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(5)	**11(23)**
2.	Solutions	1(1)	1(2)	–	–	
3.	Electrochemistry	1(1)	–	1(3)	–	
4.	Chemical Kinetics	2(2)	1(2)	–	–	
5.	Surface Chemistry	1(4)	1(2)	–	–	
6.	The *p*-Block Elements	2(2)	1(2)	1(3)	–	**8(19)**
7.	The *d*- and *f*-Block Elements	1(4)	1(2)	–	–	
8.	Coordination Compounds	1(1)	–	–	1(5)	
9.	Haloalkanes and Haloarenes	1(1)	1(2)	1(3)	–	**14(28)**
10.	Alcohols, Phenols and Ethers	1(1)	1(2)	–	1(5)	
11.	Aldehydes, Ketones and Carboxylic Acids	2(2)	1(2)	–	–	
12.	Amines	1(1)	1(2)	1(3)	–	
13.	Biomolecules	1(1)	–	1(3)	–	
	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 :**

Colour is an optical property of materials. It results from the absorption of a relatively narrow wavelength of radiation within visible high range (400-700 nm). The absorption causes electron transitions. There are four types of electron transitions :

1. Intrinsic band gap electron transition.

2. Intrinsic electron transitions within 3*d* (transition metals V, Cr, Mn, Fe, CO, Ni and Cu) and 4*f* (rare earth elements) levels.

3. Electron transfer from one ion to another.

4. Electron transitions associated with crystal imperfection.

The first type of transition is decided by intrinsic property of the material (band gap energy). The last three transitions are related to the small amounts of impurities and crystal defects.

The visible colour is the complementary colour of the absorbed colour. For example, the blue colour of the $[Cu(NH_3)_4]^{2+}$ ion results because this ion absorbs orange and red light, leaving the complementary colours of blue and green.

The striking colours exhibited by transition-metal complexes are caused by excitation of an electron from a lower energy *d*-orbital to a higher-energy *d*-orbital, which is called a *d-d* transition.

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

(i) The colour of the transition metal ions is due to

(a) *d-d* transition (b) charge transfer (c) both (a) and (b) (d) neither (a) nor (b)

(ii) The colour of $KMnO_4$ is due to

(a) electron transfer from one ion to another.

(b) intrinsic band gap electronic transition.

(c) electron transition associated with crystal imperfection.

(d) Internal electronic transition.

(iii) In which of the following pairs, both the ions are coloured in aqueous solutions?
(a) Sc^{3+}, Ti^{3+} (b) Sc^{3+}, Co^{2+} (c) Ni^{2+}, Cu^{+} (d) Ni^{2+}, Ti^{3+}
(Atomic number of Sc = 21, Ti = 22, Ni = 28, Co = 27, Cu = 29)

OR

The colour of zinc sulphide is
(a) blue (b) white (c) orange (d) yellow.

(iv) The dark blue colour of the solution formed when excess of ammonia is added to a solution of copper(II) sulphate is due to the presence of the ion
(a) $[Cu(OH)_4(H_2O)_2]^{2-}$ (b) $[Cu(NH_3)_4]^{2+}$
(c) $[Cu(NH_3)_4(H_2O)_2]^{2+}$ (d) $[Cu(NH_3)(H_2O)_4]^{2+}$

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

Adsorptions is the adhesion of molecules from gases, solutes or liquids to the surface of solid bodies or liquids with which they are in contact. The adsorption creates a thin film of the adsorbate on the surface of the solid (termed as adsorbent) and it is different from absorption in which the adsorbate permeates or dissolved by a liquid or solid. In other words, adsorption is surface based physio-chemical process and is a consequence of surface energy.

The surface concentration of the gas molecules by adsorption depends on nature of the gas, nature and surface area of adsorbent, temperature and pressure. Adsorption may include the physical adsorption that originates from attractive or repulsive forces between the molecules and chemical adsorption that involves changes in the structure of bonding molecules.

Adsorption techniques are used as high quality treatment processes for the removal of dissolved organic pollutants, such as dyes, from industrial waste water or air. Activated charcoal or mixture of absorbents is generally used in gas masks to adsorb toxic gases from air and activated carbon is used as adsorbent for removal toxic pollutants from sewage waste water.

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 :** Physical adsorption of molecules takes place on surface only.
Reason : In this process, the bonds of the adsorbed molecules are broken.

(ii) **Assertion :** Adsorption is generally temperature dependent.
Reason : Adsorption decreases with increasing temperature.

OR

Assertion : In chemisorption, all gases are adsorbed on solids.
Reason : Chemisorption takes place at elevated temperature.

(iii) **Assertion :** On mixing an organic dye with activated charcoal, the solution turns colourless.
Reason : An organic dye gets adsorbed on the surface of activated charcoal.

(iv) **Assertion :** Adsorption is a surface phenomenon.
Reason : In adsorption, there is a high concentration of adsorbate on the surface than in bulk.

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

3. Which of the following statements is incorrect?
(a) In $K_3[Fe(CN)_6]$, the ligand has satisfied only the secondary valency of ferric ion.
(b) In $K_3[Fe(CN)_6]$, the ligand has satisfied both primary and secondary valencies of ferric ion.
(c) In $K_4[Fe(CN)_6]$, the ligand has satisfied both primary and secondary valencies of ferrous ion.
(d) In $[Cu(NH_3)_4]SO_4$, the ligand has satisfied only the secondary valency of copper.

OR

Amongst $[Ni(CO)_4]$, $[Ni(CN)_4]^{2-}$ and $[NiCl_4]^{2-}$

(a) $[Ni(CO)_4]$ and $[NiCl_4]^{2-}$ are diamagnetic and $[Ni(CN)_4]^{2-}$ is paramagnetic

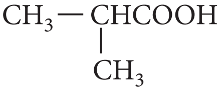
(b) $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ are diamagnetic and $[Ni(CO)_4]$ is paramagnetic

(c) $[Ni(CO)_4]$ and $[Ni(CN)_4]^{2-}$ are diamagnetic and $[NiCl_4]^{2-}$ is paramagnetic

(d) $[Ni(CO)_4]$ is diamagnetic and $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ are paramagnetic.

4. An organic compound '*A*' on treatment with NH_3 gives '*B*' which on heating gives '*C*', '*C*' when treated with Br_2 in the presence of KOH produces ethylamine. Compound '*A*' is

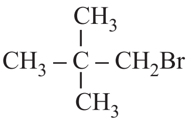
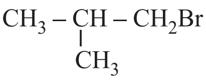
(a) CH_3COOH (b) $CH_3CH_2CH_2COOH$

(c) 
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}HCOOH$
(d) CH_3CH_2COOH

5. For the reaction, $2A + 3B \longrightarrow$ product, *A* is in excess and on changing the concentration of *B* from 0.1 M to 0.4 M, rate becomes doubled. Thus, rate law is

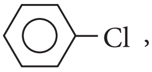
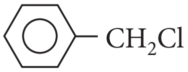
(a) $\frac{dx}{dt} = k[A]^2[B]^3$ (b) $\frac{dx}{dt} = k[A][B]$ (c) $\frac{dx}{dt} = k[A]^0[B]^2$ (d) $\frac{dx}{dt} = k[B]^{1/2}$

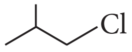
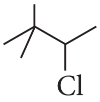
6. In S_N2 substitution reaction of the type, $R - Br + Cl^- \xrightarrow{DMF} R - Cl + Br^-$ which one of the following has the highest relative rate?

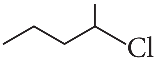
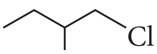
(a) 
$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_2Br$
(b) CH_3CH_2Br (c) $CH_3CH_2CH_2Br$ (d) 
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}H-CH_2Br$

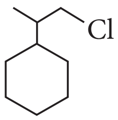
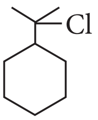
OR

Among the following in which pair the first compound is more reactive than second for S_N1 reaction?

(a)  , 

(b)  , 

(c)  , 

(d)  , 

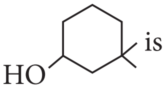
7. 0.1 M H_2SO_4 is diluted to 0.01 M H_2SO_4. Hence, its molar conductance will be

(a) 10 times (b) $\frac{1}{10}$th (c) 100 times (d) 10000 times.

OR

For the fuel-cell reaction, $2H_2 + O_2 \longrightarrow 2H_2O$, $\Delta G^\circ = -475$ kJ. Hence, E°_{cell} is

(a) 1.23 V (b) 2.45 V (c) 0.615 V (d) 0.31 V

8. The IUPAC name of the compound,  is

(a) 3,3-dimethyl-1-hydroxy cyclohexane (b) 1,1-dimethyl-3-hydroxy cyclohexane

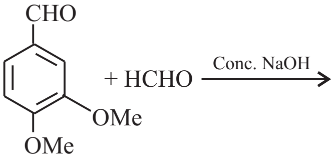
(c) 3,3-dimethyl-1-cyclohexanol (d) 1,1-dimethyl-3-cyclohexanol.

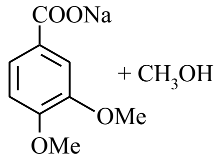
OR

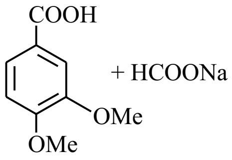
Which of the following compounds on oxidation gives ethyl methyl ketone?

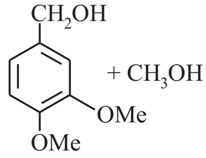
(a) 2-propanol (b) 1-butanol (c) 2-butanol (d) *tert*-butyl alcohol

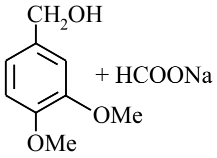
9. The following reaction gives



(a) 

(b) 

(c) 

(d) 

10. Which one of the following oxides of nitrogen is blue solid?

(a) NO (b) N_2O_3 (c) N_2O (d) N_2O_5

11. Carbohydrates are stored in human body as the polysaccharide

(a) maltose (b) glycogen (c) cellulose (d) amylose.

In the following questions (Q. No. 12-16) 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.

12. **Assertion :** Acetone and aniline show negative deviations.
Reason : H-bonding between acetone and aniline is stronger than that between acetone-acetone and aniline-aniline.

13. **Assertion :** Rate of reaction doubles when concentration of reactant is doubled if it is a first order reaction.
Reason : Rate constant also doubles.

14. **Assertion :** Mixture of benzaldehyde and acetaldehyde in hot alkaline medium gives cinnamaldehyde.
Reason : Benzaldehyde is strong electrophile than acetaldehyde.

15. **Assertion :** *bcc* and *hcp* has same packing efficiency.
Reason : Both have same number of atoms per unit cell and same arrangement.

OR

Assertion : The presence of a large number of Schottky defects in NaCl lowers its density.
Reason : In NaCl, there are approximately 10^6 Schottky pairs per cm^3 at room temperature.

16. **Assertion :** Liquid NH_3 is used for refrigeration.
Reason : Liquid NH_3 quickly vapourises.

SECTION - B

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

17. H_2S is a toxic gas with rotten egg like smell. It is used for qualitative analysis. If the solubility of H_2S in water at STP is 0.195 m, calculate Henry's law constant.

OR

What is molar concentration of solute particle in a human blood if the osmotic pressure is 7.2 atm at the body temperature of 37°C? [$R = 0.0821$ L atm K^{-1} mol^{-1}]

18. A chloro derivative (A) on treatment with zinc-copper couple gives a hydrocarbon with five carbon atoms. When (A) is dissolved in ether and treated with sodium then 2, 2, 5, 5 -tetramethylhexane is obtained. What is the original compound (A)?

19. Explain giving reason which one of the following pair has the property indicated :

(a) Fe or Cu has higher melting point.

(b) Co^{2+} or Ni^{2+} has lower magnetic moment.

OR

Predict which of the following will be coloured in aqueous solution?

Ti^{3+}, V^{3+}, Cu^{+}, Sc^{3+}, Mn^{2+} and Fe^{3+}

Give reason for each.

20. Complete the following reactions : $CH_3—CH_2—COOH \xrightarrow[H^+]{C_2H_5OH} \xrightarrow[\text{(ii) } H_2O]{\text{(i) } C_6H_5MgBr}$

$$\xrightarrow{\Delta} \xrightarrow[[O]]{CrO_3}$$

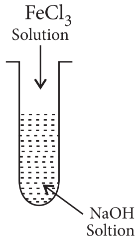
OR

An aliphatic compound '*A*' with a molecular formula of C_3H_6O reacts with phenylhydrazine to give compound '*B*'. Reaction of '*A*' with I_2 in alkaline medium on warming gives a yellow precipitate '*C*'. Identify the compounds *A*, *B* and *C*.

21. A certain reaction takes 5 minutes for initial concentration 0.5 mol L^{-1} to become 0.25 mol L^{-1} and another 5 minutes to becomes 0.125 mol L^{-1}. What is the order and specific rate constant of the reaction?

22. What is meant by hydroboration-oxidation reaction? Illustrate it with an example.

23. 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?



24. (a) Why are interhalogen compounds more reactive than its elemental form?

(b) Write the chemical reaction to show the formation of Cl_2 from bleaching powder.

25. What is acylation reaction? Acylation of amines with acid chloride is carried out in presence of stronger base. Why?

SECTION - C

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

26. Give reasons :

(i) I_3^- ion exists but F_3^- does not.

(ii) H_3PO_3 undergoes disproportionation reaction but H_3PO_4 does not.

(iii) Relative acidic strength of the hydrogen halides.

OR

(a) Arrange the following in :

(i) HOCl, $HOClO_2$, $HOClO_3$, HOClO ⇒ increasing order of thermal stability.

(ii) CO_2, N_2O_5, SiO_2, SO_3 ⇒ increasing order of acidic character.

(b) Xenon has fully filled shell configuration but is known to give compounds with fluorine.

27. Account for the following :

(i) The pK_b of aniline is more than that of methylamine.

(ii) Methylamine reacts in water with ferric chloride to precipitate hydrated ferric oxide.

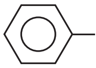
(iii) Gabriel phthalimide synthesis is the preferred method for synthesizing primary amines.

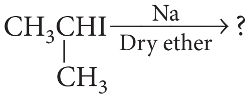
28. (i) Calculate the standard electrode potential of Ni^{2+}/Ni electrode if emf of the cell

$Ni_{(s)} \mid Ni^{2+}\ (0.01\ M) \parallel Cu^{2+}\ (0.1\ M) \mid Cu_{(s)}$ is 0.059 V. [Given : $E^{\circ}_{Cu^{2+}/Cu} = +0.34$ V]

(ii) Define the terms specific conductance and equivalent conductance.

29. Complete the following reactions :

(i)  $-CH_2-CH=CH_2 + HBr \xrightarrow{\text{Peroxide}} ?$

(ii) 
$CH_3\underset{\substack{|\\ CH_3}}{C}HI \xrightarrow[\text{Dry ether}]{\text{Na}} ?$

(iii) $CH_3CH=CH_2 \xrightarrow{\text{HBr}} ? \xrightarrow{\text{aq. KOH}} ?$

30. Predict towards which electrode would an α-amino acid migrate in an electric field at

(a) pH < pI, (b) pH > pI and (c) pH = pI

Explain.

OR

Define the following terms as related to proteins :

(i) Peptide linkage (ii) Primary structure (iii) Denaturation

SECTION - D

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

31. Write down the IUPAC name for each of the following complexes and indicate the oxidation state, electronic configuration and coordination number. Also give geometry and magnetic moment of the complexes :

(a) $K[Cr(C_2O_4)_2(H_2O)_2].3H_2O$ (b) $[CrCl_3(py)_3]$

(c) $K_4[Mn(CN)_6]$ (d) $[Co(NH_3)_5Cl]Cl_2$

(e) $Cs[FeCl_4]$

OR

(i) Write the main assumptions of valence bond theory.

(ii) What do you mean by inner orbital complexes and outer orbital complexes? Give examples of each.

32. (a) Phenol is acidic while hexanol is neutral towards a solution of NaOH. Why?

(b) *m*-Aminophenol is stronger acid than *o*-aminophenol. Explain.

(c) Name the different reagents needed to perform the following reactions :

(i) Phenol to benzene

(ii) Friedel-Crafts alkylation of anisole

(iii) Dehydrogenation of ethanol to ethanal

OR

(i) Write the structure of the products when butan-2-o1 reacts with the following :

(a) CrO_3 (b) $SOCl_2$

(ii) How is 1-propoxypropane synthesised from propan-1-ol ? Give mechanism.

33. (a) In a face centred lattice of *X* and *Y*, *X* atoms are present at the corners while *Y* atoms are at face centres.

(i) What is the formula of the compound?

(ii) What would be the formula of the compound if

(A) one of the *X* atoms is missing from a corner in each unit cell,

(B) one of the *X* atoms from a corner is replaced by *Z* atom (also monovalent)?

(b) Answer the following :

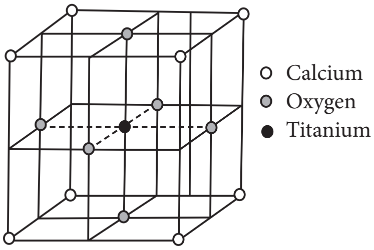
  (i) Calculate the number of unit cells in 8.1 g of aluminium if it crystallizes in a *fcc* structure. (Atomic mass of Al = 27 g mol^{-1})

  (ii) In chromium (III) chloride, $CrCl_3$, the chloride ions have *ccp* (cubic close packing) arrangement and Cr (III) ions are present in octahedral holes. What fraction of the octahedral holes is occupied? What fraction of the total number of holes is occupied?

OR

(a) An element crystallises in *fcc* lattice having edge length 400 pm. Calculate the maximum diameter of atom which can be placed in interstitial site without distorting the structure.

(b) Perovskite, a mineral containing calcium, oxygen and titanium crystallises in the given cubic unit cell.



What is the formula of perovskite and what is the oxidation number of titanium in perovskite?

SOLUTIONS

1. **(i) (c)**

(ii) (a) It is due to ligand to metal charge transfer *i.e.*, electron transfer from one ion to another

(iii) (d) : Ni^{2+} and Ti^{3+} are coloured due to the presence of unpaired electrons.

OR

(b) : Zn^{2+} has fully-filled 3*d*-subshell. Therefore, their salts are colourless.

(iv) (c) : $CuSO_4 + 2OH^- \rightarrow Cu(OH)_2 + SO_4^{2-}$

$$Cu(OH)_2 + 4NH_3 + 2H_2O \rightarrow \underset{\text{Blue colour}}{[Cu(NH_3)_4(H_2O)_2]^{2+}} + 2OH^-$$

2. **(i) (c) :** Physical adsorption involves no breaking of bond of molecules.

(ii) (a)

OR

(d) : Only those gases which can react with the adsorbent show chemisorption.

(iii) (a)

(iv) (a) The process of adsorption arises due to the presence of unbalanced or residual forces at the surface of liquid or solid phase.

3. **(a)**

OR

(c) : CO and CN^- are strong field ligands and force electrons to pair up so that a diamagnetic, low spin complex is resulted. However, Cl^- is a weak field ligand and hence does not force electrons to pair up so that a paramagnetic high spin complex results.

4. **(d) :** $\underset{\text{Propanoic acid }(A)}{CH_3CH_2COOH} \xrightarrow{NH_3} \underset{\text{Amm. propanoate }(B)}{CH_3CH_2CO\bar{O}\overset{+}{N}H_4}$

$$\xrightarrow[H_2O]{\Delta} \underset{\text{Propanamide }(C)}{CH_3CH_2CONH_2} \xrightarrow[\text{(Hoffmann bromamide reaction)}]{Br_2/KOH} \underset{\text{Ethylamine }(A)}{CH_3CH_2NH_2}$$

5. **(d) :** *A* is in excess, hence, rate is not affected by change in concentration of *A*.

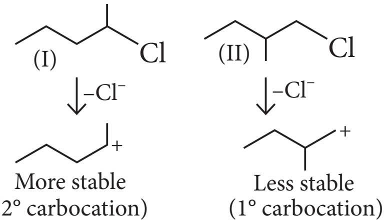
$R = k[0.1]^b$, $2R = k(0.4)^b$ or, $2 = (4)^b$, $(4)^{1/2} = (4)^b$

$$\therefore \quad b = \frac{1}{2}$$

6. **(b)**

OR

(c) : Reactivity of alkyl halide increases with increase of stability of intermediate carbocation. Stability of carbocation of I is more than II only in 'c' option due to more hyperconjugation.



7. **(a) :** If dilution is made *x*-times then molar and specific conductance becomes *x*-times.
0.1 M H_2SO_4 changes to 0.01 M H_2SO_4.
Thus, dilution is 10 times.

OR

(a) : $2H_2 + O_2 \longrightarrow 2H_2O$

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

Total electrons involved = 4

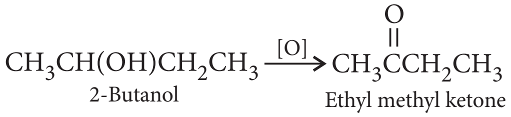
$\therefore \quad \Delta G° = -nFE°$

$-475 \times 1000 = -4 \times 96500 \times E°$

$\therefore \quad E° = 1.23$ V

8. **(c)**

OR



(c) : $\underset{\text{2-Butanol}}{CH_3CH(OH)CH_2CH_3} \xrightarrow{[O]} \underset{\text{Ethyl methyl ketone}}{CH_3\overset{\overset{O}{\parallel}}{C}CH_2CH_3}$

9. **(d) :** Two non-enolisable aldehydes and NaOH indicates that it is an example of crossed Cannizaro reaction. Benzaldehyde derivative is converted to alcohol not formaldehyde.

10. **(b) :** N_2O_3 exists as blue solid at a very low temperature.

11. **(b) :** Glycogen is the reserve carbohydrate occurring mainly in the liver.

12. **(a)**

13. **(c) :** For first order reaction, $Rate_1 = k[A_1]$
According to question,

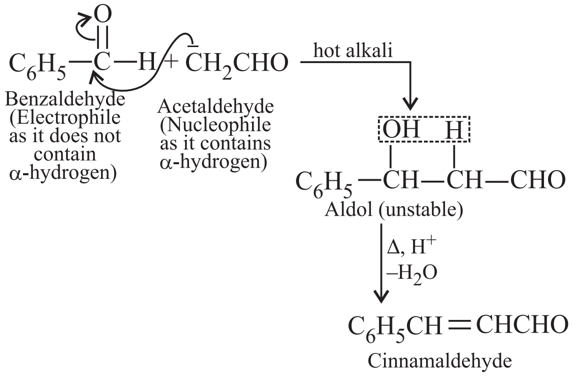
$[A_2] = [2A_1]$

$\therefore \quad Rate_2 = k[2A_1]$

$\Rightarrow \quad Rate_2 = 2\ Rate_1$

For a given reaction, rate constant is constant and independent of the concentration of reactant.

14. (a) : This is a Claisen-Schmidt reaction.



$$C_6H_5-\overset{O}{\overset{\|}{C}}-H + \bar{C}H_2CHO \xrightarrow{\text{hot alkali}} C_6H_5-\underset{OH}{CH}-\underset{H}{CH}-CHO \xrightarrow[-H_2O]{\Delta,\ H^+} C_6H_5CH=CHCHO$$

15. (d) : *bcc* has 68% and *hcp* has 74% packing efficiency.

bcc - 2 atoms per unit cell, *hcp* - 4 atoms per unit cell

OR

(b) : When an atom or an ion is missing from its normal lattice site, a lattice vacancy or defect is created, which is called Schottky defect. Due to missing ions density of crystal will be lowered.

16. (a) : Liq. NH_3 has high heat of vaporisation (327 cal/g). So, it takes up lots of heat and helps in cooling. So, it is used in ice-plants.

17. Solubility of H_2S gas = 0.195 m

$\therefore$ Moles of H_2S = 0.195, Mass of water = 1000 g

$$\text{Number of moles of water} = \frac{1000\,g}{18\,g\,mol^{-1}} = 55.55 \text{ moles}$$

$\therefore$ Mole fraction of H_2S gas in the solution (x)

$$= \frac{0.195}{0.195 + 55.55} = \frac{0.195}{55.745} = 0.0035$$

Pressure at STP = 0.987 bar

Applying Henry's law, $p(H_2S) = K_H \times x_{H_2S}$

$$\text{or} \quad K_H = \frac{p_{H_2S}}{x_{H_2S}} = \frac{0.987\,\text{bar}}{0.0035} = 282 \text{ bar}$$

OR

Given, $\pi = 7.2$ atm, $R = 0.082$ L atm K^{-1} mol^{-1}

$T = 37°C = 273 + 37 = 310$ K

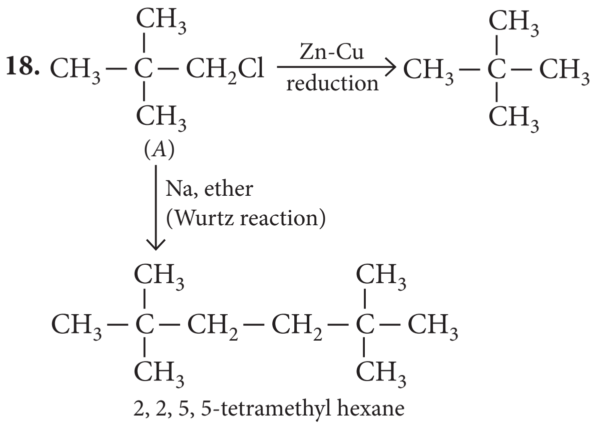
$$\pi = \frac{n}{V}RT$$

$$\pi = CRT \qquad \left[C = \frac{n}{V}\right]$$

$$7.2 = C \times 0.0821 \times 310$$

$$C = \frac{7.2}{0.0821 \times 310} \Rightarrow C = \frac{7.2}{25.451} = 0.283 \text{ mol } L^{-1}$$

18.



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2Cl \xrightarrow[\text{reduction}]{\text{Zn-Cu}} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$$

$$(A) \xrightarrow[\text{(Wurtz reaction)}]{\text{Na, ether}} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$$

2, 2, 5, 5-tetramethyl hexane

19. (a) Fe has higher melting point than Cu, because iron has four unpaired electrons in *d*-subshell ($3d^6$ $4s^2$), therefore, the metallic bonds and covalent bonds in iron are stronger but in Cu ($3d^{10}$ $4s^1$)no *d*-electron is unpaired and only one 4*s* electron is responsible for metallic bond.

(b) Co^{2+} and Ni^{2+} have $3d^7 4s^0$ and $3d^8 4s^0$ configuration respectively, hence 3 unpaired electrons are present in Co^{2+} and 2 unpaired electrons are present in Ni^{2+}. Therefore, Ni^{2+} has lower magnetic moment, because it depends upon number of unpaired electrons *i.e.*, $\mu = \sqrt{n(n+2)}$.

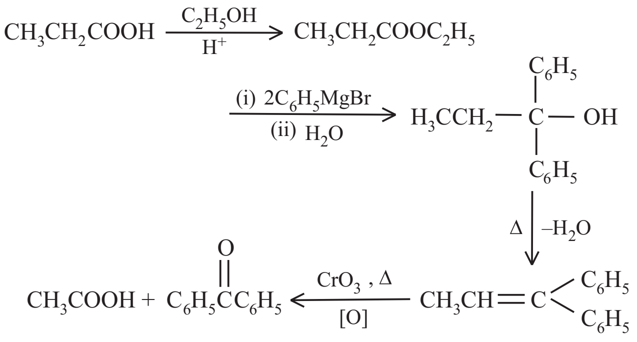
OR

The outer electronic configurations of the given ions are

Ti^{3+}	V^{3+}	Cu^+	Sc^{3+}	Mn^{2+}	Fe^{3+}
$3d^1$	$3d^2$	$3d^{10}$	$3d^0$	$3d^5$	$3d^5$
coloured (due to *d*-*d* transition)	coloured (due to *d*-*d* transition)	↑	↑	coloured (due to *d*-*d* transition)	coloured (due to *d*-*d* transition)

(no *d*-*d* transition possible, hence colourless)

20.



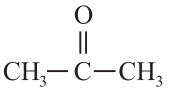
$$CH_3CH_2COOH \xrightarrow[H^+]{C_2H_5OH} CH_3CH_2COOC_2H_5 \xrightarrow[\text{(ii) } H_2O]{\text{(i) } 2C_6H_5MgBr} H_3CCH_2-\underset{C_6H_5}{\overset{C_6H_5}{C}}-OH$$

$$\xrightarrow[-H_2O]{\Delta} CH_3CH=C(C_6H_5)_2 \xrightarrow[\text{[O]}]{CrO_3,\ \Delta} CH_3COOH + C_6H_5\overset{O}{\overset{\|}{C}}C_6H_5$$

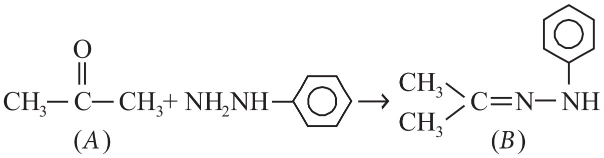
OR

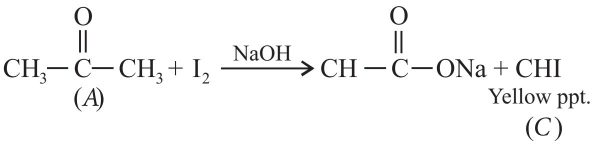
Since compound '*A*' reacts with phenylhydrazine. So, it must be either aldehyde or ketone.

As compound 'A' reacts with I_2 in alkaline medium so, it must contains CH_3CO group so, compound 'A' is ketone.



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3$$





$$\underset{(A)}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} + I_2 \xrightarrow{NaOH} CH-\overset{\overset{O}{\|}}{C}-ONa + \underset{\substack{\text{Yellow ppt.}\\(C)}}{CHI}$$

21. The given data is

$$0.5\,mol\,L^{-1} \xrightarrow{5\,min} 0.25\,mol\,L^{-1} \xrightarrow{5\,min} 0.125\,mol\,L^{-1}$$

(i) Half life period is independent of initial concentration of the reactant, hence reaction is of first order.

(ii) For first order reaction

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5\text{ min}} = 0.138\text{ min}^{-1}$$

22. This reaction is used for the preparation of alcohols from alkenes. In this reaction, alkenes are treated with diborane followed by oxidation with H_2O_2. The final alcohol is obtained by the addition of water to alkene by anti Markownikoff's rule *e.g.,* propene undergoes this reaction to yield propan-1-ol.

$$\underset{\text{Propene}}{3CH_3-CH=CH_2} + \underset{\text{Diborane}}{\frac{1}{2}B_2H_6} \longrightarrow (CH_3-CH_2-CH_2)_3B$$

$$\xrightarrow{H_2O_2} \underset{\text{Propan-1-ol}}{3CH_3-CH_2-CH_2-OH} + H_3BO_3$$

23. The sol formed will be negatively charged.

$$FeCl_3 + NaOH \longrightarrow \underset{\text{Negatively charged sol}}{Fe_2O_3 \cdot xH_2O \vdots OH^-}$$

24. (a) Since X–X bond between two dissimilar electronegative elements is weaker than two similar elements hence interhalogen compounds have low bond dissociation energy than its elemental form and correspondingly it is more reactive than elemental form.

(b) $Ca(OCl)Cl_{(s)} + 2HCl_{(aq)} \longrightarrow CaCl_{2(aq)} + H_2O_{(l)} + Cl_{2\,(g)}$

25. The process of introducing an acyl group ($R-\overset{\overset{O}{\|}}{C}-$) into any molecule is called acylation. During acylation reaction HCl acid is formed. In order to remove HCl and shift the equilibrium to the right hand side a stronger base like pyridine is added.

26. (i) If F_3^- is formed, then central F-atom would have 10 electrons in its valence shell. But that is not possible because F cannot expand its octet due to the absence of *d*-orbitals. Hence, F_3^- does not exist. On the other hand, I_3^- can expand its octet due to presence of *d*-orbital and therefore, exists.

(ii) The oxoacid of phosphorus containing +3 oxidation state, undergoes disproportionation to yield compounds in higher and lower oxidation states. Hence, H_3PO_3 undergoes disproportionation reaction but H_3PO_4 does not, as in it phosphorus is already in highest oxidation state (+5).

$$4H_3\overset{+3}{P}O_3 \xrightarrow{\Delta} \overset{-3}{P}H_3 + 3H_3\overset{+5}{P}O_4$$

(iii) The acidic strength of the hydrogen halides increases in the order : HF < HCl < HBr < HI

This order is a result of bond dissociation enthalpies of H—X bond, which decreases from H—F to H—I as the size of halogen atom increases.

OR

(a) (i) $HOCl < HOClO < HOClO_2 < HOClO_3$

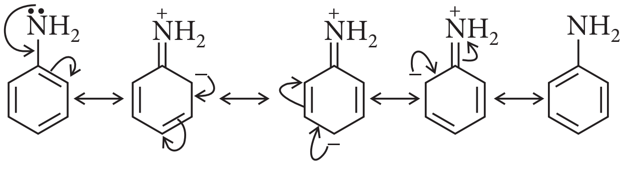
As the oxidation state of Cl increases (or the number of oxygen atoms increases), the –ve charge dispersal becomes more and more from Cl atom due to higher electronegativity value of oxygen. Lesser the charge on Cl atom more is the stability.

(ii) $SiO_2 < CO_2 < N_2O_5 < SO_3$

In case of oxides of non-metals, the acidic strength increases with increase in oxidation state. The oxidation states of various elements are Si = +4, C = +4, N = +5, S = +6 in the given oxides. Due to the small size of C-atom, CO_2 is more acidic than SiO_2.

(b) Xenon atom has large size and lower ionisation potential in comparison to He, Ne, Ar and Kr. The outermost energy shell has *d*-orbitals. The paired electrons of valence shell can be unpaired and the electrons are shifted to *d*-orbitals under suitable conditions. The unpaired electrons are shared by fluorine atoms and covalent bonds are formed. In this way, xenon forms compounds with fluorine.

27. (i) In case of aniline, the lone pair of electrons on the N-atom is delocalized with the π-electrons of the benzene ring, making the lone pair of electrons on nitrogen less available for protonation.



On the other hand, in methylamine the electron-releasing methyl group increases the electron density around nitrogen, thereby increasing the availability of the lone pair of electrons.

$$CH_3 \rightarrow \ddot{N}H_2$$

Therefore, aniline is a weaker base than methylamine and hence its pK_b value is higher than that of methylamine.

(ii) Methylamine accepts a proton from water and liberates the OH^- ion because it is a stronger base than water.

$$CH_3\ddot{N}H_2 + H{-}OH \longrightarrow CH_3\overset{+}{N}H_3 + \bar{O}H$$

The OH^- ion reacts with the Fe^{3+} ions of the solution to fom a brown precipitate of hydrated ferric oxide.

$FeCl_3 \rightarrow Fe^{3+} + 3Cl^-$

$$2Fe^{3+} + 6OH^- \rightarrow 2Fe(OH)_3 \text{ or } \underset{\substack{\text{Hydrated ferric oxide}\\ \text{(brown ppt.)}}}{Fe_2O_3 \cdot 3H_2O}$$

(iii) Gabriel phthalimide synthesis is the only method used to make primary amines because it is not possible to alkylate potassium phthalimide with either $(CH_3)_2CH{-}X$ or $(CH_3)_3C{-}X$.

28. (i) $Ni_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Cu_{(s)} + Ni^{2+}_{(aq)}$

$$E_{cell} = E^{\circ}_{cell} - \frac{0.059}{n}\log\frac{[Ni^{2+}]}{[Cu^{2+}]}$$

$$0.059 = E^{\circ}_{cell} - \frac{0.059}{2}\log\left(\frac{0.01}{0.1}\right) \qquad [\text{Here, } n = 2]$$

$$0.059 = E^{\circ}_{cell} - \frac{0.059}{2}\log\left(\frac{1}{10}\right)$$

$$0.059 = E^{\circ}_{cell} - \frac{0.059}{2}(-\log 10)$$

$$0.059 = E^{\circ}_{cell} + \frac{0.059}{2} \quad \Rightarrow \quad E^{\circ}_{cell} = 0.059 - \frac{0.059}{2}$$

$$\therefore \ E^{\circ}_{cell} = \frac{0.059}{2} = 0.0295 \approx 0.03$$

Now, $E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode}$

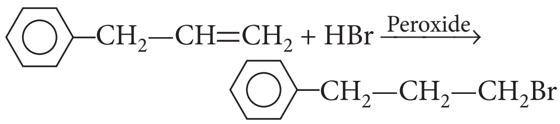
$0.03 = 0.34 - E^{\circ}_{anode}$

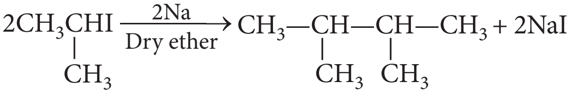
$E^{\circ}_{anode} = 0.34 - 0.03 = 0.31$ V

Hence, $E^{\circ}_{Ni^{2+}/Ni} = +0.31$ V

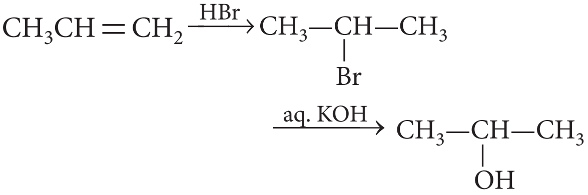
(ii) **Specific conductance :** It is the conductance due to ions present in 1 cm^3 of electrolytic solution.

Equivalent conductance (Λ_{eq}) **:** It is the conductance of an electrolytic solution containing 1 gram-equivalent of the electrolyte. The solution is contained in between two electrodes which are 1 cm apart.

29. (i)


(ii)


$$2CH_3\underset{\substack{|\\CH_3}}{C}HI \xrightarrow[\text{Dry ether}]{2Na} CH_3{-}\underset{\substack{|\\CH_3}}{C}H{-}\underset{\substack{|\\CH_3}}{C}H{-}CH_3 + 2NaI$$

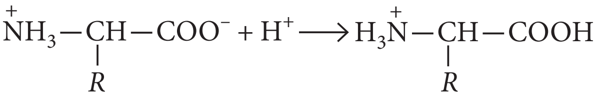
(iii)


$$CH_3CH{=}CH_2 \xrightarrow{HBr} CH_3{-}\underset{\substack{|\\Br}}{C}H{-}CH_3 \xrightarrow{\text{aq. KOH}} CH_3{-}\underset{\substack{|\\OH}}{C}H{-}CH_3$$

30. Isoelectric point of an amino acid is that pH at which there is no net migration of the amino acid occurs in an electric field. It is sometimes represented as pI.

Therefore,

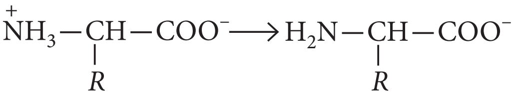
(a) Below the pI (pH < pI), the zwitter ion will accept H^+ and exist as the cation.



$$\overset{+}{N}H_3{-}\underset{\substack{|\\R}}{C}H{-}COO^- + H^+ \longrightarrow H_3\overset{+}{N}{-}\underset{\substack{|\\R}}{C}H{-}COOH$$

Therefore, migration will be towards the cathode.

(b) Above the pI (pH > pI), the zwitter ion will release proton and will exist as anion.



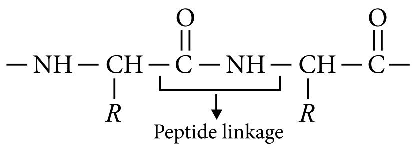
$$\overset{+}{N}H_3{-}\underset{\substack{|\\R}}{C}H{-}COO^- \longrightarrow H_2N{-}\underset{\substack{|\\R}}{C}H{-}COO^-$$

Therefore, migration will be towards the anode.

(c) At pH = pI, there is no net charge, therefore, there is no migration.

OR

(i) Proteins are the polymers of α-amino acids linked by amide formation between carboxyl and amino group. This is called peptide linkage or peptide bond *e.g.*,



$$-NH-\underset{\substack{|\\R}}{C}H-\overset{\substack{O\\ \|}}{C}-NH-\underset{\substack{|\\R}}{C}H-\overset{\substack{O\\ \|}}{C}-$$

(ii) The specific sequence in which the various α-amino acids present in a protein are linked to one another is called its primary structure. Any change in the primary structure creates a different protein.

(iii) The loss of biological activity of a protein by changing the pH, temperature or by adding some salt due to disruption of the native structure of protein is called denaturation. During denaturation secondary and tertiary structure of protein is destroyed but primary structure remains intact.

31.

Complex and IUPAC name	Oxidation state of central metal ion/ atom	Electronic configuration of central metal ion/atom (outer)	Coordination number	Geometry	Magnetic moment (B.M.)
(a) $K[Cr(C_2O_4)_2(H_2O)_2].3H_2O$ potassium diaqua*bis*(oxalto) chromate(III) trihydrate	+3	$3d^3$ or $t_{2g}{}^3$	6	Octahedral	3.87
(b) $[CrCl_3(py)_3]$ trichloridotri-pyridinechromium(III)	+3	$3d^3$ or $t_{2g}{}^3$	6	Octahedral	3.87
(c) $K_4[Mn(CN)_6]$ potassium hexacyanidomanganate(II)	+2	$3d^5$ or $t_{2g}{}^5$	6	Octahedral	1.73
(d) $[Co(NH_3)_5Cl]Cl_2$ pentaamminechloridocobalt(III) chloride	+3	$3d^6$ or $t_{2g}{}^6$	6	Octahderal	0
(e) $Cs[FeCl_4]$ caesium tetrachloridoferrate(III)	+3	$3d^5$ or $e^2\ t_2{}^3$	4	Tetrahedral	5.92

OR

(i) This theory is given by Pauling. The main assumptions of this theory are as follows :

(a) The empty *s*, *p* and *d* atomic orbitals equal to the coordination number of central metal ion, are made available by the central metal atom or ion. The vacant orbitals get hybridized to produce equal number of hybridized orbitals of same energy and shape which are arranged in definite geometry.

(b) The ligand molecules must have at least one σ-orbital containing a lone pair of electrons.

(c) These σ-orbitals (containing lone pairs) of ligand are overlapped by the vacant hybridized orbitals of metal atoms or ions to form ligand → Metal σ-bond (coordinate bond).

(ii) If the *d*-orbitals used in the hybridization (d^2sp^3) are of lower shell than the *s*- and *p*- orbitals *i.e.*, $(n - 1)d$ then the complexes formed are called inner orbital or low spin complexes. For example in $K_4[Fe(CN)_6]$, 3*d*, 4*s* and 4*p* orbitals take part in hybridization, therefore, it is an inner orbital complex.

If the *d*-orbitals used in the hybridization (sp^3d^2) are of the same principal energy level as that of *s*- and *p*-orbitals, the complexes are called outer orbital complexes or high spin complexes. For example in $[FeF_6]^{3-}$, 4*s*, 4*p* and 4*d* orbitals take part in hybridization, therefore, it is outer orbital complex.

32. (a) The phenoxide ion formed after loss of proton from phenol is resonance stabilised and thus, phenol loses H^+ ion to show acidic character.

$$C_6H_5OH \longrightarrow \underset{\text{Resonance stabilised}}{C_6H_5O^-} + H^+$$

On the other hand, alkoxide ion formed from hexanol shows no such resonance stabilisation and is unstable.

(b) In substituted phenols, the presence of electron releasing group decreases the acidic strength of phenol. This effect is more pronounced when such a group is present at *ortho* and *para*-positions. It is due to the increased negative charge in phenoxide ion. Thus *m*-aminophenol is stronger acid than *o*-aminophenol.

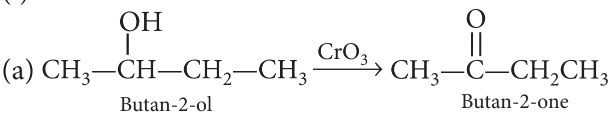
(c) (i) Zinc dust

(ii) Alkyl halide in the presence of anhydrous aluminium chloride, *i.e.*, CH_3Cl and $AlCl_3$ (anhy.)

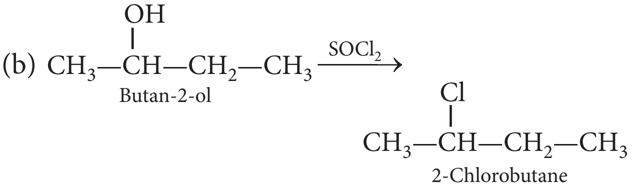
(iii) Cu/573 K

OR

(i)



$$\text{(a) } \underset{\text{Butan-2-ol}}{CH_3-\overset{\overset{\displaystyle OH}{|}}{C}H-CH_2-CH_3} \xrightarrow{CrO_3} \underset{\text{Butan-2-one}}{CH_3-\overset{\overset{\displaystyle O}{||}}{C}-CH_2CH_3}$$

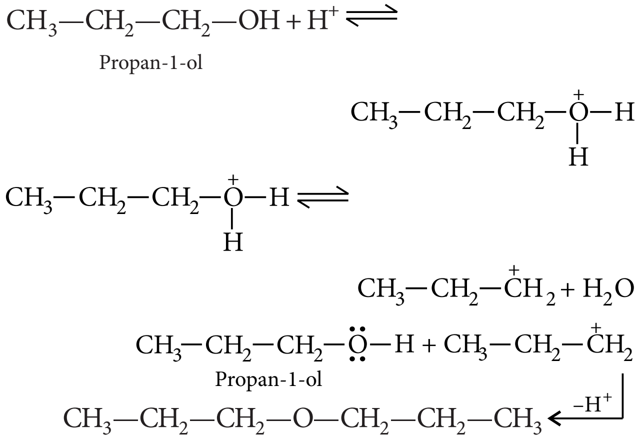


$$\text{(b) } \underset{\text{Butan-2-ol}}{CH_3-\overset{\overset{\displaystyle OH}{|}}{C}H-CH_2-CH_3} \xrightarrow{SOCl_2} \underset{\text{2-Chlorobutane}}{CH_3-\overset{\overset{\displaystyle Cl}{|}}{C}H-CH_2-CH_3}$$

(ii) Propan-1-ol on treatment with conc. H_2SO_4 at 413 K would yield 1-propoxypropane. In this method, the alcohol is continuously added to keep its concentration in excess.

$$2\underset{\text{Propan-1-ol}}{CH_3—CH_2—CH_2—OH} + H_2SO_4 \xrightarrow{413\ K} \underset{\text{1-Propoxypropane}}{CH_3—CH_2—CH_2—O—CH_2—CH_2—CH_3}$$

Mechanism :



$$\underset{\text{Propan-1-ol}}{CH_3—CH_2—CH_2—OH} + H^+ \rightleftharpoons CH_3-CH_2-CH_2-\underset{\underset{H}{|}}{\overset{+}{O}}-H$$

$$CH_3-CH_2-CH_2-\underset{\underset{H}{|}}{\overset{+}{O}}-H \rightleftharpoons CH_3-CH_2-\overset{+}{C}H_2 + H_2O$$

$$\underset{\text{Propan-1-ol}}{CH_3-CH_2-CH_2-\underset{\cdot\cdot}{\ddot{O}}-H} + CH_3-CH_2-\overset{+}{C}H_2 \xrightarrow{-H^+} CH_3—CH_2—CH_2—O—CH_2—CH_2—CH_3$$

33. (a) (i) No. of X atoms in the unit cell = 8 × 1/8 = 1

No. of Y atoms in the unit cell = 6 × 1/2 = 3

Formula = XY_3

(ii) (A) If one X atom is missing, no. of X atoms in the unit cell = 7/8

No. of Y atoms in the unit cell = 3

Formula = $X_{7/8}Y_3$ or X_7Y_{24}

(B) No. of X atoms in the unit cell = 7/8

No. of Z atoms in the unit cell = 1/8

No. of Y atoms in the unit cell = 3

Formula = $X_{7/8}Y_3Z_{1/8}$ or $X_7Y_{24}Z$

(b) (i) As 27 g of Al will contain 6.023×10^{23} atoms

∴ 8.1 g Al will contain

$$= \frac{6.023\times10^{23}}{27}\times 8.1 \text{ atoms}$$

$$= 1.8069 \times 10^{23} \text{ atoms}$$

In *fcc*, 4 atoms are present in one unit cell

∴ 1.8069×10^{23} atoms will be present in

$$\frac{1.8069\times10^{23}}{4} = 4.517 \times 10^{22} \text{ unit cells}$$

(ii) In *ccp* arrangement, each chloride ion would have one octahedral void and two tetrahedral voids associated with it.

Number of octahedral voids with 3 chloride ions = 3

Number of tetrahedral voids with 3 chloride ions = 3 × 2 = 6

Total number of voids with 3 chloride ions = 9

Number of octahedral voids occupied by Cr (III) = 1

Fraction of octahedral voids occupied = 1/3

Fraction of total number of voids occupied = 1/9

OR

(a) In a cubic crystal system, there are two types of voids known as octahedral and tetrahedral voids. If r_1 is the radius of void and r_2 is the radius of atom in close packing then,

$$\left(\frac{r_1}{r_2}\right)_{\text{octahedral}} = 0.414 \quad \text{and} \quad \left(\frac{r_1}{r_2}\right)_{\text{tetrahedral}} = 0.225$$

The above radius ratio values indicate that octahedral void has larger radius hence, for maximum diameter of atom to be present in interstital space,

$r_1 = 0.414\, r_2$

Also, in *fcc*, $r_2 = \frac{a}{2\sqrt{2}}$

Diameter required = $2r_1 = 2 \times r_2 \times 0.414$

$$= \frac{a}{2\sqrt{2}} \times 2 \times 0.414 = \frac{400 \times 0.414}{\sqrt{2}} \approx 117 \text{ pm}$$

(b) For *fcc*, $r = \frac{a}{2\sqrt{2}}$, a = 400 pm,

$$\therefore \quad r = \frac{400}{2\sqrt{2}} = \frac{400}{2\sqrt{2}} \times \frac{\sqrt{2}}{\sqrt{2}} = \frac{400\sqrt{2}}{4} = 100\sqrt{2}$$

⇒ $r = 100 \times 1.414 = 141.4$ pm

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