

2019

CHEMISTRY

( Major )

Paper : 3.2

( Chemical Bonding )

Full Marks : 60

Time : 3 hours

*The figures in the margin indicate full marks  
for the questions*

1. Answer the following as directed :  $1 \times 7 = 7$

(a) Which option best approximates  
the bond angle present in  $\text{H}_2\text{Sn}$ ?

(i)  $102.5^\circ$

(ii)  $180^\circ$

(iii)  $104.5^\circ$

(iv)  $120^\circ$

( Choose the correct option )

(b)  $\text{ClO}_3^-$  and  $\text{ClO}_4^-$  ions have same number of electron pairs around central chlorine but their geometry is different. Why?

(c) What happens when CsCl crystal is heated at high temperature?

(d) What are Keesom forces?

(e) If  $N$  is the number of tetrahedral voids in a close-packed structure, then the number of octahedral voids is \_\_\_\_\_.

( Fill in the blank )

(f) Arrange  $\text{O}_2^+$ ,  $\text{O}_2$ ,  $\text{O}_2^-$  and  $\text{O}_2^{2-}$  in order of increasing bond order.

(g) Highly charged cations are rare. Why?

2. Answer the following questions :  $2 \times 4 = 8$

(a) Anhydrous  $\text{AlCl}_3$  is covalent but  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  is ionic in nature. How would you account for this behavior?

(b) When naphthalene is hydrated, the heat released is about 80 kcal/mol. Heat of hydrogenation of an isolated cyclohexene unit is equal to 28.8 kcal/mol. Estimate the resonance energy of naphthalene.

(c) Discuss the Bent's rule by taking  $(\text{CH}_3)_2\text{CCl}_2$  molecule as an example.

(d) Why is alcohol a better drying agent than acetone?

3. Answer any *three* questions :  $5 \times 3 = 15$

(a) Draw the structure of  $\text{CO}_3^{2-}$  ion. If all the C—O bond distances are equal, then write the resonance structure to describe the bonding in  $\text{CO}_3^{2-}$  ion. Describe the bonding in  $\text{CO}_3^{2-}$  in terms of hybridization scheme.

$1+2+2=5$

(b) Calculate the maximum radius of a sphere that may be accommodated in an octahedral hole in a closed-packed solid composed of spheres of radius  $r$ . 5

(c) Compare the following pairs of molecules with respect to the parameters cited within the parenthesis :  $1 \times 5 = 5$

(i)  $\text{CO}^+$  and  $\text{CO}$  (bond length)

(ii)  $\text{SiCl}_4$  and  $\text{CCl}_4$  (boiling point)

(iii)  $\text{Na}_2\text{CO}_3$  and  $\text{Cs}_2\text{CO}_3$  (solubility)

(iv)  $\text{Cu}^{2+}$  and  $\text{Ca}^{2+}$  (polarizing power)

(v)  $\text{NH}_2^-$  and  $\text{SF}_4$  (hybrid orbitals of the central atom)

(d) Discuss the electron probable density of bonding and antibonding molecular orbitals. 5

(e) Which of the following mixtures of solvents have intermolecular hydrogen bonding between the different solvent molecules?

(i)  $\text{Et}_2\text{O}$  and THF

( 5 )

(ii) EtOH and H<sub>2</sub>O

(iii) EtNH<sub>2</sub> and Et<sub>2</sub>O

Give diagrams to show likely hydrogen-bonded interactions. 2+3=5

4. Answer any *three* questions : 5×3=15

(a) What are MOs and how are they constructed? Discuss the MO energy level diagram of the triatomic molecule NO<sub>2</sub> and hence obtain its electronic configuration. 2+2+1=5

(b) How many Bravais lattice types are there and what are they? Name the orthorhombic Bravais lattices. Determine the density of CsCl which crystallizes in bcc type structure with edge length 412.1 pm. The atomic mass of Cs and Cl are 133 and 35.5 respectively. 2+1+2=5

(c) Discuss how steric and electronic factors affect the molecular properties. 5

- (d) What are Miller indices? A certain crystal has lattice parameters of  $4.24 \text{ \AA}$ ,  $10 \text{ \AA}$  and  $3.66 \text{ \AA}$  on X, Y, Z axes respectively. Determine the Miller indices of a plane having intercepts of  $2.12 \text{ \AA}$ ,  $10 \text{ \AA}$  and  $1.83 \text{ \AA}$  on the X, Y and Z axes. 2+3=5
- (e) Predict the shapes, including the bond angles of the following : 5
- (i) The ion  $\text{PH}_4^+$
  - (ii) The molecule  $\text{PF}_5$
  - (iii) The ion  $\text{PF}_6^-$
  - (iv) The molecule  $\text{XeF}_4$

5. Answer any *three* questions : 5×3=15

- (a) When acetylene is passed through a solution of Cu(I) chloride, a red ppt of copper acetylide,  $\text{CuC}_2$  is formed. This is a common test for the presence of acetylene. Describe the bonding in the  $\text{C}_2^{2-}$  ion in terms of molecular orbital theory and compare the bond order to that of  $\text{C}_2$ . 5

( 7 )

- (b) Derive the Born-Landé equation for lattice energy calculation. Give its importance and conclusions derived. 3+2=5
- (c) Justify the following : 2½×2=5
- (i) Sodium chloride and magnesium oxide both have identical structures. However, sodium chloride melts at 1074 K and magnesium oxide melts at 3125 K.
- (ii) Cotton clothes dry slowly in comparison to synthetic clothes.
- (d) What is the effect of temperature on the conductivity of semiconductors? Write a note on the applications of semiconductors. 2+3=5

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