SAMPLE QUESTION PAPER

BLUE PRINT

Time Allowed : 3 hours **Maximum Marks :** 70

S. No.	Chapter	Passage based/ MCQs/A & R (1 mark)	SA-I (2 marks)	SA-II (3 marks)	LA (5 marks)	Total
1.	The Solid State	1(1)	1(2)	–	–	**11(23)**
2.	Solutions	2(2)	1(2)	–	–	
3.	Electrochemistry	1(1)	–	1(3)	–	
4.	Chemical Kinetics	1(1)	–	–	1(5)	
5.	Surface Chemistry	1(4)	1(2)	–	–	
6.	The *p*-Block Elements	2(2)	1(2)	1(3)	–	**9(19)**
7.	The *d*- and *f*-Block Elements	1(1)	1(2)	1(3)	–	
8.	Coordination Compounds	1(1)	–	–	1(5)	
9.	Haloalkanes and Haloarenes	1(1)	–	–	1(5)	**13(28)**
10.	Alcohols, Phenols and Ethers	1(1)	1(2)	1(3)	–	
11.	Aldehydes, Ketones and Carboxylic Acids	1(4)	1(2)	–	–	
12.	Amines	2(2)	1(2)	1(3)	–	
13.	Biomolecules	1(1)	1(2)	–	–	
	Total	**16(22)**	**9(18)**	**5(15)**	**3(15)**	**33(70)**

Subject Code : **043**

CHEMISTRY

Time allowed : 3 hours ***Maximum marks : 70***

General Instructions : Read the following instructions carefully.

(a) There are 33 questions in this question paper. All questions are compulsory.

(b) Section A : Q. No. 1 to 16 are objective type questions. Q. No. 1 and 2 are passage based questions carrying 4 marks each while Q. No. 3 to 16 carry 1 mark each.

(c) Section B : Q. No. 17 to 25 are short answer questions and carry 2 marks each.

(d) Section C : Q. No. 26 to 30 are short answer questions and carry 3 marks each.

(e) Section D : Q. No. 31 to 33 are long answer questions carrying 5 marks each.

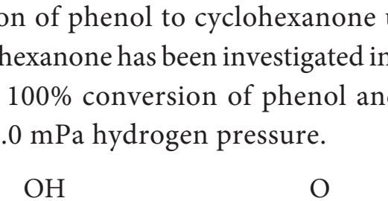
(f) There is no overall choice. However, internal choices have been provided.

(g) Use of calculators and log tables is not permitted.

SECTION - A (OBJECTIVE TYPE)

1. **Read the passage given below and answer the following questions :**

Cyclohexanone is an important intermediate in the manufacture of polyamides in chemical industry but direct selective hydrogenation of phenol to cyclohexanone under mild conditions is a challenge. Hydrogenation of phenol to cyclohexanone has been investigated in the presence of the composite catalytic system of Pd/C heteropolyacid. 100% conversion of phenol and 93.6% selectivity of cyclohexanone were achieved under 80°C and 1.0 mPa hydrogen pressure.



It has been found that a synergetic effect of Pd/C and heteropolyacid enhanced the catalytic performance of the composite catalytic system which suppressed the hydrogenation of cyclohexanone to cyclohexanol.

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) The palladium-based catalyst mention in the study above can be used to convert selectively only

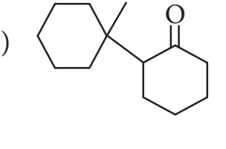
(a) cyclohexanone to cyclohexanol
(b) phenol to cyclohexanone
(c) phenol to cyclohexane
(d) phenol to cyclohexanol.

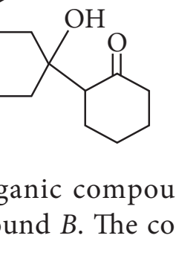
(ii) The product formed during hydrogenation of phenol by using this Pd–C + HPA catalyst can also be obtained by

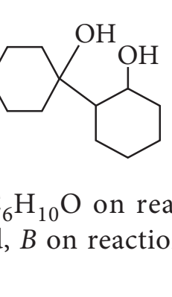
(a) oxidation of cyclohexane in air
(b) reduction of cyclohexane in Sn/HCl
(c) oxidation of cyclohexanol in air
(d) reduction of hexanone in air.

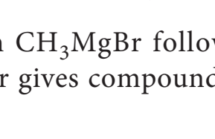
OR

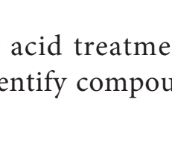
What will be the product of following reaction.



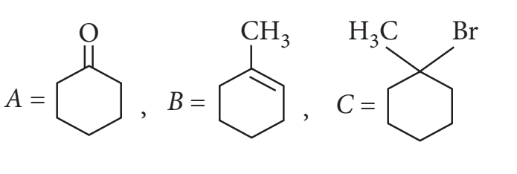
(a) 

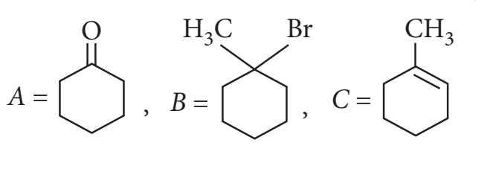
(b) 

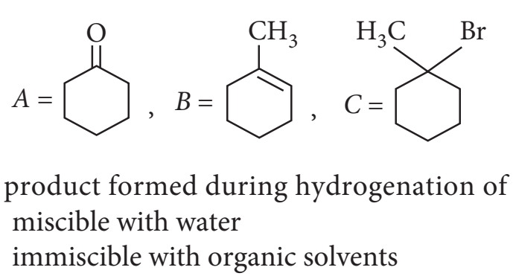
(c) 

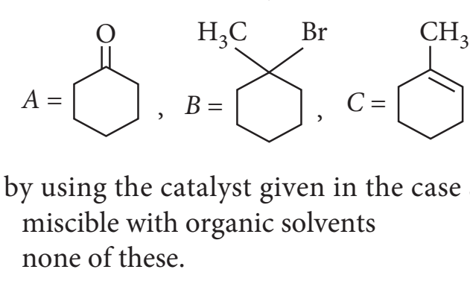
(d) 

(iii) An organic compound *A*, $C_6H_{10}O$ on reaction with CH_3MgBr followed by acid treatment gives compound *B*. The compound, *B* on reaction with HBr gives compound, *C*. Identify compound *A*, *B* and *C*.

(a) 

(b) 

(c) 

(d) 

(iv) The product formed during hydrogenation of phenol by using the catalyst given in the case study is

(a) miscible with water
(b) miscible with organic solvents
(c) immiscible with organic solvents
(d) none of these.

2. Read the passage given below and answer the following questions :

Colloids and colloidal systems are essential to life. They are extremely useful, even indispensable, in many commercial and industrial situations as well. They function in every body cell, in the blood and in all body fluids especially the intercellular fluids, formally known as "humus".

The colloidal solutions are heterogeneous in nature consisting of two phases : (i) dispersed phase and (ii) dispersion medium. The colloidal particles being bigger aggregates have high molecular masses so that the number of particles per litre of the sol is relatively very small than in a true solution. Therefore, they have low colligative properties. A critical indicator of colloidal system's quality is its color. Presence of charge on colloidal particles make them very stable.

In these questions (Q. No i-iv) , a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

(i) **Assertion :** On passing electric current in colloidal solution they do not move towards anode or cathode.
Reason : They contains positive and negative charge.

(ii) **Assertion :** Colloidal solutions show colligative properties.
Reason : Colloidal particles are bigger in size.

(iii) **Assertion :** Colloidal solution shows Tyndall effect.
Reason : Colloidal particles scatter light in all directions in space.

OR

Assertion : Sea water looks blue.
Reason : Due to scattering of light by colloidal impurities in sea water.

(iv) Assertion : Colloidal solution is a heterogenous in nature.
Reason : Colloidal solution is composed of one kind of solute particles.

Following questions (Q. No. 3-11) are multiple choice questions carrying 1 mark each :

3. In the laboratory, when crystals of NaCl are heated in an atmosphere of sodium vapour, the salt obtained is yellow in colour. The cause of yellow colour is
(a) presence of Na^+ ions in the crystal lattice
(b) presence of Cl^- ions in the crystal lattice
(c) presence of electrons in the crystal lattice
(d) presence of face-centred cubic crystal lattice.

OR

An element (density = 7.20 g/cc) exists in the body centred-cubic structure whose cell edge is 2.88 Å. The number of atoms in 104 g of the element is
(a) 2.0×10^{23}
(b) 1.209×10^{24}
(c) 2.418×10^{24}
(d) 6.045×10^{23}

4. Aryl halides are less reactive towards nucleophilic substitution reactions as compared to alkyl halides due to
(a) formation of a less stable carbonium ion in aryl halides
(b) resonance stabilisation in aryl halides
(c) presence of double bonds in alkyl halides
(d) inductive effect in aryl halides.

5. Ethylenediamine is
(a) monodentate
(b) bidentate
(c) tridentate
(d) tetradentate.

OR

The complex that does not give a precipitate with $AgNO_3$ solution is
(a) $[Co(NH_3)_3Cl_3]$
(b) $[Co(NH_3)_6]Cl_3$
(c) $[Ag(NH_3)_2]Cl$
(d) $[Cr(NH_3)_4Cl_2]Cl$

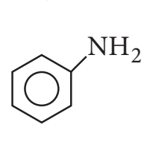
6. An azeotropic mixture of two liquids has boiling point lower than either of them when it
(a) shows negative deviation from Raoult's law
(b) shows no deviation from Raoult's law
(c) shows positive deviation from Raoult's law
(d) is saturated.

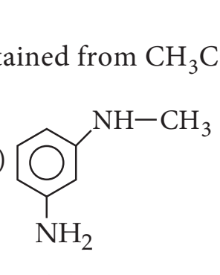
7. The element of group-17 whose half life is in milliseconds only is
(a) Ts
(b) Te
(c) At
(d) Og

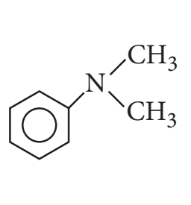
8. When ethyl bromide reacts with excess of alcoholic ammonia, the major product is
(a) ethylamine
(b) diethylamine
(c) triethylamine
(d) tetraethylammonium bromide.

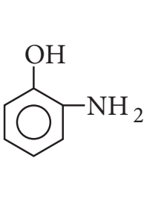
OR

N-Phenylethanamide is obtained from CH_3COCl with

(a) 

(b) 

(c) 

(d) 

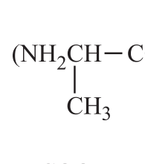
9. The common oxidation state of the elements of lanthanoid series is
(a) +2
(b) +3
(c) +4
(d) +1

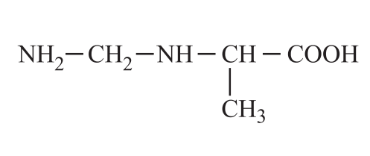
10. In a first-order reaction $A \longrightarrow B$, if k is rate constant and initial concentration of the reactant A is 0.5 M then the half-life is
(a) $\frac{\ln 2}{k}$
(b) $\frac{0.693}{0.5k}$
(c) $\frac{\log 2}{k}$
(d) $\frac{\log 2}{k\sqrt{0.5}}$

11. Hydrolysis of sucrose is called
   (a) hydration
   (b) saponification
   (c) esterification
   (d) inversion.

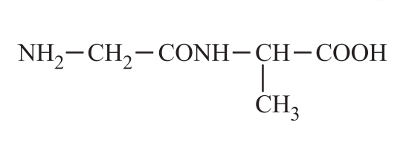
OR

The peptide linkage formed between glycine (NH_2CH_2COOH) and alanine $(NH_2\underset{\displaystyle CH_3}{\underset{|}{CH}}-COOH)$ to give glycylalanine can be shown as

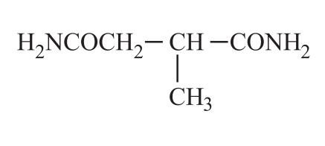


(a) 

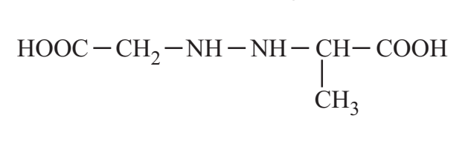
$NH_2-CH_2-NH-\underset{\displaystyle CH_3}{\underset{|}{CH}}-COOH$

(b) 

$NH_2-CH_2-CONH-\underset{\displaystyle CH_3}{\underset{|}{CH}}-COOH$

(c) 

$H_2NCOCH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CONH_2$

(d) 

$HOOC-CH_2-NH-NH-\underset{\displaystyle CH_3}{\underset{|}{CH}}-COOH$

The following questions (Q. No. 12-16) a statement of assertion following by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

12. **Assertion :** F atom has less negative electron affinity than Cl atom.
    Reason : Additional electrons are repelled more effectively by 3*p*- electrons in Cl than by 2*p*- electrons in F atom.

13. **Assertion :** Ammonolysis of alkyl halides involves reaction between alkyl halides and alcoholic ammonia.
    Reason : Ammonolysis of alkyl halides mainly produces 2° amines.

14. **Assertion :** Copper is dissolved at anode and deposited at cathode when Cu electrodes are used and electrolyte is 1 M $CuSO_{4(aq)}$ solution.
    Reason : Standard oxidation potential of Cu is less than standard oxidation potential of water and standard reduction potential of Cu is greater than that of water.

15. **Assertion :** Henry's law and Raoult's law are not independent, *i.e.*, one can be derived from the other.
    Reason : The partial pressure is directly proportional to the mole fraction of the concerned species for ideal solutions.

16. **Assertion :** Both symmetrical and unsymmetrical ethers can be prepared by Williamson's synthesis.
    Reason : Williamson's synthesis is an example of nucleophilic substitution reaction.

OR

Assertion : Anisole undergoes electrophilic substitution at *o*- and *p*-positions.
Reason : Anisole is less reactive than phenol towards electrophilic substitution reactions.

SECTION - B

The following questions Q. No. 17-25 are short answer type and carry 2 marks each.

17. (i) Which type of deviation is shown by the solution formed by mixing cyclohexane and ethanol?
    (ii) *A* and *B* liquids on mixing produced a warm solution. Which type of deviation is there and why?

OR

A 10% solution (by mass) of sucrose in water has freezing point of 269.15 K. Calculate the freezing point of 10% glucose in water, if freezing point of pure water is 273.15 K.
(Given : Molar mass of sucrose = 342 g mol^{-1}, molar mass of glucose = 180 g mol^{-1})

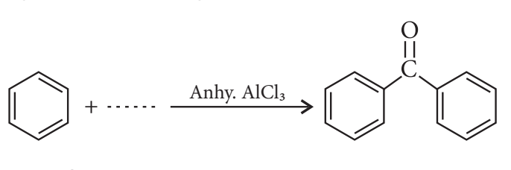
18. Which halogen will produce O_2 and O_3 as passed through water?

19. Calculate the percent change in density when *bcc* iron changes to *fcc* iron, on heating. The lengths of the edges in the *bcc* and *fcc* lattices are 286.3 pm and 359.1 pm respectively.

20. Complete each synthesis by giving the missing material, reagent or product :

(i) $C_6H_5COCl \xrightarrow[Pd-BaSO_4]{H_2}$ ......

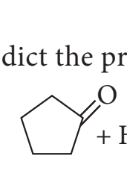
(ii)



OR

Predict the products of the following reactions :

(i)



$+ HO - NH_2 \xrightarrow{H^+}$

(ii) $CH_3COCH_2COOC_2H_5 \xrightarrow[(ii)\ H^+]{(i)\ NaBH_4}$

21. Explain why Hg(I) ion exists as Hg_2^{2+} while Cu(I) ion exists as Cu^+ ion.

OR

(i) Why do the transition metals show variability in their oxidation states?
(ii) Write formula of a compound where the transition metal is in +7 oxidation state.

22. 3,3-Dimethylbutan-2-ol loses a molecule of water in the presence of concentrated sulphuric acid to give tetramethylethylene as the major product. Suggest a suitable mechanism.

23. An optically active compound having molecular formula, $C_6H_{12}O_6$ is found in two isomeric forms (*A*) and (*B*) in nature. When (*A*) and (*B*) are dissolved in water they show the following equilibrium :

$$\begin{array}{lccc} & (A) & \rightleftharpoons \text{ Equilibrium mixture } \rightleftharpoons & (B) \\ [\alpha]_D & +111° & +52.2° & +19.2° \end{array}$$

(a) What are such isomers called?
(b) Can they be called enantiomers? Justify your answer.

24. (i) What is Helmholtz electrical double layer?
(ii) How is dialysis carried out? Mention its one application.

25. Answer the following :
(i) How is aniline obtained from benzene?
(ii) Write a chemical reaction of aniline which distinguish it from ethylamine.

SECTION - C

Q. No. 26-30 are short answer type II carrying 3 marks each.

26. A cell is prepared by dipping copper rod in 1 M copper sulphate solution and zinc rod in 1 M zinc sulphate solution. The standard reduction potential of copper and zinc are 0.34 V and –0.76 V respectively.
(i) What will be the cell reaction?

(ii) What will be the standard electromotive force of the cell?

(iii) Which electrode will be positive?

OR

Predict the products of electrolysis in each of the following :

(i) An aqueous solution of $AgNO_3$ with platinum electrodes.

(ii) An aqueous solution of H_2SO_4 with platinum electrodes.

27. Give examples and suggest reasons for the following features of the transition metal chemistry :

(i) The lowest oxide of transition metal is basic, the highest is amphoteric/acidic.

(ii) A transition metal exhibits highest oxidation state in oxides and fluorides.

(iii) The highest oxidation state is exhibited in oxoanions of a metal.

28. (i) An organic compound '*A*', C_7H_9N on reaction with nitrous acid gave benzyl alcohol. Predict the structure of the compound and give its various isomeric structures.

(ii) $CH_3CN \xrightarrow{H_2O/H^+} A \xrightarrow{NH_3} B \xrightarrow{Br_2 + KOH} C$

Identify *A*, *B* and *C*.

29. Write the equation of the reaction of the hydrogen iodide with

(i) 1-propoxypropane

(ii) methoxybenzene

(iii) benzyl ethyl ether.

30. Give reason for the following :

(i) CN^- ion is known but CP^- ion is not known.

(ii) NO_2 dimerises to form N_2O_4.

(iii) ICl is more reactive than I_2.

OR

(i) Hydrogen halides are covalent compounds but their aqueous solutions can conduct electric current. Explain.

(ii) What are the conditions to get the maximum yield of sulphuric acid by contact process?

(iii) Give two examples in which fluorine shows anomalous behaviour.

SECTION - D

Q. No. 31-33 are long answer type carrying 5 marks each.

31. (i) Why does the rate of a reaction not remain constant throughout the reaction process?

(ii) The thermal decomposition of HCOOH is a first order reaction with a rate constant of $2.4 \times 10^{-3} s^{-1}$ at a certain temperature. Calculate how long will it take for three-fourth of initial quantity of HCOOH to decompose.

(log 4 = 0.6021)

(iii) The rate for the formation of *C*, for the reaction given below, is 2.2×10^{-3} mol L^{-1} min^{-1}.

$2A + B \longrightarrow C$

What is the value of $-\frac{d[A]}{dt}$?

OR

(i) A first order reaction has a rate constant 1.15×10^{-3} s^{-1}. How long will 5 g of this reactant take to reduce to 3 g?

(ii) In a pseudo first order hydrolysis of ester in water, the following results were obtained :

t/s	0	30	60	90
[Ester]/mol L^{-1}	0.55	0.31	0.17	0.085

(a) Calculate the average rate of reaction between the time interval 30 to 60 seconds.

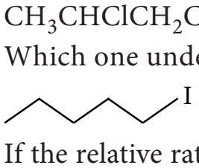
(b) Calculate the pseudo first order rate constant for the hydrolysis of ester.

32. Answer the following questions :

(i) What is meant by chirality of a compound? Give an example.

(ii) Which one of the following compounds is more easily hydrolysed by KOH and why?
$CH_3CHClCH_2CH_3$ or $CH_3CH_2CH_2Cl$

(iii) Which one undergoes S_N2 substitution reaction faster and why?



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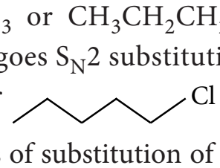


(iv) If the relative rates of substitution of 1° and 2° hydrogen are in the ratio of 1 : 3.8, show that in the presence of light at 298 K, the chlorination of *n*-butane gives a mixture of 72% 2-chlorobutane and 28% 1-chlorobutane.

OR

(i) The treatment of an alkyl chloride with aqueous KOH leads to the formation of an alcohol whereas in the presence of alcoholic KOH, alkene is the major product. Give reason.

(ii) Why is sulphuric acid not used during the reaction of alcohols with KI in the conversion of an alcohol to the alkyl iodide?

(iii) Why are haloarenes less reactive than haloalkanes towards nucleophilic substitution reactions?

(iv) Why CHF_3 is less acidic than $CHCl_3$ though fluorine is more electronegative than chlorine?

33. (i) Explain on the basis of VBT that $[Co(NH_3)_6]^{3+}$ is an inner orbital complex whereas $[Ni(NH_3)_6]^{2+}$ is an outer orbital complex.

(ii) Write the IUPAC name and draw the structures of each of the following complex entities :

(a) $\left[Co\begin{pmatrix}COO\\ |\\ COO\end{pmatrix}_3\right]^{3-}$ (b) $[Cr(CO)_6]$

(c) $[PtCl_3(C_2H_4)]^-$

OR

Explain the following :

(i) Low spin octahedral complexes of nickel are not known.

(ii) CO is a stronger ligand than NH_3 for many metals.

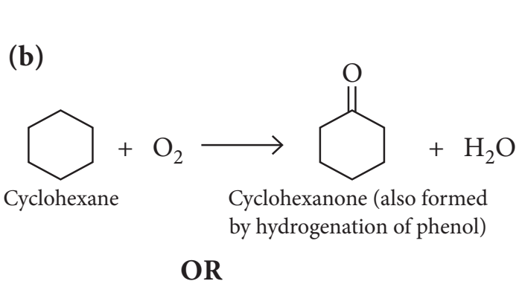
(iii) $[Ni(H_2O)_6]^{2+}$ is green and becomes violet when ethane 1, 2-diamine is added to it. Give reason.

(iv) What is the coordination number of Fe in [Fe(EDTA)]?

SOLUTIONS

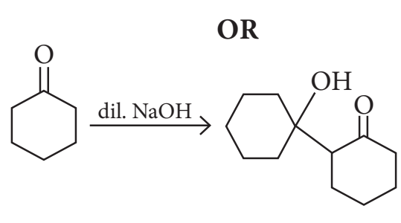
1. (i) (b)

(ii) (a) :

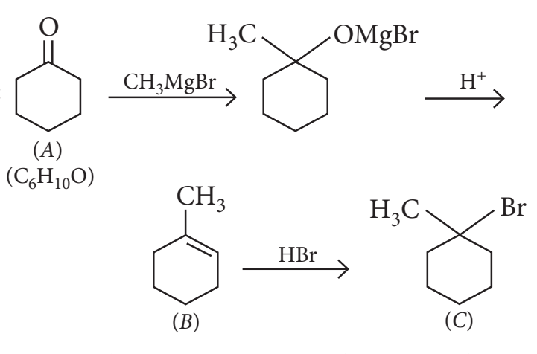


OR

(a) : 2



(iii) (c) :



(iv) (b) : Cyclohexanone is formed from hydrogenation of phenol which is slightly soluble in water and miscible with organic solvents.

2. (i) (d) : The particles of the colloidal solutions possess electric charge. On passing electric current they move towards cathode or anode.

(ii) (b)

(iii) (a) OR (a)

(iv) (c) : Colloidal solution are heterogenous in nature consisting of two phases (i) dispersed phase and (ii) dispersion medium.

3. (c) : Yellow colour on heating NaCl in presence of Na is due to presence of electrons in anion vacancies (F-centre).

OR

(b) : Density $= \dfrac{Z \times \text{Weight}}{\text{Number of atoms} \times a^3}$

$$\text{Number of atoms} = \frac{2 \times 104}{7.20 \times (2.88 \times 10^{-8})^3} = 1.209 \times 10^{24}$$

(for *bcc*, $Z = 2$)

4. (b)

5. (b) : Bidentate ligands have two donor atoms.

$$\begin{matrix} CH_2-\ddot{N}H_2 \\ | \\ CH_2-\ddot{N}H_2 \end{matrix}$$

(Ethylenediamine)

OR

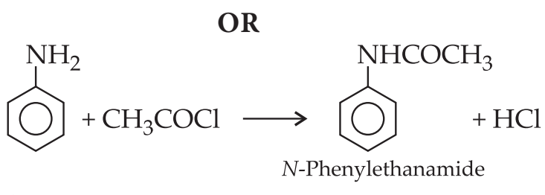
(a) : $[Co(NH_3)_3Cl_3]$ on ionisation does not give Cl^- ion, hence it does not give a precipitate of AgCl with $AgNO_3$ solution.

6. (c) 7. (a)

8. (a) : $C_2H_5-Br + \underset{\text{(Alc.)}}{NH_3} \longrightarrow \underset{\text{Ethylamine}}{C_2H_5-NH_2} + HBr$

OR

(a) :



N-Phenylethanamide

9. (b)

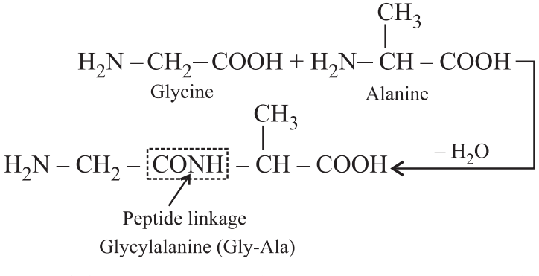
10. (a) : Half-life of a first order reaction does not depend upon initial concentration.

11. (d) : Hydrolysis of sucrose is called inversion since it results in inversion of specific rotation.

$$\underset{\substack{\text{Sucrose} \\ \text{(Dextrorotatory)}}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{HCl} \underbrace{\underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}}_{\text{(Laevorotatory mixture)}}$$

OR

(b) : The peptide linkage formed between glycine (H_2N-CH_2-COOH) and alanine ($\underset{\underset{CH_3}{|}}{H_2NCH}-COOH$) to give glycylalanine can be shown as :



12. (c) : Additional electrons are repelled more effectively by 2*p*-electrons in F than by 3*p*- electrons in Cl atom.

13. (c) 14. (c) 15. (b)

16. (b) OR (b)

17. (i) Hydrogen bonds exist among the molecules of ethanol (*i.e.*, strong forces). When cyclohexane

is added to ethanol, the cyclohexane molecule will come in between the ethanol molecules and disturb the hydrogen bondings. The forces between ethanol and cyclohexane will be weaker than the H-bonding, hence there will be positive deviation.

(ii) Negative type of deviation is present. In negative deviation the solute-solution ($A - A$) interaction and solvent-solvent ($B - B$) interaction will be weaker than solute-solvent ($A - B$) interaction. Since the new forces are stronger, therefore, the heat is evolved and solution becomes warm.

OR

Molality (m) of sucrose solution

$$= \frac{w \times 1000}{M \times \text{Mass of solvent}} = \frac{10}{342} \times \frac{1000}{90} = 0.325 \text{ m}$$

ΔT_f for sucrose solution $= T°_f - T_f$

$= (273.15 - 269.15)$ K $= 4$ K

$\because \quad \Delta T_f = K_f \times m$

$$\therefore \quad K_f = \frac{\Delta T_f}{m} = \frac{4 \text{ K}}{0.325 \text{ m}} = 12.308 \text{ K/m}$$

$$\text{Molality of glucose solution} = \frac{10}{180} \times \frac{1000}{90} = 0.617 \text{ m}$$

$\Delta T_f = K_f \times m$

$\therefore \quad \Delta T_f = 12.308$ K/m $\times$ 0.617 m $= 7.6$ K

$\therefore$ Freezing point of glucose solution,

$T_f^\circ - \Delta T_f = (273.15 - 7.60)$ K $= 265.55$ K

18. F_2 is highly reactive and has greater affinity for hydrogen. Therefore, it decomposes water at low temperature and even in dark liberating oxygen and ozone.

$2F_2 + 2H_2O \longrightarrow 4HF + O_2\uparrow$

$3F_2 + 3H_2O \longrightarrow 6HF + O_3\uparrow$

19. Density of *bcc* iron,

$$d_{bcc} = \frac{2 \times M}{N_A \times (286.3 \times 10^{-10})^3} \text{ g/cm}^3 \ (Z = 2 \text{ in } bcc \text{ lattice})$$

Density of *fcc* iron,

$$d_{fcc} = \frac{4 \times M}{N_A \times (359.1 \times 10^{-10})^3} \text{ g/cm}^3 \ (Z = 4 \text{ in } fcc \text{ lattice})$$

$$\therefore \quad \frac{d_{fcc}}{d_{fcc}} = \frac{\dfrac{4 \times M}{N_A \times (359.1 \times 10^{-10})^3} \text{ g/cm}^3}{\dfrac{2 \times M}{N_A \times (286.3 \times 10^{-10})^3} \text{ g/cm}^3}$$

$$= \frac{4 \times (286.3 \times 10^{-10})^3}{2 \times (359.1 \times 10^{-10})^3} = 1.014$$

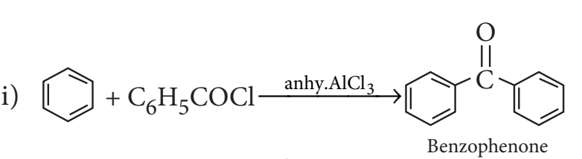
$$\therefore \quad \text{Percent change in density} = \frac{d_{fcc} - d_{bcc}}{d_{bcc}} \times 100$$

$= (1.014 - 1) \times 100 = +1.4$

Density increases by 1.4%.

20. (i) $C_6H_5COCl \xrightarrow[\text{Pd-BaSO}_4]{H_2} C_6H_5CHO$ Benzaldehyde

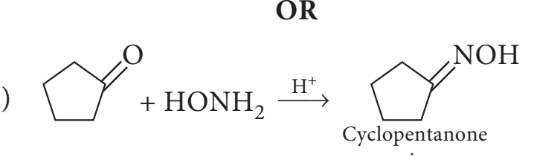
(ii)



Benzophenone

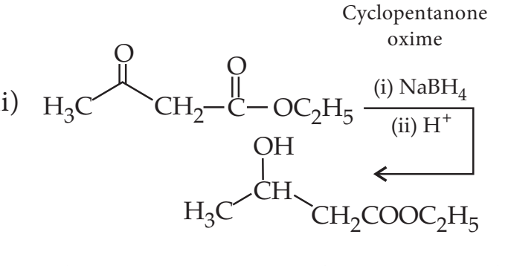
OR

(i)



Cyclopentanone oxime

(ii)



21. The electronic configuration of Hg^+ is $[Xe]4f^{14}5d^{10}6s^1$. If this were so, the mercurous, Hg(I) compounds should be paramagnetic but actually, they are diamagnetic. This behaviour can be explained by assuming that singly filled 6*s*-orbitals of the two Hg^+ ions overlap to form Hg—Hg covalent bond. Thus, Hg^+ exists as dimeric species, *i.e.*, Hg_2^{2+}.

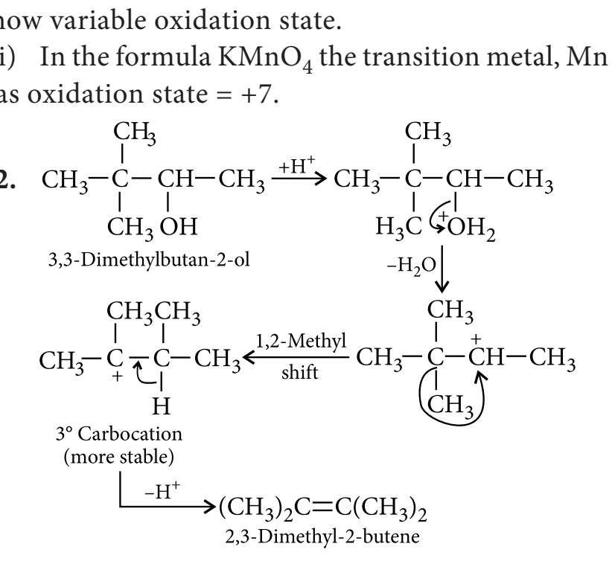
On the other hand, the electronic configuration of Cu^+ ion is $[Ar]3d^{10}$. It is stable configuration hence, it exists as Cu^+ ion.

OR

(i) Transition elements can use their *ns* and $(n - 1)d$ orbital electrons for bond formation. Therefore, they show variable oxidation state.

(ii) In the formula $KMnO_4$ the transition metal, Mn has oxidation state = +7.

22.

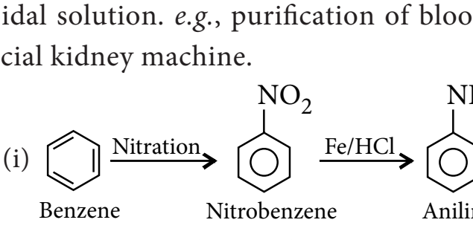


23. (a) These are called anomers.

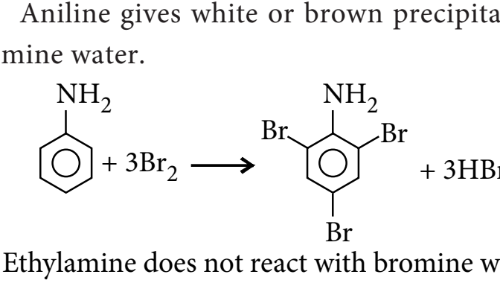
(b) They cannot be called enantiomers as they are not the mirror images of each other.

24. (i) The combination of the two layers (fixed and diffused) of opposite charges around the colloidal particles is called Helmholtz electrical double layer.
(ii) Dialysis is carried out by putting impure colloidal solution in a parchment paper bag and then dipping it in distilled water. After some time, all the crystalloids in solution diffuse through the membrane into the water leaving behind the pure colloidal solution. *e.g.*, purification of blood in the artificial kidney machine.

25. (i)



(ii) Aniline gives white or brown precipitate with bromine water.



Ethylamine does not react with bromine water

26. (i) The cell reactions are :

$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$ (Anode)

$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$ (Cathode)

Net reaction :

$Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$

(ii) $E^\circ_{cell} = E^\circ_{right} - E^\circ_{left} = 0.34\text{ V} - (-0.76\text{ V}) = 1.10\text{ V}$

(iii) Copper electrode will be positive on which reduction takes place.

OR

(i) At cathode : The following reduction reactions compete to take place at the cathode.

$Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}\ ;\ E^\circ = 0.80\text{ V}$

$H^+_{(aq)} + e^- \longrightarrow \frac{1}{2}H_{2(g)}\ ;\ E^\circ = 0.00\text{ V}$

The reaction with a higher value of E° takes place at the cathode. Therefore, the deposition of silver will take place at the cathode.

Since, Pt electrodes are inert, the anode is not attacked by NO_3^- ions. Therefore, OH^- or NO_3^- ions can be oxidized at the anode. But OH^- ions having a lower discharge potential get preference and decompose to liberate O_2.

$OH^- \longrightarrow OH + e^-$

$4OH^- \longrightarrow 2H_2O + O_2 + 4e^-$

(ii) At the cathode, the following reduction reaction occurs to produce H_2 gas.

$H^+_{(aq)} + e^- \longrightarrow \frac{1}{2}H_{2(g)}$

At the anode, the following processes are possible :

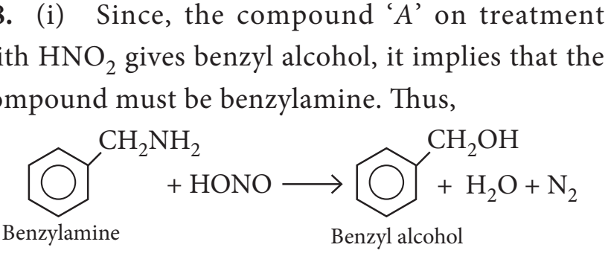
$2H_2O_{(l)} \longrightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-\ ;\ E^\circ = +1.23\text{ V}$ ...(1)

$2SO^{2-}_{4(aq)} \longrightarrow S_2O^{2-}_{8(aq)} + 2e^-\ ;\ E^\circ = +1.96\text{ V}$ ...(2)

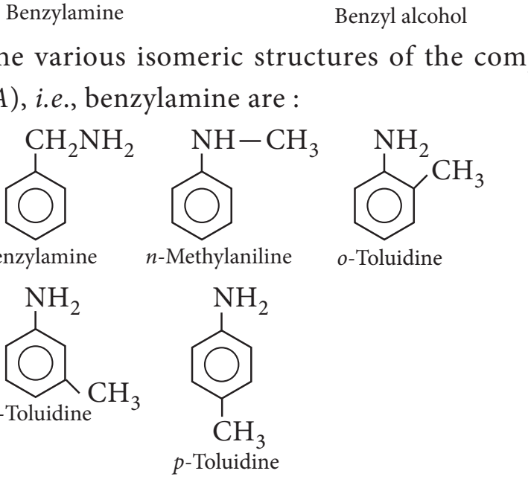
For dilute sulphuric acid, reaction (1) is preferred to produce O_2 gas but for concentrated sulphuric acid, (2) occurs.

27. (i) Lowest oxidation state oxides are basic due to their ability to get oxidised to higher oxidation state by donating electrons.
(ii) Being small in size and high in electronegativity fluorine and oxygen can bring about higher oxidation states in the compounds of transition elements. Examples are Mn_2O_7, CrO_3, OsF_6.
(iii) Transition metals showing higher oxidation states in the oxoanions are Cr and Mn, *e.g.*, CrO_4^{2-}, $Cr_2O_7^{2-}$, MnO_4^{2-}, MnO_4^-. This is due to the small size and high electronegativity of oxygen besides its ability to form multiple π-bonds with the metal (CrO_4^{2-}, MnO_4^-).

28. (i) Since, the compound '*A*' on treatment with HNO_2 gives benzyl alcohol, it implies that the compound must be benzylamine. Thus,



The various isomeric structures of the compound (*A*), *i.e.*, benzylamine are :



(ii) $CH_3CN \xrightarrow{H_2O/H^+} \underset{A}{CH_3COOH} \xrightarrow{NH_3} \underset{B}{CH_3CONH_2} \xrightarrow{Br_2+KOH} \underset{C}{CH_3NH_2}$

29. (i)

$$CH_3CH_2CH_2-O-CH_2CH_2CH_3 + \underset{\text{(Small amount)}}{HI}$$

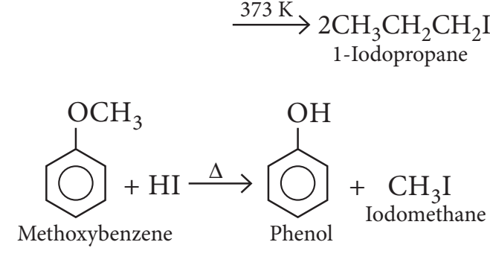
1-Propoxypropane

$$\xrightarrow{373\text{ K}} \underset{\text{1-Iodopropane}}{CH_3CH_2CH_2I} + \underset{\text{1-Propanol}}{CH_3CH_2CH_2OH}$$

$$CH_3CH_2CH_2-O-CH_2CH_2CH_3 + \underset{\text{(excess)}}{2HI}$$

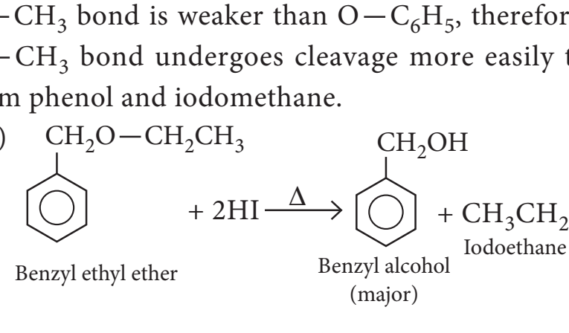
$$\xrightarrow{373\text{ K}} \underset{\text{1-Iodopropane}}{2CH_3CH_2CH_2I} + H_2O$$

(ii)



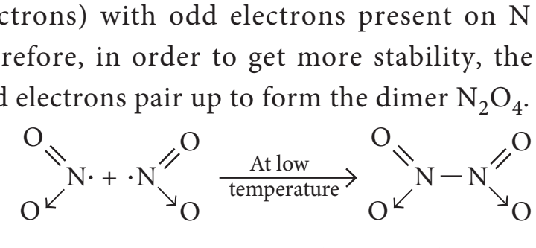
$O-CH_3$ bond is weaker than $O-C_6H_5$, therefore, $O-CH_3$ bond undergoes cleavage more easily to form phenol and iodomethane.

(iii)



30. (i) Due to smaller size and higher electronegativity than phosphorus, N is able to form *pπ-pπ* multiple bonds with C and hence, forms $:C\equiv N:$ ion but due to bigger size and lower electronegativity, P is unable to form multiple bonds with C and, hence, does not form $:C\equiv P^-:$ ion.

(ii) NO_2 is an odd electron species (7 + 8 + 8 = 23 electrons) with odd electrons present on N and therefore, in order to get more stability, the two odd electrons pair up to form the dimer N_2O_4.



(iii) As I—Cl bond is weaker and hence more reactive because of its partly ionic character due to difference in electronegativity. But in I_2, same halogen atom form covalent bond and hence less reactive.

OR

(i) All the hydrogen halides, *i.e.*, HF, HCl, HBr and HI are distinctly covalent compounds but the bond between H and halogens (*X*) is polar. In aqueous solution, these hydrogen halides are able to release proton to be accepted by H_2O and furnishes H_3O^+ and X^- ions, therefore conduct electricity.

$$H-X + H_2O \longrightarrow H_3O^+ + X^-$$

(ii) In H_2SO_4, production key step is

$$2SO_{2(g)} + O_{2(g)} \underset{}{\overset{V_2O_5}{\rightleftharpoons}} 2SO_{3(g)} :$$

$$\Delta_f H^\circ = -196.6 \text{ kJ mol}^{-1}$$

So according to Le-chatelier's principle, reaction must be carried out at optimum temperature (720 K) and at high pressure (2 bar) in the presence of V_2O_5 as a catalyst.

The two examples are :

(a) Since fluorine is most electronegative element, it shows only a negative oxidation state of –1. It does not show any positive oxidation state (except in HOF).

(b) Due to hydrogen bonding, HF can form acid salts of type KHF_2 while other halogens acids do not form such compounds.

31. (i) The rate of a reaction does not remain constant throughout the reaction process because the rate of the reaction depends upon concentration of reactants which keeps on decreasing.

(ii) Let initial concentration be $[R]_0$.

Then, first order equation, $t = \frac{2.303}{k}\log\frac{[R]_0}{[R]}$

At time t, $[R] = \frac{[R]_0}{4}$; $k = \frac{2.303}{t}\log\frac{[R]_0}{[R]}$

$$2.4\times10^{-3} = \frac{2.303}{t}\log\frac{[R]_0}{[R]_0/4} \qquad \text{...(1)}$$

$$t = \frac{2.303}{2.4\times10^{-3}}\log 4 = \frac{2.303}{2.4\times10^{-3}}\times0.6021 = 5.77\times10^2\text{s}$$

(iii) $2A + B \longrightarrow C$

According to rate law,

$$\text{Rate of reaction} = -\frac{1}{2}\frac{d[A]}{dt} = +\frac{d[C]}{dt}$$

$$\Rightarrow -\frac{d[A]}{dt} = \frac{2d[C]}{dt} = 2\times2.2\times10^{-3}\text{ mol L}^{-1}\text{ min}^{-1}$$

$$= 4.4\times10^{-3}\text{ mol L}^{-1}\text{ min}^{-1}$$

OR

(i) Here, $[R]_0 = 5$ g, $[R] = 3$ g, $k = 1.15\times10^{-3}\text{ s}^{-1}$

For first order reaction,

$$t = \frac{2.303}{k}\log\frac{[R]_0}{[R]} = \frac{2.303}{1.15\times10^{-3}}\log\frac{5}{3}$$

$$= 2.00\times10^3(\log 1.667) = 2.0\times10^3\times0.2219\text{ s}$$

$$= 443.8 \approx 444\text{ s}$$

(ii) (a) Average rate during the interval 30-60 sec

$$\text{Rate} = -\frac{C_2 - C_1}{t_2 - t_1} = -\frac{0.17 - 0.31}{60 - 30} = \frac{0.14}{30}\ \text{mol L}^{-1}\ \text{s}^{-1}$$

$= 4.67 \times 10^{-3}$ mol L^{-1} s^{-1}

(b) Using formula, $k' = \frac{2.303}{t}\log\frac{[R]_0}{[R]}$

in which $[R]_0 = 0.55$ M

At $t = 30$ sec, $[R] = 0.31$ mol L^{-1}

$$\therefore\ k' = \frac{2.303}{30}\log\frac{0.55}{0.31} = 1.91\times10^{-2}\ \text{s}^{-1}$$

At $t = 60$ sec, $[R] = 0.17$ mol L^{-1}

$$\therefore\ k' = \frac{2.303}{60}\log\frac{0.55}{0.17} = 1.96\times10^{-2}\ \text{s}^{-1}$$

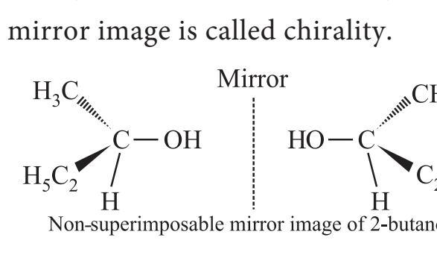
At $t = 90$ sec, $[R] = 0.085$ mol L^{-1}

$$\therefore\ k' = \frac{2.303}{90}\log\frac{0.55}{0.085} = 2.07\times10^{-2}\ \text{s}^{-1}$$

Hence, average $k' = \frac{1.91+1.96+2.07}{3}\times10^{-2}$

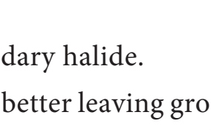
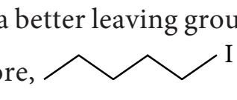
$= 1.98 \times 10^{-2}$ s^{-1}

32. (i) The molecules which are not superimposable on their mirror images are called chiral molecules. The property of non-superimposability of a structure on its mirror image is called chirality.



Non-superimposable mirror image of 2-butanol

(ii) $\underset{\displaystyle\text{Cl}}{\mathrm{CH_3CH_2\overset{}{C}HCH_3}}$ hydrolyses easily with KOH because it is secondary halide.

(iii) As iodide is a better leaving group because of its large size, therefore,  undergoes S_N2 reaction faster than .

(iv) $\mathrm{CH_3CH_2CH_2CH_3} \xrightarrow[\text{Light}]{\mathrm{Cl_2},\ 298\text{K}}$

$$\underset{\text{2-chlorobutane}}{\mathrm{CH_3 - \underset{\displaystyle Cl}{CH} - CH_2CH_3}} + \underset{\text{1-chlorobutane}}{\mathrm{CH_3CH_2\,CH_2CH_2Cl}}$$

The relative rates of formation of these two isomeric chlorobutanes will be equal to (i) their number of types of H(1°, 2° or 3°) and (ii) their relative rates of substitution, *i.e.*,

$$\frac{\text{1-Chlorobutane}}{\text{2-Chlorobutane}} = \frac{\text{Number of 1°H}}{\text{Number of 2°H}} \times \frac{\text{Reactivity of 1° H}}{\text{Reactivity of 2° H}}$$

$$= \frac{6}{4}\times\frac{1}{3.8} = \frac{6}{15.2}$$

Now, if x is the percentage of 1-chlorobutane, then percentage of 2-chlorobutane = $100 - x$

$$\therefore\ \frac{x}{100-x} = \frac{6}{15.2} \quad\Rightarrow\quad x = 28\%$$

Thus, percentage of 1-chlorobutane = 28%

Thus, percentage of 2-chlorobutane = 72%

OR

(i) In aqueous solution, KOH is almost completely ionised to give OH$^-$ ion which being a better nucleophile gives a substitution reaction on alkyl halides to form alcohol. But an alcoholic solution of KOH containing alkoxide (RO$^-$) ions which being a much stronger base than OH$^-$ ion preferentially snatches a H$^+$ ion from an alkyl chloride to form alkenes.

(ii) H_2SO_4 is an oxidant. KI reacts with H_2SO_4 and gives HI and H_2SO_4 oxidises HI to I_2.

$\mathrm{2KI + H_2SO_4 \rightarrow 2KHSO_4 + 2HI}$

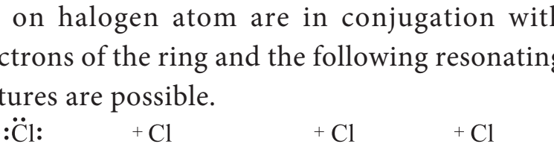
$\mathrm{2HI + H_2SO_4 \rightarrow 2H_2O + I_2 + SO_2}$

Thus, HI will not be available for reaction with alcohol to form alkyl iodide.

This is why sulphuric acid is not used during the reaction of alcohols with KI.

(iii) Haloarenes are much less reactive than haloalkanes towards nucleophilic substitution reactions due to the following reasons :

(a) Resonance effect : In haloarenes the electron pairs on halogen atom are in conjugation with π-electrons of the ring and the following resonating structures are possible.



C—Cl bond acquires a partial double bond character due to resonance. As a result, the bond cleavage in haloarene is difficult than haloalkane and therefore, are less reactive towards nucleophilic substitution reaction.

(b) In haloarenes, halogen is attached to sp^2-hybridised carbon while in haloalkanes, halogen is attached to sp^3-hybridised carbon.

(iv) $\bar{C}Cl_3$ obtained by the removal of proton from $CHCl_3$ is stabilized by resonance due to the presence of d-orbitals in chlorine while $\bar{C}F_3$ is not stabilized by resonance due to absence of d-orbitals in fluorine.

33. (i) Oxidation number of Co in $[Co(NH_3)_6]^{3+} = +3$

$$\begin{array}{ll} & \quad 3d \qquad\qquad\qquad 4s \\ Co(27) : [Ar] & \boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow} \quad \boxed{\uparrow\downarrow} \\ & \quad 3d \qquad\qquad\qquad 4s \\ Co^{3+} \quad : [Ar] & \boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow} \quad \boxed{} \\ [Co(NH_3)_6]^{3+} : [Ar] & \boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\underbrace{\boxed{\times\times}\boxed{\times\times} \quad \boxed{\times\times} \quad \boxed{\times\times}\boxed{\times\times}\boxed{\times\times}}_{d^2sp^3} \end{array}$$

(inner orbital complex)

Oxidation number of Ni in $[Ni(NH_3)_6]^{2+} = +2$

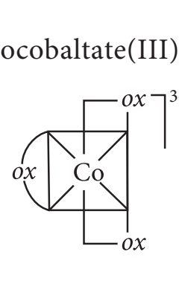
$$\begin{array}{ll} & \quad 3d \qquad\qquad\qquad 4s \\ Ni(28) : & [Ar] \boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow} \quad \boxed{\uparrow\downarrow} \\ Ni^{2+} : & [Ar] \boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow} \quad \boxed{} \end{array}$$

Ni^{2+} with NH_3 ligand :

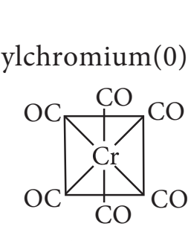
$$[Ar] \boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow} \quad \underbrace{\boxed{\times\times} \quad \boxed{\times\times}\boxed{\times\times}\boxed{\times\times} \quad \boxed{\times\times}\boxed{\times\times}}_{sp^3d^2}\boxed{}\boxed{}\boxed{}$$

(outer orbital complex)

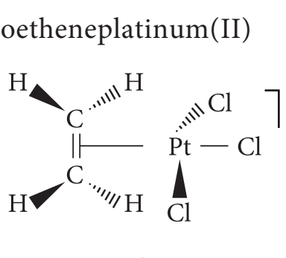
(ii) (a) Trioxalatocobaltate(III)



(b) Hexacarbonylchromium(0)



(b) Trichloroetheneplatinum(II)



OR

(i) Nickel forms octahedral complexes mainly in +2 oxidation state which has $3d^8$ configuration. In presence of strong field ligand also, it has two unpaired electrons in e_g orbital.
Hence, it does not form low spin octahedral complexes.

(ii) CO is stronger ligand than NH_3 because CO has vacant molecular orbitals with which it can form π-bond with metal through back donation.

(iii) Ethane-1,2-diamine is stronger ligand than H_2O. When H_2O molecule is replaced by ethane-1,2-diamine (*en*) the crystal field splitting energy (Δ_o) increases. Complex absorbs light of higher frequency for d-d transition. This is why colour of complex changes from green to violet.

(iv) EDTA is a hexadentate ligand, thus coordination number of Fe is 6 in [Fe(EDTA)].

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