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(4)

(b) Answer either (i) or (ii) and (iii) :

(i) Show that for a black body radiator the energy density in the region between γ and $\gamma + d\gamma$ is given by

$$E\gamma d\gamma = \frac{8\pi h\gamma^3}{C^3 (e^{h\gamma/kT} - 1)} d\gamma \qquad 10$$

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Or

- (ii) How was the spinning property of an electron experimentally demonstrated by Stern-Gerlach? Explain.
- (iii) From Pauli antisymmetry principle, prove that two electrons having same spin cannot exist in an orbital.

(c) Answer either (i) and (ii) or (iii) and (iv) :

- (i) Find the wave function for p_x orbital.
- (ii) Draw the radial probability distribution function for 2s, 3p, 4p and 5d orbitals.

Or

- (iii) Prove that an s-orbital has no angular dependance.
- (iv) Write a note on radial probability distribution function.

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2019

CHEMISTRY (Major)

Paper : 3.1

(Structure and Bonding)

Full Marks : 60 Time : 3 hours

The figures in the margin indicate full marks for the questions

1. Answer the following questions :

 $1 \times 7 = 7$

- (a) How is average value of a property associated with an operator of a normalized function expressed?
- (b) What is an eigenfunction?
- (c) Write the time independent Schrödinger equation for hydrogen atom.
- (d) What is the average distance of the electron of H atom from its nucleus?
- (e) Calculate the formal charge of P in PH_4^+ ion.

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(Turn Over)

- (f) How does bond multiplicity affect bond length?
- (g) Why is a sigma bond stronger than a pi bond?
- **2.** Answer the following questions : 2×4=8
 - (a) Calculate the wavelength for transition of the electron of H atom in 2nd line of Balmer series. $(R_{\rm H} = 1.1 \times 10^7 \text{ m}^{-1})$
 - (b) Calculate the effective nuclear charge for a 3d electron of cobalt atom.
 - (c) Draw the Lewis electron dot structures of the following :

 $ClO_{4}^{-}, CO_{3}^{2-}, CCl_{4}, NO_{2}^{-}$

- (d) Give reason why BeF₂ is linear but SF₂ is V-shaped.
- 3. Answer any three of the following questions :

5×3=15

- (a) What do you mean by bond moment and dipole moment? Give reason why NF₃ is less basic than NH₃. 1+1+3=5
- (b) Using VSEPR theory, explain the geometry of the following molecules :

21/2×2=5

XeF₂, IF₅

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(Continued)

- (c) What do you understand by percent ionic character of covalent diatomic molecule? Calculate the percent ionic character of H—F bond. (Dipole moment for HF = 1.92 D, $e = 4.8 \times 10^{-10}$ e.s.u., H—F bond length = 0.92 Å) 2+3=5
- (d) Calculate the de Broglie wavelength of an electron which is accelerated by applying a potential difference of 54 volts. $(h = 6 \cdot 6 \times 10^{-34} \text{ J-s},$ $m = 9 \cdot 1 \times 10^{-31} \text{ kg}, e = 1 \cdot 6 \times 10^{-19} \text{ C})$
- (e) Write a note on aufbau principle. 5
- **4.** Answer the following questions : . . 10×3=30
 - (a) Answer either (i) or (ii) and (iii) :
 - (i) What is resonance? What are the essential rules for writing resonating structures? Draw the different resonating structures of CO_3^{2-} ion. 2+5+3=10
 - Or
 - (ii) Explain Pauling and Mulliken scales of electronegativity. 3+3=6
 - (iii) Write the outlines of valence bond approach to bonding in diatomic molecules.

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(Turn Over)

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3 (Sem-3) CHM M 2

2019

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 H₂Sn?

(i) 102.5°

- (ii) 180°
- (iii) 104·5°
- (iv) 120°

(Choose the correct option)

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- (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?

- **2.** Answer the following questions : $2 \times 4 = 8$
 - (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 CO₃²⁻ ion. If all the C—O bond distances are equal, then write the resonance structure to describe the bonding in CO₃²⁻ ion. Describe the bonding in CO₃²⁻ in terms of hybridization scheme.

1+2+2=5

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(Turn Over)

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(Continued)

(4)

- (b) Calculate the maximum radius of a sphere that may be accommodated in an octahedral hole in a closed-packed solid composed of 5 spheres of radius r.
- Compare the following pairs of (c)molecules with respect to the cited within the parameters $1 \times 5 = 5$ parenthesis :
 - (i) CO⁺ and CO (bond length)
 - (ii) SiCl₄ and CCl₄ (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)
- Discuss the electron probable (d)density of bonding and antibonding molecular orbitals.
- Which of the following mixtures of (e) have intermolecular solvents hydrogen bonding between the different solvent molecules?
 - (i) Et₂O and THF

(5)

(ii) EtOH and H₂O (iii) EtNH₂ and Et₂O Give diagrams to show likely hydrogen-bonded interactions. 2+3=5

- 4. Answer any three questions : 5×3=15
 - (a) What are MOs and how are they constructed? Discuss the MO energy level diagram of the triatomic molecule NO2 and hence obtain its electronic configuration. 2+2+1=5
 - (b) How many Bravais lattice types are there and what are they? Name the Bravais lattices. orthorhombic 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
 - Discuss how steric and electronic (c)factors affect the molecular properties.

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(Continued)

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(6)

- (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 :
 - (i) The ion PH_4^+
 - (ii) The molecule PF₅
 - (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 .

(C)

(b) Derive the Born-Landé equation for lattice energy calculation. Give its importance and conclusions derived. 3+2=5

(7)

Justify the following : $2\frac{1}{2}\times2=5$

- (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

(Continued)

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