## $1112 / 2019(E)$

## 239101

December, 2019<br>M.Sc. (Chemistry) - I SEMESTER<br>Inorganic Chemistry (CH-101A)

Time : 3 Hours]

[Max. Marks : 75

Instructions :

1. It is compulsory to answer all the questions ( 1.5 marks each) of Part-A in short.
2. Answer any four questions from Part-B in detail.
3. Different sub-parts of a question are to be attempted adjacent to each other.

## PART - A

1. (a) Which will form stronger $\mathrm{d} \pi-\mathrm{p} \pi$ bonding with oxygen, Chlorine or Phosphorous and why?
(b) Determine the operation generated by $\mathrm{S}_{6}$ axis. Cite an example of a molecule/ion which possesses $\mathrm{S}_{6}$ axis.
(c) Prove that if $\mathrm{P}, \mathrm{Q}, \mathrm{R}$ and S are member of a group then prove,

$$
\begin{equation*}
(\mathrm{PQRS})^{-1}=\mathrm{S}^{-1} \mathrm{R}^{-1} \mathrm{Q}^{-1} \mathrm{P}^{-1} \tag{1.5}
\end{equation*}
$$

(d) Write down the mechanism for solvolysis of alkyl borane in presence of aqueous carboxylic acid. (1.5)
(e) Account for the fact $\left[\mathrm{Cr}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}$ is labile whereas $\left[\mathrm{Cr}(\mathrm{CN})_{6}\right]^{4-}$ is inert.
(f) Why CO and $\mathrm{CN}^{-}$are better trans effect ligand than $\mathrm{F}^{-} / \mathrm{Cl}^{-}$in substitution reactions of square planar complexes of platinum (II).
(g) Use Bent's rule to estimate the deviation of the $\mathrm{H}-\mathrm{C}-\mathrm{H}$ bond angle in $\mathrm{FCH}_{3}$ and $\mathrm{ClCH}_{3}$ from $109.4^{\circ}$.
(h) Which of these $\mathrm{Cl}_{2} \mathrm{O}$ and $\mathrm{F}_{2} \mathrm{O}$ will have the larger $\mathrm{X}-\mathrm{O}-\mathrm{X}$ bond angle and why?
(i) Predict which of the ligand would result in formation of more stable complex and why
(a) $\mathrm{Cr}^{3+}$ with $\mathrm{NH}_{3}$ or CO .
(b) $\mathrm{Hg}^{2+}$ with $\left(\mathrm{C}_{2} \mathrm{H}_{5}\right) \mathrm{O}$ or $\left(\mathrm{C}_{2} \mathrm{H}_{5}\right) \mathrm{S}$.
(j) Cite example of complexes, depicting an overlap of metal $\mathrm{d}_{\pi}$ orbital with $\sigma^{*}$ and $\pi^{*}$ types of orbital's respectively.

## PART - B

2. (a) Write down the structure, point group and symmetry operations of the following:
(i) $\left[\mathrm{Co}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)_{3}\right]^{2-}$.
(ii) cis-1, 2-dichlorocyclopropane, and
(iii) $\mathrm{CHFI}_{2}$.
and also mention which of these are/is optically active and why?
(b) (i) Write down the point group and symmetry operations of the molecule: $\mathrm{PCl}_{4} \mathrm{~F}$ when F is placed axially and equatorially respectively.
(ii) How many planes does $\mathrm{N}_{2} \mathrm{O}_{4}$ have? Depict them diagrammatically.
(iii) What is an Abelian group?
3. (a) What is meant by reducible and irreducible representations? Reduce the following representation having following characters in reducible representation

| $\mathrm{C}_{3 v}$ | E | $2 \mathrm{C}_{3}$ | $3 \sigma_{v}$ |
| :--- | :--- | :--- | :--- |
| $\mathrm{~T}_{\mathrm{R}}$ | 6 | 3 | 4 |

(b) Explain the shape of the following on the basis of VSEPR theory:
(i) $\left[\mathrm{XeF}_{5}\right]^{-}$(ii) $\mathrm{SF}_{4}$ (iii) $\mathrm{ICl}_{4}{ }^{+}$
(c) Use the Hückel theory to evaluate the energies of the $\pi$-orbital's of ethylene and depict them diagrammatically.
4. (i) Explain, how Walsh diagram is helpful in predicting the shape of $A B_{2}$ type of molecules?
(ii) Give an account of substitution reactions of Nitrogen.
(iii) Describe the spectrophotometric method of determination of binary Stability Constant.
5. (a) The rate constants for the formation of $\left[\mathrm{CoX}\left(\mathrm{NH}_{3}\right)_{5}\right]^{2+}$ for $\mathrm{X}=\mathrm{Cl}^{-}, \mathrm{Br}^{-}, \mathrm{N}_{3}{ }^{-}$and $\mathrm{SCN}^{-}$differ by not more than a factor of two. What does this reveal about the mechanism of substitution? Justify your reasoning.
(b) (i) Cite examples of inner sphere electron transfer reactions of octahedral complexes having a chloro and azido ligand respectively, which will react faster and why?
(ii) Differentiate between the spectrochemical and the nephelauxetic series? How does nephelauxetic effect explain the limitation of crystal field theory and is an evidence for ligand field theory for complex formation?
(7. (a) (i) Explain which of the following is expected to show greater Jahn Teller distortions and why? $\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]^{3-},\left[\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+},\left[\mathrm{Cr}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}$.
(ii) With appropriate example explain the thermodynamic origin of stability of chelates.
(b) Discuss molecular orbital theory of metal-ligand bonding in Square planar complexes with $\pi$-bonds.
7. (i) Explain crystal field effect with reference to tetrahedral complexes.
(ii) Identify the similarities and differences between CFT and MOT in reference to metal complexes.
(iii) Derive the group multiplication table for $\mathrm{C}_{3 \mathrm{v}}$ point group and show that set of planes form a class. Also give 2 examples of molecules having $\mathrm{C}_{3 v}$ point group with different structures.

