Chemistry
Question Paper
2019 (Set-3)

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
Arrange the following in decreasing order of solubility in water:
$(CH_3)_3N$, $(CH_3)_2NH$, CH_3NH_2
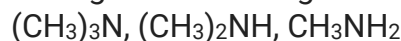
SOLUTION:

Higher the value of hydration enthalpy, more is the solubility. Also, larger the hydrocarbon part attached to the nitrogen of amine, lower is the tendency to form hydrogen bonds and lower is the solubility.
Thus, the decreasing order of solubility in water is $CH_3NH_2 > (CH_3)_2NH > (CH_3)_3N$

Question 2
What type of stoichiometric defect is shown by ZnS and why?

SOLUTION:

The stoichiometric defect shown by ZnS is Frenkel defect which is due the large difference in the size of the ions, i.e. due to small size of Zn^{2+}.

Question 3
Write one stereochemical difference between S_N1 and S_N2 reactions.

SOLUTION:

S_N1 reactions lead to the formation of racemic mixture whereas S_N2 reactions lead to inversion in configuration of product.

Question 4
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.
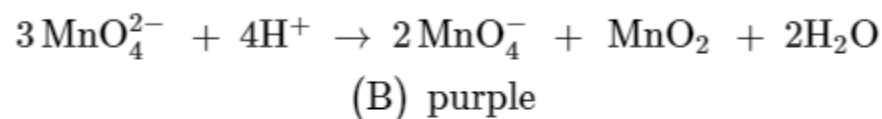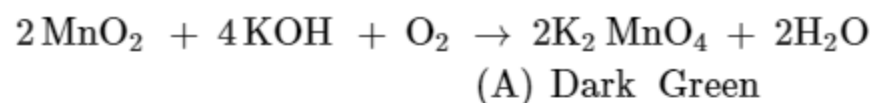Gel: It is a colloid in which the dispersed phase i.e. liquid has combined with the dispersion medium i.e. solid to produce a semisolid material. Example: jellies.

Question 6

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).
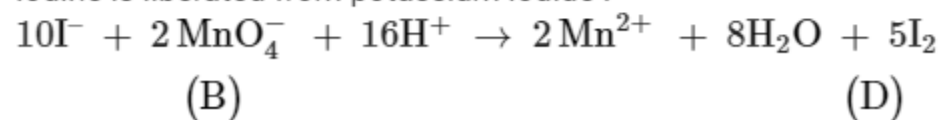
SOLUTION:

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.
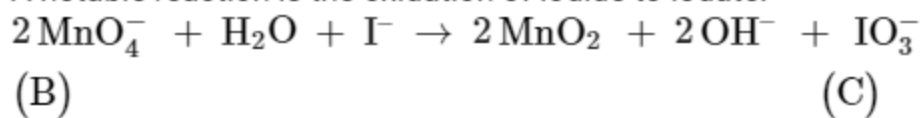
$$2\,MnO_2 + 4\,KOH + O_2 \rightarrow 2K_2\,MnO_4 + 2H_2O$$
$$\text{(A) Dark Green}$$

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

In acid solutions:
Iodine is liberated from potassium iodide :

$$10I^- + 2\,MnO_4^- + 16H^+ \rightarrow 2\,Mn^{2+} + 8H_2O + 5I_2$$
$$\text{(B)} \qquad\qquad\qquad\qquad \text{(D)}$$

In neutral or faintly alkaline solution:
A notable reaction is the oxidation of iodide to iodate:

$$2\,MnO_4^- + H_2O + I^- \rightarrow 2\,MnO_2 + 2\,OH^- + IO_3^-$$

(B)   (C)

Question 7
State Henry's law and write its two applications.

SOLUTION:

Henry's law states that partial pressure of a gas in the vapour phase is proportional to the mole fraction of the gas in the solution

Applications of Henry's law are mentioned as follows:

(i) Bottles are sealed under high pressure to increase the solubility of CO_2 in soft drinks and soda water.
(ii) Aquatic species feels uncomfortable in hot water.

Question 8
Write IUPAC name of the complex $[Pt(en)_2Cl_2]$. Draw structures of geometrical isomers for this complex.
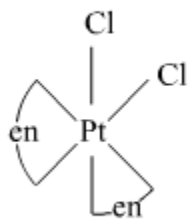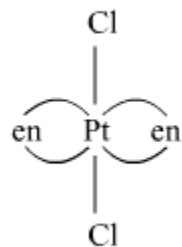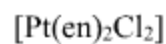**OR**
Using IUPAC norms write the formulae for the following:
(i) Hexaamminecobalt(III) sulphate
(ii) Potassium trioxalatochromate(III)

SOLUTION:

IUPAC name of the complex $[Pt(en)_2Cl_2]$ is Dichlorido bis(ethane-1,2-diammine) platinum(II).
The structures of geometrical isomers for this complex are:
$[Pt(en)_2Cl_2]$

trans-isomer   cis-isomer

(i) Hexaamminecobalt(III) sulphate - $[Co(NH_3)_6]_2(SO_4)_3$
(ii) Potassium trioxalatochromate(III) - $K_3[Cr(C_2O_4)_3]$

Question 9

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

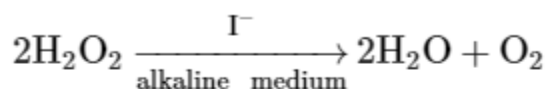(ii) HF, HCl, HBr, HI - decreasing bond enthalpy

SOLUTION:

(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 10

For a reaction

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

the proposed mechanism is as given below:
(1) $H_2O_2 + I^- \rightarrow H_2O + IO^-$ (slow)
(2) $H_2O_2 + IO^- \rightarrow H_2O + I^- + O_2$ (fast)

(i) Write rate law for the reaction.
(ii) Write the overall order of reaction.
(iii) Out of steps (1) and (2), which one is rate determining step?

SOLUTION:

$$2H_2O_2 \xrightarrow[\text{alkaline medium}]{I^-} 2H_2O + O_2$$
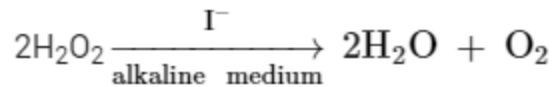
In Some cases, the rate of reaction depends not only on the reactant but may also depend on the substance present as a catalyst. This is also seen in the above reaction. The rate of reaction depends on the slowest step in case of a complex reaction.

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

(2) $H_2O_2 + IO^- \xrightarrow{\text{Fast}} H_2O + I^- + O2$
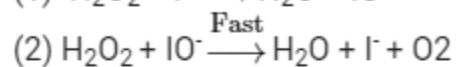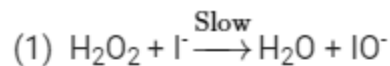
(i) Rate law:

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

(ii) The overall order of reaction:
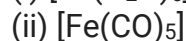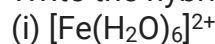
$\text{Rate} = k[H_2O_2][I^-]$

Order = 1+1 = 2

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

Question 11
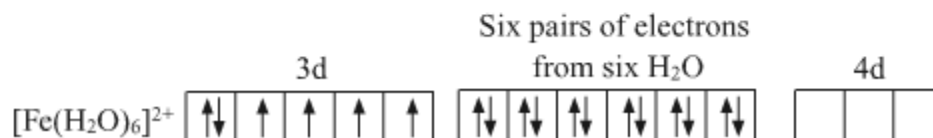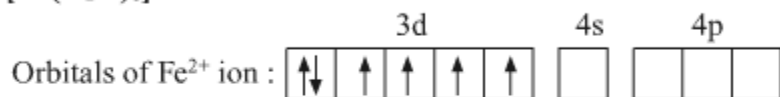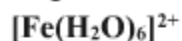Write the hybridization and magnetic character of following complexes:
(i) $[Fe(H_2O)_6]^{2+}$
(ii) $[Fe(CO)_5]$
(Atomic no. of Fe = 26)

SOLUTION:

(i) Hybridisation - sp^3d^2
  Magnetic character- Strongly paramagnetic
  $[Fe(H_2O)_6]^{2+}$

(ii) Hybridisation - dsp^3
Magnetic character - Diamagnetic

[Fe(CO)₅]

	3d	4s	4p

Orbitals of Fe ion : $\boxed{\uparrow\downarrow}\;\boxed{\uparrow}\;\boxed{\uparrow}\;\boxed{\uparrow}\;\boxed{\uparrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\;}\boxed{\;}\boxed{\;}$

dsp³ hybridised   3d   dsp³ hybrid
orbitals of Fe ion : $\boxed{\uparrow\downarrow}\;\boxed{\uparrow\downarrow}\;\boxed{\uparrow\downarrow}\;\boxed{\uparrow\downarrow}$ $\boxed{\;}\boxed{\;}\boxed{\;}\boxed{\;}\boxed{\;}$

Five pairs of electrons
3d   from five CO
[Fe(CO)₅] $\boxed{\uparrow\downarrow}\;\boxed{\uparrow\downarrow}\;\boxed{\uparrow\downarrow}\;\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}\;\boxed{\uparrow\downarrow}\;\boxed{\uparrow\downarrow}\;\boxed{\uparrow\downarrow}\;\boxed{\uparrow\downarrow}\;\boxed{\uparrow\downarrow}$
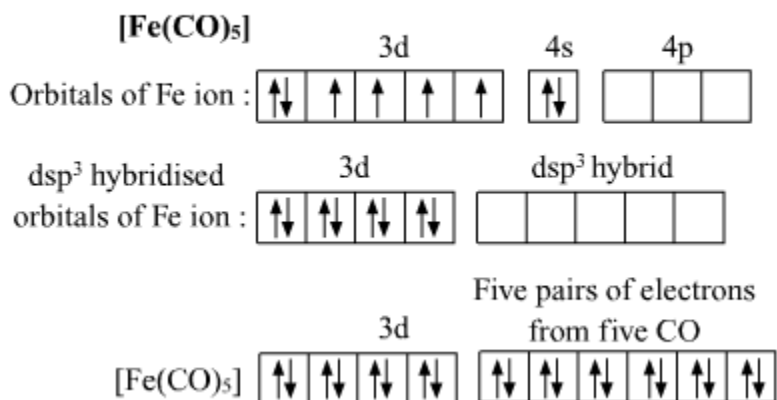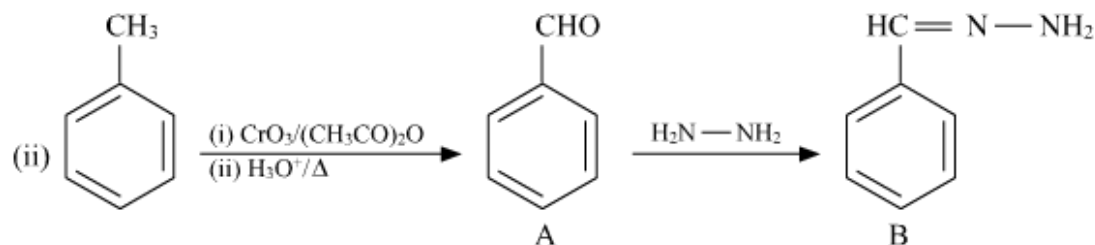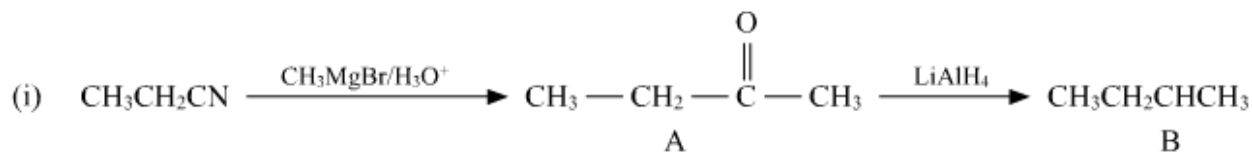
Question 12

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

(i) $CH_3CH_2CN \xrightarrow{CH_3MgBrH_3O^+} A \xrightarrow{LiAlH_4} B$

(ii) $\xrightarrow[\text{(ii) H}_3\text{O}^+/\Delta]{\text{(i) CrO}_3/(CH_3CO)_2O} A \xrightarrow{H_2N-NH_2} B$

SOLUTION:

(i) $CH_3CH_2CN \xrightarrow{CH_3MgBr/H_3O^+}$ $CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$ $\xrightarrow{LiAlH_4}$ $CH_3CH_2CHCH_3$
                                                          A   B

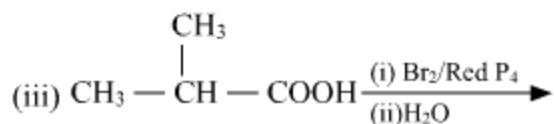(ii) $\xrightarrow[\text{(ii) H}_3\text{O}^+/\Delta]{\text{(i) CrO}_3/(CH_3CO)_2O}$ $\xrightarrow{H_2N-NH_2}$
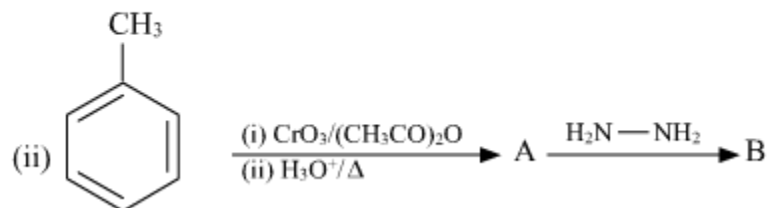
Question 13

Complete the following reactions:

(i) Reaction scheme with CHO on benzene ring and NaCN/HCl

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

(iii) $CH_3 - \underset{\underset{CH_3}{|}}{CH} - COOH \xrightarrow[\text{(ii)}H_2O]{\text{(i) } Br_2/\text{Red } P_4}$
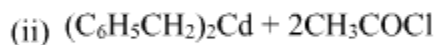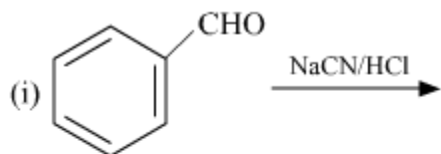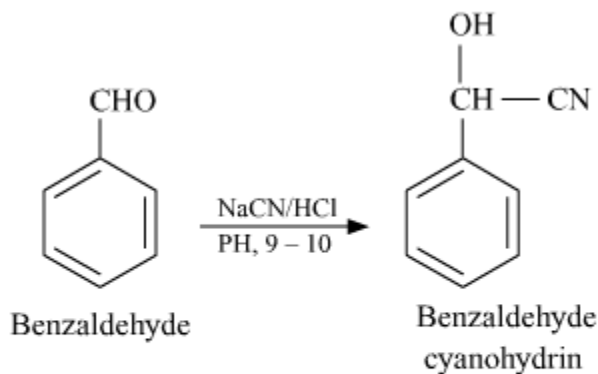
OR

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:

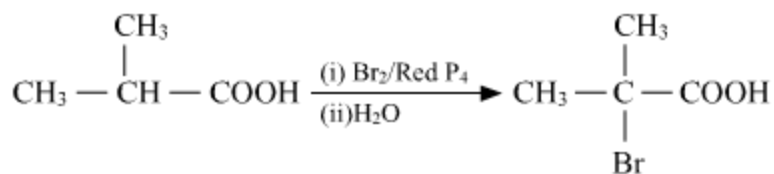(i). Reaction of benzaldehyde with NaCN/HCl gives **cyanohydrin**.

Benzaldehyde → Benzaldehyde cyanohydrin

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

$$2 \, CH_3\text{-}CO\text{-}Cl + (C_6H_5\text{-}CH_2)_2 \, Cd \rightarrow 2 \, CH_3\text{-}CO\text{-}CH_2\text{-}C_6H_5 + CdCl_2$$
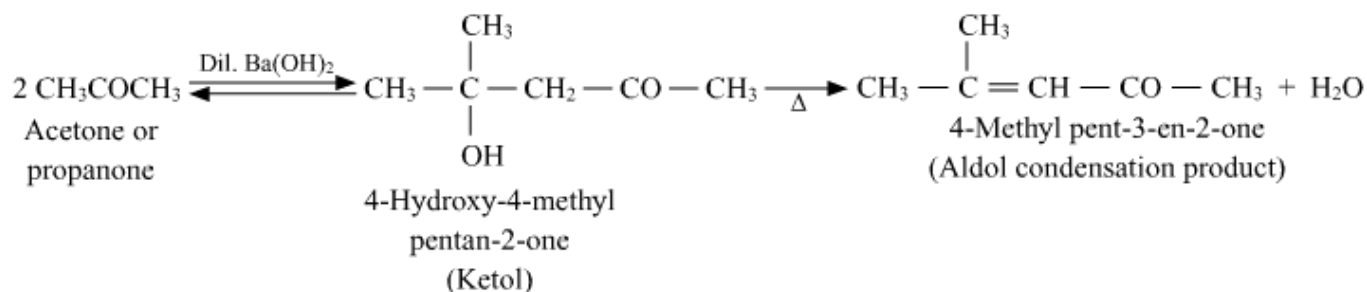1-Phenylpropan-2-one
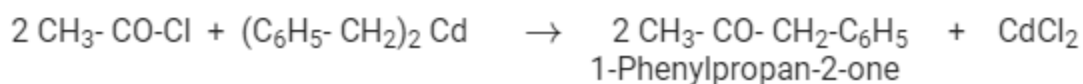
(iii) Carboxylic acid having α-hydrogen are halogenated at α-position on treatment with Br_2 in presence of red phosphorous to give α-halocarboxylic acids. This is **Hell-Volhard-Zelinsky reaction.**

$$CH_3-\underset{\underset{CH_3}{|}}{CH}-COOH \xrightarrow[\text{(ii)}H_2O]{\text{(i) } Br_2/\text{Red } P_4} CH_3-\underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{C}}-COOH$$

OR

(i) This is a self-aldol condensation reaction.

$$2\ CH_3COCH_3 \underset{\text{propanone}}{\overset{\text{Acetone or}}{\underset{\rightleftharpoons}{\xleftarrow{\text{Dil. } Ba(OH)_2}}}} CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-CO-CH_3 \xrightarrow{\Delta} CH_3-\overset{\overset{CH_3}{|}}{C}=CH-CO-CH_3 + H_2O$$

4-Hydroxy-4-methyl pentan-2-one (Ketol)

4-Methyl pent-3-en-2-one (Aldol condensation product)

(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.**
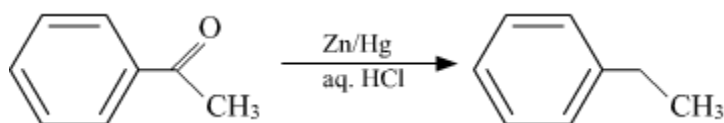

(iii) Benzoyl chloride is hydrogenated over catalyst Pd-BaSO$_4$ to give benzaldehyde. This reaction is called **Rosenmund Reaction**.

Benzoyl chloride   Benzaldehyde
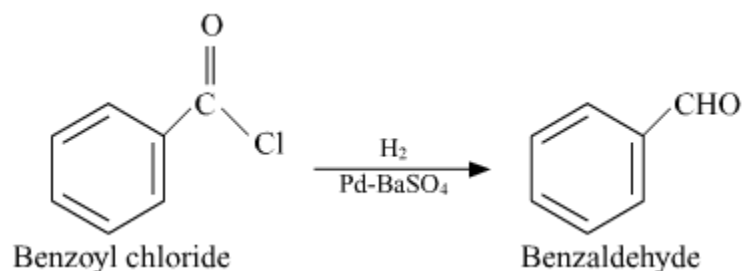
Question 14
(i) What is the role of activated charcoal in gas mask?
(ii) A colloidal sol is prepared by the given method in figure. What is the charge on hydrated ferric oxide colloidal particles formed in the test tube? How is the sol represented?

FeCl₃
solution

NaOH
solution
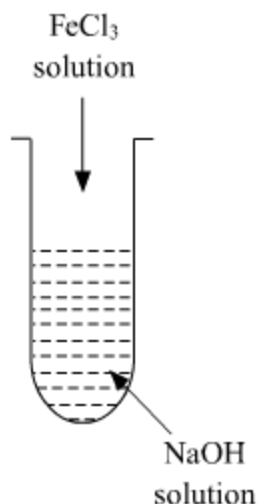
(iii) How does chemisorption vary with temperature?

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 $Fe_2O_3.xH_2O$ / OH^-

FeCl₃
solution

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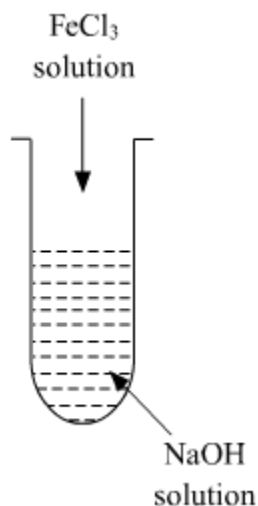
(iii) Effect of temperature on chemisorption: Even though chemical adsorption is an exothermic process, but like most chemical changes, the extent of chemisorption increases with increase in temperature up to a certain limit and then after that, it starts decreasing..

Question 15
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 ⇒ 4 g sucrose in 96 g water
w_2 (solute) = 4 g
w_1 (solvent) = 96 g
M_2 (solute) = 342 g mol⁻¹
$\Delta T_f = k_f\, m$
$T_f = 271.15$
$T_f^\circ = 273 \cdot 15$

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

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

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

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

$\Delta T_f = k_f\, m.$
* 5% solution(w/w) of glucose in water ⇒ 5 g glucose in 95 g H_2O
w_2 = 5 g
w_1 = 95 g
M_2 = 180 g

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

$\Delta T_f \cong 0.48$

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

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

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

$$= 272 \cdot 67$$

Question 16
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   (1pm $= 10^{-10}$ cm)
Density, $(\rho) = 10.8$ g/cm^3

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

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

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

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

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

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

$N = 14.8 \times 10^{23}$ atoms

Question 17
How will you convert the following:
(i) Impure Nickel to pure Nickel
(ii) Zinc blende to Zinc metal
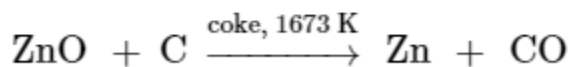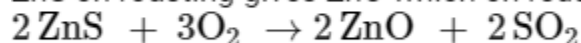(iii) $[Ag(CN)_2]^-$ to Ag

SOLUTION:

(i) Impure Nickel to pure Nickel is obtained by Mond process in which nickel is heated in a stream of carbon monoxide forming a volatile complex, nickel tetracarbonyl which is subjected to higher temperature to obtain pure metal.

$Ni + 4CO \xrightarrow{330 - 350 \text{ K}} Ni(CO)_4$

$Ni(CO)_4 \xrightarrow{450 - 470 \text{ K}} Ni + 4CO$
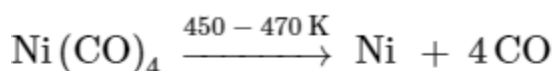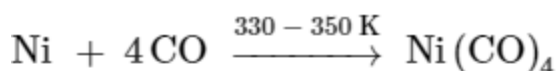
(ii) Zinc blende to Zinc metal
ZnS on roasting gives ZnO which on reduction gives zinc metal.
$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$

$ZnO + C \xrightarrow{\text{coke, 1673 K}} Zn + CO$

(iii) $[Ag(CN)_2]^-$ to Ag

The metal is recovered from the complex by reduction or displacement method using a more electropositive zinc metal.

$$2[\text{Ag(CN)}_2]^- + \text{Zn} \rightarrow 2\,\text{Ag} + [\text{Zn(CN)}_4]^{2-}$$
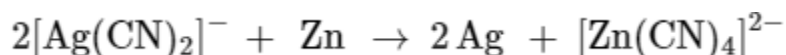
Question 18
Give reasons for the following:

(i) The transition metals generally form coloured compounds.

(ii) E^0 value for ($Mn^{3+}|Mn^{2+}$) is highly positive than that for ($Cr^{3+}|Cr^{2+}$) couple.

(iii) The chemistry of actinoids elements is not so smooth as that of the lanthanoids.

SOLUTION:
(i) Most of the complexes of transition metals are coloured. This is because of the absorption of radiation from visible light region to promote an electron from one of the d - orbitals to another. In the presence of ligands, the d - orbitals split up into into two sets of orbitals having different energies. Therefore, the transition of electrons can take place from one set to another. The energy required for these transitions is quite small and falls in the visible region of radiation. The ions of transition metals absorb the radiation of a particular wavelength and the rest is reflected , imparting colour to the solution.

(ii) Much larger third ionisation energy of Mn (where the required change is d^5 to d^4) is mainly responsible for high E^0 value for ($Mn^{3+}|Mn^{2+}$) couple than that for ($Cr^{3+}|Cr^{2+}$) couple.

(iii) Lanthanoids primarily show three oxidation states (+2, +3, +4). Among these oxidation states, +3 state is the most common. Lanthanoids display a limited number of oxidation states because the energy difference between 4f, 5d, and 6s orbitals is quite large. On the other hand, the energy difference between 5f, 6d, and 7s orbitals is very less. Hence, actinoids display a large number of oxidation states. For example, uranium and plutonium display +3, +4, +5, and +6 oxidation states while neptunium displays +3, +4, +5, and +7. The most common oxidation state in case of actinoids is also +3.

Question 19
(i) Why type of drug is used in sleeping pills?
(ii) What type of detergent are used in toothpastes?
(iii) Why the use of alitame as artificial sweetener is not recommended?
              OR
Define the following terms with a suitable example in each:
(i) Broad-spectrum antibiotics

(ii) Disinfectants
(iii) Cationic detergents

SOLUTION:

(i)Tranquilizers form an essential component of sleeping pills. They are a class of chemical compounds used for the treatment of stress and mild or even severe mental diseases. These relieve anxiety, stress, irritability or excitement by inducing a sense of well-being.

(ii)Anionic detergents are used in toothpaste.
 Anionic detergents are sodium salts of sulphonated long chain alcohols or hydrocarbons. In anionic detergents, the anionic part of the molecule is involved in the cleansing action. Sodium salts of alkylbenzenesulphonates are an important class of anionic detergents.

(iii) Alitame, an artificial sweetening agent, is high potency sweetener. The control of sweetness of food is difficult while using it, hence it is not recommended to use it.

OR

(i)Antibiotics which kill or inhibit a wide range of Gram-positive and Gram-negative bacteria are said to be broad spectrum antibiotics.
Chloramphenicol, Vancomycin, and ofloxacin are broad-spectrum antibiotics.

(ii) Disinfectants are the chemicals which either kill or prevent the growth of microorganisms. They are applied to inanimate objects such as floors, drainage system, instruments, etc.
Chlorine in the concentration of 0.2 to 0.4 ppm in aqueous solution is a disinfectant.

(iii) Cationic detergents are quarternary ammonium salts of amines with acetates, chlorides or bromides. Cationic part possesses a long hydrocarbon chain and a positive charge on nitrogen atom.
Cetyltrimethylammonium bromide is a cationic detergent and is used in hair conditioners.

Question 20

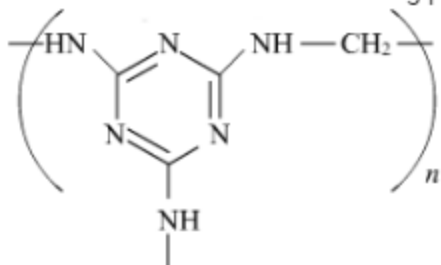Write the structures of monomers used for getting the following polymers:

(i) Nylon-6,6
(ii) Glyptal
(iii) Buna-S

OR

$$+CH_2-\overset{\overset{\displaystyle CH_3}{|}}{CH}+_n$$
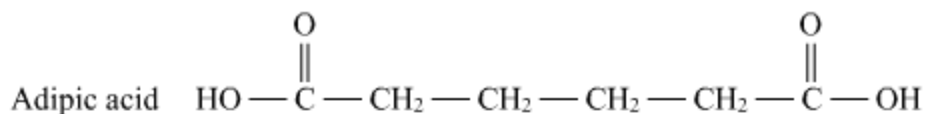
(i) Is a homopolymer or copolymer? Give reason.

(ii) Write the monomers of the following polymer:

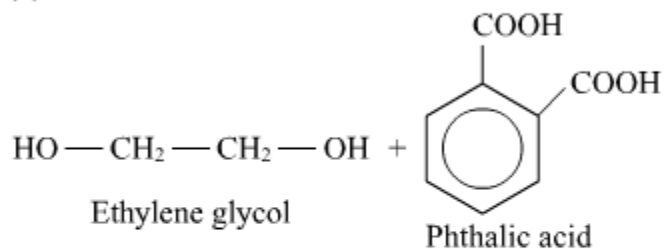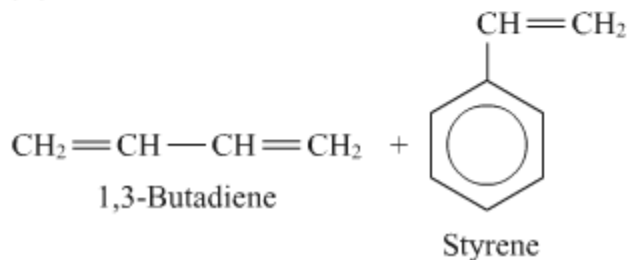(iii) What is the role of Sulphur in the vulcanization of rubber?

SOLUTION:

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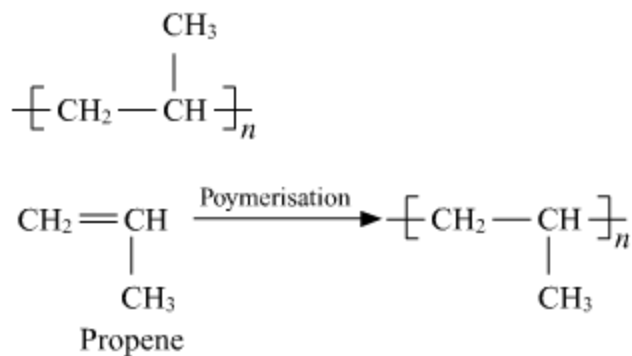
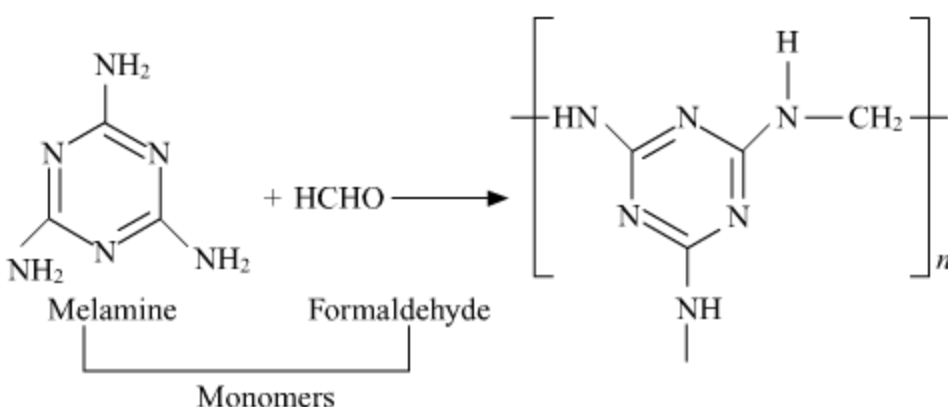

(ii) Glyptal:

(iii) Buna-S

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.

$$CH_2=CH \xrightarrow{\text{Poymerisation}} \left[CH_2-CH\right]_n$$

Propene

(ii)

Melamine + HCHO ⟶

Formaldehyde

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 21

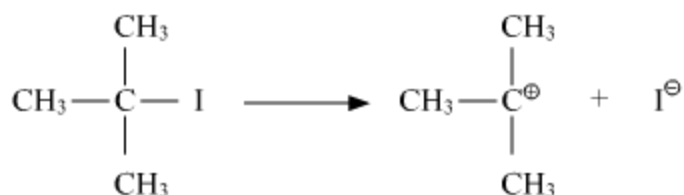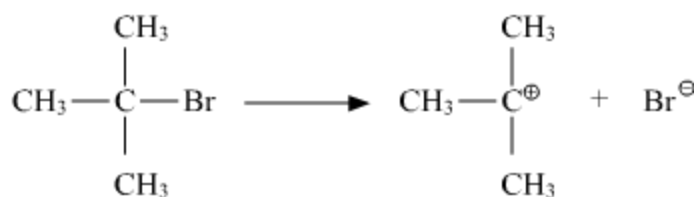(i) Out of $(CH_3)_3C-Br$ and $(CH_3)_3C-I$, which one is more reactive towards S_N1 and why?

(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_N1 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_N1 reaction will be faster in $(CH_3)_3-I$

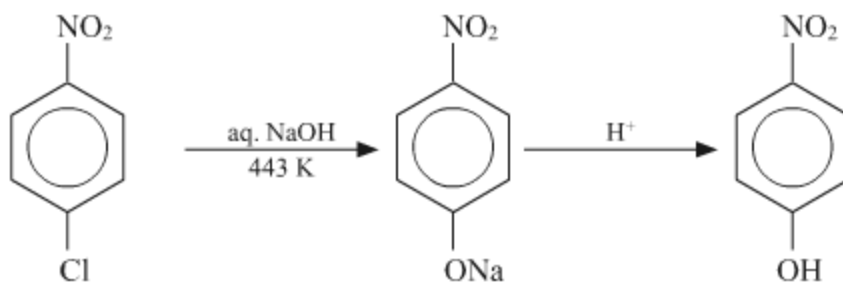$(CH_3)_3 — Br$

$$CH_3 \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} Br \longrightarrow CH_3 \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C^{\oplus}}} + Br^{\ominus}$$

$$CH_3 \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} I \longrightarrow CH_3 \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C^{\oplus}}} + I^{\ominus}$$
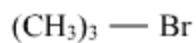
(ii)

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.

$$CH_3 — CH_2 — \overset{\overset{OH}{|}}{CH} — CH_3$$
Butan-2-ol
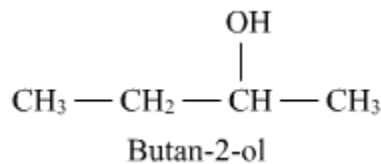
Question 22
Write equations of the following reactions:

(i) Acetylation of aniline

(ii) Coupling reaction

(iii) Carbyl amine reaction

SOLUTION:

(i)

(ii)

(iii)

$$R-NH_2 + CHCl_3 + 3\ KOH \xrightarrow{\text{Heat}} R-NC + 3\ KCl + 3\ H_2O$$
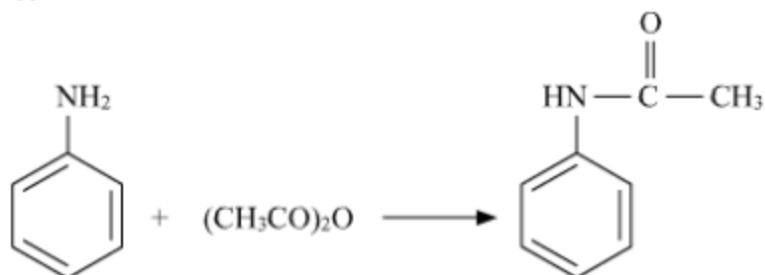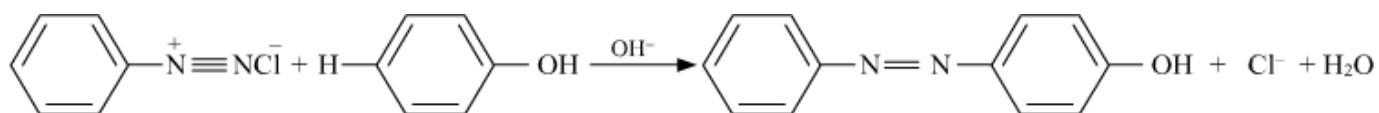
Question 23

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,

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

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

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

Question 24

Define the following with a suitable example in each:

(i) Oligosaccharides

(ii) Denaturation of protein

(iii) Vitamins

OR

Write the reactions involved when D-glucose is treated with the following reagents:

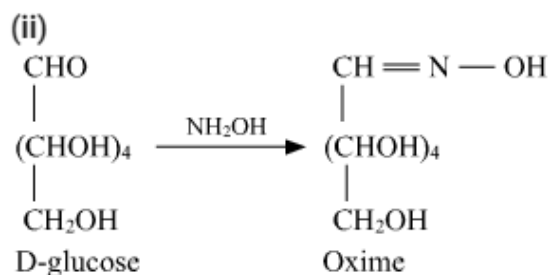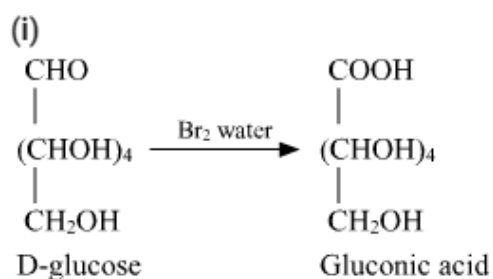(i) Br_2 water

(ii) H_2N-OH
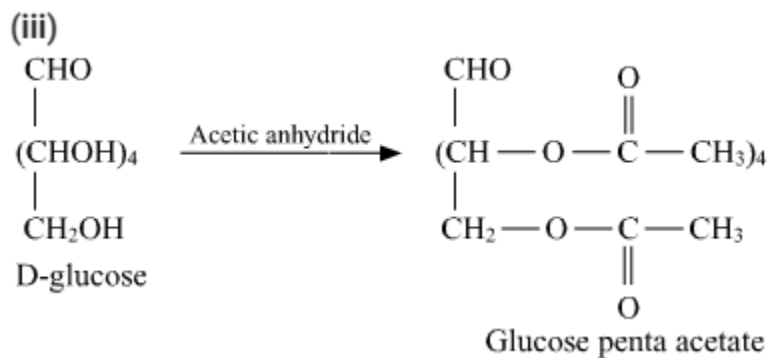
(iii) $(CH_3CO)_2O$

SOLUTION:

(i) Oligosaccharides: Carbohydrates that yield two to ten monosaccharide units, on hydrolysis are called oligosaccharides. For example: sucrose.

(ii) Denaturation of protein: When a protein in its native form, is subjected to physical change like change in temperature or chemical change like change in pH, the hydrogen bonds are disturbed. Due to this, globules unfold and helix get uncoiled and protein loses its biological activity. This is called denaturation of protein. For example: coagulation of egg white.

(iii) Vitamins: Organic compounds required in the diet in small amounts to perform specific biological functions for normal maintenance of optimum growth and health of the organism. For example: vitamin A, deficiency of which causes night blindness.

OR

(i)

$$\underset{\text{D-glucose}}{\underset{CH_2OH}{\overset{CHO}{|}} \atop (CHOH)_4} \xrightarrow{Br_2\ water} \underset{\text{Gluconic acid}}{\underset{CH_2OH}{\overset{COOH}{|}} \atop (CHOH)_4}$$

(ii)

$$\underset{\text{D-glucose}}{\underset{CH_2OH}{\overset{CHO}{|}} \atop (CHOH)_4} \xrightarrow{NH_2OH} \underset{\text{Oxime}}{\underset{CH_2OH}{\overset{CH=N-OH}{|}} \atop (CHOH)_4}$$

(iii)

D-glucose → (Acetic anhydride) → Glucose penta acetate

$$\begin{array}{c} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} \quad \xrightarrow{\text{Acetic anhydride}} \quad \begin{array}{c} CHO \\ | \\ (CH-O-\overset{\overset{\displaystyle O}{||}}{C}-CH_3)_4 \\ | \\ CH_2-O-C-CH_3 \\ \quad\quad\quad || \\ \quad\quad\quad O \end{array}$$
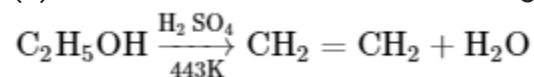
D-glucose → Glucose penta acetate

Question 25

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

(b) Write mechanism of the following reaction:

$$C_2H_5OH \xrightarrow[443K]{H_2SO_4} CH_2 = CH_2 + H_2O$$

(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.

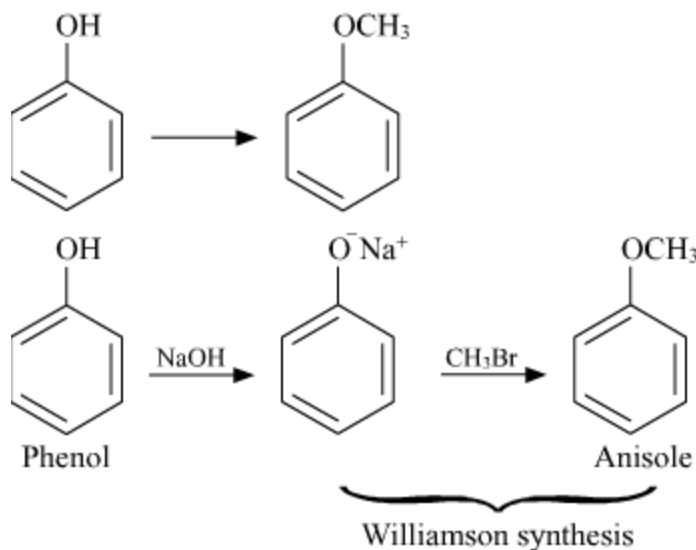(b) Write the reaction involved in the following:
    (i) Reimer-Tiemann reaction
    (ii) Friedal-Crafts Alkylation of Phenol

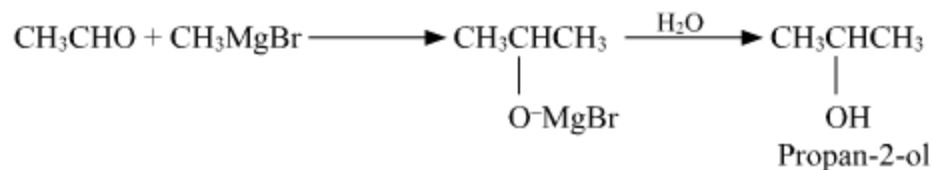(c) Give simple chemical test to distinguish between Ethanol and Phenol.

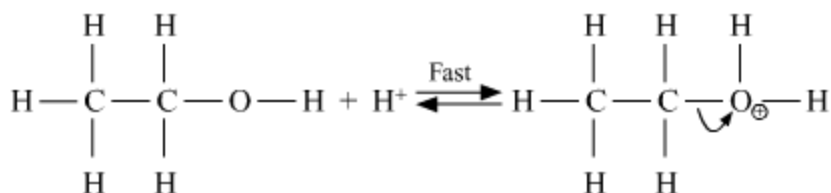SOLUTION:

(a) (i)
Phenol to anisole

Williamson synthesis

(a) (ii)

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

$$CH_3CHO + CH_3MgBr \longrightarrow \underset{\underset{O^-MgBr}{|}}{CH_3CHCH_3} \xrightarrow{H_2O} \underset{\underset{OH}{|}}{CH_3CHCH_3}$$
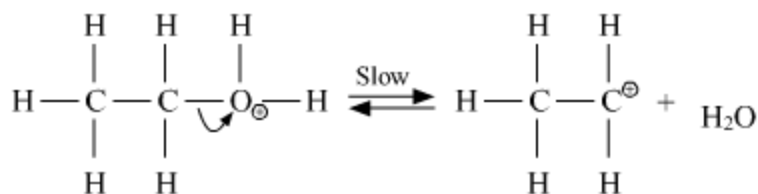Propan-2-ol

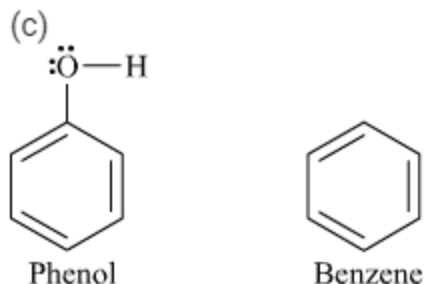## (b) Mechanism : Dehydration of ethanol
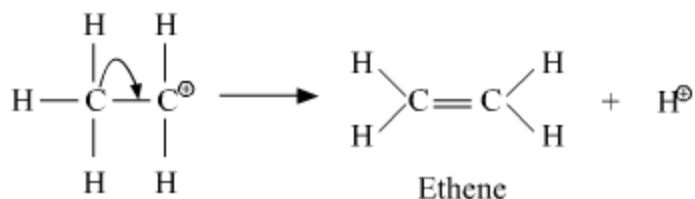Step 1: Formation of protonated alcohol

Step 2: Formation of carbocation (slow step)

Step 3: Formation of ethene
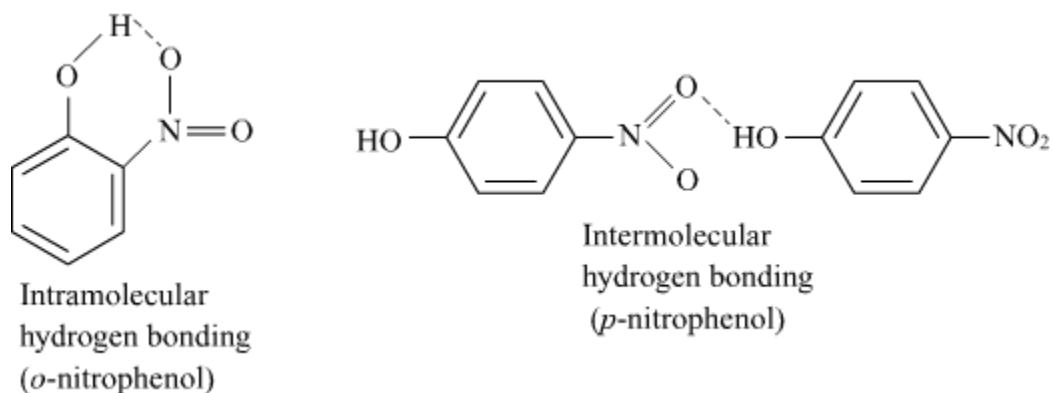

Ethene

(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)

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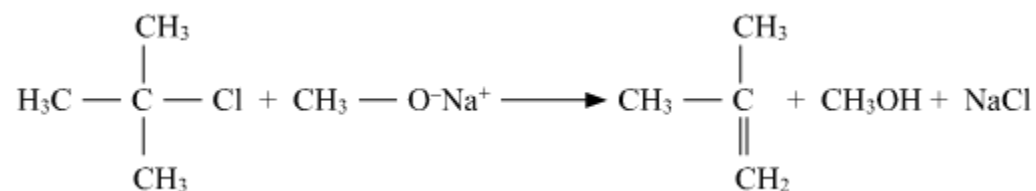
William synthesis

$$R - X + R - \overset{..}{\underset{..}{O}} - Na \longrightarrow R - \overset{..}{\underset{..}{O}} - R + NaX$$
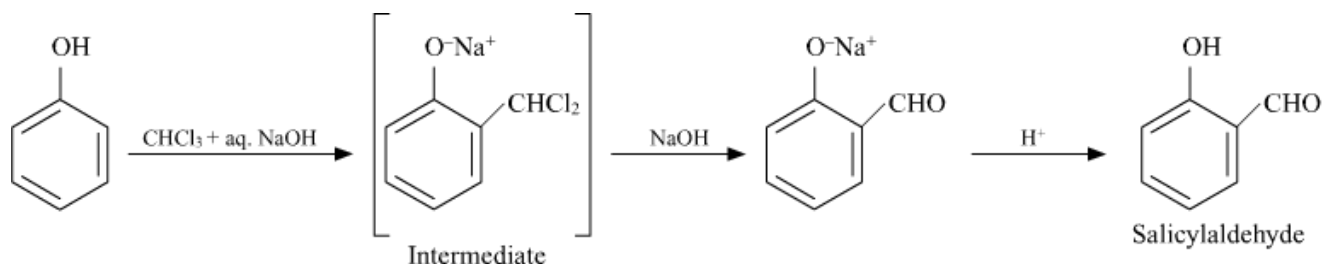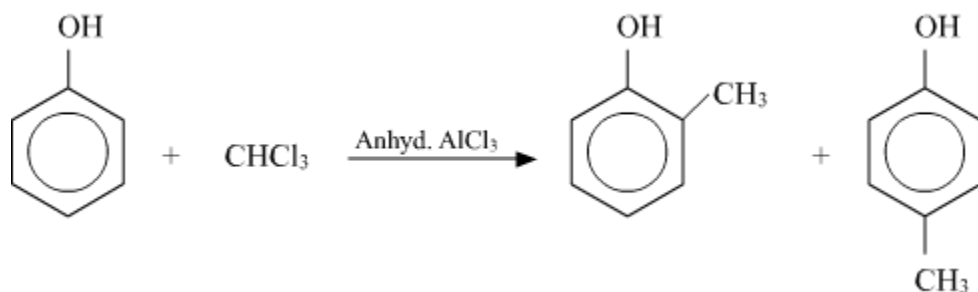
The alkyl halide must be 1^0 as the reaction involves the S_N2 reaction pathway.
If alkyl halide is 3^0 then the alkene will be the major product. Hence, 2-methylpropene is formed instead of t-butylmethylether.

(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.

Question 26
(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.

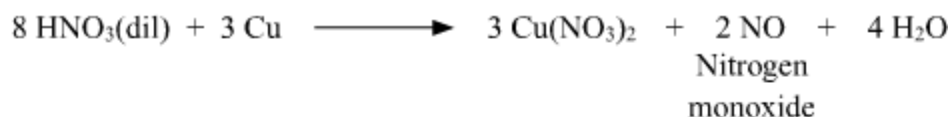(c) Write a chemical reaction to test sulphur dioxide gas. Write chemical equation involved.

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.
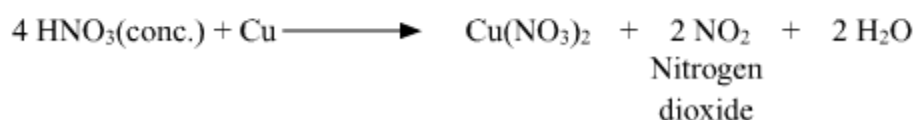
(A) (ii) The nitrogen atom is smaller in size than the Phosphorus atom. The bond length of N-N bond is smaller than that of P-P bond. Due to this, the four non-bonding electrons of the two nitrogen atoms repel each other making the bond weaker.
This does not happen in the case of phosphorus because P-P 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

$$8\, HNO_3(dil) + 3\, Cu \longrightarrow 3\, Cu(NO_3)_2 + 2\, \underset{\substack{\text{Nitrogen} \\ \text{monoxide}}}{NO} + 4\, H_2O$$

(b)(ii) Nitrogen dioxide

$$4\, HNO_3(conc.) + Cu \longrightarrow Cu(NO_3)_2 + 2\, \underset{\substack{\text{Nitrogen} \\ \text{dioxide}}}{NO_2} + 2\, H_2O$$

a). (i) $4H_3\,(PO_3) \xrightarrow{\Delta} 3H_3\,(PO_4) + PH_3$
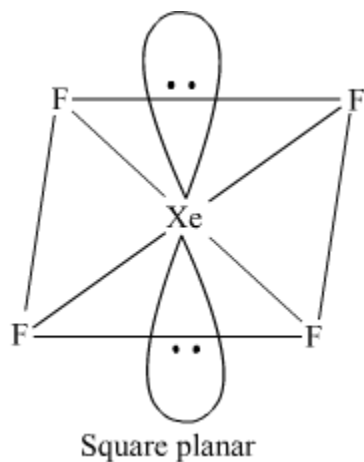 (ii) XeF_4
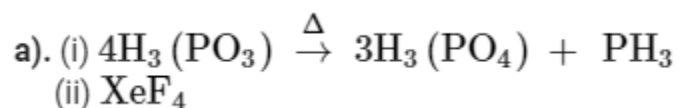
It has a square planar structure. Six electron pairs form an octahedron with two positions occupied by lone pairs.
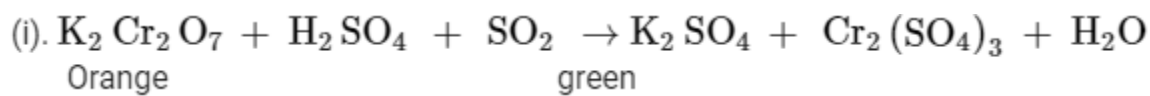

Square planar

(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.
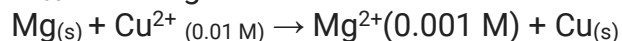
(ii).Acidic character of oxides of group 15 elements decreases and basicity increases down the group. As we move down the group, the atomic size increases, electronegativity decreases and metallic character increases. Oxides of Nitrogen and phosphorous are acidic whereas those of As and Sb are amphoteric 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 27

$E°_{cell}$ 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:
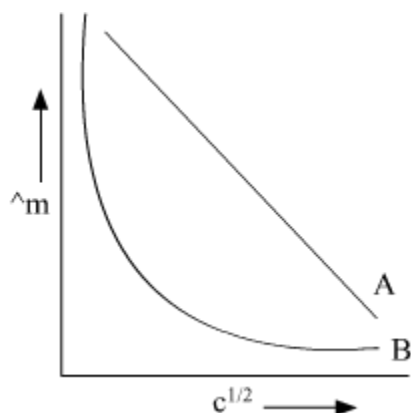
Answer the following:
(i) Predict the nature of electrolytes A and B.
(ii) What happens on extrapolation of Λ_m to concentration approaching zero for electrolytes A and B?

SOLUTION:

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

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) $Fe^{2+} \; 2e^- \rightarrow Fe$

56 g of Fe requires = 2 × 96500 C charge

$$2.8 \text{ g of Fe requires} = \frac{2 \times 96500}{56} \times 2.8 \text{ C charge}$$
$$Q = 9650 \text{ C}$$

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

(ii) $Zn^{2+} + 2e^- \rightarrow Zn$

2 × 96500 C of electricity deposit Zn = 65.3 g

$$1 \text{ C of electricity deposit Zn} = \frac{65.3}{2 \times 96500}$$

$$9650 \text{ C of electricity deposit Zn} = \frac{65.3}{2 \times 96500} \times 9650$$
$$= 3.265 \text{g}$$

(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.