Chemistry
Question Paper
2019 (Set-2)

General Instructions:
*(i) **All** questions are compulsory*
*(ii) Section A : **Q. no. 1** to **5** are very short-answer questions and carry **1** mark each.*
*(iii) Section B : **Q. no. 6** to **12** are short-answer questions and carry **2** marks each.*
*(iv) Section C : **Q. no. 13** to **24** are also short-answer questions and carry **3** marks each.*
*(v) Section D : **Q. no. 25** to **27** are long-answer questions and carry **5** marks each.*
(vi) There is no overall choice. However, an internal choice has been provided
*in **two** questions of **one** mark, **two** questions of **two** marks, **four** questions of **three** marks*
*and all the **three** questions of **five marks** weightage. You have to attempt only one of the*
*choices in **such** questions.*
*(vii) Use log tables if necessary. Use of calculators is **not** allowed.*

Question 1
Why are medicines more effective in colloidal state?
OR
What is difference between an emulsion and a gel?

SOLUTION:

Some medicines are more effective in colloidal form because medicine in colloidal form is easily absorbed by the body tissues.
For example, Antibiotics like streptomycin in the form of the colloidal sol is injected into the body for the more effective result.

OR

Emulsion: It is a colloidal mixture in which both the dispersed phase and the dispersion medium are liquids. The two or more liquids present in the mixture are generally immiscible in nature. Example: Milk.
Gel: It is a colloid in which the dispersed phase i.e. liquid has combined with the dispersion medium i.e. solid to produce a semisolid material. Example: jellies.

Question 2
Arrange the following in increasing order of base strength in gas phase:
$(C_2H_5)_3N$, $C_2H_5NH_2$, $(C_2H_5)_2NH$

SOLUTION:

$C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$

Question 3
Why conductivity of silicon increases on doping with phosphorus?

SOLUTION:

Phosphorus doping introduces phosphorus atoms in silicon crystal leading to change its electrical properties. Phosphorus atoms have 5 valence electrons which cause n-type doping. A phosphorus atom replaces silicon atom(having four valence electrons) in silicon crystal. Four out of five valence electrons of phosphorus take part in bonding while the fifth electron remains free. which lead to an increase in the conductivity of silicon crystal.
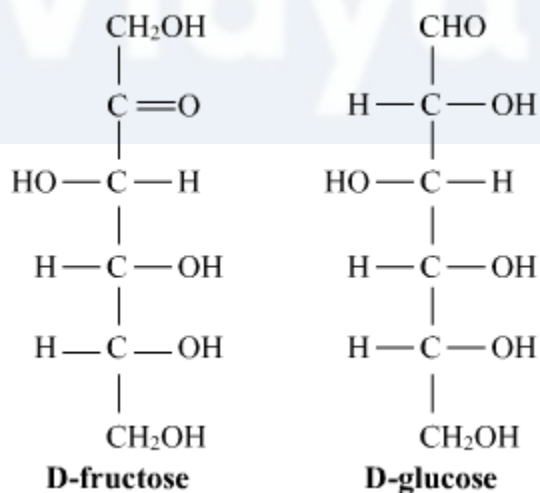
Question 4
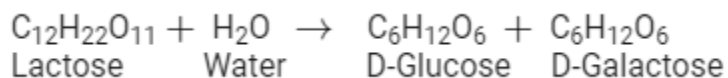What is the basic structural difference between glucose and fructose?

OR

Write the products obtained after hydrolysis of lactose.

SOLUTION:

Both Glucose and Fructose are hexose sugars with six carbon atoms but, Glucose is an aldohexose and Fructose is ketohexose which means the functional group present in glucose is aldehyde and the functional group in fructose is ketone.
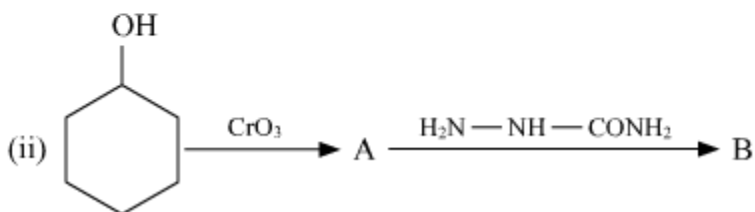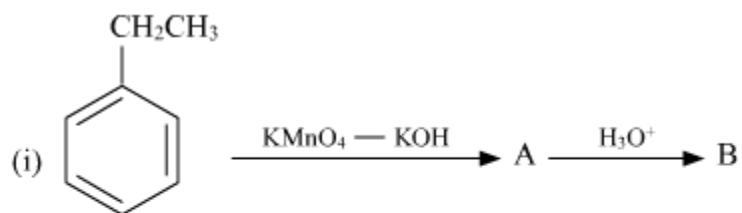

Lactose is composed of β-D galactose and β-D glucose. Thus, on hydrolysis, it gives β-D galactose and β-D glucose.

$$\underset{\text{Lactose}}{C_{12}H_{22}O_{11}} + \underset{\text{Water}}{H_2O} \rightarrow \underset{\text{D-Glucose}}{C_6H_{12}O_6} + \underset{\text{D-Galactose}}{C_6H_{12}O_6}$$

Question 5
Write IUPAC name of the given compound:

(i)

CH₂CH₃ — benzene ring
$$\xrightarrow{\text{KMnO}_4 - \text{KOH}} A \xrightarrow{\text{H}_3\text{O}^+} B$$

(ii)

OH — cyclohexane ring
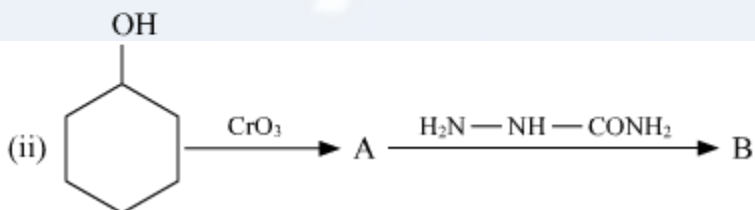$$\xrightarrow{\text{CrO}_3} A \xrightarrow{\text{H}_2\text{N} - \text{NH} - \text{CONH}_2} B$$
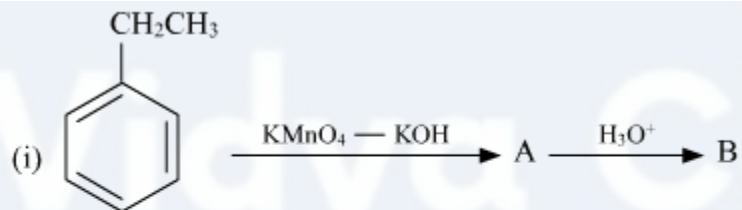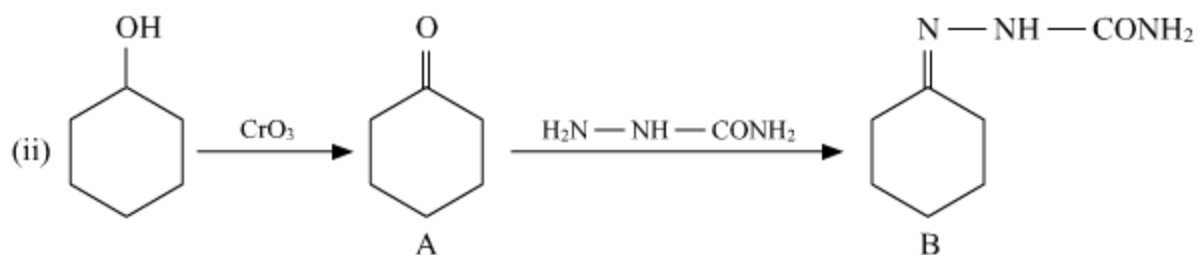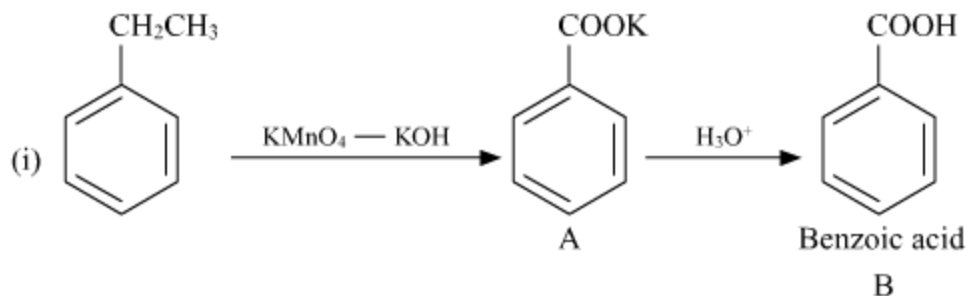
SOLUTION:

4-Chlorobenzenesulphonic acid

Question 6
Write structures of compounds A and B in each of the following reactions:

(i)

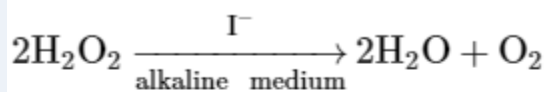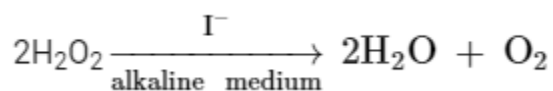CH₂CH₃ — benzene ring
$$\xrightarrow{\text{KMnO}_4 - \text{KOH}} A \xrightarrow{\text{H}_3\text{O}^+} B$$

(ii)

OH — cyclohexane ring
$$\xrightarrow{\text{CrO}_3} A \xrightarrow{\text{H}_2\text{N} - \text{NH} - \text{CONH}_2} B$$

SOLUTION:

(i)

CH$_2$CH$_3$ benzene → (KMnO$_4$ — KOH) → COOK (A) → (H$_3$O$^+$) → COOH Benzoic acid (B)

(ii)

OH cyclohexanol → (CrO$_3$) → O (A) → (H$_2$N—NH—CONH$_2$) → N—NH—CONH$_2$ (B)

$$2H_2O_2 \xrightarrow[\text{alkaline medium}]{I^-} 2H_2O + O_2$$

In Some cases, the rate of reaction depends not only on the reactant but may also depend on the substance present as a catalyst. This is also seen in the above reaction. The rate of reaction depends on the slowest step in case of a complex reaction.

(1) $H_2O_2 + I^- \xrightarrow{\text{Slow}} H_2O + IO^-$

(2) $H_2O_2 + IO^- \xrightarrow{\text{Fast}} H_2O + I^- + O_2$

(i) Rate law:

$$\text{Rate} = -\frac{1}{2}\frac{d[H_2O_2]}{dt} = k\left[H_2O_2\right]\left[I^-\right]$$

(ii) The overall order of reaction:

$\text{Rate} = k[H_2O_2][I^-]$

Order = 1+1 = 2

(iii) Slowest step is the rate determining step. Hence, step 1 is rate determining step.

Question 8

Write two differences between an ideal solution and a non-ideal solution.

SOLUTION:

(i) Ideal solutions are the homogenous mixture of two or more liquid which follows Raoult's law over the entire range of concentration.
(ii) In case of an ideal solution, $\Delta H_{mix} = 0$ and $\Delta V_{mix} = 0$, which indicates that on mixing the two solutions there is no release or absorption of heat and also there is no change in volume at constant pressure.
Example: Benzene and Toluene

(i) Non-ideal solutions are the homogeneous mixture of two or more liquid which is unable to follow Raoult's law over the entire range of concentration.
(ii) Here $\Delta H_{mix} \neq 0$ and $\Delta V_{mix} \neq 0$, which indicates that on mixing the heat is released or absorbed and also there is a change in volume.
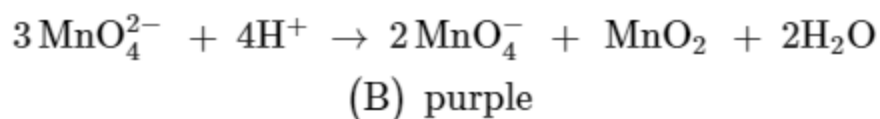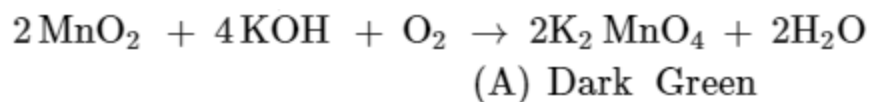Example: Acetone and Ethanol

Question 9

When MnO_2 is fused with KOH in the presence of KNO_3 as an oxidizing agent, it gives a dark green compound (A). Compound (A) disproportionates in acidic solution to give purple compound (B). An alkaline solution of compound (B) oxidises KI to compound (C) whereas an acidified solution of compound (B) oxidises KI to (D). Identify (A), (B), (C), and (D).
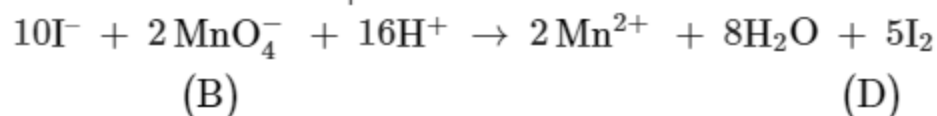
SOLUTION:

Potassium permanganate is prepared by fusion of MnO_2 with an alkali metal hydroxide and an oxidising agent like KNO_3. This produces the dark green K_2MnO_4 which disproportionates in a neutral or acidic solution to give permanganate.
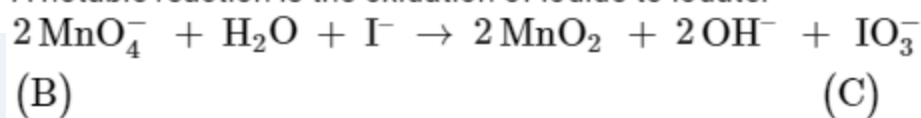
$$2\,MnO_2 + 4\,KOH + O_2 \rightarrow 2K_2\,MnO_4 + 2H_2O$$
$$\text{(A) Dark Green}$$

$$3\,MnO_4^{2-} + 4H^+ \rightarrow 2\,MnO_4^- + MnO_2 + 2H_2O$$
$$\text{(B) purple}$$

In acid solutions:
Iodine is liberated from potassium iodide :
$$10I^- + 2\,MnO_4^- + 16H^+ \rightarrow 2\,Mn^{2+} + 8H_2O + 5I_2$$
$$\text{(B)} \qquad\qquad\qquad\qquad\qquad \text{(D)}$$

In neutral or faintly alkaline solution:
A notable reaction is the oxidation of iodide to iodate:
$$2\,MnO_4^- + H_2O + I^- \rightarrow 2\,MnO_2 + 2\,OH^- + IO_3^-$$
$$\text{(B)} \qquad\qquad\qquad\qquad\qquad \text{(C)}$$

Question 10

Write IUPAC name of the complex $[Cr(NH_3)_4Cl_2]^+$. Draw structures of geometrical isomers for this complex.
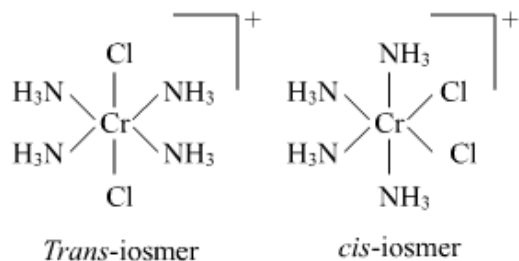
OR
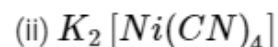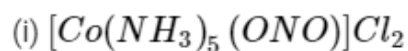
Using IUPAC norms write the formulae for the following:
(i) Pentaamminenitrito-O-cobalt(III) chloride
(ii) Potassium tetracyanidonickelate(II)

SOLUTION:

Tetraaminedichlorochromium (III)

Trans-iosmer   cis-iosmer

OR

(i) $[Co(NH_3)_5(ONO)]Cl_2$

(ii) $K_2[Ni(CN)_4]$

Question 11

Out of $[CoF_6]^{3-}$ and $[Co(C_2O_4)_3]^{3-}$, which one complex is
(i) diamagnetic
(ii) more stable
(iii) outer orbital complex and
(iv) low spin complex?
(Atomic no. of Co = 27

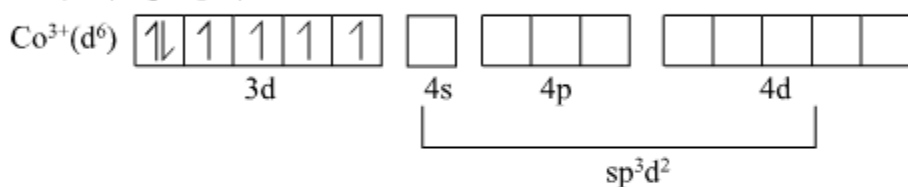$[CoF_6]^{3-}$ $[Co(C_2O_4)_3]^{3+}$
    A   B

The oxidation of Co in both cases is $(+3)$
Fluorine is weak field ligand and Oxalate is a strong field ligand.
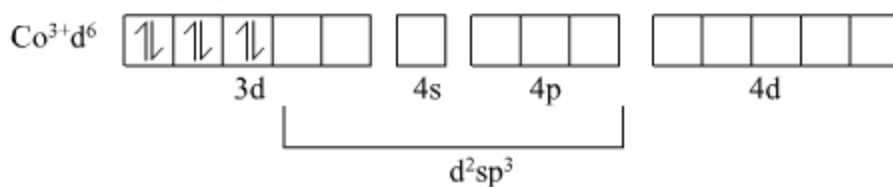According to valence bond theory.
$(CoF_6)^{3-}$ (High spin)

Hybridisation = sp^3d^2
Outer orbital complex
Paramagnetic in nature
High spin complex
$[Co(C_2O_4)_3]^{3-}$ (Low spin)

Question 12
Write balanced chemical equations for the following processes:
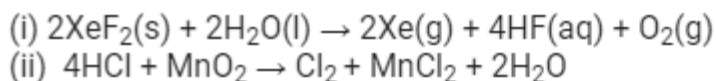
(i) XeF_2 undergoes hydrolysis.

(ii) MnO_2 is heated with conc. HCl.
                    OR
Arrange the following in order of property indicated for each set:

(i) H_2O, H_2S, H_2Se, H_2Te - increasing acidic character

(ii) HF, HCl, HBr, HI - decreasing bond enthalpy

(i) $2XeF_2(s) + 2H_2O(l) \rightarrow 2Xe(g) + 4HF(aq) + O_2(g)$

(ii) $4HCl + MnO_2 \rightarrow Cl_2 + MnCl_2 + 2H_2O$

OR

(i) The increasing order of acidic character is $H_2O < H_2S < H_2Se < H_2Te$

(ii) The decreasing order of bond enthalpy is $HF > HCl > HBr > HI$

Question 13

An element crystallizes in fcc lattice with a cell edge of 300 pm. The density of the element is 10.8 g cm^{-3}. Calculate the number of atoms in 108 g of the element.

SOLUTION:

Given: Mass of the element, W = 108 g

z (fcc) = 4

Edge length, (a) = 300 pm $\qquad$ (1pm = 10^{-10} cm)

Density, (ρ) = 10.8 g/cm^3

$$\rho = \frac{z \times M}{a^3 \times N_A}$$

$$10.8 = \frac{4 \times M}{(300 \times 10^{-10})^3 \times 6.022 \times 10^{23}}$$

$$M = \frac{10.8 \times 2.7 \times 10^{-23} \times 6.022 \times 10^{23}}{4} \text{ g}$$

$$n = \frac{N}{N_A} = \frac{W}{M}$$

$$N = \frac{W}{M} \times N_A$$

$$N = \frac{108 \times 4 \times 6.022 \times 10^{23}}{10.8 \times 2.7 \times 10^{-23} \times 6.022 \times 10^{23}}$$

N = 14.8 × 10^{23} atoms

Question 14

A 4% solution(w/w) of sucrose (M = 342 g mol^{-1}) in water has a freezing point of 271.15 K. Calculate the freezing point of 5% glucose (M = 180 g mol^{-1}) in water.

(Given: Freezing point of pure water = 273.15 K)

SOLUTION:

4% solution(w/w) of sucrose $\Rightarrow$ 4 g sucrose in 96 g water

w_2 (solute) = 4 g

w_1 (solvent) = 96 g

M_2 (solute) = 342 g mol^{-1}

$\Delta T_f = k_f \, m$

$T_f = 271.15$

$T_f^\circ = 273 \cdot 15$

$\Delta T_f = T_f^\circ - T_f = (273 \cdot 15 - 271 \cdot 15)K = 2 \cdot 0K$

$k_f = \dfrac{\Delta T_f}{m}$

$m = \dfrac{w_2}{M_2 \times w_1} \times 1000 = \dfrac{4 \times 1000}{96 \times 342} = 0 \cdot 122m$

$k_f = \dfrac{2}{0 \cdot 122} = 16 \cdot 39 \, Km^{-1}$

$\Delta T_f = k_f \, m.$

* 5% solution(w/w) of glucose in water $\Rightarrow$ 5 g glucose in 95 g H_2O

$W_2 = 5 \, g$

$W_1 = 95 \, g$

$M_2 = 180 \, g$

$\Delta T_f = 16 \cdot 39 \times \dfrac{5 \times 100}{95 \times 180} = 0 \cdot 479$

$\Delta T_f \cong 0.48$

$T_f^\circ - T_f = 0 \cdot 48$

$T_f = T_f^\circ - 0 \cdot 48$

$= 273 \cdot 15 - 0 \cdot 48$

$= 272 \cdot 67$

Question 15

The Decomposition of NH_3 on the platinum surface is zero order reaction. If rate constant (k) is $4 \times 10^{-3} \, Ms^{-1}$, how long it will take to reduce the initial concentration of NH_3 from 0.1 M to 0.064 M.

SOLUTION:

Given,

$k = 4 \times 10^{-3} \, Ms^{-1}$

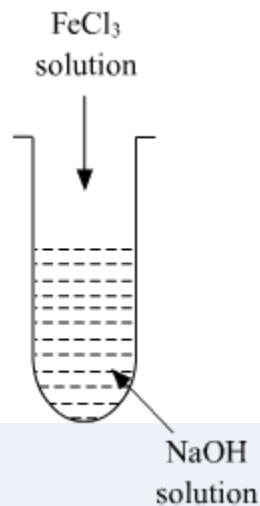$[A_o] = 0.1 \, M$

$[A] = 0.064 \, M$

For a zero-order reaction,

$k = \dfrac{1}{t} \{[A_o] - [A]\}$

$4 \times 10^{-3} \, Ms^{-1} = \dfrac{1}{t} \{[0.1] - [0.064]\}$

$t = \dfrac{0.1 - 0.064}{4 \times 10^{-3}} = 0.009 \times 10^3 = 9 \, seconds$

Question 16

(i) What is the role of activated charcoal in gas mask?
(ii) A colloidal sol is prepared by the given method in figure. What is the charge on hydrated ferric oxide colloidal particles formed in the test tube? How is the sol represented?

FeCl$_3$
solution

NaOH
solution

(iii) How does chemisorption vary with temperature?

SOLUTION:

(i) The activated charcoal containing gas masks are used by coal miners to protect them from the suffocating gases and particulate matter or ashes present in the coal mines. The activated carbon binds the materials by van der waal forces. Thus, chemical compounds with large molecules, large molecular weight and insolubility are easily absorbed.

(ii) Colloidal particles usually adsorb those ions which are in excess and are common to its own lattice. This preferential adsorption of a particular type of ions imparts a particular type of charge to colloidal particles.
When FeCl$_3$ is added in NaOH, the constituent of the sol is Fe(OH)$_3$ but the dispersion medium is having an excess of OH$^-$ ions. Hence, it gets preferentially adsorbed to the sol giving the overall negative charge. The sol is represented as Fe$_2$O$_3$.xH$_2$O / OH$^-$

FeCl₃
solution

NaOH
solution
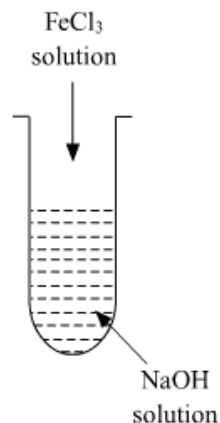
(iii) Effect of temperature on chemisorption: Even though chemical adsorption is an exothermic process, but like most chemical changes, the extent of chemisorption increases with increase in temperature up to a certain limit and then after that, it starts decreasing.
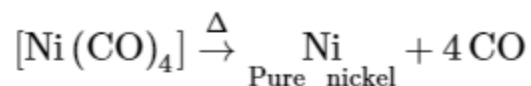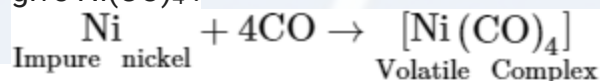
Question 17

(i) Write the role of 'CO' in the purification of nickel.
(ii) What is the role of silica in the extraction of copper?
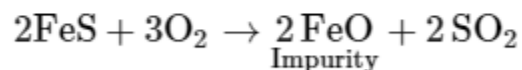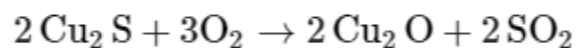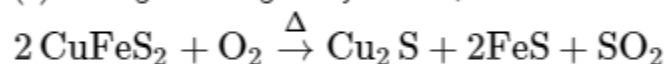(iii) What type of metals are generally extracted by electrolytic method?
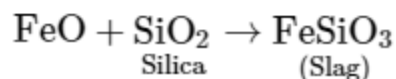
SOLUTION:

(i) Mond's process:
In the Mond process for the purification of nickel, CO is passed over metallic nickel to give Ni(CO)₄ .

$$\underset{\text{Impure nickel}}{Ni} + 4CO \rightarrow \underset{\text{Volatile Complex}}{[Ni\,(CO)_4]}$$

$$[Ni\,(CO)_4] \xrightarrow{\Delta} \underset{\text{Pure nickel}}{Ni} + 4\,CO$$

(ii) During roasting of Pyrite ore, a mixture of FeO and Cu₂O is obtained

$$2\,CuFeS_2 + O_2 \xrightarrow{\Delta} Cu_2\,S + 2FeS + SO_2$$
$$2\,Cu_2\,S + 3O_2 \rightarrow 2\,Cu_2\,O + 2\,SO_2$$
$$2FeS + 3O_2 \rightarrow \underset{\text{Impurity}}{2\,FeO} + 2\,SO_2$$

Role of Silica

$$FeO + \underset{\text{Silica}}{SiO_2} \rightarrow \underset{\text{(Slag)}}{FeSiO_3}$$

(iii) Very reactive metal like Sodium, Potassium, Calcium etc are extracted by electrolysis.
 Certain less reactive metals like Cu are purified using electrolytic refining.

Question 18
Give reasons for the following:

(i) Transition metals form alloys.
(ii) Mn_2O_3 is basic whereas Mn_2O_7 is acidic.
(iii) Eu^{2+} is a strong reducing agent.

SOLUTION:

(i) Because transition elements have almost similar sizes so that atom of one metal can easily acquire the position in the crystal lattice of other metal.

(ii)
$$Mn_2\,O_3 \quad \text{Oxidation state of Mn} = x$$
$$2x + (-2) \times 3 = 0$$
$$2x = 6$$
$$x = +3$$
$$Mn_2\,O_7 \quad \text{Oxidation state of Mn} = y$$
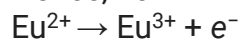$$2y + (-2) \times 7 = 0$$
$$2y = 14$$
$$y = +7$$

In case of Mn_2O_7, Mn exists in highest oxidation state and has d^0 electronic configuration. Therefore it has the tendency to accept the electron. Hence it is acid whereas in case of Mn_2O_3, Mn exists is +3 oxidation state and has d^4 electronic configuration. Therefore it has tendency to donate electron, Hence it acts as base.

(iii) Eu^{2+} is strong reducing agent
Eu can generally exist in +2, +3, +4 oxidation state. Out of these +3 is more stable.
Hence, Eu^{2+} will have the tendency to acquire +3 oxidation state.
$$Eu^{2+} \rightarrow Eu^{3+} + e^-$$
Therefore, Eu^{2+} is a strong reducing agent.

Question 19
Write the structures of monomers used for getting the following polymers:
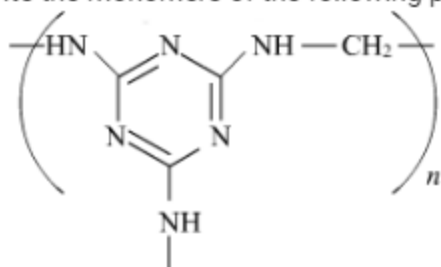(i) Nylon-6,6
(ii) Glyptal
(iii) Buna-S

OR

$$CH_3$$

$$\left[\!\!\begin{array}{c} \text{CH}_2-\text{CH} \end{array}\!\!\right]_n$$

(i) Is $\left[\!\!\begin{array}{c}\end{array}\!\!\right]_n$ a homopolymer or copolymer? Give reason.
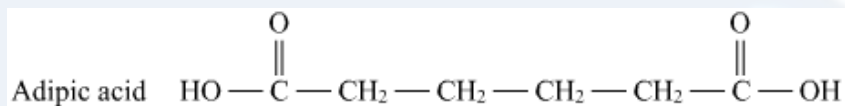
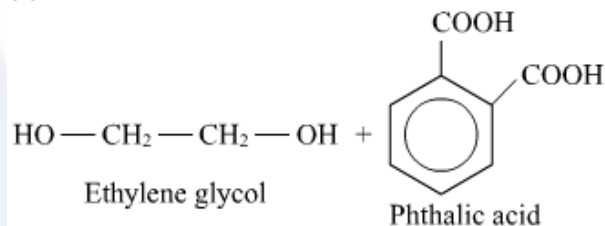(ii) Write the monomers of the following polymer:

(iii) What is the role of Sulphur in the vulcanization of rubber?
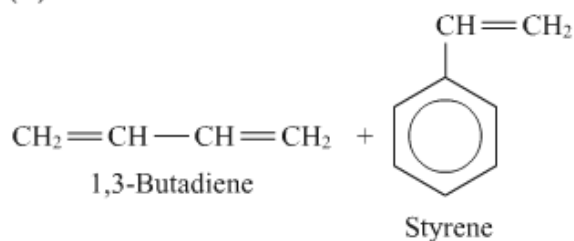
SOLUTION:

(i) Nylon-6,6: Hexamethylenediamine → H_2N-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-NH_2

Adipic acid

$$\text{HO}-\overset{\overset{\textstyle O}{\|}}{\text{C}}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\overset{\overset{\textstyle O}{\|}}{\text{C}}-\text{OH}$$

(ii) Glyptal:

$$\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH} \; + $$

Ethylene glycol

Phthalic acid (with COOH, COOH groups on benzene ring)

(iii) Buna-S

$$\text{CH}_2\!=\!\text{CH}-\text{CH}\!=\!\text{CH}_2 \; + $$

1,3-Butadiene

Styrene (benzene ring with CH=CH₂)
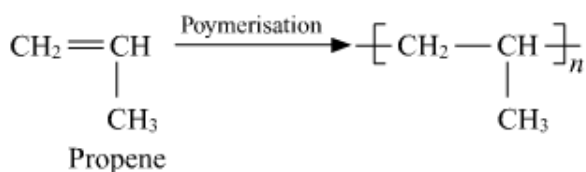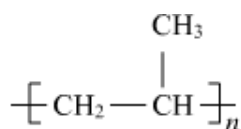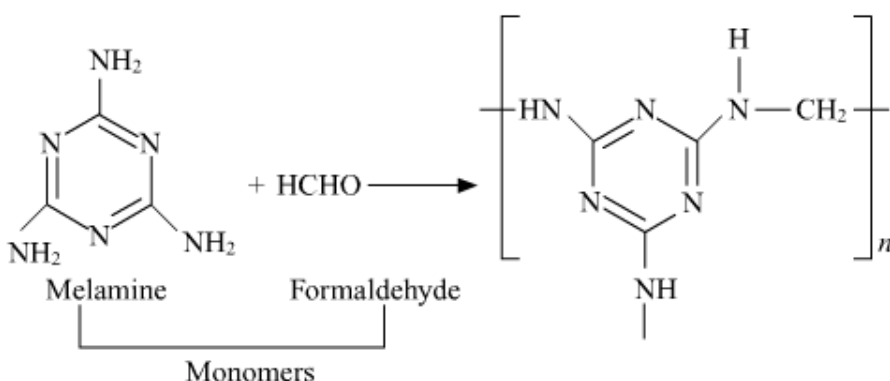
OR

(i) This is a homopolymer formed by a propene monomer because in this polymerization only one monomer is being used without losing any molecule.

$$\begin{array}{c} CH_3 \\ | \\ +CH_2-CH+_n \end{array}$$

$$CH_2=CH \xrightarrow{\text{Poymerisation}} +CH_2-CH+_n$$
with CH_3 below the first CH (Propene) and CH_3 below the product CH.

Propene

(ii)

Melamine + HCHO (Formaldehyde) → product

Monomers

(iii) Sulfur is used in vulcanization to produce cross-links between two polymer chains to produce more tensile strength, elasticity, and resistance to abrasion.

Question 20
(i) Why bithional is added in soap?
(ii) Why magnesium hydroxide is a better antacid than sodium bicarbonate?
iii) Why soaps are biodegradable whereas detergents are non-biodegradable?
<center>OR</center>
Define the following terms with a suitable example in each:
(i) Antibiotics
(ii) Artificial sweeteners
(iii) Analgesics

SOLUTION:

i). Bithional is a bacteriostatic agent which is added to impart antibacterial properties to soap.
ii). Magnesium hydroxide is a better antacid because being insoluble it does not allow the PH to increase above neutral. Hydrogen carbonate being soluble, its excess can make the stomach alkaline and trigger the production of even more acid.
iii). Soaps are sodium or potassium salts of fatty acids and they are biodegradable and can be broken down by the bacteria but detergents are not like that they are sulphonate which can't be biodegraded.

OR

i). Antibiotics are the medicine which inhibits the growth of bacteria and kill them. antibiotics act by blocking certain biochemical pathways which are essential for the survival of bacteria like cell wall formation, protein synthesis. example; penicillin.
ii). Artificial sweeteners are food additives that replace sugar and add sweetness equal to sugar to the food but with fewer calories than sugar. example: Saccharin
iii). Analgesic is the medicine which is used to relieve pain. example: aspirin, paracetamol.

Question 21

Write the structures of main products when benzene diazonium chloride reacts with the following reagents:
(i) CuCN
(ii) CH_3CH_2OH
(iii) KI

SOLUTION:
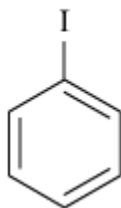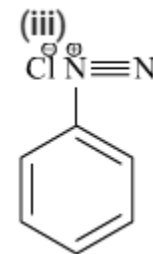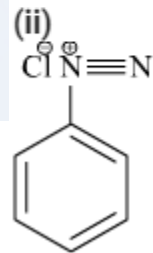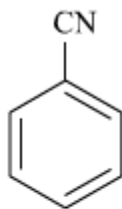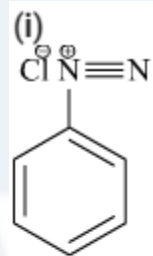
(i) Out of $(CH_3)_3C - Br$ and $(CH_3)_3 C - I$, which one is more reactive towards S$_N$1 and why?

(ii) Write the product formed when p-nitrochlorobenzene is heated with aqueous NaOH at 443 K followed by acidification.

(iii) Why *dextro* and *laevo* − rotatory isomers of Butan-2-ol are difficult to separate by fractional distillation?

SOLUTION:

(i) In S$_N$1 reactions, reactivity depends on the stability of carbocation after removing the leaving group form the reactant. Since the carbocation is same here, so, we will see the tendency of leaving group. As we can see in the following reactions Br⁻ and I⁻ are the leaving groups, out of them I⁻ is a better leaving group.
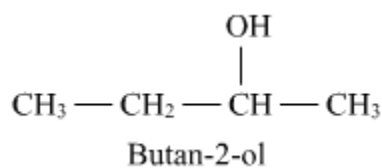Hence S$_N$1 reaction will be faster in $(CH_3)_3 - I$

$(CH_3)_3 - Br$

(ii)

p-nitrochloro benzene

4-Nitro phenol
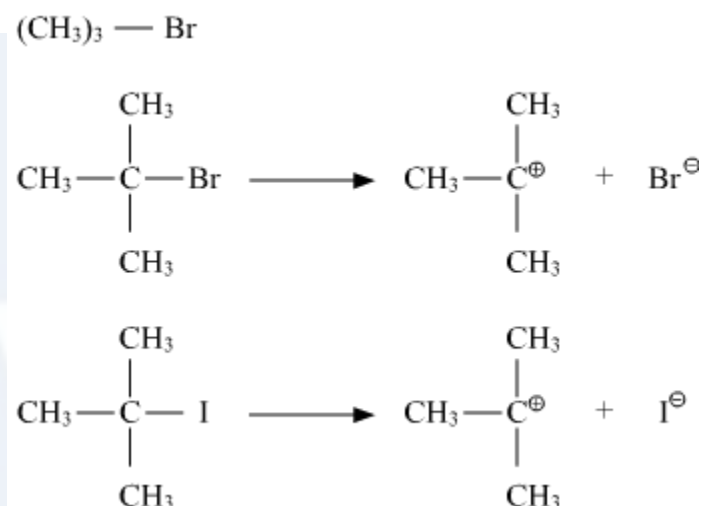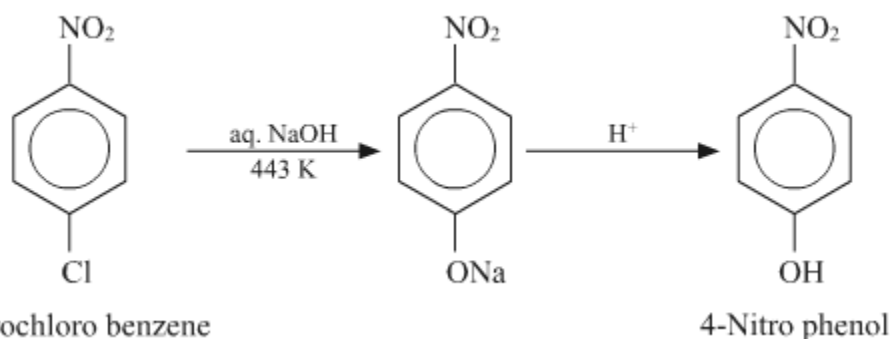
(iii) *dextro* and *laevo* rotatory isomers of butane-2-ol are difficult to separate by fractional distillation because of no difference in boiling points of these two rotatory isomers.

$$CH_3 \!-\! CH_2 \!-\! \overset{\displaystyle \overset{OH}{|}}{CH} \!-\! CH_3$$

Butan-2-ol

Question 23

Differentiate between the following:
(i) Amylose and Amylopectin
(ii) Peptide linkage and Glycosidic linkage
(iii) Fibrous proteins and Globular proteins

OR

Write chemical reactions to show that open structure of D-glucose contains the following:
(i) Straight chain
(ii) Five alcohol groups
(iii) Aldehyde as carbonyl group

SOLUTION:

(i) The differences between amylose and amylopectin are as follows:

Amylose	Amylopectin
1. It constitutes about 15-20% of starch	1. It constitutes about 80- 85% of starch.
2. It is a water-soluble component of starch	2. It is is water soluble component of starch
3. Amylose is a long unbranched chain with 200-1000 α-D-(+)-glucose units held by C1− C4 glycosidic linkage.	3. Amylopectin is a branched chain polymer of α-D-glucose units in which chain is formed by C1−C4 glycosidic linkage whereas branching occurs by C1−C6 glycosidic linkage.

(ii) The differences between peptide linkage and glycosidic linkage are as follows:

| Peptide linkage	Glycosidic linkage
1. Peptide linkage is an amide formed between −COOH group and −NH2 group.	1. A linkage between two monosaccharide units through oxygen atom is called glycosidic linkage.
2. Present in proteins	2. Present in carbohydrate/sugars.

3. Represented as -C-O-C-	3. Represented as -CONH-

(iii)The differences between fibrous protein and globular protein are as follows:

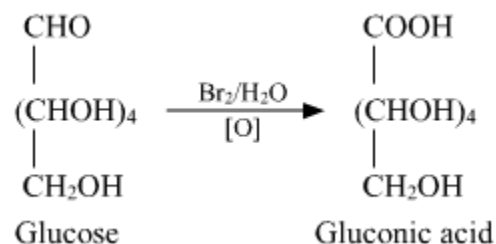| Fibrous protein	Globular protein
1. When the polypeptide chains run parallel and are held together by hydrogen and disulphide bonds, then fibrous protein is formed.	1. When the chains of polypeptides coil around to give a spherical shape, then globular protein is formed.
2. Generally insoluble in water.	2. These are usually soluble in water
3. Examples are keratin (present in hair, wool, silk) and myosin (present in muscles)	3. Examples are insulin and albumins.

OR

(i)On prolonged heating with HI, glucose forms n-hexane, suggesting that all the six carbon atoms are linked in a straight chain.

(ii)Acetylation of glucose with acetic anhydride gives glucose pentaacetate which confirms the presence of five −OH groups. Since it exists as a stable compound, five −OH groups should be attached to different carbon atoms.
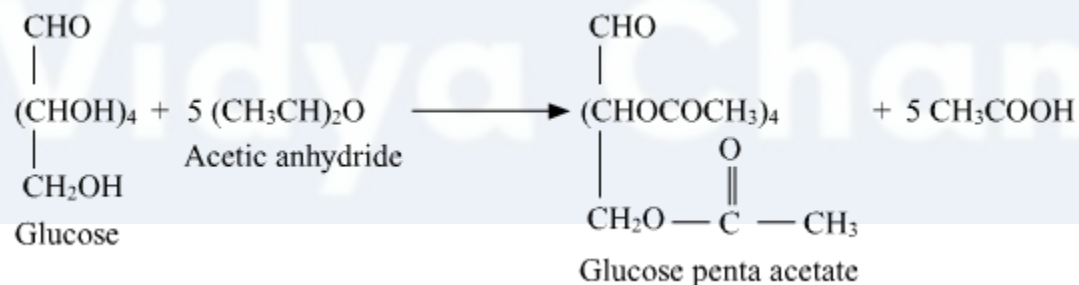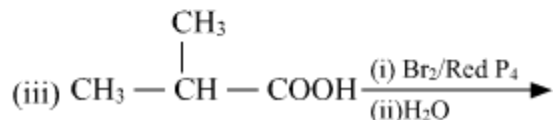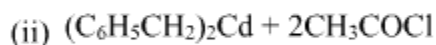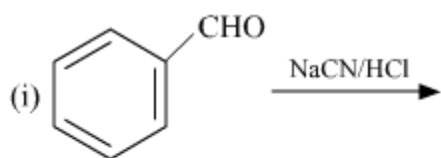

(iii)Glucose gets oxidised to six carbon carboxylic acid (gluconic acid) on reaction with a mild oxidising agent like bromine water. This indicates that the carbonyl group is present as an aldehydic group

Question 24

Complete the following reactions:

(i)

$$\text{(i)} \quad \underset{\text{}}{C_6H_5\text{-CHO}} \xrightarrow{\text{NaCN/HCl}}$$

(ii) $(C_6H_5CH_2)_2Cd + 2CH_3COCl$

(iii) $CH_3 - \underset{\underset{CH_3}{|}}{CH} - COOH \xrightarrow[\text{(ii)}H_2O]{\text{(i) Br}_2/\text{Red P}_4}$

Write chemical equations for the following reactions:

(i) Propanone is treated with dilute Ba(OH)$_2$.
(ii) Acetophenone is treated with Zn(Hg)/Conc. HCl
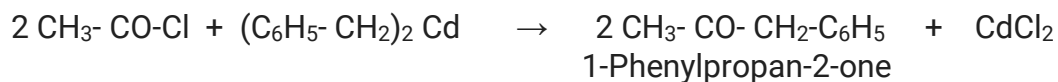(iii) Benzoyl chloride is hydrogenated in presence of Pd/BaSO$_4$.

SOLUTION:

(i). Reaction of benzaldehyde with NaCN/HCl gives **cyanohydrin**.
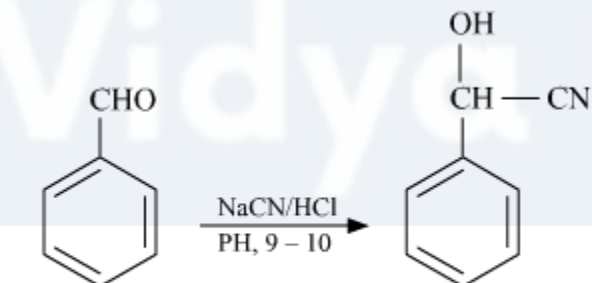
Benzaldehyde   Benzaldehyde
cyanohydrin

(ii) Treatment of acyl chlorides with dialkylcadmium gives a ketone.

2 CH$_3$- CO-Cl + (C$_6$H$_5$- CH$_2$)$_2$ Cd $\rightarrow$ 2 CH$_3$- CO- CH$_2$-C$_6$H$_5$ + CdCl$_2$
1-Phenylpropan-2-one

(iii)Carboxylic acid having α-hydrogen are halogenated at α-position on treatment with Br$_2$ in presence of red phosphorous to give α -halocarboxylic acids. This is **Hell-Volhard-Zelinsky reaction.**
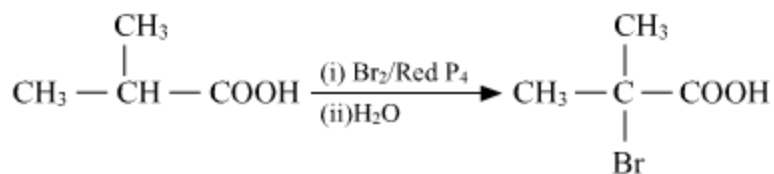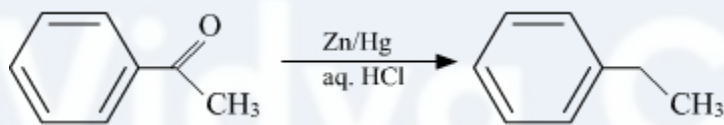
OR

(i) This is a self-aldol condensation reaction
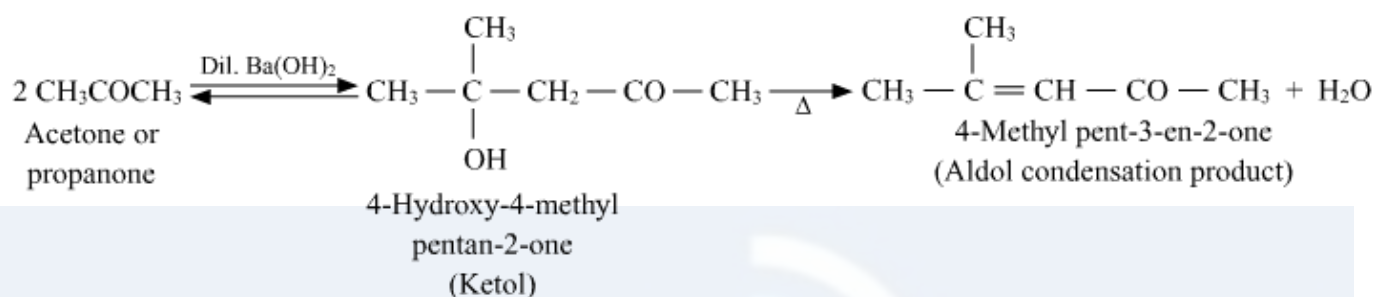
(ii) The **reaction** of aldehydes and ketones with zinc amalgam (**Zn/Hg**) in concentrated HCl, reduces the aldehyde or ketone to a hydrocarbon, and is called **Clemmensen reduction.**

(iii) Benzoyl chloride is hydrogenated over catalyst Pd-BaSO₄ to give benzaldehyde. This reaction is called **Rosenmund Reaction**.

Benzoyl chloride   Benzaldehyde
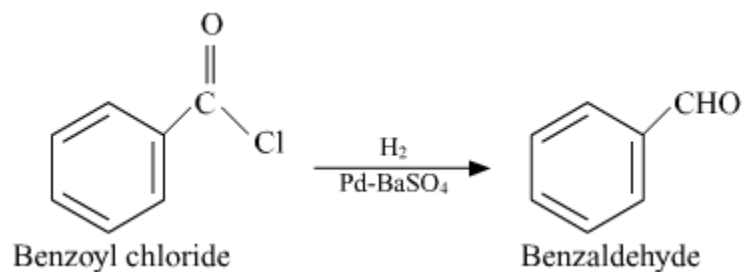
Question 25
(A) Give reasons for the following:
(i) Sulphur in vapour state shows paramagnetic behaviour.
(ii) N-N bond is weaker than P-P bond.
(iii) Ozone is thermodynamically less stable than oxygen.

(b) Write the name of gas released when Cu is added to
(i) dilute HNO_3 and
(ii) conc. HNO_3

OR

(a) (i) Write the disproportionation reaction of H_3PO_3.
(ii) Draw the structure of XeF_4.

(b) Account for the following:
(i) Although Fluorine has less negative electron gain enthalpy yet F_2 is strong oxidizing agent.
(ii) Acidic character decreases from N_2O_3 to Bi_2O_3 in group 15.

(c) Write a chemical reaction to test sulphur dioxide gas. Write chemical equation involved.
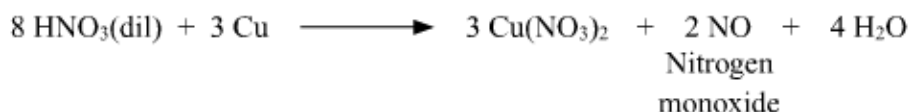
SOLUTION:

Ans:(A) (i) The paramagnetism in Sulphur in the vapour phase can be explained from the fact that in the vapour phase, S_2 is the dominant species and is therefore paramagnetic like O_2, which has two unpaired electrons. So like O_2 molecule, S_2 also has two unpaired electrons in the π*px and π*py orbital.
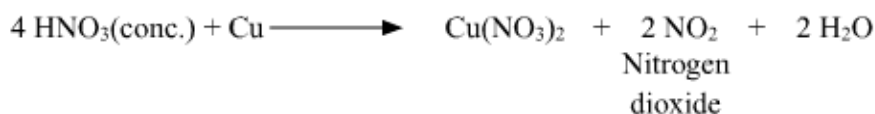
(A) (ii)   The nitrogen atom is smaller in size than the Phosphorus atom. The bond length of N-N bond is smaller than that of P-P bond. Due to this, the four non-bonding electrons of the two nitrogen atoms repel each other making the bond weaker.
This does not happen in the case of phosphorus because P-P bond length is more. So, the repulsion of non-bonding electrons is lesser than in N-N. So, the P-P sigma bond is stronger.

(A) (iii) Ozone is thermodynamically unstable with respect to oxygen since its decomposition into oxygen results in the liberation of heat (ΔH is negative) and an increase in entropy (ΔS is positive). These two effects reinforce each other, resulting in large negative Gibbs energy change (ΔG) for its conversion into oxygen.
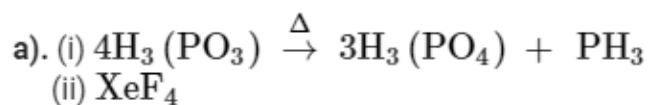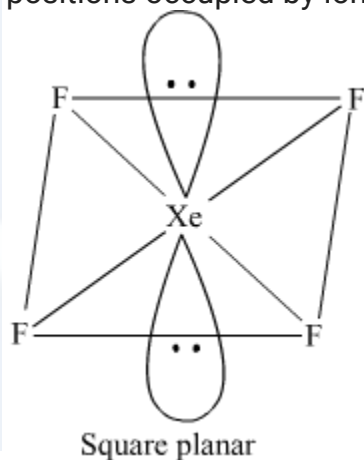
(b)(i) Nitrogen monoxide

$$8 \text{ HNO}_3(\text{dil}) + 3 \text{ Cu} \longrightarrow 3 \text{ Cu(NO}_3)_2 + 2 \text{ NO} + 4 \text{ H}_2\text{O}$$

<div style="text-align:center">Nitrogen
monoxide</div>

(b)(ii) Nitrogen dioxide

$$4 \text{ HNO}_3(\text{conc.}) + \text{Cu} \longrightarrow \text{Cu(NO}_3)_2 + 2 \text{ NO}_2 + 2 \text{ H}_2\text{O}$$

<div style="text-align:center">Nitrogen
dioxide</div>

OR

a). (i) $4\text{H}_3(\text{PO}_3) \xrightarrow{\Delta} 3\text{H}_3(\text{PO}_4) + \text{PH}_3$
(ii) XeF_4

It has a square planar structure. Six electron pairs form an octahedron with two positions occupied by lone pairs.

Square planar

(b). (i) The oxidising capability of a substance depends upon three factors: bond dissociation enthalpy, electron gain enthalpy and hydration energy.
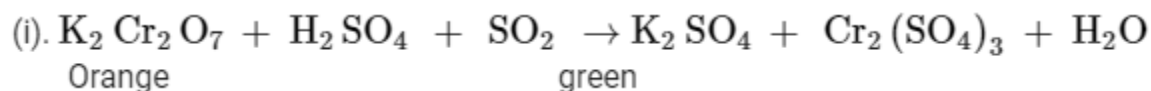Although electron gain enthalpy of fluorine is less negative as compared to chlorine, fluorine is a stronger oxidizing agent than chlorine, because of low enthalpy of dissociation of F-F bond (158.8/ kJ mol^{-1}) and high hydration enthalpy of F$^-$ (515/ kJ mol^{-1}).
Due to its small size, Fluorine's hydration energy is very high hence better the oxidizing power. Fluorine has a greater electron-electron repulsion among the lone pairs in the small-sized F_2 molecule where they are much closer to each other than in case of Cl_2, hence the enthalpy of dissociation of F_2 is lower than Cl_2 which makes it better oxidizing agent.

(ii).Acidic character of oxides of group 15 elements decreases and basicity increases down the group. As we move down the group, the atomic size increases,
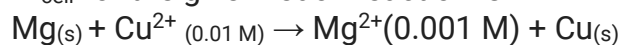
electronegativity decreases and metallic character increases. Oxides of Nitrogen and phosphorous are acidic whereas those of As and Sb are amphoteric and that of Bismuth is basic.

(c). Chemical reaction to test sulphur dioxide gas are:

(i). $\underset{\text{Orange}}{K_2\,Cr_2\,O_7} + H_2\,SO_4 + SO_2 \rightarrow K_2\,SO_4 + \underset{\text{green}}{Cr_2\,(SO_4)_3} + H_2O$

Question 26

$E°_{cell}$ for the given redox reaction is 2.71 V

$Mg_{(s)} + Cu^{2+}_{(0.01\ M)} \rightarrow Mg^{2+}(0.001\ M) + Cu_{(s)}$

Calculate E_{cell} for the reaction. Write the direction of flow of current when an external opposite potential applied is
(i) less than 2.71 V and
(ii) greater than 2.71 V

OR

(a) A steady current of 2 amperes was passed through two electrolytic cells X and Y connected in series containing electrolytes $FeSO_4$ and $ZnSO_4$ until 2.8 g of Fe deposited at the cathode of cell X. How long did the current flow? Calculate the mass of Zn deposited at the cathode of cell Y.
(Molar mass : Fe = 56 g mol^{-1} Zn = 65.3 g mol^{-1}, 1F = 96500 C mol^{-1})

(b) In the plot of molar conductivity (Λ_m) vs square root of concentration ($c^{1/2}$), following curves are obtained for two electrolytes A and B:
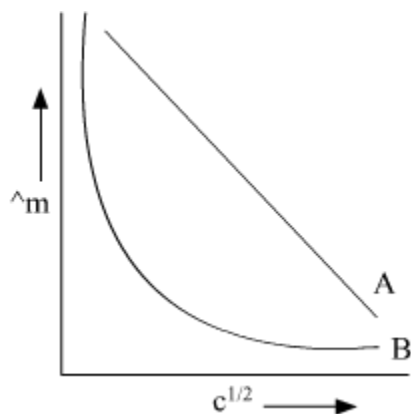
Answer the following:
(i) Predict the nature of electrolytes A and B.
(ii) What happens on extrapolation of Λ_m to concentration approaching zero for electrolytes A and B?

SOLUTION:

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log\; [Mg^{2+}]/[Cu^{2+}]$$
$$= 2.71 - \frac{0.0591}{2}\log\frac{0.001}{0.01}$$
$$= 2.71 - 0.0295 \times (-1)$$
$$= 2.7395\; V$$

i) When external potential is less than 2.71 then current will flow from copper to magnesium.
ii)When external potential is greater than 2.71 then current will flow from magnesium to copper.
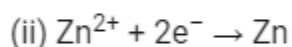
OR

(a) Given: I = 2A
(i) Fe^{2+} $2e^-$ → Fe

56 g of Fe requires = 2 × 96500 C charge

$$2.8\; g\; of\; Fe\; requires = \frac{2\times96500}{56} \times 2.8\; C\; charge$$
$$Q = 9650\; C$$

$$Q = It$$
$$t = \frac{Q}{I} = \frac{9650}{2} = 4825\; sec$$

(ii) $Zn^{2+} + 2e^-$ → Zn

2 × 96500 C of electricity deposit Zn = 65.3 g

$$1\; C\; of\; electricity\; deposit\; Zn = \frac{65.3}{2\times96500}$$

$$9650\; C\; of\; electricity\; deposit\; Zn = \frac{65.3}{2\times96500} \times 9650$$
$$= 3.265g$$

(b) (i) A = Strong electrolyte
     B = Weak electrolyte

(ii) On extrapolation of these graphs they cut the Y axis it means concentration is approaching zero and at that point, we will say infinite dilution of their respective A and B.
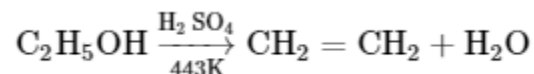
When A and B cut on Y axis then we will say molar conductivity of A and B at infinite dilution.

(a) How do you convert the following:
   (i) Phenol to Anisole
   (ii) Ethanol to Propan-2-ol

(b) Write mechanism of the following reaction:

$$C_2H_5OH \xrightarrow[443K]{H_2\,SO_4} CH_2 = CH_2 + H_2O$$

(c) Why phenol undergoes electrophilic substitution more easily than benzene?

OR

(a) Account for the following:
   (i) o-nitrophenol is more steam volatile than p-nitrophenol.
   (ii) t-butyl chloride on heating with sodium methoxide gives 2-methylpropene instead of t-butylmethylether.

(b) Write the reaction involved in the following:
   (i) Reimer-Tiemann reaction
   (ii) Friedal-Crafts Alkylation of Phenol

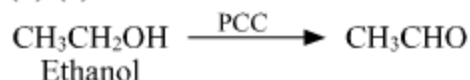(c) Give simple chemical test to distinguish between Ethanol and Phenol.

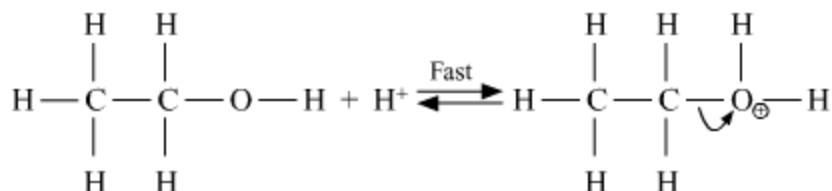SOLUTION:
(a) (i)
Phenol to anisole

Williamson synthesis

(a) (ii)

$$CH_3CH_2OH \xrightarrow{\text{PCC}} CH_3CHO$$
Ethanol

$$CH_3CHO + CH_3MgBr \longrightarrow \underset{\underset{\text{O}^-\text{MgBr}}{|}}{CH_3CHCH_3} \xrightarrow{H_2O} \underset{\underset{\text{OH}}{|}}{CH_3CHCH_3}$$
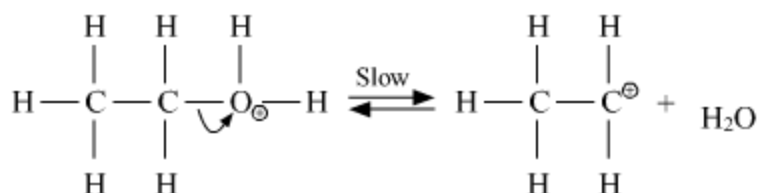Propan-2-ol
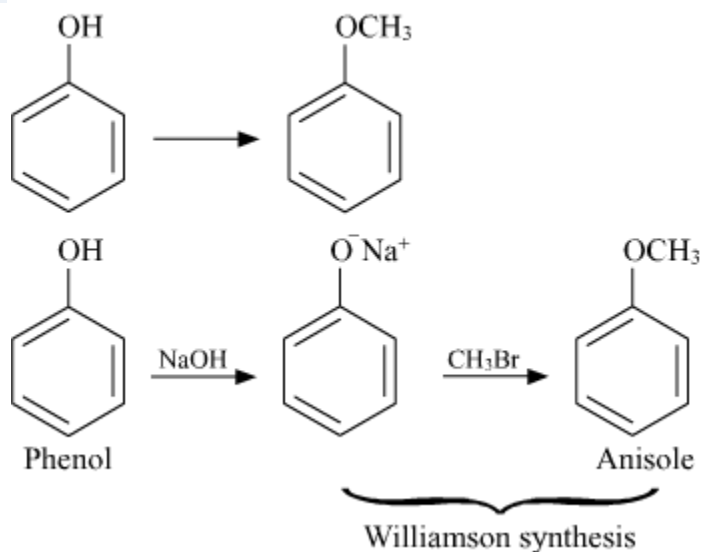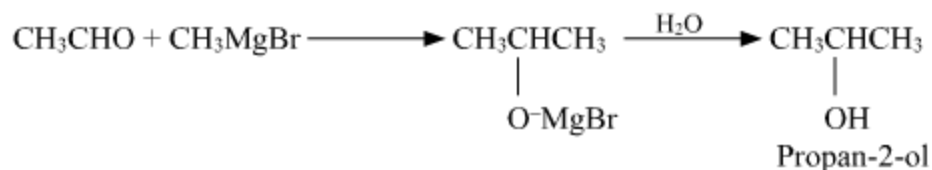
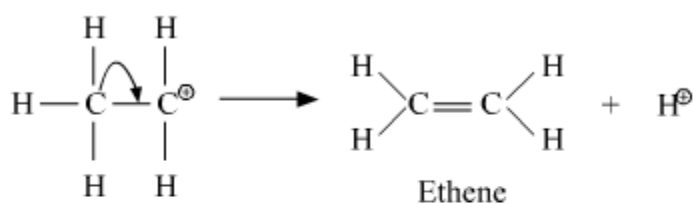(b) <u>Mechanism</u> : <u>Dehydration of ethanol</u>
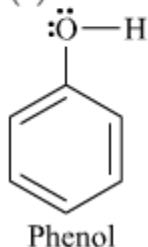
Step 1: Formation of protonated alcohol

Step 2: Formation of carbocation (slow step)

Step 3: Formation of ethene

Ethene

(c)
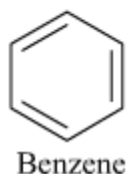
Phenol   Benzene

In case of phenol the benzene ring is more $e^\ominus$ rich due to +M effect of −OH group. Hence, electrophilic substitution takes place at much faster rate in phenol as compared to benzene.

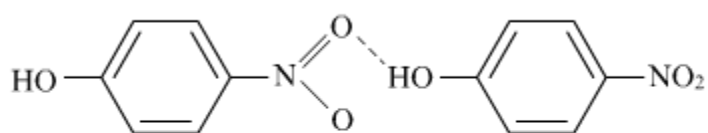**OR**

(a) (i) Incase of o-nitrophenol Intramolecular hydrogen bonding is there which is weaker than intermolecular hydrogen bonding in p-nitrophenol. Hence o-nitrophenol is steam volatile.
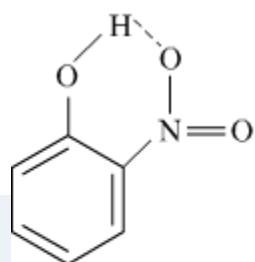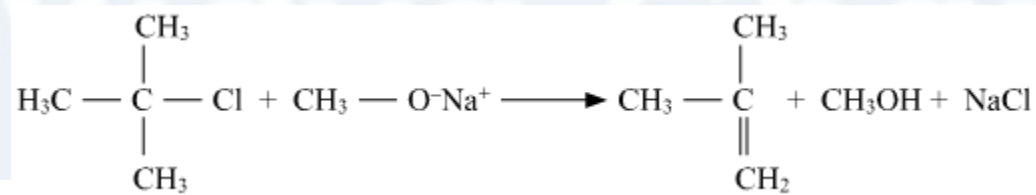
Intramolecular
hydrogen bonding
(*o*-nitrophenol)
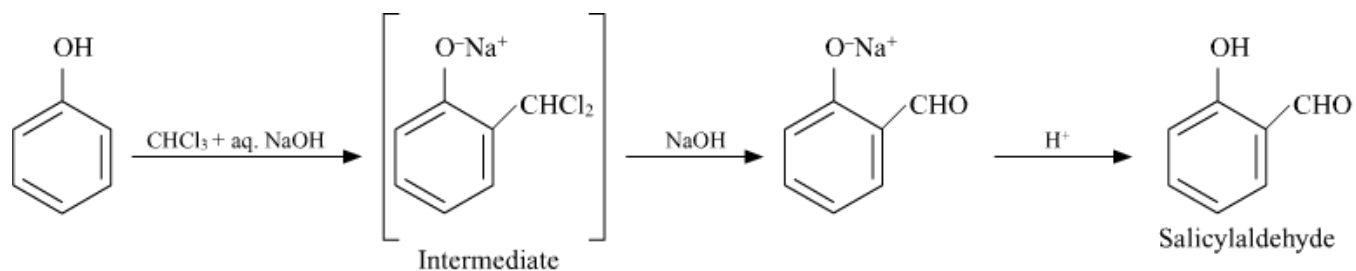
Intermolecular
hydrogen bonding
(*p*-nitrophenol)

(ii)

$$H_3C - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - Cl + CH_3 - O^-Na^+ \longrightarrow CH_3 - \underset{\underset{CH_2}{\|}}{\overset{\overset{CH_3}{|}}{C}} + CH_3OH + NaCl$$

William synthesis

$$R - X + R - \ddot{\underset{..}{O}} - Na \longrightarrow R - \ddot{\underset{..}{O}} - R + NaX$$

The alkyl halide must be 1^0 as the reaction involves the S_N2 reaction pathway.
If alkyl halide is 3^0 then the alkene will be the major product. Hence, 2-methylpropene is formed instead of t-butylmethylether.

(b) (i) Reimer-Tiemann reaction

(ii) Friedal-Crafts Alkylation of Phenol
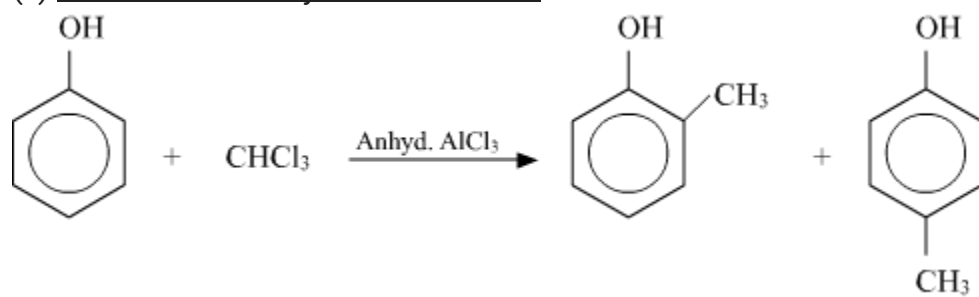
(C). Phenol is unsaturated aromatic alcohol, while ethanol is saturated aliphatic alcohol.

Ethanol reacts with triiodomethane (iodoform test) and forms the yellow precipitate, while phenol does not give this test.

Phenol has benzene ring, it undergoes diazo coupling reaction, while ethanol does not give this test.

Phenol decolorises bromine solution showing it is an unsaturated compound while ethanol does not decolorize bromine solution showing it is a saturated compound.

With neutral $FeCl_3$, phenol forms violet complex while ethanol does not.