

RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

SECOND YEAR [BATCH 2014-17]

B.A./B.Sc. FOURTH SEMESTER (January – June) 2016

Mid-Semester Examination, March 2016

Date : 17/03/2016

Time : 11 am – 1 pm

CHEMISTRY (Honours)

Paper : IV

Full Marks : 50

[Use a separate Answer Book for each group]

Group – A

Answer any one question :

1. a) Explain with the help of a μ vs T diagram the fact that freezing point/boiling point of a solvent changes when a solute is present.
[assume that the solute does not appear either in the vapour or in the solid phase] [5]
- b) i) Define an ideal solution.
ii) For such a solution prove that
$$\mu(T, X) = \mu_0(T) + RT \ln X$$

 $\mu_0 \rightarrow$ chem. potential of the pure solvent, $\mu \rightarrow$ chemical potential of the solvent in solution
 $X \rightarrow$ mole fraction of the solvent [2+1]
2. a) i) Define fugacity for a real gas. [1]
ii) Prove that fugacity and pressure of a real gas are related as
$$\ln f = \ln p + \int_0^p \frac{(Z-1)}{p} dp$$

(where Z is the compressibility factor) [5]
- b) Draw parallel between osmotic pressure of a soln. and pressure of an ideal gas. [2]

Answer any one question :

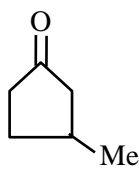
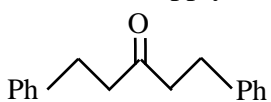

3. a) Define ionic mobility and find out its unit from the definition. [2]
b) At 298K, the resistance of a cell filled with 0.01M KCl solution is 780 ohm. The resistance of the same cell filled with water is 7422 ohm. Equivalent conductance values of H^+ and OH^- ions are 349.81 and 198.3 $S\ cm^2\ mol^{-1}$ respectively at 298K. The specific conductance of 0.01 M KCl solution at 298 K is $1.41 \times 10^{-3}\ S/cm$. Find out the value of ionic product of water at this temperature. [3]
c) Discuss the principle of conductometric titration (reasons of change of conductance before and after equivalence point, avoidance of volume effect). Draw the conductometric titration curve for the titration of NaOH solution versus acetic acid solution, the acid solution being added from a burette. [3]
4. a) Discuss the graphical method of determination of dissociation constant of a weak acid from conductance measurements at different concentrations. [3]
b) A moving boundary experiment is done to measure the transport number of Li^+ ion in 0.01mol/L LiCl solution. In a tube of cross-sectional area $0.125\ cm^2$, the boundary moves through 7.3 cm in 1490s using a current of $1.8 \times 10^{-3}\ amp$. Calculate t_+ . [2]
c) 25ml of 0.1 M HCl solution is taken in a conductivity cell having cell constant $1.00\ cm^{-1}$. The resistance of this solution is found to be A ohm. After addition of 25ml 0.1 M NaOH solution to the cell, the new resistance is B ohm. What is the sign of (A-B)? What is the expression of the equivalent conductance of the resultant solution in terms of B? Explain your answer. [3]

Group – B

Answer any one question :

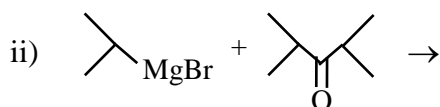
5. Carry out the following conversions as directed. Mechanism is not necessary.

[3+2.5+2.5]

- a) Diethyl adipate \rightarrow  (use Me_2CuLi)
- b) $\text{Me}_2\text{CO} \rightarrow \text{Me}_2\text{CHCHO}$ (apply Wittig reaction)
- c) $\text{PhMgBr} \rightarrow$  (Use )

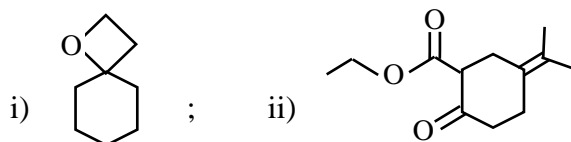
6. a) Predict the major product of the following reactions.

[2]



b) Give retrosynthetic analysis and an efficient synthesis of the following compounds starting from RASM.

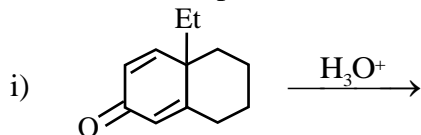
[2×3]



Answer any one question :

7. a) Write down the product(s) with mechanism.

[2×2]



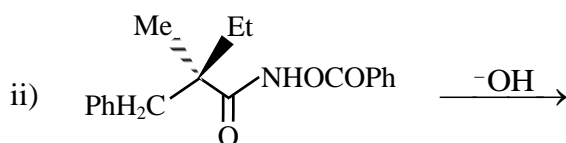
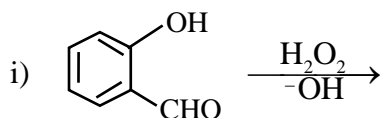
b) Carry out the following conversions.

[2×2]

- i) Benzaldehyde to Diphenylacetic acid
ii) O-xylene to anthranilic acid

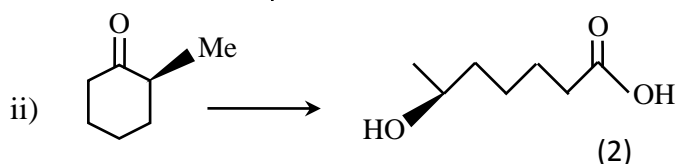
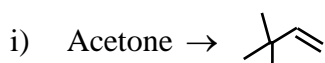
8. a) Write down the product(s) with mechanism

[2×2]



b) Carry out the following conversions

[2×2]



Group – C

Answer any one question :

9. a) Explain catenation. How does the catenating tendency of elements vary for group 14 elements. [1+3]
b) Which one, Tl^+ or Tl^{+3} , is more stable? Why? [2]
c) Which one, BF_6^{-3} or AlF_6^{-3} exists? Why? [2]
d) Draw the structure of graphitic form of boron nitride. [1]
10. a) Discuss the structure of borazine. Explain why it is more reactive than benzene. Give two reactions in support to your answer. [2+2+2]
b) What are the differences between silanes and alkanes? [3]

Answer any one question :

11. a) How did Bertlett interpret the reaction Xe and PtF_6 and how is this reaction now interpreted? [3]
b) NCl_3 (not NF_3) hydrolyses readily, while CCl_4 hydrolyses with decomposition at high temperature. Why? [3]
c) Discuss the structural features of PX_5 (where X = halogen) at gas and solid phase. [3]
12. a) Molecular formulae of nitrogen and phosphorus are different. Why? [2]
b) Discuss the molecular orbital bonding pattern of XeF_2 . [3]
c) Explain the thermal stability of MH_3 (M = As, Sb, Bi). [2]
d) What will happen when manganese (II) salt solution is treated with sodium bismuthate
i) in H_2SO_4 and
ii) HCl medium? [2]

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