

B.Sc. 5th Semester (Honours) Examination, 2021 (CBCS)

Subject: Chemistry

Paper: CC-11

Time: 2 Hours

Full Marks: 40

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

Answer any eight questions from the following:

8×5 = 40

1. (a) An octahedral complex absorbs in 545 nm. Then what would be its respective tetrahedral field splitting (Δ_{tet})?

(b) Draw the crystal field splitting pattern and calculate stabilization energy for the following configurations:

(i) d^6 octahedral high spin and low spin (ii) d^8 square planar

2. (a) Low spin tetrahedral complexes are generally not known – Explain.

(b) The mean electron pairing energy (P) for Fe^{2+} is found to be 17600 cm^{-1} . The magnitude of Δ_o for the complexes $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Fe}(\text{CN})_6]^{4-}$ are 10500 cm^{-1} and 32200 cm^{-1} respectively. Calculate the CFSE for these complex ions corresponding to high spin and low spin states and predict the possible stable configurations.

3. (a) What type of spinel structure do you expect for Co_3O_4 and NiCr_2O_4 ? Explain on the basis of CFT.

(b) Arrange the following complex ions in the order of increasing Δ_o by giving reasons:

$[\text{Ni}(\text{NH}_3)_6]^{2+}$, $[\text{Co}(\text{NH}_3)_6]^{2+}$, $[\text{Rh}(\text{NH}_3)_6]^{3+}$ and $[\text{Co}(\text{NH}_3)_6]^{3+}$.

4. (a) A complex of certain metal ion has magnetic moment 4.9 BM. Another complex of the same metal ion in the same oxidation state has zero magnetic moment. The central metal ion could be Cr(III), Mn(II), Fe(II), Fe(III) or Co(III)?

(b) For $[\text{Ni}(\text{en})_3]^{2+}$ complex (en = ethylenediamine), the bands are observed at 11000 , 18500 and 30000 cm^{-1} . Calculate the $10 Dq$ value of the complex.

5. (a) Which of the following high spin complexes would you expect to exhibit Jahn-Teller distortion: $[\text{Cr}(\text{NH}_3)_6]^{3+}$; $[\text{MnCl}_6]^{3-}$; $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$. Give reason(s).

(b) Why $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ is pale pink coloured?

6. (a) $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ is diamagnetic even though it is d^9 electronic system – Explain.
(b) Justify the trend in LMCT energies: $\text{CrO}_4^{2-} < \text{MoO}_4^{2-} < \text{WO}_4^{2-}$
(c) Find out the ground state spectroscopic term symbol for Fe^{3+} ion.
7. (a) The intense red colour of an $[\text{Fe}(\text{phen})_3]^{2+}$ solution is replaced by pale blue when cerium(IV) sulphate is added to it. Explain.
(b) Chromium(VI) oxide is strongly acidic, vanadium(V) oxide is amphoteric, titanium(IV) oxide is inert, and scandium(III) oxide is basic with some amphoteric properties. Explain the relative acidities of these oxides.
8. (a) What happens when:
(i) Reaction of sodium ferrate with aqueous ammonia solution.
(ii) Sodium nitroprusside reacts with sodium sulphide solution.
(iii) Uranyl sulphate is treated with excess of Na_2CO_3 .
(b) Comment on the structures and origin of colours of the following:
(i) Ruthenium red
(ii) Magnus green
9. (a) Lanthanoids show sharp bands in the absorption spectra in contrast to the transition metals – Explain.
(b) Why Ce(III) $4f^1$ ion is colourless, while Ti^{3+} solution ($3d^1$) is purple?
10. (a) Which is stronger base $\text{La}(\text{OH})_3$ or $\text{Lu}(\text{OH})_3$ and why?
(b) How is the magnetic behaviour of Gd^{3+} and Lu^{3+} different from the rest of the lanthanides?
(c) Lanthanide ions do not form complexes with amines in aqueous solutions. Give reason.