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

B.A./B.SC. SIXTH SEMESTER EXAMINATION, MAY 2014
THIRD YEAR

Date : 02/05/2014

Time : 11 am – 1 pm

CHEMISTRY (Honours)
Paper : VIII-A

Full Marks : 50

[Use a separate Answer book for each group]

Group - A

Unit – I

[*Answer **any one** question*]

1. a) Show that the rotational level, of a diatomic rigid rotor, whose quantum number is given by the expression : $J = \sqrt{\dfrac{1}{2}\left(\dfrac{kT}{Bhc}\right)} - \dfrac{1}{2}$

   has the maximum population. (Terms have their usual significance). [3]

   b) The pure Rotational Roman spectrum of $^{19}F_2$ (mass = 18·9984 amu) shows a series of Stokes lines separated by 3·5312 cm^{-1}, and a similar series of anti-Stokes lines. Calculate the bond length of the molecule in nanometres. [3]

   c) A hypothetical quantum mechanical system has energy levels given by the expression $E = a \cdot n(n+4)$, where n = 0,1,2,3... and 'a' is a positive constant. The selection rule for radiative transitions is $\Delta n = \pm 3$. Find the formula for the allowed absorption frequencies and draw a schematic plot of the absorption spectrum. [3]

   d) Consider linear molecules of the formula AB_2 (BAB and ABB). Pictorially describe all possible pure IR and vibration Raman active modes. Mention the relevant selection rules. [4]

   e) Two isotopically substituted molecules CD and C′D have the rotational constants B and B′. If the atomic mass of C′ is **twice** that of C then find the ratio **B′/B** [Assume that $m_D = 35 m_C$]. [2]

2. a) What are the main points of difference between the 'overtones' and 'hot bands'? Show that $\Delta \in = \overline{\omega}_e(1 - 4x_e)cm^{-1}$ is the expression for wavenumber for the **first transition** in case of 'hot bands'. [3]

   b) Write down the expression for the Morse potential including a graphical representation. Explain the meaning of the terms. Show that $a = \left(\dfrac{k}{2hc\,D_e}\right)^{\frac{1}{2}}$ (terms have their usual meaning). [4]

   c) The converse of 'mutual exclusion rule' for spectroscopy is always true. Justify or criticize. [2]

   d) The first rotational absorption of $^{12}C^{16}O$ occurs at 3·8424 cm^{-1} and that for $^{13}C^{16}O$ at 3·6734 cm^{-1}. Calculate the relative atomic mass of ^{13}C [Given : ^{16}O = 15·9994 and ^{12}C = 12·0000] [3]

   e) i) What do you mean by 'equilibrium oscillation frequency' of an anharmonic system?

   ii) The intensities of the Stokes and anti-Stokes lines are different in vibrational Raman spectra. Explain. [1+2]

Unit – II

[*Answer **any one** question*]

3. a) Photobromination of cinnamic acid to di-bromocinnamic acid was carried out in blue light of 440 nm at 35°C using light intensity of $1·5 \times 10^{-3}$ J/S. An exposure of 20 minutes produced a decrease of 0·075 millimole of bromine. The solution absorbed 80% of the light passing through it. Calculate the quantum yield of the reaction. [3]

b) Assume that the r_{min} of the potential energy curves of the ground state and the first excited state of a diatomic molecule are **equal**. Which of the v' and v'' combination will give the maximum intensity of this electronic transition? Explain, using the potential energy curves. [3]

c) What is the essential assumption of the 'activated complex' theory? Relate the entropy change for activated complex formation to the Arrhenius pre-exponential factor A. [3]

d) If the quantum yield of a photochemical reaction is **greater than unity** then the second law of photochemistry is violated. Comment. [1]

4. a) Show that for a gaseous bimolecular reaction

$A(g) + B(g) \rightarrow (AB)^{\#}(g) \rightarrow \text{Products}$; $E_a = \Delta H_m^{\#} + 2RT$ (Terms have their usual significance, 'm' denotes 'per mole') [3]

b) A 10^{-3}(M) solution of a dye 'X' shows an absorbance of 0.20 at 450 nm and an absorbance of 0.05 at 620 nm. A 10^{-4}(M) solution of another dye 'Y' shows zero absorbance at 450nm and an absorbance of 0.02 at 620 nm. Calculate the **concentration** of **each dye** present together in a solution which exhibits an absorbance of 0.38 and 0.71 at 450nm and 620 nm, respectively. [The same cell, of pathlength 1.00 cm, is used in the experiment]. What are the limitations of the Lambert-Beer's law? [3+1]

c) A solution of anthracene (A) in benzene is exposed to u-v light and the quantum efficiency of the reaction is found to be $\phi = \dfrac{[A]}{[A]+B}$ where B is a ratio of two different rate constants.

i) Obtain the expression for ϕ using a suitable reaction mechanism.

ii) What is the competitive photophysical process involved? [2+1]

Group - B

Unit – III

[*Answer **any one** question*]

5. a) When D-glucose is treated with methanol in presence of acid under reflux condition both the anomers of methyl D-glucopyranoside are formed. Give the mechanism of their formation in chair perspective formula. What happens when the α-anomer of the glycosides is treated with benzaldehyde in presence of acid. [4]

b) Write down the structures of two different D-aldohexoses which on oxidation with nitric acid yield the same aldaric acid. Explain your answer. [2]

c) Explain why glucose exhibits mutarotation but methyl glucoside does not. What is abnormal mutarotation? Give example. [3]

d) Carry out the following conversion : [3]
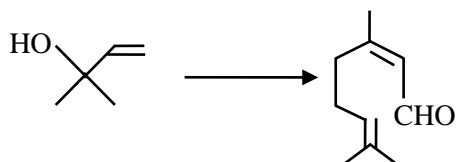
e) Who the structure of the nucleoside obtained from adenine and D-ribose. [1]

f) Apply Edman degration method to determine N-terminal residue of a protein. [2]

6. a) A D-aldopentose is oxidised to an optically active aldaric acid by nitric acid. Ruff degradation of the aldopentose leads to a monosaccharide which on oxidation with nitric acid affords an optically inactive aldaric acid. Identify the D-aldopentose. [3]

b) How the N-terminal aminoacid residue of a peptide is determined with the help on 2,4-dinitroflurobenzene? Why the cheaper 2,4-dinitrochlorobenzene is not used? [4]

c) Convert adenosine triphosphate to adenosine. [2]

d) Define terpenoids in the light of special isoprene rule. Give one example of a monoterpenoid where special isopoene rule is not obeyed. [2]

e) Write the representative structure of a trinucleotide fragment of an RNA chain. [2]

f) With a suitable chemical reaction establish that geraniol incorporates a geminal demethyl group located on an Sp^2-carbon. [2]
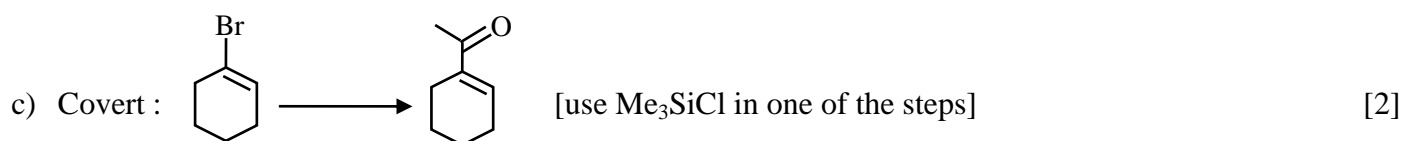
Unit – IV

[*Answer **any one** question*]

7. a) Predict the products of the following electrocyclic reactions and explain them on the basis of FMO interactions. [3+3]

i)

ii) 2Z, 4Z, 6E – 2,4,6 - octatrine $\xrightarrow{\Delta}$
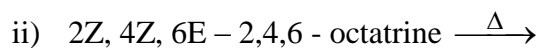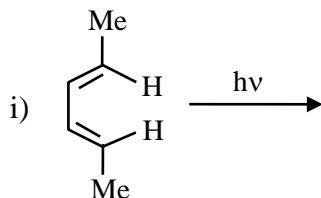
b) Explain the role of Ml_3SiCl regarding the synthesis of small ring using acyloin condensation reaction. [2]

c) Covert : [use Me_3SiCl in one of the steps] [2]

8. a) Cope rearrangement of the compound (A) leads to the formation of two diastereomeric products. Identify the products, giving mechanism. [3]

(A)
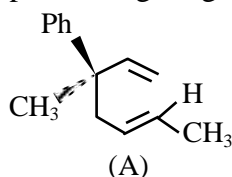
b) Complete the following reactions and write plausible mechanism to explain product formation. [2×2½]

i) $Ph-CH=CH-SiMe_3 \xrightarrow{\dfrac{Br_2}{CCl_4}}$

ii) $Ph-CHO + $ $\xrightarrow[\text{ii)}H_2O]{\text{i)}TiCl_4}$
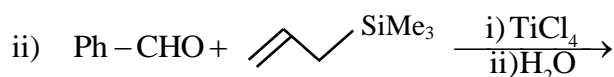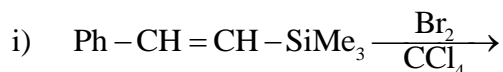
c) Predict the products(s) of the following reaction and give mechanism. [2]

 $\xrightarrow{\Delta}$

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(3)