Chemistry

Academic Year: 2017-2018 Marks: 70
Date & Time: 28th February 2018, 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: The process in which the value of ΔU = 0 is __ **[1]**

Adiabatic
Isothermal
Isobaric
Isochoric

Solution: Isothermal

Question 1.2: An ionic crystal lattice has r^+/r radius ratio of 0.320, its coordination number is __ **[1]**

(a) 3
(b) 4
(c) 6
(d) 8

Solution: An ionic crystal lattice has r^+/r radius ratio of 0.320, its coordination number is **4.**

Question 1.3: In the hydrogen-oxygen fuel cell, the carbon rods are immersed in the hot aqueous solution of __ **[1]**

(a) KCl
(b) KOH
(c) H_2SO_4
(d) NH_4Cl

Solution: In the hydrogen-oxygen fuel cell, the carbon rods are immersed in the hot aqueous solution of **KOH**

Question 1.4: The chemical formula of willemite is __ **[1]**

(a) ZnS
(b) $ZnCO_3$
(c) ZnO
(d) Zn_2SiO_4

Solution: The chemical formula of willemite is **Zn_2SiO_4**

Question 1.5: The oxidation state of nitrogen in dinitrogen trioxide is ____ **[1]**

(a) + 1
(b) + 2
(c) + 3
(d) + 4

Solution: + 3

N_2O_3 Oxidation state for O= -2

The oxidation state of N = x

∴ 2x + 3(-2) = 0

∴ 2x - 6 = 0

∴ 2x = 6

$$\therefore \ x = \frac{6}{2} = 3$$

Question 1.6: Which of the following 0.1 M will aqueous solutions exert highest osmotic pressure? **[1]**

(a) $Al_2(SO_4)_3$
(b) Na_2SO_4
(c) $MgCl_2$
(d) KCl

Solution:

$Al_2(SO_4)_3$

$Al_2SO_4 \rightarrow 2Al^{3+} + 3SO_4^{2-}$ (5 particles)

$Na_2SO_4 \rightarrow 2Na^{+} + SO_4^{2-}$ (3 particles)

$MgCl_2 \rightarrow Mg^{2+} + 2Cl^{-}$ (2 particles)

$KCl \rightarrow K^{+}Cl^{-}$ (2 particles)

Question 1.7: The half-life period of zero order reaction A → product is given by **[1]**

(a) $\frac{[A]_0}{k}$

(b) $\frac{0.693}{k}$

(c) $\frac{[A]_0}{2k}$

(d) $\frac{2[A]_0}{k}$

Solution:

$\frac{[A]_0}{2k}$

Question 2: Attempt Any Six of Following **[12]**

Question 2.1: Derive the relation between the elevation of boiling point and molar mass of solute. **[2]**

Solution:

The elevation in the boiling point is given by the expression $\Delta T_b = K_b \cdot m$ .....(1)

The molality is given by the expression m = $\frac{W_2}{M_2 . W_1}$ ...(2)

Substitute equation (2) in equation (1)

$$\Delta T_b = K_b \cdot \frac{W_2}{M_2 \cdot W_1}$$

Hence, the expression for the molar mass of the solute is

$$M_2 = \frac{K_b \cdot W_2}{\Delta T_b . W_1}$$

Question 2.2: State Third law of thermodynamics. Give 'two' uses. **[2]**

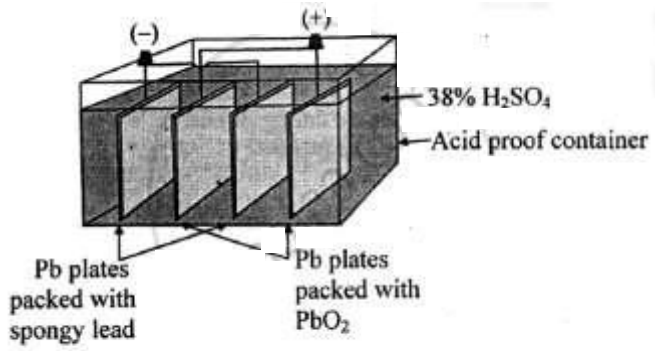
Solution: The third law of thermodynamics states that, "The entropy of a perfectly ordered crystalline substance is zero at absolute zero of temperature".

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: Draw a neat and labelled diagram of the lead storage battery. **[2]**

Solution:



Lead storage battery

Question 2.4: Explain Ionic solids are hard and brittle. **[2]**

Solution 1: The constituent particles of ionic crystals are ions. These ions are held together in three-dimensional arrangements by the electrostatic force of attraction. Since the electrostatic force of attraction is very strong, the charged ions are held in fixed positions. This is the reason why ionic crystals are hard and brittle.

Solution 2: Ionic solids are hard and brittle. Ionic solids are hard due to the presence of strong electrostatic forces of attraction. The brittleness in ionic crystals is due to the non- directional bonds in them.

Question 2.5: **[2]**

A certain reaction occurs in the following steps-

$Cl_g + O_3(g) \longrightarrow ClO(g) + O_2(g)$

$ClO_g + O(g) \longrightarrow Cl(g) + O_2(g)$

a) What is the molecularity of each of the elementary steps?

b) Identify the reaction intermediate and write the chemical equation for the overall reaction.

Solution:

a)

$$Cl_g + O_{3(g)} \rightarrow ClO_{(g)} + O_{2(g)}$$

Molacularity : Bimolecular

$$ClO_{(g)} + O_{(g)} \rightarrow Cl_{(g)} + O_{2(g)}$$

Molacularity : Bimolecular

b) Intermediate: ClO

$$Cl_g + O_{3(g)} \rightarrow ClO_{(g)} + O_{2(g)}$$

$$ClO_{(g)} + O_{(g)} \rightarrow Cl_{(g)} + O_{2(g)}$$

$$O_{3(g)} + O_{(g)} \rightarrow 2O_{2(g)}$$ Net reaction

Question 2.6: Define Semipermeable membrane **[2]**

Solution: Semipermeable membrane: It is a membrane which allows the solvent molecules, but not the solute molecules, to pass through it.

Question 2.7: What is the action of chlorine on CS_2 **[2]**

Solution: $CS_2 + 3Cl_2 \longrightarrow CCl_4 + S_2Cl_2$

Question 2.7: Answer the following. **[2]**

What is the action of chlorine on Excess NH_3.

Solution: Chlorine when reacted with excess of ammonia gives ammonium chloride and nitrogen.

$$\underset{\text{Ammonia (excess)}}{8\,NH_3} + \underset{\text{Chlorine}}{3\,Cl_2} \longrightarrow \underset{\text{Ammonium chloride}}{6\,NH_4Cl} + \underset{\text{Nitrogen}}{N_2}$$

Question 2.8: Write the chemical equations involved in van Arkel method for refining zirconium metal. **[2]**

Solution: This method is useful for removing impurities in the form of oxygen and nitrogen in metal like zirconium. The crude metal is heated in an evacuated vessel with iodine. The metal iodine volatilizes.

$$\underset{\text{Impure}}{Zr} + 2\,I_2 \longrightarrow \underset{\text{Vapour}}{ZrI_4}$$

The metal iodine is decomposed on tungsten filament, electrically heated to about 1800K. The pure metal is thus deposited on the filament

$$\underset{\text{Vapour}}{ZrI_4} \longrightarrow \underset{\text{Pure}}{Zr} + 2I_2$$

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

Question 3.1: Write balanced chemical equations for Phosphorus reacts with magnesium [3]

Solution: Balanced equations:

$6Mg + P_4 \longrightarrow 2Mg_3P_2$

Question 3.1: Write balanced chemical equations for Flowers of sulphur boiled with calcium hydroxide

Solution: $3Ca(OH)_2 + 12S \longrightarrow 2CaS_5 + CaS_2O_3 + 3H_2O$

Question 3.1: Write balanced chemical equations for Action of ozone on hydrogen peroxide.

Solution: Balanced equations:

$H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$

Question 3.2: The density of iron crystal is 8.54-gram cm−3. If the edge length of the unit cell is 2.8 A° and atomic mass is 56-gram mol−1, find the number of atoms in the unit cell. (Given: Avogadro's number = 6.022×10^{23}, 1A° = 1×10^{-8} cm) [3]

Solution:

Given a = 2.8Å = 2.8×10^{-8} cm

Molar Mass = 56 gm

Density = 8.54 g cm^{-3}

Volume = $(a)^3$

$= (2.8 \times 10^{-8})^3$

$= 21.95 \times 10^{-24} cm^3$

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

∴ Mass of unit cell = density x volume

$= 21.95 \times 10^{-24} \times 8.54$

$= 187.47 \times 10^{-24}$

56 gm of Fe contains 6.022 x 10^{23} atoms

187.47×10^{-24} gm Fe contain = $\frac{6.022 \times 10^{23} \times 187.47 \times 10^{-24}}{56}$

$= 20.15 \times 10^{-1}$

Question 3.3: How many faradays of electricity are required to produce 13 gram of aluminium from aluminium chloride solution? (Given: Molar mass of Al = 27.0-gram mol^{-1}) **[3]**

Solution: $AlCl_3 \longrightarrow Al^{+3} + 3Cl^-$

$Al^{+3} + 3e^- \longrightarrow Al$

1 mole of Al requires passage of 3 moles of electrons. The charge on 3 moles of e^- is 3 Faraday.

$$\text{Moles of Al produced} = \frac{\text{mass of Al}}{\text{molar mass of Al}}$$

= 13/27

= 0.48 moles

As 3F of electricity produces 1 mole of Al

∴ No. of faradays of electricity required to produce 0.48 mole of Al

= 0.48 x 3

= 1.44 Faraday

Question 3.4: Calculate the internal energy at 298K for the formation of one mole of ammonia, if the enthalpy change at constant pressure is – 42.0 kJ mol^{-1}. **[3]**

(Given: R = 8.314 J K^{-1} mol^{-1})

Solution: Formation of 1 mole of ammonia

$$\frac{1}{2}N_{2(g)} + \frac{3}{2}H_{2(g)} \rightarrow NH_{3(g)}$$

Δn = (no. of moles of gaseous product) - (no. of moles of gaseous reactant)

$$= 1 - \left(\frac{1}{2} + \frac{3}{2}\right)$$

= -1

ΔH = ΔU + PΔV

PΔV = -ΔnRT

$$= -(-1) \times 8.314 \times 298$$

= 2477 J

= 2.477 KJ

ΔH = -42.0 KJ

∴ -42.0 KJ = ΔU + 2.477

ΔU = -42 - 2.477

= -44.47 KJ

Question 4: Attempt Any One **[7]**

Question 4.1.i: Define the Enthalpy of atomization **[7]**

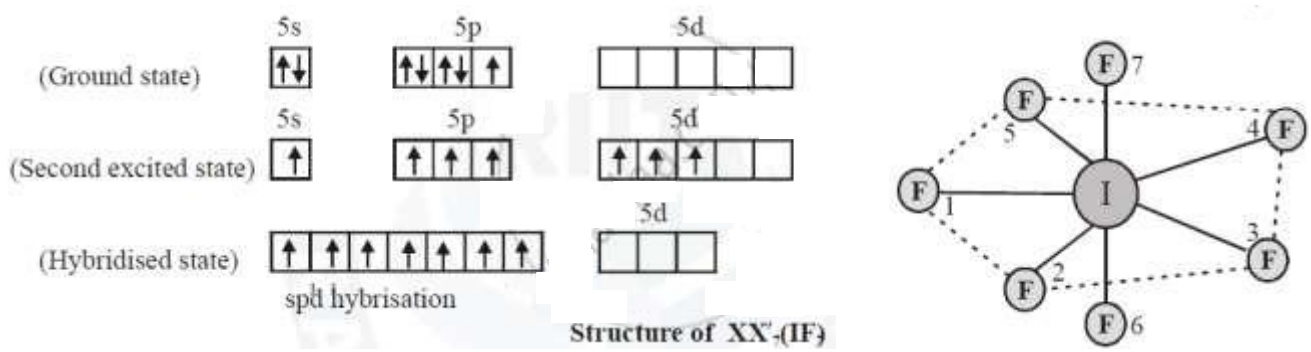
Solution: Enthalpy of atomization:-
The enthalpy change accompanying the dissociation of all the molecules in one mole of gas phase substance into gaseous atoms is called enthalpy of atomisation.

Question 4.1.ii: Define Enthalpy of vaporization

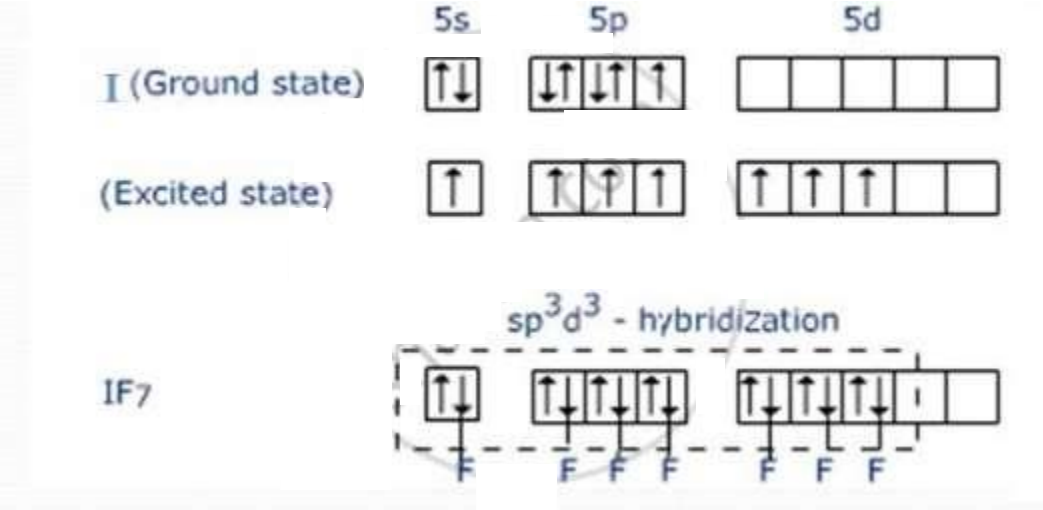
Solution: Enthalpy of vaporization ($\Delta_{vap}H$): The enthalpy change that accompanies the vaporization of one mole of liquid without changing its temperature at constant pressure is called enthalpy of vaporization.

Question 4.1.iii: Draw the structure of IF_7. Write its geometry and the type of hybridization.

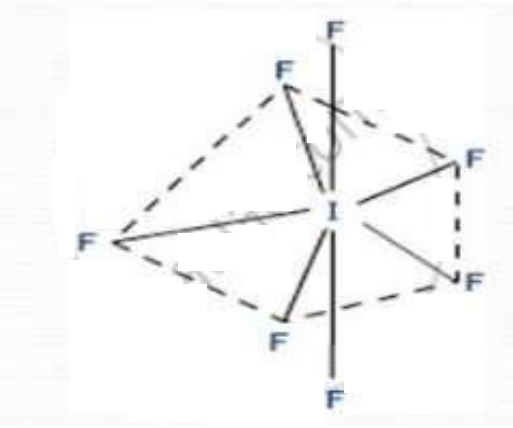
Solution 1: The only known interhalogen compound of the XX'_7 is IF_7. It is formed by sp^3d^3 hybridization of the central I atom its third excited state. The molecule has a pentagonal bipyramidal structure as shown in



Solution 2: IF_7 has seven bond pairs and zero lone pairs of electrons. The central iodine atom undergoes sp^3d^3 hybridisation which results in pentagonal bipyramidal geometry.



Formation of IF_7 molecule involving sp^3d^3 hybridization



Pentagonal bipyramidal geometry of IF_7 molecule

Question 4.1.iv: State Henry's law.

Solution 1: Henry's law: The mass of a gas dissolved in a given volume of the liquid at constant temperature is directly proportional to the pressure of the gas present in equilibrium with the liquid.

Solution 2: Henry's law relates solubility of a gas with external pressure. The law states that, "the solubility of a gas in liquid at constant temperature is proportional to the pressure of
the gas above the solution".

f S is the solubility of the gas in mol dm−3, then according to Henry's law,

$S \propto P$ i.e. $S = KP$

where, P is the pressure of the gas in atmosphere, K is constant of proportionality and has the unit of mol dm^{-3} atm^{-1}.

Question 4.1.v: 22.22 gram of urea was dissolved in 300 grams of water. Calculate the number of moles of urea and molality of the urea solution. (Given: a Molar mass of urea = 60 gram mol^{-1})

Solution:

$$\text{Moles of urea} = \frac{22.22}{60}$$

$$= 0.370 \text{ moles}$$

$$\text{Molality (m)} = \frac{\text{Moles of urea}}{\text{Mass of water}} \times 1000$$

$$= \frac{0.370 \times 1000}{300}$$

$$= 1.23 \text{ moles kg}^{-1}$$

Question 4.2.i: What is the action of carbon on the following metal oxides: **[7]**

Fe_2O_3 in the blast furnace

Solution: On reaction with carbon, ferric oxide gets reduced to iron with release of carbon monoxide gas.

$$Fe_2O_3 + 3\,C \xrightarrow{\Delta} 2\,Fe + 3\,CO\,(g)$$

Question 4.2.ii: What is the action of carbon on the following metal oxides :

ZnO in the vertical retort furnace

Solution:

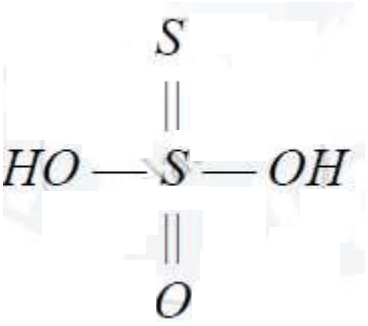
An action of Carbon on ZnO

$$ZnO + C \xrightarrow[1673k]{\Delta} Zn + CO_{(g)}$$

Question 4.2.iii:

Write the molecular and structural formulae of Thiosulphuric acid

Solution: Thiosulphuric acid ($H_2S_2O_3$)



Question 4.2.iv:

The reaction A + B → products is first order in each of the reactants
1) How does the rate of reaction change if the concentration of A is increased by factor 3?
2) What is the change in the rate of reaction if the concentration of A is halved and concentration of B is doubled?

Solution: 1) The reaction, A + B → products

Rate = K[A]'[B]'

If conc. of A is increased by factor 3 then rate also increases 3 times.

2) If conc. of A is halved and concentration of B is doubled then rate remains unchanged

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

Question 5.1: A polymer used in paints is **[1]**

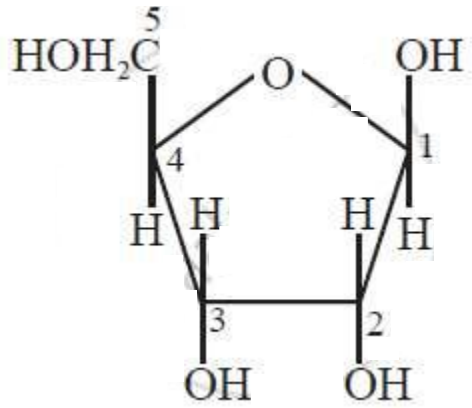
(a) Nomex
(b) Thiokol
(c) Saran
(d) Glyptal

Solution: A polymer used in paints is **Glyptal**

Question 5.2: The number of primary and secondary hydroxyl groups in ribose are - **[1]**

(a) 1, 3
(b) 2, 3
(c) 3, 1
(d) 3, 2

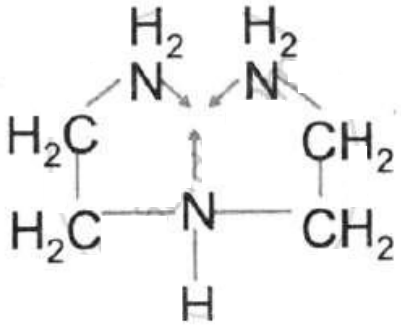
Solution: 1, 3



Question 5.3: The ligand diethylene triamine is - **[1]**

(a) monodentate
(b) bidentate
(c) tridentate
(d) tetradentate

Solution: tridentate



Question 5.4: Propene on oxidation with diborane in presence of alkaline hydrogen peroxide gives **[1]**

(a) propane-1- ol
(b) propane-2-ol
(c) allyl alcohol
(d) propane-1, 2-diol

Solution: propane-1-ol

$$6CH_3-CH=CH_2+B_2H_6\rightarrow 2(CH_3-CH_2-CH_2)_3B$$

Propene Tripropylborane

$$(CH_3-CH_2-CH_2)_3B+3H_2O_2\xrightarrow{OH^-}3CH_3-CH_2-CH_2-OH+B(OH)_3$$

Propane - 1 - ol

Question 5.5: Baeyer's reagent is -' **[1]**

(a) acidified potassium dichromate
(b) alkaline potassium dichromate
(c) alkaline potassium permanganate
(d) acidified potassium permanganate

Solution: alkaline potassium permanganate

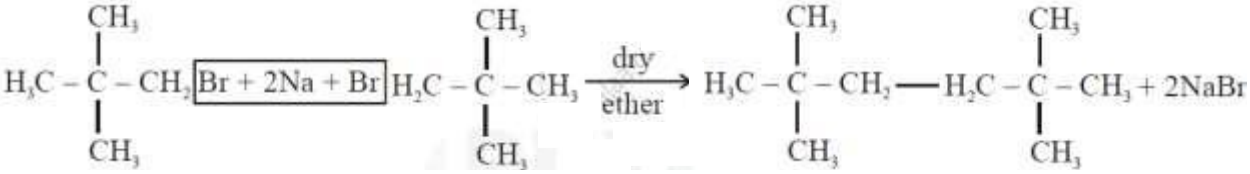
Cold and dilute alkaline $KMnO_4$

Question 5.6: Identify 'A' in the following reaction - **[1]**

$$A+2Na\xrightarrow[ether]{Dry}2,2,5,5-\text{Tetramethylhexane}+2NaBr$$

(a) 2- Bromo-2 methylbutane
(b) 1 -Bromo-2,2-dimethylpropane
(c) 1 - Bromo - 3 -methylbutane
(d) 1 - Bromo- 2 -methylpropane

Solution: 1 -Bromo-2,2-dimethylpropane



Question 5.7: An antifertility drug is - **[1]**

(a) Novestrol
(b) Histamine
(c) Vernal
(d) Equanil

Solution: Novestrol

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

Question 6.1: **[2]**

Write balanced chemical equations for the conversion of CrO_4^{2-} to $Cr_2O_7^{2-}$ in acidic medium and $Cr_2O_7^{2-}$ to CrO_4^{2-} in basic medium.

Solution:

$$K_2Cr_2O_7 + 2KOH \rightarrow 2K_2CrO_4 + H_2O$$

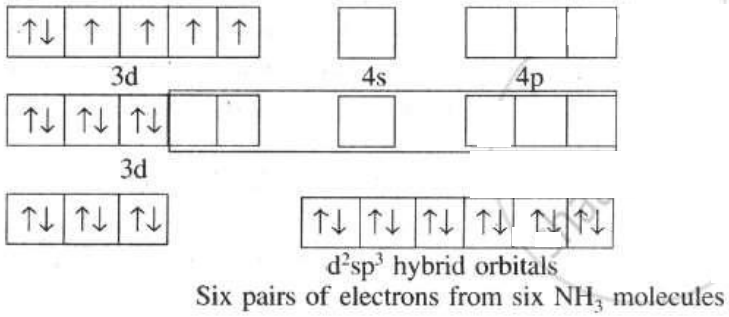
$$2K_2CrO_4 + 2HCl \rightarrow K_2Cr_2O_7 + 2KCl + H_2O$$

Question 6.2: **[2]**

Explain the geometry of $[Co(NH_3)_6]^{3+}$ on the basis of hybridisation. (Z of Co = 27)

Solution: Octahedral complex, $[Co(NH_3)_6]^{3+}$. In this complex ion, the oxidation state of cobalt is +3.

It has the electronic configuration as $3d^6$. This complex involves the d^2sp^3 hybridisation.



The six pairs of electrons, one from each NH3 molecule, occupy the six hybrid orbitals. It proves that complex has octahedral geometry. An absence of unpaired electron makes this complex diamagnetic in nature.

Question 6.3: Why ethanol has the higher boiling point than ethane? **[2]**

Solution: 1) Alcohol has higher boiling points than their corresponding alkanes due to the presence of intermolecular hydrogen bonding which is absent in the alkanes.

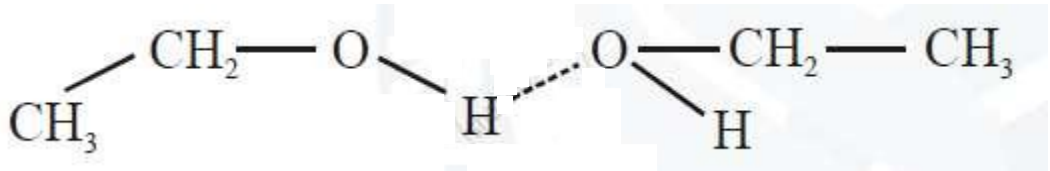
2) Hydrogen bonding arises due to the presence of electronegative atom oxygen in –OH group of the alcohol.

3) Oxygen atom attracts electron density of O–H bond towards itself and hence it gets the partial negative charge, while H atom gets partial positive change.

$$-\delta + \delta$$

R-O-H

4) Hence in alcohol, R–OH molecules become polar

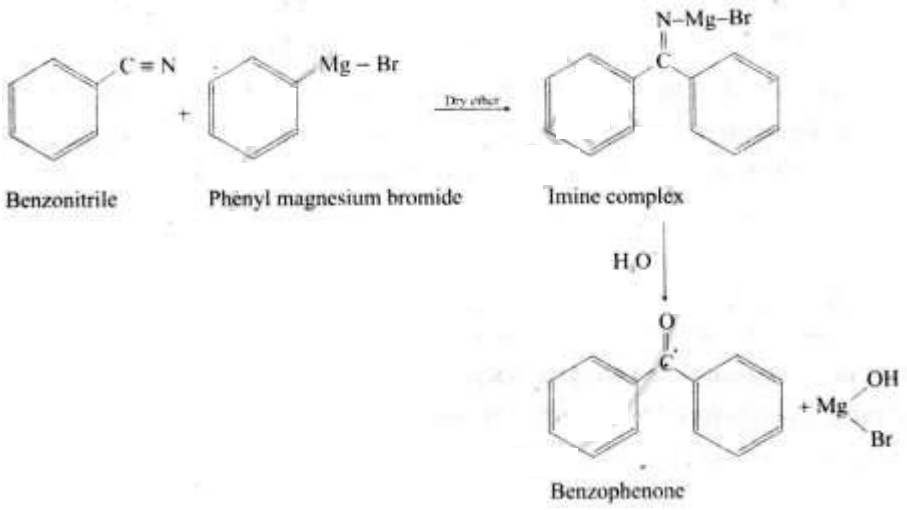


5) There arises strong intermolecular attraction between the oxygen atom of one molecule of alcohol and 'H' atom of another alcohol molecule, giving rise to strong hydrogen bonding which is not present in alkanes.

6) Hence higher thermal energy is required to separate or evaporate alcohol molecule. Therefore alcohols have higher boiling points than their corresponding alkanes.

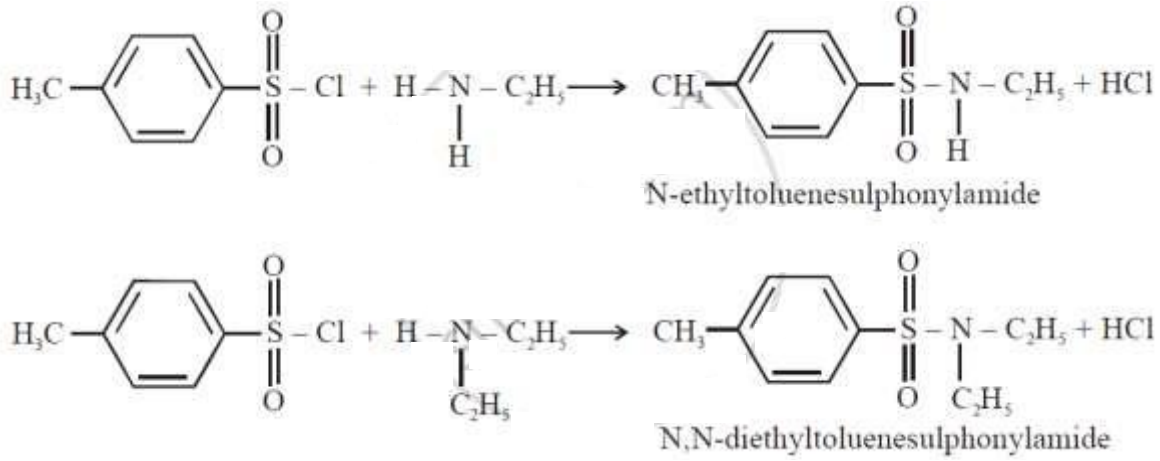
Question 6.4: Write only reactions for the preparation of benzophenone from benzonitrile. **[2]**

Solution:



Question 6.5: What is the action of p-toluenesulphonychloride on ethylamine and diethylamine? **[2]**

Solution:



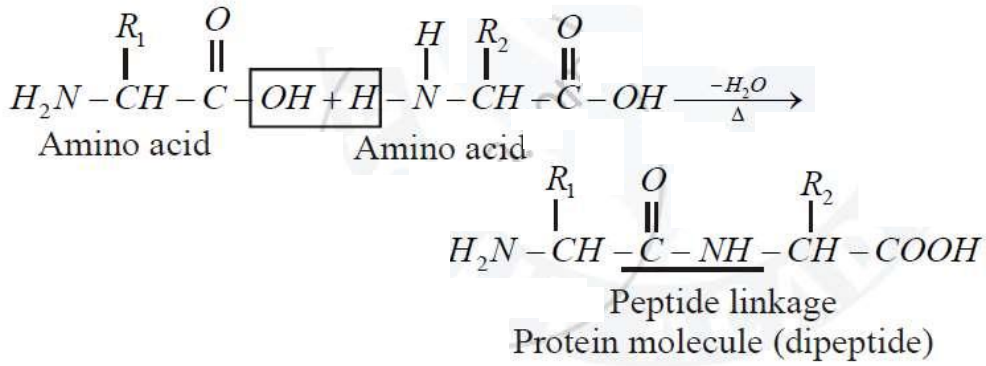
It help to distinguish between primary and secondary amines

Question 6.6.i: What are amino acids? **[2]**

Solution: Amino acids are bifunctional compounds containing a carboxylic acid group and an amino group on α - carbon.

Question 6.6.ii: Write the correct reaction for formation of the peptide bond between amino acids **[2]**

Solution:



Question 6.7: Explain the term Antiseptics **[2]**

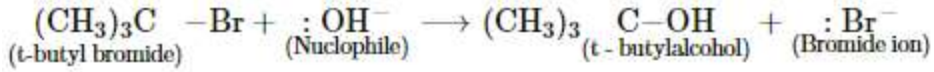
Solution 1: Antiseptic

- Chemicals which either kill or prevent the growth of microorganisms
- Antiseptics are applied to living tissues such as wounds, cuts, ulcers and diseased skin surfaces.
- Example:
- Furacine
- Soframicine
- Dettol (mixture of chloroxylenol and terpineol)

Solution 2: Anticeptic: Chemicals which either kill or prevent the growth of microorganismsn are called anticeptic drug. Antiseptics are applied to living tissues such as wounds, cuts, ulcers and diseased skin surfaces. For example: Soframicine, dettol etc.

Question 6.8: Explain only reaction mechanism for alkaline hydrolysis of tert-butyl bromide **[2]**

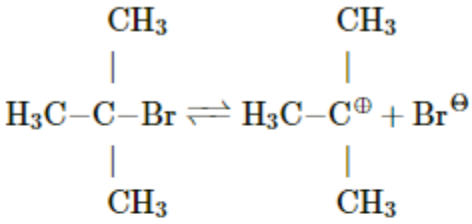
Solution:



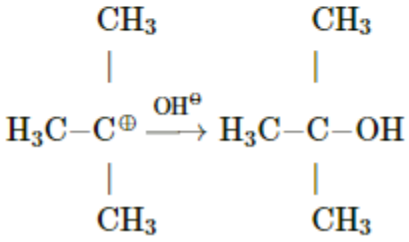
The rate of the above reaction depends upon the concentrations of the substrate, methyl bromide and the nucleophilic, OH ion.

Mechanism of SN^1 reaction: The alkaline hydrolysis of tertiary butyl bromide (a tertiary alkyl halide) proceeds through SN^1 reaction mechanism. This reaction is a two-step process. The first step is a slow step while the second one is a fast step. The hydrolysis reaction can be written as follows.

Step-1 Formation of carbocation



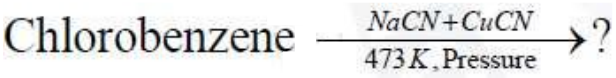
Step-2 Attack of the nucleophile on carbocation



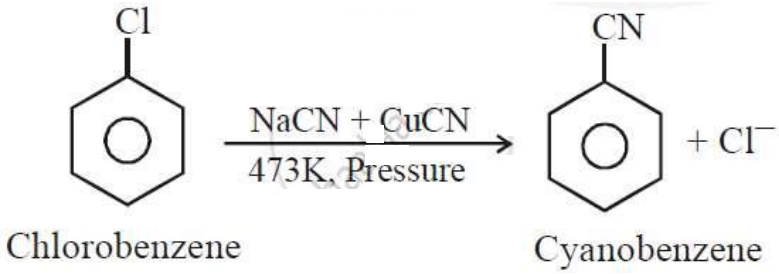
As carbocation has planar geometry, therefore, attack of nucleophile takes place from both the side to give retention inversion in configuration, therefore, the product formed is optically inactive racemic mixture.

Question 7: Answer any THREE of the following [3]

Question 7.1.i: Complete and rewrite the balanced chemical equations [3]

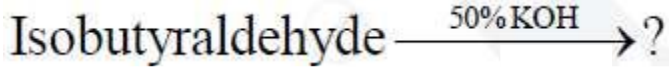


Solution:

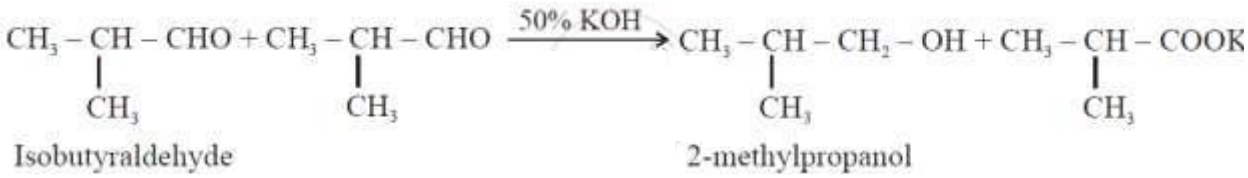


Question 7.1.ii:

Complete and rewrite the balanced chemical equations



Solution:

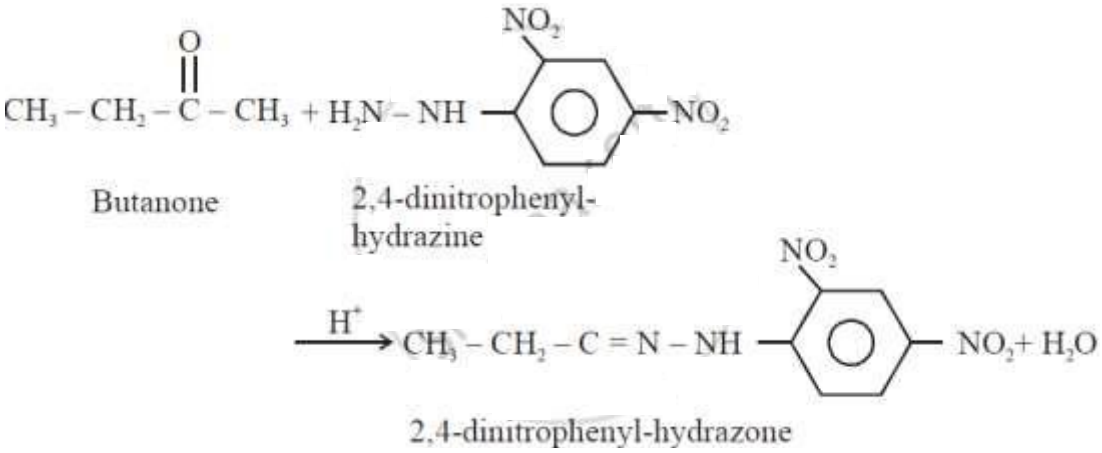


Question 7.1.iii:

Complete and rewrite the balanced chemical equations

Butanone + 2, 4-dinitro-phenylhydrazine $\xrightarrow{H^+}$

Solution:

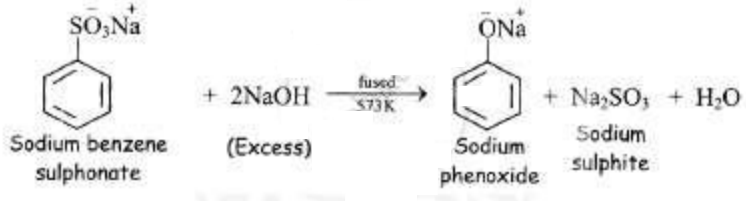


Question 7.2.i: How carbolic acid is prepared from benzene sulphonic acid? **[3]**

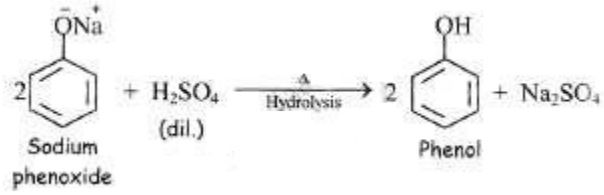
Solution: Preparation of Carbolic acid (Phenol) from Benzene sulphonic acid ($C_6H_6SO_3H$):

a) When benzene sulphonic acid is neutralised by aqueous sodium hydroxide (NaOH), sodium benzene sulphonate is obtained.

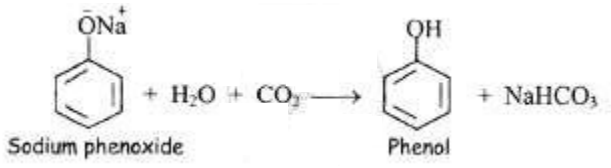
b) Dry sodium benzene sulphonate when fused with excess of sodium hydroxide at 573K,
sodium phenoxide is obtained along with sodium sulphite (Na_2SO_3).



c) Sodium phenoxide when hydrolysed by heating with dilute sulphuric acid, phenol is obtained.



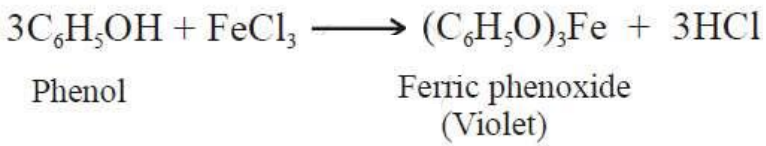
When a current of carbon dioxide is passed through aqueous sodium phenoxide, phenol is obtained as product.



Question 7.2.ii: Write a chemical equation for the action of neutral ferric chloride on phenol. **[3]**

Solution:

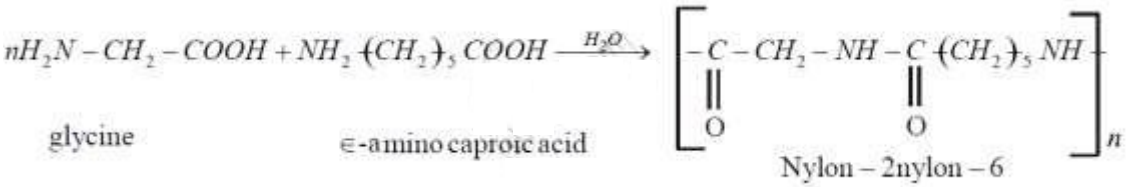
The chemical equation for the action of neutral ferric chloride on phenol :



Question 7.3: Explain the preparation and uses of nylon-2-nylon-6. **[3]**

Solution: <u>Nylon - 2 - nylon - 6</u>

It is a copolymer and contains polyamide linkages. It is obtained by condensation polymerisation of the monomers, glycine and ∈- amino caproic acid



Biodegradable polymers are used as orthopaedic devices, implants, sutures and rug release matrices. They are degraded by bacteria in the environment.

Question 7.4.i: How is glucose prepared from cane sugar? **[3]**

Solution: Preparation of glucose from cane sugar:

Cane sugar (sucrose) is boiled with dilute hydrochloric acid or sulphuric acid. Cane sugar is hydrolyside into equimolar mixture of glucose and fructose.

$$\underset{\text{cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\Delta]{\text{dil HCL or } H_2SO_4} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

The mixture is cooled and alcohol is added during cooling. Glucose crystallises out and fructose remains in solution. Glucose crystals are separated by filtration.

Question 7.4.ii: Write the formula of the complex copper (II) hexacyanoferrate (II). **[3]**

Solution: On cooling the reaction mixture, glucose separate out because it is less soluble in alcohol and fructose
remains in the solution, Crystals of glucose are then filtered and purified by recrystallization.

A formula for complex copper (II) hexacyanoferrate (II) is $Cu_2[Fe(CN)_6]$

Question 8: Attempt Any One **[7]**

Question 8.1.i: What is Lanthanoid contraction?

Solution: 1) Definition of Lanthanoid Contraction: The Lanthanoid contraction may be defined as gradual
(or small) the decrease in atomic and ionic radii of lanthanoids with the increase in atomic number.

2) In Lanthanides, after Lanthanum ($_{57}$La), the electrons are added to anti-penultimate shell i.e. 4f orbital.

3) There are 14 Lanthanoides from $_{58}$C to $_{57}$Lu

4) For each electron, one proton is also added to the nucleus of the atom of the element. Hence from $_{58}$C to $_{71}$Lu as atomic number increases, nuclear charge increases, therefore nuclear attraction increases.

5) Due to this as atomic number increases, atomic volume or radius decreases as observed with all the elements along the period.

6) But in case of Lanthanoids, this decreases in atomic volume or radius is very slow or comparatively small. This is explained in terms of Lanthanoid contraction

Question 8.1.ii:

Explain the cause of Lanthanoids contraction.

Solution: 1) In the Lanthanoid series with increasing atomic number, the atomic and ionic radii decrease from one element to another but a decrease is very small.

2) Increase in nuclear charge in a period increases force of attraction, towards outer electrons. Hence
atomic size or radius decreases

3) Filling of the electrons in the inner shells increases atomic size as inner electrons repel outer electrons. The shielding effect of electrons decreases in the order s > p > d > f

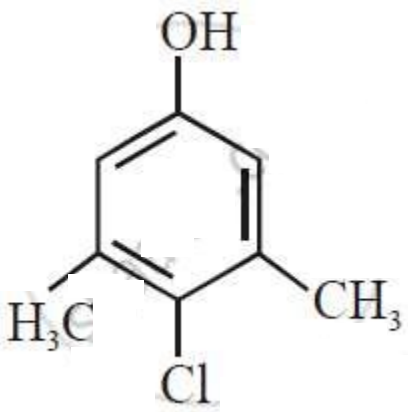
4) The new electrons are added to the same inner 4f - orbital. Hence Lanthanoids contraction is due to

- poor shielding effect due to 4f electrons
- Increase in nuclear charge.
- Non-introduction of new outer shells.

Question 8.1.iii:

Draw the structures of chloroxylenol

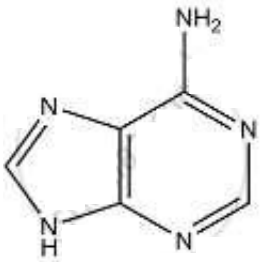
Solution: Structure of chloroxylenol



Question 8.1.iv:

Draw the structures of adenine.

Solution: Structure of adenine



adenine

Question 8.1.v:

How are ethylamine and ethyl methyl amine distinguished by using nitrous acid?

Solution: An action of nitrous acid on ethylamine

$$C_2H_5 - NH_2 + OH - N = O \xrightarrow{NaNO_2+HCl} C_2H_5 - OH + N_2\uparrow + H_2O$$

ethylamine nitrous acid ethanol

An action of nitrous acid on ethylmethylamine

$$C_2H_5 - NH - CH_3 + OH - N = O \xrightarrow{NaNO_2+HCl} C_2H_5 - \underset{\displaystyle CH_3}{\underset{|}{N}} - N = O + H_2O$$

ethylmethylamine nitrous acid N-nitrosoethyl-methylamine

When the nitrous acid reacts with primary amine like $C_2H_5NH_2$ it gives ethanol while when nitrous acid reactions with secondary amine like ethylmethylamine it gives yellow oily N-nitrosamine.

Question 8.2.i: **[7]**

What is the action of the following reagents on ethanoic acid?

1) $LiAlH_4/H_3O^+$
2) PCl_3, heat
3) P_2O_5, heat

Solution:

$$1)\ \underset{\text{ethanoic acid}}{CH_3} - COOH \xrightarrow{LiAlH_4 IH_3O^+} \underset{\text{ethanol}}{CH_3} - CH_2 - OH$$

Ethanoic acid when treated with reducing agent like $LiAlH_4$, it gives ethanol

$$2)\ \underset{\text{ethanoic acid}}{3\,CH_3 - COOH} - PCI_3 \xrightarrow{\Delta} \underset{\text{acetylcholoride}}{3\,CH_3COCI} + H_3PO_3$$

Ethanoic acid, when treated with PCl_3, gives acetyl chloride

$$3)\ \underset{\text{two molecules of ethanoic acid}}{CH_3COOH + CH_3COOH} \overset{P_2O_5}{\underset{A}{\rightleftharpoons}} \underset{\text{acetic anhydride}}{(CH_3 - CO)_2O} + OH$$

When two molecules of ethanoic acid heated with strong dehydrating agent P_2O_5, it removes water molecules to for acetic anhydride.

Question 8.2.ii:

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

$$CH_3 - CH_2 - Br + AgCN \xrightarrow{\Delta} A \xrightarrow[C_2H_5OH]{Na} B$$

Solution:

$$\Rightarrow CH_3 - CH_2 - Br + AgCN \xrightarrow{\Delta} A \xrightarrow[C_2H_5OH]{Na} B$$

$$CH_3 - CH_2 - Br + Ag\,CN \xrightarrow{\Delta} CH_3CH_2NC \xrightarrow{Na/C_2H_5OH} \underset{\text{ethylmethylamine}}{CH_3CH_2 - NH - CH_3}$$

Question 8.2.iii:

Write a short note on Hoffmann bromamide degradation.

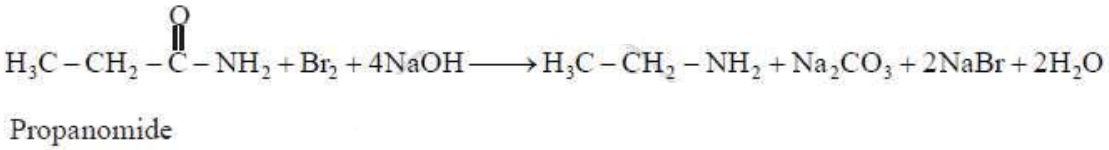
Solution 1: (a) **Hoffmann Bromanide degradation**

(1) The conversion of amides into amine in presence of bromine and alkali is known on Hoffmann degradation of amides.

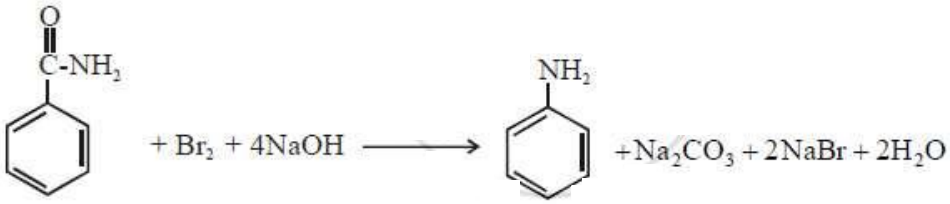
(2) An important characteristic of this reaction is that on amine with one carbon less than those in the amide is formed.

(3) This reaction is an example of molecular rearrangement and involves migration of an alkyl or aryl group from the carbonyl carbon to this adjacent nitrogen atom.

Example:

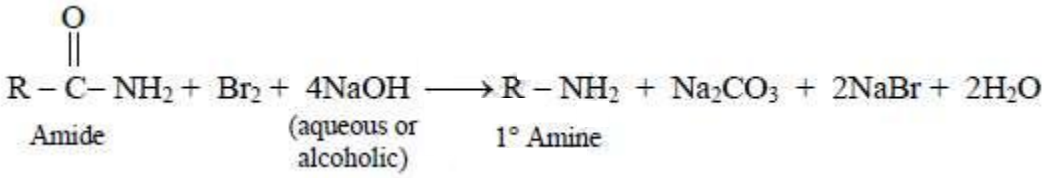


Propanomide

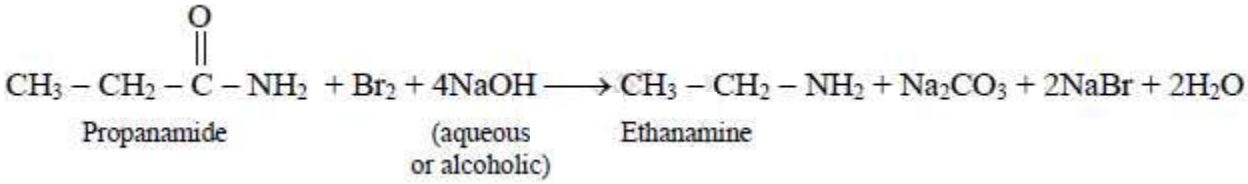


Solution 2: Hoffmann bromamide reaction:

a) Primary amine can be prepared by reaction of amide with bromine and aqueous or alcoholic sodium hydroxide.



eg. Ethanamine is prepared by reaction of propanamide with bromine and aqueous or alcoholic sodium hydroxide.



b) This reaction is known as Hoffmann bromamide degradation. It involves molecular rearrangement. An alkyl or aryl group migrates from the carbonyl carbon to the adjacent nitrogen atom.

c) This reaction is useful for decreasing the length of carbon chain by one carbon atom.