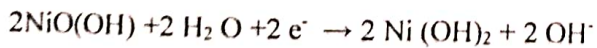
The anode material used in the battery is Cadmium, while the cathode is NiOOH. The following reactions can be observed during discharging



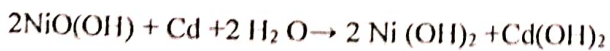
At anode : Oxidation reaction is taking place and it involves release of electrons from Cd and it can be represented as follows



At cathode, Reduction reaction taking place and it involves gaining of electrons from anode through external circuit, and it can be represented as follows



Net reaction,



Advantages

- Compared to other secondary batteries these batteries having good life cycle and performance at low temperatures
- Having high discharge rates

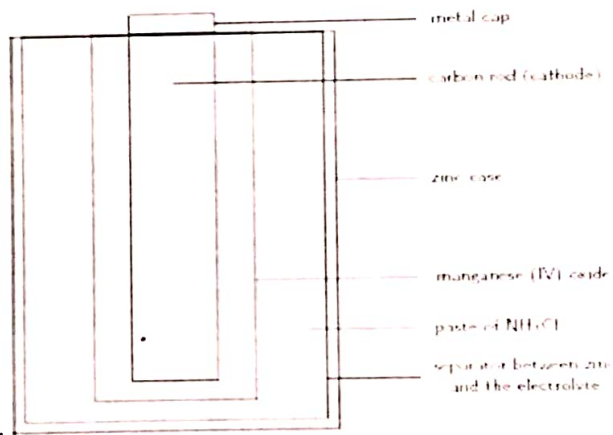
Disadvantages :

- They have high self discharge rate
- Cadmium metal is toxic to living organism
- It exhibits negative temperature coefficients(overcharging leads to destruction of battery)

4.a) Describe the working principle and cell reactions of Zinc – Carbon battery?

Ans: Zinc Carbon Battery

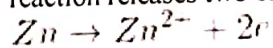
Generally there are two **types of zinc carbon battery** generally available – Leclanche battery(dry battery) and Zinc chloride battery. Leclanche himself improved his own prototype design of **zinc carbon battery**. Here he mixed a resin gum binder with manganese dioxide and carbon powder to form a compressed solid block of the mixture by hydraulic pressure. Due to this solid structure of cathode mixture, there is no further need of porous pot in Leclanche battery cell. Instead of inserting a zinc rod inside the electrolyte in glass container, he made the container by zinc itself. Hence this



container also serves as anode of the battery.

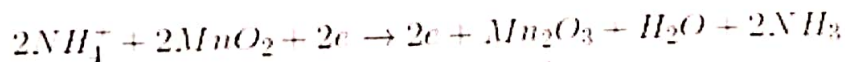
Chemical Reaction in Zinc Carbon Battery

In Leclanche battery cell, zinc is used as anode, manganese dioxide is used as cathode and ammonium chloride is used as main electrolyte but there is some percentage of zinc chloride in the electrolyte. During discharge, zinc anode involves in oxidation+ reaction and each zinc atom involved in this reaction releases two electrons.

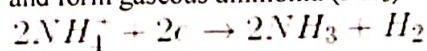


These electrons come to the cathode through external load circuit.

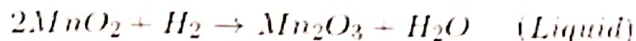
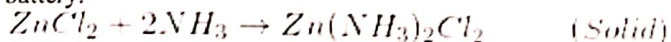
In Leclanche battery cell ammonium chloride (NH4Cl) exists in electrolyte mixture as NH4+ and Cl-. In cathode MnO2 will be reduced to Mn2O3 in reaction with ammonium ion (NH4+). In addition to Mn2O3 this reaction also produces ammonia (NH3) and water (H2O).



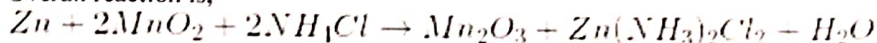
But during this chemical process some of ammonium ions (NH4+) are directly reduced by electrons and form gaseous ammonia (NH3) and hydrogen(H2).



In zinc carbon battery this ammonia gas further reacts with zinc chloride ($ZnCl_2$) to form solid zinc ammonium chloride and gaseous hydrogen reacts with manganese dioxide to form solid di-manganese trioxide and water. These two reactions prevent formation of gas pressure during discharging of battery.



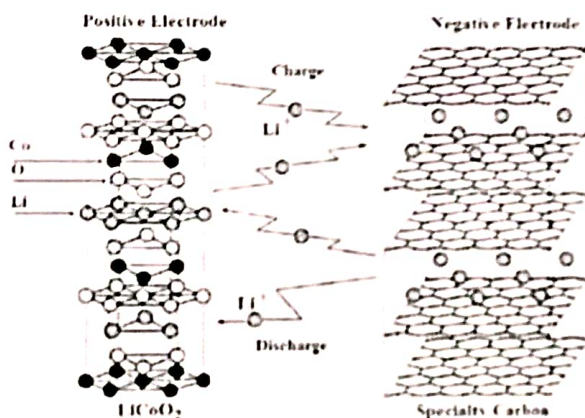
Overall reaction is,



4.b) Outline the construction, Working and chemical reaction involved in Li- ion battery. Mention its advantages?

Ans : Lithium-ion (Li-ion)

Construction: Li-ion uses liquid, gel or dry polymer electrolyte. The reactants in the electrochemical reactions in a lithium-ion cell are materials of anode and cathode, both of which are compounds containing lithium atoms. During discharge, an oxidation half-reaction at the anode produces positively charged lithium ions and negatively charged electrons.



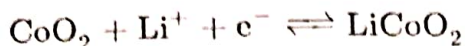
Lithium ions move through the electrolyte, electrons move through the external circuit, and then they recombine at the cathode (together with the cathode material) in a reduction half-reaction. The electrolyte and external circuit provide conductive media for lithium ions and electrons, respectively.

During charging these reactions and transports go in the opposite direction: electrons move from the positive electrode to the negative electrode through the external circuit.

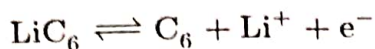
Both electrodes allow lithium ions to move in and out of their structures with a process called *insertion (intercalation)* or *extraction (deintercalation)*, respectively.

The following equations exemplify the chemistry.

The positive electrode (cathode) half-reaction in the lithium-doped cobalt oxide substrate is



The negative electrode (anode) half-reaction for the graphite is



The full reaction (left to right: discharging, right to left: charging) being



The overall reaction has its limits. Overdischarging saturates lithium cobalt oxide, leading to the production of lithium oxide, possibly by the following irreversible reaction:

In a lithium-ion cell, the lithium ions are transported to and from the positive or negative electrodes by oxidizing the transition metal, cobalt (Co), in $\text{Li}_{1-x}\text{CoO}_2$ from Co^{3+} to Co^{4+} during charge, and reducing from Co^{4+} to Co^{3+} during discharge. Liquid electrolytes in lithium-ion batteries consist of lithium salts, such as LiPF_6 , LiBF_4 or LiClO_4 in an organic solvent, such as ethylene carbonate, dimethyl carbonate, and diethyl carbonate.

Advantages :

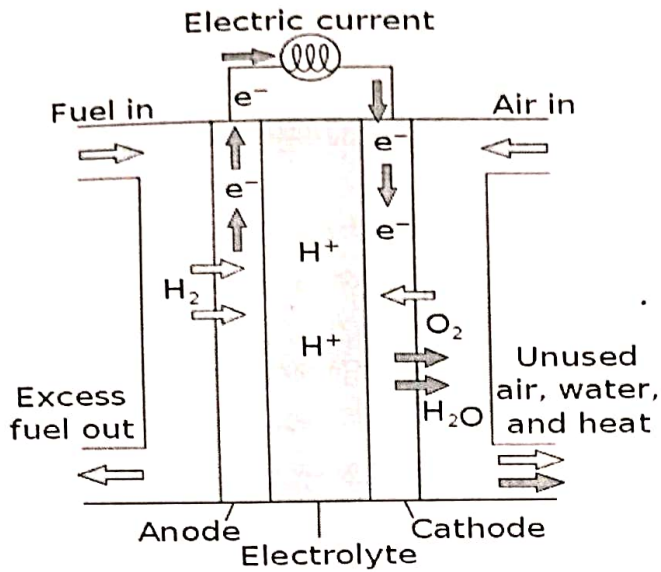
- It has high rate of discharge
- Light weight
- Charge faster

5. a) Describe the working and cell reactions of Proton Exchange membrane Fuel cell?

Ans: **Proton exchange membrane fuel cell**

Proton-exchange membrane fuel cells (PEMFC), also known as polymer electrolyte membrane (PEM) fuel cells, are a type of fuel cell being developed mainly for transport applications, as well as for stationary fuel-cell applications and portable fuel-cell applications. Their distinguishing features include lower temperature/pressure ranges (50 to 100 °C) and a special proton-conducting polymer electrolyte membrane.

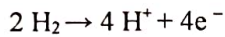
PEMFCs are built out of membrane electrode assemblies (MEA) which include the electrodes, electrolyte, catalyst, and gas diffusion layers. An ink of catalyst, carbon, and electrode are sprayed or painted onto the solid electrolyte and carbon paper is hot-pressed on either side to protect the inside of the cell and also act as electrodes. Operating temperatures above 100 °C are desired. Therefore, electricity, water along with heat was obtained



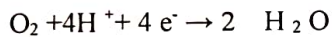
At the anode:

The protons formed at anode permeate through the polymer electrolyte membrane to the cathode side. The electrons travel along an external load circuit to the cathode side of the MEA, thus creating the current output of the fuel cell.

Oxidation reaction at anode is as follows



At the cathode: At the cathode side oxygen molecules react with the protons permeating through the polymer electrolyte membrane and the electrons arriving through the external circuit to form water molecules. This reduction half-cell reaction



Unfortunately however, splitting the oxygen molecule is more difficult, and this causes significant electric losses. An appropriate catalyst material for this process is platinum/C or Pt-alloy/C

Overall reaction: $2\text{H}_2 + \text{O}_2 \rightarrow 2 \text{H}_2 \text{O}$

Promising alternatives to Pt-based catalysts are Metal/Nitrogen/ Carbon-catalysts (M/N/C-catalysts). Recently, researchers have developed a Fe/N/C catalyst to get maximum output

PEM(POLYMER ELECTROLYTE MEMBRANE)

PEMFCs have a thin, polymeric membrane as the electrolyte. Compared to liquid electrolytes, a polymeric membrane has a much lower chance of leakage. The proton-exchange membrane is commonly made of materials such as perfluorosulfonic acid (PSFA) or Nafion

5.b) Write a note on Electrochemical sensor?

Ans: Electrochemical sensor is a device which is able to detect a change in physical/chemical quantity and produce an electrical signal suitable for a computer. Electrochemical sensors are used primarily to detect Oxygen and toxic gases. When a gas is detected, the cell generates a small current proportional to the concentration of the gas.

An Electrochemical sensor consists of –

A diffusion barrier

A Sensing electrode or working electrode or measuring electrode or anode

A counter-electrode or cathode
 An electrolyte

In an environment free of chemically reactive gases, oxygen diffuses into the cell and adsorbs on both electrode. This results in a stable potential between the two electrodes, in which little or no current flows.

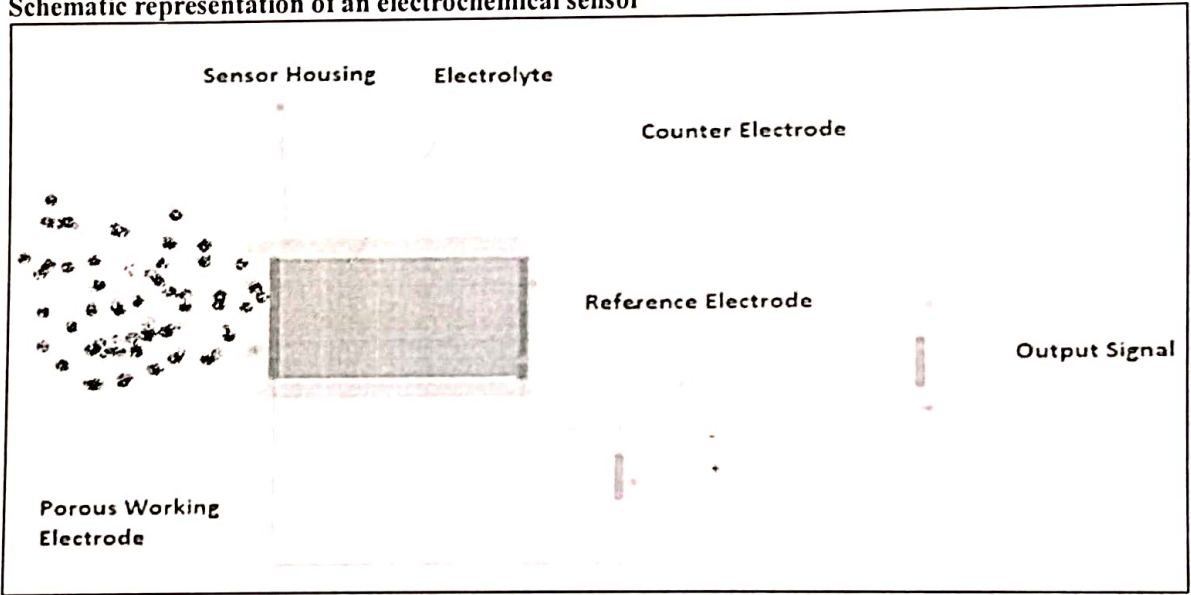
The cells chemical process at this point is:
 $O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$

When a chemically reactive gas, passes through the diffusion barrier or sensing electrode, it is either oxidized (accepts oxygen and/or gives up electrons) or reduced (gives up oxygen and/or accepts electrons) depending upon the gas.

This results in a potential difference between the two electrodes, this causes a current to flow. For example if CO, a reducing gas diffuses to the sensing electrode, it is oxidized, thereby causing the potential of the sensing electrode to shift in a negative cathodic direction.

The cells chemical process is:
 Sensing- electrode: $2CO + 2H_2O \longrightarrow 2CO_2 + 4H^+ + 4e^-$
 Counter- electrode: $O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$
 Cell Reaction : $2CO + O_2 \longrightarrow 2CO_2$

Schematic representation of an electrochemical sensor



Applications:

1. To detect oxygen and toxic gases e.g. CO, H₂S, SO₂, NO, NO₂, etc.
2. To monitor waste stream discharges.
3. To monitor composition of plating baths and rinse systems.
4. To monitor pollutants in environment.
5. To monitor continuously levels of key ingredients in oils and lubricants.
6. To monitor corrosion process.
7. To monitor blood samples and other fluids for their ionic chemical content concentrations.
8. To study chemical parameters and concentrations of gastric, tissue secretions, inner eye lid, etc.

(OR)

6.a) List out the advantages , disadvantages and environmental aspects of Fuel cell?

Ans :

Advantages:

- 1.The product is drinking water, which can be used as drinking water. Therefore, it can be used in submarine and space vehicles
- 2.It doesn't causes environmental pollution

3. High current density

4. Low temperatures (<100° C) are enough to run the battery

Disadvantages of the fuel cell :

1. Water management

Water management is crucial to performance: if water is evaporated too slowly, it will flood the membrane and the accumulation of water inside of field flow plate will impede the flow of oxygen into the fuel cell, but if water evaporates too fast, the membrane will dry and the resistance across it increases. Both cases will cause damage to stability and power output.

2. Based on the requirements to work the fuel cell , the efficiency may low

3. It may causes catalytic poisoning

4. Hydrogen or Methanol or any other reactants used at anode in fuel cell are not abundant in nature.

5. Oxygen or any other gases sent to the electrodes should be free from impurities, therefore it requires separate purifier to remove the impurities from the air

Environmental aspects of the fuel cell:

- Fuel cells have sparked considerable debate within the renewable energy community. While some argue that they offer a better alternative to batteries and solar power, others believe they may not be as sustainable as they appear. Let's take a closer look at the environmental advantages and disadvantages of fuel cell technology.

Fuel Cell Pros

- Fuel cells offer significant environmental benefits, primarily due to their lack of emissions—only water vapor and heat are produced when hydrogen and oxygen react. This contrasts with battery power, which often relies on fossil fuels.
- Hydrogen and oxygen are abundant, ensuring that fuel cells won't deplete natural resources.
- Additionally, fuel cells are more reliable, long-lasting, and efficient, with an efficiency of about 64%, much higher than traditional gas engines.

As climate change accelerates, fuel cells could help mitigate its effects on health and biodiversity.

Fuel Cell Cons

- Extracting hydrogen from chemical bonds also requires energy, and if this energy comes from fossil fuels, hydrogen power isn't fully emissions-free.
- Combining fuel cells with renewable energy sources like solar or wind for hydrogen production could eliminate emissions.
- Over time, as the technology advances, fuel cells are expected to become more affordable and efficient, making them a viable alternative to fossil fuels.
- Sustainability is complex, and while fuel cells are an improvement over fossil fuels, they are not entirely green at this stage.

6.b) Outline the construction , working and chemical reactions of direct methanol fuel cell. Mention its advantages and disadvantages?

Ans: **DIRECT METHANOL OXYGEN FUEL CELL:**

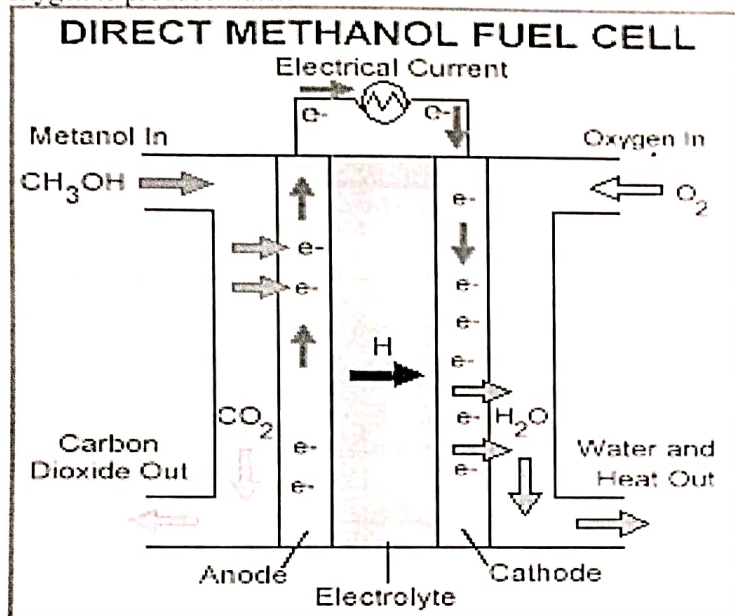
Direct-methanol fuel cells or **DMFCs** are similar to proton exchange fuel cells but methanol is used as the fuel. Their main advantage is the ease of transport of methanol (over hydrogen gas) because methanol is an energy-dense yet reasonably stable liquid in most environmental conditions.

The energy density of methanol is an order of magnitude greater than even highly compressed hydrogen, and 15 times higher than lithium ion batteries.

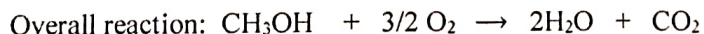
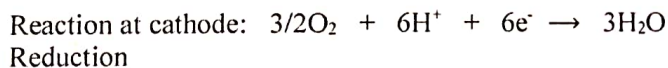
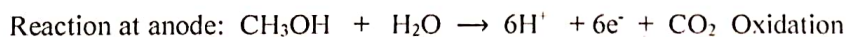
Working of DMFC:

The DMFC relies upon the oxidation of methanol on a Platinum/Ruthenium catalyst layer to form carbon dioxide.

Water is consumed at the anode and is produced at the cathode. Protons (H⁺) are transported across the proton exchange membrane—often made from polymer—to the cathode where they react with oxygen to produce water.



Electrons flow through the external circuit from anode to cathode, providing power to connected devices.



Advantages:

- Methanol has low carbon content
- The OH group is easily oxidisable
- Methanol is highly soluble in water.

Disadvantages :

- The need for water limits the energy density of the fuel
- providing water along with methanol would make the fuel supply more cumbersome, so water has to be recycled in a loop
- Cell efficiency is quite low

7. a) Categorize the factors effecting rate of corrosion?

Ans:

Factors influencing corrosion:

The rate of extent of corrosion depend on the following factors a) nature of metal b) Nature of corroding atmosphere

a) Nature of metal and corroded product

i) **Position in galvanic series:** The extent of corrosion is determined by the difference in the position of metals. The greater is difference, the faster and higher is corrosion

ii) **Relative areas of anodic and cathodic parts:** When two dissimilar metals or alloys are in contact, the corrosion of the anodic parts is directly proportional to the areas of the cathodic and anodic part.

For example, a small pipe made of steel fitted in a large copper tank, because the rapid corrosion due to smaller anodic areas is the current density at a smaller anodic area is much greater and the large cathodic area demands more electrons, which should be met by smaller anodic areas only by undergoing corrosion rapidly

iii) **Purity of metal:** Heterogeneity is produced if impurities are present in a metal, which form a tiny electrochemical cells at the exposed parts. The anodic parts are corroded

iv) **Nature of surface film:** In aerated atmosphere, practically all metal produce a thin surface film of metal oxide. If the specific volume ration is more, the rate of corrosion is less, because the surface of metal is completely covered by film, offering protection to metal surface

v) **Physical state of metal:** The smaller the grain size of the metal or alloy greater will be the rate of corrosion

vi) **Passive character of metal:** Metals like Ti, Al, Cr, and Co are passive and they exhibit much higher corrosion resistance than expected from their position in the electrochemical series

vii) **volatility of corrosion product:** If the corrosion produced volatilizes as soon as it is formed the metal surface is exposed for further attack (leads to excessive corrosion)

b) Nature of corroding environment:

i) **Temperature:** The rate of corrosion increases with increase in temperature

ii) **Humidity of air:** The humidity of air is a deciding factor for rate of corrosion. The relative humidity above which, the rate of corrosion increases sharply is called critical humidity.

iii) **presence of impurities in atmosphere:** With increase in impurities in metal, the corrosion tendency is increases

iv) **P^H value of medium:** With decreasing P^H (increase in acidity) of the medium, the corrosion tendency is increases

v) **Amount of oxygen in atmosphere:** With increase in the percentage of oxygen in atmosphere, the rate of corrosion is increases

7.b) Describe the dry corrosion mechanism with a neat sketch?

Ans:

DRY or CHEMICAL CORROSION:

This type of corrosion is due to the direct chemical attack of metal surfaces by the atmospheric gases such as oxygen, halogen, hydrogen sulphide, sulphur dioxide, nitrogen or

anhydrous inorganic liquid, etc. The chemical corrosion is defined as the direct chemical attack of metals by the atmospheric gases present in the environment.

Example: (i) Silver materials undergo chemical corrosion by Atmospheric H₂S gas

TYPES OF DRY or CHEMICAL CORROSION:

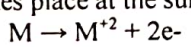
- 1. Corrosion by Oxygen or Oxidation corrosion
- 2. Corrosion by Hydrogen
- 3. Liquid Metal Corrosion

CORROSION BY OXYGEN or OXIDATION CORROSION:

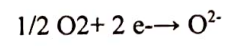
Oxidation Corrosion is brought about by the direct attack of oxygen at low or high temperature on metal surfaces in the absence of moisture. Alkali metals (Li, Na, K etc.,) and alkaline earth metals (Mg, Ca, Sn, etc.,) are rapidly oxidized at low temperature. At high temperature, almost all metals (except Ag, Au and Pt) are oxidized. The reactions of oxidation corrosion are as follows:

Mechanism:

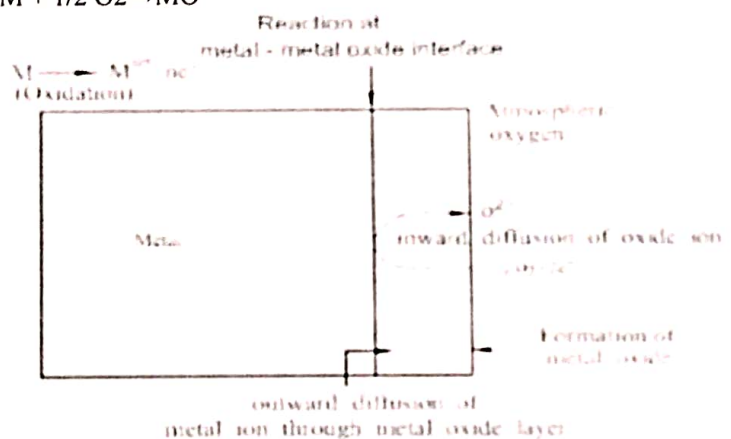
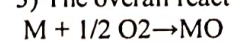
1) Oxidation takes place at the surface of the metal forming metal ions M⁺²



2) Oxygen is converted to oxide ion (O²⁻) due to the transfer of electrons from metal.



3) The overall reaction is of oxide ion reacts with the metal ions to form metal oxide film.



The Nature of the Oxide formed plays an important part in oxidation corrosion process.

Metal + Oxygen → Metal oxide (corrosion product)

When oxidation starts, a thin layer of oxide is formed on the metal surface and the nature of this film decides the further action. If the film is

(i) **Stable layer:** A Stable layer is fine grained in structure and can get adhered tightly to the parent metal surface. Hence, such layer can be of impervious nature (ie., which cuts-off penetration of attaching oxygen to the underlying metal). Such a film behaves as protective coating in nature, There by shielding the metal surface. The oxide film on Al are stable, tightly adhering and impervious in nature.

(ii) **Unstable oxide layer:**

This is formed on the surface of noble metals such as Ag, Au, Pt. As the metallic state is more stable than oxide, it decomposes back into the metal and oxygen. Hence, oxidation corrosion is not possible with noble metals.

(iii) **Volatile oxide layer:**

The oxide layer film volatilizes as soon as it is formed. Hence, always a fresh metal surface is available for further attack. This causes continuous corrosion. MoO₃ is volatile in nature.

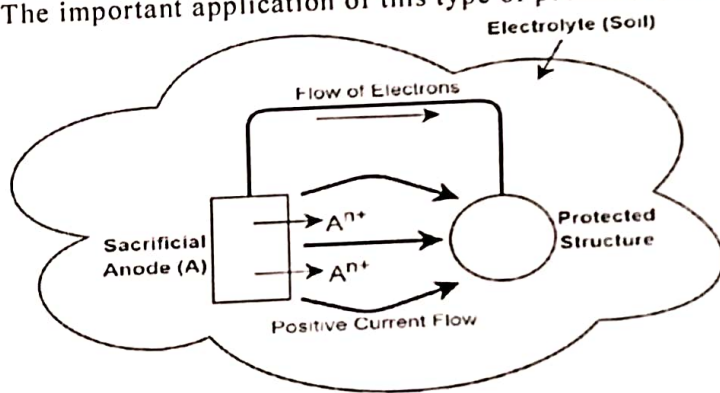
(iv) **Porous layer:** The layer having pores or cracks. In such a case, the atmospheric oxygen have access to the underlying surface of metal, through the pores or cracks of the layer, thereby the corrosion continues unobstructed, till the entire metal is completely converted into its oxide.

8.a) Define Cathodic protection? Explain Sacrificial anodic protection method?

Ans: **Cathodic protection:** The technique of providing cathodic protection to steel preserves the metal by providing a highly active metal that can act as an anode and provide free electrons. By introducing these free electrons, the active metal sacrifices its ions and keeps the less active steel from corroding.

Sacrificial anodic protection method: In this method of protection ,the metallic structure to be protected called base metal, which is connected to more anodic metal (having high oxidation potential) through a wire. The anodic metal undergoes corrosion slowly , while the base metal is protected. The corroded sacrificial anode block is replaced by a fresh one. Commonly used anodic metal are Mg and Zn

The important application of this type of protection are

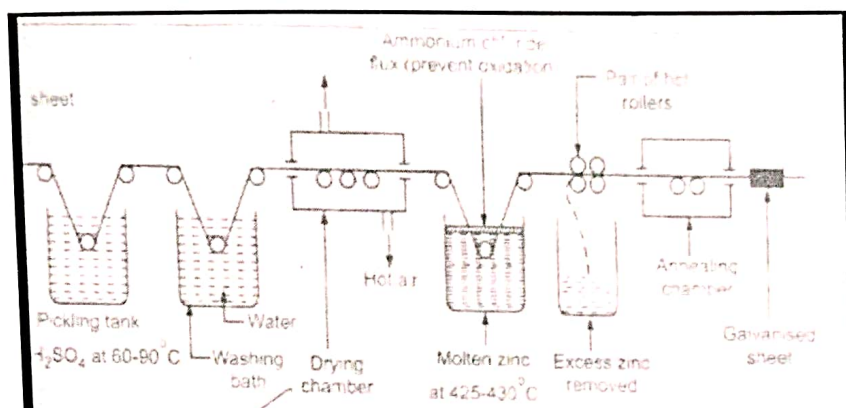


- i) to protect marine structures and ship hulls, which are made of steel are connected to a sacrificial anode, which undergoes corrosion leaving the base metal protected
- ii) protection of buried pipe line, underground cable, water tanks etc... are also protected by sacrificial anode method

8.b) Hot dipping:

Galvanization (or **galvanizing** as it is most commonly called in that industry) is the process of applying a protective zinc coating to steel or iron, to prevent rusting. The most common method is hot-dip galvanizing, in which parts are submerged in a bath of molten zinc.

The base metal iron or steel sheet is cleaned by acid pickling method with dilute sulphuric acid for 15-20 minutes at $60-90^{\circ}\text{C}$. The sheet is then washed well and dried. It is dipped in a bath of molten zinc maintained at $425-450^{\circ}\text{C}$. The surface of the bath is kept covered with ammonium chloride flux to prevent oxide formation. The sheet is taken out and excess zinc is removed by passing in between a pair of hot rollers. Then the sheet is subjected to annealing process at 650°C and cooled slowly. An alloy of iron and zinc were formed at the junction of the base metal and coating metal



Tinning: Coating of tin over iron is called tinning. In this process the surface of the base metal (iron sheet) is cleaned by acid pickling with dil. Sulphuric acid and passed through a bath of zinc chloride flux. The flux helps the molten metal to adhere to the second metal surface. Then the sheet is passed through molten tin bath and pressed between the rollers. The rollers remove excess of tin and produce a thin film of uniform concentration

9.a) Discuss the important green chemistry principles?

Ans: **Goals of green chemistry:** There are 12 principles of green chemistry

-
1. **Prevention.** It is better to prevent waste than to treat or clean up waste after it is formed.
 2. **Atom Economy.** Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
 3. **Less Hazardous Chemical Synthesis.** Whenever practicable, synthetic methodologies should be designed to use and generate substances that pose little or no toxicity to human health and the environment.
 4. **Designing Safer Chemicals.** Chemical products should be designed to preserve efficacy of the function while reducing toxicity.
 5. **Safer Solvents and Auxiliaries.** The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary whenever possible and, when used, innocuous.
 6. **Design for Energy Efficiency.** Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.
 7. **Use of Renewable Feedstocks.** A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
 8. **Reduce Derivatives.** Unnecessary derivatization (use of blocking groups, protection/ deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.
 9. **Catalysis.** Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
 10. **Design for Degradation.** Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.
 11. **Real-Time Analysis for Pollution Prevention.** Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
 12. **Inherently Safer Chemistry for Accident Prevention.** Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.
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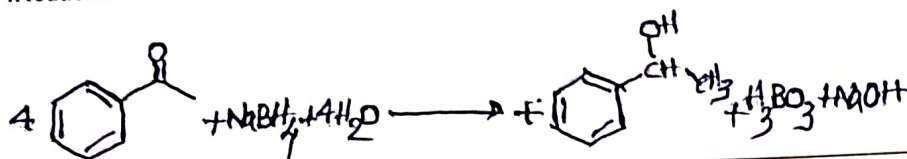
9.b) Write a note on atom economy with suitable example?

Ans : Atom economy of a reaction should be high ;

It states that "the need to incorporate maximum number of reactant molecules in product formation. Atom economy is a measure of the percentage of reactant leading to product formation. Most reactions have a yield of about 70-90 % remaining considered to be the wast

$$\text{Atom economy \%} = \frac{\text{Formula weight of the desired product}}{\text{Formula weight of all reactants}} \times 100$$

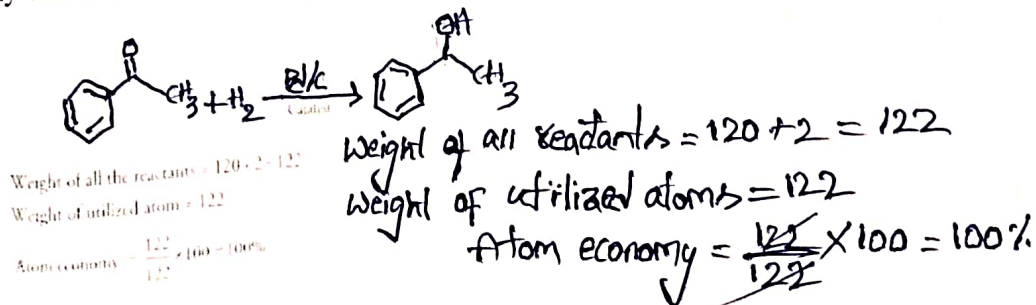
Example : Reduction of ketone to secondary alcohol using sodium boron hydride as the reductant



Reagent formula	Reagent formula weight	Utilized atoms
C ₈ H ₈ O	120X4=480	C ₈ H ₈ O
NaBH ₄	38	
H ₂ O	18	
TOTAL	590	122X4=488

$$\text{Percentage atom economy} = 488/590 \times 100 = 82.7 \%$$

Nearly 17.3 % of the reactant is wasted in unwanted side products. Green chemistry envisages a better economy which can be achieved by an alternative reaction pathway.



10.a) Explain the importance of Zeolites and ion exchange resins in green chemistry point of view?

Ans:

Zeolite catalyst in green chemistry:

Zeolite as catalyst in green chemistry:

It is difficult to spend any time in the chemical process industry without hearing about zeolite catalysts. "Zeolite" is the broad term used to describe a family of minerals called tectosilicates. Zeolites are constructed of tetrahedral AlO₄-5 and SiO₄-4 molecules bound by oxygen atoms. Currently, there are 40 known natural zeolites and in excess of 140 synthetic zeolites. Zeolites can be custom made by manipulating the structure, silica-alumina ratio, pore size, and density. Other metals can also be incorporated into zeolites to obtain specific catalytic properties.

Other examples from zeolite are ZSM-5 and ZSM-11 .

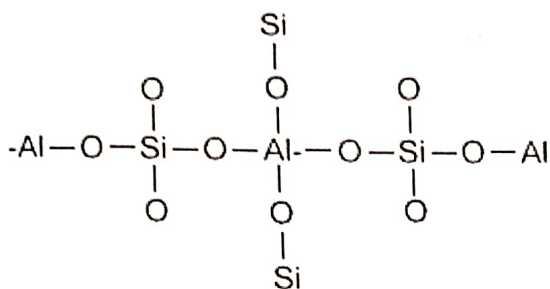
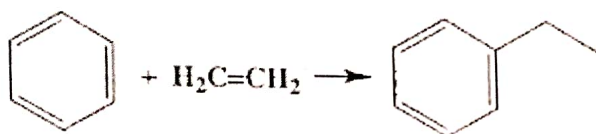


Figure 1: Basic Zeolite Structure

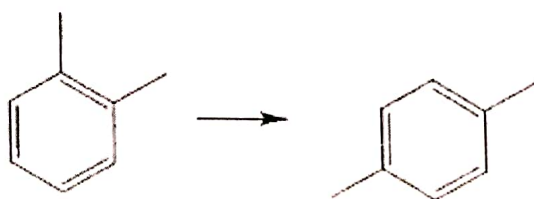
The motivations for using zeolite catalysts are primarily profit and environmental regulation compliance with low operating cost. They also are used for their superior control of reaction selectivity .

A major application of the zeolites in catalysis is in acid catalyzed reactions such as alkylation,acylation, electrophilic aromatic substitution, cyclization, isomerization and condensation.

Industrial Process	Catalyst
(1) Alkylation	H ZSM 5



(2) o-Xylene isomerisation to paraxylene	H ZSM-5
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Applications of zeolite

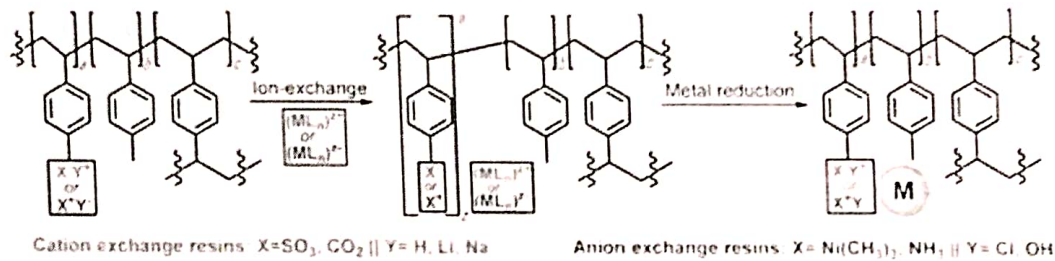
- NOx emission reductions by selective catalytic reduction (SCR)
- Ability to regenerate/recycle a process' catalyst. Many catalyst must be disposed of after they are spent, but the impregnating of zeolites is a process that can be repeated over and over(Water purification)
- Zeolites are used to thermochemically store solar heat captured from solar thermal collectors
- Zeolite-based oxygen concentrator systems are widely used to manufacture medical-grade oxygen
- Zeolites can effectively remove radioactive particles from nuclear waste. It can also be used to clean water or soil contaminated with heavy toxic metals(Due to its cage like structure)

Ion exchange resin as solid catalyst in green chemistry:

IERs are insoluble, organic materials consisting of a polymeric, amorphous backbone with a hydrophobic character with evenly distributed hydrophilic functional groups. Depending on their application, IER can present a wide variety of functional groups such as acidic or basic groups. These were prepared by free-radical crosslinking copolymerization of, for instance, styrene (ST) and divinylbenzene (DVB) monomers through suspension polymerization

Apart from water purification they are also useful in alkylation, acylation, hydration, condensation, oxidation or hydrogenation reactions

Doping IERs with metal catalysts is a well-known technique that can be roughly summarized as a two-steps procedure consisting of (a) metalation step, that is, dispersion of a metal into the IER, using a solution of a metal salt and (b) activation of the catalyst, that is, reduction of the metal in its ionic form to its zero-valence form, to produce catalytically active metal nanoparticles.



Ion-Exchange Resins Application to Hydrogenation Reactions

1. Hydrogenation of alkene, alkyne and aromatic arene using palladium supported ion exchange resin is as follows

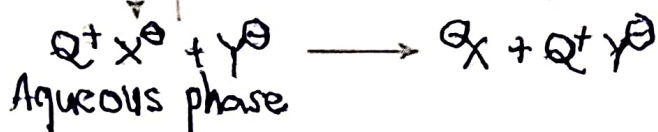
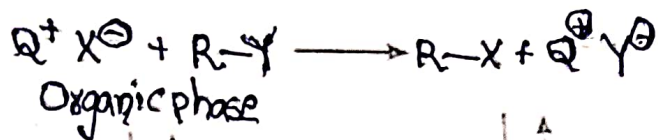
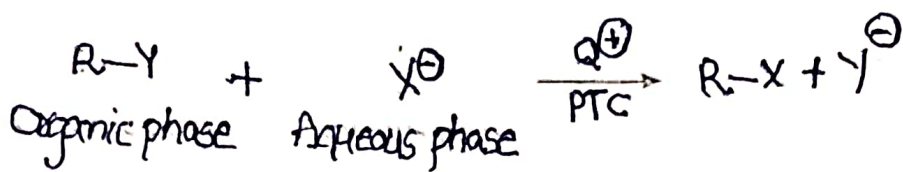


2. The simultaneous catalytic reduction of nitrate ions and reductive dehalogenation of organochlorinated pollutants from water can be done using bimetallic Pd-Cu catalysts over a strong base anion exchange resin

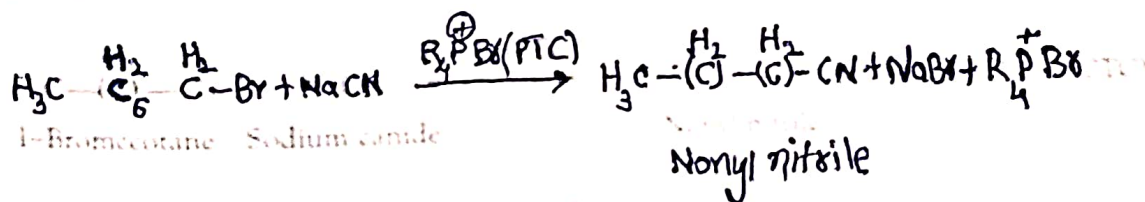
10.b) Write a note on phase transfer catalysis?

Ans: Phase transfer catalyst (PTC):

In general, aqueous and organic phase were not able to miscible with each other, i.e they were not participating in any reaction. In order to complete the reaction it requires a compound which was soluble in both organic and aqueous phase there by it produces a homegeneous solution while that compound is called "Phase transfer catalyst". Example for the PTC is quarternary ammonium or phosphonium salt.



The nucleophilic aliphatic substitution reaction of an aqueous sodium cyanide (NaCN) solution with ethereal solution of 1-bromo octane does not readily occur due to 1-bromo octane which is poorly soluble in the aqueous phase containing cyanide solution and the sodium cyanide does not dissolve well in the ether. Upon the addition of small amount of hexadecyltributylphosphonium bromide (PTC) a rapid reaction ensue to give nonyl nitrile.



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