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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 $-(h^2/m)\dfrac{d^2}{dx^2}$ 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 $13 \cdot 6$ 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 3s, 3p and 3d subshells different.   1+4=5

          (*Continued*)

(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 = $0 \cdot 529$ 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

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(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

(*Turn Over*)

    (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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CHEMISTRY

(Major)

Paper : 2.2

(Organic Chemistry)

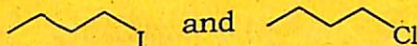*Full Marks* : 60

Time : 2½ hours

The figures in the margin indicate full marks
for the questions

1. Answer the following questions :   1×7=7

   (a) In the following pair of halogen compounds, which one would undergo S_N2 reaction faster?

       ⌃⌄⌃⌄I   and   ⌃⌄⌃⌄Cl

   (b) Find out a reagent for the conversion of RCOCl into RCHO.

   (c) What is Hinsberg's reagent?

   (d) Why are the boiling points of isopentane and neopentane less than that of *n*-pentane?

(e) What is formed when glycerol is heated with $KHSO_4$?

(f) Draw the chair form of cyclohexane and label the axial and equatorial H-atoms.

(g) What does the term 'topocity' signify?

2. Answer the following questions : 2×4=8

(a) Explain why the boat form of cyclohexane is less stable compared to the chair form.

(b) What are homotopic and heterotopic ligands? Give suitable examples.

(c) How are the H-atoms at a pro-chiral centre distinguished from one another?

(d) What are diastereotopic ligands? Give example of molecules with dia-stereotopic H-atoms and explain why they are so.

3. Answer any *three* questions : 5×3=1

(a) The bromination of toluene using bromine in aqueous acetic acid takes place 605 times faster than does the same reaction of benzene. The product ratio is 32·9% *ortho-*, 0·3% *meta-* and 66·8% *para-*bromotoluene. Calculate the partial rate factors for the reaction. 5

(Continued)

(b) Explain the formation of aniline from chlorobenzene through benzyne intermediate formation. What are the evidences in support of this mechanism? 3+2=5

(c) Discuss the mechanism of Friedel-Crafts acylation. What is the role of $AlCl_3$ in this reaction? 3+2=5

(d) Give an example of Ar S_N1 reaction. What is the mechanism involved? What are the evidences in support of this mechanism? 1+2+2=5

4. Answer any *three* questions : 10×3=30

(a) (i) Describe Corey-House method for the preparation of unsymmetrical alkane. 3

(ii) Why is peroxide effect not valid with HCl and HI? 2

(iii) Distinguish between but-1-yne and but-2-yne. 2

(iv) How is 1°-, 2°- and 3°-alcohol detected by Lucas test? 3

(b) (i) Discuss the mechanism of acid-catalysed aldol condensation. 3

(ii) Convert ethyne into propanone. 2

(**4**)

(iii) What products are obtained when nitrobenzene is reduced under acidic, neutral and alkaline conditions?   3

(iv) Using Gabriel's phthalimide method, how can you prepare a 1°-amine exclusively?   2

(c) (i) What is Wurtz-Fittig reaction?   2

(ii) Convert aniline into 4-nitroaniline.   2

(iii) Explain the mechanism involved in Reimer-Tiemann reaction.   3

(iv) How is cinnamic acid prepared from benzaldehyde? What is the name of the involved reaction?   2+1=3

(d) (i) Why does HCN not add to the $\diagup C{=}O$ part of an ester?   2

(ii) Arrange the compounds in order of increasing reactivity towards nucleophilic reagents :   2

CH_3CHO, CH_3COCH_3, CF_3CHO and $CH_3CH{=}CH{-}CHO$

(iii) p-Animobenzaldehyde does not undergo the benzoin condensation. Why?   3

(iv) Convert benzene into benzaldehyde by Gattermann-Koch synthesis.   3

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