SAMPLE OUESTION OAPER

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

An efficient catalytic system consisting of *N*-hydroxyphthalimide (NHP) and a Co ion for the oxidation of alcohols and diols with molecular oxygen has been discovered.

$$\begin{array}{c|c} \text{OH} & \xrightarrow{\text{NHP (10 mol\%)}} \\ & + \text{O}_2 & \xrightarrow{\text{additive (5 mol\%)}} \\ & \text{C}_6\text{H}_{13} & \xrightarrow{\text{Solvent}} \end{array} \qquad \begin{array}{c} \text{O} \\ \text{C}_6\text{H}_{13} & \text{C}_6\text{H}_{13} \end{array}$$

The implementation of catalysts in combination with molecular oxygen which is cheap and green stoichiometric oxidant represents an emerging alternate to the traditional procedures. This process is also environmental friendly.

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

- (i) The cobalt-based catalyst along with molecular oxygen mentioned in the study above can be used to convert
 - (a) octan-1-ol to octan-2-one

(b) octan-2-ol to octan-2-one

(c) hexanol to hexanoic acid

- (d) propanal to propanone.
- (ii) A compound (X) with molecular formula, $C_8H_{17}O$ on oxidation with the Co-based catalyst forms a compound (Y). The compound (Y) gives positive iodoform test and on reaction with CH_3MgBr followed by hydrolysis gives compound (Z). The compound (Z) is

(a)
$$CH_3 - C - C_6 H_{13}$$

(b)
$$CH_3 - \overset{n}{\overset{n}{\overset{}_{\smile}}} - C_5 H_{11}$$

(c)
$$CH_3 - C - C_6 H_{13}$$

OH

- (iii) 2-Octanol has higher boiling point than 2-octanone because of
 - (a) hydrogen bonding

(b) dipole-dipole interaction

(c) both (a) and (b)

- (d) neither (a) nor (b).
- (iv) Identify the product (*P*) in the given reaction.

$$C_{6}H_{13}+O_{2}\xrightarrow{NHP\ (10\ mol\%)} C_{Co(OAc)_{2}(0.5\ mol\%)} (P)$$

$$C_{6}H_{13}+O_{2}\xrightarrow{Additive\ (5\ mol\%)} C_{6}H_{12}$$

$$C_{6}H_{13}$$

$$C_{6}H_{13}$$

$$C_{6}H_{13}$$

$$C_{6}H_{13}$$

$$C_{6}H_{13}$$

$$C_{6}H_{13}$$

$$C_{6}H_{13}$$

Which of the following reagents can also be used instead of the catalyst mentioned in the study above for the oxidation of 2° alcohols?

(a)
$$CrO_3/C_5H_5N$$

(b)
$$Al_2O_3/\Delta$$

(c)
$$K_2CrO_7 / dil.H_2SO_4$$

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

Halogen elements have different electronegativity. Due to this they combine with each other to form covalent compounds (binary). The binary compounds formed by halogens amongst themselves are known as interhalogen compounds. These compounds have general formula; XX_n , where n=1, 3, 5 and 7. The interhalogen compounds may be regarded as the halide of the more electronegative halogen. Thus, since the electropositive character of halogens is in the order; F < CI < Br < I, fluorine cannot form any inter-halogen compounds, while iodine has the maximum tendency to form inter-halogen compounds. Inter-halogen compounds are used as non-aqueous solvents, as catalyst in few reactions and as fluorinating compounds.

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: Inter-halogen compounds have higher boiling point than halogens.

Reason : X - X' bond in inter-halogens is weaker than X - X bond in halogens.

(ii) Assertion: Inter-halogens compounds are more reactive than halogens (except fluorine).

Reason : Covalent bond between dissimilar atoms in inter-halogen compounds is weaker than that between similar atoms in halogens except F—F bond.

OR

Assertion : Inter-halogen compounds are covalent molecules except ClF.

Reason : The electropositive character of halogens is F < Cl < Br < I.

(iii) Assertion: All inter-halogen compounds are paramagnetic.

Reason: *X-X'* type of inter-halogen undergoes hydrolysis giving a halide ion derived from the smaller halogen and a hypohalite ion derived from the larger halogen.

(iv) Assertion: Iodine has maximum tendency to form inter-halogen compounds.

Reason: The electropositive character of Iodine is maximum among the halogens.

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

3. Three metals, *A*, *B* and *C*, with solutions of their respective cations are tested in a voltaic cell with the following results:

A and B: A is the cathode

B and *C* : *C* is the cathode

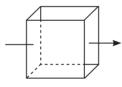
A and C: A is the anode

What is the order of reduction potentials from highest to lowest for the cations of these metals?

- (a) A > B > C
- (b) B > C > A
- (c) C > A > B
- (d) B > A > C
- **4.** A crystal is made of particles *X* and *Y*. *X* forms *fcc* packing and *Y* occupies all the octahedral voids. If all the particles along one body diagonal are removed then the formula of the crystal would be
 - (a) X_4Y_3
- (b) $X_{5}Y_{4}$
- (c) X_4Y_5
- (d) none of these.

ΩR

In NaCl unit cell, all the ions lying along the axis as shown in the figure are removed. Then the number of Na⁺ and Cl⁻ ions remaining in the unit cell are



- (a) 4 and 4
- (b) 3 and 3
- (c) 1 and 1
- (d) 4 and 3
- 5. For the given compounds, CH_3 –C– CH_3 , CH_3 – CH_2 –CHO, CH_3 –CHO

correct statement is

- (a) A and C both give iodoform test
- (b) A, B and C give aldol condensation
- (c) *A*, *B* and *C* do not give Cannizzaro reaction
- (d) all are correct.
- **6.** Which of the following is not correct?
 - (a) 1-Butene + HBr $\xrightarrow{\text{peroxide}}$ 1-Bromobutane
- (b) Propylene + $HCl \longrightarrow 2$ -Chloropropane
- (c) 1-Butene + HCl $\xrightarrow{\text{peroxide}}$ 2-Chlorobutane
- (d) 1-Butene + HBr → 1-Bromobutane

OR

Which of the following sequences would yield *m*-nitrochlorobenzene from benzene?

(a) Benzene $\xrightarrow{\text{Cl}_2/\text{FeCl}_3} \xrightarrow{\text{HNO}_3} \xrightarrow{\text{H}_2\text{SO}_4}$

- (b) Benzene $\xrightarrow{\text{H}_2\text{SO}_4/\text{HNO}_3}$
- (c) Benzene $\xrightarrow{\text{H}_2\text{SO}_4/\text{HNO}_3} \xrightarrow{\text{Cl}_2/\text{FeCl}_3}$
- (d) All of the above
- 7. If the volume of the vessel in which the reaction, $2NO + O_2 \longrightarrow 2NO_2$, is occurring is diminished to 1/3rd of its initial volume, the rate of the reaction will be increased by
 - (a) 3 times
- (b) 9 times
- (c) 27 times
- (d) 36 times.

In which of the following octahedral complexes of Co (atomic number = 27), will the magnitude of Δ_0 be the highest?

(a) $[Co(CN)_{6}]^{3-}$

(b) $[Co(C_2O_4)_3]^{3-}$ (c) $[Co(H_2O)_6]^{3+}$

(d) $[Co(NH_3)_6]^{3+}$

1000 g H₂O have 0.1 mole urea and its freezing point is − 0.2°C and now it is freezed upto −2°C, then how much amount of ice will form?

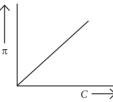
(a) 100 g

(b) 900 g

(c) 500 g

(d) 200 g

A graph showing variation of osmotic pressure (π) versus molar concentration (C) of an aqueous solution at temperature *T* is given below :



The slope of the line represent

(a) solution constant R

(b) absolute temperature T

(c) *RT*

(d) degree of ionization of solute.

10. In an electrical field, the particles of a colloidal system move towards cathode. The coagulation of the same sol is studied using K₂SO₄(I), Na₃PO₄(II), K₄[Fe(CN)₆](III) and NaCl(IV). Their coagulating power should be

(a) (I) > (II) > (III) > (IV)

(b) (III) > (II) > (IV)

(c) (III) > (I) > (II) > (IV)

(d) (IV) > (III) > (I) > (II)

11. Which of the following is an incorrect statement?

- (a) The oxide in lower oxidation state of a transition metal is acidic whereas the one in higher oxidation state is usually basic.
- (b) Transition metal usually exhibits higher oxidation states in fluorides and oxides.
- (c) Transition metal halides become more covalent with the increasing oxidation state of the transition metal and are more susceptible to hydrolysis.
- (d) The oxide in higher oxidation state of a transition metal is acidic whereas the one in lower oxidation state is usually basic.

OR

 E° values for the couples Cr^{3+}/Cr^{2+} and Mn^{3+}/Mn^{2+} are -0.41 and +1.51 volts respectively. These values suggest that

- (a) Cr^{2+} acts as a reducing agent whereas Mn^{3+} acts as an oxidizing agent
- (b) Cr^{2+} is more stable than Cr^{3+} state
- (c) Mn^{3+} is more stable than Mn^{2+}
- (d) Cr^{2+} acts as an oxidizing agent whereas Mn^{3+} acts as a reducing agent.

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: Formic acid reduces mercuric chloride to mercurous chloride on heating, while acetic acid

Reason: Formic acid is a stronger acid than acetic acid.

13. **Assertion**: $[Fe(CN)_6]^{3-}$ has d^2sp^3 type hybridisation.

Reason : $[Fe(CN)_6]^{3-}$ ion shows magnetic moment corresponding to two unpaired electrons.

14. Assertion : The overall order of the reaction is the sum of the exponents of all the reactants in the rate expression.

Reason: There are many higher order reactions.

15. Assertion: When acetamide reacts with NaOH and Br₂, methyl amine is formed.

Reason: The reaction occurs through intermediate formation of isocyanate.

16. Assertion: Solubility of proteins is minimum at the isoelectric point.

Reason: At isoelectric point, protein molecule behaves as a zwitter ion.

OR

Assertion: Nucleotides are phosphate esters of nucleosides.

Reason: The various nucleotides in nucleic acids are linked either through purine or pyrimidine bases.

SECTION - B

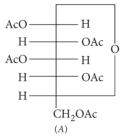
The following questions (Q.No. 17-25) are short answer type and carry 2 marks each.

- 17. Write the formula of the oxo-metal anions of the first series of the transition metals in which the metal exhibits the oxidation state equal to its group number.
- **18.** Show that half life period of a first order reaction is independent of initial concentration of the reactant.

OR

Write expression for rate constant of a zero order reaction and explain the terms involved. What is the unit of rate constant of a zero order reaction?

- 19. Outer hard shells of two eggs are removed. One of the egg is placed in pure water and the other is placed in saturated solution of sodium chloride. What will be observed and why?
- **20.** Account for the following:
 - (i) Why does compound (A) given below not form an oxime?



- (ii) How do you explain the presence of six carbon atoms in glucose in a straight chain?
- 21. Knowing the electron gain enthalpy values for $O \rightarrow O^-$ and $O \rightarrow O^{2-}$ as -141 and 702 kJ mol⁻¹ respectively, how can you account for the formation of large number of oxides having O^{2-} species and not O^- ?

OR

Answer the following:

- (i) In the ring test of NO_3^- ion, Fe^{2+} ion reduces nitrate ion to nitric oxide, which combines with $Fe_{(aq)}^{2+}$ ion to form brown complex. Write the reactions involved in the formation of brown ring.
- (ii) Account for the following: Thermal stability of water is much higher than that of H₂S.

- **22.** An aromatic compound 'A' on treatment with aqueous ammonia and on heating forms compound 'B' which on heating with Br₂ and KOH forms a compound 'C' of molecular formula C_6H_7N . Write the structure and IUPAC name of compounds A, B and C.
- **23.** Explain the following:
 - (i) What happens when dialysis is prolonged?
 - (ii) How does the precipitation of colloidal smoke take place in Cottrell precipitator?
- 24. Explain why
 - (a) the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride?
 - (b) alkyl halides, though polar, are immiscible with water?
- **25.** Write the equations involved in the following reactions:
 - (i) Stephen reaction

(ii) Etard reaction

OR

Illustrate the following name reactions giving a chemical equations in each case:

(i) Clemmensen reaction

(ii) Cannizzaro reaction

SECTION - C

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

26.
$$C_5H_{13}N \xrightarrow{aq. NaNO_2/HCl} (Y)$$
 $(X) \xrightarrow{-N_2} Tertiary$
Optically active alcohol

- (i) Identify (X) and (Y).
- (ii) Give structures of intermediate(s), if any, in the formation of (Y) from (X).

OR

Predict the products of the following reactions:

(iii)
$$C-CH_3 + CH_3CH_2NH_2 \xrightarrow{H^+}$$

27. In the button cells, widely used in watches and other devices, the following reaction takes place:

$$Zn_{(s)} + Ag_2O_{(s)} + H_2O_{(l)} \rightarrow Zn_{(aq)}^{2+} + 2Ag_{(s)} + 2OH_{(aq)}^{-}$$

Determine E° and ΔG° for the reaction.

(Given :
$$E_{Ag^+/Ag}^{\circ}$$
 = + 0.80 V, $E_{Zn^{2+}/Zn}^{\circ}$ = -0.76 V)

- **28.** Answer the following:
 - (i) What is a developer used in photography and how does it work?
 - (ii) How will you synthesise
 - (a) 1-phenylethanol from a suitable alkene?
 - (b) cyclohexylmethanol using an alkyl halide by an S_N^2 reaction?

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- **29.** (i) $[Fe(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{2+}$ are of different colours in dilute solutions. Why?
 - (ii) Write the hybridisation and number of unpaired electrons in the complex $[CoF_6]^{3-}$. (Atomic no. of Co = 27)

OR

Write the correct formulae for the following coordination compounds:

- (a) CrCl₃·6H₂O (violet, with 3 chloride ions/unit formula)
- (b) CrCl₃·6H₂O (light green colour, with 2 chloride ions/unit formula)
- (c) CrCl₃·6H₂O (dark green colour, with 1 chloride ion/unit formula)
- **30.** Answer the following :
 - (i) In a cubic close-packed structure of a mixed oxide one-eighth of tetrahedral voids are occupied by divalent ions, X^{2+} while one half of the octahedral voids are occupied by trivalent ions, Y^{3+} . What is the formula of the compound?
 - (ii) Ferric oxide crystallises in a hexagonal close packed array of oxide ions with two out of every three octahedral holes occupied by ferric ions. Derive the formula of the ferric oxide.

SECTION - D

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

- **31.** (a) What are interstitial compounds? Explain them with reference to transition metals and mention their two important properties.
 - (b) Decide giving reasons which one will exhibit the property indicated in the given pair.
 - (i) Sc^{3+} or Cr^{3+} : Paramagnetism
 - (ii) V or Mn: More number of oxidation states
 - (iii) V^{4+} or V^{5+} : Diamagnetism

OR

- (a) Why are Sm²⁺, Eu²⁺ and Yb²⁺ good reducing agents?
- (b) Can lanthanum (Z = 57) exhibit +4 oxidation state?
- (c) Why are +3 oxidation state of gadolinium (Z = 64) and lutetium (Z = 71) especially stable?
- (d) First ionisation energy of copper is higher than those of alkali metals, while second and third ionisation energies are lower. Explain.
- **32.** (a) Carry out the following transformations.

$$(i) \xrightarrow{Br} \xrightarrow{COOH}$$

(ii)
$$HC \equiv CH \longrightarrow \bigcap_{O} OH$$

- (iii) $C_6H_5CH = CH_2 \longrightarrow C_6H_5CH_2COOH$
- (b) Out of nitrobenzoic acid and chlorobenzoic acid which one is a stronger acid and why?
- (c) The C O bond in carboxylic acid is shorter than that in alcohol. Explain.

OI

- (a) Write the complete reaction for each of the following conversions stating the conditions necessary:
 - (i) Toluene to benzaldehyde
- (ii) Aldehyde to acetal.

- (b) Describe the preparation of acetic acid from acetylene.
- (c) How can the following be obtained from acetic acid:
 - (i) Acetaldehyde

- (ii) Acetone?
- 33. (a) The freezing point of a solution having 50 cm³ of ethylene glycol in 50 g water is found to be 34 °C. Calculate the density of ethylene glycol, assuming ideal behaviour.
 - $(K_f \text{ for water} = 1.86 \text{ K kg mol}^{-1})$
 - (b) What is the effect of pressure on the solubility of gas in polar solvent?
 - (c) When water and nitric acid are mixed together, a rise in temperature is observed. What type of azeotropic mixture is obtained?
 - (d) Explain the following: Boiling point elevation constant for a solvent.
 - (e) The HCl used in laboratory is 21.3% (w/v). What is its molarity?

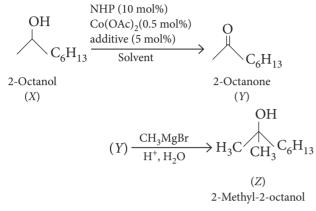
OR

- (a) An aqueous solution of glucose boils at 100.02° C. What is the number of glucose molecules in the solution containing 100 g of water? What will be the osmotic pressure of this glucose solution at 27° C? (Given K_b for $H_2O = 0.5$ K kg mol⁻¹, $N_A = 6.02 \times 10^{23}$ mol⁻¹,
 - $R = 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$
- (b) A solution of glucose in water is labelled as 20% (w/W). The density of the solution is 1.20 g mL⁻¹. Calculate
 - (i) molality
 - (ii) molarity and
 - (iii) mole fraction of each component in solution.

< SOLUTIONS >

1. (i) (b)

(ii) (c): Since compound(Y) gives iodoform test, it must be methyl ketone, $CH_3COC_6H_{13}(Y)$. It will be obtained by oxidation of 2-octanol (X).



(iii) (a): Alcohols have higher boiling points than ketones because of intermolecular hydrogen bonding.

(iv) (b)

OR

(a) : A secondary alcohol is easily oxidised by chromic anhydride (CrO₃).

2. (i) (b)

(ii) (a): Higher boiling point by inter-halogen compounds is associated with the polarity of X-X' bond.

OR

(b) : Halogen elements have different electronegativity. Due to this they combine with each other to form covalent compounds.

(iii) (d): All inter-halogens are not paramagnetic.

(iv) (a)

3. (c) : R.P. order C > A > B.

4. (b): Along one body diagonal, 2*X* atoms from 2 corners, one *Y* particle (at the centre of cube) will be removed.

So, effective no. of *X* particles in a unit cell

$$=4-\left(2\times\frac{1}{8}\right)=\frac{15}{4}$$

and effective no. of *Y* particles in a unit cell = 4-1=3 X: Y = 15/4: 3 or $5: 4 \Rightarrow X_5Y_4$

OR

(b) : On removing all the ions lying along the axis

one Na⁺ from centre and 2Cl⁻ from *fcc* centres are removed.

.. No. of Na⁺ ions =
$$12 \times 1/4 = 3$$

No. of Cl⁻ ions = $8 \times 1/8 + 4 \times 1/2 = 3$

5. (d)

6. (d): The correct reaction is
$$H_3C-CH_2-CH=CH_2+HBr$$

1-Butene

Br

 $H_3C-CH_2-CH-CH_3$
 OR

2-Bromobutane

(c): $C_6H_6 \xrightarrow{H_2SO_4/HNO_3} C_6H_5 - NO_2 \xrightarrow{Cl_2/FeCl_3} C_6$

m-Nitrochlorobenzene

7. (c): For a given reaction,

$$2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$$

Rate of reaction = $k[NO]^2[O_2]$

Rate of reaction is directly proportional to concentration of the reactants or inversely proportional to the volume of the vessel. *i.e.*, $C \propto \frac{n}{V}$

If volume of vessel is reduced to 1/3rd of its initial value, then concentration of compound is increased by 3 times and consequently the rate of reaction by will increase 27 times.

8. (a): As CN⁻ is strongest field ligand so it has highest Δ_0 .

9. (b) :
$$\Delta T_f = 0.2 = K_f \times \frac{0.1}{1000} \times 1000$$
 ...(i)

$$\Delta T_f = 2 = K_f \times \frac{0.1}{\text{wt. of solvent}} \times 1000$$
 ...(ii)

On dividing,

$$\frac{\text{wt. of solvent}}{1000} = \frac{0.2}{2}$$

or wt. of solvent = 100 g

Weight of remaining H_2O is 100 g and weight of ice is 900 g.

OR

(c) :
$$\pi = CRT$$

Comparing with y = mx + c

Slope =
$$RT$$

- 10. (b): When excess of an electrolyte is added, the colloidal particles are precipitated. The reason is that colloidal particles take up ions carrying charge opposite to that present on themselves. This causes neutralisation leading to their coagulation. Generally greater the valency of the flocculating ion added, greater is the power to cause coagulation. So the sequence of coagulating power is III > II > IV.
- 11. (a): For a transition metal, the oxide in lower oxidation state is basic while higher oxidation state is acidic.

OR

(a) : Lesser and negative reduction potential indicates that Cr^{2+} is a reducing agent. Higher positive reducing potential indicates that Mn^{3+} is a stronger oxidizing agent.

12. **(b)**:
$$HCOOH + 2HgCl_2 \xrightarrow{\Delta} Hg_2Cl_2 + CO_2 + 2HCl_2$$

Reducing property of formic acid is due to -CHO group.

- 13. (c): $[Fe(CN)_6]^{3-}$ ion shows magnetic moment corresponding to one unpaired electron.
- **14. (c)**: Reactions of higher order are rare because chances for larger number of molecules to come simultaneously for collision are less.

15. (a) :
$$CH_3CONH_2 + Br_2 + 4NaOH \rightarrow CH_3NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

The reaction occurs through intermediate formation of alkyl isocyanate which on hydrolysis gives methylamine and sodium carbonate.

$$CH_{3}-C-NH_{2}\xrightarrow{Br_{2}/NaOH}CH_{3}-C-NHBr$$

$$OH^{-}+H_{2}O$$

16. (a): At isoelectric point, protein molecules behave as zwitter ions and hence, do not move toward any electrode or act as neutral molecules. This reduces their solubility to minimum and thus, helps in their separation and purification.

OR

(c) : The various nucleotides in nucleic acids are linked through phosphate ester groups.

17. ScO_2^- ; Group number = Oxidation state of Sc = 3. TiO_3^{2-} : Group number = Oxidation state of Ti = 4 VO_3^- : Group number = Oxidation state of V = 5 $Cr_2O_7^{2-}$: Group number = Oxidation state of Cr = 6 CrO_4^{2-} : Group number = Oxidation state of Cr = 6 MnO_4^- : Group number = Oxidation state of Mn = 7

18. For first order reaction,

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}, \text{ at } t_{1/2}, [R] = \frac{[R]_0}{2}$$

$$\therefore \quad k = \frac{2.303}{t_{1/2}} \log \frac{[R]_0}{[R]_0/2} \text{ or, } t_{1/2} = \frac{2.303}{k} \log 2$$

$$t_{1/2} = \frac{2.303 \times 0.3010}{k} \Rightarrow t_{1/2} = \frac{0.693}{k}$$

In first order reaction, $t_{1/2}$ is independent of initial concentration.

OR

Expression for rate constant of a zero order reaction is $k = \frac{[R]_0 - [R]}{t}$

where $[R]_0$ is the initial concentration, [R] is the final concentration and t is time.

k = proportionality constant called rate constant of reaction.

For zero order reaction, rate may be expressed as: Rate = $k[A]^0$ or k

$$\frac{\text{mol } L^{-1}}{s} = k$$

or $k = \text{mol } L^{-1} s^{-1}$

- 19. The egg placed in pure water will swell because the concentration of proteins is high inside the egg as compared to water. Therefore, endosmosis occurs and water diffuses through the semipermeable membrane. The egg which is placed in sodium chloride solution will shrink due to exosmosis of water out of the egg.
- **20.** (i) Glucose pentaacetate (*A*) does not have a free –OH at C-1 and so cannot be converted to the open chain form to give –CHO group hence, it does not form the oxime.
- (ii) On prolonged heating with HI and red P, glucose gives *n*-hexane which shows it has six carbon atoms in a straight chain.

$$CH_2OH(CHOH)_4CHO \xrightarrow{HI, red P} CH_3(CH_2)_4CH_3$$
Glucose

 n -Hexane

21. This can be explained with the help of electronic configuration.

$$\begin{array}{cccc}
O & \longrightarrow & \stackrel{1s}{\uparrow} \downarrow & \stackrel{2s}{\uparrow} \downarrow & \stackrel{2p}{\downarrow} \uparrow \downarrow & \uparrow \uparrow \uparrow \uparrow \uparrow \\
O^{-} & \longrightarrow & \uparrow \downarrow \downarrow & \uparrow \downarrow \downarrow & \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \\
O^{2-} & \longrightarrow & \uparrow \downarrow \downarrow & \uparrow \downarrow \downarrow & \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow
\end{array}$$

As O^{2-} has most stable configuration amongst these. So, formation of O^{2-} is much more easier. In solid state, large amount of energy (lattice enthalpy) is released when oxides are formed with divalent O^{2-} ions. It is greater lattice enthalpy of the crystal lattice of oxide (O^{2-}) which compensates for the high energy required to add the second electron.

OR

(i)
$$NO_3^- + 3Fe^{2+} + 4H^+ \rightarrow NO + 3Fe^{3+} + 2H_2O$$

 $[Fe(H_2O)_6]^{2+} + NO \rightarrow [Fe(H_2O)_5(NO)]^{2+} + H_2O$
Brown ring

- (ii) As the size of central atom increases, M-H bond becomes weaker and longer and hence, thermal stability decreases while going from H_2O to H_2Te .
- **22.** Since the compound 'C' with molecular formula C_6H_7N is obtained from compound B on heating with Br_2 and KOH, the compound 'B' must be an amide and the compound 'C' must be an amine. Thus, aromatic amine having molecular formula C_6H_7N is $C_6H_5NH_2$, *i.e.*, aniline.

$$C_6H_5CONH_2 \xrightarrow{Br_2+KOH} C_6H_5NH_2$$
(B)
(C)
(C)
(B)

Since, the compound 'B' is formed from compound 'A' by treating with ammonia and then heating, the compound 'A' must be benzoic acid.

$$C_6H_5COOH \xrightarrow{\text{(i) aq. NH}_3} C_6H_5CONH_2$$
(A)
(B)

- 23. (i) When dialysis is prolonged, the traces of electrolytes are also removed. These electrolytes stabilise the colloid and when removed completely, make the colloid unstable and the colloid gets coagulated.
- (ii) Smoke is a colloidal solution of carbon particles in air. In Cottrell precipitator, when smoke is allowed to pass through a chamber having a number of metal plates attached to a metal, will be connected to a source of high potential. The charged particles of smoke get attracted by oppositely charged electrode and get precipitated after losing their charges.
- **24.** (a) In case of chlorobenzene, carbon to which chlorine is attached is sp^2 hybridised and is more electronegative than the corresponding carbon in cyclohexyl chloride which is sp^3 hybridised. So, the net dipole moment is lower in chlorobenzene.

(b) Alkyl halides are polar but are insoluble in water because energy required to break the intermolecular H – bonding among water molecules is much higher than energy released by water–halide interaction.

25. (i) Stephen reduction:

$$R$$
—CN + SnCl₂ + HCl \longrightarrow R —CH—NH
$$\xrightarrow{\text{H}_3\text{O}^+} R$$
 —CHO

(ii) Etard reaction:

CH₃ +
$$CrO_2Cl_2$$
 $\xrightarrow{CS_2}$ $CH(OCrOHCl_2)_2$
Chromium complex
$$\downarrow H_3O^+$$
CHO
Benzaldehyde

(i) Clemmensen reduction: The carbonyl group of aldehydes and ketones is reduced to CH_2 group on treatment with zinc amalgam and concentrated hydrochloric acid.

$$CH_3$$
 $C=O$ EH_3 CH_3 CH_3 $CH_2 + H_2O$ CH_3 CH_3 $CH_2 + H_2O$ CH_3 CH_3 CH_3 CH_3 CH_4 CH_3 CH_5 C

(ii) Cannizzaro reaction : Aldehydes which do not contain α -H atom undergo disproportionation when heated with concentrated (50 %) NaOH.

$$\begin{array}{ccc} \text{HCHO} + \text{HCHO} & \xrightarrow{50\% \text{ NaOH}} \\ \\ \text{Methanal} & \text{HCOONa} + \text{CH}_3\text{OH} \\ \\ \text{Sodium formate} & \text{Methanol} \end{array}$$

26. (i) As the compound (X) on treatment with HNO_2 evolves N_2 gas, therefore, (X) must be a primary amine. The compound (X) is optically active, it must contain a chiral carbon. The $-NH_2$ group cannot be directly attached to chiral carbon since such amines undergo racemisation due to nitrogen inversion. Therefore, the structure of the compound (X) is

$$\begin{array}{c|c} CH_3 & CH_3 \\ | & | \\ CH_3CH_2CHCH_2NH_2 \xrightarrow{aq.NaNO_2/HCl} CH_3CH_2CCH_3 \\ \text{2-Methylbutanamine} \\ \text{(Optically active)} & OH \\ (X) & (Y) \end{array}$$

(ii) The formation of the compound (*Y*) from the compound (*X*) may be explained as follows:

$$\begin{array}{c} \text{CH}_{3} \\ \text{CH}_{3}\text{CH}_{2}\text{CHCH}_{2}\text{NH}_{2} \xrightarrow{\text{NaNO}_{2}/\text{HCl}} \\ \text{CH}_{3}\text{CH}_{2}\text{-CH}\text{-CH}_{2}\text{-CH}_{2} \xrightarrow{\text{N}_{2}\text{Cl}} \xrightarrow{\text{-N}_{2},\text{-Cl}} \\ \text{CH}_{3} \\ \text{CH}_{3}\text{CH}_{2}\text{-CH}\text{-CH}_{2} \xrightarrow{\text{-N}_{2}\text{Cl}} \xrightarrow{\text{-N}_{2},\text{-Cl}} \\ \text{CH}_{3} \\ \text{CH}_{3}\text{CH}_{2} \xrightarrow{\text{-C}\text{-CH}_{2}} \xrightarrow{\text{-CH}_{3}\text{-CH}_{2}} \xrightarrow{\text{-Cl}} \xrightarrow{\text{-N}_{2},\text{-Cl}} \\ \text{CH}_{3}\text{CH}_{2} \xrightarrow{\text{-Cl}} \xrightarrow{\text{-Cl}} \xrightarrow{\text{-Cl}} \xrightarrow{\text{-N}_{2},\text{-Cl}} \\ \text{CH}_{3}\text{CH}_{2} \xrightarrow{\text{-Cl}} \xrightarrow{\text{-Cl}} \xrightarrow{\text{-Cl}} \xrightarrow{\text{-Cl}} \xrightarrow{\text{-Cl}} \\ \text{-N}_{2}\text{-Cl} \xrightarrow{\text{-Cl}} \xrightarrow{\text{-N}_{2},\text{-Cl}} \xrightarrow{\text{-Cl}} \xrightarrow{\text{-N}_{2},\text{-Cl}} \xrightarrow{\text{-Cl}} \\ \text{-N}_{3}\text{CH}_{2} \xrightarrow{\text{-Cl}} \xrightarrow{\text{-Cl}} \xrightarrow{\text{-Cl}} \xrightarrow{\text{-N}_{2},\text{-Cl}} \xrightarrow{\text{-Cl}} \xrightarrow{\text{-N}_{2},\text{-Cl}} \xrightarrow{\text{-Cl}} \xrightarrow{\text{-N}_{2},\text{-Cl}} \xrightarrow{\text{-Cl}} \xrightarrow{\text{-N}_{2},\text{-Cl}} \xrightarrow{\text{-Cl}} \xrightarrow{\text{-N}_{2},\text{-Cl}} \xrightarrow{\text{-Cl}} \xrightarrow{\text{-Cl}} \xrightarrow{\text{-N}_{2},\text{-Cl}} \xrightarrow{\text{-Cl}} \xrightarrow{\text{-N}_{2},\text{-Cl}} \xrightarrow{\text{-Cl}} \xrightarrow{\text{-N}_{2},\text{-Cl}} \xrightarrow{\text{-Cl}} \xrightarrow{\text{-N}_{2},\text{-Cl}} \xrightarrow{\text{-Cl}} \xrightarrow{\text{-N}_{2},\text{-Cl}} \xrightarrow{\text{-Cl}} \xrightarrow{\text{-N}_{2},\text{-Cl}} \xrightarrow{\text{-Cl}} \xrightarrow{\text{-Cl}$$

(i)
$$O$$
+ HONH₂ $\xrightarrow{H^+}$
Cyclopentanone oxime

(ii)
$$O_2N$$
 O_2N
 $O_$

$$(iii) \begin{picture}(200,0) \put(0,0){\ootalign{\hfill (0,0){\hfill (0,0){\ootalign{\hfill (0,0){\hfill (0,0){\ootalign (0,0){\hfill (0,0){$$

27. Since, $E_{Ag^+/Ag}^{\circ} > E_{Zn^{2+}/Zn}^{\circ}$, the zinc electrode is the anode. The half-cell reactions are as follows:

At anode : $Zn \rightarrow Zn^{2+} + 2e^{-}$

At cathode : $Ag^+ + e^- \rightarrow Ag$

Overall cell reaction is

$$Zn + 2Ag^{+} \rightarrow Zn^{2+} + 2Ag$$

 $E_{cell}^{o} = E_{cathode}^{o} - E_{anode}^{o} = 0.80 \text{ V} - (-0.76) \text{ V}$
 $= 0.80 \text{ V} + (0.76) \text{ V} = 1.56 \text{ V}$

Number of electrons involved is 2. Therefore, ΔG° value is given by the formula,

$$\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ} = -2 \times 96500 \text{ C mol}^{-1} \times 1.56 \text{ V}$$

= -301080 J mol⁻¹ = -301.08 kJ mol⁻¹

28. (i) Hydroquinone (or benzene-1,4-diol) is used as a developer in photography because it reduces Ag⁺ ions present on the exposed film to metallic silver.

$$HO \longrightarrow OH + 2Ag^+ \longrightarrow O \longrightarrow O + 2H^+ + 2Ag$$

Iydroquinone

-Benzoquinone

(ii) (a) Addition of $\rm H_2O$ to ethenylbenzene (or styrene) in presence of dil. $\rm H_2SO_4$ gives 1-phenylethanol.

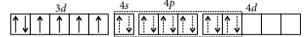
(b) Hydrolysis of cyclohexylmethyl bromide by aqueous NaOH gives cyclohexylmethanol.

$$\begin{array}{c} CH_2Br \\ + \text{NaOH} \xrightarrow{\Delta} \\ Cyclohexylmethyl \\ \text{bromide} \end{array}$$

$$\begin{array}{c} CH_2OH \\ \hline \\ Cyclohexylmethanol \\ Cyclohexylmethanol \\ \hline \\ Cyclohexylmethanol \\ Cyclohexylmethan$$

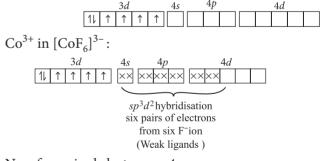
29. (i) In $[Fe(CN)_6]^{4-}$, CN^- is a strong field ligand hence, pairing of electrons takes place.

In $[Fe(H_2O)_6]^{2+}$, H_2O is a weak field ligand hence, pairing does not take place.



Both ligands show different magnitude of crystal field splitting energy due to different nature hence, absorb different wavelengths and show different colours.

(ii) Oxidation state of Co ion in $[CoF_6]^{3-}$ is +3. Co^{3+} :



No. of unpaired electrons = 4

OR

The given three coordination compounds are examples of special form of ionisation, called hydrate isomerism. Water can exist as a part of coordination entity or a part outside the coordination entity.

(a) $[Cr(H_2O)_6]Cl_3$: all three Cl^- ions are outside the coordination entity.

- (b) $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$: one Cl^- ion is part of coordination entity and two are outside of it.
- (c) $[CrCl_2(H_2O)_4]Cl\cdot 2H_2O$: two Cl^- ions are part of coordination entity and one is present outside of it. The Cl^- ions outside the coordination entity are ionisable and forms white precipitate with $AgNO_3$ while Cl^- ions which are part of coordination entity are not ionisable.
- **30.** (i) Let the number of O^{2-} ions in the crystal be N.
- \therefore Number of tetrahedral voids = 2NNumber of octahedral voids = N
- .. Number of X^{2+} ions = $\frac{1}{8} \times 2N = \frac{N}{4}$ Number of Y^{3+} ions = $\frac{1}{2} \times N = \frac{N}{2}$ $X^{2+}: Y^{3+}: O^{2-} = \frac{1}{4}: \frac{1}{2}: 1 = 1: 2: 4$
- \therefore The formula of the compound is XY_2O_4 .
- (ii) There is one octahedral hole for each atom in hexagonal closed packed arrangement. If the number of oxide ions (O^{2-}) per unit cell is x, then

Number of Fe³⁺ ions = $2/3 \times$ octahedral holes = $\frac{2}{3} \times x = \frac{2x}{3}$

= $\frac{2}{3}$ × $x = \frac{2x}{3}$ ∴ Ratio of Fe³⁺ : O²⁻ = $\frac{2x}{3}$: x = 2 : 3

Thus, formula of compound is Fe₂O₃.

31. (a) Small atoms like B, C, N, etc., can occupy positions in the voids among the atoms of transition metals. Such combinations are termed as interstitial compounds. They are usually non-stoichiometric materials having formulae like $VH_{0.56}$, $TiH_{1.7}$, etc.

Steel is an interstitial compound in which voids among iron atoms are occupied by carbon atoms.

Two important properties:

- (i) Transition metals become more harder and rigid.
- (ii) Melting points of interstitial compounds are higher than parent metals.
- (b) (i) $Sc : [Ar]3d^14s^2, Sc^{3+} : [Ar];$ It has no unpaired electron.

 $Cr : [Ar]3d^54s^1, Cr^{3+} : [Ar]3d^3;$

It has three unpaired electrons. Hence, Cr³⁺ is paramagnetic.

(ii) V : $[Ar]3d^34s^2$, Mn : $[Ar]3d^54s^2$; Mn exhibits more number of oxidation states.

The expected oxidation states in V are +2, +3, +4, +5. The expected oxidation states in Mn are +2, +3, +4, +5, +6, +7.

(iii) V^{4+} : [Ar] $3d^1$; One unpaired electron V^{5+} : [Ar]; No unpaired electron Hence, V^{5+} is diamagnetic in nature.

OR

- (a) The most stable oxidation state of lanthanides is +3. Hence, ions in +2 state tend to change to +3 oxidation state by loss of electron and act as reducing agents.
- (b) La³⁺ has a stable configuration of an inert gas $[Xe]5d^06s^0$. To obtain +4 oxidation state, the stable configuration is to be disturbed which is not possible under ordinary conditions and hence, La⁴⁺ does not exist.
- (c) This is because gadolinium in +3 oxidation state has half filled 4f-subshell $(4f^{7})$ and lutetium in +3 state has completely filled 4f-subshell $(4f^{14})$ which are very stable configurations.
- (d) Copper has small size compared to alkali metals in their period. Its electronic configuration is $[Ar]3d^{10}4s^1$. As filled 3d-subshell is less effective in shielding than s- and p-subshells, so s-electron in copper is more tightly held by the nucleus than that in alkali metals. Hence, its first ionisation energy is higher than for alkali metals. However, second and third ionisation energy values of copper are lower as compared to those of alkali metals due to removal of electrons from diffused d-orbitals.

32. (a) (i)

Br

MgBr

COOH

$$\frac{Mg}{\text{ether}}$$
 $\frac{1. \text{CO}_2}{2. \text{H}_3 \text{O}^+}$

(ii)
$$HC \equiv CH \xrightarrow{HBr} CH_2 = CHBr \xrightarrow{Mg}_{ether} OH$$

 $H_2C = CHMgBr \xrightarrow{1. CO_2}_{2. H_3O^+} OH$

(iii)
$$C_6H_5CH = CH_2 \xrightarrow{1. B_2H_6/THF} C_6H_5CH_2CH_2OH$$

$$\xrightarrow{\text{KMnO}_4/\text{H}^+}$$
 $\xrightarrow{\text{C}_6\text{H}_5\text{CH}_2\text{COOH}}$

- (b) Nitrobenzoic acid is more acidic than chlorobenzoic acid due to greater -I effect of nitro group than chloro group.
- (c) Due to resonance structure of carboxylate ion the C O bond acquires some double bond character, due to which its length is less than that in alcohol.

$$R - C \leqslant_{O^{-}}^{O} \longleftrightarrow R - C \leqslant_{O}^{O^{-}}$$

$$OR$$

(a) (i)
$$\underbrace{\bigcup_{\text{Toluene}}^{\text{CH}_3}}_{\text{Toluene}} \xrightarrow{\text{(i) CrO}_2\text{Cl}_2 + \text{CH}_3\text{COOH}}_{\text{Benzaldehyde}} \xrightarrow{\text{CHO}}_{\text{Benzaldehyde}}$$

(ii)
$$R-\text{CHO} \xrightarrow{R'\text{OH}} \left[R-\text{CH} \xrightarrow{\text{OR}'} \right]$$

$$\xrightarrow{R'\text{OH}} R-\text{CH} \xrightarrow{\text{OR}'} + \text{H}_2\text{O}$$
Acetal

(b)
$$CH \equiv CH \xrightarrow{H_2O} CH_3CHO \xrightarrow{[O]} CH_3COOH$$

(c) (i)
$$CH_3$$
 $C-OH$ $\xrightarrow{PCl_5}$ CH_3 $C-Cl$ $\xrightarrow{H_2}$ CH_3CHO

(ii)
$$2CH_3-C-OH \xrightarrow{Ca(OH)_2} (CH_3COO)_2Ca$$

$$\xrightarrow{\Delta} CH=C-CH$$

33. (a) Amount of ethylene glycol,

$$w_2 = \frac{M_2 \times \Delta T_f \times w_1}{K_f \times 1000} = \frac{62 \times 34 \times 50}{1.86 \times 1000} = 56.67 \text{ g}$$
(As, molar mass of ethylene glycol is 62 g mol⁻¹)
Density, $d = \frac{\text{Mass}}{\text{Volume}} = \frac{56.67}{50} = 1.13 \text{ g cm}^{-3}$

- (b) Solubility of a gas in polar solvent increases with increase in pressure and is governed by Henry's law.
- (c) Since a rise in temperature is observed when water and nitric acid are mixed together, the mixture is showing negative deviation from Raoult's law. Maximum boiling azeotropes are obtained by liquid mixtures showing negative deviation.
- (d) Molal elevation constant may be defined as the elevation in boiling point when the molality of the solution is unity (*i.e.*, 1 mole of the solute is dissolved in 1 kg (1000 g) of the solvent). The units of K_b are therefore, degree/molality *i.e.*, K/m or °C/m or K kg mol⁻¹.
- (e) 21.3% (w/v) means 100 mL of the HCl solution contains 21.3 g of HCl.

Molarity =
$$\frac{21.3 \text{ g HCl}}{100 \text{ mL solution}} \times \frac{1 \text{ mol HCl}}{36.5 \text{ g HCl}} \times \frac{1000 \text{ mL}}{1 \text{ L}}$$

= 5.8 M

OR

(a)
$$\Delta T_b = 100.02 - 100 = 0.02$$
°C
 $K_b = 0.5 \text{ K kg mol}^{-1}$

$$\therefore \quad \Delta T_b = m \times K_b$$

$$m = \frac{\Delta T_b}{0.5} = \frac{0.02}{0.5} = 0.04$$

Now, no. of glucose molecules = $0.04 \times N_A$ = $0.04 \times 6.022 \times 10^{23} = 2.4088 \times 10^{22}$ molecule Again, $\pi = CRT$

$$\Rightarrow \pi = 0.04 \times 0.0821 \times 300$$

$$\Rightarrow \pi = 12 \times 0.0821 = 0.985 \text{ atm}$$

Hence, osmotic pressure $(\pi) = 0.985$ atm

(b) 20% (w/W) solution of glucose means that 20 g of glucose is present in 100 g of solution or in 80 g of water

(i) Molality =
$$\frac{\text{Moles of solute}}{\text{Mass of solvent in g}} \times 1000$$

Moles of glucose =
$$\frac{20}{180}$$
 = 0.1111

Mass of solvent (water) = 80 g

:. Molality =
$$\frac{0.1111}{80} \times 1000 = 1.388 \text{ m}$$

(ii) Molarity =
$$\frac{\text{Moles of solute}}{\text{Volume of solution}} \times 1000$$

Moles of glucose = 0.1111

Volume of solution = $\frac{\text{Mass}}{\text{Density}} = \frac{100}{1.20} = 83.3 \text{ mL}$

:. Molarity =
$$\frac{0.1111}{83.3} \times 1000 = 1.333 \text{ M}$$

(iii) Moles of glucose = 0.1111

Moles of water
$$=\frac{90}{18} = 5.0$$

Total moles = 5.0 + 0.1111 = 5.1111

Mole fraction of glucose =
$$\frac{0.1111}{5.1111}$$
 = 0.021

Mole fraction of water =
$$\frac{5.0}{5.1111}$$
 = 0.978

 \odot \odot \odot