ST. JOSEPH'S COLLEGE (AUTONOMOUS), BENGALURU-27 M.Sc. CHEMISTRY: I SEMESTER SEMESTER EXAMINATION: OCTOBER 2019 CH-7118 : INORGANIC CHEMISTRY

<u>Note</u> : (i) The question paper has **three printed pages** and **three parts**. All parts are compulsory.

(ii) Answer any <u>SIX</u> out of eight questions from part – A, Any <u>FOUR</u> out of six questions from part – B, and any <u>TWO</u> out of three questions from part – C.

Time : 2 1/2 hrs

Max .Marks : 70

<u>PART A</u>

<u>2 x 6 = 12</u>

- 1. Write the shape of SNF_3 using VSEPR theory and predict the approximate bond angle F-S-F in the same.
- 2. Using Ketelaar's triangle would you classify $Sr_2Ga [\chi(Sr) = 0.95 \text{ and } \chi(Ga) = 1.81]$ as an alloy or a Zintl phase? Give reason.
- 3. Calculate the percentage p character in the O-H bond in water.
- 4. The photoelectron spectrum of N_2 is given below. Assign the peaks to the respective



5. How are graphite intercalation compounds classified? Give one example each.

- 6. Draw the structure of $(NPCI_2)_4$.
- 7. How is S_4N_4 prepared? Write chemical equation.
- 8. Give a reaction in supercritical fluid.

<u>PART B</u>

<u>12 x 4 = 48</u>

 a) Draw the shapes of the following molecules using VSEPR theory (i) XeO₂F₂ and (ii) XeOF₂.

b) Construct an approximate molecular orbital energy diagram of NH_3 . The energies in eV of the atomic orbitals are given : The energy levels of atomic orbitals of N are (2s = -25.6; 2p = -15.5) and H (-13.5). Draw the shapes of molecular orbitals showing the overlap of atomic orbitals.

c) Using the mean bond enthalpy (kJ mol⁻¹) values in the table provided below, calculate the standard enthalpy of the reaction, $2H_{2(q)} + O_{2(q)} \rightarrow 2H_2O_{(q)}$.

	н	С	N	0
н	436			
С	412	348 (1)		
		612 (2)		
		837 (3)		
		518 (a)		
N	388	305 (1)	163 (1)	
		613 (2)	409 (2)	
		890 (3)	946 (3)	
0	463	360 (1)	157	146 (1)
		743 (2)		497 (2)

(3+6+3)

10. a) Calculate the density of silver, with a cubic close-packed structure. (the atomic mass of silver = 107.9 g mol⁻¹ and cubic lattice parameter a = 409×10^{-12} m).

b) Draw the rock-salt structure and its projection representation. Identify the nearest neighbour of a sodium ion in the first shell, second shell and third shell at a distance of r, 2r and 3r respectively in sodium chloride crystals.

c) Calculate lattice enthalpy of $Bk(NO_3)_4$, the ionic / thermodynamic radii are given: r(Bk⁴⁺) = 96 pm & r (NO³⁻)= 189 pm. The constants d* = 34.5 pm and κ = 1.21 X 10⁵ kJ pm mol⁻¹. (4+4+4)

11. a)Identify the following metal oxide as insulators, p- and n-type extrinsic semiconductors.
(i) Fe₂O₃ (ii) MgO and (iii) CoO. Give reason for your conclusion.

b) Draw the ccp unit cell and mark all octahedral holes in the projection representation.
c) The enthalpy change and entropy change for the decomposition of strontium carbonate are 234.6 kJ mol⁻¹ and 171 J mol⁻¹ respectively. Calculate the decomposition temperature. Will the decomposition temperature of calcium carbonate be higher or lower than that of strontium carbonate? Give explanation for your conclusion. (4+4+4)

12. a) With the help of a diagram explain the preparation of carbon nanotubes by chemical vapour deposition method.

b) Differentiate between symmetric and unsymmetric cleavages of diborane by Lewis bases. Give the mechanism.

c) Give geometrical and Lipscomb's semitopological structure of B_5H_{11} (4+4+4)

13. a) Starting from B₆H₁₀, arrive at the structures of any three carboranes.
b) How are metallocarboranes prepared from 1,2-dicarba-closo-dodecaborane. Write chemical equations.

c) Write the chemical equations for the reactions each at 100° C, between borazine and (i) HCl (ii) CH₃OH. (4 + 4 + 4)

14. a) Differentiate between 'B' strain and 'F' strain with suitable examples.

b) Account for the fact that secondary amines are stronger bases than primary amines. Explain using suitable example.

- c) What are ionic liquids? Give one method of preparation of ionic liquids.
- d) $R_2OBH_3 + R_2SBF_3 \approx R_2OBF_3 + R_2SBH_3$. In which direction does the equilibrium shifts more, right or left? Give reason. (3+ 3+3+3)

PART C

<u>5 x 2 = 10</u>

15. Write the Lewis structure of SCN⁻. Write the resonance structures for the same. Calculate the formal charges for each atom in all resonance structures. Arrange the resonance structures according to their stability (write the most stable structure first). Give reason/s for your conclusion. Predict the approximate bond lengths of C-S & C-N in this radical using the data given in the table:

Bond	Bond length (pm)	Bond	Bond length (pm)
C-N	147	C-S	181
C=N	128	C=S	155
C≡N	116	-	-

16. a) Calculate the number of 2c-2e (α) and 3c-2e (β) bonds of the B₁₀H₁₂²⁻.

b) The number of 2c-2e (α) and 3c-2e(β) bonds in a borane are 8 and 5 respectively. Arrive at the formula of the borane. (2+3)

17. a) Give the formula of an acid which can protonate $C(CH_3)_4$.

b)The ReO_3 structure is cubic with a Re atom at each corner of the unit cell and one O atom on each unit cell edge midway between the Re atoms. Sketch this unit cell and determine (a) the coordination numbers of the ions and (b) the identity of the structure type that would be generated if a cation were inserted in the centre of each ReO₃ unit cell. (2+3)