RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. FIRST SEMESTER EXAMINATION, DECEMBER 2016

FIRST YEAR [BATCH 2016-19]

Date : 14/12/2016 **CHEMISTRY [Honours]**

Time : 11 am – 1 pm **Paper : I [Gr-B]** Full Marks : 35

[Use one Answer Book for Unit I and another Answer Book for Unit II, III & IV]

(Attempt one question from each Unit)

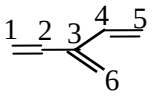
Unit I

[10 marks]

3. a) Draw the orbital diagram of the following compound, $CH_3-CH=C=O$. [2]

   b) Draw all the canonical forms of $Me_2\overset{\oplus}{N}CHOMe$ and identify the most contributing one. [2]

   c) Give the possible canonical forms of the following compound and predict the relative double bond character of the three double bonds $(C_1-C_2, C_4-C_5, C_3-C_6)$. [2]



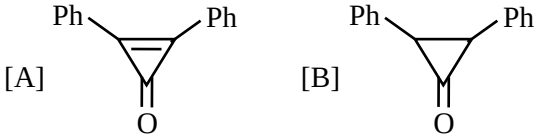
   d) Answer the following questions for the 2,4,6-heptatrienyl cation. [2]

      i) Which MO is nonbonding?

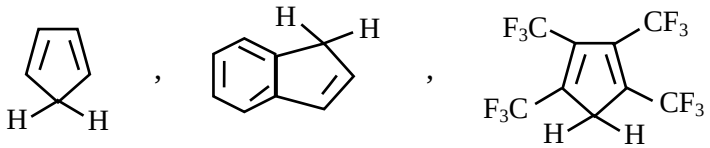
      ii) Classify each MO as symmetric or antisymmetric.

   e) Show relative energies of π–M.O's, distribution of electrons, and state aromaticity or anti-aromaticity of cyclopentadienyl cation. [2]

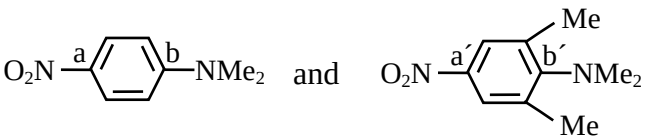
4. a) Which of the following two compounds has higher dipole moment? Give reasons. [2]



   b) Arrange the following in order of increasing pKa values : [2]



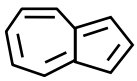
   c) Compare the C-N bond lengths (a vs a′) and (b vs b′) in the following compounds : [2]



   d) Explain why reactivity of anions is greater in polar aprotic solvent like DMSO or DMF than in protic solvent like ethanol. [2]

   e) State with reasons the following species as aromatic, non-aromatic or anti-aromatic. [2]

   i) 

   ii) 

Unit II [9 marks]

9. a) An electron circles a nucleus of charge Ze. Of the two orbits 1 and 2 of radii r_1 and r_2 respectively, its total energy is greater while in orbit 1. Prove that $r_1 > r_2$. [3]

   b) Compare the penetrating ability of 4s and 3d orbitals by drawing qualitatively the radial probability distribution curves of the orbitals. [3]

   c) What led Sommerfeld to modify Bohr's theory? What were his assumptions? [2+1]

10. a) Radius of the first Bohr orbit of H atom is 0·529 Å, Find the radii of the first and second Bohr orbits of Li^{2+} ions. [3]

   b) State the Hund's rules and hence find out the ground state term symbol for Cr. [2+2]

   c) Establish Bohr's assumption from de-Broglie's wave particle duality. [2]

Unit III [8 marks]

11. a) Rationalize the trends in the specific atomic properties in the following atoms. [3]

	C	N	O
First electron affinity (eV) :	1·263	–0·070	1·461

   b) What is 'inert-pair' effect? Comment on the oxidation state of Bi in sodium bismuthate. [3]

   c) What is the relation between Pauling scale of electronegativity and Allred-Rochow electronegativity? [2]

12. a) Electronegativity of hydrogen and fluorine are 2·1 and 4·0 respectively. Calculate the percentage of ionic character in HF. [2]

   b) The interatomic distance in chlorine molecule is 1·98Å. Calculate the Allred-Rochow electronegativity using Slater rules. [3]

   c) Compare feasibility of the following decomposition reactions. Give probable reasons. [2]

   $SnCl_4 \rightarrow SnCl_2 + Cl_2$, $PbCl_4 \rightarrow PbCl_2 + Cl_2$

   d) Arrange the following ions in increasing order of their ionic radii, N^{3-}, Mg^{2+}, Na^+ and F^-. [1]

Unit IV [8 marks]

13. a) Draw the possible resonance structure of N_2O molecule and indicate with justifications the most stable structure. [3]

   b) Explain how the presence of 'Non-stoichiometric Defects' in solids influence the properties of the solid with at least one representative example. [3]

   c) Explain with reasons : $PbCl_4$ is unstable but PbF_4 is stable. [2]

14. a) Define 'Formal charge'. Draw the Lewis structure of NO_2F molecule and calculate the formal charge of each atom in it. [3]

   b) $NaClO_3$ is about 1000 times as soluble as $KClO_4$ is water. Explain. [2]

   c) Define with example Schottky defect and Frenkel defect. Mention the differences between Schottky defect and Frenkel defect. [3]

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