RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College under University of Calcutta)

THIRD YEAR
B.A./B.SC. FIFTH SEMESTER (July – December) 2014
Mid-Semester Examination, September 2014

Date : 15/09/2014

Time : 2 pm – 4 pm

CHEMISTRY (Honours)

Paper : V

Full Marks : 50

[Use a separate answer book for each group]

Group – A

(*Answer **Question No. 1 or 2** and **Question No. 3 or 4***)

1. a) When all energies are measured relative to $\in_0 = 0$, the population of the i-th quantum state is given

   by $n_i = \dfrac{Ne^{-\beta\in_i}}{z}$

   The actual population, n_i must remain unchanged whenever we choose our reference zero of energy. Demonstrate that if all energies are measured on a scale relative to $\in_0 = c$, the above equation continues exactly the same result for n_i. [2]

   b) For a macroscopic body consisting of species of loosely coupled distinguishable units, the energy of body E_i is slightly increased by input of a minute amount of heat. Find out the operative relation between W and E. [The distribution in different levels is according to Boltzmann distribution]. [4]

   c) The gaseous NO present in the vibrational states as the fraction given below

v	0	1	2	3	4
f	0·7344	0·1936	0·0521	0·0143	0·004

   What is the energy spacing between quantum states v = 0 and v = 1? [2]

   d) For a two level system (e.g Har. Osc) at high temperature, the population at '0' (zero) level is given as a function of the energy gap between the two levels. True or False. Explain. [2]

   e) For an ideal gas [indistinguishable particles] obeying $z_{trans} = \left(\dfrac{2\pi m}{h^2\beta}\right)^{3/2} V$ show that $E_{trans} = \dfrac{3}{2}RT$

   for 1 mole of gas. [3]

2. a) We encounter the energy distribution $P(\in) = Ae^{-\in/K_B T}$ where $P(\in)$ is the probability of a molecule occupying a given energy state, $\in$. Imagine that there are three energy states at 0, 100 and 500J mol^{-1}.

   i) Determine the normalization constant for this distribution.

   ii) What is the probability of occupying the highest energy state at 298K?

   iii) What is the average energy at 298K? [5]

   b) For a system, with N distinguishable particles distributed in different energy levels, show that $n_i = n_0 e^{-\beta\in_i}$

   where n_i and n_0 are the populations at ith and '0'th level, respectively. And energy values for '0'th level is 0(zero) and $\in_i$ being the energy of ith level. [4]

   c) For an ensemble consisting of a mole of particles having 2 energy levels separated by $h\nu = 1·00 \times 10^{-20} J$. At what temperature will internal energy of system equal to 1·00KJ? [2]

   d) Could a calculated partition function ever have a value less than one? Explain. [2]

3. a) A closed system contains graphite, O_2, CO and CO_2 at equilibrium at 1000K. Find out the number of components and the degrees of freedom for this system. [2]

   b) The normal boiling point of benzene is 80·2°C and its molar heat of vapourization is 30·78 KJ/mol. Find out the vapour pressure of benzene at 30°C. [2]

c) Derive Duhem-Margules equation. [3]

d) The phenol-water system has an upper consolute temperature of 65·85°C at 1 atm. what happens if the observation is made at a higher pressure? Explain. [2]

e) i) Sketch the phase diagram of water and mark the following in the diagram : Normal freezing point and critical point.

   ii) Trace a path from a point in vapour to that in solid phase b minimum change of variables at a time. [3]

4. a) Explain why ice melts but dry ice sublimes when exposed to room temperature and pressure. [2]

   b) A gaseous mixture of two substances A and B under a total pressure of 0·8 atm is in equilibrium with an ideal liquid solution. The mol fraction of substance A is 0·5 in the vapour phase and 0·2 in the liquid phase. What are the vapour pressures of the pure liquids A and B? [3]

   c) Derive Konowaloff's rules when $\dfrac{dP}{dx_A} > 0$ and when $\dfrac{dP}{dx_A} = 0$, where P is the total vapour pressure and x_A is the mol fraction of the more volatile liquid in the liquid phase. [3]

   d) What are the criteria of a first order phase transition? [1]

   e) Draw a suitable phase diagram for Phenol-water system and calculate the number of degrees of freedom on the curve, above and below the curve. What will be the 'F' at UCST? [3]

Group – B

(*Answer **Question No. 5 or 6** and **Question No. 7 or 8***)

5. a) Which of the following vibrational modes shows no IR absorption bands?
   i) symmetrical CO_2 stretch
   ii) antisymmetrical CO_2 stretch
   iii) symmetrical $O = C = S$ stretch
   iv) $C = C$ stretching in O-xylene
   v) $C = C$ stretching in p-xylene and
   vi) $C = C$ stretching in p-bromo toluene. [2]

   b) Is it possible to distinguish following two compounds by IR spectroscopy? [1]


(A)   (B)
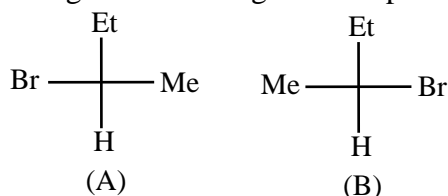
   c) Trace the oxidation of 2-propanol to acetone by 1R. [1]

   d) Which of the following atoms are not NMR active?
   $^{12}C, \ ^{16}O, \ ^{14}N, \ ^{2}H, \ ^{15}N, \ ^{19}F, \ ^{31}P, \ ^{13}C, \ ^{32}S$ [1]

   e) Explain why TMS is chosen as the reference compound. [2]

   f) Why is twist boat a lower energy conformer than a true boat? [1½]

   g) Draw the stable conformer, (with reason) of cis-1, 3-cyclohexane diol. [1½]

   h) The conformational free energies of Cl, Br, I are same, though their size increases from Cl to I —explain. [2]

   i) State the stereochemical relationship between (B) and its flipped form. [1]


$(R \ne R_1)$
(B)   R
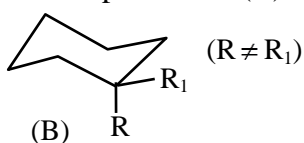
6. a) What is the effect of hybridisation of carbon on the stretching frequency of C – H bonds? [2]
   b) How will you distinguish between the following pairs on the basis of IR spectroscopy? [2]

   i) and   ii)   and
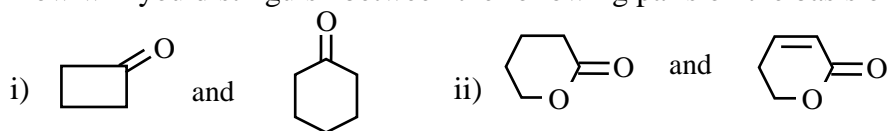
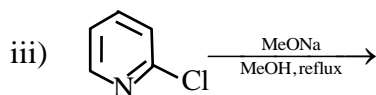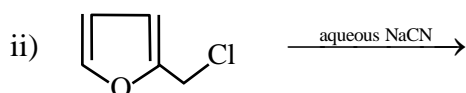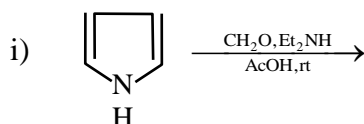   c) Indicate what NMR spectra you expect from the following compounds. [2]

   i) $H_3C-CH_2-CH_2-CH_3$ ii) $H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_3$
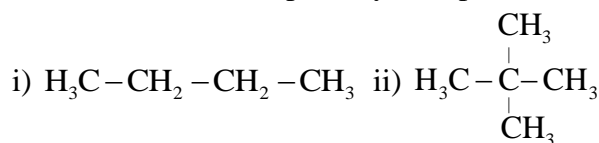
   d) Give the relative decreasing order of δ values for 3°, 2°. 1° and CH_4 (super 1°) H's. [1]
   e) State the stereochemical relationship between (A) and its flipped form. [1]
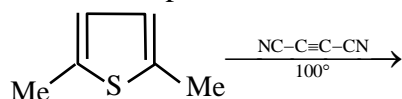

   (A)
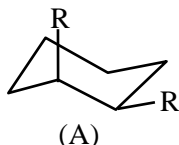
   f) Why is cyclohexane called a strainless ring? [1·5]
   g) Draw with reason, the stable conformer of trans-1, 3-ditertiary butyl cyclohexane. [1·5]
   h) Amount of equatorial conformer does increase in the order Me < Et < i–Pr << t-Bu —Explain [2]

7. a) Give Retrosynthetic analysis and efficient synthesis of the following compounds : [3×2]

   i)   ii)   iii)
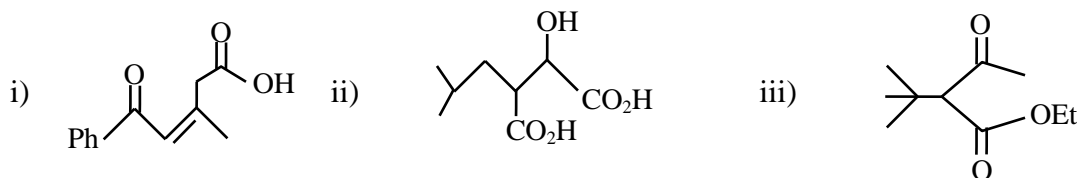
   b) Indole undergoes electrophilic substitution primarily at C–3 but pyrrole does at C–2. Explain. [2]
   c) Write the product(s) with plausible mechanism in the following reactions (any two) [1·5×2]
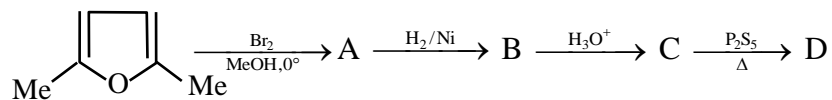
   i) $\xrightarrow[\text{AcOH,rt}]{CH_2O,Et_2NH}$

   ii) $\xrightarrow{\text{aqueous NaCN}}$

   iii) $\xrightarrow[\text{MeOH,reflux}]{\text{MeONa}}$

   d) Predict the product in the following reaction. [1]

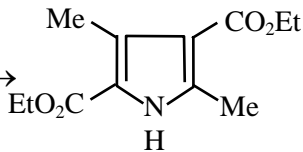 $\xrightarrow[100°]{NC-C\equiv C-CN}$

8. a) Outline the total synthesis of papaverine starting from Resorcinol. [4]
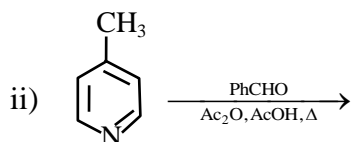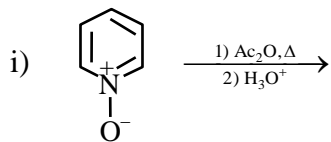   b) Carry out the following conversion : [2]

(3)
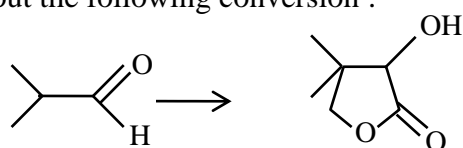
c) Identify A, B, C, D in the following sequence of reactions. [2]

$$\underset{\underset{Me}{}}{\text{Me}} \xrightarrow[\text{MeOH,0°}]{\text{Br}_2} A \xrightarrow{\text{H}_2/\text{Ni}} B \xrightarrow{\text{H}_3\text{O}^+} C \xrightarrow[\Delta]{\text{P}_2\text{S}_5} D$$

d) Convert : $CH_3COCH_2CO_2Et \rightarrow$ [2]

Me — CO$_2$Et
EtO$_2$C — N — Me
H

e) Write the products with suitable mechanism in the following reactions. (**any one**) [2]

i)

$$\xrightarrow[\text{2) H}_3\text{O}^+]{\text{1) Ac}_2\text{O,}\Delta}$$

CH$_3$

ii)

$$\xrightarrow[\text{Ac}_2\text{O, AcOH,}\Delta]{\text{PhCHO}}$$

————— × —————

(4)