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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 : 1×7=7

   (a) Which option best approximates the bond angle present in H_2Sn?

   (i) 102·5°

   (ii) 180°

   (iii) 104·5°

   (iv) 120°

   (Choose the correct option)

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(*Turn Over*)

(2)

(b) ClO_3^- and 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 O_2^+, O_2, O_2^- and O_2^{2-} in order of increasing bond order.

(g) Highly charged cations are rare. Why?

(3)

2. Answer the following questions : 2×4=8

(a) Anhydrous $AlCl_3$ is covalent but $AlCl_3 \cdot 6H_2O$ 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 $(CH_3)_2CCl_2$ molecule as an example.

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

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

(a) Draw the structure of CO_3^{2-} ion. If all the C—O bond distances are equal, then write the resonance structure to describe the bonding in CO_3^{2-} ion. Describe the bonding in CO_3^{2-} in terms of hybridization scheme.

1+2+2=5

(4)

(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) CO^+ and CO (bond length)

   (ii) $SiCl_4$ and CCl_4 (boiling point)

   (iii) Na_2CO_3 and Cs_2CO_3 (solubility)

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

   (v) NH_2^- and 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) Et_2O and THF

(5)

   (ii) EtOH and H_2O

   (iii) $EtNH_2$ and Et_2O

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

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

(a) What are MOs and how are they constructed? Discuss the MO energy level diagram of the triatomic molecule NO_2 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 crystalizes 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 Å, 10 Å and 3·66 Å on X, Y, Z axes respectively. Determine the Miller indices of a plane having intercepts of 2·12 Å, 10 Å and 1·83 Å 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 PH_4^+

  (ii) The molecule PF_5

  (iii) The ion PF_6^-

  (iv) The molecule 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, CuC_2 is formed. This is a common test for the presence of acetylene. Describe the bonding in the C_2^{2-} ion in terms of molecular orbital theory and compare the bond order to that of C_2. 5

(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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