ST. JOSEPH'S COLLEGE (AUTONOMOUS), BENGALURU-27

M.Sc. CHEMISTRY: I SEMESTER

SEMESTER EXAMINATION: OCTOBER 2019

CH-7116 : INORGANIC CHEMISTRY

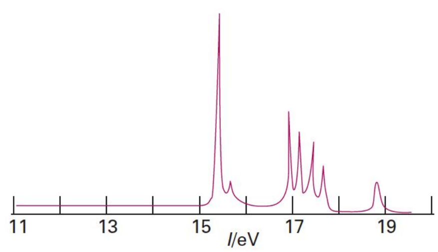
Note : (i) The question paper has **three printed pages** and **three parts**. All parts are compulsory.

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

Time : 2 ½ hrs Max .Marks : 70

PART A

1. Assign the molecular orbitals for the spectral lines in the UV photoelectron spectrum of CO shown:



2. What are the expected changes in bond orders that accompany the following ionization processes? (i) $O_2 \rightarrow O_2^+$; (ii) $N_2 \rightarrow N_2^+$.
3. Deduce the shape of the given species using VSEPR theory: (i) IOF_4^- (ii) $SeOCl_2$ (Se belongs to the oxygen family).
4. Predict the crystal structure of TlCl using the ionic radii given: r(Tl) = 159 pm and r(Cl) = 181 pm.
5. What are phosphazenes? Give two examples.
6. Discuss the structure of C_{60} fullerene.
7. Give the structures of pentaiodide and octaiodide ions.
8. What are supercritical fluids? Give a reaction in supercritical carbon dioxide.

PART B $4 \times 12 = 48$

9. (a) Write the Lewis structure of $POCl_3$. Verify it with the formal charge calculation. Predict the shape of $POCl_3$ using VSEPR theory and explain the same using VB theory by assuming suitable hybridisation.

   (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. (6+6)
10. (a) Metallic sodium adopts a bcc structure with a density of 970 kg m^{-3}. What is the length of the edge of the unit cell? Atomic mass of sodium = 23×10^{-3} kg mol^{-1}.

    (b) Draw the structure of sphalerite (zinc-blende) and its projection representation.

(c) Calculate the affinity enthalpy of chlorine using the data given. In sodium chloride, the Madelung constant = 1.748, $r_{Na+} + r_{Cl-}$ = 283 pm (2.83×10^{-10} m), the permittivity of free space = 8.854×10^{-12} J^{-1} C^2 m^{-1}, the constant d* = 34.5 pm, elementary charge = 1.602 10^{-19} C, ΔH^0_f for NaCl = - 411kJ. $\Delta H_{subblimation}$ and IE for sodium are +108kJ mol^{-1} and +496 kJ mol^{-1}respectively. The dissociation energy of chlorine is 244kJ $mole^{-1}$.

(4+4+4)

11. a) Describe the difference between a semiconductor and a semimetal.
b) Calculate the percentage of unoccupied space in a close-packed arrangement of identical spheres.
c) Construct an approximate molecular orbital energy diagram of H_2O. The energies in eV of the atomic orbitals are given: O (2s = -32.38; 2p = -15.85) and H (1s = -13.61). The bond angle H-O-H in water is 107^0. Explain this using the Walsh diagram. (4+4+4)

12. a) Discuss the classification of carbon nanotubes.
b) What are the products formed when NH_3 and $N(C_2H_5)_3$ react with diborane? Give the mechanism for one of the reactions.
c) Give geometrical and Lipscomb's semitopological structure of B_5H_9. (4+4+4)

13. a) Give the general formulae of nidocarboranes and arachno carboranes. Give the structure of nido $C_2B_4H_8$.
b) What is a dicarbollide? How are metallocarboranes prepared from a dicarbollide?
c) Give two chemical differences between inorganic benzene and benzene. Write chemical equations. (4+4+4)

14. a) How steric factor affect the acid- base strength? Explain using suitable examples.
b) Arrange primary, secondary and tertiary amines in the increasing order of base strength and give reason.
c) Give two applications of ionic liquids by selecting a suitable example.
d) i) Give Drago-Wayland equation and explain the terms.
ii) Which is more stable, $[AgI_2]^-$ or $[AgF_2]^-$? Give reason. (3+ 3+3+3)

PART C **2 X 5 = 10**

15. (a) Explain the instability of fulminate ion, CNO^- by writing its resonance Lewis structures and calculating the formal charges of each atom in all structures.
(b) The bond dissociation energies of some molecules are given: D(H-H) = 436 kJ mol^{-1}; D(Cl-Cl) = 242 kJ mol^{-1} ; D(Br-Br) = 193 kJ mol^{-1}; D(I-I) = 151 kJ mol^{-1}. Calculate the bond dissociation energies of HCl, HBr and HI. Compare these values with the experimental values given below: D(H-Cl) = 432 kJ mol^{-1} ; D(H-Br) = 366 kJ mol^{-1} ; and D(H-I) = 293 kJ mol^{-1}. Give reason/s for the difference between the experimental value and the calculated value, if any, in each case. (2+3)

16. (a) Cu-Ni alloy crystallises over the whole concentration range in a face-centred cubic lattice. If Cu occupies all corners of the cube and Ni all faces of the cube, calculate mass percentage of copper in the alloy. (Atomic mass of Cu= 63.55 U and Ni = 58.70 U)
b) Complete the following reaction: SO_3^{-2} + HF → ----- +----- . In which direction this reaction proceeds more, right or left? Give reason. (2+3)

17. The styx numbers of two boranes, A and B are [4012] and [4620] respectively. Which one of these is an arachno borane? Draw the structure of the borane with 6, BBB bonds.
