2014

CHEMISTRY

(Major)

Paper : 3.2

(Chemical Bonding)

Full Marks : 60

Time : 2½ hours

The figures in the margin indicate full marks for the questions

1. Answer the following as directed : 1×7=7

(a) Arrange the following bonds in the increasing order of bond lengths :

C—H; O—H; N—H

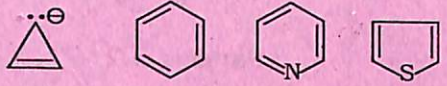
(b) The molecule with bond angle of 120° out of the following is ——.

Fill in the gap from NH_3, BF_3, CO_2 and CH_4.

(c) Arrange the diatomics O_2^+, O_2, O_2^- and O_2^{2-} in order of increasing internuclear distance.

(d) Methylbromide reacts much faster than ethylbromide when treated with ethyl alcohol. Explain the underlying cause.

(e) Which of the following does not possess aromaticity?



(i) (ii) (iii) (iv)

(f) State the number of Na^+ and Cl^- in the unit cell of NaCl, if NaCl forms f.c.c. lattice.

(g) What is a spinel structure?

2. Answer the following : 2×4=8

(a) The dipole moment of water is 1·84 D. Bond moment of O—H bond is 1·5 D. Calculate the ∠H—O—H bond angle in water.

(b) How is bond order defined for a diatomic molecule in MO theory? Comment on the molecule A_2 of which the bond order is zero.

(c) What is solvation? Explain by taking an example of ionic solid.

(d) The density of ice is less than that of water. Explain why.

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

(a) State and explain the postulates of VSEPR theory. Predict the shape of ClF_3. 3+2=5

(b) What are the three important types of hybrid orbitals that can be formed by an atom with only *s*- and *p*-orbitals in its valence shell? Describe the molecular geometry that each of these produces. Which one of the above hybrid orbitals is supposed to form the longest bond? 1½+3+½=5

(c) Discuss the structures of PCl_5 and SF_6 highlighting the hybridization of atoms, shape of molecules and bond angles in each. Give reasons why P—Cl bonds in PCl_5 are of two different lengths. 4+1=5

(d) Explain why—

(i) dipole moment of NH_3 is higher than that of NF_3;

(ii) bond angle $\angle$H—O—H in H_2O is higher than bond angle $\angle$H—S—H in H_2S;

(iii) PH_3 is pyramidal in shape whereas $PH_4^{\oplus}$ is tetrahedral. 2+1½+1½=5

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

(a) Draw the molecular orbital diagram of carbon monoxide molecule. Mention, how oxygen has higher effective nuclear charge reflected in the MO diagram. State which species out of CO^+ and CO has stronger bond. Give reasons in support of your answer. 2+1½+1½=5

(b) State the rules for linear combination of atomic orbitals. The wave function of two hydrogen atoms are given by ψ(1) and ψ(2). Apply the principle of LCAO to generate the wave functions corresponding to molecular orbitals in H_2 molecule. 3+2=5

(c) Why does B_2H_6 not have the same kind of structure as C_2H_6? Draw the structure that B_2H_6 does have and describe the nature of two types of BH bonds therein. 1+2+2=5

(d) Discuss and draw the molecular orbital diagram of BeH_2 molecule. Mention the total bond order of the B—H bonds. 4+1=5

(e) Draw the appropriate electronic formula for resonance forms which contribute to the structures of $CO_3^{=}$ and $NO_3^{\ominus}$. Discuss the hybridization of the central atoms and mention the shapes in the two. 3+2=5

(f) Explain the terms 'permitted band', 'forbidden zone' and 'Fermi level' in the light of band theory of bonding in metals. What is an *n*-type semiconductor? Prepare a diagram of its band structure as a part of your answer. 3+2=5

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

(a) (i) Write any two different types of unit cells on the basis of cell parameters. Mention the cell parameters.

(ii) How many Bravais lattices are known?

(iii) Define Miller indices. A plane in an ionic crystal is indicated as (1 2 1). What are the Miller indices for the plane? 2+1+(1+1)=5

(b) Explain (i) radius ratio and (ii) coordination number in an ionic crystal. In an ionic crystal composed of $A^{\oplus}$ and $B^{\ominus}$ ions, all the $B^{\ominus}$ ions touch

each other as well as the $A^{\oplus}$ ions. Find a probable radius ratio and predict its structure. 2+3=5

(c) What is Born-Haber cycle? Construct Born-Haber cycle for formation of LiCl (s). Explain each step.

Using Born-Haber cycle, calculate the missing parameter of LiCl (s) from the following data : 1+2+2=5

	ΔH (kJ mol^{-1})
Sublimation of Li (s)	160·7
Ionisation of Li (g)	520·0
Dissociation of Cl_2 (g)	242·0
Electron gain by Cl (g)	−365·0
Lattice energy of LiCl (s)	−838·4

(d) Arrange the following molecules in increasing order with respect to melting point within the groups :

Group (i) : $NaCl$, $MgCl_2$, $AlCl_3$

Group (ii) : $BeCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$

Group (iii) : CaI_2, $CaBr_2$, CaF_2

Support your answer on the basis of Fajans' rules. 2+3=5

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