

RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College under University of Calcutta)

FIRST YEAR

B.A./B.SC. SECOND SEMESTER (January – June), 2012

Mid-Semester Examination, March 2012

Date : 19/03/2012

CHEMISTRY (Honours)

Time : 11 am – 1 pm

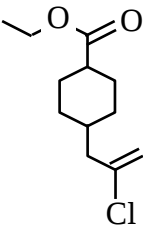
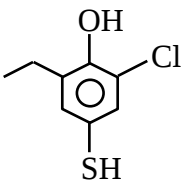
Paper : II

Full Marks : 50

[Use separate Answer Books for each group]

Group – A

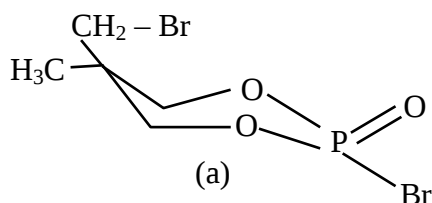
(Answer any two from the following)

1. a) Carry out the following conversion : [4]
(R) – 2 – butanol $\longrightarrow$ (s) – 2 – butanol
- b) Explain the following observation : [3]
(R) – 2 – chlorooctane when treated with 80% acetone / 20% water it gives 83% (s) – 2 – octanol and 17% (R) – 2 – octanol whereas (R) – α – phenylethyl chloride by the similar treatment gives 51% (s) – α – phenylethanol and 49% (R) – α – phenylethanol
- c) Cite an example of S_N2 reaction which is attended by racemisation [1]
2. Complete the following reactions and write down mechanism in each case : [2×4]
 - a) cis – 1, 2 – dimethylcyclohexene $\xrightarrow[\text{RhCl(PPh}_3)_3, 25^\circ, 1 \text{ atm}]{\text{H}_2}$
 - b) $\text{F}_3\text{C} - \text{CH} = \text{CH}_2 + \text{HCl} \longrightarrow$
 - c) $\text{MeO} - \text{CH} = \text{CH}_2 + \text{HCl(aq)} \longrightarrow$
 - d) cis – But – 2 – ene $\xrightarrow{\text{Br}_2 / \text{CCl}_4}$
3. a) Predict which reaction in the following pair has the greater entropy of activation [2]
 $\text{Me}_2\text{S} + \text{MeI} \longrightarrow \text{Me}_3\text{S}^+ + \text{I}^-$
Or, $\text{SH}^- + \text{MeI} \longrightarrow \text{MeSH} + \text{I}^-$
- b) Account for the relative K_{eqm} values for the following two reactions : [2]
 - i) $\text{H}_3\text{CCOCH}_3 + 2\text{EtOH} \rightleftharpoons (\text{CH}_3)_2\text{C}(\text{OEt})_2 + \text{H}_2\text{O}$
 - ii) $\text{Me}_2\text{CO} + \text{HO}(\text{CH}_2)_2\text{OH} \rightleftharpoons \text{Me}_2\text{C} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{array} (\text{CH}_2)_2 + \text{H}_2\text{O}$
- c) Write the IUPAC name of the following compounds :
 - i) 
 - ii) 
- d) 2, 6 – di – t – butylpyridine is a better scavenger than pyridine itself —Explain [2]

Group – B

(Answer **any two** from the following)

4. a) Name the Principal ore of Beryllium with composition. How Beryllium is extracted from that ore :
Give chemical reactions for that extraction. [1+3]
b) Explain why Group IA hydroxides are much more corrosive than that of Group IIA hydroxides. [2]
c) Write notes on Zintl salt. [2]
d) Write with example the existence of the sodide ion. [1]
5. a) Draw the complexes formed by Li^+ , Na^+ , and K^+ with acetyl acetone and with salicaldehyde. [3]
b) Write down the name of an important occurrence of lithium with its composition. How can you obtain extra pure lithium from that occurrence. [1+2]
c) State the basis of radius ratio rule for ionic compounds. [1]
d) Arrange (increasing order) and explain the solubility of LiClO_4 , NaClO_4 and KClO_4 in water. [2]
6. a) Discuss the structure of XeF_2 . [2]
b) Draw the important resonance structure for NO_2 showing the formal charges on each atom and indicate the relative importance of the various structures. [2]
c)



In the cyclic bromo phosphate ester (a) nearly 40% 's' character is involved in the σ bond to the exocyclic oxygen. Explain the fact with Bent's rule and comment. [3]

- d) What do you mean by Limiting radius ratio? Deduce the Limiting radius ratio for a body centered cubic Lattice. [2]

Group – C

7. Answer **any two** :
- a) i) Starting from Clausius inequality prove that for a spontaneous process at constant S and U, $\Delta E < 0$. [2]
ii) Starting from the expression of combined first and second law derive the thermodynamic equation of state (in terms of internal energy). [2]
- b) i) Any spontaneous endothermal process must always be associated with an increase of entropy. Explain. [2]
ii) 3 mole of an ideal gas (monoatomic) is expanded adiabatically from 27°C , 1 atm to 2 atm. Compute the corresponding entropy change. [2]
- c) i) Starting from the definition of G show that for any liquid $\bar{G} - \bar{G}_0 = \bar{V}(p - p_0)$ at const. temperature where G_0 is the free energy/mole at $p = p_0$. [2]
ii) Starting from Clausius inequality show that the entropy of the universe increases with time. [2]
8. Answer **any two** :
- a) i) For the reaction $3\text{H}_2(\text{g}) + \text{N}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$, the rate can be expressed in three ways. Write the rate expressions. [2]
ii) The decomposition of A to produce B can be written as $\text{A} \rightarrow \text{B}$. When the initial concentration of A is 0.012 M, the rate is 0.0018M min^{-1} and when the initial concentration of A is 0.024 M, the rate is 0.0036M min^{-1} . Write the rate law for the reaction. [2]
- b) i) The kinetics of acid-catalysed hydrolysis of ethyl acetate can be observed as the first order reaction with respect to the ester only. Explain. If it is a single step reaction, what is its molecularity? [2]

- ii) Use the following data for the reaction $\text{SO}_2 + \text{Cl}_2 \rightarrow \text{SO}_2\text{Cl}_2$, find out the partial orders. [2]

$[\text{SO}_2]/(\text{M})$	$[\text{Cl}_2]/(\text{M})$	Initial rate/ (Ms^{-1})
2.3×10^{-4}	3.1×10^{-5}	5.25×10^{-4}
4.6×10^{-4}	6.2×10^{-5}	4.20×10^{-3}
9.2×10^{-4}	6.2×10^{-5}	1.70×10^{-2}

- c) i) If the half-life for the reaction $\text{C}_2\text{H}_5\text{Cl} \rightarrow \text{C}_2\text{H}_4 + \text{HCl}$ is the same when the initial concentration of $\text{C}_2\text{H}_5\text{Cl}$ is 0.0050 M and 0.0078 M, what is the rate law for this reaction? Comment on the dimension of its rate constant. [2]
- ii) A hypothetical reaction goes as $\text{A} \rightarrow \text{P}$, $\text{A} \rightarrow \text{Q}$ and $\text{A} \rightarrow \text{R}$, simultaneously with 1st order kinetics. What will be the amount of P, Q and R after 't' time? Which one will be the kinetically controlled product? [2]

