

**Solutions of Engineering Chemistry Question paper for VTU  
B.E./B. Tech. Degree Examination, July/August 2022**

**CBCS SCHEME**

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21CHE12/22

**First/Second Semester B.E. Degree Examination, July/August 2022  
Engineering Chemistry**

Time: 3 hrs.

Max. Marks: 100

**Note: Answer any FIVE full questions, choosing ONE full question from each module.**

**Module-1**

- 1 a. Define Single Electrode Potential. Derive Nernst equation for Single Electrode Potential. (07 Marks)  
b. Explain the construction and working of glass electrode. (07 Marks)  
c. Describe the construction and working of lithium ion battery. Mention its applications. (06 Marks)

**OR**

- 2 a. What are Reference Electrodes? Discuss the construction and working of Calomel electrode. (07 Marks)  
b. Calculate the single electrode potential of copper electrode at 28°C. Given that standard electrode potential of Cu is 0.34V and concentration of  $\text{Cu}^{2+}$  ions is 0.012m. (07 Marks)  
c. Distinguish between Primary, Secondary and Reserve batteries. (06 Marks)

**Module-2**

- 3 a. Explain the following factors which affect the rate of corrosion :  
i) Ratio of Anodic and Cathodic area    ii) Nature of corrosion product. (07 Marks)  
b. What is Electroless Plating? Distinguish between Electroplating and Electroless plating. (07 Marks)  
c. Describe differential Metal corrosion and Water line corrosion. (06 Marks)

**OR**

- 4 a. Explain Sacrificial anode and Impressed current method of corrosion control. (07 Marks)  
b. What is meant by Metal finishing? Mention technological importance of Metal finishing. (07 Marks)  
c. A steel sheet area  $400\text{cm}^2$  ( $62\text{ in}^2$ ) is exposed to moist air. After one year period it was found to experience a weight loss of 375g due to corrosion. If the density of steel is  $7.9\text{ g/cm}^3$ , calculate the CPR in mpy and  $\text{mm}^{-1}$ . Given that  $K = 534\text{ in mpy}$  and  $87.6\text{ in mmy}^{-1}$ . (06 Marks)

**Module-3**

- 5 a. What are Polymer Composites? Explain the synthesis, properties and applications of Kevlar. (07 Marks)  
b. Describe the mechanism of conduction in Polyaniline. (07 Marks)  
c. Discuss the properties and applications of Carbon nanotubes. (06 Marks)

**OR**

- 6 a. Explain the synthesis, properties and application of Polyurethane. (07 Marks)  
b. What are Biodegradable polymers? Explain the synthesis, properties and applications of Polylactic acid. (07 Marks)  
c. What are Nanomaterials? Describe the synthesis of Nano materials by Sol – Gel process. (06 Marks)

Important Note : 1. On completing your answers, compulsorily draw diagonal cross lines on the remaining blank pages.  
2. Any revealing of identification, appeal to evaluator and/or equations written eg. 42+8 = 50, will be treated as malpractice.

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**Module-4**

- 7 a. Define Green chemistry. Briefly explain basic principles of Green chemistry. (07 Marks)  
b. Discuss the synthesis of Adipic acid by conventional route from benzene and green route from glucose. (07 Marks)  
c. Describe the construction and working of Methanol – Oxygen fuel cell. (06 Marks)

**OR**

- 8 a. Explain the synthesis of Paracetamol by conventional and green route from phenol. (07 Marks)  
b. Describe the production of hydrogen by photocatalytic water Splitting method. (07 Marks)  
c. Explain the construction and working of Photovoltaic cell. (06 Marks)

**Module-5**

- 9 a. Explain the Theory, Instrumentation and Applications of Colorimetry. (07 Marks)  
b. Discuss the determination of hardness of water by EDTA method. (07 Marks)  
c. Define the following terms : (06 Marks)  
i) Normality      ii) Molarity      iii) Mole fraction.

**OR**

- 10 a. Explain the theory and any two applications of Conductometric Analysis. (07 Marks)  
b. In a COD experiment, 24.8 and 16.6cm<sup>3</sup> of 0.2N FAS solutions are required for blank and sample titration respectively. The volume of test sample used was 25cm<sup>3</sup>. Calculate COD of the sample solution. (07 Marks)  
c. What are Primary and Secondary standards? Explain the requirements of Primary Standard solution. (06 Marks)

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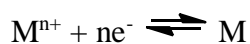
## Module 1

**Answer 1a**    **Single Electrode Potential:** It is defined as the potential developed at the interface between metal and solution, when it is in contact with solutions of its ions. It is denoted by E. It indicates measure of tendency of an electrode to gain electrons i.e. to undergo reduction.

### Nernst Equation

The potential of an electrode depends on concentration and temperature. In 1889, W. H. Nernst derived a quantitative relationship between electrode potential and concentration of electrolyte species.

Consider an electrode assembly undergoing a spontaneous reaction.



The equilibrium constant (K<sub>c</sub>) is related to change in free energy by Vant Hoff equation as follows

$$\Delta G = \Delta G^{\circ} + RT \ln K_c \text{ -----(1)}$$

For above reaction  $K_c = \frac{[M]}{[M^{n+}]} \text{ -----(2)}$

According to thermodynamics, decrease in free energy (-ΔG) represents maximum amount of work that can be obtained from a chemical reaction.

$$-\Delta G = W_{\max} \text{ ----- (3)}$$

Work done in electrochemical reaction depends on

(i) Number of coulombs of electricity that flow and    (ii) Energy available per coulomb.

Number of coulombs = n × F (Where n = number of electrons involved in the cell reaction and F = Faraday constant)

Energy available per coulomb = E (V) or J C<sup>-1</sup>

Thus,

$$W_{\max} = n \times F \times E \text{ ----- (4)}$$

n = moles of electrons, F = C mol<sup>-1</sup>, E = J C<sup>-1</sup>

Equating equations (3) & (4)

$$-\Delta G = n \times F \times E \text{ or}$$

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$$\Delta G = -n \times F \times E \text{ ----- (5)}$$

Under standard conditions, when concentrations of all species is unity, standard free energy change is given by equation

$$\Delta G^\circ = -n \times F \times E^\circ \text{ -----(6)}$$

Where  $\Delta G^\circ$  = Change in free energy under standard conditions,  $E^\circ$  is a constant called **standard electrode potential**.

$E^\circ$  is the potential when a metal is dipped in 1M solution of its ions or when an inert electrode is in contact with a gas at a pressure of 1 atm at 298 K.

Therefore by substituting values of  $\Delta G$ ,  $\Delta G^\circ$  and  $K_c$  from equation (2), (5) and (6) into equation (1), we get

$$-nFE = -nFE^\circ + RT \ln \left[ \frac{[M]}{[M^{n+}]} \right]$$

$$-nFE = -nFE^\circ + RT \ln [M] - RT \ln [M^{n+}]$$

Dividing whole equation by  $-nF$

$$\frac{-nFE}{-nF} = \frac{-nFE^\circ}{-nF} + \frac{RT \ln[M]}{-nF} - \frac{RT \ln[M^{n+}]}{-nF}$$

$$E = E^\circ - \frac{RT \ln[M]}{nF} + \frac{RT \ln[M^{n+}]}{nF}$$

Under standard condition  $[M] = 1$ ,

$$\therefore E = E^\circ + \frac{RT \ln[M^{n+}]}{nF} \text{ ----- (7)}$$

Converting natural log to base 10 in eqn (7) we get

$$E = E^\circ + \frac{2.303RT \log[M^{n+}]}{nF} \text{ ----- (8)}$$

Substituting the values for R (8.314 JK<sup>-1</sup>mol<sup>-1</sup>), F (96500 Cmol<sup>-1</sup>) and T (298K) in eqn (8) we get

$$E = E^\circ + \frac{0.0591 \log[M^{n+}]}{n}$$

This is the mathematical representation of Nernst equation.

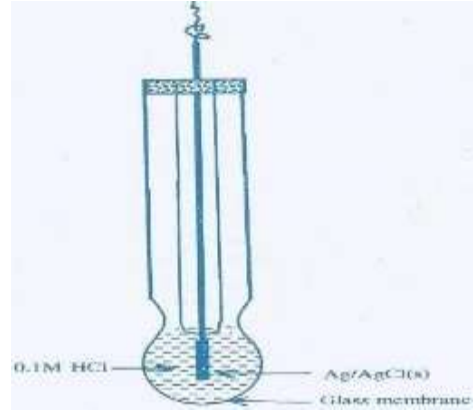
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## Answer 1(b)

**Definition:** Ion selective electrodes selectively respond to a specific ion in a mixture and potential developed is a function of concentration of that ion in the solution. Eg. Glass electrode.

### Glass Electrode:

**Construction:** The glass electrode consist of glass tube, the bottom of the glass tube is glass bulb covered with glass membrane made up of special glass of low melting point and high electrical conductivity (  $\text{SiO}_2, \text{Na}_2\text{O}, \text{Al}_2\text{O}_3$  etc., and it allows only  $\text{H}^+$  ions). Glass bulb consists of 0.1 N HCl (Assume concentration is  $C_2$ ) and Ag/AgCl electrode, which serves as internal reference electrode .



**Working:** The glass electrode is dipped into any solution containing  $\text{H}^+$  ions then glass electrode develops potential called as glass electrode potential. It is represented as  $E_G$ .

Then,  $E_G = E_b + E_{\text{Ag/AgCl}} + E_{\text{assy}} \dots \dots \dots (1)$

Where,  $E_b$ = Boundary potential,  $E_{\text{Ag/AgCl}}$  = Potential due to Ag/AgCl and

$E_{\text{assy}}$ = asymmetric potential

**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.

Mathematically it is represented as,  $E_b = E_1 - E_2$

Where,  $E_1$ = Potential due to  $\text{H}^+$  present inside the bulb (Unknown solution)

$E_2$  = Potential due to  $\text{H}^+$  present in outside solution (Unknown solution)

According to Nernst equation

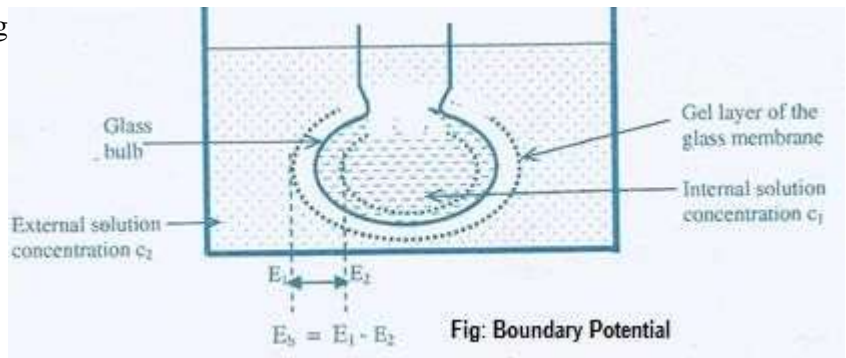
$$= E^\circ + \frac{0.0591}{n} \log C_1 - (E^\circ - \frac{0.0591}{n} \log C_2)$$

$$= \frac{0.0591}{n} \log C_1 - \frac{0.0591}{n} \log C_2$$

Where,  $C_2 = 0.1 \text{ M}$  and  $n = 1 (\text{H}^+)$

$$= \frac{0.0591}{n} \log C_2 - K \text{ or}$$

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



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Glass selects only H<sup>+</sup> ions ignoring other ions.

Hence  $C_1 = H^+$

$E_b = K + 0.0591 \log [H^+]$ , Where,  $\log [H^+] = -pH$

Hence  $E_b = K - 0.0591pH$  -----(2)

Substituting eqn (2) in (1)

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

$E_G = E_G^\circ - 0.0591pH$

## Answer (1c)

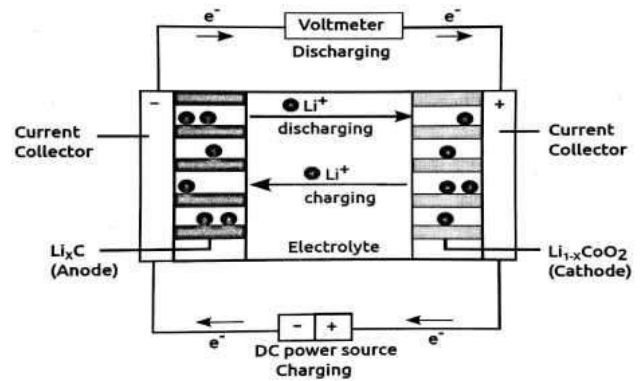
This is a rechargeable battery in which Li ions move from the negative electrode to the positive electrode during discharge and back when charging. (Anode and cathode are layered structure and they are able to insert lithium ion into their layer structure reversibly).

### Construction

**Anode:** The negative electrode of a conventional lithium ion cell is made up of graphite C (Lithiated intercalated material, LiC)

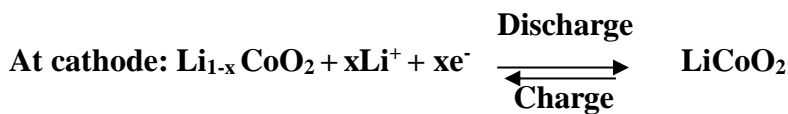
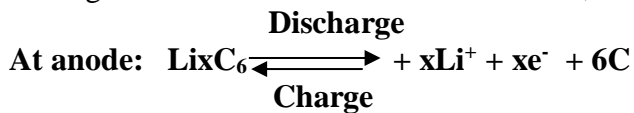
**Cathode:** It is made up of lithiated transition metal intercalated compound i.e. metal oxide (M = Mn, Co).

**Electrolyte:** Lithium salt (LiPF<sub>6</sub>) in an org solvent or mixture of organic carbonates such as ethylene carbonate or diethyl carbonate containing complex of Li-ions.



### Working:

In the electrochemical reaction in a Li-ion battery both electrodes allow lithium ions to move in and out of their interiors. When a lithium ion cell is discharging, the positive Li ions moves from the negative electrode and enters the cathode, and when the cell is charging reverse occur.



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## Charge

Electrochemical process is uptake of Li-ions at the anode during charge and their release during discharge.

The voltage of LIB is about **3.5-3.7 V**.

### Applications:

1. Mobile phones, smartphone, Laptops and tablets, digital cameras camcorders and torches.
2. They are used for energy storage for many electric vehicles.
3. Li-ion batteries are used in telecommunications applications.

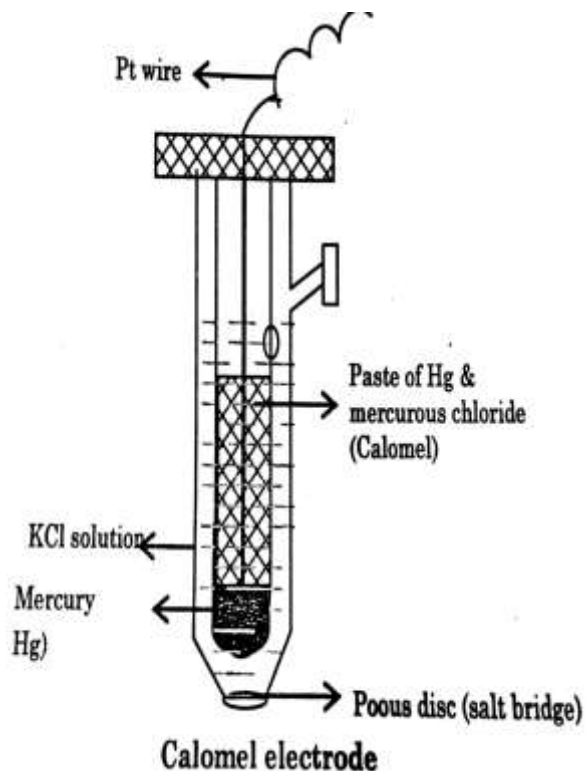
## Answer 2a.

**Reference electrode:** It is an electrode whose electrode potential is arbitrarily fixed or known and is reliable.

This can be used to measure the electrode potentials of other electrodes by constructing a galvanic cell using the reference electrode.

**Calomel electrode** It is a metal – metal salt ion electrodes and also a secondary reference electrode.

**Construction:** It consists of mercury, mercurous chloride and a solution of KCl. It is made up of glass tube, Hg is placed at the bottom of the glass tube. It is covered with a paste of calomel ( $\text{HgCl}_2$ ) and KCl solution. A solution of KCl is introduced above the paste through the side tube. Electrical contact is made through Pt wire (dipped in Hg). This glass tube is taken into another glass tube, which has a side tube and a porous plug at the bottom. This porous plug act as salt bridge. The conc of KCl solution used is either decinormal, normal or saturated. Correspondingly, the electrode is known as decinormal, normal or saturated calomel electrode. This constitutes one half cell. Calomel electrode can act as either anode or cathode. It is connected to the other half cell through salt bridge.



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## Half cell representation

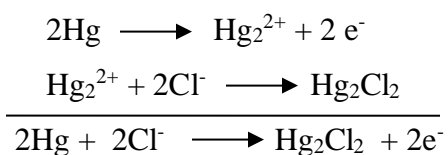
The calomel electrode is represented as,  $\text{Hg} / \text{Hg}_2\text{Cl}_2 (\text{s}) / \text{Cl}^-$  (anode)

Or  $\text{Cl}^- / \text{Hg}_2\text{Cl}_2 (\text{s}) / \text{Hg}$  (Cathode)

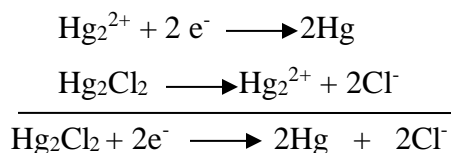
## Working

Depending on the potential of electrode with which the calomel electrode is connected, calomel electrode acts as anode or cathode.

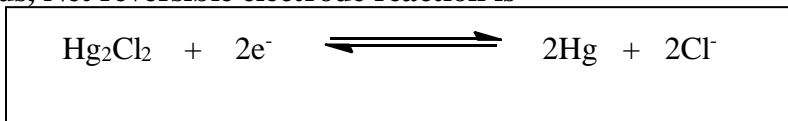
(a). When it acts as anode, electrode reaction is



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



Thus, Net reversible electrode reaction is



Electrode potential is calculated using Nernst equation,

$$\begin{aligned} E_{\text{cal}} &= E^\circ - \frac{2.303RT}{2F} \log [\text{Cl}^-]^2 \\ &= E^\circ - \frac{2.303RT}{F} \log [\text{Cl}^-] \\ &= E^\circ - 0.0591 \log [\text{Cl}^-] \text{ at } 298 \text{ K} \end{aligned}$$

From the above equation it is evident that, the electrode potential of the calomel electrode is mainly depends on the concentration of KCl used. At 298 K the electrode potential are as follows-



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For,        0.1 N KCl = 0.334V  
              1 N KCl = 0.280V  
              Sat KCl = 0.242 V

### Applications:

1. It is used as secondary reference electrode in all potentiometric determinations.
2. Used in glass or combined electrode to determine the pH of the unknown solution.

### Advantages:

1. Construction is simple and electrode is portable.
2. The cell potential is stable and reproducible.
3. Cell potential does not vary with temperature.

### Limitations:

1. Calomel electrode cannot be used beyond a temperature of 60 °C.
2. Hg employed in construction poses pollution problem.

### Answer 2b:

Solution: Given  $E^\circ = 0.34 \text{ V}$

$[\text{Cu}^{2+}] = 0.012 \text{ M}$

$T = 28 \text{ }^\circ\text{C} = (273 + 28) \text{ K} = 301\text{K}$

$$E = E^\circ + \frac{2.303 RT}{nF} \log [M^+]$$

Reaction at cathode:  $\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}$

$$E = 0.34 + \frac{2.303 \times 8.314 \times 300}{2 \times 96500} \log [\text{Cu}^{2+}]$$

$$E = 0.34 + 0.02986 \times \log [0.012]$$

$$E = 0.34 - 0.02986 \times (-1.92)$$

$$E = 0.283 \text{ V}$$

### Answer 2c

#### Classification of batteries

Batteries are classified into mainly three types:

- (i) Primary batteries                      (ii) Secondary batteries                      (iii) Reserve batteries

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**1. Primary batteries:** In primary batteries, the cell reaction is not reversible and hence these are not rechargeable. Once discharged they have no further use.

For example: Zn – MnO<sub>2</sub>, Li-MnO<sub>2</sub> batteries etc.

**2. Secondary batteries:** In secondary batteries, the net cell reaction is completely reversible and hence these are rechargeable. They are known as storage batteries. The discharged cell can be recharged by passing current through it in the direction opposite to that discharge current.

For example: Lead storage battery, Ni – Cd battery etc.

**3. Reserve batteries:** In these batteries one of the key components is stored separately and is incorporated into the battery when required. Usually electrolyte is stored separately. When one of the key components is separated from battery, chemical reaction between cell components (self discharge) is prevented and battery can be stored for a long period of time.

For example: Mg-AgCl, Mg-CuCl, Zinc – Silver oxide reserve batteries, etc.

## Module 2

### Answer 3 (a)

(i) **The ratio of anodic and cathodic areas** : The rate of corrosion largely depends on the relative size of anode and a cathode.

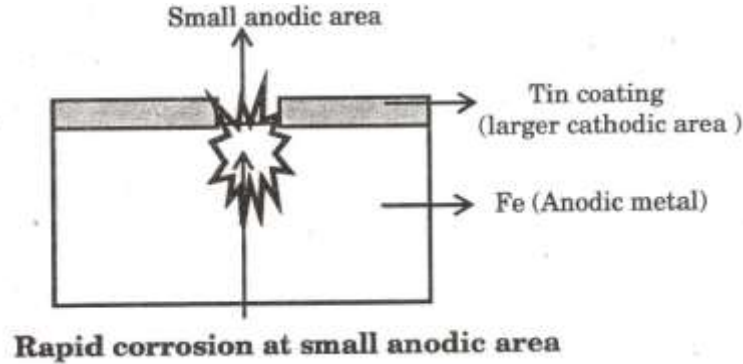
(a) If the metal has a **small anodic and large cathodic area** (i.e; the ratio of anode to cathode is small) then the corrosion is **more intensive and faster in rate**. This is explained as follows

At anode oxidation takes place and electrons are liberated. At the cathode these electrons are consumed when the anode is smaller and cathode region is large, the electrons liberated at the anode, are rapidly consumed, at the cathode region. This process makes the anodic reaction to take place faster, thus increasing the corrosion rate.

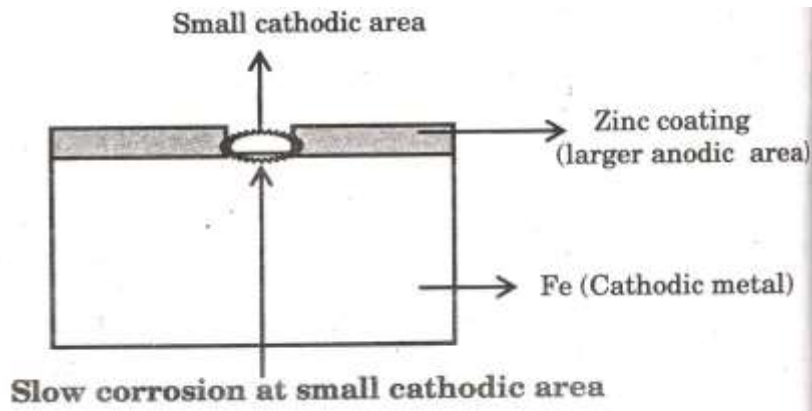
Ex: A broken coating of tin on iron surface, tin is cathodic to iron and the small exposed part of

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iron acts as anodic region and rest of the large tin coated surface acts as cathodic region. Because of small ratio of anodic to cathodic area, the corrosion rate is very high



(b) If the **cathode is smaller and anode is larger**, the rate of corrosion will be **less**, because the consumption of electrons will be slower and the corrosion reaction as a whole will be slower.



Eg. The broken coating of Zn over Fe, Zn plating on Fe gives an anodic coating to iron (Zn is above Fe in electrochemical series). Thus even if Zn plating peels off at some point, Fe does not get corroded.

## (ii) Nature of the corrosion product

The nature of the corrosion product largely decides the rate of further corrosion. The corrosion product formed on the surface of the metal may or may not act as a protective layer.

(a) The nature of the oxide layer largely decides the rate of further corrosion. If its composition is stoichiometric, highly insoluble and non porous with low ionic and electrical

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conductivity, the layer acts as protective film and prevent further corrosion. For eg. Al, Ti and Cr develops such a layer on their surface and become passive to further corrosion. Stainless steel (18% Cr, 8% Ni) builds up a thin but a highly protective film of  $\text{Cr}_2\text{O}_3$  which resist attack in a highly corrosive environment. Metals such as Zr and Mo not only form such protective layer but are also capable of self repairing the oxide films when it is damaged. Hence these metals are extremely resistant to corrosion.

- (b) If the oxide layer is non stoichiometric, highly porous, soluble, unstable, it cannot control further corrosion. In such cases the fresh metal surface is continuously exposed to corrosion environment and corrosion takes place continuously. Eg. Fe and Zn

### Answer 3b

**Electroless-plating:** Deposition of metal or alloy over a conducting or non-conducting substrate surface by **chemical reduction of the metal ions by use of reducing reagent** and without the use of electrical energy is called electroless-plating.

Electroless-plating is generally autocatalytic in nature. Schematically, it can be represented as,

Metal ions + Reducing agent  $\xrightarrow{\text{catalytically active surface}}$  Metal atom + Oxidized product

- There is a difference in the method and quality of metal deposition by electroplating and electroless-plating. Following is the comparison between the two.

	Property	Electroplating	Electroless-plating
1	Driving force	Power supply	Autocatalytic redox reaction
2	Site of oxidation reaction	Separate anode	Object surface to be plated
3	Site of reduction reaction	Object surface to be plated	Surface activated object
4	Oxidation reaction	when anode is active: $\text{M} \longrightarrow \text{M}^{n+} + n\text{e}^-$ when anode is inert: $\frac{n}{2} \text{H}_2\text{O} \longrightarrow n\text{H}^+ + \frac{n}{2} \text{O}_2 + n\text{e}^-$	$\text{R} \longrightarrow \text{O} + n\text{e}^-$ where R = Reducing agent O = Oxidised species
5	Reduction reaction	$\text{M}^{n+} + n\text{e}^- \longrightarrow \text{M}$	$\text{M}^{n+} + n\text{e}^- \longrightarrow \text{M}$
6	Time taken for deposition	Short	Long
7	Throwing power	Low	High
8	Plating cost	Low	High
9	Nature of deposit	Pure metal or definite alloy, hard deposit	Usually, metal contaminated with R/O derived species, harder deposit

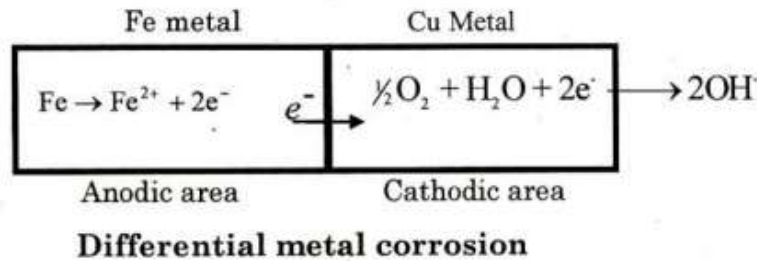
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10	Features of deposit	May be porous, & less corrosion resistant	Non-porous, relatively hard & more corrosion resistant

**ANSWER 3(c):** Differential metal corrosion: Galvanic corrosion or differential metal corrosion: This occurs when two dissimilar metals are in contact with each other in a corrosive conductive medium; a potential difference is set up resulting in a galvanic current. The two metals differ in their tendencies to undergo oxidation. The metal with lower electrode potential or more active metal acts as anode and the metal with higher electrode potential acts as cathode. The potential difference is main factor for corrosion to take place. The anodic metal undergoes corrosion whereas cathodic metal gets unattacked. Example: When iron contact with copper iron has lower electrode potential acts as anode and undergo oxidation as,



Whereas copper which is having higher electrode potential acts as cathode gets unaffected. The rate of galvanic corrosion depends upon potential difference between anodic and cathodic metals, ratio of anodic and cathodic area and environmental factors and tendency of the metal to undergo passivity etc.

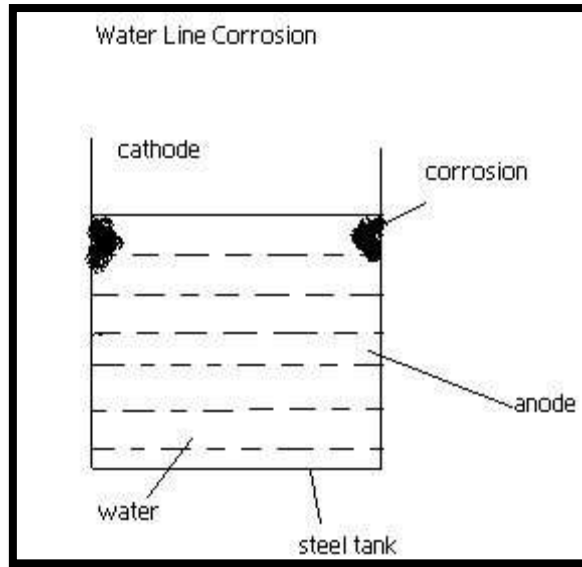


**Waterline corrosion:** Water line corrosion is a case of differential aeration corrosion. The water line corrosion takes place due to the formation of differential oxygen concentration cells. The part of the metal below the water line is exposed only to dissolved oxygen (acts as anode) while the part above the water is exposed to higher oxygen concentration (acts as cathode) of the atmosphere. A distinct brown line is formed below the water line due to deposition of rust

At the anode (less O<sub>2</sub> concentration)  $\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^-$

At the cathode (more O<sub>2</sub> concentration),  $\text{H}_2\text{O} + \frac{1}{2}\text{O}_2 + 2e^- \rightarrow 2\text{OH}^-$

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***Answer 4a***

**(I) SACRIFICIAL ANODIC METHOD:**

In this method, the base metal structure is converted into a cathode by connected it to a more active [higher up in galvanic series or less noble] metal. This active metal actually acts as an auxiliary anode. Mostly Zn, Mg, Al are the common auxiliary anodes used in this method. These metals being more active, acts as anode and undergo destruction and protect the metal structure.

Since the anode material sacrifice to protect the metal structure, the method is known as sacrificial anode method. After continuous use exhausted sacrificial anodes are replaced by new ones as and when required.

Ex: 1. A Mg block connected to buried oil storage tank.

2. Mg base areas fixed to the side of ocean going ships.

3. Mg blocks area connected to the buried pipe lines.

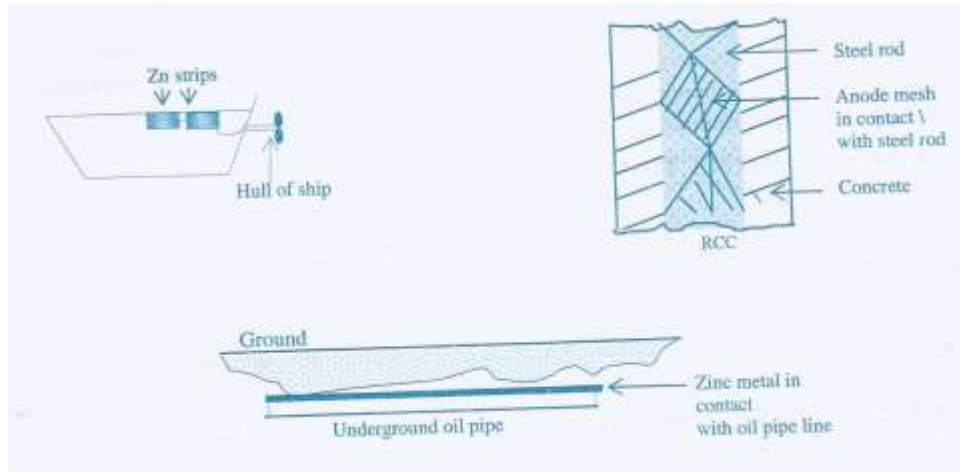
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(i) The method is simple. (ii) Low installation cost. (iii) Minimum maintenance cost. (iv) Doesn't require power supply.

## Disadvantage:

(i) Involves recurring expenditure for replacement of consumed anodes.



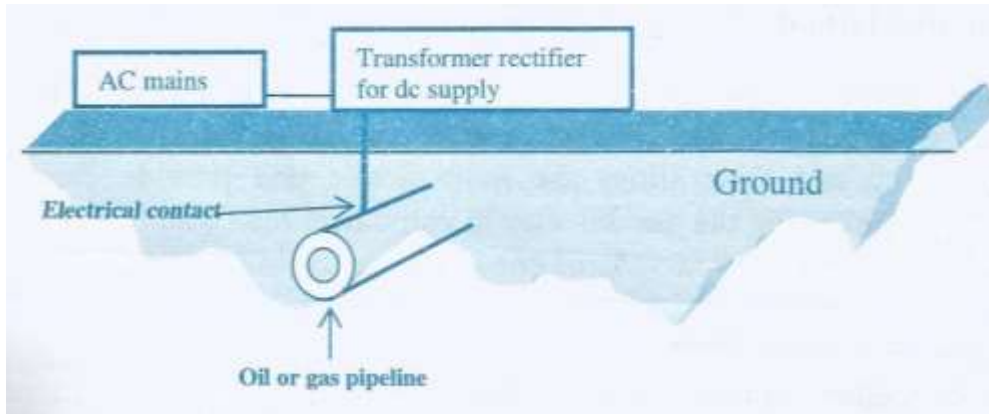
**Fig:** Cathodic Protection by sacrificial anode

## (II) IMPRESSED CURRENT METHOD:

In this method, by applying a direct current larger than the corrosion current, the base metal is made cathodic by connecting it to the cathode of the external source of current and the anode of the source is connected to an inert electrode (lead or graphite). The cathode is the structure to be protected and anode is resin bonded graphite rod, high silicon-iron alloy or platinized Ti connected to the positive terminal.

The metal structure being cathode, doesn't undergo corrosion. Anode being inert, remains unaffected [electrons for protection are supplied by a source of direct current].

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**Fig:** Protection using an impressed voltage

### **Advantages:**

- (i) One installation can protect larger area of metal.
- (ii) Low maintenance cost.

### **Disadvantages:**

- (i) It is very expensive, because it needs continuous current.
- (ii) If the impressed current is not uniform on the entire surface of the protected structure, localized corrosion takes place on the protected metal.

## ***Answer 4b***

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

### **Technological Importance:**

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

- (i) Better corrosion resistance,



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

**Answer 4c:** Corrosion Penetration Rate (CPR) is defined in three ways: (1) the speed at which any metal in a specific environment deteriorates due to a chemical reaction in the metal when it is exposed to a corrosive environment, (2) the amount of corrosion lost per year in thickness, (3) the speed at which corrosion spreads to the inner portions of a material.

<p>Corrosion penetrating rate in mpy  <math>CPR = KW/DAT</math>            Weight loss, <math>W = 375 \times 10^3 \text{ mg}</math>            Density, <math>D = 7.9 \text{ g/cm}^3</math>; Time, <math>T = 1 \times 24 \times 365</math>            Area <math>A = 62 \text{ in}^2</math>  <math display="block">CPR = \frac{534 \times 375 \times 10^3}{7.9 \times 62 \times 1 \times 24 \times 365}</math> <b>CPR = 46.67 mpy</b></p>	<p>Corrosion penetrating rate mm/y  <math>CPR = KW/DAT</math>            Weight loss, <math>W = 375 \times 10^3 \text{ mg}</math>            Density, <math>D = 7.9 \text{ g/cm}^3</math>; Time, <math>T = 1 \times 24 \times 365</math>            Area <math>A = 400 \text{ cm}^2</math>  <math display="block">CPR = \frac{87.6 \times 375 \times 10^3}{7.9 \times 400 \times 1 \times 24 \times 365}</math> <b>CPR = 1.187 mm/y</b></p>
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## Module 3

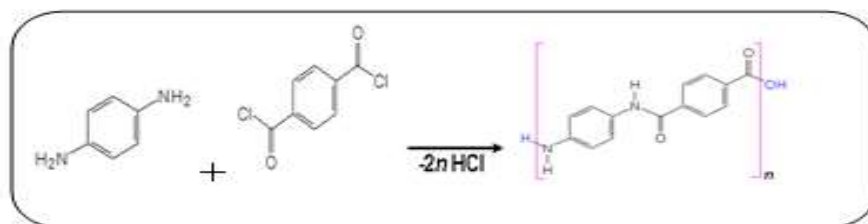
### **Answer 5a**

**Answer:** Polymer composites are a combination of polymers (i.e., thermosets or thermoplastics) with various continuous and noncontinuous reinforcements/fillers, principally added to polymers to improve the material performance.

**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

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to form mostly planar sheets, similar to those of silk. This is due to the Para-orientation 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 radially, 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.

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**6. Kevlar in Fiber Optics:** Kevlar is used to safeguard against mechanical stresses in optical fibre cables.

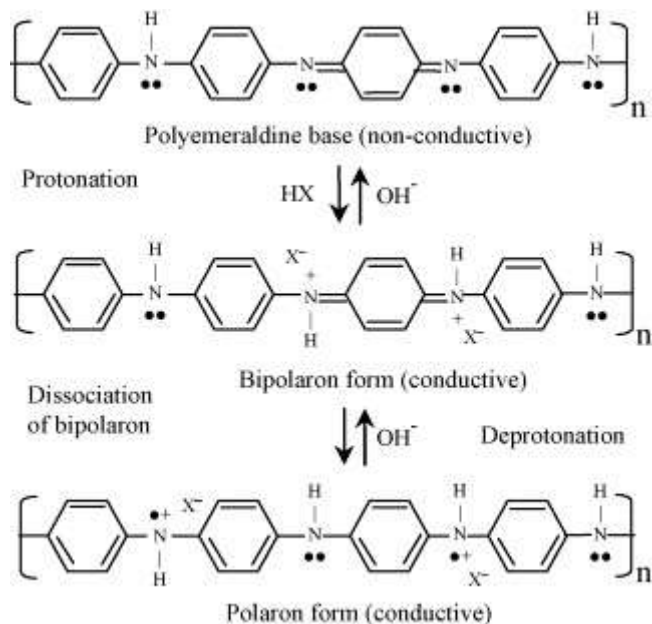
**7. Ropes and Cables:** Its resistance to chemicals and temperature extremes make it an ideal component for ropes and cables under severe loads in harsh environments.

### Answer 5b

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

**Mechanism of Conduction:** These conjugated organic polymers in their pure state are insulators or semi-conductors. The  $\pi$ -electrons are normally localized and do not take part in conductivity. But, these electrons delocalize on doping and conduct electricity.

Polyaniline exists in a variety of forms (Oxidation states) that differ in their conductivity. The emeraldine form of polyaniline can also be electrochemically oxidized or reduced in aqueous acid resulting in pernigraniline (PS) and leuco-emeraldine (LS) salts, respectively. This process is known as protonic acid doping. The addition of protons and electrons to nitrogen is observed during the reduction. This leads to change of ring from phenyl to quinoid structure upon oxidation and vice versa during reduction. The generation of these charged carriers is responsible for conductivity of the polymer.



### Mechanism of Conduction

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## **ANSWER 5C:**

**Carbon Nanotubes (CNTs):** Carbon Nanotubes (CNTs) are cylindrical tubes with a central hollow core formed by rolling up of graphene sheets. The CNT is a one dimensional material like nanowire, but with the length to width ratio greater than 1000. CNTs are categorized as Single-Walled CNTs (SWCNTs) and multi-walled nanotubes (MWCNTs).

1. **Single-Walled CNT (SWCNTs):** They are formed by rolling up of single graphene layer. The diameter of SWCNT is 1-4 nm and length can go up to few micrometers.
2. **Multi-Walled CNT (MWCNTs):** They consist of two or more concentric graphene cylinders. The diameter of MWCNTs is in the range of 30-50 nm and length can go up to few micrometers.

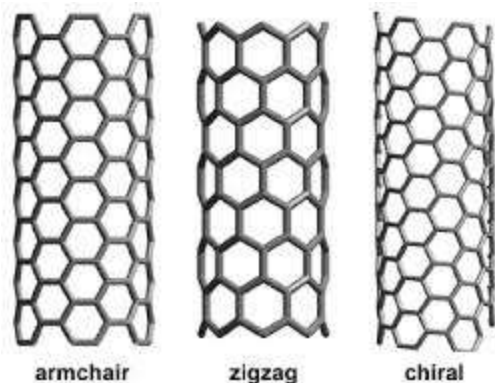
### **Properties:**

1. CNTs exhibit high electrical and thermal conductivity.
2. They have low density and very high mechanical strength due to these properties they are used as electrode material.
3. CNTs can emit electrons when subjected to high electrical field. Due to this property they are used in X-ray tubes.
3. The CNTs are about 20 times stronger than steel and hence find applications in making automobiles and aircraft body parts.
4. SWCNTs absorb radiation in the near IR range (700-1100 nm) and convert it to heat. This property is used in cancer thermotherapy to selectively kill cancer cells.
5. SWCNTs are used in solar panels.
6. CNTs are used for hydrogen storage to be used as fuel source.

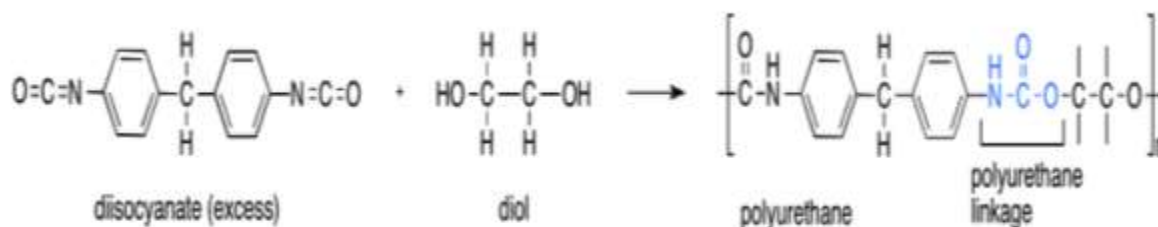
### **Applications:** In the field of

1. Biosensors, chemical sensor and gas sensors,
2. Water purification
3. Cancer treatment
4. Drug delivery
5. Battery
6. Construction with steel

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**Answer 6a** : 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.



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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.,

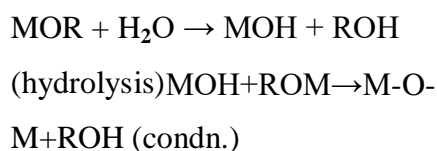
**Answer 6c:** Nanomaterials or Nanoparticles are defined as substances which contain nano size particles with at least one dimension in the range of 1 nm to 100 nm.

The sol-gel method of synthesizing nanomaterial is very popular amongst chemists and is widely employed to prepare oxide materials.

The sol-gel process can be characterized by a series of distinct steps.

**Step 1:** Formation of different stable solutions of the alkoxide or solvated metal precursor (**the sol**).

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



Step 3: Aging of the gel (Syneresis), during which the polycondensation reactions continue until the gel transforms into a solid mass, accompanied by contraction of the gel network and expulsion of solvent from gel pores. The aging process of gels can exceed 7 days and is critical to the prevention of cracks in gels that have been cast.

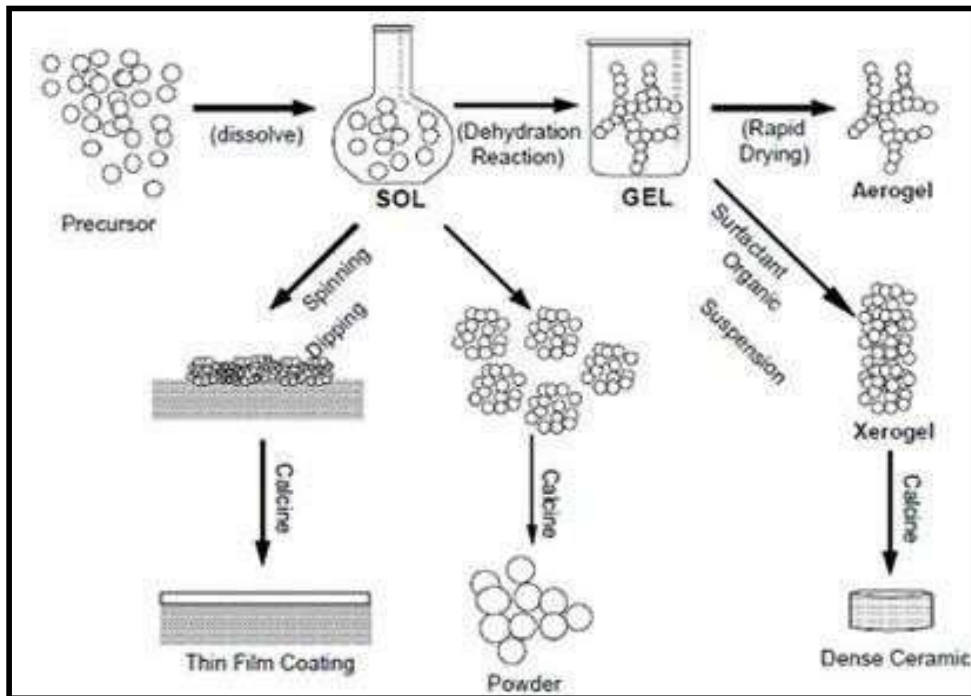
Step 4: Drying of the gel, when water and other volatile liquids are removed from the gel network. This process is complicated due to fundamental changes in the structure of the gel. The drying process has itself been broken into four distinct steps: (i) the constant rate period, (ii) the critical point, (iii) the falling rate period, (iv) the second falling rate period. If isolated by thermal evaporation, the resulting monolith is termed a xerogel. If the solvent (such as water) is extracted under supercritical or near supercritical conditions, the product is an

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aerogel.

Step 5: Dehydration, during which surface- bound M-OH groups are removed, thereby stabilizing the gel against rehydration. This is normally achieved by calcining the monolith at temperatures up to 8000C.

Step 6: Densification and decomposition of the gels at high temperatures ( $T > 8000C$ ). The pores of the gel network are collapsed, and remaining organic species are volatilized. The typical steps that are involved in sol-gel processing are shown in the schematic diagram below.



### Advantages:

1. Nanomaterials of high purity with good homogeneity can be obtained.
2. Samples can be prepared at lower temperature.
3. Easy to control synthesis parameters to control physical characteristics like shape and size of resulting materials.
4. Simple and inexpensive equipment.
5. Size can be controlled.



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## Module 4

**Answer 7a:** 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”

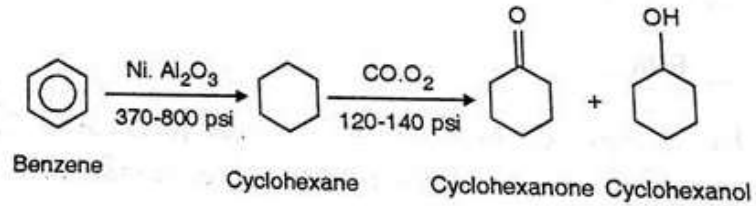
Basic principles of green chemistry

- 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.

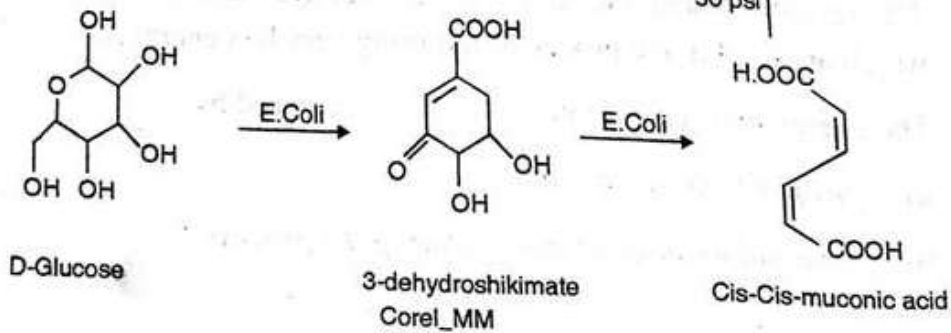
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**Answer 7b**

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



**(B) Greener pathway :  
Using glucose (absolutely safe)**



**Answer 7c**

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.

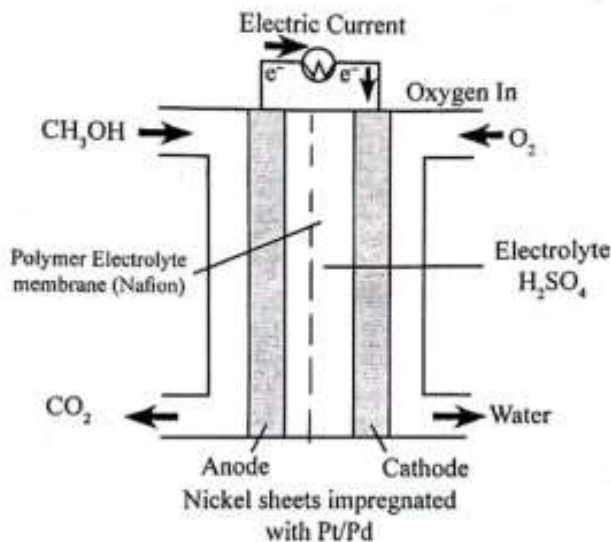
**Cathode** - It is a porous Nickel (Ni) electrode coated with Pt/Pd catalyst.

**Electrolyte** – Aqueous sulphuric acid (H<sub>2</sub>SO<sub>4</sub>), 3.7 M.

**Fuel** – Methanol mixed with sulphuric acid supplied at

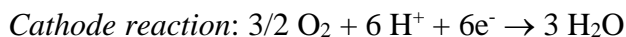
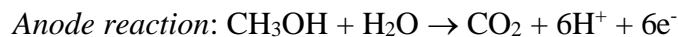
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*Oxidant* – Pure oxygen is supplied at cathode.



**Figure. Methanol – oxygen fuel cell**

**Working:** Cell reaction;



H<sub>2</sub>O and CO<sub>2</sub> 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:**

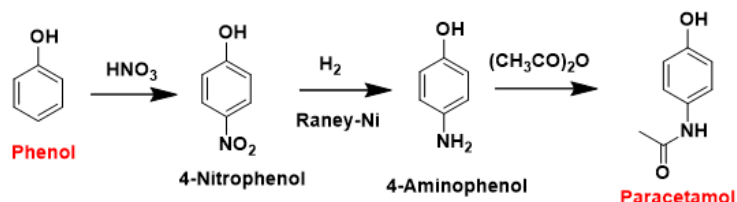
- (1) used in automobiles, military applications.
- (2) Power backup and portable instruments.
- (3) in large scale power production.

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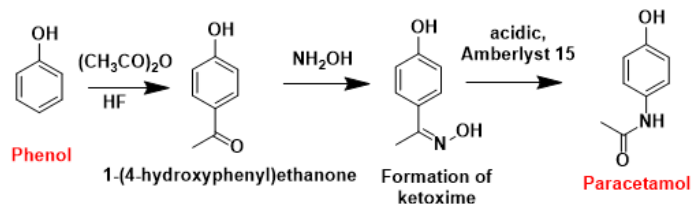
## Answer 8a

Synthesis of Paracetamol:

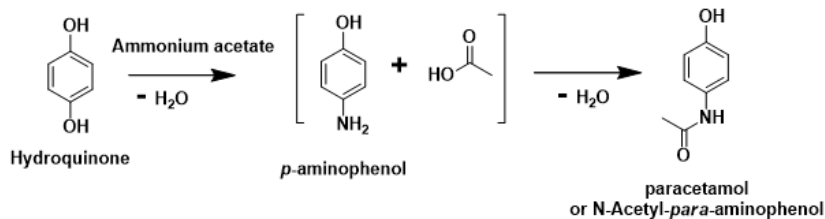
**Traditional/Conventional synthesis:** Involves the nitration of phenol to 4-nitrophenol. The nitro group is then reduced to an amine, giving 4-aminophenol. Finally, the amine is acetylated with acetic anhydride.



**Green Synthesis of Paracetamol:** Involves direct acylation of phenol with acetic anhydride catalyzed by HF, conversion of the ketone to a ketoamine with hydroxylamine, followed by the acid-catalyzed Beckmann rearrangement to give the amide. :



More recently (2014) a "one-pot" synthesis from hydroquinone has been described. The process called "direct synthesis"



## Answer 8b

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

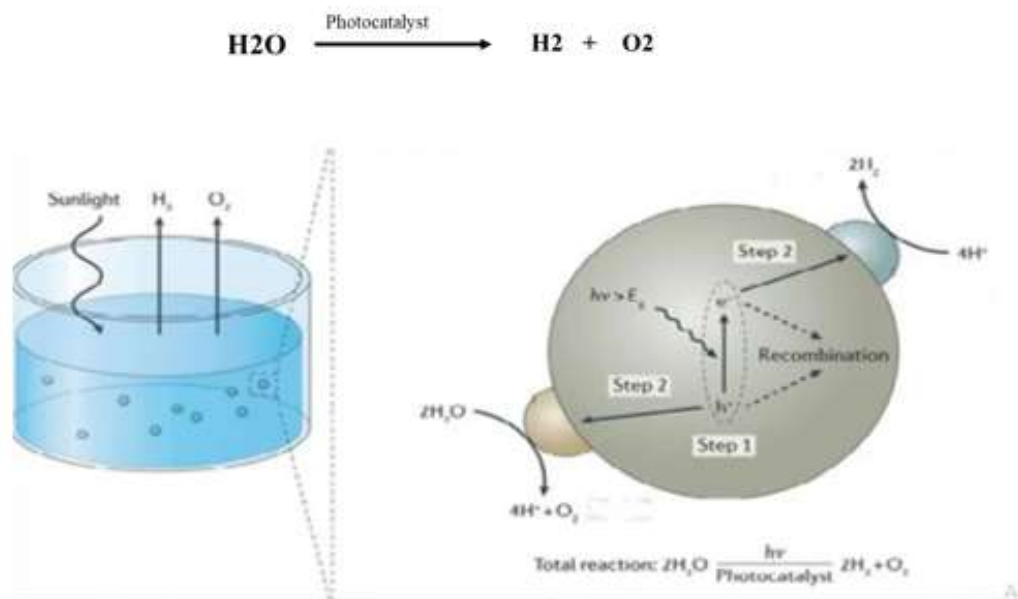
Photocatalytic reaction

Input: Photocatalyst particles, sunlight and water

Output: Oxygen and hydrogen

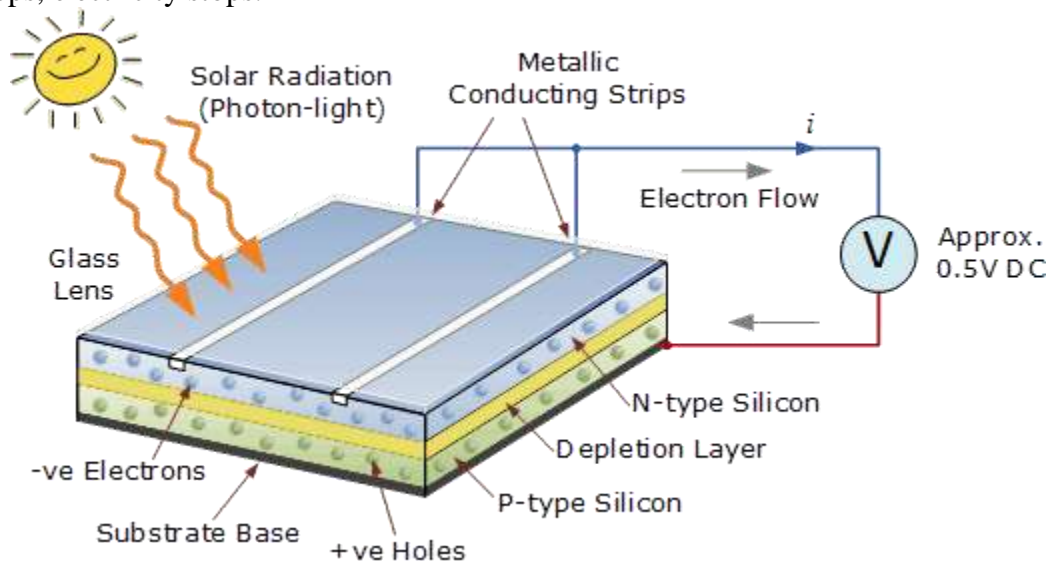
Photocatalyst in the form of particles is immersed in water based electrolyte and it produces charge carriers holes and electrons after absorbing sunlight. Charges are moved to surface of the photocatalyst to start the chemical reaction. Holes are oxidizing the water and electrons reduces hydrogen ions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

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### *Answer 8c*

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-

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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  $\text{TiO}_2$

### Working:

Electromagnetic radiation consists of particle called photon ( $h\nu$ ). 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

## Module 5

### *Answer 9a*

#### COLORIMETRY

**Theory:** Colorimetry is an analytical technique used for the determination of concentration of compounds in a solution. It is used for solutions which are themselves coloured or which give a colour when mixed with a suitable reagent. A measure of the variation of the color of a solution with change in concentration of the solute forms the basis of colorimetry. Colorimetric estimation is based on the Beer-Lambert's law.

**Beer-Lambert's Law:** When a monochromatic radiation of intensity  $I$  is passed through a solution of a sample, a portion of light is absorbed ( $I_a$ ), a portion is reflected ( $I_r$ ) and the remainder is transmitted ( $I_t$ ), then,

$$I_o = I_a + I_r + I_t$$

For glass cell,  $I_r$  is negligible, hence,

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$$I_o = I_a + I_t$$

**Lambert's Law:** It states that when a monochromatic light passes through a transparent medium, the rate of decrease in intensity with the thickness of the medium is proportional to the intensity of the light.

**Beer's Law:** It states that when a monochromatic light passes through a solution, the rate of decrease in intensity with concentration of the light absorbing species is proportional to the intensity of the light.

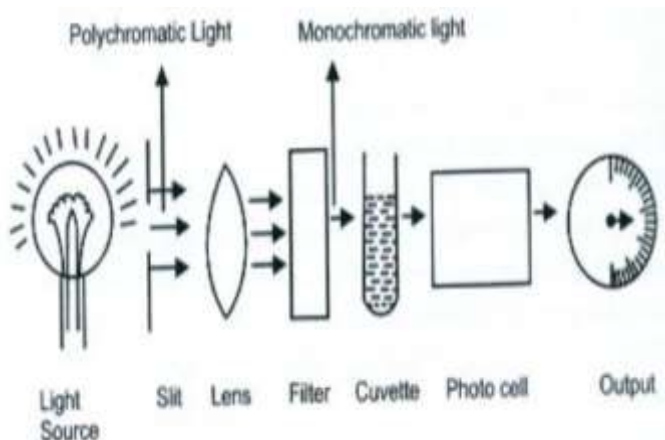
$$\log \frac{I_o}{I_t} = \epsilon ct \quad \text{Or} \quad A = \epsilon ct$$

where  $\epsilon$  called *molar absorptivity* or *molar absorption coefficient*, is a constant for a given substance at a given wavelength. If  $c$  is expressed in  $\text{mol. dm}^{-3}$  and  $t$  in centimeters,  $\epsilon$  has the unit  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ . **This equation is referred to as Beer-Lambert's law.** If the path length of the cell is kept constant, then, absorbance  $A$  is proportional to the concentration  $c$ .

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

It consist of

- (i) Tungsten lamp as the light source.
- (ii) A filter which provides the desired wavelength range wherein the solution gives the maximum absorbance.
- (iii) A sample cell
- (iv) A photocell detector



**Fig: Schematic layout of colorimeter**

Light from a tungsten lamp is allowed to fall on the solution taken in the sample call after passing through the filter. First a blank solution is taken in the sample cell and placed in the path of the

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light beam. Its absorbance is adjusted to zero on the meter. Next the analyte solution is placed in the path of the light beam and the quantity of light absorbed is measured as its absorbance.

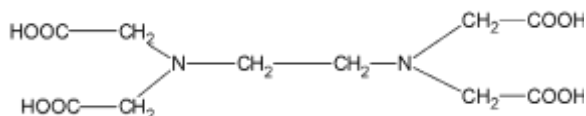
**Application:** Colorimetry is versatile method of determining the concentration of metals and nonmetals present in small quantities in ores, soil, samples and alloys. **Colorimetric estimation of Cu in CuSO<sub>4</sub>**. Draw out 2, 4, 6, 8, and 10 ml cm<sup>3</sup> of the Copper sulphate solution into 50cm<sup>3</sup> volumetric flask. Add 5cm<sup>3</sup> of ammonia solution to each of them and dilute upto the mark with distilled water and mix well. Prepare a blank solution by diluting 5cm<sup>3</sup> of ammonia solution in 50cm<sup>3</sup> volumetric flasks. For test solution add 5ml of NH<sub>3</sub> and make up to the mark. Measure the absorbance of each of these against blank solution at 620 nm. Plot a graph of absorbance (OD) against volume of copper sulphate solution and determine the volume of copper sulphate solution in the test sample as shown in the figure and find the amount of copper present in it.

### Answer 9b

Hardness of water is determined by EDTA method, which involves complexometric titration

#### Principle

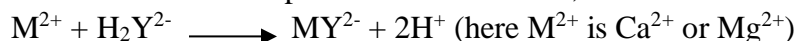
EDTA (Ethylene diamminetetra acetic acid) is a hexadentate ligand and forms complexes with Ca<sup>2+</sup> & Mg<sup>2+</sup> ions. EDTA commonly represented as H<sub>4</sub>Y. It has structure,



The ionization of EDTA in solution is represented as



The anion forms complexes with metal ions, M<sup>2+</sup>



The total hardness of water is determined by titrating a known volume of water against standard EDTA solution at pH 10 using Eriochrome black – T (EBT) indicator. The colour of indicator at pH 10 is blue

EBT forms a wine-red complex with M<sup>2+</sup> ion. On adding EDTA, it forms a complex with free metal ions. At the end point when all the free metal ions are exhausted in the solution, added EDTA dissociates wine red coloured metal – EBT complex, consumes the metal ion and releases blue coloured free indicator. Therefore the colour changes from wine red to blue.

#### Procedure:



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- (i) **Total hardness:** Pipette out 50ml of the sample of water into a clean titration flask, add 1ml of  $\text{NH}_3\text{-NH}_4\text{Cl}$  buffer solution and 3-4 drops of EBT indicator. Titrate against 0.01M EDTA till the color changes from wine-red to clear blue. Let the volume of EDTA required be  $v_1$  ml.
- (ii) **Permanent hardness:** Transfer 50ml of the sample of water into a clean 500ml beaker and boil gently for 20-30 minutes. Cool and filter it directly into a 250ml conical flask. Add 1ml of buffer solution followed by 3-4 drops of EBT indicator. Titrate against standard 0.01M EDTA. Let the volume of EDTA required be  $v_2$ ml.

### Calculations:

#### Total hardness

1000 ml of 1M EDTA = 100g  $\text{CaCO}_3$  (Molecular mass of  $\text{CaCO}_3$  = 100g)

1ml of 1M EDTA =  $\frac{100}{1000}$  g of  $\text{CaCO}_3$

$V_1$  ml of 0.01M EDTA =  $\frac{v_1 \times 0.01 \times 100}{1000}$  g of  $\text{CaCO}_3$

50 ml of water sample =  $\frac{v_1 \times 0.01 \times 100}{1000}$  g of  $\text{CaCO}_3$

$10^6$  (1 million parts) ml of water sample contains =  $\frac{v_1 \times 0.01 \times 100 \times 10^6}{1000 \times 50}$  g of  $\text{CaCO}_3$   
 $= 20 \times v_1$  ppm  $\text{CaCO}_3$  equivalent

#### Permanent hardness

Permanent hardness =  $\frac{v_2 \times 0.01 \times 100 \times 10^6}{1000 \times 50}$  g of  $\text{CaCO}_3$   
 $= 20 \times v_2$  g of  $\text{CaCO}_3$

#### Temporary hardness

Temporary hardness =  $20 \times (v_1 - v_2)$  ppm of  $\text{CaCO}_3$

## Answer 9c

i) Molarity ii) Normality iii) ppm

**Answer: Molarity:** It is one of the most widely used unit of concentration and is denoted by M. It is defined as no. of moles of solute present in 1 liter of solution. Thus,

**Molarity = No of moles of solute / Volume of solution (in Liters)**

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**Normality:** It is described as the number of gram or mole equivalents of solute present in one litre of a solution.

$$\text{Normality} = \text{No of gram equivalents of solute} / \text{Volume of solution (in Liters)}$$

**Mole Fraction:** The mole fraction or molar fraction ( $x_i$ ) is defined as the amount of a constituent (expressed in moles),  $n_i$ , divided by the total amount of all constituents in a mixture (also expressed in moles),  $n_{\text{tot}}$ :

$$x_i = n_i / n_{\text{tot}}$$

The sum of all the mole fractions is equal to 1.

### *Answer 10a*

**Theory:** Conductometry is based on Ohm's law which 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.

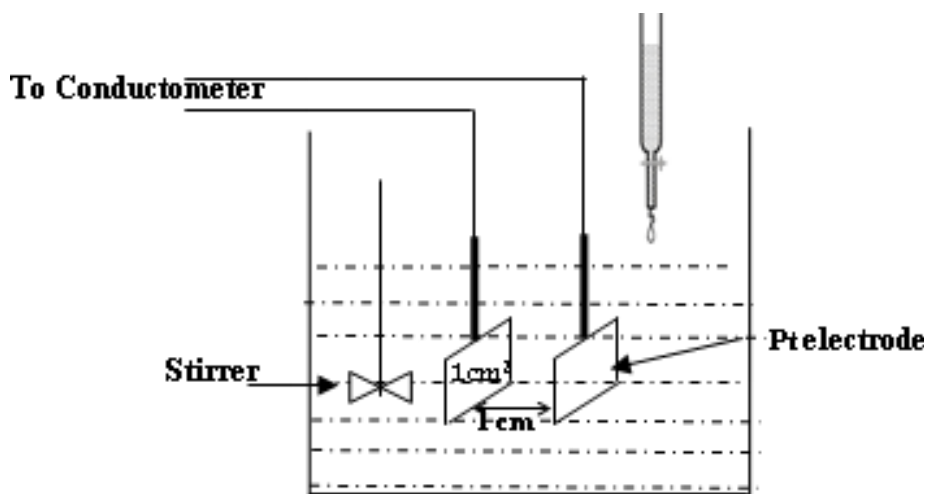
$$i = \frac{E}{R}$$

The reciprocal of the resistance is called the conductance (Ease with which electric current flows through a conductor). Specific conductance of a solution is defined as the conductance of a solution present between two parallel electrodes which have  $1\text{cm}^2$  area of cross section and which have kept 1 cm apart.

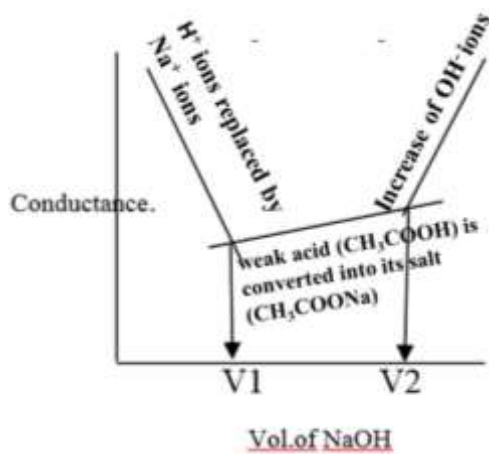
The conductance of solution depends on the number and mobility of ions. The substitution of ions with different ionic mobility affects the electrolytic conductivity. Therefore, the equivalence point can be determined by means of conductivity measurement for a neutralization reaction between an acid and a base. Equivalence point is determined graphically by plotting conductance against titer values.

**Instrumentation:** Conductometer consists of: (i) conductivity cell having two platinum electrodes; and a (ii) conductometer. A simple arrangement of conductometric titration is depicted in figure. The solution to be titrated is taken in the beaker.

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**Application:** (i) used to check water pollution in lakes as well as rivers.  
 (ii) used to check the alkalinity of the fresh water  
 (iii) Purity of distilled water and de ionised water can determined.  
 (iv) **Conductometric titrations of acids and base:** Pipette out 50ml of sample (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 point from the graph as shown below.



Explanation of conductometric titrations

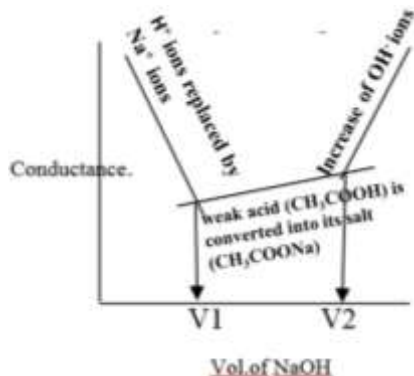
**These 3 cases must be explained only when mentioned in question.**

**Case j) Mixture of acids with a Strong base [(HCl+CH<sub>3</sub>COOH) Vs NaOH]:**

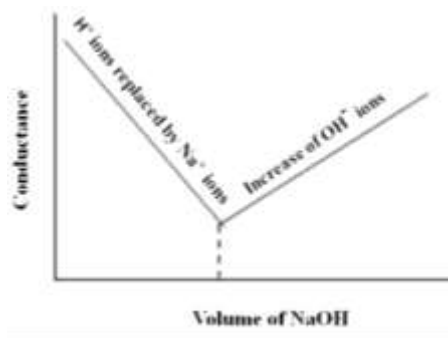
(1) The conductance decreases upon adding NaOH to acid mixture due to substitution of highly mobile H<sup>+</sup> ions by the less mobile Na<sup>+</sup> ions. (2) This trend continues till the strong acid is

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neutralized. (3) Continued addition of NaOH raises the conductance moderately due to salt ( $\text{CH}_3\text{COONa}$ ). (4) Further addition of NaOH raises the conductance steeply due to the presence of  $\text{OH}^-$  ions.

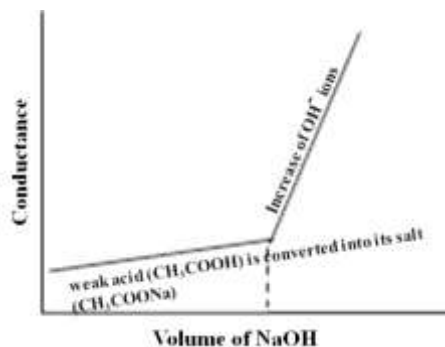


**ii) Strong acid with a Strong base (HCl Vs NaOH):** The conductance first falls, due to the replacement of highly mobile  $\text{H}^+$  ion by the added cation. After the neutralization point, the conductance rapidly rises with further additions of strong base and is due to increase in the concentration of the  $\text{OH}^-$  ions.



**iii) Weak acid with a strong base: ( $\text{CH}_3\text{COOH}$  Vs NaOH):** In the conductometric titration of a weak acid with a strong base, the conductance of the acid will be initially low due to poor dissociation of acetic acid. On complete neutralization of the acid, further addition of base leads to an increase in the number of more mobile  $\text{OH}^-$  ions. Hence conductance increases sharply.

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**Answer 10(b)**

$$\begin{aligned}\text{COD of sample} &= \frac{N_{\text{FAS}} \times (b-a) \times 8}{V_s} \text{ g.dm}^{-3} \\ &= \frac{N_{\text{FAS}} \times (b-a) \times 8000}{V_s} \text{ mg.dm}^{-3}\end{aligned}$$

$$\text{COD} = \frac{0.2 \times (24.8 - 16.6) \times 8000}{25} = 524.8 \text{ mg of O}_2/\text{litre}$$

***Answer 10 c***

**Primary and Secondary standards**

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In Pharmaceutical Analysis, the word standard means a material containing a substance of our interest with a known concentration. We can express this with definite numbers with proper units.

## Primary standard

- Primary standard is a reagent which is very pure, generally representative of the number of moles the substance contains and easily weighed.
- A primary standard is a reagent that's stable, it's not a hydrate /has no water of hydration, and has a high molecular weight.
- Primary standards are typically used in titration to determine an unknown concentration and in other analytical techniques.
- Not hygroscopic (to reduce changes in mass in humid versus dry environments), non-toxic, inexpensive and readily available.
- It should have a high relative molecular weight so that weighing errors may be negligible.
- The substance should be readily soluble under the conditions in which it is employed.

The substance commonly employed as primary standards are mention below,

- **Acid-base reactions:** sodium carbonate  $\text{Na}_2\text{CO}_3$ , sodium tetraborate  $\text{Na}_2\text{B}_4\text{O}_7$ , potassium hydrogenphthalate  $\text{KH}(\text{C}_8\text{H}_4\text{O}_4)$ , potassium hydrogeniodate  $\text{KH}(\text{IO}_3)_2$ .
- **Complex formation reactions:** pure metals (zinc, copper, magnesium and manganese) and salts, depending upon the reaction used.
- **Precipitation reactions:** silver, silver nitrate, sodium chloride, potassium chloride and potassium bromide.
- **Oxidation-reduction reaction:** potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ), potassium bromate ( $\text{KBr}$ ), potassium iodate ( $\text{KIO}_3$ ), sodium oxalate  $\text{Na}_2\text{C}_2\text{O}_4$  and pure iron.

## Secondary standard

- Secondary standard is a chemical that has been standardized against a primary standard for use in a specific analysis. Secondary standards are commonly used to calibrate analytical methods.
- A secondary standard is a substance which may be used for standardization.
- A secondary standard is a standard that is prepared in the laboratory for a specific analysis. It is usually standardized against a primary standard.
- It follows that a secondary standard solution is a solution in which the concentration of dissolved solute has not been determined from the weight of the compound dissolved but by reaction (titration) of a volume of the solution against a measured volume of a primary standard solution.
- It is less stable and more reactive than primary standard.

Examples:  $\text{NaOH}$ ,  $\text{HCl}$ ,  $\text{CH}_3\text{COOH}$ ,  $\text{KMnO}_4$  etc.,

## Requirement of a primary standard solution

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- ✓ High purity
- ✓ Stability (low reactivity)
- ✓ Low hygroscopicity (to minimize weight changes due to humidity)
- ✓ High equivalent weight (to minimize weighing errors)
- ✓ Non-toxicity
- ✓ Ready and cheap availability