Reg. No.

## CHH/ACH/OCH/CAH 451

## Second Semester M.Sc. Degree Examination, Sept./Oct. 2022 (Freshers and Repeaters) (CBCS – 2016-17 Syllabus) CHEMISTRY/APPLIED CHEMISTRY/ORGANIC CHEMISTRY/ANALYTICAL CHEMISTRY Advanced Inorganic Chemistry

Time : 3 Hours

Max. Marks : 70

Note: i) Answer Part – A and four questions from Part – B. ii) Figures to the **right** indicate marks.

## PART – A

- 1. Answer the following sub-divisions :
  - a) Define improper axis of symmetry  $(S_n)$ . Mention the number of operations generated when n = 3 in  $S_n$ .
  - b) What is a point group ? Identify the point group of trans-[PECl<sub>2</sub>Br<sub>2</sub>] or staggered ethane.
  - c) What is an irreducible representation ? How many irreducible representations are possible in  $C_{2h}$  point group ?
  - d) Which among the complexes  $[CuL_6]^{2+}$  and  $[CrL_6]^{3+}$  undergo Jahn Teller distortion ? Why ?
  - e) Write the structures of all possible isomers of [Co(en)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup>. Which of them is optically active ?
  - f) The  $\Delta$  values (in cm<sup>-1</sup>) of the octahedral complexes,  $[Co(NH_3)_6]^{3+}$ ,  $[Co(en)_3]^{3+}$ ,  $[Rh(en)_3]^{3+}$  and  $[Ir(en)_3]^{3+}$  are 22,900, 23,200, 34,600 and 41,400 respectively. Justify this observation.
  - g) Carbon may be used to reduce any metal oxide above 710°C. Why ?
  - h) The trivalent oxidation state is common for lanthanides but Ce<sup>4+</sup>, Tb<sup>4+</sup> and Eu<sup>2+</sup> are quite stable. Give reasons.
  - i) Why actinides show variable valencies ?

 $(9 \times 2 = 18)$ 

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PART – B

Answer any four full questions :

(4×13=52)

- 2. a) What is group multiplication table ? Construct the group multiplication table for  $C_{3v}$  point group.
  - b) Derive matrix representation for reflection operation of a vector in YZ-plane.
  - c) Explain the mathematical rules for the matrix representation of a point group with suitable examples. (5+4+4=13)
- 3. a) Illustrate the rules followed in assigning the Mulliken's symbol for irreducible representations.
  - b) Explain how character table could be used in identifying the type of hybridization in NH<sub>3</sub> molecule.
  - c) Identify the subgroups present in D<sub>2h</sub> and C<sub>2h</sub> point groups. Give the order of each group. (5+4+4=13)
- 4. a) Derive the possible sets of 'styx' numbers and draw the most reasonable structures of  $B_5H_9$  and  $B_5H_{11}$ .
  - b) Outline the synthesis of  $\alpha$ -C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>. Draw the structures of its possible isomers and explain their properties.
  - c) Explain the method of preparation of  $S_4N_4$ . Draw its structure and explain geometry in terms of S-S and S-N bond distances. (5+4+4=13)
- 5. a) How does CFT successfully explain the d-orbitals splitting in an octahedral and tetrahedral ligand fields ? Mention its limitations.
  - b) Give examples for complexes of coordination number five and seven, sketch the possible geometries.
  - c) Describe the structure and bonding in  $\operatorname{Re}_{2}\operatorname{Cl}_{8}^{2-}$ . (5+4+4=13)
- 6. a) Describe the different chemical methods adapted for the reduction of oxide ores with suitable examples.
  - b) Discuss the salient features of Ellingham diagram.
  - c) What are NMR shift reagents. Give examples. (5+4+4=13)
- 7. a) What is lanthanide contraction ? How does it affect the chemical behaviour of Zr/Hf, Nb/Ta and Mo/W ?
  - b) Explain in details the chemistry of halides and oxides of nickel group elements.
  - c) Discuss the general principles involved in ion-exchange separation of lanthanide ions. (5+4+4=13)