

2016

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 as directed : 1×7=7

(a) The state of hybridization of the central atom and the number of lone pairs over the central atom in  $\text{POCl}_3$  are

(i)  $sp$ , 0

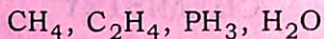
(ii)  $sp^2$ , 0

(iii)  $sp^3$ , 0

(iv)  $dsp^2$ , 1

(Choose the correct option)

- (b) Arrange the following compounds in order of increasing H—X—H bond angles :



- (c) Two ice cubes are pressed over each other until they unite to form one block. Which force is responsible for holding them together?

- (d) Why do the crystalline solids have sharp melting points?

- (e) Which substance would you expect to have the greatest lattice energy— $\text{MgF}_2$ ,  $\text{CaF}_2$  or  $\text{ZrO}_2$ ?

- (f) The edge lengths of the unit cells in terms of the radius of spheres constituting f.c.c, b.c.c. and simple cubic unit cell are respectively \_\_\_\_\_.

(Fill up the blank)

- (g) What is meant by angular wave function of atomic orbitals?

2. Answer all questions : 2×4=8

(a) The bond dissociation enthalpies for  $N_2$  and  $N_2^-$  are  $945 \text{ kJ mol}^{-1}$  and  $765 \text{ kJ mol}^{-1}$  respectively. Using an argument based on MO theory, explain why  $N_2^-$  has smaller bond dissociation energy than  $N_2$ .

(b) Solid phosphorous pentachloride is an ionic solid composed of  $PCl_4^+$  cations and  $PCl_6^-$  anions but the vapour phase is molecular. What are the shapes of the ions in the solid?

(c) Using the values of ionic radii (nm) given below, propose the packing pattern of lithium fluoride  $LiF$  and rubidium bromide  $RbBr$  :

$$Li^+ = 0.074, Rb^+ = 0.149, F^- = 0.131, Br^- = 0.196$$

(d) Write the resonating structures of  $CO$  and explain the cause of its low dipole moment.

3. Answer any *three* of the following :  $5 \times 3 = 15$

(a) Draw the resonance structures for the isoelectronic ions  $\text{NSO}^-$  and  $\text{SNO}^-$  and assign formal charges. Which ion is likely to be more stable?  $2+2+1=5$

(b) What is cubic close packing arrangement of spheres? Show that the volume of space occupied for a cubic close packed lattice of spheres is 74%.  $2+3=5$

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

(i)  $\text{NO}^+$  and  $\text{NO}$  (bond energy)

(ii)  $\text{H}_2\text{Se}$  and  $\text{H}_2\text{O}$  (boiling point)

(iii)  $\text{XeO}_3$  and  $\text{SO}_2\text{Cl}_2$  (hybridization of the central atom)

(iv)  $\text{PI}_3$  and  $\text{SbI}_3$  (bond angle)

(v) HCP and  $\text{COF}_2$  (shape)

- (d) What are intrinsic and extrinsic semiconductors? Which of the oxides  $\text{WO}_3$ ,  $\text{MgO}$  and  $\text{CdO}$  are likely to show  $p$ - or  $n$ -type extrinsic semiconductivity?

3+2=5

4. Answer any *three* questions :

5×3=15

- (a) Develop the molecular orbital energy-level diagram for  $\text{LiF}$ . Show the orbital occupancy in  $\text{LiF}$  and estimate the bond order.

3+2=5

- (b) How many orthorhombic Bravais lattices are there and what are they? Lithium borohydride,  $\text{LiBH}_4$ , crystallizes in an orthorhombic system with four molecules per unit cell. The unit cell dimensions are  $a = 6.81 \text{ \AA}$ ,  $b = 4.43 \text{ \AA}$  and  $c = 7.17 \text{ \AA}$ . If the molar mass of  $\text{LiBH}_4$  is  $21.76 \text{ g mol}^{-1}$ , calculate the density of the crystal.

2+3=5

- (c) Explain the Bent's rule with suitable examples. Why are the axial bonds of  $\text{PCl}_5$  longer than those of equatorial bonds? Which  $d$ -orbital takes part in  $sp^3d$  hybridization and why?

2+1+2=5

- (d) Discuss the structure and bonding in electron-deficient compound diborane,  $\text{B}_2\text{H}_6$ .

2+3=5

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

- (a) What is lattice enthalpy? Discuss the factors on which lattice enthalpy depends. Calculate the lattice enthalpy of magnesium chloride ( $\text{MgCl}_2$ ) using a Born-Haber cycle and the information given below :

$$1+2+2=5$$

$$\begin{aligned} \text{Enthalpy of sublimation of Mg (s)} \\ = + 148 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \text{First ionization energy of Mg (g) to} \\ \text{Mg}^+ \text{ (g)} \quad = + 738 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Second ionization energy of Mg}^+ \text{ (g)} \\ \text{to Mg}^{2+} \text{ (g)} \quad = + 1450 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Dissociation energy of Cl}_2 \text{ (g)} \\ = + 244 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Electron gain enthalpy of Cl (g)} \\ = - 355 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Enthalpy of formation of MgCl}_2 \text{ (s)} \\ = - 641 \text{ kJ mol}^{-1} \end{aligned}$$

- (b) Giving suitable examples, explain how electronic effects influence the structure, reactivity or properties of a molecule.

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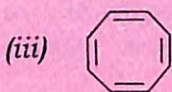
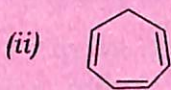
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(c) Justify the following :  $2\frac{1}{2} \times 2 = 5$

(i) When burn in oxygen, lithium forms the oxide  $\text{Li}_2\text{O}$  but sodium forms the peroxide  $\text{Na}_2\text{O}_2$ .

(ii) Water contracts when heated between  $0^\circ\text{C}$  and  $4^\circ\text{C}$ .

(d) Discuss Huckel's rule for aromaticity. Explain why each of the following is not aromatic :  $2+3=5$



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