RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College under University of Calcutta)

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

FIRST YEAR

Date : 05/01/2015
CHEMISTRY(Honours)
Time : 11 am – 1 pm
Paper : I (Gr. A&B)
Full Marks : 50

[Use a separate Answer Book for each group]

Group – A

(*Answer one question from each Unit*)

Unit – I

1. a) Assuming Maxwellian 3D distribution of molecular speed, what will be the magnitude of the average linear momentum, $\langle p \rangle$, of sulphur trioxide molecules in the gaseous state at 127°C? Will the average kinetic energy, $\langle \in \rangle$, be given as $\langle p \rangle^2 / 2m$? Give arguments in favour of your answer. [3]

b) Define mean free path of gas molecules. Associate the concept of mean free path of gas molecules to find out the expression of molecular collisions as $z_1 = \sqrt{2}\pi\sigma^2 c_a \hat{N}$, where the terms are having usual meanings. [3]

c) i) State the 'equipartion of energy' principle. Apply it to find the C_v, m of a diatonic gas, explaining all the steps.

ii) For Chlorine gas at 300K the C_v, m is close to 3·0R, suggest an explanation for this observation. [4]

d) Describe the nature of interactive forces in action in a gas mixture of H_2 and NH_3. [qualitatively]. Name the force which is both temperature and dipole moment dependent. [3]

2. a) Derive an expression for the van der Waals constant **b**, in terms of the radius of the gas molecule. Assume that in a gas assembly binary collisions **only** are taking place between molecules which act as **hard spheres**. Hence find the radius of a molecule of a van der Waals gas with $b = 3 \cdot 94 \times 10^{-2}\, L.mol^{-1}$, in picometre units. [3]

b) Explain the followings with probable reasons (**<u>any two</u>**): [2×2]

i) The kinetic energies of lighter molecules are exactly equal to those for the heavier molecules. True or false.

ii) The mean free path of gas molecules is inversely proportional to the pressure. Justify.

iii) For a van der Waals gas, $T_B = a/Rb$. Show it.

c) Arrive at the "reduced equation of state" for a van der Waals gas. (You may assume that the relevant expressions for the critical constants of the gas are known to you) Are the characteristics of the gas really removed, or are they hidden? Explain. [3]

d) Express the van der Waals gas equation as virial equation of state in terms of P, T. And find out the 2nd virial coefficient. [3]

Unit – II

3. a) One mole of an ideal gas of $C_v = 6$ cal K^{-1} $mole^{-1}$ expands adiabatically from STP to 0·1 atm.

i) Calculate the final temperature and w, if the expansion is reversible.

ii) Calculate the final temperature, if the process is irreversible and such that work done is 10% of the value in (i). The final pressure is still 0·1 atm. [3]

b) Classify the followings as intensive or extensive properties for a system consisting of a pure liquid only—

i) density ii) internal energy iii) surface tension iv) heat capacity [2]

c) Given the following information :

Heat of combustion at 298K : $CH_2 = CHCN(g)$ = +488·67 KCal, C (graphite) = +94·05 KCal, $H_2(g)$ = +68·33 KCal.

Heat of formation at 298 K : HCN (g) = –31·00 KCal, C_2H_2 = – 54·19 KCal

i) Calculate ΔH_{298K} for the reaction:

$$HCN(g) + C_2H_2(g) \rightarrow CH_2 = CHCN(g)$$

ii) Also calculate the difference between ΔH and ΔE for this reaction. [4]

d) Show the following (any one) :

i) $$\left(\frac{\partial U}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_v = -\left(\frac{\partial U}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T$$

ii) For van der Waals gas, $\bar{C}_P - \bar{C}_v = R\left(1+\frac{2aP}{R^2T^2}\right)$ at high T and low P. [3]

4. a) One mole of an ideal monatomic gas initially at P_1 = 2 atm, T_1 = 273 K is taken to a pressure of P_2 = 4 atm by the reversible path defined by P/V = constant. Calculate V_1, V_2 and T_2. Calculate ΔE, ΔH, q and w. [4]

b) Calculate $\Delta H^\circ_f (298K)$ of sucrose (solid) from the following data :

$\Delta H^o_f(H_2O, \ell) = -285 \cdot 8\,KJ\,mol^{-1}$, $\Delta H^o_f(CO_2, g) = -393 \cdot 5\,KJ\,mol^{-1}$,

$\Delta H^0_{combustion}(Sucrose, s) = -5665\,KJmole^{-1}$. [3]

c) For a closed system undergoing a transformation the change in internal energy is always given by the relation, du = $C_v dT$. Justify or criticize the statement. [2]

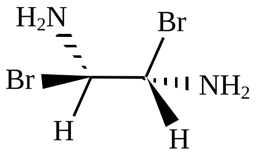
d) 1 mole of an ideal monatomic gas is confined in a leak proof, variable volume container at 0°C and 1 atm. pressure. It absorbs 840 J of heat and increases in volume by 4·0 L at the constant pressure of 1 atm. Calculate the work done, internal energy change and final temperature. [3]

Group – B

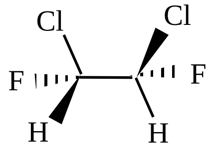
(*Answer one question from each Unit*)

Unit – I

5. a) Determine whether each of the following molecules is chiral or achiral. [2]



A



B

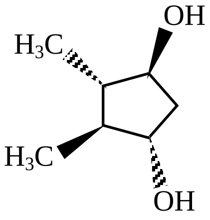
b) An optically active pure compound having configuration R exhibits its specific rotation +13·6°. A partially resolved variety of this compound showed its sp. rotation –6·8°. Find out the % of R and S in this compound. [3]

c) Draw Newman projection formula of the stable conformer of erythro 3-bromo-2-butanol. Designate this conformation on the basis of tortional angle by Klyne-Prelog terminology. Explain the cause of stability. [3]

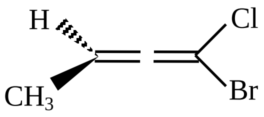
d) i) How many stereogenic centers are present in the following compound?

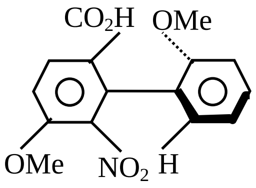
ii) Is this compound chiral or achiral?

iii) What symmetry element(s) are present in this compound? [3]



e) Assign R/S configuration of [2]

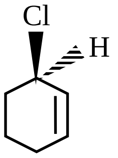
i) 

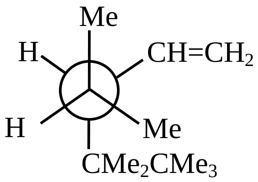
ii) 

f) Explain : Meso–tartaric acid is optically inactive on the basis of Newman projections of its all possible conformers for rotation about C2–C3 bond. [2]

6. a) Pro-R hydrogen of ethanol is transferred as H^- to NAD^+ to produce acetaldehyde. On which face of acetaldehyde that H^- ion will come back to get the original ethanol molecule? [2]

b) Give R/S designation at the chiral centres of the following compounds showing the priority sequence order. [2]

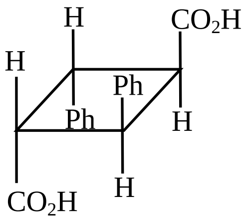
i) 

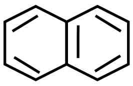
ii) 

c) Draw the conformational energy profile diagram of 1,2-dibromoethane. Comment on the relative % of anti form of 1,2-dibromoethane and n-butane in gaseous phase. [4]

d) Write the Flying-Wedge formula of D-2-butyl methyl ethers and predict its R/S configuration. [2]

e) Indicate the symmetry elements present in the following compounds: [3]

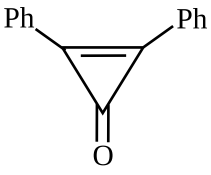
i) 

ii) 

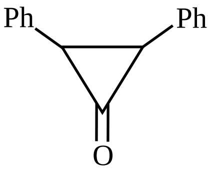
f) 1,2-Dibromoethane has a zero dipole moment, whereas ethylene glycol, CH_2OHCH_2OH, has a measurable dipole moment. Explain. [2]

Unit – II

7. a) Which of the following two compounds has higher dipole moment? Give reasons. [3]

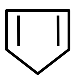
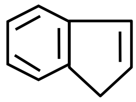
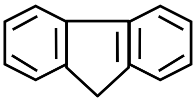


(A)



(B)

b) Compare the acidity of the following compounds with proper justification. [2]

 ,  and 

c) Write down the difference between : Polarity and polarisability [1]

d) Draw the orbital picture of the following compound indicating the state of hybridization of C and O atoms. $H_3C-CH=C=O$ [2]

e) Answer the following questions for 1,3,5-hexatriene. [2]

i) How many π MO's are there?

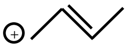
ii) Classify each MO as symmetric or antisymmetric about a reference plane through the center of the molecule.

iii) Which MO's are bonding? Which are antibonding?

iv) Which MO's are frontier molecular orbitals?

8. a) Use curly arrows to show how cations A, B and C are stabilised by resonance, and draw the resonance structure(s). Would you expect A, B or C to be more stable? Briefly explain your reasoning. [2]


A


B


C

b) Show relative energies of π MO's, distribute pi-electrons, and state of aromaticity of (i) cyclobutadiene, (ii) cyclopentadienyl anaion, (iii) Cycloheptatrienyl anion. [3]

c) Compare the properties mentioned in the parenthesis of the following pair of compounds (any two) : [3]

i) n-pentane and neo-pentane (b.p)

ii) 1-Butene and 2-butene (heat of hydrogenation)

iii) n-Butanol and t-Butanol (Miscibility with water)

iv) $Me_2\underline{C}H_2$ and $\underline{C}H_4$ (H–C–H bond angles on underlined carbon)

d) Which one of the following pair is more stable and why? [1]

$$Ph-CH=CH-\overset{+}{C}H_2 \text{ and } CH_3-CH=CH-\overset{+}{C}H_2$$

e) Write down the difference between conjugation and hyperconjugation. [1]

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