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CHEMISTRY

(Major)
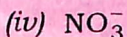
Paper : 3.2

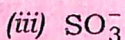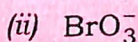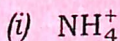**(Chemical Bonding)**

Full Marks : 60

Time : 3 hours

The figures in the margin indicate full marks for the questions

1. Answer the following questions as directed :

$1 \times 7 = 7$

(a) Which of the following ions have the planar geometry?

   (i) NH_4^+

   (ii) BrO_3^-

   (iii) SO_3^-

   (iv) NO_3^-

   (Choose the correct answer)

(b) Determine if the molecule below has conjugation, aromaticity, both or neither :

(*Turn Over*)
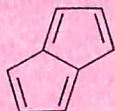
(c) What is the number of tetrahedral voids per unit cell in NaCl crystal?

(d) Why are ionic solids generally poor conductors of electricity?

(e) Arrange the following in order of their increasing bond length :

$$NF_3, \ BF_3, \ NH_3 \ \text{and} \ PH_3$$

(f) What hybridization is predicted for sulfur in the HSO_3^- ion?

(g) The atomic diameter of a bcc crystal (where a is the lattice parameter) is ____.

(Fill in the blank)

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

(a) Sodium chloride melts at 1074 K; magnesium oxide melts at 3125 K. Both have identical structures. Why is there such a difference in their melting points?

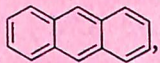(b) Draw the structures of NO_2^+, NO_2 and NO_2^-. Arrange them in the increasing order of O—N—O bond angle.

(c) Explain why water can form hydrogen bond more effectively than hydrogen fluoride.

(d) Explain why iodine is a solid with a low melting and boiling point, almost insoluble in water, but soluble in organic solvents such as hexane.

3. Answer any *three* of the following questions :

$$5 \times 3 = 15$$

(a) What do you mean by resonance energy? Explain giving suitable examples. Calculate the resonance energy of anthracene , using the data provided below : $3 + 2 = 5$

Heat of hydrogenation, $\Delta H_R = -28 \cdot 6 \ \text{kcal mol}^{-1}$
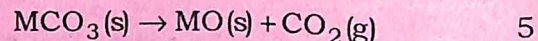

$\Delta H_R = -116 \cdot 2 \ \text{kcal mol}^{-1}$
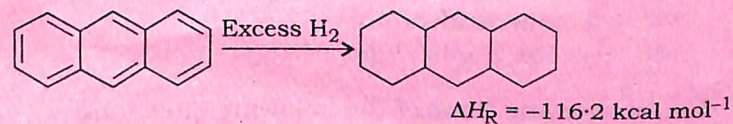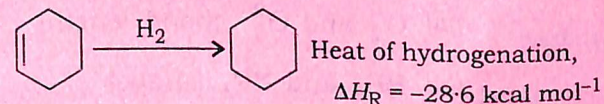
(b) What is theoretical density of a crystal? At room temperature, Po crystallizes in a primitive cubic unit cell. If $a = 3 \cdot 36 \ \text{Å}$, calculate the density of Po. Its atomic mass is 209 g mol^{-1}. $2 + 3 = 5$

(c) Discuss the trend in decomposition temperatures of alkaline earth metal carbonates in the reaction

$$MCO_3(s) \rightarrow MO(s) + CO_2(g) \qquad 5$$

(d) Discuss how steric effects influence the reactivity and other properties of a molecule. How is it differ from electronic effects? 4+1=5

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

(i) CaF_2 and TiO_2 (radius ratio)

(ii) HCN and H_2O (dipole moment)

(iii) O_2^- and O_2^{2-} (bond length)

(iv) BF_3 and NF_3 (shape)

(v) SeF_2 and SiO_2 (hybridization of the central atom)

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

(a) Predict the hybridization and draw the structure of the following molecule ions based on VSEPR theory : 5

$P(CH_3)_3F_2$, BrF_3, PF_6^-, ICl_2^- and TeF_4

(b) What are radial and angular wave functions? Give the radial wave functions for $2s$ and $2p$ orbitals. Show, from its angular wave function, that the distribution of electronic charge in an s orbital is spherically symmetrical. 1+2+2=5

(c) What is meant by bcc arrangement of spheres? Show that the volume of space occupied for a bcc lattice of spheres is 68%. 1+4=5

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

(i) Perovskite structure

(ii) Molecular solids

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

(a) The theoretical and experimental lattice enthalpies obtained for silver halides are listed in the table below. On the basis of these data, answer the following :

Silver halides	Lattice enthalpy	
	Experimental value (kJ mol^{-1})	Theoretical value (kJ mol^{-1})
AgF	+967	+953
AgCl	+915	+864
AgBr	+904	+830
AgI	+889	+808

(i) For AgF, the experimental and theoretical values are very close. What does that show?

(ii) For AgI, there is a much greater difference between the two values. What does that suggest?

(iii) Why do you think the difference between the two values increases as you go from AgF to AgI?

$$1\frac{1}{2}+1\frac{1}{2}+2=5$$

(b) What are aromatic, anti-aromatic and non-aromatic compounds? If a molecule contains an aromatic ring, such as a benzene ring, attached to a non-aromatic ring, how does that affect the overall aromaticity of the molecule? Give suitable examples. $3+2=5$

(c) Discuss the radius ratio rule for determining the shapes of ionic crystals. The ionic radii of Rb^+, Br^- and I^- ions are   1·47 Å,   1·95 Å   and   2·16 Å respectively. Predict the most probable type of geometry exhibited by RbBr and RbI on the basis of radius ratio rule.

$$3+2=5$$

(d) What is band gap? Differentiate semiconductors, conductors and insulators on the basis of band gap. Why does a semiconductor behave like an insulator at absolute zero temperature? $1+3+1=5$

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