

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

CBCS SCHEME

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21CHE12

First Semester B.E./B.Tech. Degree Examination, Feb./Mar. 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. What are Reference Electrodes? Explain the construction and working of Calomel Electrode. (07 Marks)
- b. Define Single Electrode Potential. Derive Nernst equation for Single Electrode Potential. (07 Marks)
- c. Explain the construction and working of Li-ion battery. Mention its applications. (06 Marks)

OR

- 2 a. Explain Primary, Secondary and Reserve batteries with an example. (06 Marks)
- b. Explain the experimental determination of pH by using glass electrode. (07 Marks)
- c. A cell consists of Copper rod dipped in 5M CuSO₄ solution and Iron rod dipped in 0.05 M FeSO₄ solution. Given $E_{Cu}^{\circ} = +0.34V$ and $E_{Fe}^{\circ} = -0.44V$. Write Cell representation, Cell reactions and calculate Emf of the cell. (07 Marks)

Module-2

- 3 a. Define Corrosion. Describe Electrochemical theory of corrosion by taking Iron as an example. (07 Marks)
- b. What is Cathodic Protection? Explain Sacrificial Anodic method and Impressed Current method of Cathodic protection. (07 Marks)
- c. What is Metal Finishing? Mention technological importance of Metal Finishing. (06 Marks)

OR

- 4 a. Explain the factors affecting the corrosion rate :
 - i) Ratio of anodic to cathodic areas.
 - ii) Nature of the corrosion product.
 - iii) pH. (06 Marks)
- b. What is Corrosion Penetration Rate? A piece of corroded plate was found in the submerged ocean vessel. It was estimated that the original area of the plate was 10 inch² and that approximately 2.6kg had corroded away during the submersion for a period of 10 years. Calculate Corrosion Penetration Rate (CPR) in terms of mpy and mmy. Given density of iron = 7.9 g/dm³
mpy → k = 534
mmy → k = 87.6. (07 Marks)
- c. What is Electroless Plating? Write the differences between Electroplating and Electroless plating. (07 Marks)

Module-3

- 5 a. What are Conducting Polymers? Explain the mechanism of conduction in Polyaniline. (07 Marks)
- b. Explain the synthesis, properties and applications of Poly Lactic Acid. (06 Marks)
- c. What are Nanomaterials? Explain the synthesis of Nanomaterials by Sol-gel process. (07 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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OR

- 6 a. What are Polymer Composites? Explain the synthesis and applications of Kevlar fibre. (07 Marks)
b. Explain any two size dependent properties of Nanomaterials. (06 Marks)
c. Write a note on Fullerene and mention its applications. (07 Marks)

Module-4

- 7 a. What is Green Chemistry? Explain briefly any six basic principles of Green Chemistry. (07 Marks)
b. Describe the production of hydrogen by Photocatalytic Water Splitting Method. (06 Marks)
c. Explain the synthesis of Paracetamol by Conventional and Green Route Method. (07 Marks)

OR

- 8 a. Explain the impacts of Oxides of Nitrogen (NO_x) and Oxides of Sulfur (SO_x) on the Environment. (06 Marks)
b. Explain the working of Photovoltaic cell, with a neat diagram. (07 Marks)
c. Describe working of Methyl alcohol – Oxygen fuel cell [$\text{CH}_3\text{OH} - \text{O}_2$] with a neat diagram. Mention its applications. (07 Marks)

Module-5

- 9 a. Explain Theory, Instrumentation and Applications of Colorimeter. (07 Marks)
b. Explain the principle of Volumetric analysis and requirement of Volumetric analysis. (06 Marks)
c. Define Biological Oxygen demand and Chemical Oxygen demand. 25 ml of waste water required 18.0ml and 25.2ml of 0.1N FAS solution for sample and blank titration respectively. Calculate COD of the waste water sample. (07 Marks)

OR

- 10 a. Explain applications of Conductometry :
i) Strong acid Vs Strong base ii) Weak acid Vs Strong base. (07 Marks)
b. Define the following units of Standard Solution :
i) Normality ii) Molarity iii) PPM. (06 Marks)
c. 25 m^3 of hard water sample titrated against 0.01M EDTA solutions consumed 18.0 cm^3 of EDTA solution. 25 cm^3 same sample of hard water was boiled, filtered and titrated against 0.01M EDTA solution consumed 12.0 cm^3 EDTA solution. Calculate Total, Permanent and Temporary hardness of the water sample. (07 Marks)

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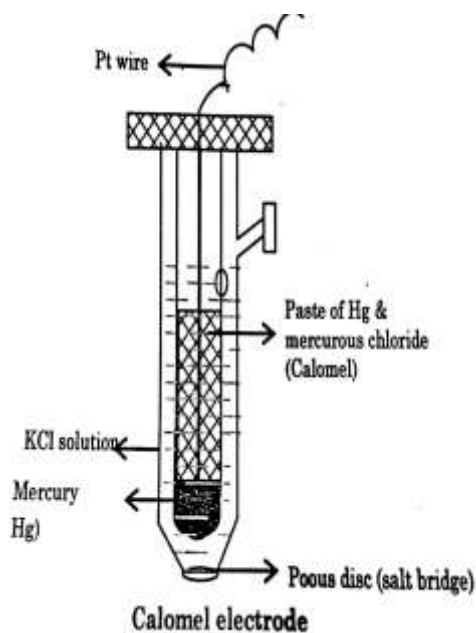
Answer 1a.

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 (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

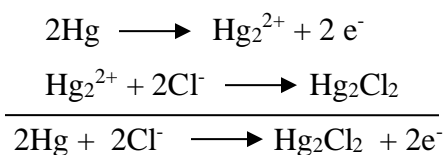
The calomel electrode is represented as, $\text{Hg} / \text{Hg}_2\text{Cl}_2 (\text{s}) / \text{Cl}^-$ (anode)

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

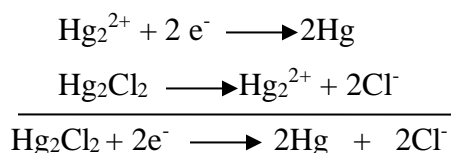
Working

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

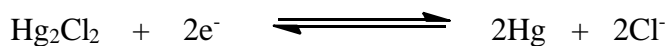
(a). **When it acts as anode, electrode reaction is**



(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 1b

Single Electrode Potential: When a metal is in contact with its own ions it has natural tendency to undergo oxidation and reduction, because of this potential develops which is known as single electrode potential. Or 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 (Kc) is related to change in free energy by Vant Hoff equation as follows

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

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

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According to thermodynamics, decrease in free energy ($-\Delta G$) 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 = $n \times F$ (Where n = number of electrons involved in the cell reaction and F = Faraday constant)

Energy available per coulomb = E (V) or JC^{-1}

Thus,

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

n = moles of electrons, $F = Cmol^{-1}$, $E = JC^{-1}$

Equating equations (3) & (4)

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

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

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 ΔG° = Change in free energy under standard conditions, E° is a constant called **standard electrode potential**.

E° 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 ΔG , ΔG° 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 $-nF$

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

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

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 ($8.314 \text{ JK}^{-1}\text{mol}^{-1}$), F (96500 Cmol^{-1}) 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.

Answer 1c.

Lithium ion Batteries

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).

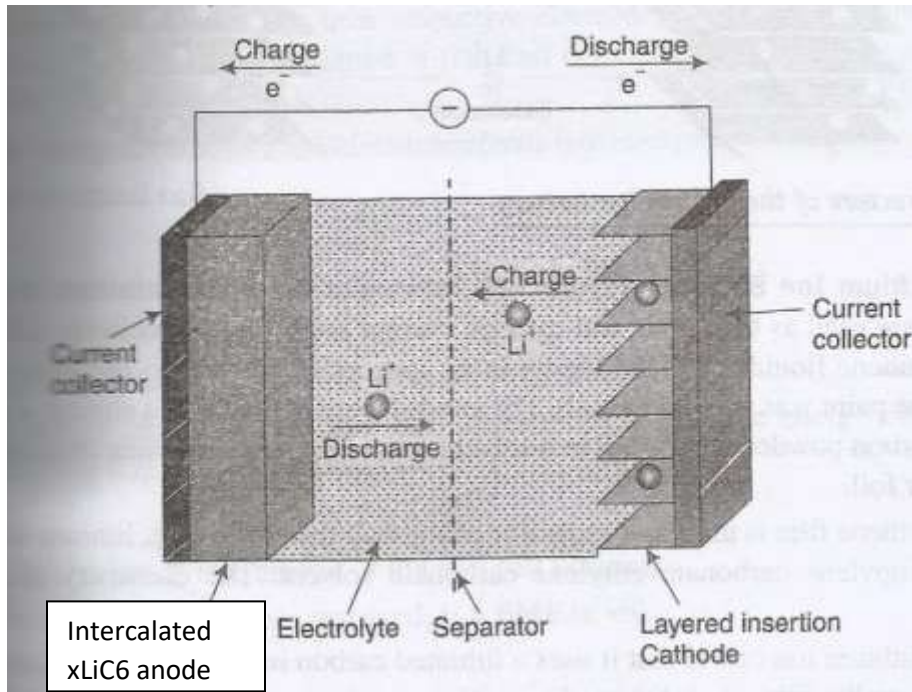
Construction

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).

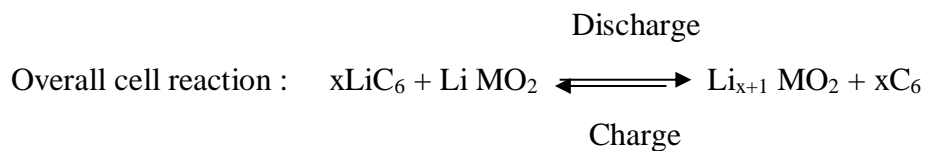
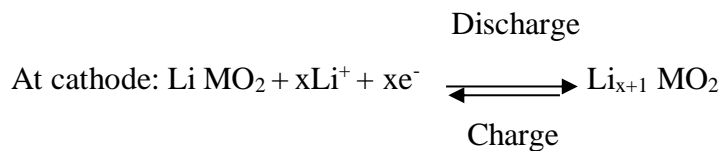
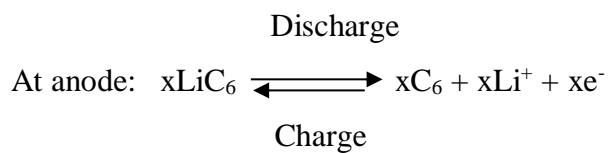
Electrolyte: Lithium salt (LiPF_6) in an org solvent or mixture of organic carbonates such as ethylene carbonate or diethyl carbonate containing complex of Li-ions.

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In the electrochemical reaction in a Li-ion battery both electrodes allow lithium ions to move in and out of their interiors. During insertion ions move into the electrode and during reverse process (extraction) ions move back out. 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.

Working:



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

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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

Classification of batteries

Batteries are classified into mainly three types:

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

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 – MnO₂, Li-MnO₂ 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.

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Answer 2b

Determination of pH using glass electrode

To determine the pH of given solution, glass electrode is dipped in a solution whose pH is to be determined. It is combined with a saturated calomel electrode (ref electrode) through a salt bridge.

The cell assembly is represented as



EMF of the So formed cell is determined by using electronic voltmeter.

$$E_{\text{cell}} = E_{\text{Cathode}} - E_{\text{anode}} \quad (\text{Conventionally glass electrode is cathode})$$

$$E_{\text{cell}} = E_G - E_{\text{cal}}$$

Substituting value of E_G from Eq. 5 into above equation

$$E_{\text{cell}} = E_G^\circ - 0.0591\text{pH} - E_{\text{cal}}$$

$$\text{pH} = \frac{E_G^\circ - E_{\text{cal}} - E_{\text{cell}}}{0.0591}$$

$$\text{pH} = \frac{K - E_{\text{cell}}}{0.0591}$$

where, K is known as glass electrode assembly constant.

E_G° value or K is evaluated by dipping the glass electrode in a solution of known pH and measuring emf of the cell formed when coupled with a calomel electrode. Next the same assembly is dipped into test solution and the pH of test solution can be determined.

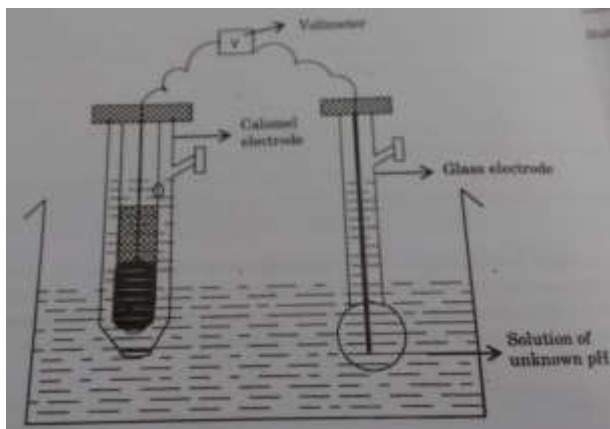


Fig : determination of pH using Glass electrode

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Answer 2c:

Fe/FeSO₄ (0.05)//CuSO₄ (5M)/Cu



Equation: E_{cell} = E^o_{cell} + (0.0591/n) log [Cu²⁺]/[Fe²⁺]

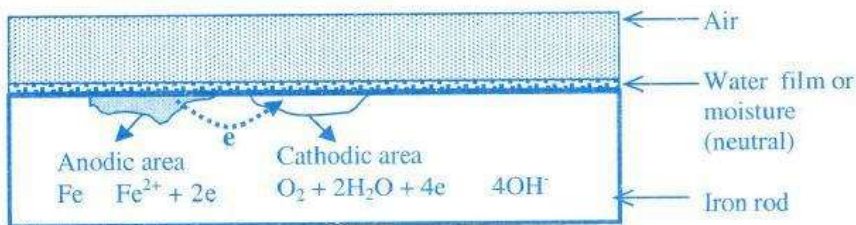
E_{cell} = 0.78 + (0.0591/2) log [5]/[0.05]

E_{cell} = 0.8391V

Answer 3a

Answer: Destruction of metal or alloy surface by the surrounding environment through chemical or electrochemical changes. Eg Rusting of iron

Electrochemical theory of corrosion:



(i) According to electrochemical theory, corrosion of metals takes place due to the formation of minute galvanic cells over the surface of metal. Thus anodic and cathodic regions are formed on the same metal surface or when two metals are in contact with each other in the presence of a conducting medium.

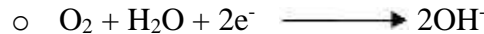
(ii) At the anodic region oxidation reaction takes place and the metal gets converted into its ions by liberating electrons. Consequently, metal undergoes corrosion at the anodic region.



(iii) The electrons flow from the anodic to cathodic area and at the cathodic region, reduction takes place. Since metal cannot be reduced further, metal atoms at the cathodic region are unaffected by the cathodic reaction. Some constituents of the corrosion medium take part in the cathodic reaction. There are three possible ways in which the reduction can take place.

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- If the solution is aerated and almost neutral,



- If the solution is deaerated and almost neutral:



- If the solution is deaerated and acidic:



(iv) Corrosion of iron produced Fe^{2+} ions and OH^- ions at the anode and cathode sites respectively. These ions diffuse towards each other and produce insoluble $\text{Fe}(\text{OH})_2$.



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



Answer 3b

CATHODIC PROTECTION:

Cathodic protection is a method of protecting a metal or alloy from corrosion by converting it completely into cathodic and no part of it is allowed to act as anode. This can be achieved by providing electrons from an external source.

Principle: Metals normally undergo corrosion by electrochemical process with the formation of anodic and cathodic regions in contact with each other. The corrosion of metal takes place at the anodic region whereas at the cathodic region the metal is unaffected. Therefore, corrosion can be prevented by eliminating the anode sites and converting the entire metal into cathodic area.

There are two methods of cathodic protection.

- (i) Sacrificial anodic method.

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(ii) Impressed current method.

(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.

Advantages:

(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.

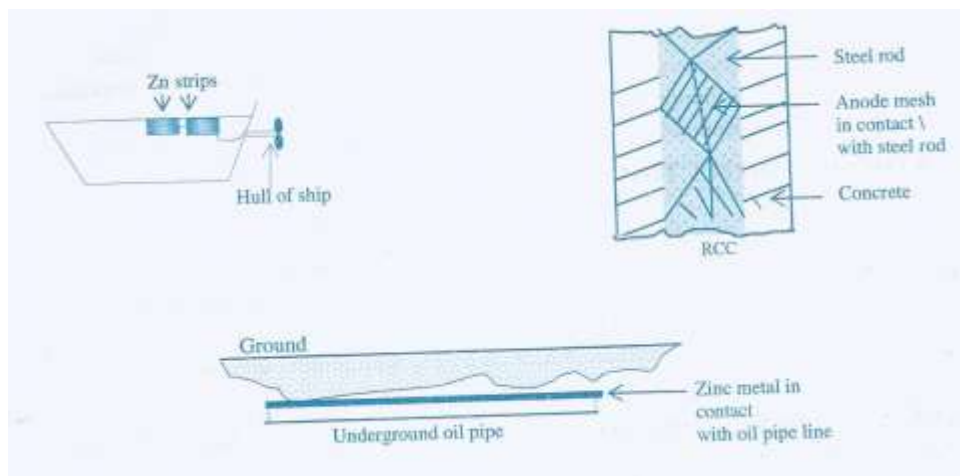


Fig: Cathodic Protection by sacrificial anode

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(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].

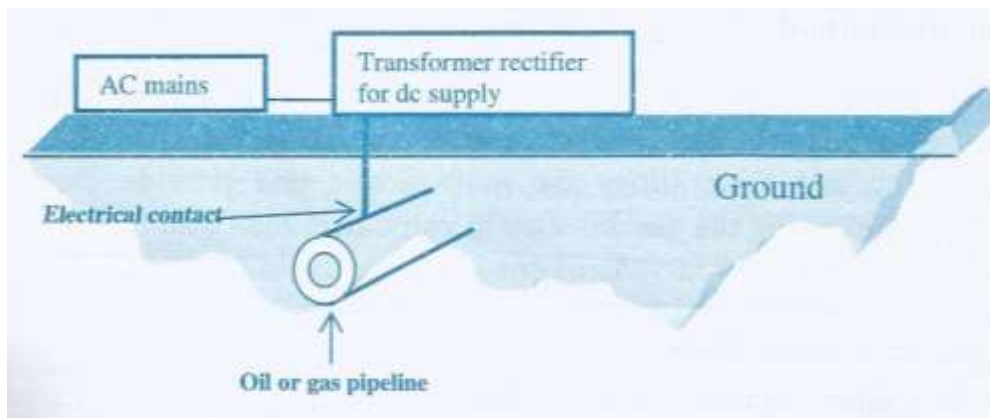


Fig: Protection using an impressed voltage

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.

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Answer 3c

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,
- (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 4a

FACTORS AFFECTING THE RATE OF CORROSION:

Primary Factors:

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

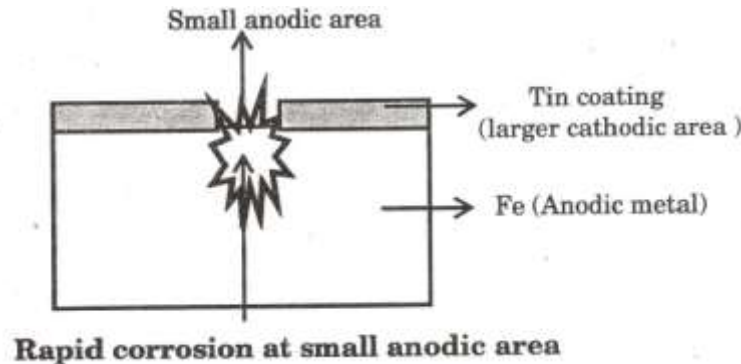
(a) If the metal has a **small anodic and large cathodic area** (i.e; the ratio of anode to cathode is small) then the corrosion is **more intensive and faster in rate**. This is explained as follows

At anode oxidation takes place and electrons are liberated. At the cathode these electrons

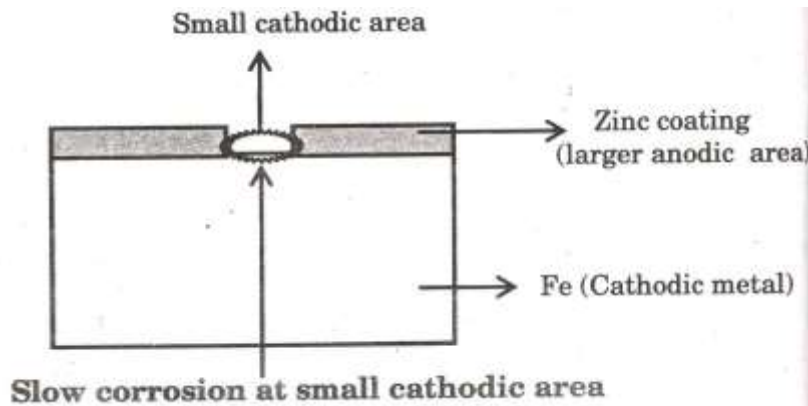
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consumed when the anode is smaller and cathode region is large, the electrons liberated at the anode, are rapidly consumed, at the cathode region. This process makes the anodic reaction to take place faster, thus increasing the corrosion rate.

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

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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 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 Cr_2O_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

(iii) **pH** : In general, the rate of corrosion is high when the nature of the environment is acidic.

(a) If the $\text{pH} < 3$, severe corrosion occurs even in the absence of air due to the continues evolution of hydrogen at the cathodic region.

(b) If the $\text{pH} > 10$, corrosion of the metal practically ceases, due to the formation of a protecting coating of hydrogen oxide of iron.

Answer 4b: 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.

Corrosion penetrating rate in mpy $\text{CPR} = \text{KW}/\text{DAT}$ Weight loss, $W = 2.6 \times 10^6 \text{ mg}$ Density, $D = 7.9 \text{ g/cm}^3$; Time, $T = 10 \times 24 \times 365$ Area $A = 10 \text{ in}^2$ $\text{CPR} = \frac{534 \times 2.6 \times 10^6}{7.9 \times 10 \times 10 \times 24 \times 365}$ CPR = 200.62 mpy	Corrosion penetrating rate mm/y $\text{CPR} = \text{KW}/\text{DAT}$ Weight loss, $W = 485000 \text{ mg}$ Density, $D = 7.9 \text{ g/cm}^3$; Time, $T = 10 \times 24 \times 365$ Area $A = 10 \times 6.45 \text{ cm}^2$ $\text{CPR} = \frac{87.6 \times 2.6 \times 10^6}{7.9 \times 10 \times 6.45 \times 10 \times 24 \times 365}$ CPR = 5.10 mm/y
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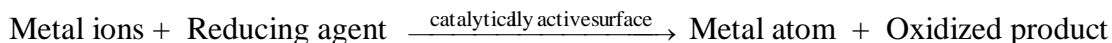
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Answer 4c

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,



- 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: $M \longrightarrow M^{n+} + ne^{-}$ when anode is inert: $\frac{n}{2} H_2O \longrightarrow nH^{+} + \frac{n}{2} O_2 + ne^{-}$	$R \longrightarrow O + ne^{-}$ where R = Reducing agent O = Oxidised species
5	Reduction reaction	$M^{n+} + ne^{-} \longrightarrow M$	$M^{n+} + ne^{-} \longrightarrow M$
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
10	Features of deposit	May be porous, & less corrosion resistant	Non-porous, relatively hard & more corrosion resistant

Answer 5a

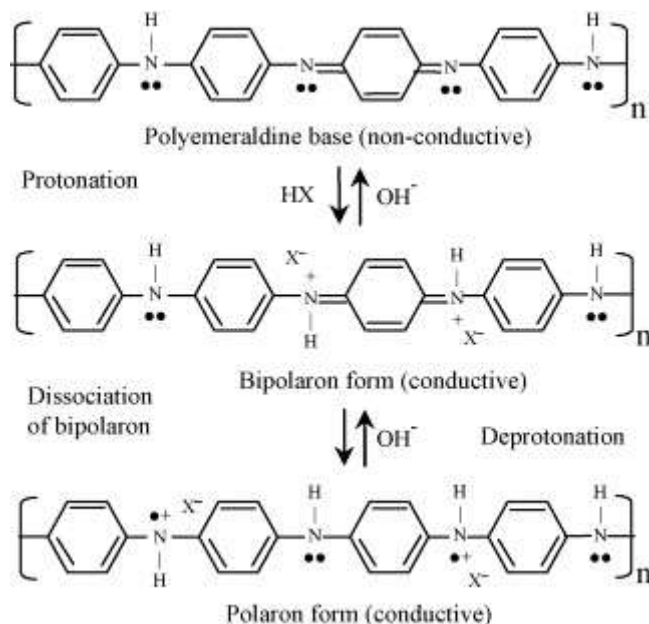
Ans: Conducting polymers are organic polymers that conduct electricity. Example: polyaniline (PANI)

Mechanism of Conduction: These conjugated organic polymers in their pure state are insulators or semi-conductors. The π -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

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and vice versa during reduction. The generation of these charged carriers is responsible for conductivity of the polymer.

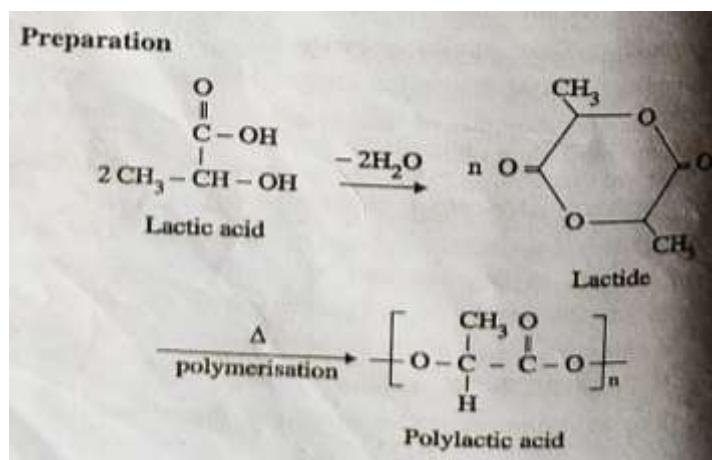


Mechanism of Conduction

Answer 5b

Answer: Polylactic Acid (PLA)

Preparation



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

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monomer.

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

Properties

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

Applications:

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

Answer 5c

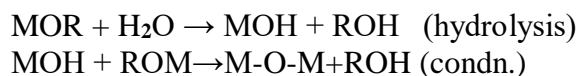
Nanomaterials or Nanoparticles are defined as substances which contain nano size particles with at least one dimension in the range of 1 nm to 100 nm.

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.

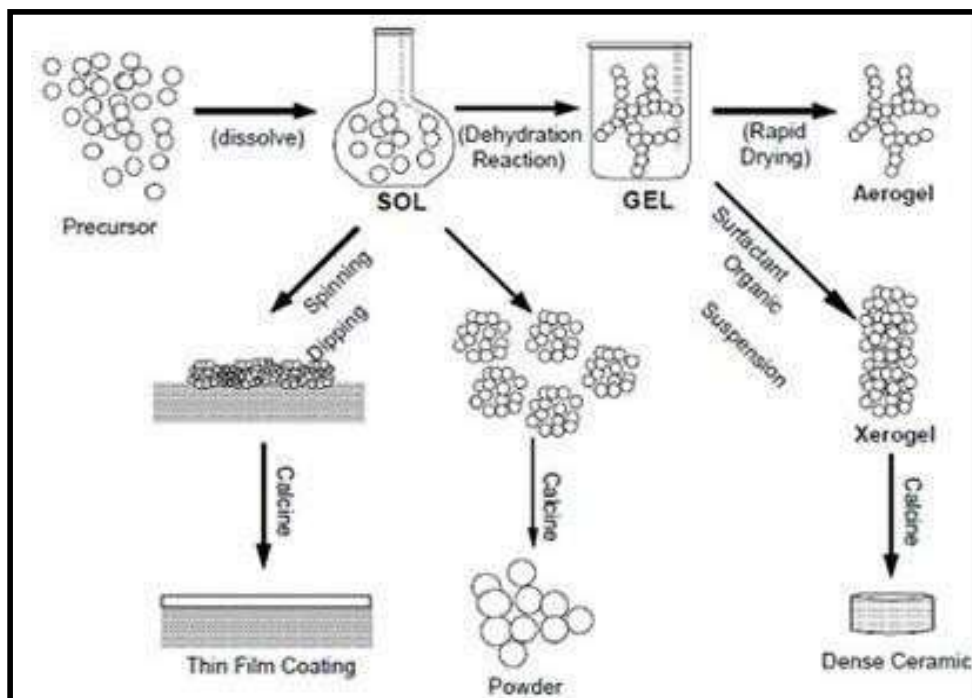
Step 4: Drying of the gel, when water and other volatile liquids are removed from the gel network. This process is complicated due to fundamental changes in the structure of the gel.

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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 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 high temperature.

Step 6: Densification and decomposition of the gels at high temperatures ($T > 8000\text{C}$). 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.

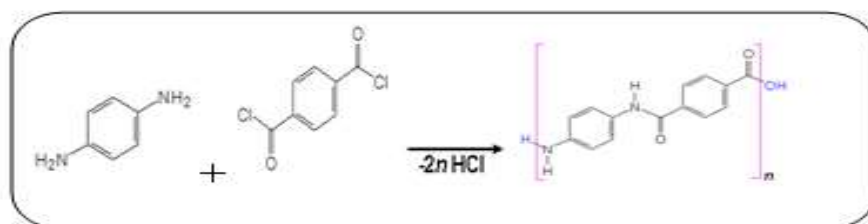
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5. Size can be controlled.

Answer 6a

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-phenylenediamine) and acid chloride (terephthaloyl chloride). The Kevlar chains are relatively rigid and tend to form mostly planar sheets, similar to those of silk. This is due to the 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 radically, like the spokes on a wheel, allowing additional interactions between the face-to-face aromatic groups on neighbouring sheets to help to increase the strength of the overall fibre.



Properties of Kevlar

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

Applications

1. Military Body Armor & Jackets: Kevlar fibre is five times stronger than steel on an equal weight basis, offering superior protection in military body armour and flak jackets.

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2. Protection Vests: From higher-level bullets to knives, needles and explosions, protection vests made with Kevlar

3. Military Helmets: Kevlar meet demanding requirements for protection against a wide range of threats, including bullets, shrapnel and fragmentation.

4. Automotive Uses: It is not uncommon for a new vehicle to have several crucial parts that employ products Belts, Brake pads, Clutches, Gaskets, Hoses made of Kevlar brand fibre.

5. Kevlar as a Composite: Formula 1 cars and HANS Device uses Kevlar straps to supports the driver's head and neck— Kevlar absorbs impact forces that are strong enough to pulverize neck vertebrae.

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

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

Answer 6b

Answer: 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.

Nanoparticles can exhibit size-dependent properties which is different from those of bulk materials.

Size dependent properties of Nanoparticles:

Optical Property: It is dependent on electronic structure. A change in the particle size, brings about change in electronic structure and band gap, which leads to the change in absorption and emission properties. Example: Bulk gold appears yellow in colour, whereas nanogold appears red in colour.

Surface area and Catalytic Property: Surface area is enormously increased on moving from bulk to nanoscale. Nanomaterials have a significant proportion of atoms existing at the surface. Nanomaterials have high surface to volume ratio therefore they exhibit good catalytic activity. Example: Bulk gold is catalytically inactive while nano gold is catalytically very active for selective redox reactions.

Answer 6c

Fullerenes:

1). Fullerenes are class of molecules made only carbon atoms having closed cage like structure. Fullerenes can be of a different type C_{60} , C_{70} , C_{76} , C_{78} , C_{80} etc. depending on the number of carbon atoms. The most important fullerene is C_{60} containing 60 carbon atoms.

Fullerenes having spherical shape resemble soccer ball and are also called buckyballs. Fullerenes structure is built of fused pentagons and hexagons.

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2). Fullerenes contain carbon atoms arranged as a combination of 12 pentagonal rings and n hexagonal rings. All the C-atoms are sp^2 hybridized. The C_{60} molecule has two bond lengths. The hexagonal ring bonds can be considered double bonds and are shorter than the pentagonal bonds. Fullerene C_{60} molecule is composed of 60 carbon atoms arranged as 12 pentagons and 20 hexagons and is commonly known as Buckminster fullerene

3) Fullerenes are stable, but not totally unreactive. The characteristic reaction of fullerenes is electrophilic addition. Fullerenes are heat-resistant and

4) Solubility: Fullerenes are soluble in many organic solvents, such as toluene, chlorobenzene etc. Solutions of pure buckminsterfullerene have a deep purple color. Solutions of C_{70} are a reddish brown. The higher fullerenes C_{76} to C_{84} have a variety of colors.

5) Superconductivity: Fullerenes are normally electrical insulators, but when crystallized with alkali metals, the resultant compound can be conducting or even superconducting

Applications: In the field of 1. Biosensors, chemical sensor and gas sensors, 2. Water purification
3. Cancer treatment 4. Super conductor 5. Fuel cells 6. Textiles, Food packaging etc..



Figure: Fullerene C_{60}

Answer 7a

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

Basic principles of green chemistry

- 1) **Prevention of waste:** preventing the formation of waste products is always preferable to the clean-up of the waste once it is generated.
- 2) **Atom economy:** the synthetic processes and methods that are devised 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.

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- 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 minimized since they tend to require the use of additional reagents and chemicals, resulting in the generation of excess waste.

Answer 7b

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

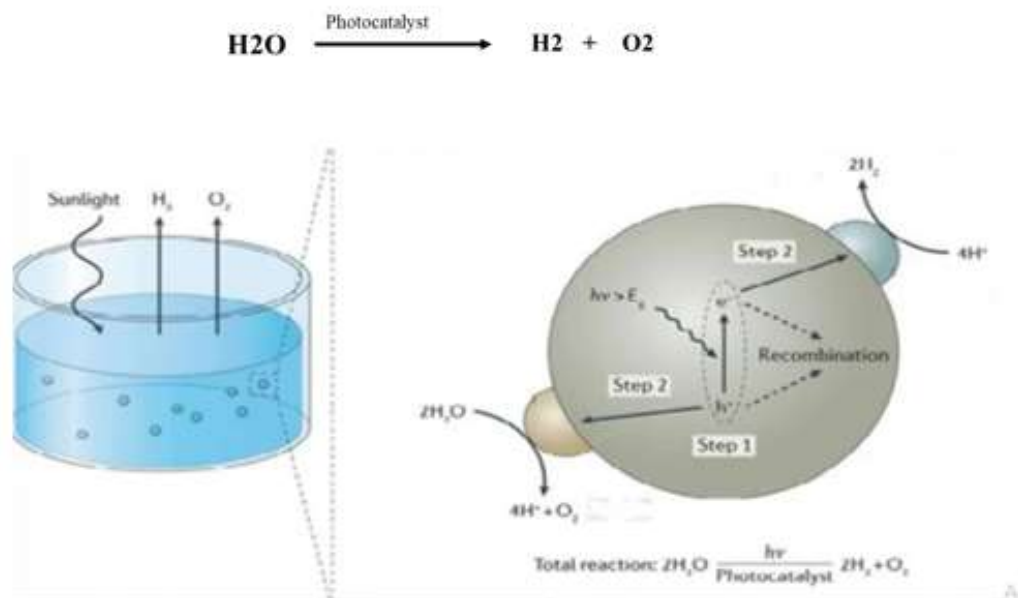
Photocatalytic reaction

Input: Photocatalyst particles, sunlight and water

Output: Oxygen and hydrogen

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

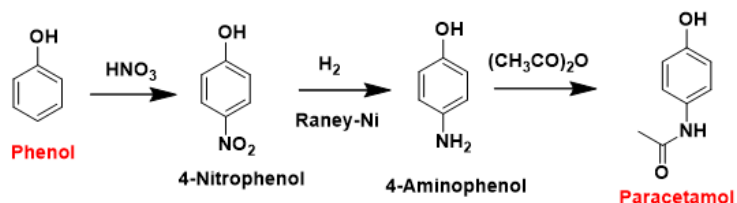
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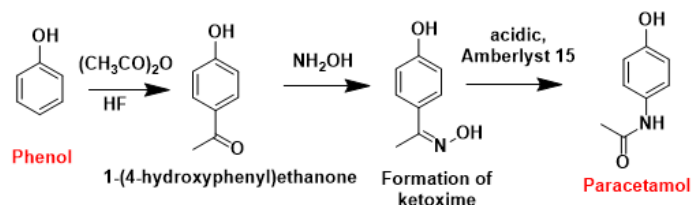
Answer 7c

Synthesis of Paracetamol:

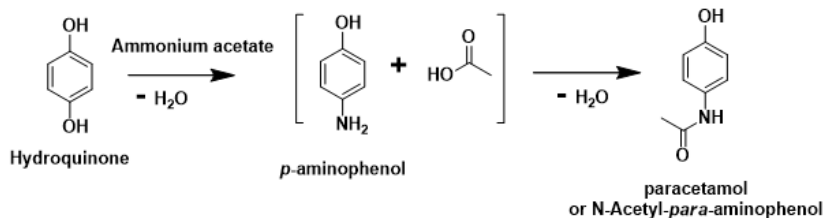
Traditional/Conventional synthesis: Involves the nitration of phenol to 4-nitrophenol. The nitro group is then reduced to an amine, giving 4-aminophenol. Finally, the amine is acetylated with acetic anhydride.



Green Synthesis of Paracetamol: Involves direct acylation of phenol with acetic anhydride catalyzed by HF, conversion of the ketone to a ketoxime 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"



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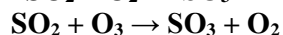
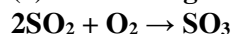
Answer 8a

Oxides of Sulphur: Sulphur oxides (SO_x) are a group of compounds made up of sulphur and oxygen molecules. The most common sulphur oxide is sulphur dioxide (SO₂), which is a colourless gas with a burnt match type smell. It includes SO₂ and SO₃

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

(c) Pulp and paper manufacture: The sulphite process for wood pulping emits SO₂ in air. The kraft pulping process produces H₂S, which is then burned to produce SO₂

(d) **Oil refining:** H₂S is released as a gas during catalytic cracking and it is burned to produce SO₂.



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

(b) Sulphur dioxide causes irritation to the eyes, resulting in tears and redness

(c) It is also *toxic to plants* and can cause *acid rain* when it reacts with moisture in the air.

(d) Damage to limestone and marble, damage to leather, increased rate of corrosion of iron, steel, zinc and aluminium.

Oxides of Nitrogen: Nitrogen oxides (NO_x) are a group of gases made up of varying amounts of oxygen and nitrogen molecules. One of the most common nitrogen oxides is nitrogen dioxide (NO₂) which is a reddish, brown gas that has an unpleasant smell and is poisonous in high concentrations

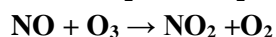
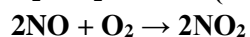
Sources:

(a) The main sources of NO_x pollution are vehicles and thermal power plants.

(b) NO_x are formed when fossil fuels are burned at high temperatures, but they can also be formed naturally by lightning strikes.

(c) However significant amount of NO & NO₂ are emitted in to the atmosphere by natural activity. Rate of production of NO₂ is faster when nitric oxide reacts with ozone in the stratosphere

(d) Nitrogen oxides are released during manufacturing of nitrogen fertilizers.



Effects of NO_x pollution:

(a) It cause respiratory problems, as it inflames the lining of the lungs, and can reduce immunity to cause lung infections. This can cause problems such as coughing, colds, flu and bronchitis.

(b) Higher concentrations of NO₂ damage the leaves of plants and retard the rate of photosynthesis.

(c) These can form secondary pollutants and can result in environmental problems such as acidification and nitrogen enrichment. NO₂ and other NO_x interact with water, oxygen and other chemicals in the atmosphere to form acid rain.

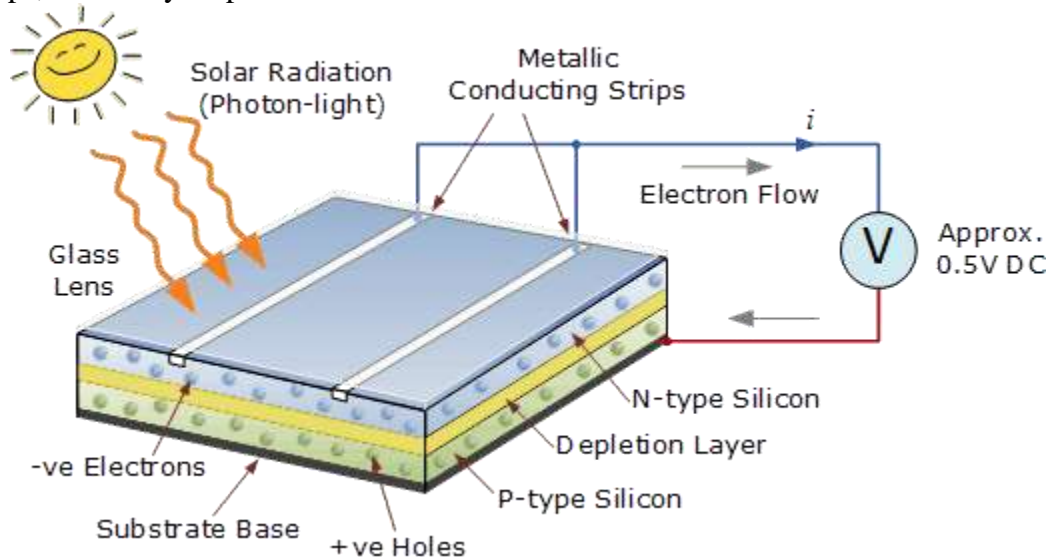
(d) The nitrate particles that result from NO_x make the air hazy and difficult to see though and accounts for global warming.

(e) In the presence of hydrocarbons and sunlight, oxides of nitrogen form photochemical smog.

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Answer 8b

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



Construction:

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

Working:

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

$$E = hc/\lambda$$

Where, h = Planck's constant, c = velocity of light, λ = 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

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- iv. For Operating water pumps for domestic and agricultural purpose.
- (v) For toys, watches, calculators solar water heaters etc.

Answer 8c

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

Construction: Methanol – oxygen fuel cell consist of

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

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

Electrolyte – Aqueous sulphuric acid (H_2SO_4), 3.7 M.

Fuel – Methanol mixed with sulphuric acid supplied at

Oxidant – Pure oxygen is supplied at cathode.

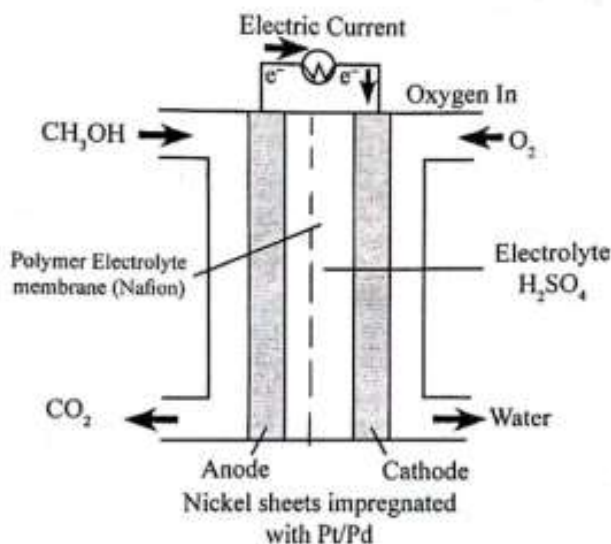
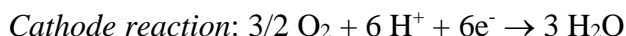
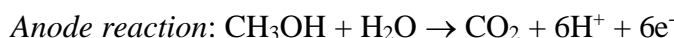


Figure. Methanol – oxygen fuel cell

Working: Cell reaction;



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

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Cell Potential : 1.2 V

Applications:

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

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 colored 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,

$$I_o = I_a + I_t$$

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 ϵ called *molar absorptivity* or *molar absorption coefficient*, is a constant for a given substance at a given wavelength. If c is expressed in mol. dm^{-3} and t in centimeters, ϵ 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.

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

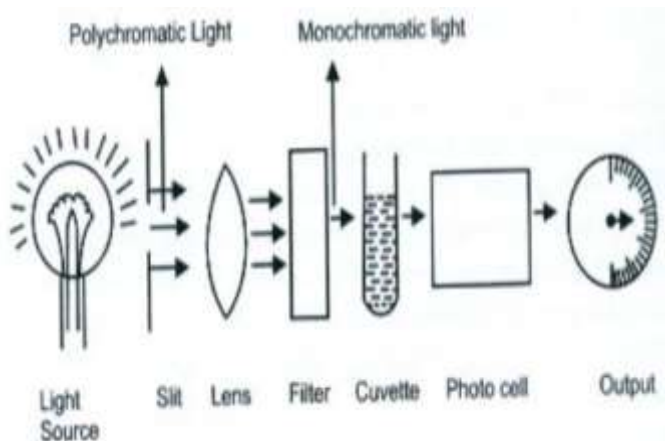
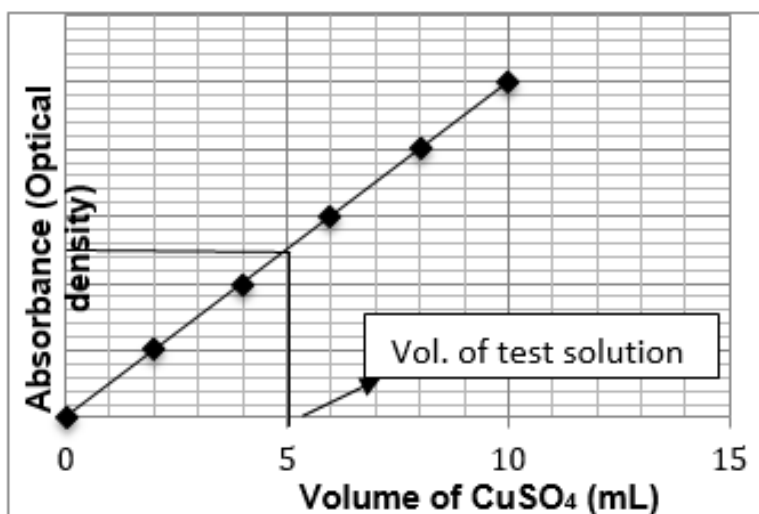


Fig: Schematic layout of colorimeter

Light from a tungsten lamp is allowed to fall on the solution taken in the sample cell after passing through the filter. First a blank solution is taken in the sample cell and placed in the path of the 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 CuSO₄**. Draw out 2, 4, 6, 8, and 10 ml cm³ of the Copper sulphate solution into 50cm³ volumetric flask. Add 5cm³ of ammonia solution to each of them and dilute upto the mark with distilled water and mix well. Prepare a blank solution by diluting 5cm³ of ammonia solution in 50cm³ volumetric flasks. For test solution add 5ml of NH₃ 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.

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Answer 9b

Answer: Principles of Volumetric analysis

1. The solution to be analyzed contains an unknown amount of chemicals.
2. The reagent of unknown concentration reacts with a chemical of an unknown amount in the presence of an indicator (mostly phenolphthalein) to show the end-point. It's the point indicating the completion of the reaction.
3. The volumes are measured by titration which completes the reaction between the solution and reagent.
4. The volume and concentration of reagent which are used in the titration show the amount of reagent and solution.
5. The amount of unknown chemical in the specific volume of solution is determined by the mole fraction of the equation.

When the endpoint of the reaction is reached, the volume of reactant consumed is measured and applied to carry volumetric analysis calculations of the analyte by the following formula,

$$C_a = C_t \times (V_t \times M / V_a)$$

Where,

C_a is the analyte concentration, typically in molarity.

C_t is the titrant concentration, typically in molarity.

V_t is the volume of the titrant which is used, typically in liters.

M is the mole ratio of the analyte and reactant from the balanced equation.

V_a is the volume of the analyte, typically in liters.

Many non-acid-base titrations are needed a constant pH throughout the reaction. Therefore, a buffer solution can be added to the titration chamber to maintain the pH value.

Requirement of titrimetric analysis

1. Reaction between reagent and analyte must be specific. Titrant cannot react with impurities or additions of analyte solution.
2. Reaction must be stoichiometric.
3. Titrant must react rapidly with the analyte so that the time required between additions of reagent

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is minimised.

4. Titrant must react more or less completely with the analyte so that satisfactory end points are realised.
5. Undergo a selective reaction with the analyte that can be described by simple balanced equation. Equilibrium constant must have high value

Answer 9c

Definition of Biological Oxygen Demand (BOD): Biological oxygen demand, BOD is defined as the amount of oxygen required by microorganisms to oxidize the organic wastes present in one liter of waste water at 20°C over a period of 5 days. It is expressed in mg dm^{-3} .

Chemical Oxygen Demand (COD): COD is defined as the amount of oxygen consumed in the complete chemical oxidation of organic and inorganic wastes present in 1 litre of waste water by using strong oxidizing agent, such as acidified $\text{K}_2\text{Cr}_2\text{O}_7$. It is represented in mg dm^{-3} or ppm.

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

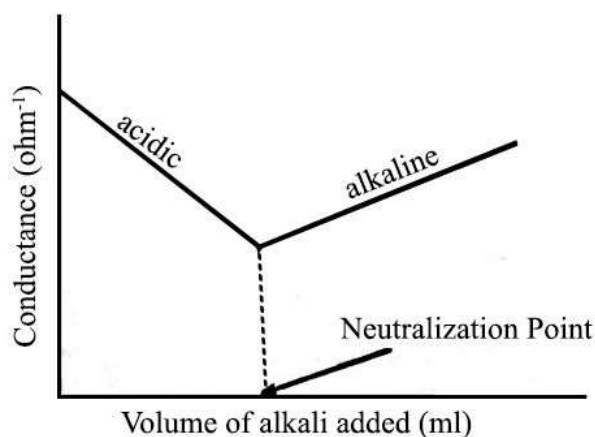
$$\text{COD} = \frac{0.1 \times (25.2 - 18) \times 8000}{25} = 230.4 \text{ mg of O}_2/\text{dm}^3$$

Answer 10a

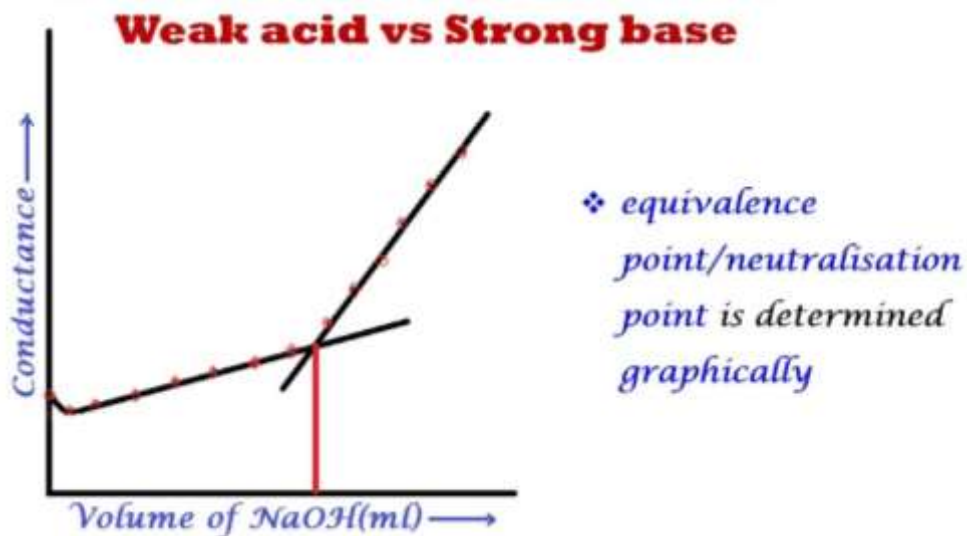
Conductometric titration of Strong acid vs Strong base

Strong Acid with a Strong Base, e.g. HCl with NaOH: Before NaOH is added, the conductance is high due to the presence of highly mobile hydrogen ions. When the base is added, the conductance falls due to the replacement of hydrogen ions by the added cation as H^+ ions react with OH^- ions to form undissociated water. This decrease in the conductance continues till the equivalence point. At the equivalence point, the solution contains only NaCl. After the equivalence point, the conductance increases due to the large conductivity of OH^- ions.

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Weak Acid with a Strong Base, e.g. acetic acid with NaOH: Initially the conductance is low due to the feeble ionization of acetic acid. On the addition of base, there is decrease in conductance not only due to the replacement of H⁺ by Na⁺ but also suppresses the dissociation of acetic acid due to common ion acetate. But very soon, the conductance increases on adding NaOH as NaOH neutralizes the un-dissociated CH₃COOH to CH₃COONa which is the strong electrolyte. This increase in conductance continues raise up to the equivalence point. The graph near the equivalence point is curved due the hydrolysis of salt CH₃COONa. Beyond the equivalence point, conductance increases more rapidly with the addition of NaOH due to the highly conducting OH⁻ ions



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Answer 10b

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)

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

Normality = No of gram equivalents of solute / Volume of solution (in Liters)

ppm: Parts per million (ppm) is a unit of measurement used when expressing a very dilute concentration level of pollutants in the air, water and other fluids. It also can be expressed as milligrams per liter (mg/L).

Answer 10c

Calculations:

Total hardness

1000 ml of 1M EDTA = 100g CaCO₃ (Molecular mass of CaCO₃ = 100g)

1ml of 1M EDTA = $\frac{100}{1000}$ g of CaCO₃

$$18 \text{ cm}^3 \text{ of } 0.01\text{M EDTA} = \frac{18 \times 0.01 \times 100}{1000} = 0.018 \text{ g of CaCO}_3$$

25 cm³ of water sample = 0.018 g of CaCO₃

$$10^6 \text{ (1 million parts) ml of water sample contains} = \frac{0.018 \times 10^6}{25} \text{ g of CaCO}_3$$
$$= 720 \text{ ppm}$$

Permanent hardness

1000 ml of 1M EDTA = 100g CaCO₃ (Molecular mass of CaCO₃ = 100g)

