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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 : $1 \times 7 = 7$

(a) In a face centered cubic lattice, atom A occupies the corner position and atom B occupies the face centered position. If one atom B is missing from one of the face centered points, the formula of the compound is _____ .

(Fill in the blank)

(b) PCl_5 undergoes

(i) $sp^3 d_{xy}$ hybridization

(ii) $sp^3 d_{x^2 - y^2}$ hybridization

(iii) $sp^3 d_{z^2}$ hybridization

(iv) $sp^3 d_{zx}$ hybridization

(Choose the correct answer)

(c) What type of intrinsic defect would you expect to find in MgO and CdTe?

(d) Why is boiling point of NH_3 higher than PH_3?

(e) Which of the following can be expected to be more soluble in water?

$$NaClO_4 \quad \text{or} \quad KClO_4$$

(f) What is the angle (degree) between [1 1 1] and [1 1 2] directions in a cubic crystal?

(g) What is the coordination number of Ti^{4+} ion in perovskite structure? Name three compounds with such a structure.

2. Answer the following :   2×4=8

(a) What do you mean by the term 'hypervalence' in polyatomic molecules?

(b) Metallic sodium adopts a bcc structure with density 970 kg m^{-1}. What is the length of the unit cell?

(c) An organic compound crystallizes in an orthorhombic system with two molecules per unit cell. The unit cell dimensions are 12·05 Å, 15·05 Å and

2·69 Å. If the density of the crystal is 1·419 g cm^{-3}, calculate the molar mass of the organic compound.

(d) Explain the trends in bond angles and bond lengths of the following ions :

	X—O (pm)	O—X—O (°)
ClO_3^-	149	107
BrO_3^-	165	104
IO_3^-	181	100

3. Answer any *three* of the following :   5×3=15

(a) How many LCAOs are possible for four 1s orbitals? Draw and arrange these MOs for hypothetical linear H_4 and square H_4 molecules in order of increasing energy. Also comment on the magnetic behavior of the molecules.

                              1+3+1=5

(b) What do you mean by Fermi level? What is the forbidden energy gap? How does it occur? What is its magnitude for Ge and Si?

                              1+2+2=5

(c) The stronger the intermolecular attractions, the greater the boiling point of a molecular substance. Explain the trend in boiling points of the halogens :   5

	F_2	Cl_2	Br_2	I_2
Boiling point (K)	85	238	332	457

(d) What are Miller indices? Determine the Miller indices of a plane that makes intercepts of 4 Å, 3 Å and 8 Å on the coordinate axes of an orthorhombic lattice with the ratio of the axial lengths as $a : b : c = 2 : 3 : 1$.   2+3=5

4. Answer any *three* of the following :   5×3=15

(a) Draw the MO energy level diagram of CO molecule. Why is the bond length of CO^+ less than that of CO?   3+2=5

(b) What is lattice enthalpy? How can the relative stabilities of different oxidation states in solids be predicted on the basis of lattice enthalpies? Arrange the following ionic solids in order of their increasing lattice enthalpies :   1+3+1=5

LiCl, NaCl, KCl

(c) Giving suitable examples, discuss the correlation among bond order, bond angle and bond strength.   5

(d) When propanone and trichloromethane are mixed, a hydrogen bond is formed between the two molecules, although no hydrogen bonding exists in either of the pure liquids.

(i) Explain why there is no hydrogen bond in either propanone or trichloromethane when the liquids are pure.

(ii) Suggest a reason why hydrogen bonds are formed when the two liquids are mixed.   2½+2½=5

(e) Compare the following pairs of molecules with respect to the parameters cited within the parenthesis :   1×5=5

(i) Benzene and Pyridine (resonance energy)

(ii) $SiCl_4$ and CCl_4 (bond length)

(iii) CH_3Cl and $CHCl_3$ (dipole moment)

(6)

(iv) CO and N_2 (bond dissociation energy)

(v) $SOCl_2$ and SOF_2 (halogen–S–halogen angle)

5. Answer any *three* of the following :   5×3=15

(a) Solid phosphorous pentachloride is an ionic solid composed of PCl_4^- cations and PCl_6^- anions, but the vapour is molecular. What are the shapes of the ions in the solid? Predict the shape of the following molecules/ions :   2+3=5

$$HCP, SeF_3^+, NH_2^-$$
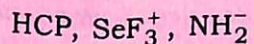
(b) The solubility and stability of ionic solids largely depend upon their lattice energies. Explain giving suitable examples.   5

(c) Write notes on the following :   2½×2=5

(i) Spinel

(ii) Volume occupied in ccp arrangement

A9/90

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(7)

(d) What is Hückel's rule of aromaticity? Does an aromatic molecule need to have conjugation and resonance? Identify the aromatic and non-aromatic species from the following :   2+1+2=5

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A9—6000/90

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