

2009  
CHEMISTRY - II (Optional)

100073

Standard : Degree

Total Marks : 200

Nature : Conventional

Duration : 3 Hours

Note :

- (i) Answers must be written in **English**.
- (ii) Question No. 1 is **Compulsory**. Of the remaining questions, attempt **any four** selecting one question from **each section**.
- (iii) Figures to the **RIGHT** indicate marks of the respective question.
- (iv) Use of log table, non-programmable calculator is permitted, but any other table/code/reference book are not permitted.
- (v) Make suitable assumptions, wherever be necessary and state the same.
- (vi) Number of optional questions upto the prescribed number in the order in which they have been solved will only be assessed. Excess answers will not be assessed.
- (vii) Credit will be given for orderly, concise and effective writing.
- (viii) Candidate should not write roll number, any name (including their own), signature, address or any indication of their identity anywhere inside the answer book otherwise he/she will be penalised.
- (ix) For each slab of 10 and 15 marks, the examinee is expected to write answers in 125 and 200 words respectively.

1. Answer **any four** of the following questions :

- (a) What product would be obtained from the hydroboration oxidation of  $(\text{CH}_3)_2\text{-C=CH}_2$  ? Explain with a suitable mechanism. 10
- (b) Explain Fischer Indole synthesis with a suitable example along with the reaction mechanism. 10
- (c) What are nucleotides ? Draw the structures of bases that are present in DNA and RNA. 10
- (d) Explain how photochemical reactions occur and state Grothus - Draper law and Stark - Einstein law of photochemistry. 10
- (e) Write the products and mechanism of the reaction of  $\text{Na/NH}_3(l)/\text{C}_2\text{H}_5\text{OH}$  with 2-butyne. 10

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## SECTION - A

2. (a) Discuss the hybridization of carbon in  $\text{CH}_4$  and  $\text{C}_2\text{H}_2$ . What is the shape and bond angles of these molecules ? 10
- (b) (i) Write the structures of all the possible conformers of methyl cyclohexane. Indicate the most stable conformer with suitable explanation. 10
- (ii) Write the Fischer projection formula of 2-bromo-3-chlorobutane. Indicate the R and S configurations of all the possible stereoisomers and indicate their relationship with each other.
- (c) What is Beer-Lambert's law ? Discuss the application of this law in UV spectroscopy. 10
- (d) An organic compound has the molecular formula  $\text{C}_9\text{H}_{10}\text{O}$ . Its IR spectrum contains bands at  $1680\text{ cm}^{-1}$ ,  $3000\text{ cm}^{-1}$ ,  $1600\text{ cm}^{-1}$  and  $1440\text{ cm}^{-1}$ . No absorption was observed at  $2700\text{ cm}^{-1}$ . Its NMR spectrum shows the following. A triplet at 1.2 ppm, a quartet at 3.0 ppm and a multiplet at 7.4–8.0 ppm with integration ratio 3 : 2 : 5 respectively. Identify the compound with reasoning. 10
3. (a) (i) Arrange the carbocations  $\text{CH}_3\text{CH}_2^+$ ,  $(\text{CH}_3)_3\text{C}^+$  and  $(\text{CH}_3)_2\text{CH}^+$  in the increasing order of stability and justify your answer. What is the hybridization of C in  $\text{CH}_3^+$  ? 10
- (ii) What is the reactive intermediate formed when 1-chloro-4-methylbenzene is treated with  $\text{NaNH}_2$  ? The rate constant for the elimination reaction of 1-bromo-2-phenyl ethane is 7.0 times higher than that of the reaction of 2-bromo-1, 1-dideuterio-1-phenyl ethane. Explain why ?
- (b) (i) A sample of (S) – (+) lactic acid was found to have an optical purity of 72%. What is the percentage of R isomer present in the sample ? 10
- (ii) Explain in detail any one method of resolution of enantiomers with a suitable example.
- (c) An organic compound with molecular formula  $\text{C}_7\text{H}_6\text{O}$  shows a positive silver mirror test and it burn with a sooty flame. Its IR spectrum contains bands at  $3080\text{ cm}^{-1}$ ,  $2760\text{ cm}^{-1}$ ,  $1735\text{ cm}^{-1}$ ,  $1615\text{ cm}^{-1}$  and  $1500\text{ cm}^{-1}$ . Predict the structure of the molecule with suitable reasoning. 10
- (d) An organic compound has the molecular formula  $\text{C}_5\text{H}_{10}\text{O}$ . Its NMR spectrum contains the following peaks. 1.2 ppm (triplet) ; 2.5 ppm (quartet) with integration ratio 3 : 2. Identify the compound with suitable explanation of the spectral data. 10

## SECTION - B

4. (a) (i) Write the major product of the reaction of benzonitrile with nitric acid and small amount of sulphuric acid at high temperatures. Explain the reaction with a suitable mechanism. 10
- (ii) Discuss the mechanism of the reaction of benzoyl chloride with excess aniline.
- (b) Discuss the mechanism of the acid catalysed pinacol - pinacolone re-arrangement. 10
- (c) Write the product of the following reaction cyclohexanone  $\xrightarrow[\text{heat}]{\text{H}_2\text{N}-\text{NH}_2, \text{KOH}}$ . 10
- Suggest a suitable mechanism for the reaction.
- (d) What is the product of the following reaction ? 10
- Phthalimide + KOH +  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br} \xrightarrow[\text{heat}]{\text{H}_2\text{N}-\text{NH}_2}$  ?
- Explain the mechanism of the reaction.
5. (a) (i) Predict the product of the following reaction : 10
- $\text{C}_6\text{H}_5\text{COOH} + \text{Na}/\text{NH}_3(l) + \text{C}_2\text{H}_5\text{OH} \longrightarrow ?$
- Write the major steps of the reaction.
- (ii) What is the product formed in the reaction
- $\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl} + \text{Na}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}_6\text{H}_5$  ? Write the major steps of the reaction.
- (b) Phenol is treated with  $\text{K}_2\text{CO}_3$  at  $150^\circ\text{C}$  and under 100 bar pressure of  $\text{CO}_2$ . Suggest a mechanism for the reaction and predict the product. 10
- (c) How does  $\text{CH}_3\text{CHO}$  react with aq. NaOH at high temperatures ? Explain the reaction mechanism. 10
- (d) Aniline is treated with  $\text{NaNO}_2 / \text{HCl}$  at  $5^\circ\text{C}$ . Write the product of this reaction. The product is further treated with KI. What is the reaction ? Suggest the mechanism of the first reaction. 10

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## SECTION - C

6. (a) What product is expected when 2 moles of  $\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OC}_2\text{H}_5$  are treated with  $\text{NaOC}_2\text{H}_5$  in  $\text{C}_2\text{H}_5\text{OH}$ ? Write the mechanism of this reaction. 10
- (b) What are monosaccharides? Explain their classification with suitable examples. Based on the structure, how is their configuration determined? 10
- (c) What is condensation polymerization? Explain the formation of polyesters and polyamides with suitable stoichiometric equations. 10
- (d) (i) Discuss the synthesis of Indigo dye. 10  
(ii) Write in brief any five principles of green chemistry.
7. (a) In the following conversion, 10
- $$\text{C}_2\text{H}_5\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OC}_2\text{H}_5 \xrightarrow[\text{(ii) R-X}]{\text{(i) NaOC}_2\text{H}_5} \text{A} \xrightarrow[\text{heat}]{\text{H}_3\text{O}^+} \text{B}$$
- Identify A and B. Write the mechanism for the formation of A and B.
- (b) Write a short note on disaccharides and polysaccharides. 10
- (c) Discuss the polymerization of ethylene in presence of  $\text{R}_3\text{Al} / \text{TiCl}_4$  catalyst. 10
- (d) (i) Write a short note on the classification of synthetic dyes. 10  
(ii) Discuss the concept of 'Atom Economy' in green chemistry with a suitable example.

## SECTION - D

8. (a) (i) State Kohlrausch's law of independent migration of ions. If the equivalent conductance at infinite dilution ( $\lambda_\infty$ ) of  $\text{HCl}$ ,  $\text{NaCl}$  and  $\text{CH}_3\text{COONa}$  are 426.16, 126.45 and 91.01  $\text{ohm}^{-1} \text{cm}^2 \text{eq.}^{-1}$  respectively, calculate  $\lambda_\infty$  of  $\text{CH}_3\text{COOH}$  at the same temperature,  $25^\circ\text{C}$ . 10  
(ii) Discuss the Debye-Huckel theory of strong electrolytes.
- (b) (i) An electrochemical cell is made of Standard Hydrogen Electrode (SHE) and a  $\text{Ag} / \text{AgCl}$  electrode.  $E^\circ \text{Ag}^+ / \text{Ag} = 0.222 \text{ V}$  at  $25^\circ\text{C}$ . Write the half cell reactions at both the electrodes. 10

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- (ii) Calculate  $E^\circ$  of the reaction  $\text{Cu}^+ + e^- \longrightarrow \text{Cu}$ , using the following  $E^\circ$  values.  
( $F = 96,500$  Coulombs).
- (1)  $\text{Cu}^{2+} + e^- \longrightarrow \text{Cu}^+ \quad E_1^\circ = 0.153 \text{ V}$
- (2)  $\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu} \quad E_2^\circ = 0.337 \text{ V}$
- (c) (i) State any two postulates of quantum mechanics. 10
- (ii) Write the time independent Schrodinger equation. What information can be obtained from this equation ?
- (d) (i) Give any three applications of computers in chemistry. 10
- (ii) State any two devices on which computer data can be stored. What is CPU of a computer ?
9. (a) (i) Discuss the conductometric titration of  $\text{NaOH}$  vs  $\text{HCl}$  with the suitable plot of titration. 10
- (ii) Discuss the Standard Hydrogen Electrode (SHE). Give one application of the electrochemical series.
- (b) (i) The emf of the following cell  
 $\text{Pt}, \text{H}_2 (1 \text{ bar}) | \text{HCl} (0.01\text{M}) | \text{AgCl} (s) | \text{Ag}$  is  $0.2002 \text{ V}$  at  $25^\circ\text{C}$ . Write the cell reactions. Calculate the free energy change ( $\Delta G$ ) of the overall cell reaction. 10
- (ii) Discuss galvanic corrosion. Give any one method for its prevention.
- (c) (i) Explain magnetic quantum number and spin quantum number. 10
- (ii) What is the significance of the wave function,  $\psi$  ? Write the expression for the possible stationary-state energies for a particle in a one dimensional box.
- (d) (i) Write a brief note on molecular modelling. 10
- (ii) Give any one application of each of the following softwares.  
 $\text{MS-Excel}$ ,  $\text{MS-Power Point}$ .

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