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

Time : 11 am – 1 pm **Paper : I [Gr-A]** Full Marks : 40

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

(Attempt one question from each Unit)

Unit I

[15 marks]

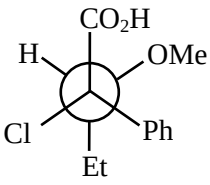
1. a) Indicate the symmetry elements present in *trans*-1, 3-dimethylcyclobutane. [2]

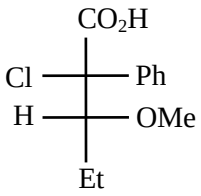
   b) Justify or criticize : [2+2]

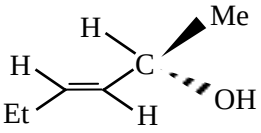
   i) 180° rotation is allowed but 90° rotation is not allowed for a Fischer projection formula.

   ii) Meso-tartaric acid is optically inactive not due to plane of symmetry.

   c) Label the following pairs of molecules as homomers, enantiomers or diastereomers. [2]

   i) 

and


   ii) 

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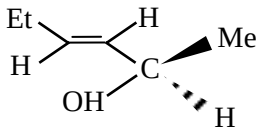


   d) Draw the Fischer projection formulae for all the possible stereoisomers of 2,3,4-trihydroxyglutaric acid. Comment on the stereogenicity of C-3 in the active and meso isomers. [3]

   e) $:NR^1R^2R^3$ is not resolvable but $:PR^1R^2R^3$ is resolvable —Explain. [2]

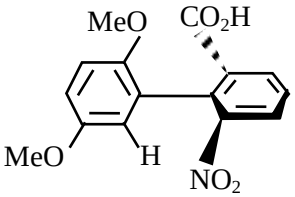
   f) In between ethylene glycol and 1, 2-dibromoethane which one has higher dipole moment? [2]

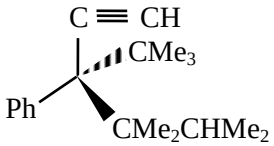
2. a) Draw all the stereoisomers for the given molecule with proper explanation:

   $CH_3CH=CH-CH(OH)CH_3$ [2]

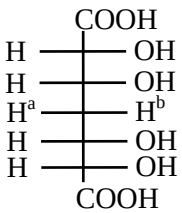
   b) An optically pure sample of (–) 2-butanol shows a specific rotation of –13·6°. What relative molar proportion of (+) 2-butanol and (–) 2-butanol would give a specific rotation of +6·8°? [3]

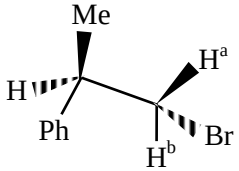
   c) Designate following compounds by R, S configurational nomenclature with reason. [2]

   i) 

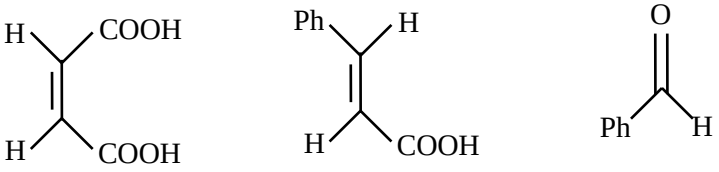
ii) 

   d) Identify the *pro-R* and *pro-S* hydrogen atoms (marked) in each of the following compounds. [2]

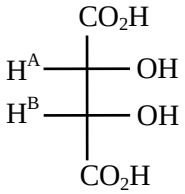
   i) 

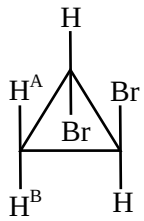
ii) 

e) Give *Re* and *Si* descriptor to the following π–faces. [3]



f) Identify H^A and H^B in each of the following structures as homotopic, enantiotopic or diastereotopic and explain. [3]

i) 

ii) 

Unit II

[13 marks]

3. a) Consider two separate but equivalent containers of CO_2 and NH_3 gas molecules at T_1 and T_2, respectively, where molecules are continuously colliding among themselves, as well as with the walls.

i) Show that ratio of rate of collisions on wall for CO_2 gas molecules to that of NH_3 molecules is

$$\frac{(dN_W/dt)_{CO_2}}{(dN_W/dt)_{NH_3}} = \frac{\tilde{N}_{CO_2} < v >_{CO_2}}{\tilde{N}_{NH_3} < v >_{NH_3}} = \frac{P_1}{P_2} \times \sqrt{\frac{T_2}{T_1}}$$

where P_1 and P_2 are pressures at CO_2 and NH_3 containers, respectively. [4]

ii) Describe the important forces present in two different containers. [3]

iii) How does the ratio of mean free path for this two containers vary with T, P and size of gas molecules? [2]

b) From the one-dimensional velocity distribution, derive the expression of two-dimensional speed distribution function. [2]

c) Write down the condition for the determination of critical temperature and Boyle temperature with suitable explanation. [2]

4. a) Deduce the reduced equation of state for the gas obeying van der Waals' equation. Mention the significance of the equation. [4]

b) Explain why the equipartition principle predicts more correct value of heat capacity for He than HCl at room temperature. [3]

c) Express the van der Waals equation of state as a virial expansion in process of $1/V_m$ and obtain expression for B and C in terms of parameters 'a' and 'b'. Measurements on Ar gave B = – 21·7 $cm^3 mol^{-1}$ and C = 1200 cm^6 mol^{-2} for the 2nd and 3rd virial coefficients, respectively, at 273K. What are the values of 'a', 'b'? [4]

d) Calculate the compressibility factor for a van der Waals' gas at 1 atm and 300 K. [a = 1·39 atm lit^2 mol^{-2}, b = 0·039 lit mol^{-1}] [2]

Unit III

[12 marks]

5. a) Starting with the definitions of the terms prove that $C_P - C_V = \left[p + \left(\frac{\partial u}{\partial v} \right)_T \right] \left(\frac{\partial v}{\partial T} \right)_p$. [3]

b) State the Zeroth Law of Thermodynamics and hence define temperature. [3]

c) Adiabatic free expansion is isothermal —justify or criticise. [2]

d) One mole of a monoatomic ideal gas initially at a pressure of 2·00 bar and a temperature of 273K is taken to a final pressure of 4·00 bar by the reversible path defined by P/V = const. Calculate the values of ΔU, ΔH, q and W for this process. [$\overline{C_V}$ to be equal to 12·5 J $mol^{-1}K^{-1}$] [4]

6. a) Derive the expression for adiabatic reversible expansion work for an ideal gas. [2]

b) One mole of an ideal gas $\left(\overline{C_V} = \frac{5}{2}R\right)$ is expanded adiabatically against a constant pressure of 1 atm until it doubles in volume. If the initial temperature is 25°C and the initial pressure is 5 atm, calculate final temperature, ΔU and W. [4]

c) The enthalpy change associated with the neutralisation of 10ml 1·05 $\left(\frac{N}{10}\right)$ acetic acid by $\left(\frac{N}{10}\right)$ NaOH is –53·13J. Find out the dissociation of acetic acid if the heat of neutralisation of strong acid and strong base is –55·9 KJ eqv^{-1}. [3]

d) For the reaction : C (graphite) + H_2O (g) $\rightarrow$ CO(g) + H_2 (g); $\Delta H^{o}_{298} = 131\cdot28$ KJ / mol. The values of $\overline{C_p}$ / (J/K mol) are :

graphite : 8·53, H_2O (g) : 33·58, CO(g) : 29·12, H_2(g) : 28·82

Calculate the value of ΔH^{o} at 125°C (assume the $\overline{C_p}$ values are independent of temp). [3]

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