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E - 305

M. Sc. (First Semester) EXAMINATION, Dec.-Jan., 2020-21

CHEMISTRY

Paper First

(Group Theory and Chemistry of Metal Complexes)

Time: Three Hours [Maximum Marks: 80

Note: Attempt all Sections as directed.

Section—A

1 each

(Objective/Multiple Choice Questions)

Note: Attempt all questions.

Choose the correct answer:

- 1. The molecule (i) $\,SO_2$, (ii) $\,XeOCl_4$ and (iii) $\,PH_3\,$ belongs to :
 - (a) (i) C_1 (ii) D_{4h} (iii) D_{3h}
 - (b) (i) $C_{2\nu}$ (ii) $C_{4\nu}$ (iii) $C_{3\nu}$
 - (c) (i) C_{2v} (ii) D_{4h} (iii) D_{3v}
 - (d) (i) D_{2h} (ii) C_{4v} (iii) D_{3v}

- 2. In the ionic solid state PCl₅ exists as an ionic solid composed of PCl₄⁺ cation and PCl₆⁻ anions but the vapour is molecular. To what point groups do the ionic species in the solid belong?
 - (a) C_{4v} and O_h respectively
 - (b) T_d and D_{6h} respectively
 - (c) T_d and O_h respectively
 - (d) D_{4h} and O_h respectively
- 3. Which of the following does not contain a C_3 axis?
 - (a) POCl₃
 - (b) $[NH_4]^+$
 - (c) $[H_3O]^+$
 - (d) ClF₃
- 4. The number of symmetry elements in diborane molecule:
 - (a) 2
 - (b) 4
 - (c) 6
 - (d) 8

- 5. Among the following the correct statement is:
 - (a) The no. of irreducible representation is equal to the classes of symmetry operation.
 - (b) The no. of irreducible representation is equal to the order of symmetry point group.
 - (c) The irreducible representation contained in any point are always of one dimension.
 - (d) Symmetry point group may not contain a totally symmetric irreducible representation.
- 6. The rate of the reaction depends on:

$$Ni(CO)_4 + PPh_3 \xrightarrow{hv} [Ni(CO)_3(PPh)_3] + CO$$

- (a) Concentration of both the reactant
- (b) Concentration of Ni(CO)₄ only
- (c) Concentration of PPh3 only
- (d) The steric bulk of PPh₃
- 7. The decreasing order of Δt of the following complexes are :
 - (A) $[CoCl_4]^{2-}$
 - (B) $[CoBr_4]^{2-}$
 - (C) $[Co(NCS)_4]^{2-}$
 - (a) (C) > (A) > (B)

- (b) (A) > (B) > (C)
- (c) (B) > (A) > (C)
- (d) (C) > (B) > (A)
- 8. The correct *d*-electron configuration showing spin-orbit coupling is :
 - (a) $t_{2g}^6 + e_g^2$
 - (b) $t_{2g}^6 + e_g^0$
 - (c) $t_{2g}^4 + e_g^0$
 - (d) $t_{2g}^3 + e_g^2$
- 9. Which of the following is hexadentate ligand?
 - (a) Acetyl acetonato
 - (b) 1, 10-phenonthrline
 - (c) Ethylene diamine
 - (d) Ethylene diamine tetraacetic acid
- 10. CrO_4^{2-} is coloured due to :
 - (a) d-d transition
 - (b) $M \rightarrow L$ charge transfer
 - (c) $L \rightarrow M$ charge transfer
 - (d) None of the above

- 11. The ring size and the number of linked tetrahedral present in $[Si_6O_8]^{12-}$ respectively are :
 - (a) 6 and 6
 - (b) 12 and 6
 - (c) 12 and 12
 - (d) 6 and 12
- 12. Silicate with continuous 3D framework are:
 - (a) *Neso*-silicates
 - (b) Soro-silicates
 - (c) Phyllo-silicates
 - (d) Tecto-silicates
- 13. Number of chelating rings present in [Ni(DMG)₂] is/are:
 - (a) Four (2-five membered, 2-two membered)
 - (b) Four (2-five membered, 2-three membered)
 - (c) Four (2-five membered, 2-four membered)
 - (d) Four (2-five membered, 2-six membered)
- 14. Which statement is correct?
 - (a) A dissociative mechanism is a 2-step mechanism with the leaving group departing in the second step.

- (b) An associative mechanism is a 2-step mechanism; the intermediate has a lower coordination number than the starting complex.
- (c) In a dissociative interchange mechanism, bond breaking dominates over bond formation.
- (d) In an associative interchange mechanism, the entering group associates with the substrate after the leaving group has departed.
- 15. Three of the following ions are kinetically inert, one is labile. Which ion is labile?
 - (a) Rh^{3+}
 - (b) Ti³⁺
 - (c) Ru^{2+}
 - (d) Cr³⁺
- 16. Arrange the following cluster in decreasing order of metalmetal bond length:
 - (A) $[Re_2Cl_4(PMe_2Ph)_4]^{2+}$
 - (B) $\left[\text{Re}_{2}\text{Cl}_{4}\left(\text{PMe}_{2}\text{Ph}\right)_{4}\right]^{1+}$
 - (C) $[Re_2Cl_4(PMe_2Ph)_4]$
 - (a) (A) > (B) > (C)
 - (b) (C) > (B) > (A)
 - (c) (B) > (A) > (C)
 - (d) (C) > (A) > (B)

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- 17. Find out the bond order of the following $[Mo_2Cl_8]^{4-}$ and $[Os_2Cl_8]^{2-}$:
 - (a) Both 4
 - (b) Both 3
 - (c) 3 and 4 respectively
 - (d) 4 and 3 respectively
- 18. The reaction of BCl₃ with NH₄Cl gives product A which upon reduction by NaBH₄ gives product B. Product B upon reacting with HCl affords compound C, which is:
 - (a) $B_3N_3H_6$
 - (b) [ClBNH]₃
 - (c) $Cl_3B_3N_3H_9$
 - (d) $(ClH)_3B_3N_3(ClH)_3$
- 19. According to isolobal principle, structure of $[Ni(CO)_2]PB_{10}H_{11}$ is :
 - (a) closo
 - (b) nido
 - (c) archano
 - (d) hypho

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- 20. Which among the following is isolobal with Fe(CO)₅?
 - (a) CH₃
 - (b) CH₃⁺
 - (c) CH₃
 - (d) CH_4

Section—B

2 each

(Very Short Answer Type Questions)

Note: Attempt all questions.

- 1. Write the symmetry elements and point group of PCl₅.
- 2. What are sub-group? Explain with suitable example.
- 3. Write the limitation of CFT.
- 4. How many metal-metal bond present in $Ir_4(CO)_{12}$ and $Os_4(CO)_{15}$.
- 5. Discuss the stability of the complex with respect to ligands.
- 6. What are silicones?
- 7. What are carboranes?
- 8. Calculate framework electron of $Fe_6C(CO)_{16}$.

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Section—C

3 each

(Short Answer Type Questions)

Note: Attempt all questions.

- 1. What are abelian and non-abelian group?
- 2. Find out the point group of the following:
 - (i) SF₄
 - (ii) I_3^-
 - (iii) IF₇
- 3. Apply vibrational spectroscopy to distinguish terminal metal carbonyl from the bridging metal carbonyl.
- 4. Write notes on metal nitrosyls and tertiary phosphene as ligands.
- 5. What are iso- and hetero-polyacids? Briefly discuss the iso- and heteropolyacids and Mo and W.
- 6. Describe the spectrophotometry method for determining the stability constant of metal complexes in solution.
- 7. Discuss the structure and bonding of phosphazene.
- 8. Describe the types of bonds in higher boranes.

Section—D

5 each

(Long Answer Type Questions)

Note: Attempt all questions.

1. Discuss the properties, character and spectroscopy active modes of C_{3V} point group.

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Or

For H₂O molecules:

- (a) Obtain a reducible representation for the different motion.
- (b) Reduce this reducible representation using standard formula and character table of C_{2V} point group.
- (c) Obtain irreducible representation of each kind.
- (d) Show which irreducible representation will be IR and Raman active.
- 2. Discuss the molecular orbital theory for the bonding of octahedral complex.

Or

What is π -acidity? Discuss the type of π -bonding in metal complexes. Why π -bonding ligands behave as strong field ligand?

3. What do you understand by mean of stability constant of metal complexes? On what factors does the stability of a complex ion depends?

Or

What are the silicates ? How are they classified ?

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4. What do you mean by quadruple bonding ? Discuss the structure and bonding of $Re_2Cl_8^{2-}$.

Or

Borazine is isoelectronic structure of benzene and known as inorganic benzene :

- (a) How can borazine be synthesized? Write its reactions.
- (b) Despite parallel physical properties of benzene and isoelectronic borazine why chemical properties of both the compounds are different.