RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College under University of Calcutta)

B.A./B.SC. SIXTH SEMESTER EXAMINATION, MAY-JUNE 2013

THIRD YEAR

Date : 24/05/2013 — **Chemistry (Honours)**

Time : 11am – 1pm — Paper : VIII(A) — Full Marks : 50

(Use separate answer book for each group)

Group-A

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

Unit-I

1. a) To explain the kinetics of unimolecular reactions, Lindemann proposed a mechanism of activation by collision and the subsequent rate law may be first order in certain situations. Illustrate this point clearly. 3

   b) What is Franck-Condon Principle? Using appropriate potential energy curves discuss the phenomena of normal dissociation and pre-dissociation from the excited state after usual excitation from the ground state. 1+2+2

   c) Absorption spectra and Fluorescence spectra are almost mirror image to each other, as well as later one is red shifted to former one. Do you agree with above fact? Explain. 3

   d) A second order reaction in solution has rate constant 5.7×10^{-5} dm^3 mol^{-1} s^{-1} at 25ºC and 1.64×10^{-4} dm^3 mol^{-1} s^{-1} at 40ºC. Calculate the activation energy and the pre-exponential factor. Also calculate $\Delta^{\ddagger} G^{o}$ and $\Delta^{\ddagger} H^{o}$ at 25ºC. 2+2

2. a) Write down the Lambert-Beer's Law and explain the terms. What are the assumptions involved for writing down the law in this form. 2+1

   b) What do you understand by quantum yield? Does a quantum yield less than one or greater than one contradict Stark Einstein's Law of photochemical equivalence? Give one example of each. 1+2+1

   c) Explain the mechanism of photochemical dissociation of HI and hence show that its quantum efficiency (φ) is 2. 3

   d) In between phosphorescence and fluorescence which one is of long duration? Explain. 2

   e) A 10^{-3} (M) solution of *A* also contains some *B*, and the solution when placed in a 2 cm cell absorbs 80% of the incident light at a certain wavelength. If the extinction coeff of *A* and *B* at this wavelength are 250 and 1000 respectively, then find the concentrations of *B* in the solution. 3

Unit-II

3. a) For Harmonic Oscillator, the transition moment integral $\langle \psi_v | \mu | \psi_{v'} \rangle$ exists only if $\Delta v = v - v' = \pm 1$. Justify or criticise. 3

   b) Can rotational spectroscopy be used to find out the mass of an isotope? Explain. 2

   c) The vibrational spectrum of $^{1}H^{35}Cl$ shows the fundamental at 2886 cm^{-1}, first overtone at 5668 cm^{-1}. Calculate –

      (i) the anharmonicity constant

      (ii) harmonic oscillator frequency 1+2

   d) Explain why? Raman lines for bending modes of H_2O are not observed. 2

4. a) What do you understand by hot bands? "The intensity of a hot band increases with temperature." – Justify or criticize. 3

b) Using the CO_2 molecule as a test case, explain mutual exclusion principle. (Take any two modes) 4

c) The consecutive lines in the rotational spectrum of $^1H^{79}Br$ are observed at 84.544, 101.355, 118.112 cm^{-1}.

(i) Assign the lines to their $J'' \rightarrow J'$ transitions

(ii) Deduce the values of rotational constant and centrifugal distortion in cm^{-1}. 3

Group-B

Unit-I

Answer **any one** question

5. a) Provide an explanation to each of the following:–

(i) β-D glucopyranose gets oxidised more rapidly than α-D glucopyranose by bromine water. 2½

(ii) Oxidation of D-fructose with Tollens' reagent yields a mixture of D-mannonic acid and D-gluconic acid. 2

(iii) α-D galactose readily forms diacetonide with acetone in presence of dry HCl but α-D glucose does so only in furanose form. 2½

b) Two different D-aldohexores produce the same aldaric acid on oxidation with HNO_3 – write their structures with reason. 2

c) How can you prepare phenyl alanine by the azalactone method? 2

d) What would happen when D-glucose is treated with benzaldehyde in presence of dry HCl? 2

6. a) How can you cleave the methionine residue in a polypeptide using BrCN? 3

b) How can you synthesise the tripeptide Gly-Ala-Phe by the Merrifield method? 3

c) Write down the product(s) with mechanism: 3

$$\text{Alanine} \xrightarrow[\Delta]{AC_2O/\text{Pyridine}} ?$$

d) Explain the role of '<u>DNF B</u>' for the determination of N-terminal amino acid of a peptide. 2

e) Write down the product(s) of the reaction – 2

$$D-\text{Glucose} \xrightarrow[HCl(Dry)]{>=0}$$

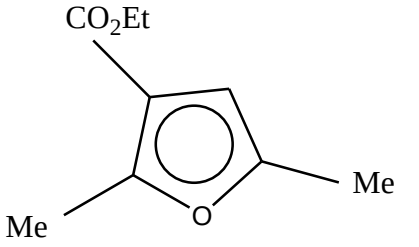
Unit-II

Answer any **one** question

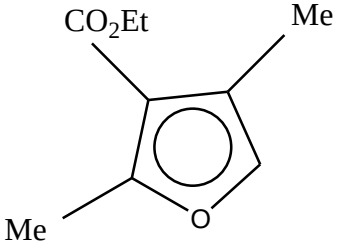
7. a) Synthesis chloroquine and mention its one use. 3

b) Write down the structures of guanosine and adenosine. Why does guanosine hydrolyse more rapidly than adenosine? 2

c) Make the following heterocycles using the same starting materials, showing the reagents and probable mechanism – 5



,

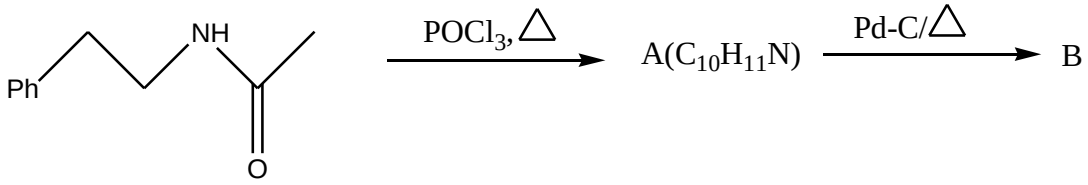


d) Convert pyridine to 4-nitorpyridine. 2

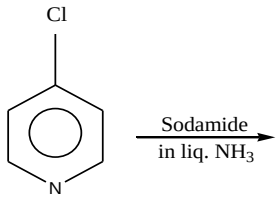
8. a) Indicate the structural differences between nucleosides and nucleotides, with example. 2

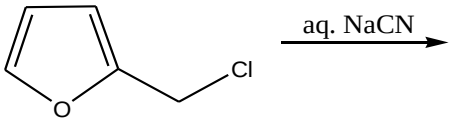
b) Outline the synthesis of phenobarbital. 2

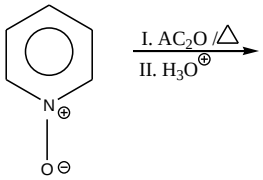
c) Identify *A* and *B* in following reaction sequence and indicate the mechanism leading to *A*. 2



d) Write the product(s) with possible mechanism (any three):– 2+2+2

(i) 

(ii) 

(iii) 

(iv)