

B.Sc. 5th Semester (Honours) Examination, 2020 (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**

- What are the limitations of crystal field theory? Write down the Laporte Selection Rule and Spin Selection Rule in words and in mathematical form. Find out the hybridization and geometry of the following complexes: $\text{Ni}(\text{CN})_4^{2-}$ and NiCl_4^{2-} .
- Mention the conditions for orbital contribution to spin only magnetic moment value. What is Racah parameter? Explain why Racah parameter B for $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ is only about 70% of that for free Ni^{2+} .
- What is meant by high spin-low spin cross overs? What are the pre-requisite for a coordination compound to be amenable to such cross overs? Give an example of a d^5 system known to exhibit this behaviour. An octahedral complex absorbs in 545 nm. Then calculate its respective tetrahedral field splitting (Δ_{tet}) value?
- Explain why the $\text{Mn}(\text{H}_2\text{O})_6^{2+}$ ion has extremely pale pink colour? What is the origin of intense yellow colour of CrO_4^{2-} ? Find out the ground state spectroscopic term symbol for Cr^{3+} ion.
- What are spinels? Using crystal field model, explain why Fe_3O_4 has an inverse spinel structure while Mn_3O_4 has a normal spinel structure. A complex of a transition metal ion with d^6 electronic configuration is diamagnetic; is it an octahedral or a tetrahedral one?
- The octahedral complex ions, $[\text{FeF}_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{3-}$ are paramagnetic but to different extent. Identify the d -electron configurations in these two octahedral complex ions. In which case the octahedral field splitting is greater? How does the crystal field stabilization energy differ between them? How do d -orbitals split in square planar geometry?
- Explain why Cu^{2+} does not form a regular octahedral complex whereas Ni^{2+} does. What is spectrochemical series? Why is it so called?

8. In aqueous solutions, the VO_4^{3-} ion forms a large series of polyvanadates; but CrO_4^{2-} ion, also d^0 , condenses mainly upto the $\text{Cr}_2\text{O}_7^{2-}$ ion. Comment on the statement.

Outline the preparatory methods of the following indicating the reaction conditions and comment on the structures:

- Wilkinson's catalyst
- Vaska compound and
- Reineck's salt

9. Write the half-cell reaction for reduction of TcO_4^- and ReO_4^- ions in acidic aqueous medium.

Are they stronger or milder oxidising agents than MnO_4^- ?

In presence of cyanide ion, Co(II) salts are readily oxidized to the Co(III) state while Cu(II) salts are reduced to the Cu(I) state. Comment.

10. Give the important oxidation states of lanthanides. How would you account for them? What are Shift reagents? What is their importance? Actinides form oxocations but lanthanides don't. Explain