RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

FIRST YEAR [2015-18]

B.A./B.Sc. FIRST SEMESTER (July – December) 2015

Mid-Semester Examination, September 2015

Date : 14/09/2015 **CHEMISTRY (Honours)**

Time : 11 am – 1 pm Paper : I Full Marks : 50

[Use a separate Answer Book for each group]

Group – A

1. a) Starting from the mathematical definition of the first law of thermodynamics prove that
   i) Energy of the universe is constant.
   ii) Work is a state function under adiabatic condition. [2×2]

   b) A system is divided into 'n' subsystems (i = 1,2,3,...n). x_i (i = 1,2, ...,n) are the values of a certain property measured on the different subsystems. The value for the same property comes out to be X when the measurement is done on the whole system. Write down how X and x_is are related when the property is extensive in nature. [2]

   c) Three moles of an ideal gas are compressed isothermally from 60L to 20L using a constant external pressure of 5 atm. Calculate Q, W, ΔE and ΔH. [2]

OR

2. a) Starting with the definition of C_P and C_V, show that for an ideal gas $C_P - C_V = nR$. [4]

   b) Show graphically the work done in a process when a gas at (P_i, V_i) is expanded to (P_f, V_f) isothermally in a single step with the constant external pressure as P_f. [2]

   c) One mole of an ideal gas ($\bar{C}_V = 20{\cdot}8\,J/K\,mol$) is transformed at constant volume from 0°C to 75°C. Calculate Q, W, ΔE and ΔH. [2]

3. a) Two flasks are filled with N_2 gas and when both are immersed in boiling water, the gas pressure inside the system is 0·5 atm. One of the flasks is then immersed in an ice-water mixture, keeping the other in the boiling water. Calculate the new pressure for the system. [3]

   b) Define law of equipartition of energy and apply the law to calculate $\bar{C}_V$ of CO_2 molecule. [3]

   c) The 1D distribution of gas molecular velocity becomes flattened at higher temperature keeping the area constant. Explain. [2]

OR

4. a) Answer **any one** of the following: [1×3]
   i) Express the 3D distribution of gas molecular velocity according to Maxwell-Boltzmann and explain all terms.
   ii) Find out the total energy for 3D distribution of 1 mole of Ar gas molecules from energy distribution equation.

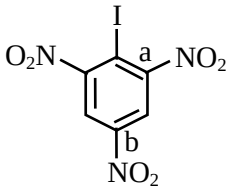
   b) From the definition of average quantity, related to velocity, show that $< p_x >= \int_{-\infty}^{\infty} p_x f(u_x) du_x$, where $< p_x >$ is meant for average momentum along X direction. [3]

   c) Explain— with height the molecules with higher mass will be less. [2]

Group – B

5. a) Draw the orbital picture of $CH_2 = CH - CN$. [2]

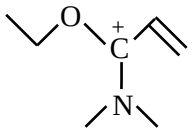
   b) Explain which C-N bond 'a' or 'b' has a shorter bond length in the following compound. [2]



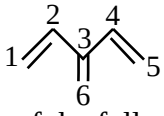
   c) Draw all the π molecular orbital of 1,3 butadiene. Arrange them in order of increasing energy level, designate the HOMO and LUMO in the ground state. [4]

OR

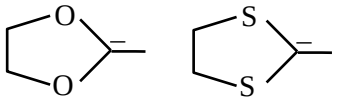
6. a) Write down the canonical forms of the following cation and select the most contributing structure with reason. [2]



   b) Give the possible canonical forms of the following compound and hence compare the bond length of the three double bonds $(C_1 - C_2, C_4 - C_5, C_3 - C_6)$. [2]

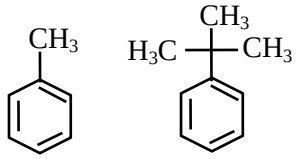


   c) Comment on the relative stabilities of the following carbanions. [2]



A B

   d) Explain with reason which of the following compounds has greater electron density at the para position. [2]



A B

7. a) Cite examples through their structures according to the instructions given :

   i) A molecule having S_2-axis showing the axis

   ii) A molecule having pseudoasymmetric centre showing the structure in Fischer projection formula. [1·5×2]

   b) Distinguish : conformation and configuration. [1·5]

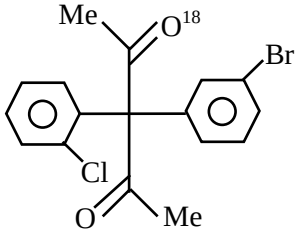
   c) Define with an example : Stereogenic centre [1·5]

   d) Write down all possible stereoisomers represented by 4-chloropheta-2, 5-diene and designate them by R/S and E/Z notations. [2]

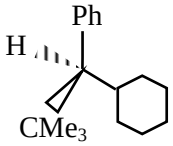
OR

8. a) Assign R/S configurational descriptor to the following molecules showing the priority order : [4]

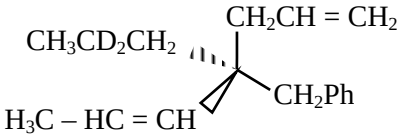
i)



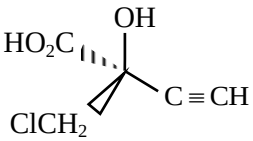
ii)



iii)



iv)



b) Write the structure of the following molecules as indicated :

i) Erythro 3-phenyl-2-butyl acetate (Fisher projection)

ii) Butanone – (Z) – hydrazone [2]

c) Justify or criticise (**<u>any one</u>**) : [2]

i) A molecule having (R) configuration must be dextrorotatory.

ii) C_3-centre of (Z) – 2- butene is a sterocentre.

Group – C

9. a) Find the energy required to release the electron from the hydrogenic ion, if the energy required to excite the electron from the ground state to first excited state is 40·8 ev. [3]

b) i) Calculate the wave length (Å) of an electron (mass = $9{\cdot}108 \times 10^{-31}$ kg) which is revolving around the nucleus of hydrogen atom with velocity one-third of the velocity of light. [3]

ii) Compare the value evaluated with that of a massive body (mass = 10 kg) which is moving with velocity 10% of the velocity of light. [2]

c) Draw the conclusion comparing above two results. [1]

OR

10. a) Establish the following (each term has usual significance) : [2+2+2]

i) $r_n = \{0 \cdot 529 \times 10^{-10} \times n^2\} / Zm$

ii) $v_n = \{0 \cdot 2185 \times 10^7 \times Z\} / n \text{ m/s}$ and

iii) Number of revolutions made by the electron at n^{th} orbit = $\{65 \cdot 711 \times 10^{14} \times Z^2\} / n^3 s^{-1}$

[Given : $h = 6 \cdot 626 \times 10^{-34}$ Js, $\varepsilon_0 = 8 \cdot 85 \times 10^{-12} J^{-1} C^2 m^{-1}$, $m = 9 \cdot 108 \times 10^{-31}$ Kg, $e = 1 \cdot 602 \times 10^{-19}$ C)

b) Derive Bohr's assumption from the (i) Sommerfeld's assumptions and (ii) de-Broglie relation. [1·5+1·5]

11. a) First ionisation potentials of coinage metals falls in the order Cu > Ag < Au, Give reasonable explanation. [2]

b) Electron affinity of SF_5 is among the highest known but that of SF_6 is quite modest. Explain. [2]

c) The correct electronic configuration of Cu is $[Ar]3d^{10}4s^1$ but not $[Ar]3d^9 4s^2$, explain with reasons. [2]

d) Explain the following electron affinity value ($KJmol^{-1}$) [3]

Li	Be	B	C	N	O	F	Ne
59·6	–50	26·7	121·9	–7	141·0	328·0	–116

OR

12. a) What is the basis of Pauling's electronegativiey? Electronegativity is not its inherent property explain with an example. [3]

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

c) Successive electron affinity have negative value. Explain. [2]

d) Arrange the following ions in increasing order of their ionic radii. $H^-, Br^-, Cl^-, I^-, F^-$. [1]

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