# ST. JOSEPH'S COLLEGE (AUTONOMOUS), BENGALURU-27 <br> M.Sc. CHEMISTRY: I SEMESTER 

## SEMESTER EXAMINATION: OCTOBER 2019 <br> CH-7118: 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: $21 / 2 \mathrm{hrs}$
Max .Marks : 70
PART A
$\underline{2 \times 6=12}$

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

5. How are graphite intercalation compounds classified? Give one example each.
6. Draw the structure of $\left(\mathrm{NPCl}_{2}\right)_{4}$.
7. How is $\mathrm{S}_{4} \mathrm{~N}_{4}$ prepared? Write chemical equation.
8. Give a reaction in supercritical fluid.

## PART B

$12 \times 4=48$
9. a) Draw the shapes of the following molecules using VSEPR theory (i) $\mathrm{XeO}_{2} \mathrm{~F}_{2}$ and
(ii) $\mathrm{XeOF}_{2}$.
b) Construct an approximate molecular orbital energy diagram of $\mathrm{NH}_{3}$. The energies in eV of the atomic orbitals are given : The energy levels of atomic orbitals of N are ( $2 \mathrm{~s}=$ $-25.6 ; 2 p=-15.5$ )and $H(-13.5)$. Draw the shapes of molecular orbitals showing the overlap of atomic orbitals.
c) Using the mean bond enthalpy $\left(\mathrm{kJ} \mathrm{mol}^{-1}\right)$ values in the table provided below, calculate the standard enthalpy of the reaction, $2 \mathrm{H}_{2(\mathrm{~g})}+\mathrm{O}_{2(\mathrm{~g})} \rightarrow 2 \mathrm{H}_{2} \mathrm{O}_{(\mathrm{g})}$.

|  | H | C | N | 0 |
| :---: | :---: | :---: | :---: | :---: |
| H | 436 |  |  |  |
| C | 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) |

10. a) Calculate the density of silver, with a cubic close-packed structure. (the atomic mass of silver $=107.9 \mathrm{~g} \mathrm{~mol}^{-1}$ and cubic lattice parameter $\mathrm{a}=409 \times 10^{-12} \mathrm{~m}$ ).
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 $r$, $2 r$ and $3 r$ respectively in sodium chloride crystals.
c) Calculate lattice enthalpy of $\mathrm{Bk}\left(\mathrm{NO}_{3}\right)_{4}$, the ionic / thermodynamic radii are given: $r\left(\mathrm{Bk}^{4+}\right)=96 \mathrm{pm} \& r\left(\mathrm{NO}^{3-}\right)=189 \mathrm{pm}$. The constants $\mathrm{d}^{*}=34.5 \mathrm{pm}$ and $\kappa=1.21 \mathrm{X} 10^{5} \mathrm{~kJ}$ $\mathrm{pm} \mathrm{mol}{ }^{-1}$.
$(4+4+4)$
11. a)Identify the following metal oxide as insulators, p - and n -type extrinsic semiconductors.
(i) $\mathrm{Fe}_{2} \mathrm{O}_{3}$ (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 $234.6 \mathrm{~kJ} \mathrm{~mol}^{-1}$ and $171 \mathrm{~J} \mathrm{~mol}^{-1}$ 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 $B_{5} H_{11}$
13. a) Starting from $B_{6} H_{10}$, 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 $100^{\circ} \mathrm{C}$, between borazine and (i) HCl (ii) $\mathrm{CH}_{3} \mathrm{OH}$.
$(4+4+4)$
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) $\mathrm{R}_{2} \mathrm{OBH}_{3}+\mathrm{R}_{2} \mathrm{SBF}_{3} \leftrightharpoons \mathrm{R}_{2} \mathrm{OBF}_{3}+\mathrm{R}_{2} \mathrm{SBH}_{3}$. In which direction does the equilibrium shifts more, right or left? Give reason.
(3+3+3+3)

## PART C

$5 \times 2=10$
15. Write the Lewis structure of $\mathrm{SCN}^{-}$. 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 $2 c-2 e(\alpha)$ and $3 c-2 e(\beta)$ bonds of the $B_{10} H_{12}{ }^{2-}$.
b) The number of $2 \mathrm{c}-2 \mathrm{e}(\alpha)$ and $3 \mathrm{c}-2 \mathrm{e}(\beta)$ bonds in a borane are 8 and 5 respectively. Arrive at the formula of the borane.
17. a) Give the formula of an acid which can protonate $\mathrm{C}\left(\mathrm{CH}_{3}\right)_{4}$.
b)The $\mathrm{ReO}_{3}$ 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 $\mathrm{ReO}_{3}$ unit cell.
(2+3)
