Chemistry

Academic Year: 2014-2015 Marks: 70
Date & Time: 5th October 2015, 4:00 pm
Duration: 3h

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

Question 1.1: The hybridisation of phosphorus in phosphorus pentachloride is _______.

(A) dsp^3
(B) sp^3 d
(C) d^2 sp^3
(D) sp^3 d^2

Solution: (B) sp^3d

Question 1.2: The rate constant for a first order reaction is 100 s^{-1}. The time required for completion of 50% of reaction is _______. [1]

(A) 0.0693 milliseconds
(B) 0.693 milliseconds
(C) 6.93 milliseconds
(D) 69.3 milliseconds

Solution: (C)

6.93 milliseconds
$t_{1/2}$ = 0.693/100
= 6.93 x 10^{-3} seconds
= 6.93 milliseconds

Question 1.3: Silica is added to roasted copper ore during smelting process to remove _______. [1]

(A) ferrous sulphide
(B) ferrous oxide
(C) cuprous sulphide
(D) cuprous oxide
Solution: (B) ferrous oxide

Question 1.4: 96500 coulombs correspond to the charge on how many electrons? [1]

1.6 X 10^{19}
6.022 X 10^{20}

6.022×10^{23}
6.022×10^{24}

Solution: 6.022×10^{23}

Question 1.5: For the reaction: $Cl_2(g) \rightarrow 2Cl(g)$, ______. **[1]**

(A) ΔH is positive, ΔS is positive
(B) ΔH is positive, ΔS is negative
(C) ΔH is negative, ΔS is negative
(D) ΔH is negative, ΔS is positive

Solution: (A) ΔH is positive, ΔS is positive
ΔH is positive as energy is required for bond breaking. ΔS is positive as the number of gaseous species increases.

Question 1.6: The substance 'X', when dissolved in solvent water gave molar mass corresponding to the molecular formula 'X3'. The van't Hoff factor (i) is ______. **[1]**

(A) 3
(B) 0.33
(C) 1.3
(D) 1

Solution: (B) 0.33
van't Hoff factor (i) = Theoretical molecular mass/Observed molecular mass
= 1/3
= 0.33

Question 1.7: The relation $a \neq b \neq c$ and $\alpha \neq \beta \neq \gamma$ represents which crystal system? **[1]**

(A) Orthorhombic
(B) Tetragonal
(C) Triclinic
(D) Monoclinic

Solution: (C) Triclinic

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

Question 2.1: Define ebullioscopic constant. Write its unit. **[2]**

Solution: Ebullioscopic constant:
Ebullioscopic constant or Molal elevation constant is the elevation in the boiling point produced when one mole of the solute is dissolved in one kilogram of solvent. Its unit is K kg mol^{-1}.

Question 2.2.i: State Second law of thermodynamics in terms of entropy. **[2]**

Solution: Second law of thermodynamics in terms of entropy:
The second law of thermodynamics states that, “The total entropy of the system and its surroundings (universe) increases in a spontaneous process”.

Question 2.2.ii: State Third law of thermodynamics. Give ‘two’ uses.

Solution: The third law of thermodynamics states that, “The entropy of a perfectly ordered crystalline substance is zero at absolute zero of temperature”.

Usefulness :
(a) It helps in calculating thermodynamic properties.
(b) It is helpful in measuring chemical affinity.
(c) It is used to determine the absolute entropy of any substance either in solid, liquid or gaseous state at
any desired temperature.

Question 2.3.i: What is the hybridisation of carbon atom in diamond and graphite? **[2]**

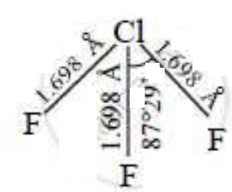
Solution: Hybridisation of carbon atom in diamond is sp^3 and that in graphite is sp^2.

Question 2.3.ii: 0.1 mole of Buckminster fullerene contains how many kg of carbon? [Atomic mass of carbon = 12]

Solution: 1 mole of C60 contains 60 moles of C.
0.1 mole of C60 will contain 6.0 moles of C.
Weight of C-atoms = Number of moles of C x atomic mass of C
= 6.0 x 12
= 72.0 g
= 0.072 kg
0.1 mole of Buckminster fullerene contains 0.072 kg of carbon.

Question 2.4.1: Draw structure of Chlorine trifluoride **[1]**

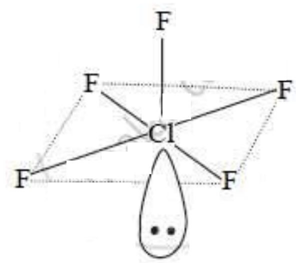
Solution:



Structure of Chlorine trifluoride

Question 2.4.2: Draw structure of Chlorine pentafluoride **[1]**

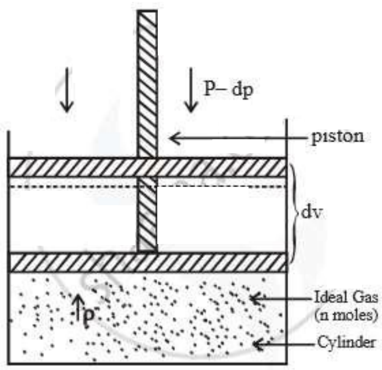
Solution:



Structure of Chlorine pentafluoride

Question 2.5: Derive an expression for maximum work in isothermal reversible expansion of two moles of an ideal gas. **[2]**

Solution:



a. Consider the expansion of 'n' moles of an ideal gas enclosed in a cylinder fitted with a weightless and frictionless piston at a constant temperature T.

b. Let the pressure of the gas be P which is equal to the external pressure.

c. Let the external pressure be reduced by an infinitesimally small amount dp so that the new external pressure becomes (P-dp).

d. Let the corresponding small increase in volume by dv.

e. Therefore amount of work done in the expansion of the gas, dw = - [(p dp)dv] = -[pdv - dp.dv] ..(i)

f. Since dp and dv are very small, their product (dp.dv) will be much smaller and can be neglected ∴ dw = -pdv ...(ii)

g. During expansion of the gas, if the initial volume V_1 changes to volume V_2 then total amount of work alone (Wmax) can be obtained by integrating the work, dw between the two limits, V_1 and V_2.

$$\therefore W_{max} = \int_{v_2}^{v_1} -dw$$

$$= \int_{v_1}^{v_2} -pdv \quad ...(iii)$$

But pv = nRT (Ideal gas Equation for n moles of a gas)

$$\therefore p = \frac{nRT}{v}$$

Substitute pressure value in equation (iii)

$$\therefore W_{max} = \int_{v_1}^{v_2} -\frac{nRT}{v} dv$$

$$= nRT \int_{v_1}^{v_2} \frac{dv}{v} \quad \text{(n,R,T are constatnt)}$$

$$= -nRT \, [\log v]_{v_1}^{v_2}$$

$$= -nRT \ln \frac{v_2}{v_1}$$

$$\therefore W_{max} = -2.303 nRT \log \frac{v_2}{v_1}$$

(ln = 2.303 $\log_{10}$) ...(iv)

Question 2.6: Can copper sulphate solution be stored in an iron vessel? Explain. **[2]**

Solution: Higher the standard reduction potential (E°) value, greater the tendency of the species to accept electrons and undergo reduction.

$Cu^{2+} + 2e^- \rightarrow Cu$, E° = + 0.337 V; $Fe^{2+} + 2e^- \rightarrow Fe$, E° = - 0.440 V

Therefore, Cu^{2+} has a greater tendency to undergo reduction than Fe^{2+} or Fe can reduce (or displace) Cu^{2+} ions from its salt solution.

$Fe_{(s)} + Cu^{2}_{(aq)} \rightarrow Fe^{2}_{(aq)} + Cu_{(s)}$

Hence, copper sulphate solution cannot be stored in an iron vessel as the iron vessel dissolves forming Fe^{2+} ions and Cu^{2+} ions from copper sulphate solution forms Cu.

Question 2.7.i: Define Average rate of reaction. **[2]**

Solution: Average rate of a reaction: The average rate of a reaction is defined as the change in concentration of a reactant or product divided by the time interval over which the change occurs.

Question 2.7.ii:

Define Instantaneous rate of reaction.

Solution: Instantaneous rate of a reaction: The rate of a reaction at a specific instant is called instantaneous rate.

Question 2.8.i: Define Hydrometallurgy? **[2]**

Solution: Hydrometallurgy: A process of extracting metals from aqueous solutions of their salts using suitable reducing agents is called hydrometallurgy.

Question 2.8.ii: Define Electrometallurgy?

Solution: Electrometallurgy: A process of extraction of metals by electrolytic reduction of molten (fused) metallic compounds is called electrometallurgy.

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

Question 3.1.i: What is the action of dioxygen on Calcium **[3]**

Solution: Action of dioxygen on calcium:
Dioxygen reacts with calcium at room temperature to form calcium oxide.

$2Ca_{(s)} + O2 \rightarrow 2CaO$

Calcium Calcium oxide

Question 3.1.ii: What is the action of dioxygen on Iron

Solution: Action of dioxygen on iron:
Dioxygen combines with iron on heating to form ferric oxide.
$4Fe + 3O_2 \rightarrow 2Fe_2O_3$
Iron Ferric oxide

Question 3.1.iii: What is the action of dioxygen on Carbon disulfide

Solution: Action of dioxygen on carbon disulfide:

Combustion of carbon disulfide in presence of air (dioxygen) gives carbon dioxide and sulfur dioxide.

$CS_2 + 3O_2 \rightarrow CO_2 + 2SO_2$
Carbon Carbon Sulphur
disulphide dioxide dioxide

Question 3.2: A solution of glucose in water is labelled as 10% (W/W). **[3]**

Calculate:
a. Molality
b. Molarity of the solution.
[Given: Density of solution is 1.20 g mL^{-1} and molar mass of glucose is 180 g mol^{-1}]

Solution: Given: Glucose solution is 10% W/W, Density of solution = 1.20 g mL^{-1}

To find: a. Molality b. Molarity

$$1.\ \text{Molality} = \frac{\text{Number of moles of solute}}{\text{Mass of solvent in kg}}$$

$$2.\ \text{Molarity} = \frac{\text{Number of moles of solute}}{\text{Volumeof solution in L}}$$

Calculation: 10 % W/W of glucose solution means 100 g of solution contains 10 g of glucose.

Mass of glucose = 10 g
Mass of solution = 100 g
Mass of H2O = 100 – 10 = 90 g = 0.090 kg
Molar mass of glucose = 180 g mol^{-1}

$$\text{Number of moles of glucose} = \frac{\text{Massof glucose}}{\text{Molar massof glucose}}$$

$$= \frac{10g}{180gmol^{-1}} = 0.0556mol$$

From formula (1),

$$\text{Molality of glucose solution} \quad = \frac{\text{Number of molesof glucose}}{\text{Massof H2Oin kg}}$$

= 0.0556 mol/0.090 kg

= 0.618 m

$$b.\ \text{Density of solution} = \frac{\text{Massof solution}}{\text{Volumeof solution}}$$

Volume of solution = 100g/1.20g mL^{-1} = 83.33 mL = 0.08333 L

$$\text{Molarity of glucose solution} \quad = \frac{\text{Number of molesof glucose}}{\text{Volume of solution in L}}$$

= 0.0556 mol/0.08333 L
= 0.67 M

Question 3.3: Resistance of conductivity cell filled with 0.1 M KCl solution is 100 ohms. If the resistance of the same cell when filled with 0.02 M KCl solution is 520 ohms, calculate the conductivity and molar conductivity of 0.02 M KCl solution. [Given: Conductivity of 0.1 M KCl solution is 1.29 S m^{-1}.] **[3]**

Solution:

Given: For 0.1 M KCl, k = 1.29 S m^{-1} = 0.0129 S cm^{-1}, R = 100 ohms or 0.02 M KCl, R = 520 ohms

To find: Conductivity and molar conductivity of 0.02 M KCl solution.

Formulae: a. Cell constant, b = k x R

b. Conductivity, $k_{(KCl,\ 0.02\ M)}$ = Cell constant /Resistance

c. Molar conductivity = 1000 k/C

Calculation: From formula (a),
b = k x R
= 0.0129 x 100 = 1.29 cm^{-1}

From formula (b),
Conductivity, $k_{(KCl,\ 0.02\ M)}$ = Cell constant/Resistance

= 1.29/520
= 2.48 x 10^{-3} ohm^{-1} cm^{-1}

From formula (c),
Molar conductivity of 0.02 M KCl solution = 1000k/C

=(1000 x 2.48 x 10^{-3})/0.02

=124 ohm^{-1} cm^2 mol^{-1}

Question 3.4: Ammonia and oxygen react at high temperature as: **[3]**

$4NH_{3(g)} + 5O_{2(g)} \rightarrow 4NO_{(g)} + 6H_2O_{(g)}$ In an experiment, rate of formation of $NO_{(g)}$ is 3.6 x 10^{-3} mol L^{-1} s^{-1}.
Calculate:
a. Rate of disappearance of ammonia.
b. Rate of formation of water.

Solution:

Rate of formation of NO(g) = d[NO]/dt= 3.6 x 10^{-3} mol L^{-1} s^{-1}

Rate of reaction $= \frac{1}{4}\frac{d[NH_3]}{dt} = -\frac{1}{5}\frac{d[O_2]}{dt} = +\frac{1}{4}\frac{d[NO]}{dt} = +\frac{1}{6}\frac{d[H_2O]}{dt}$

$$\frac{1}{4}\frac{d[NO]}{dt} = \frac{1}{4} \times 3.6 \times 10^{-3} = 9.0 \times 10^{-4} molL^{-1}s^{-1}$$

a. Rate of disappearance of $NH_3 = -\frac{d[NH_3]}{dt}$

$$-\frac{1}{4}\frac{d[NH_3]}{dt} = \frac{1}{4}\frac{d[NO]}{dt} = 9.0 \times 10^{-4} molL^{-1}s^{-1}$$

$$-\frac{d[NH_3]}{dt} = 3.6 \times 10^{-3} molL^{-1}s^{-1}$$

Rate of formation of $H_2O = \frac{d[H_2O]}{dt}$

$$\frac{1}{6}\frac{d[H_2O]}{dt} = \frac{1}{4}\frac{d[NO]}{dt} = 9.0 \times 10^{-4} molL^{-1}s^{-1}$$

$$\frac{d[H_2O]}{dt} = 5.4 \times 10^{-3} molL^{-1}s^{-1}$$

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

Question 4.1.i: What is the effect of temperature on solubility of a gas in a liquid? [7]

Solution: Effect of temperature on solubility of a gas in a liquid:
1. According to Charles' law, volume of a given mass of a gas increases with increase in temperature.

2. Therefore, volume of a given mass of dissolved gas in solution also increases with increase in temperature, so that it becomes impossible for the solvent in solution to accommodate gaseous solute in it and gas bubbles out. Hence, solubility of gas in liquid decreases with increase in temperature.

Question 4.1.ii:

Explain refining of nickel by Mond process.

Solution: Mond process for refining nickel:
1. In this process, nickel is heated in a stream of carbon monoxide forming a volatile complex, nickel tetracarbonyl.

$$\underset{\text{(Impure)}}{Ni} + 4CO \xrightarrow{330-350K} \underset{\substack{\text{Nickel tetracarbonyl} \\ \text{(Volatile)}}}{Ni(CO)_4}$$

2. The nickel carbonyl complex is subjected to higher temperature so that it is decomposed giving the pure metal.

$$\underset{\text{Nickel tetracarbonyl complex}}{Ni(CO)_4} \xrightarrow{450-470K} \underset{\text{(Pure)}}{Ni} + 4CO$$

Question 4.1.iii:

State Kohlrausch’s law of independent migration of ions.

Solution: Kohlrausch law states that, “at infinite dilution, each ion migrates independently of its co-ion and makes its own contribution to the total molar conductivity of an electrolyte irrespective of the nature of other ion with which it is associated.”

Question 4.1.iv:

Silver crystallises in F.C.C. (face-centred cubic crystal) structure. The edge length of the unit cell is found to be 408.7 pm. Calculate density of the unit cell.
[Given: Molar mass of silver is 108 g mol^{-1}]

Solution: Given: Edge length (a) = 408.7 pm = 408.7 x 10^{-12} m = 408.7 x10^{-10} cm,
Molar mass/Atomic mass of silver = 108 g mol^{-1}
To find: Density (d)

Formulae:

$$1.\ \text{Mass of one atom} = \frac{\text{Atomic mass}}{\text{Avogardo Number}}$$

$$2.\ Volumeofunitcell = a^3$$

$$3.\ \text{Density} = \frac{\text{mass of unit cell}}{\text{Volume of unit cell}}$$

Calculation: For fcc lattice, number of atoms per unit cell is 4.

Mass of one atom of silver= $\frac{\text{Atomic mass}}{\text{Avogadro number}}$

$$= \frac{108}{6.023 \times 10^{23}} = 17.9 \times 10^{-23} g$$

Mass of unit cell = 4 x 17.9 x 10^{-23} = 71.7 x 10^{-23} g

Volume of unit cell = a^3 = (408.7 x 10^{-10} cm)^3 = 6.827 x10^{-23} cm^3

$$\text{Density} = \frac{\text{mass of unit cell}}{\text{Volume of unit cell}}$$

$$= \frac{71.7 \times 10^{-23} g}{6.827 \times 10^{-23} cm^3} = 10.5g$$

Question 4.2.i: Write ‘four’ uses of hydrochloric acid. [7]

Solution: Uses of hydrogen chloride: Hydrogen chloride is used,
1. in the manufacture of chlorine and chlorides such as ammonium chloride.
2. for extracting glue from bones. It is also used for purifying bone black.
3. in medicine and as a laboratory reagent.
4. in dyeing, calico printing and tanning industries.
5. in pickling (cleaning metallic surfaces) before tinning, galvanising and electroplating.
6. in the manufacture of glucose by the hydrolysis of corn starch.
7. in the preparation of aqua regia which is used to dissolve noble metals like gold.
8. for the laboratory preparation of H2 gas by reaction with metals.
$Zn + 2HCl \rightarrow ZnCl_2 + H_2$

Question 4.2.ii:

Write chemical formula of the following oxoacids of chlorine:
a. Hypochlorous acid
b. Chlorous acid
c. Chloric acid
d. Perchloric acid

Solution:

Oxoacid of chlorine	Chemical formula
Hypochlorous acid	HOCl or HClO
Chlorous acid	HOClO or $HClO_2$
Chloric acid	$HOClO_2$ or $HClO_3$
Perchloric acid	$HOClO_3$ or $HClO_4$

Question 4.2.iii:

The equilibrium constant Kp for the reaction,
$H_{2(g)} + I_{2(g)} \rightarrow 2HI_{(g)}$ is 130 at 510 K. Calculate ΔG° for the following reaction at the same temperature: $2HI_{(g)} \rightarrow H_{2(g)} + I_{2(g)}$ [Given: R = 8.314 J K^{-1} mol^{-1}]

Solution: Given: $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$; Kp = 130, T = 510 K, R = 8.314 J K^{-1} mol^{-1}

To find: ΔG° for reaction, $2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$

Formula: $\Delta G^o = -2.303\ RT \log_{10}K_p$

Calculation:

$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$; Kp = 130,

$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$; Kp = 1/130

$\Delta G^o = -\ 2.303\ RT \log_{10}K_p$

$= -2.303 \times 8.314 \times 510 \times \log_{10} (1/130)$

= 20642.7 J mol^{-1}
=20.64 kJ mol^{-1}

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

Question 5.1: Which among the following reducing agents is NOT used to reduce acetaldehyde to ethyl alcohol? [1]

(A) Na-Hg and water
(B) Zn-Hg and conc. HCl
(C) H2-Raney Ni
(D) LiAlH4/H+

Solution: (B) Zn-Hg and conc. HCl

Question 5.2: Acetaldehyde, when treated with which among the following reagents does NOT undergo addition reaction? [1]

(A) Ammonia

(B) Hydroxylamine
(C) Ammoniacal silver nitrate
(D) Semicarbazide

Solution: (C) Ammoniacal silver nitrate

Question 5.3: What is natural rubber? [1]

(A) Cis-1,4-polyisoprene
(B) Neoprene
(C) Trans-1,4-polyisoprene
(D) Butyl rubber

Solution: (A) Cis-1,4-polyisoprene

Question 5.4: What is salvarsan? [1]

(A) An antiseptic
(B) An antibiotic
(C) An antifertility drug
(D) An analgesic

Solution: (B) An antibiotic

Question 5.5: Which among the following vitamins is also known as riboflavin? [1]

(A) B1
(B) B2
(C) B6
(D) B12

Solution: (B) B2

Question 5.6: The amine which reacts with nitrous acid to give yellow oily compound is _______. [1]

(A) ethylamine
(B) isopropylamine
(C) secondary butylamine
(D) dimethylamine

Solution: (D) dimethylamine

Question 5.7: What is the molecular formula of chromyl chloride? [1]

(A) CrO_2Cl_2
(B) $CrOCl_2$
(C) $CrCl_3$

(D) Cr_2OCl_2

Solution: (A) CrO_2Cl_2

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

Question 6.1: [2]

Identify 'A' and 'B' in the following reaction :

$$CH_3-CH=CH_2 \xrightarrow{HBr} 'A' \xrightarrow{alc \cdot KOH} 'B'$$

Solution:

$$\underset{\text{Propene}}{CH_3-CH=CH_2} \xrightarrow{HBr} \underset{\text{Isopropyl bromide (A)}}{CH_3-\underset{\underset{Br}{|}}{CH}-CH_3} \xrightarrow{alc \cdot KOH} \underset{\text{Propene(B)}}{CH_3-CH=CH_3}$$

Question 6.2: Distinguish between lanthanoid and actinoids. [2]

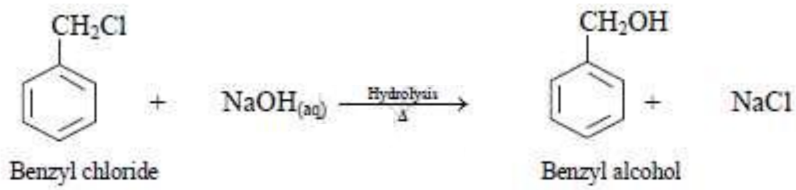
Solution:

Lanthanoids	Actinoids
Differentiating electron enters 4f orbitals	Differentiating electron enters 5f orbitals
Belong to the sixth period and form part of the third transition series. They constitute the first inner transition series.	Belong to the seventh period and form part of the fourth transition series. They constitute the second inner transition series.
Binding energy of 4f orbitals is higher.	Binding energy of 5f orbitals is lower.
Besides the +3 oxidation state, lanthanoids show +2 and + 4 oxidation states in few cases.	Besides the +3 oxidation state, actinoids show higher oxidation states such as +4, +5 and +7.
They show lesser tendency to form complexes.	They show greater tendency to form complexes.
Some of the lanthanoids are fairly coloured.	Most of the ions of actinoids are deeply coloured. Examples: U3+ (red), U4+ (green)
Only promethium is radioactive.	All the members of this series are radioactive.

Question 6.3.i: How are the following compounds prepared? [2]

Benzyl alcohol from benzyl chloride.

Solution: Benzyl alcohol from benzyl chloride:



Question 6.3.ii:

How are the following compounds prepared?
Propan-1-ol from propanal

Solution:

Propan-1-ol from propanal:

$CH_3 - CH_2 - C = O + H_2 \xrightarrow[\Delta]{} CH_3 - CH_2 - CH_2 - OH$

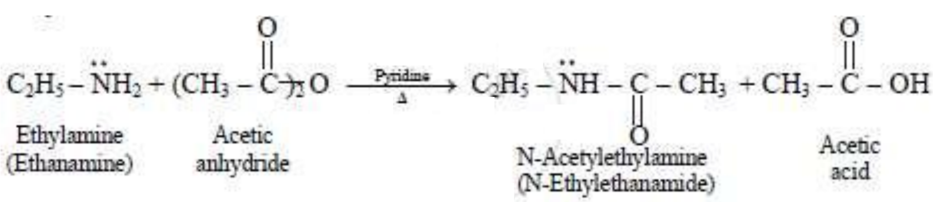
| Propan-1-ol

H

Propanal

Question 6.4.i: What is the action of acetic anhydride on ethylamine? **[2]**

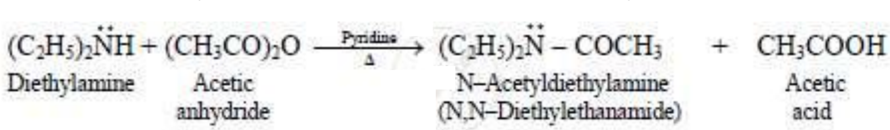
Solution: a. Ethylamine reacts with acetic anhydride to give N-acetylethylamine.



Question 6.4.ii:

What is the action of acetic anhydride on diethylamine?

Solution: Diethylamine reacts with acetic anhydride to give monoacetyl derivative



Question 6.5.i: What are monosaccharides? **[2]**

Solution 1: Monosaccharides: A carbohydrate that cannot be hydrolysed further to give simpler units of polyhydroxy aldehyde or polyhydroxy ketone is called a

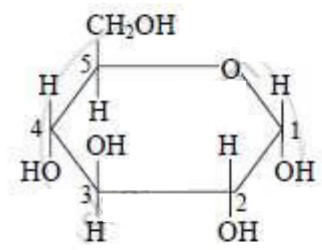
monosaccharide.
eg. Glucose, fructose, ribose, etc.

Solution 2: Monosaccharides are carbohydrates that cannot be hydrolysed further to give simpler units of polyhydroxy aldehyde or ketone.

Monosaccharides are classified on the bases of number of carbon atoms and the functional group present in them. Monosaccharides containing an aldehyde group are known as aldoses and those containing a keto group are known as ketoses. Monosaccharides are further classified as trioses, tetroses, pentoses, hexoses, and heptoses according to the number of carbon atoms they contain. For example, a ketose containing 3 carbon atoms is called ketotriose and an aldose containing 3 carbon atoms is called aldotriose.

Question 6.5.ii: Draw ring structure of α - D - (+) - glucopyranose.

Solution: Ring ring structure of α-D-(+)-glucopyranose:



α-D-(+)-Glucopyranose (trans)

Question 6.6.i:

Explain Tranquilizers

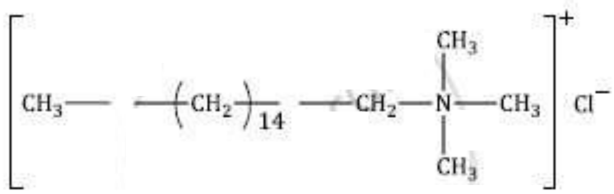
Solution 1: Tranquilizers:
The chemical substances used to relieve or reduce the stress and anxiety leading to calmness are called tranquilizers. They affect the mechanism for the transfer of message from nerve to receptors.
eg. Equanil, Valium, Chlordiazepoxide, Meprobamate, Veronal, Serotonin, etc. are mild tranquilizers.

Solution 2: Tranquilizers: The drugs which are useful for the treatment of mental stress, mild or acute mental disorders are known as tranquilizers. These are neurologically active drugs.
Example: Chlordiazepoxide.

Question 6.6.ii:

Explain cationic detergents.

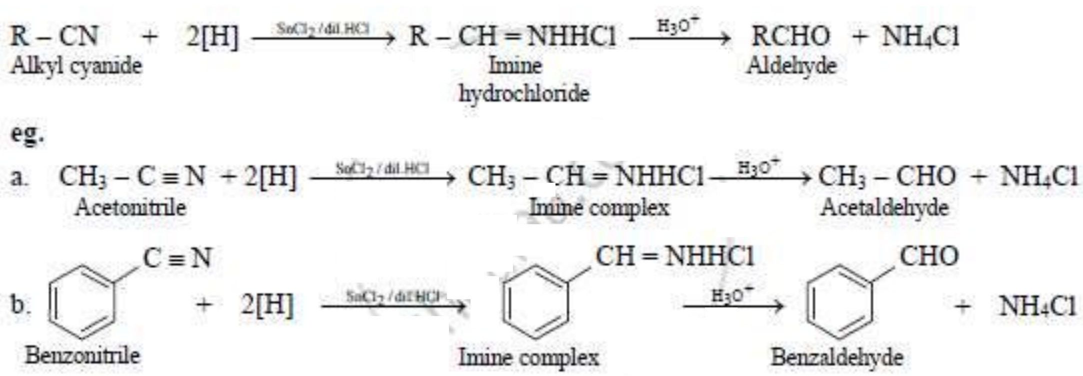
Solution: Cationic detergents:- Cationic detergents are quaternary ammonium salts of amines with chlorides, acetates or bromides. They have cations at the soluble ends of the chain. Anions are chlorides, acetates or bromides, and cations are long chain hydrocarbons with a positive charge on the nitrogen 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.



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

Question 6.7: What is Stephen reaction? **[2]**

Solution: Alkyl nitriles on reduction with stannous chloride and hydrochloric acid in dry ether give corresponding imine hydrochlorides which on acid hydrolysis, give corresponding aldehydes. This reaction is known as Stephen reaction. Ketones cannot be prepared by Stephen reaction.

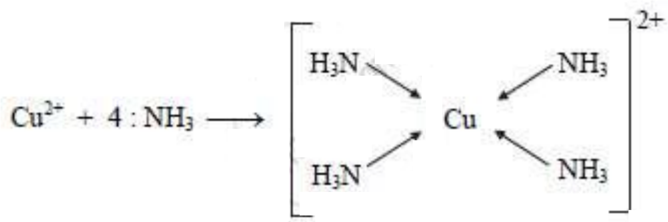


(Any one example)

Question 6.8: Explain Sidgwick's electronic theory with suitable example **[2]**

Solution: The Sidgwick's electronic theory explains the formation of coordination compounds. According to this theory, coordinate bonds are formed when the ligands donate the electron pairs to the central metal ion.

a. Four ammonia molecules donate four electron pairs to Cu^{2+} ion to form the complex cup ammonium ion, $[Cu(NH_3)_4]^{2+}$.



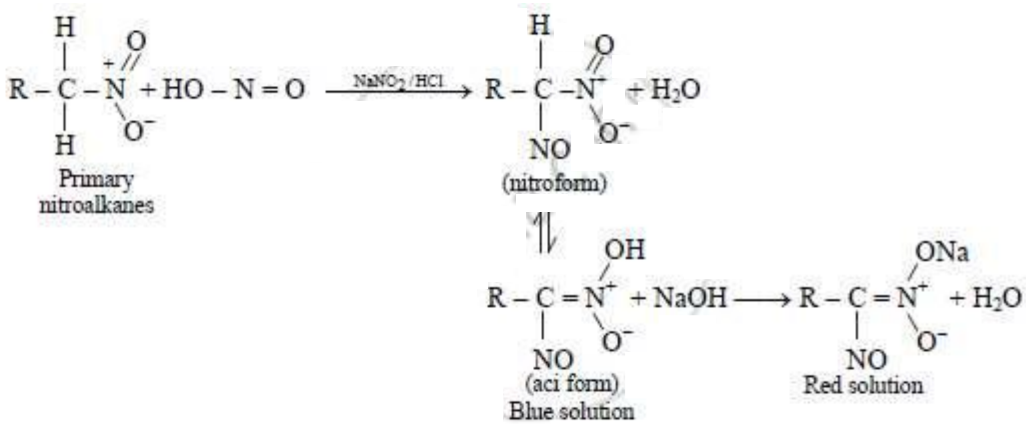
b. Six CN^- ligands donate six electron pairs to Fe^{2+} and Fe^{3+} ion to form the complex ion ferrocyanide, $[Fe(CN)_6]^{4-}$ and ferricyanide, [Fe(CN)6

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

Question 7.1.i: What is the action of nitrous acid on primary nitroalkane? [3]

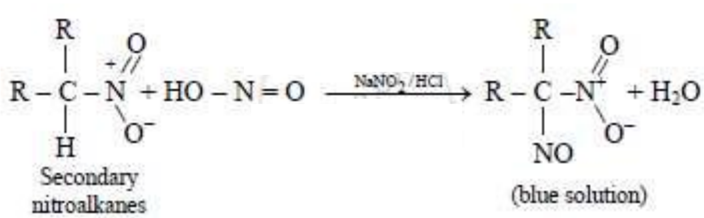
Solution: Reaction with nitrous acid: The reaction is used to distinguish between primary, secondary or tertiary nitroalkanes. With nitrous acid, α-hydrogen is replaced by nitroso group.

a. Primary nitroalkanes react with nitrous acid to form blue coloured nitroso-nitroalkanes (aci form) which on dissolution in sodium hydroxide gives red solution.



Question 7.1.ii: What is the action of nitrous acid on secondary nitroalkane?

Solution: Secondary nitroalkanes react with nitrous acid to form corresponding blue coloured nitroso-nitroalkanes, which are insoluble in sodium hydroxide as they no more contain replaceable α-hydrogen atom.



Question 7.1.iii:

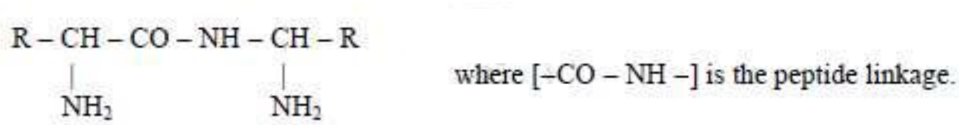
What is the action of nitrous acid on tertiary nitroalkane

Solution: Tertiary nitroalkanes do not react with nitrous acid because there is no replaceable α-hydrogen atom on the carbon atom carrying the - NO2 group.

Question 7.2.i: What is peptide linkage? **[3]**

Solution: A peptide linkage (a peptide bond) is the amide linkage (-CONH-), which is formed between the two amino acid molecules.

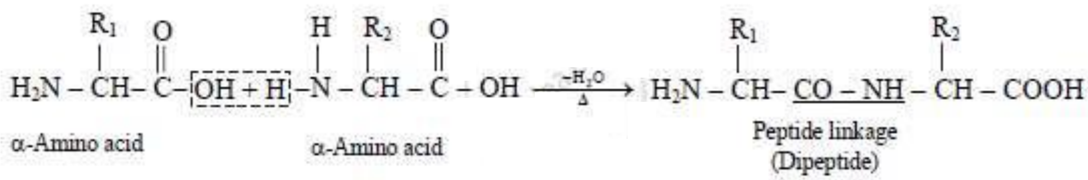
The general formula of a peptide bond can be written as follows:



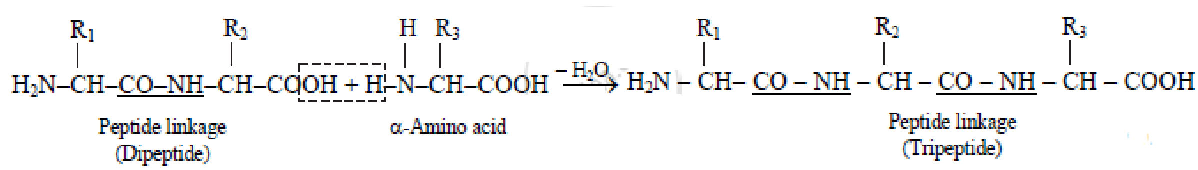
Question 7.2.ii:

How is tripeptide formed?

Solution: b. The reaction of the COOH group of one amino acid molecule and NH2 group of the neighbouring amino acid molecule forms peptide having -CO-NH- linkage by elimination of water



The dipeptide formed reacts with another molecule of amino acid to form tripeptide

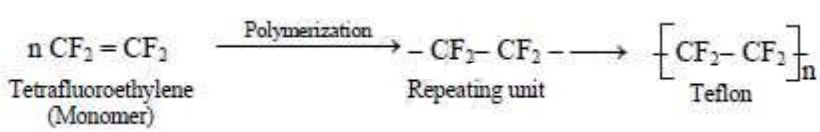


Question 7.3.i: Write the reactions involved in the preparation of Teflon **[3]**

Solution: Preparation of teflon:

Teflon is the addition polymer made from the monomer tetrafluoroethylene. Tetrafluoroethylene is heated under high pressure in presence of oxygen (which acts as a catalyst) to form Teflon.

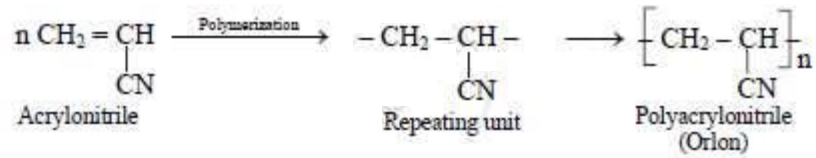
Teflon:



Question 7.3.ii:

Write the reactions involved in the preparation of Orlon

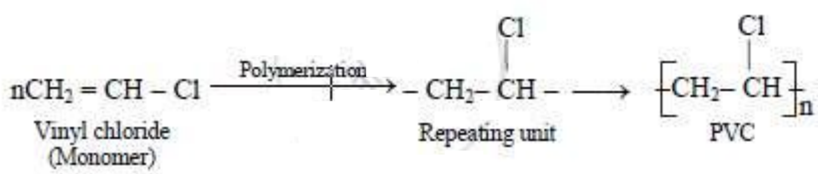
Solution: Orlon :



Question 7.3.iii:

Write the reactions involved in the preparation of PVC

Solution: PVC :



Question 7.4.i: What is the position of iron (Z = 26) in periodic table? **[3]**

Solution: Iron (Fe) is placed in the 4th period and group 8 of the modern periodic table.

Question 7.4.ii:

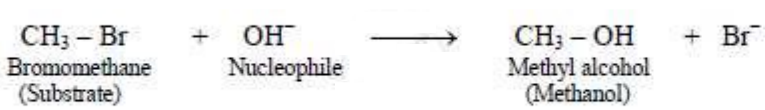
Explain why is Fe3+ more stable than Fe2+?

Solution: Electronic configuration of Fe^{2+} : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$
Electronic configuration of Fe^{3+} : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$
Due to the presence of half filled 'd' orbital, Fe^{3+} is more stable than $Fe^{2+.}$

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

Question 8.i: Discuss the mechanism of alkaline hydrolysis of bromomethane. **[7]**

Solution: a. Alkaline hydrolysis of bromomethane follows bimolecular nucleophilic substitution (SN2)mechanism. The hydrolysis reaction can be written as follows:

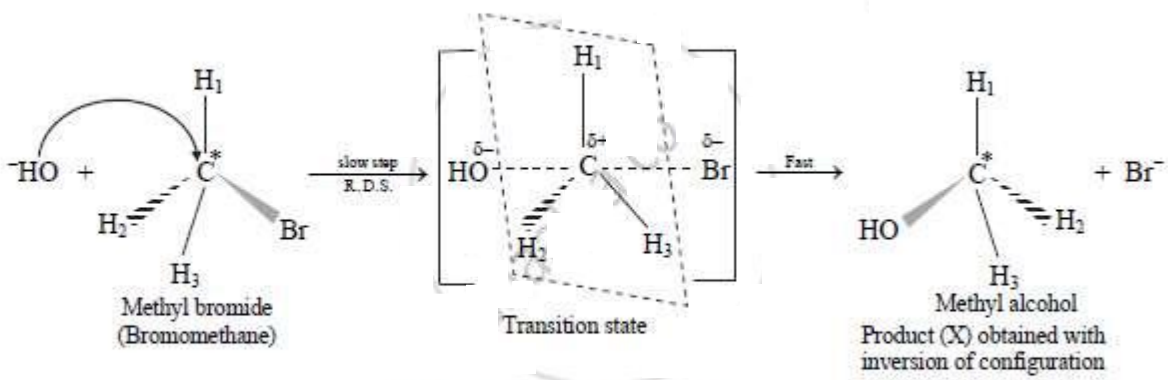


1. Approach of the nucleophile (Backside attack):
i. The nucleophile ($OH^{-)}$ slowly approaches the carbon atom from the opposite side

of the C - Br bond.
ii. C – OH weak bond is formed, while the existing C – Br bond gradually weakens.
iii. It is a slow process and hence, it is the rate determining step (R.D.S.).

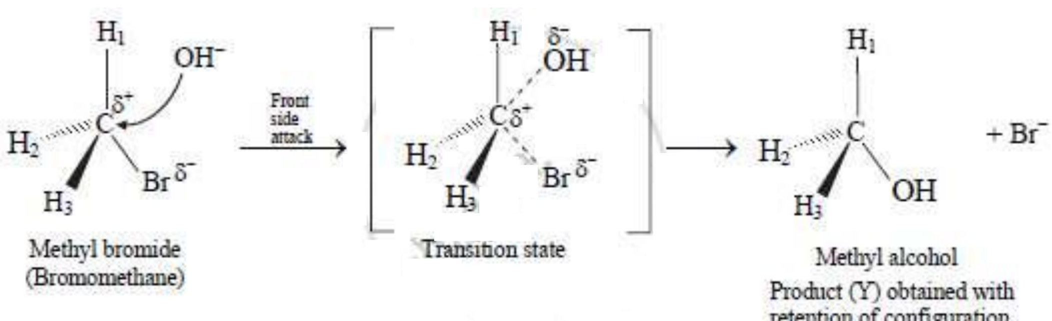
2. Transition state (Activated complex): With the approach of OH^- group and the gradual departure of Br–, a stage comes where the central atom is attached to five substituents. This state is known as transition state of reaction.
At this stage, the three hydrogen atoms lie in a plane perpendicular to the HO – C – Br axis.

3. Stereochemistry of SN2 reaction:
The attack might take place from back as well as from front side.
i. If backside attack takes place:
As shown in the figure given below, the OH– group occupies a position in the product which is opposite to the position of Br–. Similarly the positions of H2 and H3 in the reactant and in the product are on opposite sides i.e., inverted due to the back side attack. This is known as inversion of configuration. Thus, backside attack of nucleophile leads to inversion of configuration.



Backside attack of nucleophile

ii. If front side attack takes place: In this situation, the OH^- occupies the same position which was occupied by Br– in the reactant and the position of H1, H2 and H3 also remain the same. Therefore, the configuration of the carbon is retained. This is known as retention of configuration.



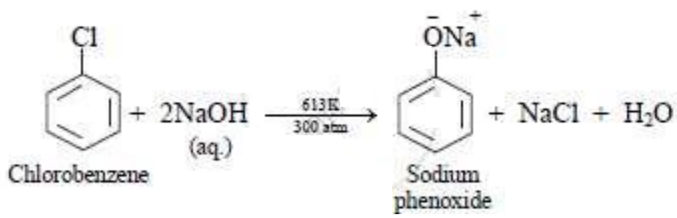
Front side attack of nucleophile

The product X is obtained with inversion of configuration and not Y, with retention of configuration (X and Y are enantiomers). Thus, in SN2 reaction, the nucleophile attacks from back side leading to the inversion of configuration.

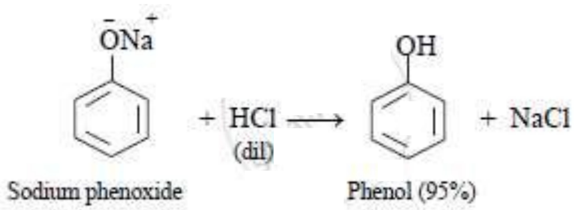
Question 8.ii:

How is carbolic acid prepared from chlorobenzene?

Solution: 1. Dow's process:
i. When chlorobenzene is heated with excess of aqueous sodium hydroxide (NaOH) at 613 K under a pressure of 300 atmosphere, sodium phenoxide is formed.

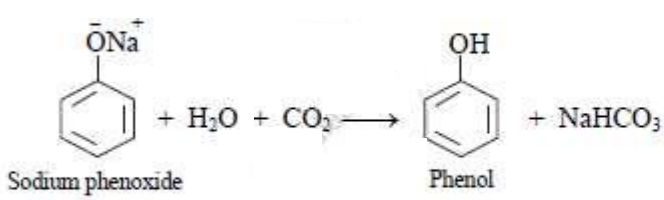


ii. Sodium phenoxide when hydrolysed using dilute hydrochloric acid (HCl), phenol is obtained.

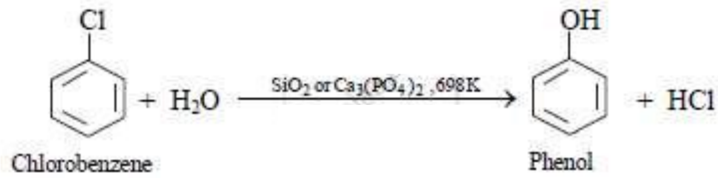


OR

Phenol can also be obtained by passing CO2 (carbon dioxide) gas, through aqueous solution of sodium phenoxide.



2. Raschig process (Industrial method):
i. When chlorobenzene is treated with steam (H2O) at 698 K in the presence of $Ca_3(PO_4)_2$ or SiO_2 as a catalyst, phenol is obtained.

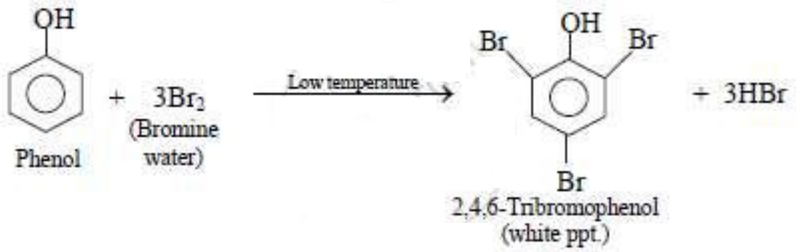


ii. The hydrolysis can also be carried out by using water in the presence of copper catalyst at 673 K and under pressure.

Question 8.iii:

What is the action of bromine water on carbolic acid?

Solution: Action of bromine water on carbolic acid (phenol): Phenol when treated with bromine water at low temperature forms 2,4,6-tribromophenol.



Question 8.iv:

Write chemical test to distinguish between carbolic acid and alcohol.

Solution: Action of neutral ferric chloride ($FeCl_3$) is a distinguishing test (colour test) between phenol and an alcohol.
1. Action on phenol: When phenol is treated with aqueous neutral $FeCl_3$, it gives red to violet colouration. The colour obtained is due to the formation of violet coloured ferric phenoxide complex.

$$\underset{\text{Phenol}}{3C_6H_5OH} + \underset{\text{(aq./neutral)}}{FeCl_3} \longrightarrow \underset{\substack{\text{Ferric phenoxide}\\\text{(Violet colour)}}}{Fe(C_6H_5O)_3} + 3HCl$$

2. Action on alcohol: When an alcohol (eg. ethanol) is treated with aqueous neutral $FeCl_3$, it does not give any colouration.
Ethanol + aq./neutral $FeCl_3$ → No colouration

Question 8.2.i: Explain cationic complexes and anionic complexes of co-ordination compounds. **[7]**

Solution: 1. Cationic complexes: A complex in which the complex ion carries a net positive charge is called a cationic complex.

eg. $[Fe(H_2O)_6]Cl_3$, $[Co(NH_3)_6]Cl_3$, $[Ni(NH_3)_6]Cl_2$ are cationic complexes. This can be seen from the following reactions:

$[Co(NH_3)_6]Cl_3 \rightleftharpoons [Co(NH_3)_6]^{3+} + 3Cl^-$

$[Fe(H_2O)_6]Cl_3 \rightleftharpoons [Fe(H_2O)_6]^{3+} + 3Cl^-$

$[Ni(NH_3)_6]Cl_2 \rightleftharpoons [Ni(NH_3)6]^{2+} + 2Cl^-$

2. Anionic complexes: The complexes in which the complex ion carries a net negative charge are called anionic complexes.
eg. $K_4[Fe(CN)_6]$, $K[Ag(CN)_2]$, $K_2[HgI_4]$ are anionic complex ions as indicated in the following reactions:

$K_4[Fe(CN)_6] \rightleftharpoons 4K^+ + [Fe(CN)_6]^{4-}$

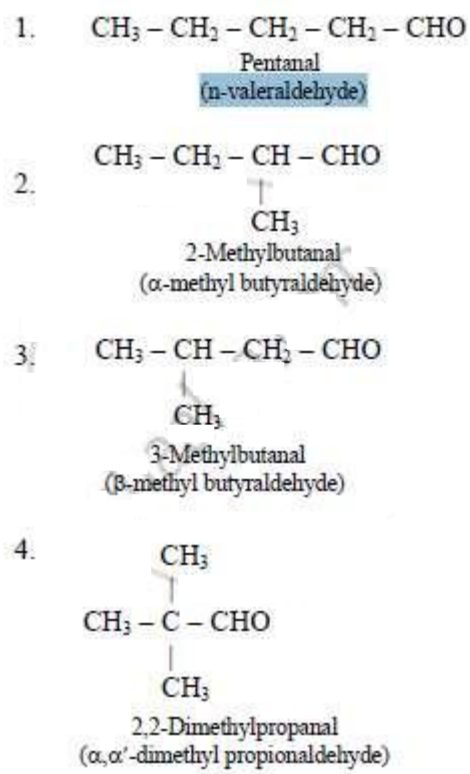
$K[Ag(CN)_2] \rightleftharpoons K^+ + [Ag(CN)_2]^{1-}$

$K_2[HgI_4] \rightleftharpoons 2K^+ + [HgI_4]^{2-}$

Question 8.2.ii:

Write the structure and IUPAC names of isomeric aldehydes having molecular formula $C_5H_{10}O$.

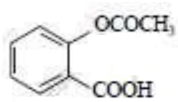
Solution: There are four isomeric aldehydes having molecular formula $C_5H_{10}O$.



Question 8.2.iii:

Draw the structure of aspirin.

Solution: The structural formula of aspirin is :



Aspirin
(O-Acetyl salicylic acid)