RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. FIRST SEMESTER EXAMINATION, DECEMBER 2015

FIRST YEAR [BATCH 2015-18]

Date : 14/12/2015 **CHEMISTRY [Hons]**

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

[Use a separate Answer Book for each Group]

Group – A

[Answer **one** question from **each unit**]

Unit - I

1. a) Determine the heat capacity at constant volume for H_2O using equipartition principle. [2]

   b) Draw the qualitative P vs V curve for a real gas and explain the continuity of states defining the critical point of the real gas. [3]

   c) The critical constants for water are 374°C, 221 MPa and 0·0566 $Lmol^{-1}$. Calculate values of a, b, R using van-der-Waals equation and compare the value of R with correct value. [3]

   d) If the speed distribution for a gas confined to move in 2-dimensions is given as $\frac{dn_c}{N} = \left(\frac{m}{k_B T}\right) e^{-\frac{mc^2}{2k_B T}} cdc$, Calculate the probability of a molecule having kinetic energy greater than a given value E. [3]

   e) Calculate the number of wall-molecule collisions per m^3 per second for O_2 at 25°C and 1 atm pressure. [2]

2. a) Write down the expression for energy distribution (3D) according to Maxwell and convert it into 3D speed distribution equation. [3]

   b) How does the viscosity of a gas change with increase in temperature. Justify. [2]

   c) Assume that 0·800 mol of N_2 and 0·200 mol of O_2 are contained in 24·45 L at 298 K.
   [N_2 and O_2 molecules measure roughly 300 pm and 292 pm, respectively]

      i) Find out z_{O_2} and $Z_{N_2O_2}$.

      ii) Also calculate λ_{N_2}. [3+1]

   d) Give a graphical representation of molecular velocities and its x-component at two different temperatures, for a gas obeying the kinetic theory model and confined to move in x-direction only.
   Hence justify qualitatively (without derivation) that the average velocity is equal to zero but not the average speed. [2+2]

Unit - II

3. a) A gas obeying the van-der-Waals equation of state undergoes a reversible isothermal volume change from V_1 to V_2. Obtain the expression for the work W. [3]

   b) 2L of a gas, initially maintained at 0°C and 10 atm pressure, expands adiabatically against a constant pressure of 1 atm. till equilibrium is reached. Find out the final temperature of the gas, if the heat capacity at constant volume for the gas is 3 cal mol^{-1}. [2]

   c) For the reaction $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(\ell)$ at 300K $\Delta H = -68\cdot8\,KCal$. Calculate ΔU for the reaction assuming ideal behaviour of the gases. [2]

   d) Prove that work (consider pressure volume work only) done in a process cannot be written as a change of state function. [3]

e) A gas is made to undergo the following change of state—

(P_i, V_i) to (P_f, V_f) in a single step with the external pressure fixed at P_f (isothermally)

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If both the processes were carried out involving infinite number of steps what would have been the amount of net work done? [2]

4. a) Define temperature as a consequence of the zeroth law of thermodynamics. [2]

b) 1 mole of an ideal monoatomic gas is compressed adiabatically at a constant pressure of 1·0 MPa till equilibrium is reached. If the gas initially was at 300K and 0·1 MPa pressure. Calculate the final temperature of gas, W, and ΔH. $\left(\text{Use } C_V = \frac{3}{2}R\right)$. [3]

c) Consider the following reaction : $aA + bB \rightarrow cC + dD$.

Establish a relation between ΔH of the reaction at two different temperatures T_1 and T_2 in terms of the individual molar heat capacities of the reactants and products. [3]

d) Derive the equation for the work done in an isothermal, reversible compression of one mole of a gas obeying the van der Waal's equation of state. [2]

e) Derive an expression for $(C_P - C_V)$ for a gas obeying $P(V-b) = RT$. Given $\left(\frac{\partial u}{\partial v}\right)_T = 0$ for the gas. [2]

Group – B

[Answer **one** question from **each unit**]

Unit - I

5. a) i) Write down the structure of the following compound :

2R, 3R – 2, 3 – dihydroxy-3-methyl pentanoic acid [1·5]

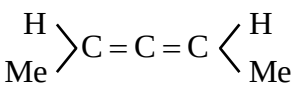
ii) Draw Fisher projection formula of (2R, 3S)-3-phenyl-2-butanol and convert it into flying wedge notation. [1·5]

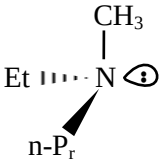
b) An optically pure sample of *R*-(–)-2-butanol shows specific rotation of –13·6°. What relative molar proportion of S-(+)-2-butanol and R-(–)-2-butanol would give a specific rotation of +6·8°? [3]

c) Indicate the symmetry elements present in (i) 1,3-dichloroallene (ii) $CHCl_3$. [2]

d) What is gauche-butane interaction? Draw the conformers of 2-methylbutane for rotation about $C_2 - C_3$ bond in Newman projection formula and compare their relative stabilities. [4]

e) Explain whether the following compounds are resolvable or not. [2]

i) 

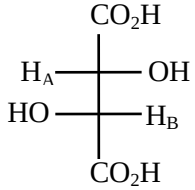
ii) 

f) Assign Re/Si descriptors for the enantiotopic faces of acetaldehyde. [1]

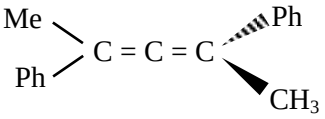
6. a) How would you resolve a racemic alcohol? [2]

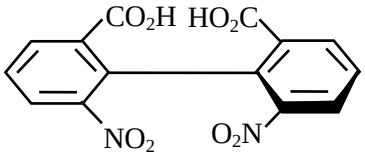
b) Draw all possible stereoisomers of $CH_3CH = CH - CHBr - CH = CHCH_3$ and mention whether they are 'R' or 'S' and optically active or not. [4]

c) Identify H_A and H_B in the following structure as homotopic, enantiotopic or diastereotopic and explain [1]



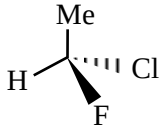
d) Assign R/S configuration to the following compounds : [2]

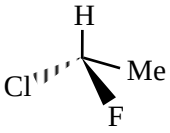
i) 

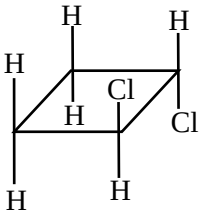
ii) 

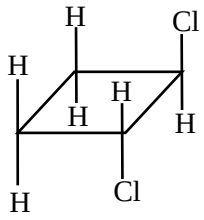
e) Comment on the stereogenicity of C-3 centre in all the stereoisomers of 2,3,4-tri-hydroxyglutaric acid. [3]

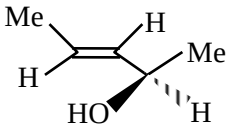
f) Label the following molecules as homomers, enantiomers or diastereomers : [3×1]

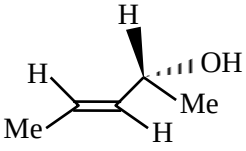
i) 

and 

ii) 

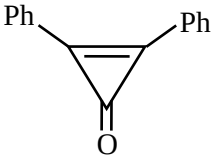
and 

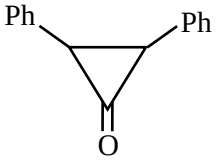
iii) 

and 

Unit - II

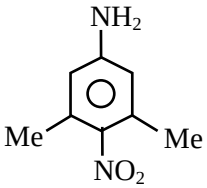
7. a) Which of the following two compounds has higher dipole moment? Give reason. [2]



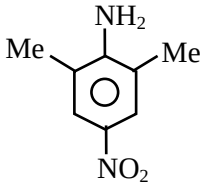
and 

b) Draw the π molecular orbital diagram of allyl anion and indicate the HOMO and LUMO in the ground state. [2]

c) Explain why 'A' is more basic than 'B'. [2]

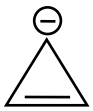


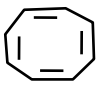
A



B

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

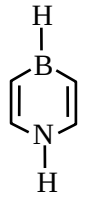
i) 

ii) 

e) Difference of molecular weight alone can not explain the large difference in boiling points between benzene (78°C) and nitrobenzne (211°C). Explain which other factor is responsible for this large difference of boiling points. [2]

8. a) Why cyclopropylmethyl carbocation shows exceptional stability? [2]

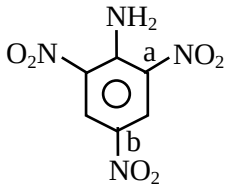
b) Draw the resonating structure of the following two compounds and indicate the most stable structure in each case. [2]

i) 

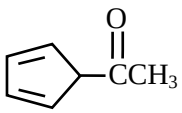
ii) $CH_3 - \overset{+}{C} = O$

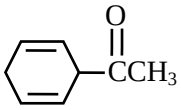
c) Draw the orbital picture of $CH_3CH = C = O$. [2]

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



e) Compare acid strength of the following molecules : [2]





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