

Five Year Integrated M.Sc. Examination 2021-2022

Semester - V

Course: CH-3-5-1

(Chemistry)

Time: Four Hours

Full Marks: 80

Questions are of value as indicated in the margin

Group-A

1. Answer **any ten** questions: 10 × 2
= 20
- (a) Arrange H_3^+ , H_3 and H_3^- according to bond order.
 - (b) Calculate the bond order of H_{14} molecule.
 - (c) Compare the stability of H_{14} and H_{10} molecules.
 - (d) What are the shapes of BeH_2 and BH_2 molecules?
 - (e) Why tetrahedral complexes are always high spin?
 - (f) Au(II) disproportionates to Au(I) and Au(III) . Explain
 - (g) Calculate the spin only magnetic moment of MnBr_4^{2-} .
 - (h) Predict a crystal field splitting diagram for a complex in a linear field assuming that the ligands lie on the z-axis.
 - (i) Give an example of $\text{S}_{\text{N}}1'$ reaction.
 - (j) Compare the nucleophilicity of HO^- and HOO^- .
 - (k) Give an example of NGP where π -bond acts as neighboring group.
 - (l) What do you mean by $\text{S}_{\text{N}}i$ reaction?

Group-B

Answer **any two** questions

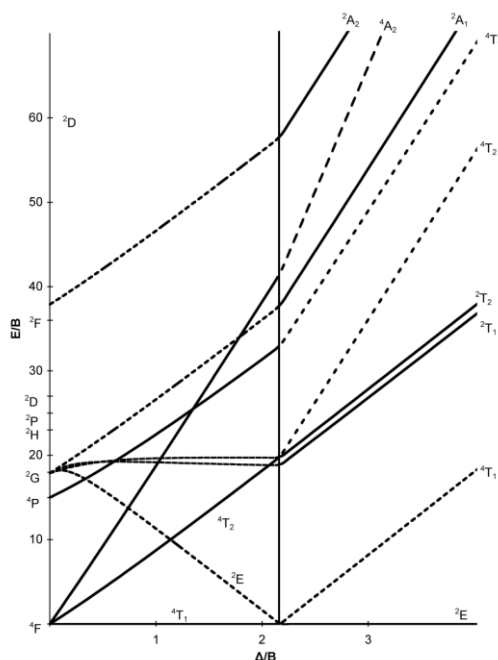
2. Draw the involved molecular orbitals of BH_2^+ molecule by considering participation of H-group orbitals. Write the mathematical formulations for the MO formation after LCAO in this regard. Draw the MO energy diagram of BH_2^+ molecule. 4+3+3
3. Draw the Walsh diagram of species like XH_2 (X is a second period element) and give reasons for variation of energy of molecular orbitals with the change of bond angle showing the involved MOs. 3+7
4. Draw the involved molecular orbitals considering symmetry adapted linear combination for H_3^+ species and show the involved MO diagram. What is the difference between H_3^+ and H_3 in this regard? 6+3+1

Group-C

Answer *any two* questions

5. (a) What information can you obtain from the following diagram?

2



- (b) Explain the difference between a d-d transition and charge-transfer transition.

2

- (c) For the $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ ion, the mean pairing energy P is found to be $23,500 \text{ cm}^{-1}$. The magnitude of Δ is $13,900 \text{ cm}^{-1}$. Calculate the CFSE for the complex in high-spin and low-spin configurations. Which spin state is more stable and why?

3

- (d) Discuss about the electronic spectra of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ complex ion.

3

6. (a) Explain the difference in spectral properties of ClO_4^- and MnO_4^- ions.

2

- (b) The magnetic susceptibility of two compounds, **A** and **B**, increase gradually with the decrease in temperature. After a certain temperature the susceptibility of **B** is found to increase abruptly. What type of compounds are **A** and **B**? Explain the reason behind such observation in the compounds and write the laws governing such behavior.

1+2+1

- (c) Explain why the nephelauxetic effect for CN^- is larger than that for NH_3 .

2

- (d) Which of the following should have comparatively more intense d-d transition and why?

2

- (i) $\text{trans}-[\text{CrCl}_2(\text{H}_2\text{O})_4]^+$ or $\text{cis}-[\text{CrCl}_2(\text{H}_2\text{O})_4]^+$ (ii) $\text{Ni}(\text{CO})_4$ or $\text{Fe}(\text{CO})_5$

7. (a) Comment on the magnetic properties of hexacyanidoferrate(II) and hexafluoridoferrate(III) ions. Calculate the CFSE of the metal ions and the magnetic moments of the species.

4

- (b) Justify the difference in energy between the $d_{x^2-y^2}$ and d_{xy} orbitals in a square planar field is identical to the difference between the same orbitals in the octahedral field.

2

- (c) Explain why $[\text{FeF}_6]^{3-}$ is colorless whereas $[\text{CoF}_6]^{3-}$ is colored. 2
- (d) Discuss about the structure of NiCr_2O_4 . 2

Group-D

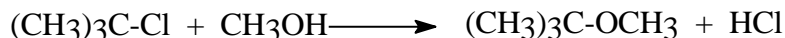
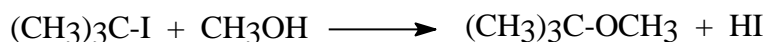
Answer *any two* questions

8. (a) The strongly nucleophilic reagents favor $\text{S}_{\text{N}}2$ mechanism, whereas weakly nucleophilic reagents favour $\text{S}_{\text{N}}1$ mechanism. Justify. 3
- (b) Why CH_3OH cannot form CH_3Br with NaBr but does so with HBr ? Explain your answer. 3
- (c) How can you distinguish between an $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ reaction? Explain your answer with proper example. 4
9. (a) Arrange the following in increasing order of basicity with explanation. 4



Will this order of basicity be same for nucleophilicity? Explain your answer.

- (b) Reactivity of the halides towards *n*-butyl brosylate in acetone is $\text{Cl}^- > \text{Br}^- > \text{I}^-$ when $(\text{C}_4\text{H}_9)_4\text{N}^+$ is the cation of the halide salt, but $\text{I}^- > \text{Br}^- > \text{Cl}^-$ when Li^+ is the cation. Justify 3
- (c) $\text{CH}_3\text{COCH}_2\text{Cl}$ undergoes $\text{S}_{\text{N}}2$ reaction faster than *n*-propyl chloride but it undergoes $\text{S}_{\text{N}}1$ reaction much more slowly. Justify the statement. 3
10. (a) Which of the following $\text{S}_{\text{N}}1$ reactions would you expect to take place more rapidly? Explain your answer: 3



- (b) Explain the relative $\text{S}_{\text{N}}2$ rate of the following (as substrate or solvent): 4
- (i) $\text{CH}_3\text{CH}_2\text{Br} > \text{CH}_3\text{CH}_2\text{CH}_2\text{Br} > (\text{CH}_3)_2\text{CHCH}_2\text{Br} > (\text{CH}_3)_3\text{CCH}_2\text{Br}$ (Substrate)
- (ii) $\text{CH}_3\text{OH} < \text{HCONH}_2 < \text{HCONMe}_2$ (Solvents in reaction between CH_3I with Cl^-).
- (c) Base catalyzed hydrolysis of 2-bromo propanoic acid proceeds with retention of configuration. – Explain. 3