2022

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

1. Answer any **two** questions: 1×2=2

   a) Give structure of a molecule which is optically active but has no chiral centre.

   b) Calculate the CFSE of $[NiCl_4]^{2-}$ in terms of Dq. The complex is paramagnetic having $\mu_{s.o.} = 2.83\,BM$.

   c) Give the appropriate mathematical expression of μ_{eff}.

   d) Calculate the spin only magnetic moment of tetrahedral $[CoCl_4]^{-}$ complex.

2. Answer any **two** questions: 2×2=4

   a) Calculate the CFSE of d6 ion in tetrahedral ligand field in terms of Δ_0.

   b) List the elements of symmetry present in D_{5d} point group.

   c) Find the symmetry point group of staggered ferrocene indicating the symmetry elements present.

   d) d orbitals of transition metal ions split into t_{2g} and e_g levels in octahedral ligand field. Why 'g' subscript is used in t_{2g} and e_g? Illustrate.

3. Answer any **four** questions: 6×4=24

   a) Explain the experimental procedure (with diagram) for determining the magnetic moment by Gouy method. 6

   b) i) '$[Fe(phen)_2(NCS)_2]$ is high spin at room temperature while it is low spin below 175K.' – Explain.

      ii) State the structures of Mn_3O_4 and Fe_3O_4 in terms of spinel and inverse spinel. 3+3

   c) i) Comment on the dipole moments of $CHCl_3$, CH_3Cl and CH_2Cl_2 employing symmetry arguments.

ii) 'Presence of C_6 symmetry element confirms presence of C_3'– Justify.

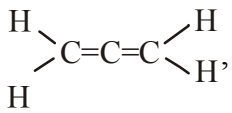
iii) Compare the magnetic moments of $[NiBr_4]^{2-}$ and $[PdCl_4]^{2-}$. 2+2+2

d) i) One complex of Fe^{2+} is colored due to d-d transition, but another Fe^{2+} complex very pale colored. Explain with appropriate illustration.

ii) The Δ_0 value of $[Mn(H_2O)_6]^{3+}$ is 15,800 cm^{-1} while the mean pairing energy in this complex is 28000cm^{-1}. Predict whether the complex is high spin or low spin.

iii) Why CO is a better ligand than CN^- for stabilization of lower oxidation state of transition metal ions? $1+2\frac{1}{2}+2\frac{1}{2}$

e) i) Find the symmetry point groups of the following species and write down all the symmetry elements present

$[Co(en)_3]^{2+}$,  , $[FeCl_6]^{3-}$

ii) State two limitations of crystal field theory.

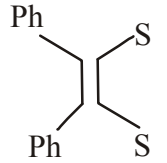
iii) Why $[CoCl_4]^{2-}$ is tetrahedral whereas $[PtCl_4]^{2-}$ is square planar? Explain using VBT. 3+1+2

f) i) Calculate the CFSE of d^2 metal ion in terms of Δ_{oct} under tetrahedral ligand field.

ii) What would be the CFSE of $t_{2g}^5e_g^0$ configuration?

iii) Give example of a molecule having S_4 symmetry element. Illustrate.

iv) 'The structure of $[(L)_3Mn]$ is not octahedral'– Predict its structure and draw.

L ≡  2+1+1+2

4. Answer any **one** question: 10×1=10

a) i) Discuss the bonding (VBT) and magnetic properties of high-spin and low-spin Co(III) complexes in octahedral ligand field.

ii) Explain why the stability of octahedral Cu(II) complexes with bidentate ligands.

iii) Explain the pattern of variation of hydration enthalpy of M^{2+} ions across the 1st transition series considering octahedral field only.

iv) Prove that S_2 is nothing but an inversion. 3+2+3+2

b) i) Explain how magnetic susceptibility is measured by Gouy method. Give experimental set up, measurements, calculation, theory and diamagnetic corrections.

ii) Give example of a molecule where S_6 symmetry element is present.

iii) If the molecular plane of H_2O is XZ plane, then which p orbital is symmetric with respect to all the symmetry elements of H_2O.

$6+1\frac{1}{2}+2\frac{1}{2}$

GROUP–B

5. Answer any **two** questions: 1×2=2

a) Write down the IUPAC nomenclature of $K_2[Pt(C_2H_4)Cl_3]$.

b) Draw the structure of Tebbe's reagent.

c) What are the common oxidation states of Ir?

d) Name an enzyme associated with ion transport across the cell membrane.

6. Answer any **two** questions: 2×2=4

a) Draw the structural formula of $[W_2Cl_9]^{3-}$ and comment on W-W bond order.

b) Draw the structure of $\left[\left(\eta^5-Cp\right)_2 TiCl_2\right]$ and its Lewis acid base property.

c) Name the enzymes containing Mo and Fe. Name one natural source of the enzyme.

d) How Pb^{2+}/Pb^{4+} can be detoxified?

7. Answer any **four** questions: 6×4=24

a) Discuss the mechanism of Wacker oxidation process catalysed by Pd complexes. 6

b) i) Draw the structure of tetraphenyl porphyrin.

ii) How the tetraphenyl porphyrin can be prepared?

iii) Show its number of π electrons.

2+3+1

c) Draw the active site structure of chlorophyl. What is its role in synthesis of glucose from CO_2 and H_2O. 6

d) Compare and contrast the chemistries of Nb and Ta with respect to separation and halo compounds. 3+3

e) What is meant by 'active transport'? Is Na^+ and K^+ transport across the cell membrane active transport? Furnish the mechanism of the transport. 2+1+3

f) i) Give two methods of synthesizing alkyl zinc compounds (Equations only). "Alkyl zinc compounds are utilised for chemical synthesis"– Give two examples.

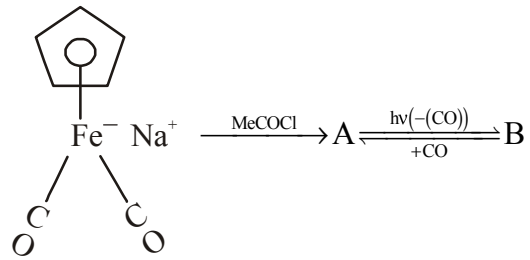
ii) Draw the structural formulae of two organozinc complexes incorporating cyclopenta dienlyl ligands. State whether the complexes obey 18 electron rule or not. (2+2)+2

8. Answer any **one** question: 10×1=10

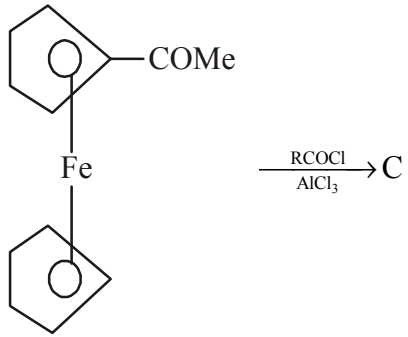
a) i) Draw the structure of the active site of Myoglobin and discuss its role in oxygen transport by haemoglobin.

ii) Discuss on the calcium ion transport across cell membrane indicating the roles of plasma membrane Ca^{2+} ATPase and Sarcoplasmic Reticulum Ca^{2+} ATPase. 6+4

b) i) Draw the structural formulae of A, B and C.



ii)



iii) Discuss on the photosystems– PS-I and PS-II showing the Z scheme and electron transfer. Draw the structure of chlorophyl. $(1\frac{1}{2}\times3)+5\frac{1}{2}$

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