

West Bengal State University
B.A./B.Sc./B.Com (Honours, Major, General) Examinations, 2015

PART - I
CHEMISTRY — HONOURS

Paper - I

Duration : 4 Hours]

[Full Marks : 100

The figures in the margin indicate full marks.

Use separate answer scripts for
[CEMAT-11 IA & CEMAT-11 IB] & [CEMAT-11 OA & CEMAT-11 OB]

CEMAT-11-IA

Answer any *two* questions taking *one* from each Unit.

UNIT - I

1. a) The last electron of an atom in the ground state enters as d^5 configuration. What will be the electronic configuration of the element ? Show the distribution of electrons in the valence shell. 2
- b) What do you understand by K-electron capture ? 2
- c) Who explained the fine structure of spectral lines in the hydrogen spectrum ? What were his extensions ? 2
- d) An atom 'X' is bombarded with α -particle and produce (i) an atom 'Y' and proton in one path, (ii) atom 'M' and neutron in another path. 'M' disintegrates to ^{30}Si and positron. Identify 'X', 'Y', 'M' and explain the phenomenon with reactions. 4
- e) Energy of an excited electron of He^+ ion is - 6.04 eV. Calculate the angular momentum of that excited electron from Bohr's theory. (Given energy of 1st Bohr orbit of hydrogen = - 21.8 $\times 10^{-19}$ J, 1 eV = 1.6 $\times 10^{-19}$ J, $h = 6.6203 \times 10^{-34}$ Js) 3
2. a) Find out the spectroscopic ground state term symbols for MO^{3+} ion. 2
- b) A sample of ^{238}U ($\lambda = 0.154 \times 10^{-9}$ year $^{-1}$) ore is found to contain 23.8 gm of ^{238}U and 'X' gm of ^{206}Pb . The age of the ore is 4.5×10^9 years. Calculate the amount of ^{206}Pb (X) present in the ore. 2

- c) Identify X and Y and classify the following two radioactive reactions into spallation and fission reactions :

When ${}^{63}_{29}\text{Cu}$ is bombarded with protons it produces one proton, one neutron, six ${}^4_2\text{He}$ and 'X' in one path. In another path ${}^{38}_{17}\text{Cl}$, 'Y' and one neutron is formed.

- d) State Hund's rule of maximum multiplicity. Explain it with example. 1 + 2
 e) What do you understand by liquid drop model ? 2
 f) Calculate the principal quantum number where the electron is revolving in a H-atom, when its kinetic energy is 217.945×10^{-20} J.
 (Given : E_1 for H = -871.78×10^{-20} J) 2

UNIT - II

3. a) Explain the irregularities in the increase of I.E. on going from nitrogen to oxygen. Also explain the 2nd I.E. of Be and B. 3
 b) Calculate the E.N. of Si in the compound SiO_2 .
 (Given, $X_p(\text{O}) = 3.53$, $E_{\text{O-Si}} = 372.46$ kJ/mol, $E_{\text{O-O}} = 138.1$ kJ/mol, $E_{\text{Si-Si}} = 179.95$ kJ/mol) 3
 c) Why does lithium resemble magnesium more than sodium ? 2
 d) "Ionization enthalpy of hydrogen is 1312 kJ mol $^{-1}$ compared to that of Li, 520 kJ mol $^{-1}$." Explain. 2
 e) Why the atomic radii of Nb and Ta are 147 pm although they do not belong to the same position of the periodic table ? 2
 4. a) Write down the electronic configuration of Gd^{3+} ion ($Z = 64$). 1
 b) " PbCl_4 is very unstable and oxidising." Explain. 2
 c) Discuss whether coinage metals and Zn-families can be considered as transition metals or not. 2
 d) Establish a relation of r_+ and r_- with Z^+ in Pauling's univalent radii method. For which ion pairs is the relation applicable ? Give examples. 3
 e) Calculate $X_p(\text{F})$ from the following data :
 $\text{EA}(\text{F}) = 3.62$ eV/atom, $\text{I.P.}(\text{F}) = 17.4$ eV/atom. 2
 f) What is lanthanide contraction ? What is its effect ? 2

CEMAT-11-IB

Answer any two questions taking one from each Unit.

UNIT - I

5. a) Draw the canonical structures of SCN^- and OCN^- ions showing the formal charges on each atom and predict therefrom the most stable structure with proper reasons. 3
- b) The μ_{obs} of KCl is 3.336×10^{-29} C-m. The distance between K^+ and Cl^- ion (d_{KCl}) is 2.6×10^{-10} m. Calculate the % ionic character of KCl. 2
- c) Write down Born-Landé's equation for one mole ionic lattice. Explain the term involved in the equation and mention the physical significances of the terms A and n . 3
- d) Predict between CsCl and AuCl, which is likely to be more ionic and why? 2
- e) Using Bent's rule, explain why $\dot{\text{C}}\text{H}_3$ radical is planar whereas $\dot{\text{C}}\text{F}_3$ radical is pyramidal. 3
6. a) Predict the actual structures of ClF_3 and SF_4 on the basis of VSEPR theory and Bent's rule and hence state the hybridization of the central atom. 4
- b) "Carbon atom prefers to form π -bonds whereas silicon in the same group prefers to form σ -bonds." Explain this statement with proper example. 3
- c) Define proton affinity with example. Calculate proton affinity of NH_3 from the following data for the formation of NH_4Br .
(Given, $I_{\text{H}} = 1311.7$ kJ/mol, $D_{\text{HBr}} = 411$ kJ/mol,
 $\Delta H_{\text{NH}_4\text{Br}} = -170.02$ kJ/mol, $E_{\text{A}_{\text{Br}}} = -328$ kJ/mol, $U = -670.19$ kJ/mol) 1 + 2
- d) Explain the following order of polymerisation tendency of the following anions : 3
 $\text{SiO}_4^{4-} > \text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{ClO}_4^-$

UNIT - II

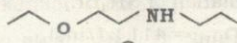
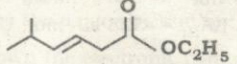
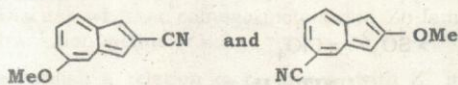
7. a) Show the auto ionisation of HF. On that basis does CH_3COOH act as a base in liquid HF? 3
- b) Predict the direction of the reaction and give explanation : 3
- i) $\text{CuI}_2 + \text{Cu}_2\text{O} \rightleftharpoons 2\text{CuI} + \text{CuO}$
- ii) $\text{La}_2(\text{CO}_3)_3 + \text{Tl}_2\text{S}_3 \rightleftharpoons \text{La}_2\text{S}_3 + \text{Tl}_2(\text{CO}_3)_3$

- c) Write down the Pauling's rule for predicting acid strength of oxyacids. Using these rules explain the first pK_a values of H_3PO_2 ($pK_1 = 2.0$) and H_3BO_3 ($pK_1 \approx 9$) with respect to their structural difference if any. 4
- d) Classify the following species into acids and bases and give their corresponding conjugate bases or acids : 2
 NH_4^+ , HS^- , HCO_3^- , H_2O
8. a) 20 ml of a weak acid HX of strength 0.02 (N) is titrated with 20 ml of a strong base YOH of strength 0.02(N). Calculate the pH when (i) 19.9 ml of YOH is added and (ii) at the equivalent point. Choose a suitable indicator from the above pH values. ($pK_{HX} = 4.7$) $1\frac{1}{2} + 1\frac{1}{2} + 1$
- b) What are levelling and differentiating solvents? Give suitable example and explain their functions. 3
- c) Give examples of buffer solutions which can be obtained by (i) mixing two salts, (ii) using a bi-salt. 1
- d) What are the criteria of soft and hard acids & bases? 2
- e) Calculate the pH of a solution by mixing 40 ml 0.125 (M) NH_3 and 60 ml of 0.03334(M) HCl. (Given K_b of $NH_3 = 1.8 \times 10^{-5}$) 2

CEMAT-11-OA

Answer any two questions taking one from each Unit.

UNIT - I

1. a) Give the I.U.P.A.C. names of the following compounds : 2
- i) 
- ii) 
- b) Compare dipole moments of the following compounds with proper reason : 2
- 
- c) Draw orbital picture of $CH_3CH=C=O$. 2
- d) What is meant by the term 'nucleophilicity'?
 Arrange the following anions in the order of increasing nucleophilicity and give reasons for your answer :
 R_2N^- , R_3C^- , F^- , RO^- 1 + 2

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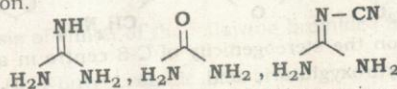
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1 + 2

- e) Tertiary butyl alcohol is miscible in water in all proportions but 1-butanol is only partially miscible. Account for the observation. 2
- f) Show the HOMO of allyl free radical (Ground state configuration) and LUMO of 1, 3, 5-hexatriene (excited state). 2
2. a) Compare and explain the difference in 'C = C' bond lengths in CH₂=CH₂ and CH₃CH=CH₂. 2
- b) Arrange the following compounds in order of increasing basic strength. Give reason. 3

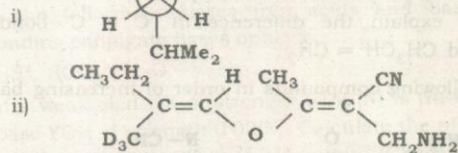
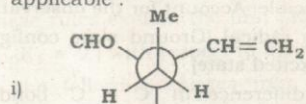


- c) Arrange the following ions in order of increasing stability. Give reason. 2
- (i) $\text{CH}_3\text{C}^+\text{HCH}_3$ (ii) Cyclopropyl^+ (iii) Cyclopropyl^+ (iv) Cyclopropyl^+
- d) Account for the following observations: 2 + 2
- i) 18-crown-6 greatly increases the nucleophilicity of cyanide ion where KCN is used as the source of the cyanide ion.
- ii) The heat of combustion of isobutene is lower than that of 1-butene, even though the two isomers have the same number of C-C, C=C and C-H bonds.
- e) While the pK_{a1} of maleic acid is 1.9 and that of fumaric acid is 3.03; pK_{a2} of fumaric acid is 4.44 and that of maleic acid is 6.07. Explain. 2

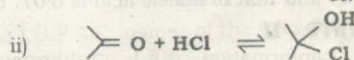
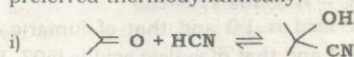
UNIT - II

3. a) Draw the most stable conformation of 1, 2-dibromoethane and HOCH₂CH₂F and justify your answer. 2
- b) Draw Fischer projection formula of (2R, 3S)-3-phenyl-2-butanol and convert it into flying wedge notation. 2
- c) A and B react at a certain temperature to give C as the major product. At a higher temperature they give a product D, which is more stable than C as the major product. Explain this phenomenon with suitable energy profile diagram and comment on the product ratio with variation of temperature. 3
- d) Indicate the symmetry elements present in
- i) 1, 3-dichloroallene
- ii) 2
- e) Draw the conformational energy profile for rotation around C₂-C₃ bond of meso-2,3-butane-diol and draw the conformers. 3

4. a) Assign R/S or E/Z descriptors to the following stereostructure as applicable: 2



- b) Comment on the stereogenicity of C-3 centre in all the stereoisomers of 2, 3, 4-trihydroxyglutaric acid. 3
- c) Bromination of toluene and isopropyl benzene by NBS show $K_H/K_D = 4.9$ and 1.8 respectively. What type of kinetic isotope effect is observed in these reactions? Draw an energy profile diagram by showing the relative positions of the transition states of the rate determining steps. 3
- d) Calculate ΔH° for the following two reactions from the bond dissociation energy (BDE) data provided and identify with reasoning which one is preferred thermodynamically.



BDE (kcal/mole): H-Cl (103) H-CN (130)
C-Cl (84) C-CN (122)

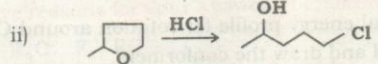
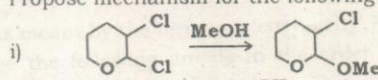
- e) Calculate the optical purity of a sample of 2-butanone which has specific rotation $+3.4$. What is the enantiomeric composition of the above mixture? (Optically pure sample of (R)-2-butanol is $+13.6$) 2

CEMAT-11-OB

Answer any *two* questions taking *one* from each Unit.

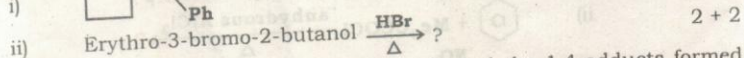
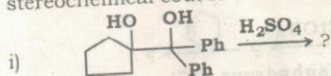
UNIT - I

5. a) Propose mechanism for the following reactions and explain.

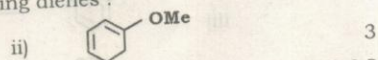
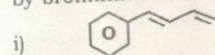


2 + 2

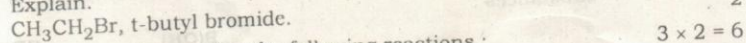
- b) Predict the product(s) of the following reactions. Suggest mechanism and stereochemical course of these reactions as applicable :



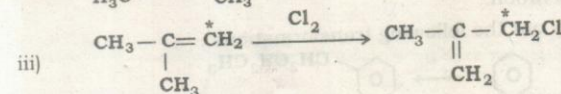
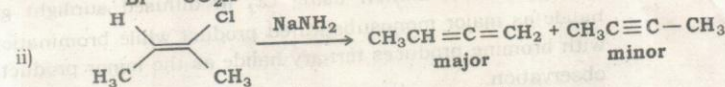
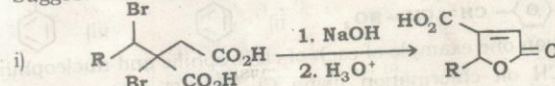
- c) Predict the regiochemistry of both the 1,2- and the 1,4-adducts formed by bromination of each of the following dienes :



- d) Hydrolysis of which of the following bromides may be catalysed by NaI ? Explain. 2



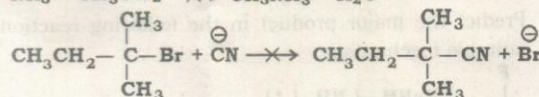
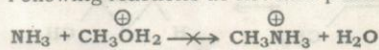
6. a) Suggest mechanism for the following reactions :



- b) Explain the following observations :

- i) Electrophilic additions of H-X to alkenes are much faster in water than that of in gas phase. 2

- ii) Following reactions do not take place as indicated : 2

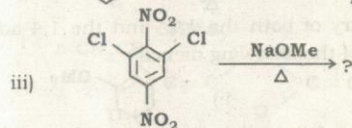
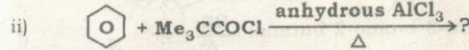
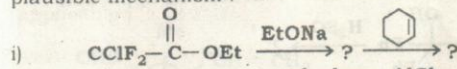


- c) Write down the structure of the ozonides if 2, 3-dimethyl-1-butene is subjected to ozonolysis in presence of formaldehyde. Give mechanism of ozonide formation. 3

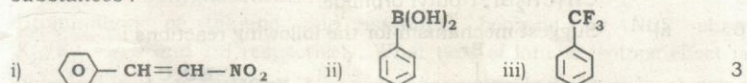
UNIT - II

7. a) What are electrophilic and nucleophilic radicals ? Give appropriate examples. 2

- b) Predict the major product of the following reactions and suggest plausible mechanism : $3 \times 2 = 6$

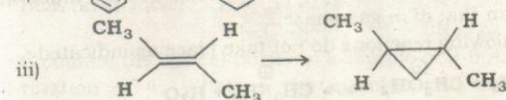
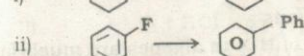
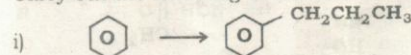


- c) Explain the fate of aromatic electrophilic substitution for the following substances :

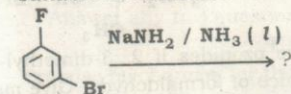


- d) Mention one example of each of electrophilic and nucleophilic carbene. 1
8. a) Me_3CH on chlorination using Cl_2 in diffused sunlight gives primary halide as major monosubstituted product while bromination by heating with bromine produces tertiary halide as the major product. Justify this observation. 3

- b) Carry out the following transformations : $3 \times 2 = 6$



- c) Predict the major product in the following reaction and explain with a suitable mechanism : 2



- d) "Both $\text{C}_6\text{H}_5\text{NO}_2$ and $\text{C}_6\text{D}_5\text{NO}_2$ undergo nitration at the same rate." Justify the statement. 1