Reg. No. $\square$

## 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. <br> ii) Figures to the right indicate marks.

PART - A

1. Answer the following sub-divisions:
( $9 \times 2=18$ )
a) Define improper axis of symmetry $\left(\mathrm{S}_{\mathrm{n}}\right)$. Mention the number of operations generated when $\mathrm{n}=3$ in $\mathrm{S}_{\mathrm{n}}$.
b) What is a point group ? Identify the point group of trans-[ $\left[\mathrm{PECl}_{2} \mathrm{Br}_{2}\right]$ or staggered ethane.
c) What is an irreducible representation ? How many irreducible representations are possible in $\mathrm{C}_{2 h}$ point group ?
d) Which among the complexes $\left[\mathrm{CuL}_{6}\right]^{2+}$ and $\left[\mathrm{CrL}_{6}\right]^{3+}$ undergo Jahn Teller distortion? Why?
e) Write the structures of all possible isomers of $\left[\mathrm{Co}(\mathrm{en})_{2} \mathrm{Cl}_{2}\right]^{+}$. Which of them is optically active ?
f) The $\Delta$ values (in $\mathrm{cm}^{-1}$ ) of the octahedral complexes, $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]^{3+}$, $\left[\mathrm{Co}(\mathrm{en})_{3}{ }^{3++},\left[\mathrm{Rh}(\mathrm{en})_{3}{ }^{3+}\right.\right.$ and $\left[\operatorname{lr}(\mathrm{en})_{3}\right]^{3+}$ 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 $710^{\circ} \mathrm{C}$. Why?
h) The trivalent oxidation state is common for lanthanides but $\mathrm{Ce}^{4+}, \mathrm{Tb}^{4+}$ and $\mathrm{Eu}^{2+}$ are quite stable. Give reasons.
i) Why actinides show variable valencies ?

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PART - B

Answer any four full questions :
( $4 \times 13=52$ )
2. a) What is group multiplication table ? Construct the group multiplication table for $\mathrm{C}_{3 v}$ 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.
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 $\mathrm{NH}_{3}$ molecule.
c) Identify the subgroups present in $\mathrm{D}_{2 \mathrm{~h}}$ and $\mathrm{C}_{2 \mathrm{~h}}$ 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 $\mathrm{B}_{5} \mathrm{H}_{9}$ and $\mathrm{B}_{5} \mathrm{H}_{11}$.
b) Outline the synthesis of $\alpha-\mathrm{C}_{2} \mathrm{~B}_{10} \mathrm{H}_{12}$. Draw the structures of its possible isomers and explain their properties.
c) Explain the method of preparation of $\mathrm{S}_{4} \mathrm{~N}_{4}$. 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 $\mathrm{Re}_{2} \mathrm{Cl}_{8}^{2-}$.
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.
7. a) What is lanthanide contraction ? How does it affect the chemical behaviour of $\mathrm{Zr} / \mathrm{Hf}, \mathrm{Nb} / \mathrm{Ta}$ and $\mathrm{Mo} / \mathrm{W}$ ?
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)

