

2021
CHEMISTRY
[HONOURS]
Paper : VII

Full Marks : 80

Time : 4 Hours

*The figures in the right-hand margin indicate marks.**Candidates are required to give their answers in their own words as far as practicable.***GROUP-A****(Marks : 40)**

1. Answer any **two** questions: 1×2=2
- a) What is the spin only magnetic moment of $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ in its first ligand field excited state ($t_{2g}^2 e_g^1$)?
- b) Δ_0 for high spin $[\text{FeF}_6]^{3-}$ is 13900 cm^{-1} . Predict the colour of the complex ion.
- c) Identify the symmetry point group of PBrClF .
- d) What is the CFSE of $[\text{NiCl}_4]^{2-}$ in terms of Δ_0 ? [μ_{so} of $[\text{NiCl}_4]^{2-}$ is 2.83 B.M.]

2. Answer any **two** questions: 2×2=4
- a) Compare the magnetic moments of $[\text{NiBr}_4]^{2-}$ and $[\text{PdCl}_4]^{2-}$ combining the concepts of valence bond and crystal field theory.
- b) In CuF_2 crystals Cu^{2+} ions occupy the octahedral holes. Comment on the Cu-F distances.
- c) Write down all the symmetry elements present in D_{5d} point group.
- d) Calculate the CFSE of high and low spin $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ when mean pairing energy is 23500 cm^{-1} and Δ_0 is 13900 cm^{-1} .
3. Answer any **four** questions: 6×4=24
- a) i) Explain whether Mn_3O_4 and Fe_3O_4 will adopt a normal spinel structure or inverse spinel structure.
- ii) The magnetic moment of $[\text{Fe}(\text{NCS})_2(\text{o-phenanthroline})_2]$ increases above 160 K. Explain. 3+3
- b) i) Why the intensity of d-d transitions of octahedral metal complexes is of weak intensity? Compare the intensities of such transitions of

- octahedral complexes with tetrahedral complexes.
- ii) Assign the three d-d electronic transitions of (high spin) $[\text{Cr}(\text{NH}_3)_6]^{2+}$.
3+3
- c) i) How does spin-orbit coupling influence the magnetic moment of octahedral complexes of Ni^{2+} ? Explain with appropriate expressions.
- ii) Give a brief account of Curie-Weiss law.
3+3
- d) i) Assign the point group of the following:
 $\text{B}_3\text{N}_3\text{H}_3\text{Cl}_3$ (B,B,B-trichloroborazine) and HOCl
- ii) By symmetry arguments discuss the dipole moments of CHCl_3 , CH_3Cl and CH_2Cl_2 .
- iii) Comment on the colours of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{K}_2[\text{Cu}(\text{CN})_4]$ with reasons.
2+2+2
- e) i) Mention the symmetry properties of s, p and d orbitals with respect to rotational axis and inversion centre.
- ii) Compare the Δ_0 of $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Co}(\text{NH}_3)_6]^{2+}$ and $[\text{Co}(\text{NH}_3)_4]^{2+}$ with explanation.
3+3
- f) i) Although ionisation energy of $\text{Cr}^{2+}(\text{g})$ is greater than $\text{V}^{2+}(\text{g})$ but Cr^{2+} is stronger oxidising agent than V^{2+} . Explain. [Given Δ_0 for V^{2+} and V^{3+} are 12300 and 18600 cm^{-1} respectively whereas Δ_0 for Cr^{2+} and Cr^{3+} are 14100 and 17000 cm^{-1} respectively]
- ii) Define Jahn-Teller theorem. Which of the following high spin complexes would you expect to exhibit Jahn-Teller distortions? Give reasons.
 $[\text{Cr}(\text{NH}_3)_6]^{3+}$, $[\text{MnCl}_6]^{3-}$ and $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$
3+3
4. Answer any **one** question: 10×1=10
- a) i) Write down all the symmetry operations of C_{2v} point group. Prove that S_2 is nothing but an inversion operation. Does the mer- $[\text{Ru}(\text{CO})_3\text{Cl}_3]$ possess C_3 axis? Give reason.

- ii) Draw the splitting pattern of d orbital in square pyramidal crystal field.
- iii) Give a brief outline of experimental determination of magnetic susceptibility.
- iv) Draw the ground state Orgel diagram for tetrahedral metal complexes of d^3 and d^7 metal ion. Hence predict the probable d-d electronic transitions.
(1+2+1)+1+3+2
- b) i) Explain the pattern of variation of hydration enthalpy of M^{2+} ions where M is the transition metal of 1st transition series. [Assume octahedral coordination only].
- ii) "[$CuCl_4$] $^{2-}$ is a square planar complex." – True or false? Give reasons using VB theory.
- iii) Can you explain the bonding of low spin octahedral complexes of Co^{2+} metal ion according to VB theory? Give reason in support of your answer.
- iv) Comment on the anomalous magnetic moment of [$EuCl_6$] $^{4-}$. $3+2\frac{1}{2}+2+2\frac{1}{2}$

GROUP-B

(Marks : 40)

5. Answer any **two** questions: $1 \times 2 = 2$
- a) Draw the structure of Tungsten (V) chloride.
- b) Draw the structural formula of Tebbe's reagent.
- c) How many Fe-Fe bonds do you expect in $Fe_2(CO)_9$.
- d) Mention the main feature of electronic spectrum of haemoglobin.
6. Answer any **two** questions: $2 \times 2 = 4$
- a) Draw the structural formula of [W_2Cl_9] $^{3-}$ and comment on the W-W bond order.
- b) Give two chemical equations of preparing organozinc compounds by two methods.
- c) Why does solution of Grignard reagent conduct electricity?
- d) Draw the structure of protoporphyrin.
7. Answer any **four** questions: $6 \times 4 = 24$
- a) Draw the active site structure of chlorophyll. What is its role in synthesis of glucose from CO_2 and H_2O ? 6
- b) i) Drawing appropriate chemical structure show the coordination

behaviour of ATP in biology. Why the metal complex of ATP is important in biological processes? Discuss with an example.

- ii) Give a brief account on sulphide complexes of M_O . 4+2
- c) i) Draw the structural formula of Vaska's complex. Give one chemical reaction catalysed by Vaska's complex. Give the catalytic cycle.
- ii) Compare the oxidation states and coordination behaviour of Pd and Pt. $(1+\frac{1}{2}+2\frac{1}{2})+2$
- d) i) Explain the structure of methyl lithium.
- ii) " $(\eta^5-C_5H_5)_2TiCl$ can act as good catalyst." – explain by drawing the structure of the complex. 2+4
- e) Explain the working of the Na^+-K^+ pump with appropriate illustration. 6
- f) i) Why ring nitration in ferrocene cannot be carried out at ease? How will you prepare the nitro derivative of ferrocene?
- ii) Name one chelating drug in chelation

therapy in metal ion detoxification. Draw the structure of the drug.

$$1\frac{1}{2}+1\frac{1}{2}+3$$

8. Answer any **one** question: 10×1=10
- a) i) What is meant by hapticity of alkene ligands? What is the hapticity of cyclopentadienyl in-ferrocene? How the C_p can be alkylated in ferrocene? Give chemical equations.
- ii) Write down the principle of a method of Nb and Ta separation.
- iii) Why olefines are utilised for stabilisation of lower oxidation states of transition metals?
- iv) Write a note on Wilson disease. $(1+\frac{1}{2}+1\frac{1}{2})+3+2+2$
- b) i) Describe the mechanism of O_2 transport by myoglobin.
- ii) What is the significance of Oxygen-Haemoglobin Dissociation Curve (ODC)?
- iii) Write a short note on arsenic poisoning.
- iv) How would you prepare $MoCl_5$ from $MoOCl_3$? 3+2+3+2