2012

CHEMISTRY

(Major)

Paper : 2.1

(Structure and Bonding)

Time : 3 hours

The figures in the margin indicate full marks for the questions

*Candidates **eligible** for Internal Assessment shall answer from PART—I only* (*Marks* : 65)

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*Candidates **not eligible** for Internal Assessment shall answer both from PART—I and PART—II* (*Marks* : 75)

This part is for all students.

Physical constants :

Planck's constant = $6 \cdot 626 \times 10^{-34}$ J-s

Mass of electron = $9 \cdot 109 \times 10^{-31}$ kg

PART—I

(*Marks* : 65)

1. Answer question *(a)* and any *four* from the rest : 22

(a) Show that at all small wavelengths, the Planck's distribution law approximately becomes Wien distribution law. 2

(b) (i) What do you understand by an eigenfunction of an operator? Find whether $\sin(kx)$ is an eigenfunction of the $-(h^2/m)\frac{d^2}{dx^2}$ operator, and if so, find the eigenvalue. 1+2=3

(ii) The electronic energy of the H-atom with the electronic principal quantum number n is 13·6 eV. Calculate the wavelength for the second line within the Balmer series of hydrogen atomic line spectra. 2

(c) (i) Calculate the number of photons emitted by a 35 W sodium vapour lamp emitting yellow light at 5890 Å wavelength. How many waves reach one's eyes every second? 3

(ii) Explain why wave property of a macroscopic particle is not detectable. 2

(d) What is meant by effective nuclear charge? Explain how the shielding effect and the penetration effect act together to make the orbital energies and the effective nuclear charges of the 3*s*, 3*p* and 3*d* subshells different. 1+4=5

(e) State and explain Heisenberg's uncertainty principle. Calculate the minimum uncertainty in the speed of an electron within a hydrogen atom assuming it to remain confined with a sphere of diameter 2 Bohrs.

(1 Bohr = 0·529 Å) 2+3=5

(f) (i) Write down the Schrödinger's wave equation for an electron moving in an one-dimensional box and identify the terms involved. 2

(ii) The wave function for the lowest energy orbital in the He^+ is $\psi \propto e^{-2r/a_0}$, with $a_0 = 52 \cdot 9$ pm and r the distance from the nucleus. Calculate the relative probabilities of finding the electron inside a small volume of magnitude $1 \cdot 0\ pm^3$ located at—

(1) the nucleus;

(2) at distance a_0 from the nucleus. 3

2. Answer question *(a)* and any *four* from the rest : 22

(a) Give one example of each of the following point groups : 2

(i) C_2

(ii) C_{2v}

(iii) D_{4h}

(iv) C_s

(b) Give a brief description of the formation of the hydrogen molecule, in light of Valence Bond Theory. Give the graphical presentation of the potential energy change during the formation of the molecule. 2+3=5

(c) (i) Define dipole moment of a bond. What is the conventional unit of dipole moment and what is its value in SI unit? 2

(ii) What is meant by ionic character of a covalent bond? The percent ionic character and the theoretical dipole moment of the hydrogen fluoride molecule are 45% and 4·42 D respectively. Calculate the actual dipole moment. 1+2=3

(d) Write Lewis structures of (i) XeF_4, (ii) PF_5, (iii) BrF_3, (iv) $TeCl_4$ and (v) ICl_2^-. Determine the geometries about the central atoms using VSEPR theory. 5

(e) (i) Discuss briefly the dependence of electronegativity of the carbon atom on the type of its hybridization. 2

(ii) Arrange the basic strength of $MeNH_2$, Me_2NH and Me_3N in the increasing order. Justify your answer. 3

(f) Discuss Pauling's method of determining electronegativity of elements. 5

(g) (i) What is meant by resonance? Define resonance energy. Draw the resonating structures of the N_2O molecule. 1+1+1=3

(ii) Define formal charge on an atom. Calculate the formal charge on the sulphur atom of the sulphate ion. 1+1=2

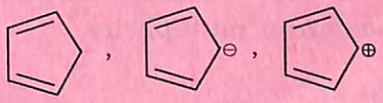
3. Answer question *(a)* and any *four* from the rest : 13

(a) Define bond order. Draw the MO diagram of the NO molecule. Predict the magnetic property and bond order of the molecule. ½+1½+½+½=3

(b) Explain the structure of diborane on the basis of MO theory. 2½

(c) What is meant by delocalized molecular orbital? Explain with a suitable example. 1+1½=2½

(d) State Hückel's rule of aromaticity. Examine the following species for their aromaticity : 1+1½=2½



(e) Discuss the formation of the H_2O molecule using MO theory. 2½

(f) With the help of band theory, explain the properties of conductors. 2½

4. Answer any *two* : 4×2=8

(a) Define unit cell. How many basic or primitive unit cells have been recognized among crystals? Draw neat sketches of cubic space lattices. 1+1+2=4

(b) Define lattice energy of ionic solids. How is the lattice energy of sodium chloride calculated using Born-Haber cycle? 1+3=4

(c) Define hydrogen bond. Explain the effect of hydrogen bond on the boiling points of the hydrides of 14 Group elements. Why is benzene insoluble in water? 1+2+1=4

PART—II

(*Marks* : 10)

(In lieu of Internal Assessment)

5. Answer any *four* : 2½×4=10

(a) State and explain Hund's rule of maximum multiplicity. 2½

(b) Write briefly about the different series of line spectra for atomic hydrogen and explain. 2½

(c) Using VSEPR theory, explain why the bond angle in NF_3 is less than that of the NH_3 molecule. Which molecule has more dipole moment and why? 2½

(d) Draw a neat diagram of the BF_3 molecule showing all the symmetry elements present. To which point group the molecule belong? 2½

(e) Is the B_2 molecule paramagnetic or diamagnetic? Give reason for your answer. What is its bond order? 2½

(f) Define ionic radius and radius ratio. How is coordination number related to radius ratio? 2½

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