2025

CHEMISTRY — HONOURS

Paper : DSCC-8

(Inorganic Chemistry - II)

Full Marks : 75

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

Answer ***question nos.* 1, 2, 3 & 4 *(Compulsory)*** and ***any four*** from the rest.

1. Answer ***any ten*** questions : 2×10

(a) Write two postulates of Werner's theory.

(b) Identify the complex with larger 10Dq value and justify $[Mn(H_2O)_6]^{2+}$ or $[Fe(H_2O)_6]^{3+}$.

(c) Name the origin of colour for the following compounds :

$CuSO_4.5H_2O$ and $KMnO_4$.

(d) Give examples of one molecule each which shows hydrogen bonding and halogen bonding. Show their interactions.

(e) MnO_4^- is reduced to Mn^{2+} in acid medium. Write down the half cell reaction and the corresponding Nernst equation at 25°C.

(f) Find the potential at the equivalence point for the titration of Fe^{2+} with $KMnO_4$ in presence of 1(M) H_2SO_4.

$$E^o_{Fe^{3+}/Fe^{2+}} = +0.77 \text{ V and } E^o_{MnO_4^-/Mn^{2+}} = +1.51 \text{ V}$$

(g) Draw the crystal field splitting diagram of d^n configuration for square pyramidal geometry and label the *d* orbitals.

(h) Predict the geometry of the following complex on the basis of its magnetic moment value –

$[MnBr_4]^{2-}$ (5.90 BM)

(i) Which force is responsible for the condensation of the inert gases into liquid? Find the order of liquefaction temperature of He, Ne and Ar.

(j) Give one example each for disproportionation and comproportionation reaction.

(k) Predict the hybridization involved in the complex $[Fe(CN)_6]^{4-}$ and classify it as inner orbital or outer orbital complex according to VB theory.

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(l) Give one example each for molecules showing antiferromagnetic and super exchange interactions.

2. (a) Write short note on the crystal field splitting pattern for Ni^{2+} based on the following points –

(i) Diagrams in octahedral, square planar and tetrahedral geometrics.

(ii) Preferences for ligands for tetrahedral and square planar geometrics. 3+2

Or

(b) Write short note on selection rules for electronic spectral transitions based on the following points :

(i) Selection rules and ways of relaxation of any one selection rule.

(ii) Justification of the observation that *cis*– $[Co(NH_3)_4Cl_2]^+$ is more intensely coloured than its trans-isomer. 3+2

3. (a) Write short note on Π-interaction based on the following points :

(i) Cation – Π

(ii) Anion – Π

(iii) Edge to face and face to face Π – Π

(iv) NH – Π. 1+1+2+1

Or

(b) Write short note on Redox titrations and Redox indicators based on the following points :

(i) Indicator range and conditions for a suitable redox indicator

(ii) Explanation of the fact that addition of H_3PO_4 of F^- ion is essential in the titration of Fe^{2+} by $K_2Cr_2O_7$ in acid medium using BDS as redox indicator.

$$\left[E^{o}_{Cr_2O_7^{2-}/2Cr^{3+}} = 1.33V,\ E^{o}_{Fe^{3+}/Fe^{2+}} = 0.77V,\ E^{o}_{Ind(ox)/Ind(red)} = 0.76V\right]$$

2+3

4. (a) Write short note on Jahn Teller distortion based on the following points :

(i) Statement

(ii) Conditions for distortion in octahedral complexes

(iii) Types of distortion with examples. 1+1+3

Or

(b) Write short note on spin only moments of d^n ions and their correlation with μ_{eff} based on the following points :

(i) Expression of $\mu_{spin\ only}$.

(ii) Causes of deviation of μ_{eff} from $\mu_{spin\ only}$.

(iii) Comparison of μ_{eff} values of Co^{2+} (HS, Oct) and Co^{2+} (Td) complexes. 1+1+3

5. (a) Define geometrical isomerism. sketch all the possible isomers of $[Co(NH_3)_2\ (py)_2\ Cl_2\ ]^+$. Among them identify the pair of optical isomers.

(b) Justify the stability sequence of the following polyhalide ions :

$I_3^- > Br_3^- > Cl_3^-$

(c) Calculate the E° for reduction of MnO_4^- to Mn^{2+} in acid solution from the following Latimer diagram–

$$MnO_4^- \xrightarrow{0.56V} MnO_4^{2-} \xrightarrow{2.26V} MnO_2 \xrightarrow{1.23V} Mn^{2+}$$

Identify the species that will undergo disproportionation. (1+2+1)+3+(2+1)

6. (a) Electronic absorption spectra of $[Co(H_2O)_6]^{2+}$ exhibits bands at 8100, 16000 and 19400 cm^{-1}. Assign the bands to electronic transitions using Orgel diagram and calculate the 10 Dq value.

(b) What is Zimmermann-Reinhardt solution? Why it is used in the titration of Fe^{2+} ion by $KMnO_4$ in presence of hydrochloric acid?

$$\left[E^\circ_{MnO_4^-/Mn^{2+}} = +1.51\ V,\ E^\circ_{Fe^{3+}/Fe^{2+}} = +0.77\ V,\ E^\circ_{\frac{1}{2}Cl_2/Cl^-} = +1.36\ V \right]$$

(c) Both $[Ni(CN)_4\ ]^{2-}$ and $[\ Ni(CO)_4]$ are diamagnetic but they have different geometrics. — Explain. 4+(1+2)+3

7. (a) Predict the thermodynamic redox stability of H_2O_2 and construct the Fröst diagram from the following data :

$$O_2 \xrightarrow{+0.70\ V} H_2O_2 \xrightarrow{+1.76\ V} H_2O$$

(b) The electronic spectrum of $[Ti\ (H_2O)_6]^{3+}$ shows a peak at 490 nm and a broad shoulder at 580 nm. Assign the transitions and explain the reason for the appearance of the shoulder.

(c) Give IUPAC name for $[Co\ (en)_2(CO_3)]Cl$ and write the formula of [μ – oxo – bis pentaammine–chromium(III)] chloride. 4+3+3

8. (a) What do you mean by ion-dipole and dipole-induced dipole interactions? Explain with suitable examples.

(b) Calculate the CFSE for the complexes given below :

(i) $K_2[NiF_6]$ (ii) $[CoCl_4]^{2-}$ (iii) $[Mn(H_2O)_6]^{2+}$

(c) Wavelength of LMCT transition bands for isoelectronic ions runs in the sequence :

$VO_4^{3-} < CrO_4^{2-} < MnO_4^-$ — Explain and justify. (2+2)+3+3

9. (a) The order of ligand field strength in the spectrochemical series is :

$F^- < H_2O < CO$

Explain the order on the basis of M.O. approach.

(b) Which non-covalent interaction is strongest : hydrogen bonding, van der Waals forces or ionic interactions? Justify.

(c) Explain how does the formal potential affect the oxidation of potassium iodide to iodine by cupric ion.

$$\left(E^o_{Cu^{2+}/Cu^+} = 0.15\ V,\ E^o_{\frac{1}{2}I_2/I^-} = 0.54\ V \right)$$

4+3+3

10. (a) What do you mean by charge transfer transition? Write down the conditions for different kinds of the transitions.

(b) Calculate the OSSE value for Ni(II) ion. State the significance of the result.

(c) Fe(III) cannot be estimated iodometrically with high accuracy. Justify this statement.

$$\left[E^o_{Fe^{3+}/Fe^{2+}} = 0.77\,V,\ E^o_{\frac{1}{2}I_2/I^-} = 0.54\ V \right]$$

4+3+3
