RAMAKRISHNA MISSION VIDYAMANDIRA
(Residential Autonomous College under University of Calcutta)

B.A./B.SC. FIRST SEMESTER EXAMINATION, DECEMBER 2011
FIRST YEAR
CHEMISTRY (Honours)
Paper : I

Date : 15/12/2011
Time : 11am – 1pm
Full Marks : 50

[Use separate answer-books for each group]

Group–A
Unit – I

Answer **any one** from the following

1. a) Define compressibility factor (z) of a gas. The virial equation of state in terms of P is given by $z = 1 + \frac{1}{RT}\left(b - \frac{a}{RT}\right)P + \frac{a}{(RT)^3}\left(2b - \frac{a}{RT}\right)P^2 + \cdots\cdots$. Find the expression for Boyle temperature. 3

   b) A gas obeys the equation of state $P(V-b) = RT$. Would it be possible to liquefy the gas? Would it have critical temperature? Explain. 2

   c) For N_2 molecules, the volume correction parameter is found as 39.1 cc/mole. Assuming the gas as Vander Waals real gas, find out its molecular diameter. 3

   d) The potential energy of attraction between neutral molecules is given by $U = A/r^n$. Remark on the sign of A and its dependence on molecular property. Comment on the value of 'n'. 3

   e) (i) For CH_4 at 400K, what value of $\bar{C}_p$ is predicted? 2

   (ii) Comment on the $\bar{C}_p$ at very low temperature. Why is this so? 2

2. a) Probability density of finding gas molecule in one dimension is $P(u_x) = Ae^{-\lambda u_x^2}$, where A is normalization constant and u_x is one dimensional velocity.

   (i) Give justification of the appearance of the square term. 1

   (ii) Find out the value of A. 2

   b) Stating with the Maxwell Speed distribution in three dimensions derive the expression of the number of molecules with translational kinetic energy greater than $\in$, $(\in \gg kT)$. 4

   c) How many collisions does a single H_2 molecule make per second when the temperature is 25ºC and the pressure is 1 atm. (Molecular diameter of H_2 = 0.292 nm) 3

   d) (i) Two gas constants of Vander Waals equation explains both the rise and fall of experimental compressibility factors. Explain. 2

   (ii) Explain the continuity of states using P–V isothermal curves. 2

   e) The most probable velocity of the molecules moving in one direction, v_x is zero. Explain. 1

Unit – II

Answer **any one** from the following

3. a) Heat and work are equivalent ways of changing a system's internal energy. Explain from molecular point of view. 2

b) " $\Delta H = \int_{T_i}^{T_f} Cpdt$ is valid for any process involving any system". Justify or criticize. 2

c) Derive the relation $c_p - c_v = \left[P + \left(\frac{\partial u}{\partial v}\right)_T\right]\left(\frac{\partial v}{\partial T}\right)_p$.

Hence find the value of $c_p - c_v$ for a gas obeying $P(V-b) = RT$. $\left[\left(\frac{\partial u}{\partial v}\right)_T = 0 \text{ for the gas}\right]$. 3

d) The constant pressure heat capacity of a sample of a perfect gas was fond to vary with temperature according to the expression $C_P / JK^{-1} = 20.17 + 0.3665T$.

Calculate *q, w,* Δu and ΔH, when the temperature is raised from 25ºC to 200ºC at constant pressure. 3

4. a) A gas enclosed in a cylinder with a diabatic and non-rigid wall is an isolated system. Justify or criticise. 2

b) Consider the combustion of propane gas. The equation is $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$. Measurement at 298K gives 4U = –2195 KJ mol^{-1} of propane. What do you expect about ΔH at same temperature in constant pressure combustion? 2

c) 1 mol · H_2O (liq, 100ºU, 1 atm) $\rightarrow$ 1 mol H_2O (vap, 100ºC, 1 atm)

Calculate Q, W & ΔV for the process. Assume ideal behaviour of the vapour. Given: Enthalpy of vaporization = 43.7 KJ mol^{-1}. 3

d) One mole of an ideal monatonic gas initially at STP is compressed reversibly to 2 atm pressure along the path: PT = constant.

(i) Calculate the final T and V for the gas. 1

(ii) Sketch qualitatively the appearance of path on a P vs V plot. 1

(iii) Calculate ΔH for the process. 1

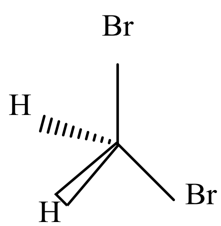
Group – B

Unit–I

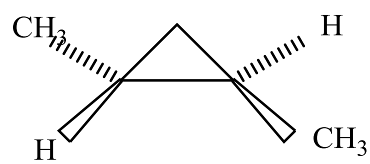
Answer **any one** from the following

5. a) Find the symmetry elements of the following: 2

(i)



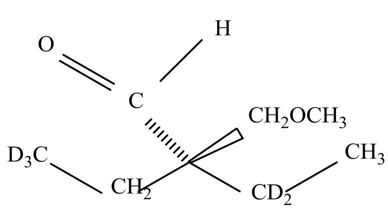
(ii)



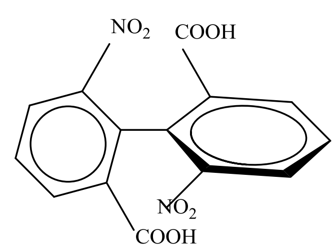
b) Write down one each of Fischer and Newman projection formulae of (2S, 3S)-3-bromobutan-2-ol. 2

c) Give R/S notations of the stereogenic centre/axis of the following: 2

(i)



(ii)



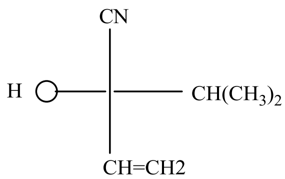
d) C_3 atom of meso-2,3,4-trihydroxyglutaric acid is a pseudoasymmetric centre — comment. Examine the stereogenicity and chirotopicity of C_3. 3

e) Draw the energy profile of conformations obtained by rotation around C_2–C_3 bond of meso-butane-2,3-diol. Indicate the dihedral angle of the conformers. Label the energy maxima and minima of the curve with appropriate conformations. 4

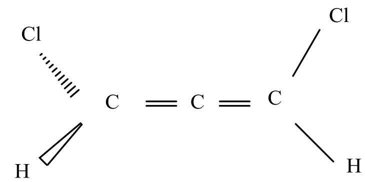
f) (+)Mandelic acid [PhCH(OH)COOH] undergoes racemisation when boiled in alkali, but (+) atrolactic acid [PhC(CH_3)(OH)COOH] does not — explain. 2

6. a) Give R/S notations of configurations of the following: 2

(i)



(ii)

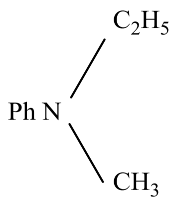


b) Explain whether the following compounds are resolvable. Comment on their chirality. 3

(i) $CH_2 = C = C(CH_3)_2$

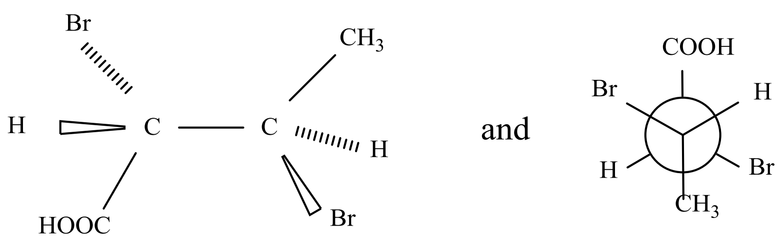
(ii) $CH_3CH = C = CHCH_3$

(iii)

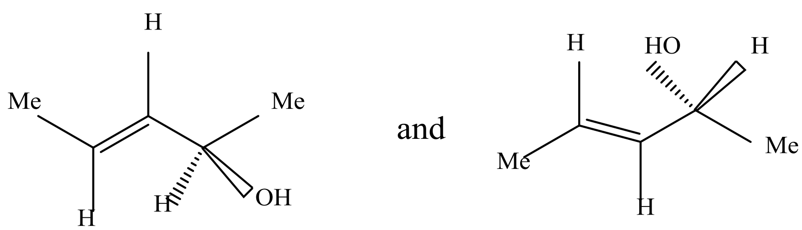


c) Give the stereochemical relationship between the following pairs. 2

(i)



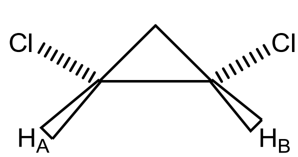
(ii)



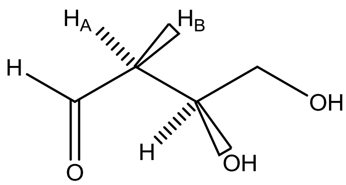
d) A pure enantiomer of a certain chiral compound has $[\alpha]_D^{25} = +55^\circ$. A mixture of two enantiomers of the same compound shows the $[\alpha]_D^{25}$ as –11º. Calculate the percentage composion of the enantiomers in the mixture. 3

e) Identify the labelled *H* atoms as homotopic, enantiotopic or diastereotopic in the following: 3

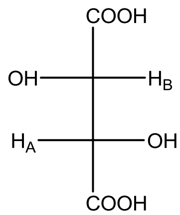
(i)



(ii)



(iii)



f) How many steroisomers are possible for 2-methylpent-3-enoic acid. Draw their structures. 2

Unit–II

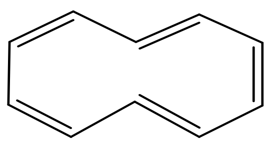
Answer **any one** from the following

7. a) Which carbocation of the following pair is more stable and why? 3

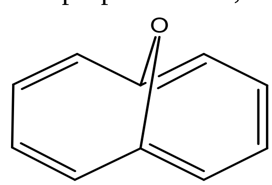
$CH_3OCH = CH\overset{+}{C}H_2$ and $CH_3OC(=CH_2){-}\overset{+}{C}H_2$

b) Draw the orbital picture of $CH_3CH = C = O$ indicating the state of hybridisation of *C* atoms. 2

c) Of the following two structures, ascertain, with proper reasons, the structure with greater stability. 2



and



d) Calculate the approximate values of dipolemoments of (i) *p*-chloronitrobenzene and (ii) *p*-nitrotoluene from the following data. 3

$\mu_{toluene} = 0.43D,\ \mu_{nitrobenzene} = 4.21D, \mu_{chlorobenzene} = 1.70D$

8. a) Calculate the resonance energy of benzene from the following heats of hydrogenation (ΔH) values. 2

Cyclohexene + H_2 = Cyclohexane, ΔH = –30 Kcal mol^{-1}

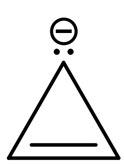
Benzene + $3H_2$ = Cyclohexane, ΔH = –54 Kcal mol^{-1}

b) C–H bonds in fluoromethane are shorter than in methane — explain. 2

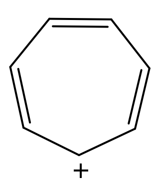
c) Draw the π MOs of allyl carbocation and allyl carbonion. Explain on the basis of MO pictures, (i) the electron enriched C atoms in allyl carbanion and (ii) the electron deficient C atoms in allyl carbocation. 3

d) State, with reasons, whether the following are aromatic, nonaromatic or antiaromatic. 3

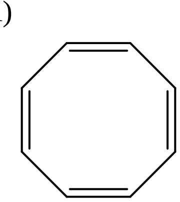
(i)



(ii)



(iii)



————