

West Bengal State University
B.A./B.Sc./B.Com. (Honours, Major, General) Examinations, 2013
Part - I

CHEMISTRY — HONOURS

Paper - I

Duration : 4 Hours

[Maximum Marks : 100

Candidates are required to give their answers in their own words as far as practicable.

The figures in the margin indicate full marks.

Use separate answer scripts for CEMAT-11-IA/IB and CEMAT-11-0A/OB

CEMAT - 11-IA

(Full Marks : 50)

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

UNIT - I

1. a) What are nuclear isomers ? Cite an example where a metastable nucleus has been used. 2 + 1
- b) Explain with the help of a binding energy curve why the heavier nuclides undergo fission to produce stable nuclides. 2
- c) Obtain an expression for the total energy of an electron in the He^+ ion. On the basis of Bohr's equation for energy levels of single electron system, calculate the 2nd I.E. of He [given that the 1st I.E. of H is 1312 kJ/mol]. 3 + 2
- d) Find out the spectroscopic ground state term symbols for Cu^{2+} and Cr^{2+} ions. 3

2. a) A piece of wood sample is found to have activity 20% compared to that of a fresh wood. Find the age of the wood sample [given that the $t_{1/2}$ of ^{14}C is 5578 years]. 4
- b) Why does ^{235}U undergo fission on capture of slow neutrons whereas ^{238}U requires fast neutrons for fission ? 3
- c) What is spallation reaction ? How does it differ from nuclear fission ? 3
- d) Comment on the penetrating power and relative energy of the $3p$ and $3d$ orbitals with the help of the radial probability distribution curve. $2 \times 1 \frac{1}{2}$

UNIT - II

3. a) Calculate the electronegativity of As [given that r_{cov} for As is 120 pm]. 4
- b) How do you account for the similarities in the properties of Zr and Hf ? 2
- c) Define electron affinity. Explain the electron affinity values given below with reasons.

$\text{C} (122) : \text{N} (203) : \text{O} (141) \text{ kJ/mol.}$ 2 + 3

- d) Write the IUPAC names of the elements with atomic numbers 117 and 118. 1
4. a) Calculate Z^* for a $3p$ electron in P, S, Cl and Ar. Hence predict the relative size of the atoms. 4 + 2
- b) How can you explain the noble like character of the post lanthanide elements like Pt and Au ? 3
- c) How does electronegativity change with hybridisation and bond order ? 3

CEMAT - 11-IB

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

UNIT - I

5. a) Calculate the electron affinity of chlorine from the following data :
- $\Delta H_f(\text{LiCl}) = -405.9 \text{ kJ/mol}$, $\Delta H_{\text{sub}}(\text{Li}) = 163.2 \text{ kJ/mol}$,
 $\Delta H_{\text{diss}}(\text{Cl}_2) = 242.7 \text{ kJ/mol}$, $\Delta H_{\text{IE}}(\text{Li}) = 518.9 \text{ kJ/mol}$ and
 $U_{\text{LiCl}} = -841.2 \text{ kJ/mol}$. 4
- b) Why does ZnO change colour to yellow when heated? 2
- c) Which of the following molecules have permanent dipole moment?
 PCl_3 , BCl_3 , XeF_4 and SF_4 2
- d) Why are the hydrolytic products of NCl_3 and PCl_3 different? 2
- e) NH_4F crystallizes in ZnS structure though a NaCl structure is expected from the radius ratio value. Explain. 3
6. a) How do you calculate the lattice energy values for the ionic solids with unknown crystal structures? 3
- b) Predict the shapes of the following ion and molecule from VSEPR theory.
 I_3^- and XeO_2F_2
- Show an example where VSEPR theory fails to explain the shape. 4 + 2
- c) Explain why the molecular formulae of nitrogen and oxygen are N_2 and O_2 respectively but those of phosphorus and sulphur are P_4 and S_8 respectively. 2
- d) How can you account for the lower *mp* of AgCl (455°C) than KCl (776°C)? 2

UNIT - II

7. a) Why does SbF_5 increase the acidity and conductivity of liquid HF but NaF reduces its acidity ? 3
- b) Why do the heavier transition metal ions prefer to bind with the S-donor ligands than the O-donor ligands ? 2
- c) Draw an acid-base neutralisation curve for the titration of a weak acid by a strong base and hence predict the choice of indicator. 2 + 1
- d) Calculate the concentration of NH_4^+ and H_3O^+ ions in a 0.1 (m) solution of ammonia. ($K_b = 1.8 \times 10^{-5}$) . 2
- e) Why the pH of the ammonium acetate solution is independent of its concentration ? 2
8. a) Predict the pK_1 values of the following oxo-acids using Pauling's rule :
 HClO , H_3PO_4 and H_3PO_3 .
 Will the pK_1 value of H_3PO_3 deviate from that of the expected value ? If so, why ? 3 + 2
- b) The colour of the metal-ammonia solution is independent of the nature of the metal used. Explain. 2
- c) Arrange the following in the increasing order of Lewis acidity :
 SiF_4 , SiCl_4 , SiBr_4 and SiI_4 . 2
- d) Find out the pH of a mixture containing 9 ml 0.2 (N) CH_3COOH and 191 ml 0.2 (N) CH_3COONa .
 ($K_a = 1.8 \times 10^{-5} \text{ mol/dm}^3$) 3

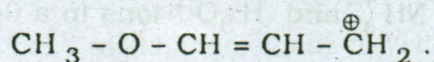
CEMAT - 11-0A

(Full Marks : 50)

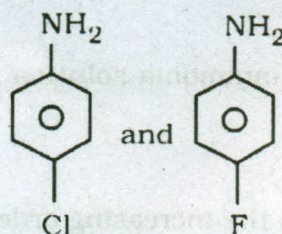
Answer any two questions, taking one from each Unit.

UNIT - I

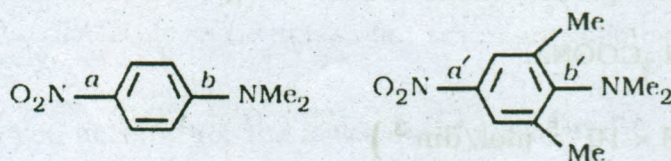
1. a) Show the canonical forms of the following carbocation and which has the greater contribution towards the resonance hybrid.



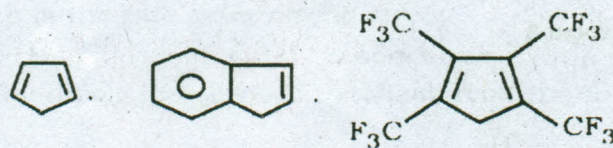
- b) Calculate the double bond equivalent (DBE) of $\text{C}_{12}\text{H}_{15}\text{N}_2\text{Cl}$.
- c) Draw the orbital picture of $\text{CH}_3\text{CH} = \text{C} = \text{CHCl}$. Indicate the state hybridisation of each carbon atom.
- d) Diethyl ether is less soluble than tetrahydrofuran in water. Explain.
- e) Compare the dipole moments of ethyl chloride and vinyl chloride.
- f) Explain which one of the following two molecules has higher basicity.



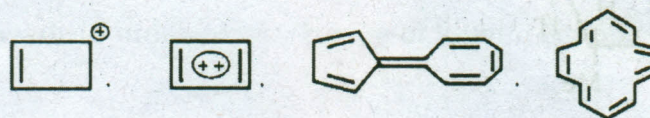
- g) Compare the C - N bond lengths (a vs a') and (b vs b') in the following compounds :



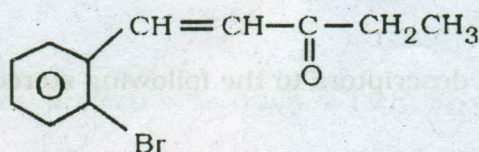
2. a) Arrange the following compounds in order of increasing pKa values. Give reason. 2



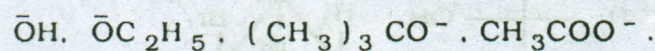
- b) State with reason whether the following species are aromatic, anti-aromatic or non-aromatic : 2



- c) Write down the IUPAC name of the following compound : 1

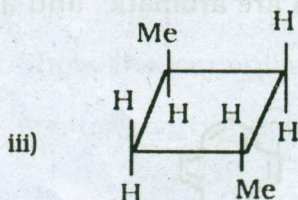
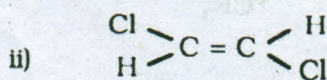
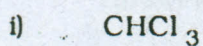


- d) Can you compare the stabilities of all the isomers having molecular formula C_5H_{10} by measuring their heats of hydrogenation ? Explain. What other method could you use ? 2
- e) What do you mean by bond polarity and bond polarisability ? Explain with proper example. 2
- f) Show the HOMO of allyl free radical (Ground state configuration) and LUMO of 1, 3-butadiene (excited state). 2
- g) Arrange the following in the increasing order of basicity and justify : 2



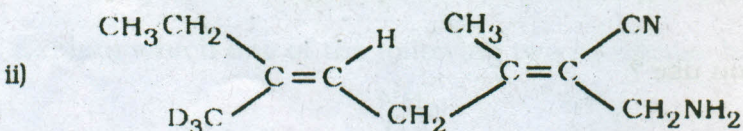
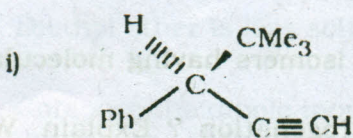
UNIT - II

3. a) Find out the symmetry elements (C_n , σ , i) present in the following molecules (any two) : 3



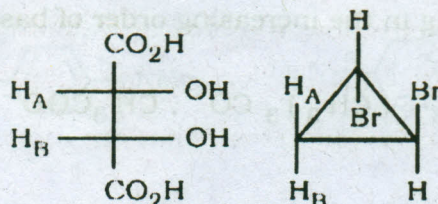
- b) Draw all stereoisomers of $\text{CH}_3\text{CH} = \underset{\text{Br}}{\text{CH}}\text{CH} = \text{CHCH}_3$ and comment on their optical activity. 3

- c) Assign *R/S* or *E/Z* descriptors to the following stereostructures as applicable : 2



- d) Draw the conformational energy diagram for rotation around $\text{C}_2 - \text{C}_3$ bond of *meso*-2,3-butane diol with proper labelling. 3

- e) Identify H_A and H_B in each of the following structures as homotopic, enantiotopic or diastereotopic. 2



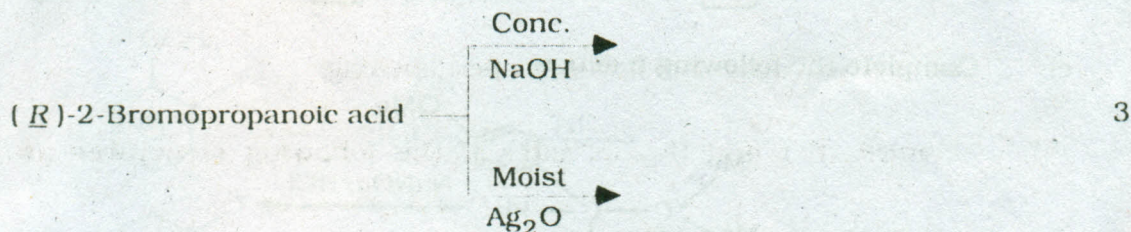
4. a) Draw the energy profile diagram of a two-step exothermic reaction of which the activation energy of the first step is greater than the second step, but the second step is the rate determining step. 3
- b) Compare the dipole moments of the diastereomers of 1, 2-dichloro-1, 2-diphenyl ethane. 2
- c) What is primary kinetic isotope effect ? Write the mechanism of oxidation of Me_2CHOH with $\text{Cr}(\text{VI})$ oxide in glacial acetic acid. Cite a labelling experiment and its result to indicate which type of kinetic isotope effect is operative here. 3
- d) Comment on the relative energy barriers for rotation across C - C bond in $\text{CH}_3\text{CH}_2\text{X}$ (X = F, Cl, Br and I). 2
- e) Draw the Fischer projection formula of (2R, 3S)-2-bromo-3-hydroxy butanoic acid and represent it in Newman projection form. 2

CEMAT - 11-0B

Answer any two questions, taking one from each Unit.

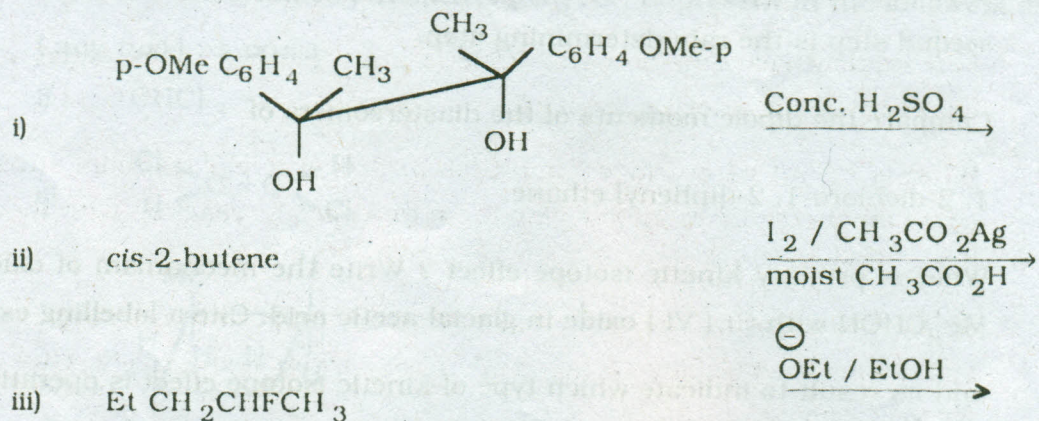
UNIT - I

5. a) Give the products with the configurational descriptors (R/S) in the following reaction :

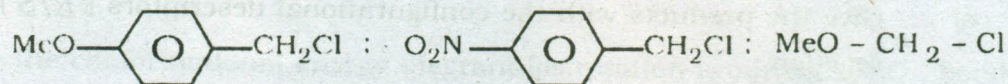


- b) Acetylene is less reactive towards bromine addition than ethylene. Explain. 2
- c) Treatment of $\text{Me}_3\text{C} - \text{CH} = \text{CH}_2$ and $\text{Me}_3\text{C} - \text{CHOH} - \text{CH}_3$ with conc. HCl gives two same isomeric chlorides. What are the two products ? Explain. 2

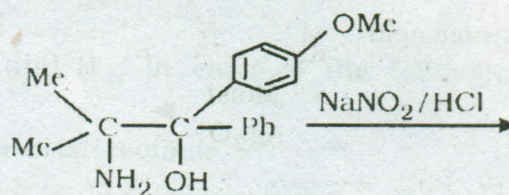
- d) Predict the product(s) with mechanism indicating major/minor, and the stereochemistry wherever applicable (any two) : 2 × 3 = 6



6. a) Though conjugated dienes are more stable than the non-conjugated dienes, former dienes undergo addition reaction more rapidly than the latter. Explain. 2
- b) What happens when an optically active α -phenyl ethanol is allowed to react with thionyl chloride (i) in absence of and (ii) in presence of pyridine ? Explain with mechanism. 2
- c) How would you synthesize CH₃OC(CH₃)₃ by adopting Williamson's synthesis ? 2
- d) Which mechanism S_N1 or S_N2 is favourable for reactions with each of the following substrates ? Explain. 3



- e) Complete the following reaction : 2

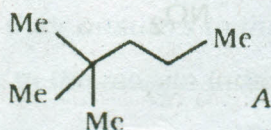


- f) Carry out the following conversion : 2

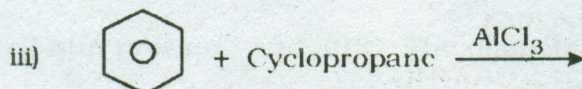
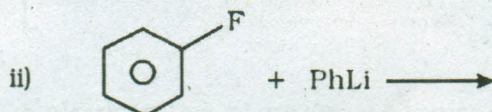
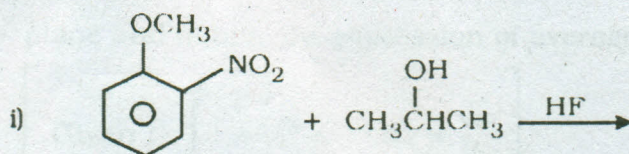


UNIT - II

7. a) What is *ipso*-substitution? Explain with an example. 2
- b) Free radical reaction between toluene and chlorine takes place at the side chain not at the nucleus. Explain. 2
- c) What is meant by σ and π complexes in aromatic electrophilic substitution? Draw an energy diagram showing them in a specific reaction with mechanism. 4
- d) Apply Corey-House method to synthesize compound A using two suitable substrates having four carbon and three carbon respectively. Give argument for your choice. 2



- e) Compare the stabilities of the following radicals : 2
- $\dot{\text{C}}\text{H}_3$: $\dot{\text{C}}\text{H}_2\text{F}$: $\dot{\text{C}}\text{F}_3$.
8. a) Give one example for each of the following : $4 \times \frac{1}{2} = 2$
- Ylide
 - Zwitterion
 - Electrophilic radical
 - Nucleophilic radical.
- b) Predict the product(s) with plausible mechanism : $3 \times 2 = 6$



- c) Me_3CH on chlorination using Cl_2 in diffused sunlight gives primary halide as major monosubstituted product while bromination by heating with Br_2 produces tertiary halide as major. Justify this observation. 3
- d) Arrange the following compounds in increasing order of reactivity towards nucleophilic substitution reaction. 1

