Chemistry

Academic Year: 2014-2015 Marks: 70
Date & Time: 4th March 2015, 11:00 am
Duration: 3h

Question 1: Select and write the most appropriate answer from the given alternatives for each sub-question [7]

Question 1.1: p - type semi-conductors are made by mixing silicon with impurities of [1]

a. germanium
b. boron
c. arsenic
d. antimony

Solution: (c) Boron
Boron (electronic configuration 1s2 2s2 2p1) is one electron deficient as compared to the valence electrons in the silicon atom. On adding boron to silicon, some atoms of boron occupy some sites of silicon atoms.

Question 1.2: Amongst the following identify the criterion for a process to be at equilibrium - [1]

a. $\Delta G < 0$
b. $\Delta G > 0$
c. $\Delta S_{total=0}$
d. $\Delta S < 0$

Solution:
(c) $\Delta S_{\text{total}} = 0$

$\Delta S_{\text{total}} = 0$ must be zero for the process at equilibrium.

Question 1.3: Colligative property depends only on .... in a solution. [1]

Number of solute particles.
Number of solvent particles.
Nature of solute particles
Nature of solvent particles

Solution: Colligative properties of solutions depend only on the **number of solute particles.**

Question 1.4: The charge of how many coulomb is required to deposit 1.0 g of sodium metal (molar mass 23.0 g mol^{-1}) from sodium ions is - `[1]`

a. 2098
b. 96500
c. 193000
d. 4196

Solution: Colligative properties of solutions depend only on the **number of solute particles.**

Question 1.5: What is the chemical composition of malachite? `[1]`

a. $CuO . CuC0_3$
b. $Cu(OH)_2\ CuC0_3$
c. $CuO.Cu(OH)_2$
d. $Cu_2O . Cu(OH)_2$

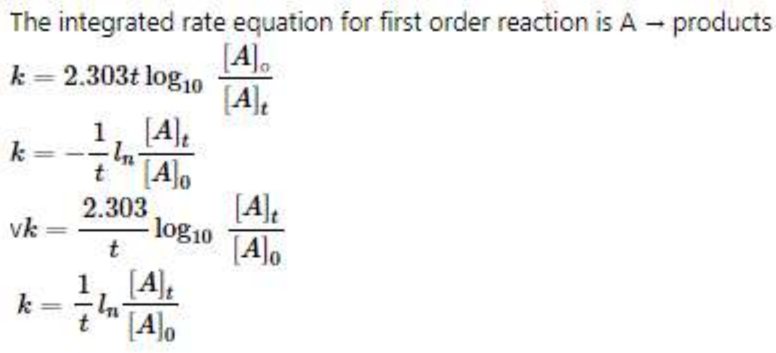
Solution: $Cu(OH)_2.CuCO_3$
The chemical composition of malachite is $Cu(OH)_2.CuCO_3$.

Question 1.6: The element that does NOT exhibit allotropy is `[1]`

a. As
b. Sb
c. Bi
d. N

Solution: (c) Bi
With the exception of Bismuth, all other elements exhibit allotropy.

Question 1.7: `[1]`



The integrated rate equation for first order reaction is A → products

$$k = 2.303t \log_{10} \frac{[A]_o}{[A]_t}$$

$$k = -\frac{1}{t} l_n \frac{[A]_t}{[A]_0}$$

$$\surd k = \frac{2.303}{t} \log_{10} \frac{[A]_t}{[A]_0}$$

$$k = \frac{1}{t} l_n \frac{[A]_t}{[A]_0}$$

Solution:

$$k = -\frac{1}{t} l_n \frac{[A]_t}{[A]_0}$$

Question 2: Answer any SIX of the following [12]

Question 2.1: Define the Enthalpy of fusion [2]

Solution: Enthalpy of fusion:-
The enthalpy change which accompanies the fusion of one mole of a solid without change in temperature at constant pressure is called its enthalpy of fusion.

Question 2.2: Derive van’t Hoff general solution equation [2]

Solution: (a) According to van't Hoff-Boyle's law, osmotic pressure of a dilute solution is inversely proportional to the volume containing 1 mole of solute at constant temperature and according to van't Hoff-Charles' law, osmotic pressure of a dilute solution is directly proportional to the absolute temperature, at constant concentration.

(b) If π is the osmotic pressure, V is the volume of the solution and T is the absolute temperature, then $\pi \propto 1/V$ ...(1) ...[van't Hoff-Boyle's law at constant temperature]
$\therefore \pi V = \text{constant}$
$\pi \propto T$ .....(2) ...[van't Hoff-Charles' law at constant concentration]

$$\therefore \frac{\pi}{T} = \text{constant}$$

c. Combining (1) and (2) we get,

$$\pi \propto \frac{T}{V}$$

$$\therefore \pi = \text{Constant} \times \frac{T}{V}$$

$\therefore \pi V = R'T$, where R' is a constant.

(d) This equation is parallel to the ideal gas equation PV = RT (n = 1)
Since, the calculated value of R' is almost same as R, the equation can be written as $\pi V = RT$ (for 1 mole of solute)

(e) This equation was derived for 1 mole of solute dissolved in V dm^3. If n moles of solute are dissolved in V dm^3 of solution, the equation becomes

$$\pi V = nRT$$

$$\therefore \pi = \frac{nRT}{V}$$

f. $C = \frac{n}{V}$

$$\therefore \pi = CRT$$

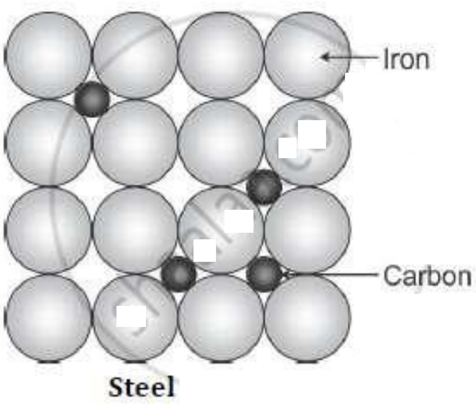
Where,
π = osmotic pressure,

C = concentration of solution in moles/litre
R = gas constant = 0.082 L atm mol^{-1} K^{-1} or 8.314 J mol^{-1} K^{-1}
T = absolute temperature
n = number of moles of solute,
V = volume of the solution.

Question 2.3: Explain impurity defect in stainless steel with diagram **[2]**

Solution: Pure iron is soft and malleable, whereas stainless steel is hard, strong, less ductile, shiny and bright in appearance.

Stainless steel is an interstitial alloy formed by introducing carbon atoms as impurity.



Question 2.4: Derive the relation between half-life and rate constant for a first order reaction **[2]**

Solution: The integrated rate law for the first order reaction is given by the equation

$$k = \frac{2.303}{t}\log_{10}\frac{[A]_o}{[A]_t}$$

Where $[A]_0$ = initial concentration of the reactant at t = 0

The concentration falls to $[A]_t$ at time t from the start of the reaction.

The concentration of the reactant falls to $[A]_0/2$ at time $t_{1/2}$.
Therefore, $t = t_{1/2}$
$[A]_t = [A]_0/2$
So, the equation can be written as

$$k = \frac{2.303}{t_{\frac{1}{2}}} \log_{10} \frac{[A]_o}{\frac{[A]_o}{2}}$$

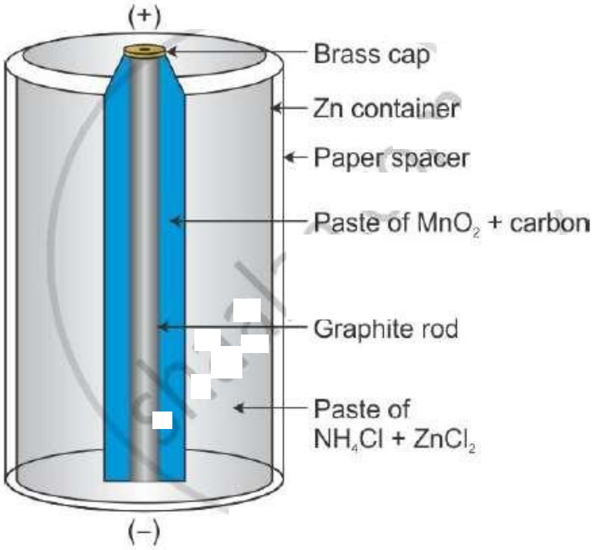
$$= \frac{2.303}{\frac{t_1}{2}} \log_{10} 2$$

$$= \frac{2.303}{\frac{t_1}{2}} \cdot 0.301 = \frac{0.693}{\frac{t_1}{2}}$$

$$t_{\frac{1}{2}} = \frac{0.693}{k}$$

Question 2.5: Draw neat and labelled diagram of dry cell. [2]

Solution:



Question 2.6: Explain the structure of sulphur dioxide. [2]

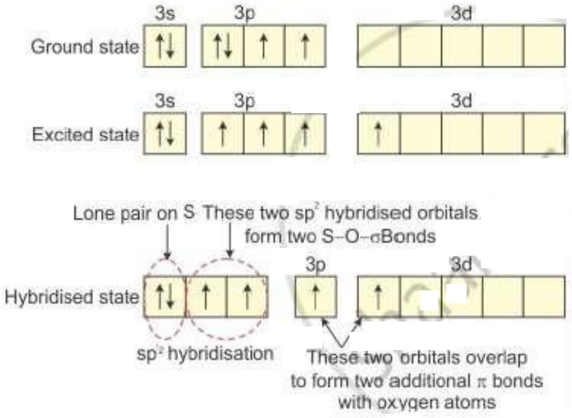
Solution: SO2 molecule has a bent structure with an O–S–O bond angle of 119°.

Sulphur is sp2 hybridised and the lone pair of electrons of sulphur reduces the bond angle from 120° to 119°.

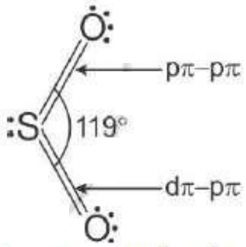
In the structure, each oxygen atom is attached to sulphur by an σ and a π bond.

The σ bonds between S and O are formed by sp^2–p overlap, while one of the π bonds is formed from pπ– pπ overlap and other from pπ–dπ overlap.

Both S–O bonds are identical because of resonance.



Hybridisation of S in SO₂ molecule



Bonding in SO₂ molecule

Question 2.7.i: What is calcination? **[2]**

Solution: Calcination is a process in which the ore is heated to a high temperature below its melting point in the absence of air or in a limited supply of air.

Ex: $ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2$

Question 2.7.ii:

Explain calcination with reactions.

Solution: a. Calcination is a process in which the ore is heated to a high temperature below its melting point in the absence of air or in a limited supply of air.

b. Carbonate ores are decomposed to give metal oxides and carbon dioxide.

$$\underset{\substack{\text{Zinc carbonate}\\\text{(Calamine ore)}}}{ZnCO_{3(s)}} \xrightarrow[\Delta]{\text{Calcination}} \underset{\substack{\text{Zinc}\\\text{oxide}}}{ZnO_{(s)}} + CO_{2(g)}$$

c. The hydrated ore loses its water of hydration.

$$\underset{\text{Malachite}}{CuCO_3.Cu(OH)_2} \xrightarrow[\Delta]{\text{Calcination}} \underset{\substack{\text{Cupric}\\\text{oxide}}}{2CuO} + H_2O + CO_2$$

Question 2.8: Arrange the following reducing agents in the order of increasing strength under standard state conditions. Justify the answer **[2]**

Element	Al(s)	Cu(s)	Cl(aq)	Ni(s)
E°	-1.66V	0.34V	1.36V	-0.26V

Solution: Cl < Cu < Ni < Al

Reason: Substances which have lower electrode potential are stronger reducing agents, while those which have high electrode potential are stronger oxidising agents.

Question 3: Answer any THREE of the following [9]

Question 3.1: Determine whether the reactions with the following ΔH and ΔS values are spontaneous or non-spontaneous. State whether the reactions are exothermic or endothermic. [3]

(a) $\Delta H = -110 kJ, \Delta S = +40 JK^{-1}$ at 400 K
(b) $\Delta H = +40 kJ, \Delta S = -120 JK^{-1}$ at 250K

Solution: (a) ΔH = −110 kJ, ΔS = +40 JK−1 at 400 K

ΔH = −ve; heat is evolved in an exothermic reaction

In the above case, ΔH < 0 and ΔS > 0. Under these conditions, both ΔH and TΔS terms will be negative, so ΔG will be negative regardless of the temperature.

So, the reaction will be spontaneous and exothermic.

(b) ΔH = +40 kJ, ΔS = − 120 JK−1 at 250 K

ΔH = +ve; heat is absorbed in an endothermic reaction

In the above case, ΔH > 0 and ΔS < 0. Under these conditions, ΔG is always positive and the reaction is always non-spontaneous.

So, the reaction will be non-spontaneous and endothermic.

Question 3.2: 1.0×10^{-3}Kg of urea when dissolved in 0.0985 Kg of a solvent, decreases freezing point of the solvent by 0.211 k. 1.6x10 Kg of another non-electrolyte solute when dissolved in 0.086 Kg of the same solvent depresses the freezing point by 0.34 K. Calculate the molar mass of the another solute. (Given molar mass of urea = 60) [3]

Solution: Mass of solute (A), i.e. urea = 1.0×10^{-3} kg

Molar mass of solute (A) = 60

Mass of solvent in which solute A is dissolved = 0.0985 kg

Mass of solute (B) = 1.6×10^{-3} kg

Molar mass of solute (B) =?

Mass of solvent in which solute B is dissolved = 0.086 kg

$$\frac{\Delta T_{f_A}}{\Delta T_{f_B}} = \frac{m_A}{m_B}$$

$$\frac{0.211}{0.34} = \frac{\frac{\text{Mass of solute (A)}}{\text{Molecular mass of solute(A)} \times \text{Kg of solvent}}}{\frac{\text{Mass of solute(B)}}{\text{Molecular mass of solute(B)} \times \text{Kg of solvent}}}$$

$$\frac{0.211}{0.34} = \frac{\frac{1 \times 10^{-3}}{60 \times 0.0985}}{\frac{1.6 \times 10^{-3}}{\text{Molecular mass of solute(B)} \times 0.086}}$$

$$\frac{0.211}{0.34} = \frac{1 \times 10^{-3} \times \text{Molecular mass of solute(B)} \times 0.086}{60 \times 0.0985 \times 1.6 \times 10^{-3}}$$

$$\text{Molecular mass of solute(B)} = \frac{0.211 \times 60 \times 0.0985 \times 1.6 \times 10^{-3}}{0.34 \times 1 \times 10^{-3} \times 0.086}$$

Molar mass of another solute = 68.24

Question 3.3: Sucrose decomposes in acid solution into glucose and fructose according to the first order rate law with $t_{1/2}$= 3 hours. What fraction of the sample of sucrose remains after 8 hours? **[3]**

Solution:

$$t_{\frac{1}{2}} = 3 Hours$$

Now we know that,

$$k = \frac{0.693}{t_{\frac{1}{2}}} = \frac{0.693}{3} = 0.231 h^{-1}$$

Put above value in the formula of first order reaction,

$$k = \frac{2.303}{t} \log\left(\frac{[R]_0}{[R]}\right) = \frac{2.303}{8} \log\left(\frac{[R]_0}{[R]}\right)$$

So,

$$\log\left(\frac{[R]_0}{[R]}\right) = \frac{0.231 \times 8}{2.303} = 0.8024$$

Taking antilog on both sides,

$$\frac{[R]_0}{[R]} = 6.3445$$

$$\frac{R}{[R]_0} = 0.158$$

Fraction of the sample of sucrose remaining after 8 hours = 0.158

Question 3.4: Explain how does nitrogen exhibit anomalous behaviour amongst group 15 elements. **[3]**

Solution: Nitrogen shows anomalous behaviour as follows:-

a. Nitrogen is a gas, whereas the other members of the family are solids.
b. Nitrogen is diatomic, while the other elements such as phosphorus and arsenic form tetra-atomic molecules (P_4, As_4).
c. Nitrogen forms five types of oxides (N_2O, NO, N_2O_3, N_2O_4 and N_2O_5), while the other members form two types of oxides—trioxides and pentoxides.
d. Hydrides of nitrogen consist of H-bonding, which is absent in members of other elements.
e. Nitrogen does not show penta-covalency because of the absence of d-orbitals, but all other elements show penta-covalency.
f. Nitrogen dose not form complexes because of the absence of d-orbitals, while the other elements show complex formation (e.g. $[PCl_6]^-$, $[AsCl_6]^-$).
g. The hydride of nitrogen (NH_3) is highly basic in nature, whereas the hydrides of other elements are slightly basic.

Question 4: Answer any one of the following : [7]

Question 4.1.i: Niobium crystallises as body centred cube (BCC) and has density of 8.55 Kg / dm^{-3} . Calculate the atomic radius of niobium. **[7]**
Given : Atomic mass of niobium = 93).

Solution: Crystal structure of Niobium = bcc

Density (d) = 8.55 kg dm-3

Atomic mass of Niobium = 93

$$d = \frac{n \times M}{V \times N_A}$$

No. of atoms per unit cell (n) in bcc = 2

Total volume of unit cell = a3

$$d = \frac{2 \times 93}{a^3 \times 6.022 \times 10^{23}}$$

$$a^3 = \frac{2 \times 93}{8.55 \times 6.022 \times 10^{23}} = 36.12 \times 10^{-24}$$

$$a = \sqrt[3]{36.12 \times 10^{-24}}$$

a= 3.305 x 10-8

In BCC unit cell,

$$r = \frac{\sqrt{3} \times a}{4} = \frac{\sqrt{3} \times 3.305 \times 10^{-8}}{4} = 1.431 \times 10^{-8}$$

Question 4.1.ii:

Write one statement of first law of thermodynamics and its mathematical expression.

Solution: First law of thermodynamics:-

If the quantity of heat supplied to a system is capable of doing work, then the quantity of heat absorbed by the system is equal to the sum of the increase in the internal energy of the system and the external work done by it.

The equation which supports the first law of thermodynamics mathematically is

$\Delta U = q + w$

When expressed in the differential form, the same relationship takes the following form:

$dQ = dU + dL$

Question 4.1.iii:

Write the reactions involved in the zone of reduction in blast furnace during extraction of iron.

Solution: Zone of reduction:-

Carbon monoxide reduces ferric oxide to spongy iron (porous solid) at about 900 K.

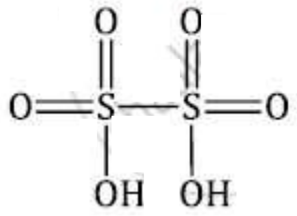
$$3\,Fe^{2}O^{3} + CO \longrightarrow 2\,Fe^{3}O^{4} + CO^{2}$$
$$Fe^{3}O^{4} + 4\,CO \longrightarrow 3\,Fe + 4\,CO^{2}$$
$$Fe^{2}O^{3} + CO \longrightarrow 2\,FeO + CO^{2}$$

Question 4.2.i: Write molecular formulae and structures of Dithionic acid **`[7]`**

Solution:

Dithionic acid

Molecular formula: $H_2S_2O_6$



$$O{=}S(=O)(OH){-}S(=O)(OH){=}O$$

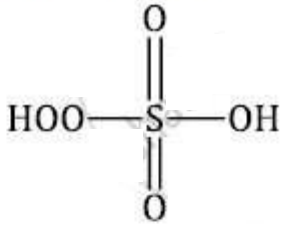
Question 4.2.ii:

Write molecular formulae and structures of the Peroxy monosulphuric acid

Solution:

Peroxymonosulphuric acid

Molecular formula: H_2SO_5

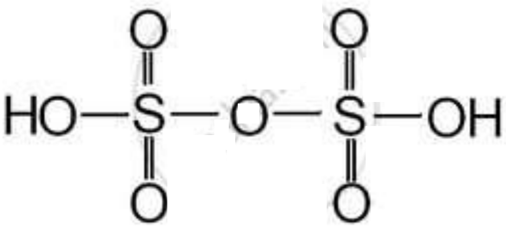


$$HOO{-}S(=O)_2{-}OH$$

Question 4.2.iii:

Write molecular formula and structure of Pyrosulphuric acid

Solution: Pyrosulphuric acid molecular formula: $H_2S_2O_7$



$$HO{-}S(=O)_2{-}O{-}S(=O)_2{-}OH$$

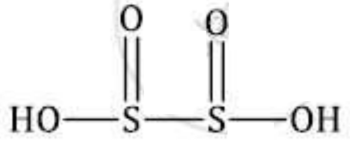
Question 4.2.iv:

Write molecular formulae and structures of the Dithionous acid

Solution:

Dithionous acid

Molecular formula: $H_2S_2O_4$



Question 4.2.v:

Calculate E_{cell} and ΔG for the following at 28°C :

$Mg_{(s)} + Sn^{2+}(0.04M) \rightarrow Mg^{2+}(0.06M) + Sn_{(s)}$

E°_{cell} = 2.23V. Is the reaction spontaneous ?

Solution:

$$Mg_s + Sn^{2+}_{aq} \rightarrow Mg^{2+}_{aq} + Sn_s$$

$$[Sn^{2+}] = 0.04M [Mg^{2+}] = 0.06M$$

$$Q = \frac{Mg^{2+}}{Sn^{2+}} = \frac{0.06}{0.04} = 1.5$$

$$E^\circ_{cell} = 2.23V$$

R = 8.314 JK^{-1} mol^{-1}

T = 28°C = 28 + 273 = 301K

n = 2

F = 96500 C/mol e^-

$$\therefore E_{cell} = E^\circ_{cell} - \frac{2.303RT}{nF} \log_{10} Q$$

$$= 2.23 - \frac{2.303 \times 8.314 \times 301}{2 \times 96500} \log_{10}(1.5)$$

$$= 2.23 - \frac{2.303 \times 8.314 \times 301}{2 \times 96500} \times (0.1760)$$

= 2.23 - 0.005255

E_{cell} = -2.2247 V

$\Delta G = nFE_{cell}$

$\Delta G = -2 \times 96500 \times 2.2247$

ΔG = - 429367 J

∵ ΔG is negative therefore reaction is **spontaneous**.

Question 5: Select and write the most appropriate answers from the given alternatives for each sub-question [7]

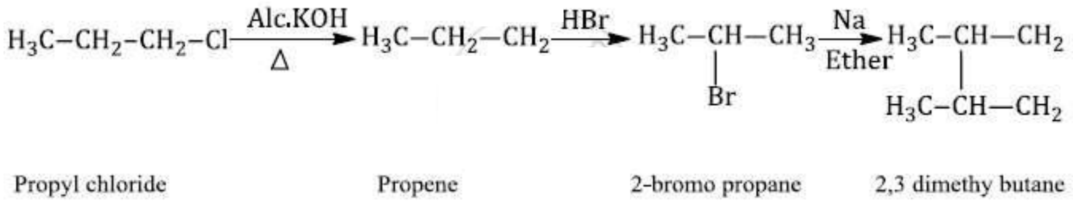
Question 5.1: [1]

Identify the product 'D' in the following sequence of reactions:

$H3C - CH2 - CH2 - Cl \xrightarrow[KOH]{Alc} 'B' \xrightarrow{HBr} 'C' \xrightarrow[Ether]{Na} 'D'$

a. 2,2 - dimethyl butane
b. 2,3- dimethylbutane
c. hexane
d. 2,4 - dimethylpentane

Solution: (b) **2, 3-dimethyl butane**



Question 5.2: Which of the following complexes will give a white precipitate on treatment with a solution of barium nitrate? **[1]**

a. $[Cr(NH_3)_4SO_4]$ Cl
b. $[Co(NH_3)_4Cl_2]$ NO_2
c. $[Cr(NH_3)_4Cl_2]SO_4$
d. $[CrCl_2(H_2O)_4]Cl$

Solution: (c) $[Cr(NH_3)_4Cl_2]SO_4$

$[Cr(NH_3)_4Cl_2]SO_4$ complex will give a white precipitate on treatment with a solution of barium nitrate. The white precipitate is of barium sulphate ($BaSO_4$).

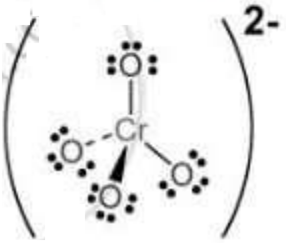
Question 5.3: What is the geometry of chromate ion? **[1]**

a. Tetrahedral
b. Octahedral
c. Trigonal planer
d. Linear

Solution:

(a) Tetrahedral

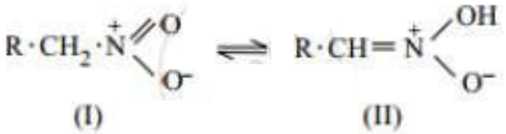
The chromate anion CrO_4^{2-} has tetrahedral geometry.



Question 5.4: Primary and secondary nitroalcanes containing α - H atom show property of - [1]

a. chain isomerism
b. tautomerism
c. optical isomerism
d. geometrical isomerism

Solution: (b) **Tautomerism**
Primary and secondary nitroalkanes containing α-hydrogen atoms show tautomerism. Here, the isomers are obtained by 1,3-migration of a proton from one polyvalent atom to the other within the same molecule.



Question 5.5:

In phenol carbon atom attached to -OH group undergoes -

a. SP^3 hybridisation
b. SP hybridisation
c. SP^2 hybridisation
d. No hybridisation

Solution: (c) **sp^2 hybridisation**
The carbon to which the hydroxyl group is bonded in phenol is sp^2 hybridised. The increased s-character of the carbon orbital used to form the C—O bond makes it more electron-withdrawing. Thus, conjugation with the aromatic ring would make the sp^2 hybridised oxygen atom more likely.

Question 5.6: Identify the strongest acid amongst the followings: [1]

a. Chloroacetic acid
b. Acetic acid
c. Trichloroacetic acid
d. Dichloroaceticacid

Solution: (c) **Trichloroacetic acid**
As the number of chlorine atoms increases, the electronegativity of that end of the molecule increases and the molecule adopts a progressively more ionic character (e.g. density, boiling point and acidity).

Question 5.7: Which of the following vitamins is water soluble? `[1]`

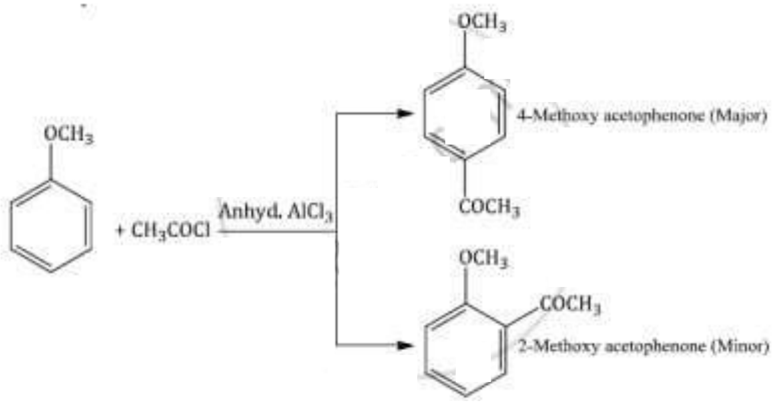
a. A
b. D
c. E
d. B

Solution: (d) **B**
Vitamin B is water soluble, whereas vitamins A, D, E and K are fat soluble.

Question 6: Answer any SIX of the following : `[12]`

Question 6.1: Write a note on Friedel Craft's acylation. `[2]`

Solution: Friedel Crafts acylation
Introduction of the acyl group at the ortho and para positions in anisole on reaction with acyl halide in the presence of anhydrous aluminium chloride (a Lewis acid) as a catalyst is called Friedel Crafts acylation.



Question 6.2: How is ethyl amine prepared from methyl iodide? `[2]`

Solution: Methyl iodide reacts with alcoholic solution of potassium cyanide (KCN) to give ethane nitrile (or methyl cyanide) as the major product with a small amount of potassium iodide.

$$\underset{\text{Iodomethane}}{CH_3{-}I} + KCN \rightarrow \underset{\substack{\text{Ethane nitrile}\\\text{(or methyl cyanide)}}}{CH_3{-}C\equiv N} + KI$$

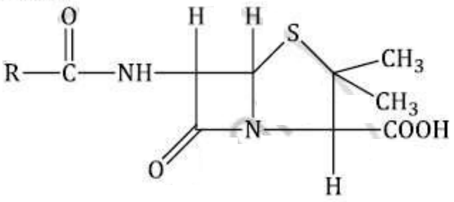
Ethane nitrile (or methyl cyanide) on reduction with sodium and alcohol (Mendius reaction) forms ethyl amine.

$$\underset{\substack{\text{Ethane nitrile}\\\text{(or methyl cyanide)}}}{CH_3{-}C\equiv N} + 4H \xrightarrow[\text{(Mendius reaction)}]{Na/C_2H_5OH} \underset{\text{Ethyl amine}}{CH_3{-}CH_2{-}NH_2}$$

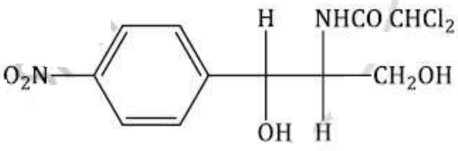
Question 6.3: What are antibiotics? Give ‘two’ examples **[2]**

Solution: An antibiotic is a drug derived from living matter or microorganisms which is used to kill or prevent the growth of other microorganisms. The antibiotics are classified into two types—bactericidal (killing bacteria) and bacteriostatic (inhibits growth of bacteria).

Examples of antibiotics:



Penicillin (bactericidal)



Chloramphenicol (bacteriostatic)

Question 6.4: Explain, why boiling points of carboxylic acids higher than corresponding alcohols are **[2]**

Solution: The boiling points of carboxylic acids are higher than the corresponding alcohols because

- Carboxylic acids have a high boiling point because of their ability to form intermolecular hydrogen bonds.
- Hydrogen bonds formed in carboxylic acids are stronger than those in alcohols.
- The –OH bond in –COOH is more strongly polarised than the –OH bond of alcohols. This is because of the presence of an electron-withdrawing carboxyl group in an adjacent position in carboxylic acids.

Question 6.5: How are proteins classified on the basis of molecular shapes? **[2]**

Solution: On the basis of molecular shape, proteins are classified into two types—fibrous proteins and globular proteins.

1. **Fibrous proteins:-** They are insoluble in water, long, thread-like and tend to lie side by side to form fibres. The polypeptide chains are held together by hydrogen bonds. Examples: Collagen in tendons; keratin in hair, skin, nails, horn and feathers; myosin in muscle; fibroin in silk

2. **Globular proteins:-** They are soluble in water and aqueous solutions of bases, acids and salts. They are folded to form a spherical shape, have intramolecular hydrogen bonding and have weak intermolecular forces as compared to fibrous proteins.

Question 6.6.i: What are interstitial compounds ? **[2]**

Solution 1: Interstitial compounds :
Interstitial compounds are formed when small atoms such as H, C or N are trapped inside the crystal lattices of metals. They are usually nonstoichiometric and are neither typically ionic nor covalent.

Solution 2: (a) Interstitial compounds are those which are formed when small atoms like H, C, N, B etc. are trapped inside the crystal lattice of metals.
(b) They have melting point higher than metals due to stronger metal-non metal bonds or compared to metal-metal bonds in pure metals.

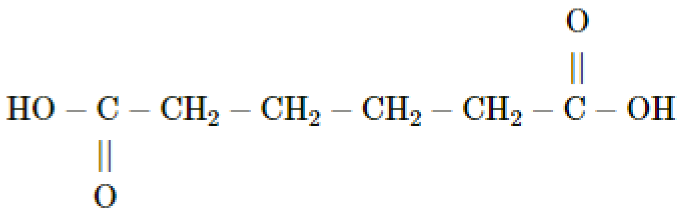
Question 6.6.ii:

Why do interstitial compounds have higher melting points than corresponding pure metals?

Solution: The melting points of interstitial compounds are higher than those of pure metals because of bonding between the metal and the non-metal, which is stronger than metal–metal bonding.

Question 6.7.i: Write the structures and IUPAC names of the : Adipic acid compound **[2]**

Solution: Structure and IUPAC name of the compounds are :
Adipic acid Structure :



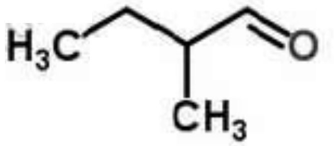
$HO-\underset{\underset{O}{||}}{C}-CH_2-CH_2-CH_2-CH_2-\overset{\overset{O}{||}}{C}-OH$

IUPAC name : Hexanedioic acid.

Question 6.7.ii: Write the structures and IUPAC names of the α - methyl butyraldehyde.

Solution:

α-methyl butyraldehyde

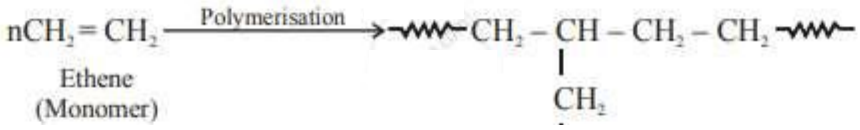


IUPAC: 2-Methyl butanal

Question 6.8: Explain with examples, branched and linear polymers. `[2]`

Solution: **__Branched polymers :-__** These polymers consist of a chain structure having one main chain of molecules with smaller chains as branches of the main chain. They have low density.

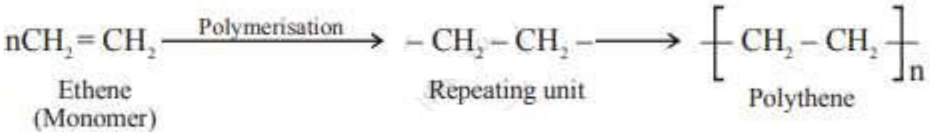
Example : Polypropylene with methyl groups as branches, LDPE



$\underset{\text{(Monomer)}}{\underset{\text{Ethene}}{nCH_2=CH_2}} \xrightarrow{\text{Polymerisation}} \sim\!\sim CH_2-\underset{\underset{CH_2}{|}}{CH}-CH_2-CH_2\sim\!\sim$

__Linear polymers :-__ They are made of long continuous chains without any excess attachments (branches). The repeating units are joined to form a long chain.

Examples : Polyethene, PVC.

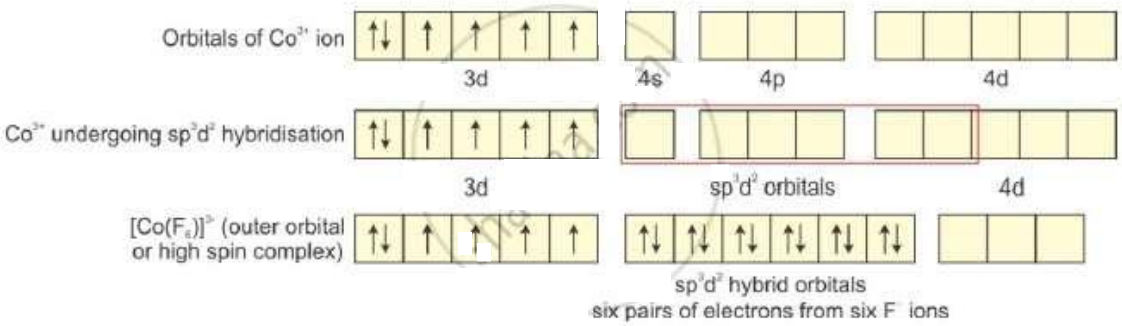


$\underset{\text{(Monomer)}}{\underset{\text{Ethene}}{nCH_2=CH_2}} \xrightarrow{\text{Polymerisation}} \underset{\text{Repeating unit}}{-CH_2-CH_2-} \longrightarrow \underset{\text{Polythene}}{\left[CH_2-CH_2 \right]_n}$

Question 7: Answer any THREE of the following : `[9]`

Question 7.1.i: On the basis of valence bond theory explain the nature of bonding in $[CoF_6]^3$ ion. `[3]`

Solution: The oxidation state of cobalt in this complex is +3. Hence, we have



F^- ion provides a weak ligand field and is unable to pair up the unpaired electrons of the 3d orbitals. Hence, six equivalent hybrid orbitals are obtained by mixing of one 4s, three 4p and two 4d orbitals. Six empty sp^3d^2 hybrid orbitals are filled up by six electron pairs provided by F^- ion. The highly paramagnetic nature of the complex further confirms the presence of four unpaired electrons.

As d-orbitals of the outermost shell take part in hybridisation, the complexes thus formed are called outer orbital complexes.

Question 7.1.ii: Write the IUPAC name of $[Co(NO_2)_3(NH_3)_3]$.

Solution: IUPAC name of the compound is **Trinitroamine cobalt (III)**

Explanation :
The given compound IUPAC name is as follows : $Co(NH_3)_3(NO_2)_3$

- The given compound has Cobalt metal atom, which is surrounded by six ligand. Among them three are ammonia groups and three are nitro groups.
  According to the IUPAC, ammonia groups are mentioned as amino groups.
- The oxidation state of cobalt atom in the given coordination compound is +3.
- Hence, the name of given coordinated compound is Trinitroamine cobalt (III).

Question 7.2.i: Define lanthanoid contraction. [3]

Solution 1: Lanthanoid contraction:-

With an increasing atomic number in the lanthanoid series, there is a progressive decrease in the atomic as well as ionic radii of trivalent ions from La3+ to Lu3+.

This regular decrease (contraction) in the size of the atoms and ions with increasing atomic number is known as lanthanoid contraction.

Solution 2: Lanthanoid Contraction : In the lanthanoids , the electrons are getting filled in the 4f-subshell. On moving from left to right, the nuclear charge increases and this increase is expected to be compensated by the increase in the magnitude of shielding effect by the 4 f- electrons However,
the f-electrons have very poor shielding effect. Consequently, the atomic and ionic radii decrease from left to right and this is knwon as lanthanoid contraction.

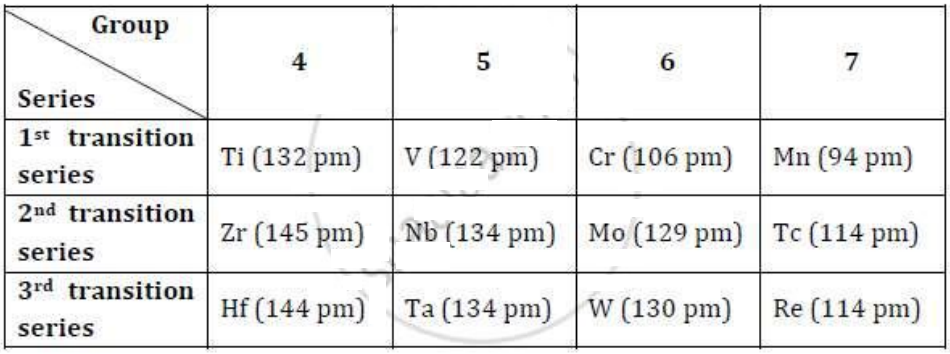
Question 7.2.ii:

Explain effects of lanthanoid contraction

Solution 1: Effects of lanthanoid contraction:-

(a) Effects on the basic strength of hydroxides: As the size of the lanthanoid ions decreases from La^{3+} to Lu^{3+}, the covalent character of the hydroxides increases. Thus, the basic strength decreases. Hence, $La(OH)_3$ is most basic, while $Lu(OH)_3$ is the least basic.

(b) Ionic radii of post lanthanoids: The elements which follow the lanthanoids in the third transition series are known as post lanthanoids. As a result of lanthanoid contraction, the atomic radii (size) of the elements which follow lanthanum (Hf, Ta, W etc.) are similar to those of the elements of the previous period. There is normal increase in size from Sc to Y to La. This trend disappears after the lanthanoids, and pairs of elements Zr–Hf (group 4), Nb–Ta (group 5), Mo–W (group 6) and Tc–Re (group 7) have almost identical sizes. These atoms possess similar number of valence electrons and similar properties. These pairs of elements are called ‘chemical twins’. The elements of the second and third transition series resemble each other more closely than the elements of the first and second transition series.



Group Series	4	5	6	7
1st transition series	Ti (132 pm)	V (122 pm)	Cr (106 pm)	Mn (94 pm)
2nd transition series	Zr (145 pm)	Nb (134 pm)	Mo (129 pm)	Tc (114 pm)
3rd transition series	Hf (144 pm)	Ta (134 pm)	W (130 pm)	Re (114 pm)

(c) Difficulty in separation of lanthanoids:- Because the changes in ionic radii (size of the ions) in the lanthanoids are very small, their chemical properties are similar. This makes the separation of the lanthanoids in the pure state difficult. However, lanthanoid contraction results in slight difference in the size of the lanthanoids which results in the differences in properties such as solubility, complex formation, hydration, basic character of their hydroxides etc. Because of these differences, the lanthanoids can be separated by the ion exchange method.

Question 7.2.iii:

What are the consequences of lanthanoid contraction?

Solution: Consequences of lanthanoid Contraction
(a)Separation Lanthanoids: All the lanthanoids have quite similar properties and due to this reason they are difficult to separate.

(b)Variation in basic strength of hydroxides: Due to lanthanoid contraction, size of M^{3+} ions decreases and thus there is a corresponding increase in the covalent character in M—OH bond. Thus basic character of oxides and hydroxides decreases from $La(OH)_3$ to $Lu(OH)_3$.

(c)Similarity in the atomic sizes of the elements of second and third transition series present in the same group. The difference in the value of atomic radii of Y and La is quite, large as compared to the difference in the value of Zr and Hf. This is because of the lanthanoid contraction.

(d)Variation in standard reduciton potential: Due to lanthanoid contraction there is a small but steady increase in the standard reduction potential (E°) for the reduction process.

M^{3+} (aq) + $3e^-$ ––> 4 M(aq)

(e)Variation in physical properties like melting point, boiling point, hardness etc.

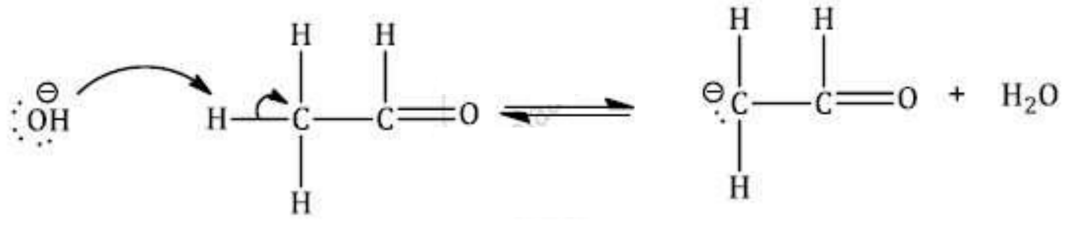
Question 7.3: Write mechanism of Aldol addition reaction. `[3]`

Solution:

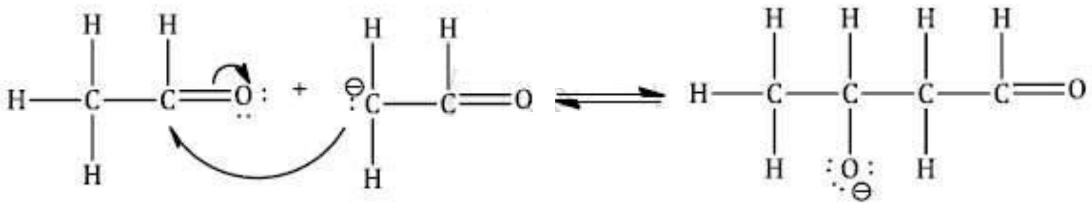
Aldol addition reaction:-

'Aldol' is an abbreviation of aldehyde and alcohol. When the enolate of an aldehyde or a ketone reacts at the α-carbon with the carbonyl of another molecule under basic or acidic conditions to obtain β-hydroxy aldehyde or ketone, the reaction is called an aldol reaction.

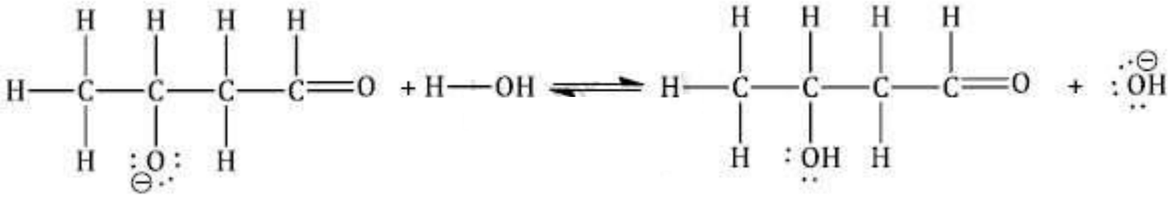
Step I: Base OH− ion abstracts a hydrogen atom from an α-carbon of aldehyde to form carbanion.



Step II: The nucleophilic carbanion or enolate ion attacks the electrophilic carbonyl carbon of the second aldehyde molecule to form an intermediate alkoxide ion. A new C–C bond is formed.



Step III: Alkoxide ion abstracts a hydrogen ion from water to form β-hydroxy aldehyde. Base OH− ion is regenerated.



Question 7.4.i: Define carbohydrates. [3]

Solution: Carbohydrates are optically active polyhydroxy aldehydes or polyhydroxy ketones or the compounds which can be hydrolysed to polyhydroxy aldehydes or polyhydroxy ketones.

Question 7.4.ii:

What are reducing and non-reducing sugars?

Solution: Carbohydrates are classified as

(a) Reducing sugars:- They reduce Fehling’s solution and Tollens’ reagent. All monosaccharides, whether aldoses or ketoses, are reducing sugars. Disaccharides in which aldehydic and ketonic groups are free behave as reducing sugars.

Examples: Maltose, lactose

(b) Non-reducing sugars: They do not reduce Fehling’s solution and Tollens’ reagent. Disaccharides in which aldehydic or ketonic groups are bonded behave as nonreducing sugars.

Example: Sucrose

Question 8: Answer any ONE of the following [7]

Question 8.1.i: What are biodegradable polymers and non-biodegradable polymers? Write ‘one example’ of each. [7]

Solution: Biodegradable polymers and non-biodegradable polymers: After a certain period of time, the natural polymers degrade on their own but synthetic polymers do not. These are non-biodegradable polymers and are resistant to environmental degradation processes and are accumulated as solid waste materials. Hence, efforts were made to synthesise biodegradable polymers to avoid environmental problems.

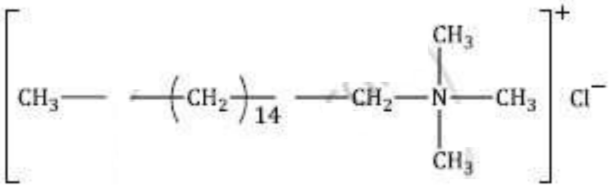
Example of biodegradable polymer: Dextron

Example of non-biodegradable polymer: 1-polyethylene

Question 8.1.ii:

Explain cationic detergents.

Solution: Cationic detergents:- Cationic detergents are quaternary ammonium salts of amines with chlorides, acetates or bromides. They have cations at the soluble ends of the chain. Anions are chlorides, acetates or bromides, and cations are long chain hydrocarbons with a positive charge on the nitrogen atom. They are used as germicides and are expensive, for example, cetyltrimethyl ammonium chloride is used in hair conditioners. Hence, these cationic detergents are alkyl ammonium salts.

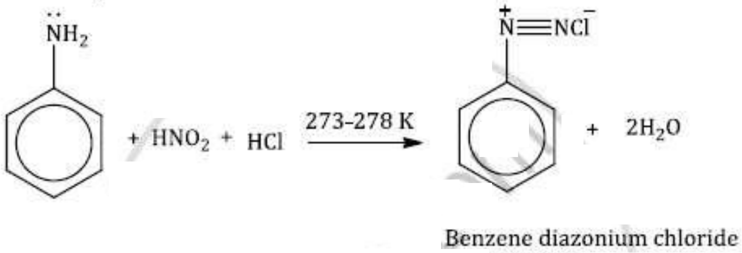


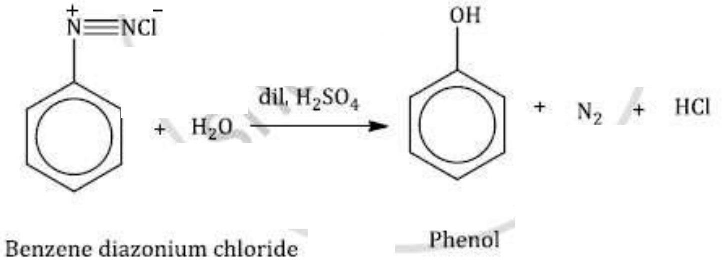
$$\left[CH_3-(CH_2)_{14}-CH_2-\overset{CH_3}{\underset{CH_3}{N}}-CH_3\right]^+ Cl^-$$

n-hexadecyl trimethyl
ammonium chloride or
(cetyltrimethyl ammonium chloride)

Question 8.2.i: How is carbolic acid prepared from the given compounds : `[7]`
Aniline

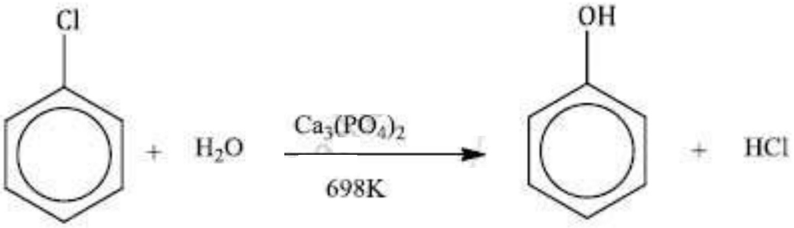
Solution: Aniline:-
When aniline (a primary aromatic amine) is treated with nitrous acid ($NaNO_2$ and HCl) under ice-cold conditions, it gives benzene diazonium salt. This process is called diazotization. The aqueous solution of the diazonium salt is hydrolyzed with dilute sulphuric acid to give phenol. The reaction can be shown as follows:





Question 8.2.ii:
How is carbolic acid prepared from the given compounds :
Chlorobenzene and steam at 698K?

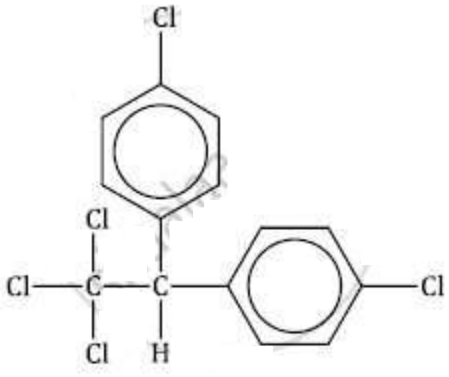
Solution: Preparation of carbolic acid from Chlorobenzene and steam at 698 K:-
Phenol is obtained by heating chlorobenzene with steam at 698 K using Ca3(PO4)2 or SiO2 as a catalyst. The hydrolysis can also be affected by water in the presence of copper as a catalyst at 673 K and under pressure.



Question 8.2.iii:

Draw structure of DDT.

Solution: Structure of dichlorodiphenyltrichloroethane (DDT) is as follows:



Question 8.2.iv:

Write the environmental effects of DDT.

Solution:

1. It is not completely biodegradable i.e. it is not very rapidly metabolized by animals. Instead, it gets deposited and store in fatty tissues. It is exists for longtime in soil, plants and animals as well. It produces unforeseen ecological effects.

2. It is replaced by better and safer insecticide due to ecological problems.

Question 8.2.v:

Mention ‘two’ physical properties of carbolic acid.

Solution: Physical properties of carbolic acid:
(a) Pure phenol is a colourless, crystalline solid.
(b) Phenol has characteristic smell known as phenolic or carbolic odour.
(c) Melting point of phenol is 315 K.
(d) Boiling point of phenol is 455 K.