RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. FIRST SEMESTER EXAMINATION, DECEMBER 2017

FIRST YEAR (BATCH 2017-20)

Date : 14/12/2017 **CHEMISTRY (Honours)**

Time : 11.00 am – 1.00 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

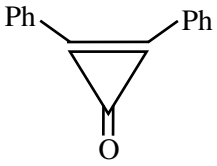
[10 marks]

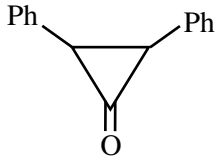
1. a) Draw the π–molecular orbital diagram of allyl anion $(CH_2 = CH - CH_2^-)$ and indicate the HOMO and LUMO in the ground state of the anion. [2]

   b) Why $C_2 - C_3$ bond in propene is shorter than C – C bond in propane. [1]

   c) Between toluene and *t*-butylbenzene, which molecule will have higher electron density at the *para*-carbon atom? Explain your answer. [2]

   d) Which of the following two molecules has higher dipole moment? Give reason. [2]

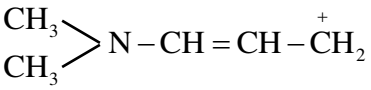




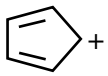
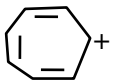
   f) Unlike benzyl bromide, 1-bromocyclohepta–2,4,6–triene is highly soluble in water yielding bromide ion in solution. Explain. [2]

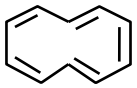
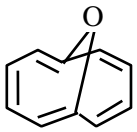
   g) Write down the difference between conjugation and hyperconjugation. Use suitable example(s) for illustration. [1]

2. a) Write the cannonical forms of the following carbocation and indicate which one has the greatest contribution towards the resonance hybrid. [2]



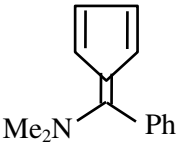
   b) Ascertain which species in each of the following pairs is more stable and why? [3]

   i)  and 

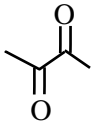
   ii)  and 

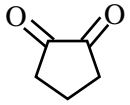
   c) State, with reasons, the following species as aromatic, non-aromatic or antiaromatic. [2]

   i) 

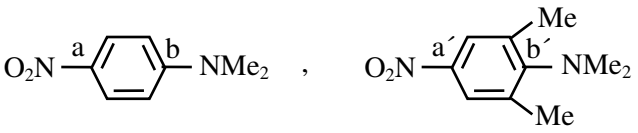
   ii) 

   d) Which one of the following α-diketones has higher dipole moment? Explain. [1·5]



and 

e) Compare the C–N bond lengths (a vs. a′) and in (b vs b′) in cases of the following compounds. [1·5]



UNIT-II

[9 marks]

3. 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 $r_1 > r_2$. Also show that the velocity and acceleration in orbit 2 are greater than those in orbit 1. 2+2

b) Draw the probability density versus distance from the nucleus for the following radial distribution functions. 2

$$\Psi_1 = N_1 \frac{r^2}{a_0^2} e^{-\frac{r}{3a_0}}$$

$$\Psi_2 = N_2 \frac{r}{a_0}\left(2 - \frac{r}{3a_0}\right) e^{-\frac{r}{3a_0}}$$

N_1 and N_2 are constants. Rest of the terms has usual meaning.

c) Electronic configuration of Lithium is written as $1s^2\ 2s^1$, not $1s^2\ 2p^1$, despite the fact that $n = 2$ in both 2s and 2p and according to Bohr model 2s and 2p should have the same energy. What is the reason of this apparent anomaly? 2

d) Determine the ground state term for V^{3+}. 1

4. a) 'The orbital angular momentum of an electron does not give its total angular momentum' — Explain. Which quantum number is used to supplement the orbital angular momentum? 2+1

b) State and explain Hund's rule. 3

c) Discuss the origin and physical significance of magnetic quantum number. 1+1

d) Using Slater's rule, calculate the effective nuclear charge on a valence electron in N atom. 1

UNIT-III

[8 marks]

5. a) Reduction of Fe^{3+}, the electron can enter either 3d or 4s. Explain with the reason. 3

b) Calculate Pauling's electronegativity of hydrogen atom from the following data: 3

Bond energies (KJ $mole^{-1}$): H_2 (458), F_2 (155), HF (565) and Pauling's electronegativity of F = 4.0.

c) What are the advantages of mulliken electronegativity scale over Pauling's scale? 2

6. a) Explain why:

(i) The electronegativity value of Ga is higher than Al. 2

(ii) Au shows the highest electron affinity amongst all the metals. 2

b) The F-F bond distance in F_2 is 141.3 pm. Calculate Allred-Rochow electronegativity of Fluorine using Slater's rule. 3

c) What are the disadvantages of Allred-Rochow electronegativity scale? 1

UNIT-IV

[8 marks]

7. a) What do you mean by inert pair effect? Explain the effect with proper examples. 2+1

   b) Comment on the following dipole moment values – CH_3Cl (1.94D), CH_2Cl_2 (1.6D), $CHCl_3$(1.03D), CCl_4 (0). 3

   c) Draw the resonance structures of N_3^- and comments on their relative stabilities. 2

8. a) How can you explain — (i) ZnO is white when cold but yellow when hot. (ii) When NaCl is treated with Na-vapour form yellow colour. 2+2

   b) What type of Crystal defect is expected in FeO? 2

   c) Explain the following:

   $MgSO_4$ is freely soluble in water whereas $BaSO_4$ is almost insoluble in it. 2

———— × ————