



CEMA(HN)-01

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 = -21.8×10^{-19} J, $1 \text{ eV} = 1.6 \times 10^{-19}$ 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

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[Turn over

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

When ${}_{29}^{63}\text{Cu}$ 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. 2

- 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^{\wedge} 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 :
 $\text{SiO}_4^{4-} > \text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{ClO}_4^-$. 3

UNIT - II

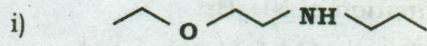
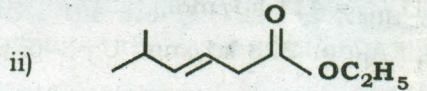
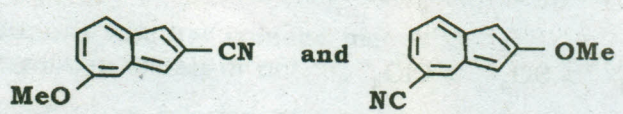
7. a) Show the auto ionisation of HF. On that basis does CH_3COOH act as a base in liquid HF? 3
- b) Predict the direction of the reaction and give explanation :
 i) $\text{CuI}_2 + \text{Cu}_2\text{O} \rightleftharpoons 2\text{CuI} + \text{CuO}$
 ii) $\text{La}_2(\text{CO}_3)_3 + \text{Tl}_2\text{S}_3 \rightleftharpoons \text{La}_2\text{S}_3 + \text{Tl}_2(\text{CO}_3)_3$ 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 :
 NH_4^+ , HS^- , HCO_3^- , H_2O 2
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

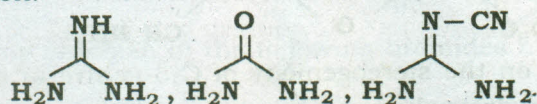
CEMAT-11-OA

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

- 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 $\text{CH}_2 = \text{CH}_2$ and $\text{CH}_3\text{CH} = \text{CH}_2$. 2
- b) Arrange the following compounds in order of increasing basic strength. Give reason. 3

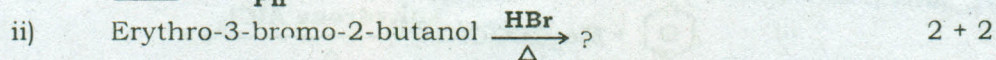
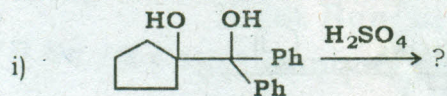


- c) Arrange the following ions in order of increasing stability. Give reason. 2
- (i) $\text{CH}_3\text{CHCH}_3^{\oplus}$ (ii) (iii) (iv)
- d) Account for the following observations : 2 + 2
- i) 18-crown-6 greatly increases the nucleophilicity of cyanide ion where KCN is used as the source of the cyanide 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 $\text{p}K_{a1}$ of maleic acid is 1.9 and that of fumaric acid is 3.03; $\text{p}K_{a2}$ of fumaric acid is 4.44 and that of maleic acid is 6.07. Explain. 2

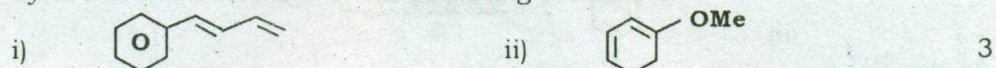
UNIT - II

3. a) Draw the most stable conformation of 1, 2-dibromoethane and $\text{HOCH}_2\text{CH}_2\text{F}$ 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 $\text{C}_2 - \text{C}_3$ bond of meso-2,3-butane-diol and draw the conformers. 3

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



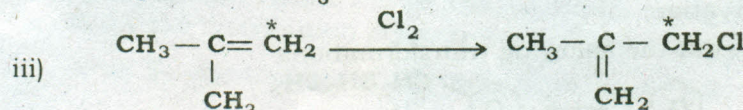
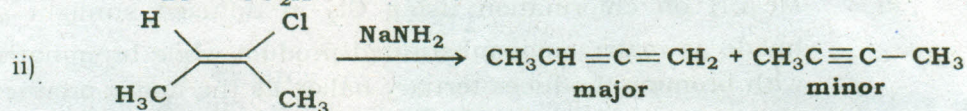
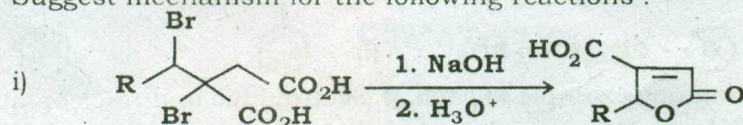
- c) Predict the regiochemistry of both the 1,2- and the 1,4-adducts formed by bromination of each of the following dienes :



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



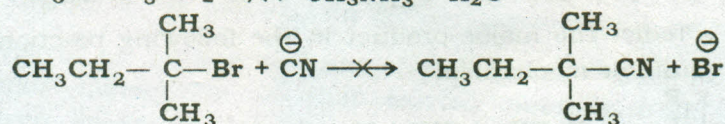
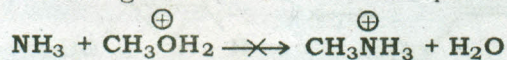
6. a) Suggest mechanism for the following reactions : 3 × 2 = 6



- 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

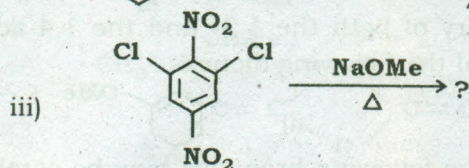
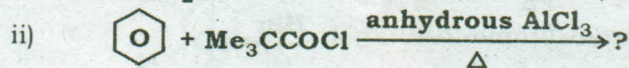
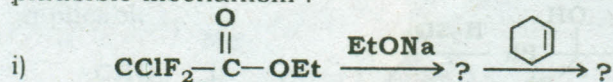


- c) Write down the structure of the ozonides if 2, 3-dimethyl-1-butene is subjected to ozonolysis in presence of formaldehyde. Give mechanism of ozonide formation. 3

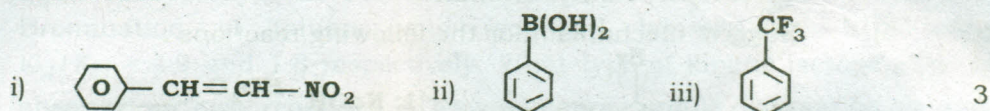
UNIT - II

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 × 2 = 6



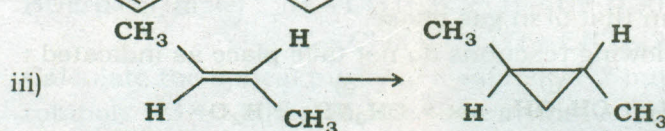
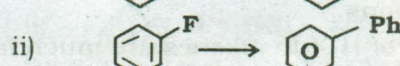
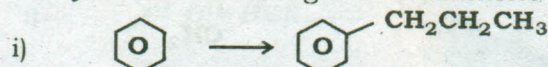
- c) Explain the fate of aromatic electrophilic substitution for the following substances :



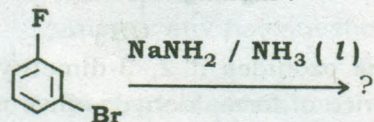
- d) Mention one example of each of electrophilic and nucleophilic carbene. 1

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 × 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