RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College under University of Calcutta)

B.A./B.SC. FIRST SEMESTER EXAMINATION, DECEMBER 2013

FIRST YEAR

Date : 14/12/2013 CHEMISTRY (Honours)

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

[Use separate Answer Books for each group]

Group – A

(*Answer **one** question from each unit*)

Unit – I

1. a) i) Depict Maxwell's speed distribution curves for ID at two different temperatures T_1 and T_2 ($T_2>T_1$). [2]

ii) Explain their natures by analysing Maxwell's equation. [2]

iii) How is it affected, if the gas is changed from He to Ar? [1]

b) Indicate the nature of intermolecular force operative between nonpolar molecules. [2]

c) Molecular diameter of carbon monoxide is 3·19Å. At 27°C and 100 mm of Hg pressure what will be the—

i) collision frequency ii) mean free path [1+2]

d) The value of C_p for gaseous benzene at 50°C is 14 $\text{CalK}^{-1}\text{mole}^{-1}$. Calculate the number of vibrational degrees of freedom this corresponds to, assuming equipartition. To what fraction of the total number of vibrational degrees of freedom for benzene does the above number correspond? Assume ideal behaviour. [3]

2. a) The critical temperature and pressure for gas A are 177 K and 64 atm, respectively and for gas B they are 550K and 45 atm, respectively. Which gas has

i) smaller value of van der Waals' constant, b? [1]

ii) smaller value of Boyle temperature? [2]

iii) larger value of critical volume? [2]

b) Derive an expression for the average time required for a gas molecule moving in 3D to travel unit distance, i.e., $\left\langle \frac{1}{c} \right\rangle$. [3]

c) The compressibility factor, Z, of a van der Waals gas is given by the following equation :

$$Z = 1 + \frac{1}{RT}\left(b - \frac{a}{RT}\right)P + \frac{a}{(RT)^3}\left(2b - \frac{a}{RT}\right)P^2 + \ldots$$

At what temperature does the slope of Z versus p curve (at P = 0) have a maximum value for the van der Waals gas? What is the value of the maximum slope? [3]

d) Calculate the number of methane molecules at 25°C and one torr that strike a 1·0 cm^2 surface in one millisecond. [2]

Unit – II

3. a) Classify each of the following properties as intensive or extensive :

(i) H (ii) T (iii) $\left(\frac{\partial u}{\partial v}\right)_T$ (iv) $V^{-1}\left(\frac{\partial V}{\partial T}\right)_P$ [½×4]

b) Justify or criticize the statements (**<u>any two</u>**) : [2×2]

i) For every process in an isolated system, $\Delta U = 0$

ii) $\left(\partial u/\partial v\right)_T = 0$ for a gas obeying $P(v-b) = RT$.

iii) As no heat enters a system under adiabatic conditions its energy is conserved during expansion.

c) Show that the work involved in a reversible, adiabatic pressure change of one mole of an ideal gas is given by

$$W=\bar{C}_V T_1\left[\left(\frac{P_2}{P_1}\right)^{\frac{R}{\bar{C}_P}}-1\right]$$

where T_1 is the initial temperature and P_1 and P_2 are the initial and final pressures respectively. [4]

d) For the reaction :

$$NH_3(g)=\frac{1}{2}N_2(g)+\frac{3}{2}H_2(g)\quad \Delta H^o_{298K}=11{,}040\ \text{cal}.$$

Find the value of ΔE^o of the reaction at 298K. [2]

4. a) Show that : $C_P-C_V=\left[V-\left(\frac{\partial H}{\partial P}\right)_T\right]\left(\frac{\partial P}{\partial T}\right)_V$ [3]

b) Show that : $dq=C_V(T)dT+\frac{nRT}{V}dv$ is not exact differential but $\frac{dq}{T}$ is. [2]

c) For $H_2(g)+\frac{1}{2}O_2(g)\rightarrow H_2O(\ell)$, find $\Delta H^o_{298}-\Delta U^o_{298}$, neglecting the volume of $H_2O(\ell)$. [2]

d) 1 mole of an ideal monatomic gas initially at P_1=2atm, T_1=273 K is taken to a pressure of P_2=4 atm by the reversible path defined by P/V = const.

i) Calculate V_1, V_2 and T_2. ii) Calculate q, w, ΔH [(½+½+1)+(1+1+1)]

Group – B

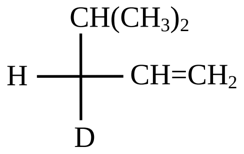
(*Answer **one** question from each unit*)

Unit – I

5. a) Define, with suitable example, each of the following terms : [2×2]

i) Centre of symmetry ii) Atropisomerism

b) assign R/S-descriptor to the chiral centres present in the following compounds (**any two**) : [2]

i)


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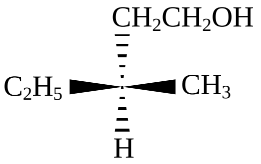

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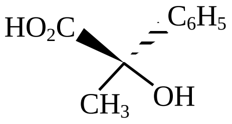
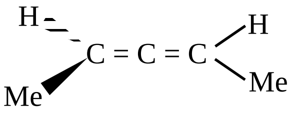


c) Draw the energy profile diagram of 1,2-dichloroethane for rotation about C–C bond and label the maxima and minima with appropriate conformations. Compare the relative stability of the conformations with explanation. [3]

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

i)


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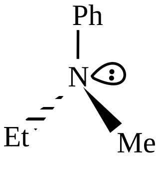
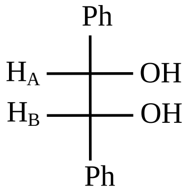


e) Identify H_A and H_B in each of the following structures as homotopic, enantiotopic or diastereotopic and explain. [2]



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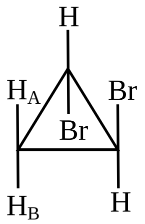
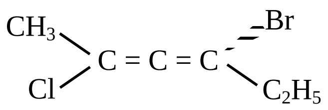


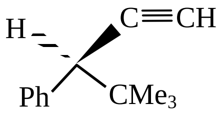
f) Draw the Fischer projection formula of (2S, 3S) – 3 – bromobutan – 2 – ol and represent it in Newman projection formula. [2]

6. a) Draw the Newman projection formula of the most stable conformation of meso–butane–2, 3–diol along $C_2 - C_3$ bond and justify. [2]

b) Give the principle of a method of resolution of a racemic mixture of a chiral alcohol. [3]

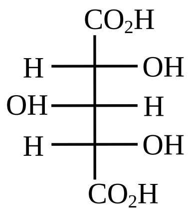
c) Assign R/S descriptors to the following compounds : [2]

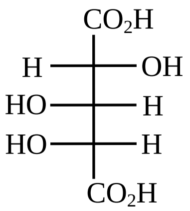
i) 

ii) 

d) What is meant by 'enantiomeric excess (ee)'? The pure (+) enantiomer of a compound shows a specific rotation of +80°. Calculate the percentage of the (–) –enantiomer of the same compound in a partially resolved sample showing a specific rotation of –20°. [3]

e) Label the C–3 centres of a the following molecules as stereogenic / non-stereogenic and chirotopic / achirotopic. Justify your answer. [2]





f) Draw all stereoisomers of $CH_3CH=CH-CH(OH)-CH=CH-CH_3$ and mention their optical activity. Assign R/S designation at the chiral centres of the active molecules. [3]

Unit – II

7. a) Between toluene and t-butylbenzene which compound will have higher electron density at the para-carbon atom. —Explain. [2]

b) Unlike benzyl bromide 1-bromocyclohepta 2,4,6-triene is highly soluble in water yielding bromide ions in solution —Explain. [2]

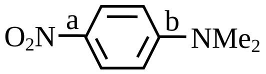
c) Draw the $\pi -$M.O. diagram of :

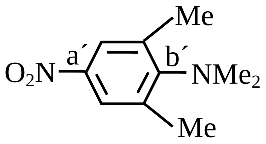
i) HOMO of 1,3–butadiene in the excited state.

ii) LUMO of allyl cation in the ground state. [2]

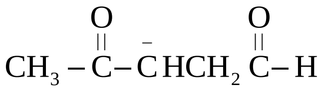
d) Write canonical forms of the following carbocation and indicate which one has the greatest contribution towards the resonance hybrid. $(CH_3)_2NCH=CH-\overset{+}{C}H_2$ [2]

e) Compare the C–N bond lengths (a vs a´) and (b vs b´) in the following compounds. [2]

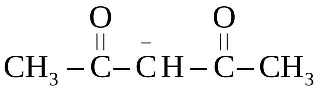




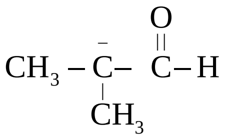
8. a) Which species in each of the following cases is more stable? Explain. [2]

i) 

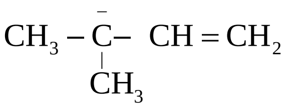
$CH_3-\overset{\overset{O}{||}}{C}-\overset{-}{C}HCH_2\overset{\overset{O}{||}}{C}-H$

or 

$CH_3-\overset{\overset{O}{||}}{C}-\overset{-}{C}H-\overset{\overset{O}{||}}{C}-CH_3$

ii) 

$CH_3-\underset{\underset{CH_3}{|}}{\overset{-}{C}}-\overset{\overset{O}{||}}{C}-H$

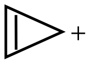
or 

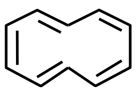
$CH_3-\underset{\underset{CH_3}{|}}{\overset{-}{C}}-CH=CH_2$

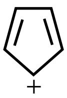
b) Compare the dipole moments of o, m and p – dichlorobenzenes. [2]

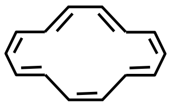
c) Draw orbital picture of the following compound indicating the state of hybridisation of carbon and nitrogen. $CH_3-CH=C=CH-NO_2$ [2]

d) Assign the following as aromatic, non-aromatic and antiaromatic with reasoning. [4]

i) 

ii) 

iii) 

iv) 

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