

**West Bengal State University**  
**B.A./B.Sc./B.Com. (Honours, Major, General) Examinations, 2012**

**PART-I**

**CHEMISTRY - Honours**

**Paper- I**

Duration : 4 Hours

Full 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.*

**Group-A**

**CEMAT-11-IA**

(Full Marks - 50)

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

**UNIT - I**

1.
  - a) What is meant by artificial transmutation ? Give two example. 2 + 2
  - b) State Hund's rule of maximum spin multiplicity. Calculate the exchange energy for  $d^6$  system. 2
  - c) Explain magic number with the help of nuclear shell model. 3
  - d) What is radial probability function of a hydrogenic orbital ?  
 Compare the relative penetration of 4s and 3d orbitals from their radial probability plots against  $r$ . 2 + 2
2.
  - a) The isotopic masses of two atoms,  ${}_{26}\text{X}^{56}$  and  ${}_{57}\text{Y}^{139}$  are 55.9521244 and 138.9621461  $u$  respectively. Compare their nuclear stability. [Given masses (in  $u$ ) of electron = 0.0005486, proton = 1.0072765 and neutron = 1.0086650]. 4
  - b) Explain any *three* of the following : 6
    - (i) Critical mass of fissionable nuclei
    - (ii) Moderators in nuclear reactors
    - (iii) Breeder reactor
    - (iv) Units rad or gray.
  - c) Find out spectroscopic ground term symbols for  $d^5$  and  $d^8$  system.  $1\frac{1}{2} + 1\frac{1}{2}$

## UNIT - II

3. a) Lanthanides behave more or less identically with respect to chemical properties while *d*-block elements differ widely in this respect. Explain
- b) In case of *3d* block elements, ionization of first electron may take place either from *3d* or *4s* orbital. On the basis of Slater's rule, show that the first electron goes from *4s* orbital in case of vanadium (atomic number 23).
- c) The second electron attachment enthalpy of oxygen is positive — yet oxygen forms many compounds in oxidation state—2. Explain.
- d) Calculate the radii of  $\text{Na}^+$  and  $\text{F}^-$ , given their interionic distance = 231 pm.
4. a) Comment on the term "inert pair effect".  
Why does thallium form an iodide only in +1 oxidation state.
- b) The drop in first ionization energy from N to O is larger than that from P to S. Explain.
- c) Discuss Allred-Rochow's scale of electronegativity.
- d) Explain the variation in colour :  
 $\text{ZnO}$  (white);  $\text{CdO}$  (orange);  $\text{HgO}$  (red).

## CEMAT-11-IB

Answer two questions, taking one from each Unit.

## UNIT - I

5. a) Explain Lattice energy. Write Born-Landé equation. Explain the terms 'Madelung constant' and 'Born exponent'.  $1 + 1 + 1 + \frac{1}{2} + \dots$
- b) (i) State the basis of radius-ratio for structure of ionic crystals. Calculate the limiting radius ratio for tetrahedral coordination.
- (ii) Why does KCl adopt NaCl structure though its radius ratio suggests tetrahedral coordination no.8? Explain qualitatively.
- c) The dipole moment of  $\text{NH}_3$  is 1.49 D while that of  $\text{BF}_3$  is zero. Explain.
6. a) State Bent's rule and predict the geometry of the following molecules with the help of Bent's rule and VSEPR theory :  $2 + 2 = 4$
- (i)  $\text{PF}_2\text{Cl}_3$
- (ii)  $\text{XeOF}_4$ .

- b) Give two examples where the VSEPR theory fails to predict the shape of a molecule. 2
- c) Give an example of a fluxional molecule. 1
- d)  $N(\text{SiH}_3)_3$  is planar while  $N(\text{CH}_3)_3$  is pyramidal. Explain with sketch of *d-p*  $\pi$ -overlap. 4

## UNIT-II

7. a) Which one is stronger Lewis acid  $\text{BCl}_3$  or  $\text{BF}_3$ ? Explain. 2
- b) The B-F distance in  $\text{BF}_3$  is 130 pm. Comment on the following bond distances :  
 $\text{H}_3\text{NBF}_3$                       B-N = 160 pm, B - F = 138 pm  
 $\text{Me}_3\text{NBF}_3$                       B-N = 158 pm, B-F = 139 pm. 3
- c) Predict the directions of the following equilibria : 3
- (i)  $2\text{CH}_3\text{MgF} + \text{HgF}_2 \rightleftharpoons (\text{CH}_3)_2\text{Hg} + 2\text{MgF}_2$
- (ii)  $\text{La}_2(\text{CO}_3)_3 + \text{Bi}_2\text{S}_3 \rightleftharpoons \text{La}_2\text{S}_3 + \text{Bi}_2(\text{CO}_3)_3$
- d) What are super acids? Give one example. How the acidity of such solutions is expressed? 1 + 1 + 2
8. a) What will the effect of acidity on the following?
- (i)  $\text{CH}_3\text{COOK}$  is added to liquid  $\text{NH}_3$ .
- (ii)  $\text{CuSO}_4$  is added to an aqueous solution of  $(\text{NH}_4)_2\text{SO}_4$ .  $1\frac{1}{2} + 1\frac{1}{2}$
- b) Explain the following reaction in the light of Acid-Base interaction. :  
 $6\text{CaO} + \text{P}_4\text{O}_{10} \longrightarrow 2\text{Ca}_3(\text{PO}_4)_2$ . 2
- c) Define buffer capacity. When does it become maximum? 2 + 2
- d) How does an acid-base indicator work in showing the equivalent point in an acid-base reaction? 3

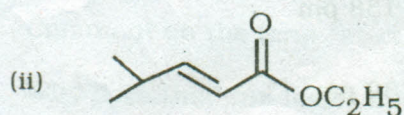
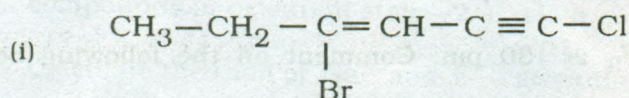
## CEMAT-11-0A

( Full Marks - 50 )

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

## UNIT - I

1. a) Write down the IUPAC names of the following compounds:



- b) Critically comment on the delocalization :



- c) Stability of the three alkenes is shown as :

isobutene > E-butene > Z-2-butene.

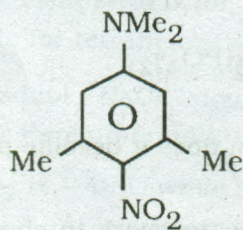
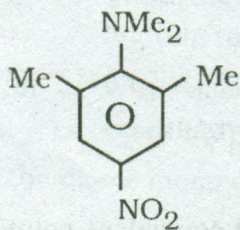
Explain the order as given.

- d) Arrange the following compounds in order of increasing acid strength. Give reason.



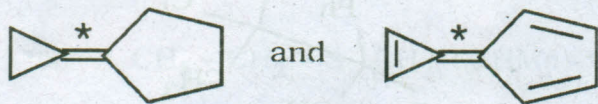
- e) Draw the  $\pi$  M.O (S) for the HOMO of allyl-anion and LUMO of 1,3-butadiene.

- f) Which of the following compounds has the higher dipole-moment and why ?

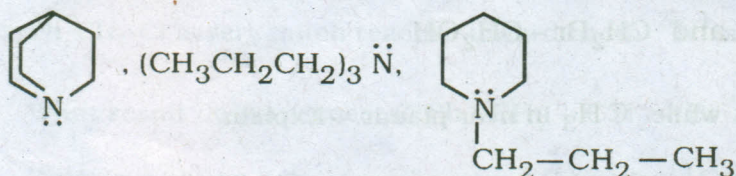


- g) Define homoaromaticity.

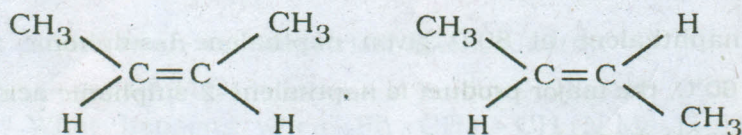
2. a) Comment on the energy barrier of the rotation around the marked double bonds of the following : 2



- b) State with reason the order of nucleophilicity of four halide ions ( $F^-$ ,  $Cl^-$ ,  $Br^-$  and  $I^-$ ) in a protic solvent and in an aprotic solvent. 2
- c) Draw the orbital picture of  $CH_2 = CH - CN$ . Indicate the state of hybridization of each carbon atom. 2
- d) The boiling point of 2, 3-pentanediol ( $188^\circ C$ ) is much lower than the isomeric 1,5-pentanediol ( $238^\circ C$ ). Explain. 2
- e) Arrange the following compounds in order of increasing basicity. Give reason. 2

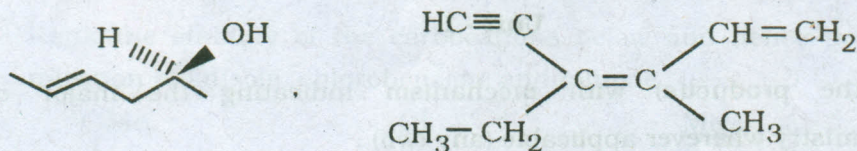


- f) Write down the structures of the singlet and triplet carbenes. 2
- g) Comment on the stability of the following isomeric alkenes considering heat of hydrogenation. 2



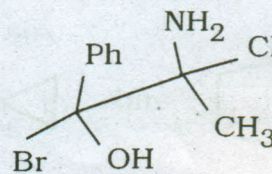
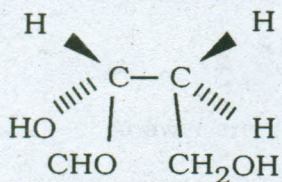
### UNIT - II

3. a) Find out R/S or E/Z descriptors wherever applicable in the following stereostructures : 2

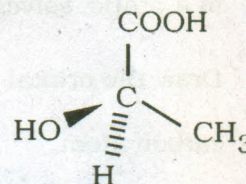
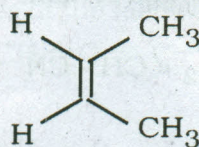
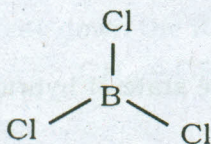


- b) Draw the energy diagram for the conformations of *n*-butane arising out of rotation C(2) - C(3) bond with proper explanation. 3

- c) Draw the Fischer projection of the following compounds :



- d) Find out the symmetry elements present in the following molecules :



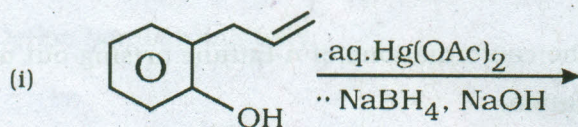
- e) Specific rotation of (S)-alanine is  $+8.5^\circ$ . Calculate the observed specific rotation of a sample of alanine containing 80% of (R)-alanine and 20% of (S)-alanine.
4. a) Draw the preferred conformation of the following :  
 $\text{CH}_2\text{Br} - \text{CH}_2\text{Br}$  and  $\text{CH}_2\text{Br} - \text{CH}_2\text{OH}$
- b)  $\text{CF}_3$  is pyramidal, while  $\text{CH}_3$  is near planar.—Explain.
- c) Draw the Fischer projection formula of the following :  
 (i) (R)-2-Deuteropropanoic acid  
 (ii) (2R, 3S)-3-Phenyl-2-butanol
- d) Define secondary kinetic isotope effect with suitable example.
- e) Sulphonation of naphthalene at  $80^\circ\text{C}$  gives naphthalene-1-sulphonic acid as major product while at  $160^\circ\text{C}$ , the major product is naphthalene-2-sulphonic acid. Explain with a suitable energy profile diagram.

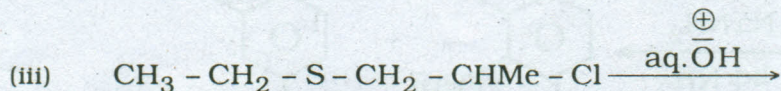
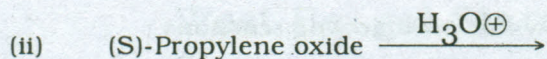
### CEMAT-11-0B

Answer any two questions, taking one from each Unit.

#### Unit - I

5. a) Predict the product(s) with mechanism indicating the major one and the stereochemistry wherever applicable (any two) : 3 × 2

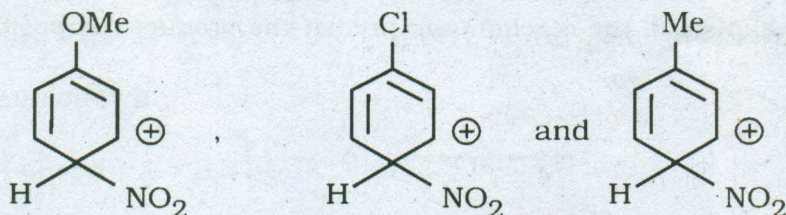




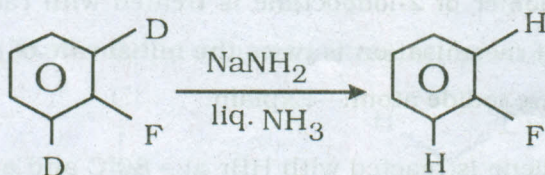
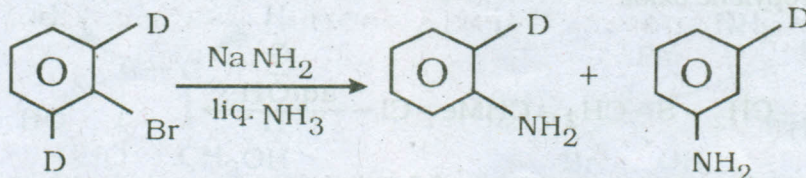
- b) When an optically active enantiomer of 2-iodooctane is treated with radioactive iodide ion in solution, the initial rate of racemisation is twice the initial rate of displacement of normal iodine atom by radioactive iodide atom.—Explain. 3
- c) What happens when buta-1,3-diene is reacted with HBr at  $-80^\circ\text{C}$  and at  $40^\circ\text{C}$ ? Predict the product composition in each case and offer proper explanation in support of your answer. Also draw the energy diagram for the reactions. 4
6. a) Starting from E-butane, how would you prepare *meso*-butane-2,3-diol and dl-butane-2, 3-diol separately? Show the reagents and stereo-chemistry of the reaction in each case. 3
- b) Ph-CH<sub>2</sub>-Cl is very much reactive towards both S<sub>N</sub><sup>1</sup> and S<sub>N</sub><sup>2</sup> reactions. Explain. 2
- c) What result do you expect if Ph - CH<sub>2</sub> - <sup>\*</sup>CH<sub>2</sub> - Br is reacted with anhydrous AlBr<sub>3</sub>? Explain with the help of mechanism (C means <sup>14</sup>C). 2
- d) Show how many ozonides are expected to form when 2-pentene is reacted with ozone in the presence of formaldehyde. 2
- e) Among the halogen hydracids, only HBr is capable of showing peroxide effect when added to an unsymmetrical alkene. Justify. 2
- f) What happens when Ph - CH<sub>2</sub> - CH(<sup>+</sup>NMe<sub>3</sub>) - CH<sub>2</sub> - CH<sub>3</sub> is heated with moist Ag<sub>2</sub>O? Explain with the help of mechanism. 2

### UNIT-II

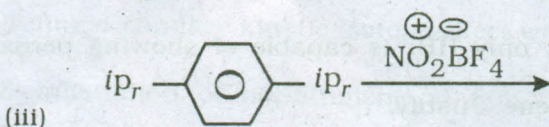
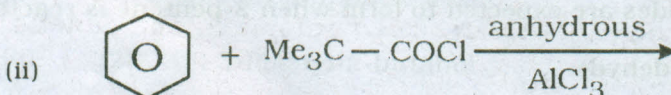
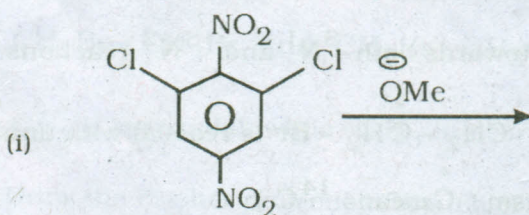
7. a) Rank the stability of the carbocations below and hence predict the relative rates of nitration of anisole, chlorobenzene and toluene. 3



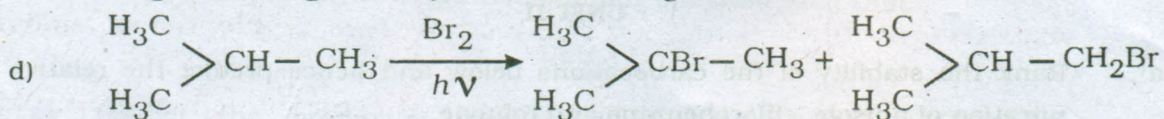
- b) Explain the observations as shown in the following reactions :



- c) What are singlet and triplet carbenes? Explain the reaction of a singlet carbene with Z-butene and E-butene separately. 3
- d) Friedel-Craft's alkylations of benzene separately with  $\text{Me}_3\text{C}-\text{CH}_2\text{Cl}$  and  $\text{Me}_2\text{C}(\text{Cl})-\text{CH}_2\text{Me}$  give the same product. Identify the product and rationalise mechanistically. 3
8. a) Predict the product(s) with plausible mechanism in the following reactions (any two) :



- b) When *p*-chlorotoluene is reacted with  $\text{NaNH}_2$  in  $\text{liq. NH}_3$  at  $-33^\circ\text{C}$ , a mixture of *m*- and *p*-toluidines is obtained, with the former predominating. Explain. 3
- c) How would you synthesise  $\text{Me}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_3$  using a suitable organo-copper reagent? Also give the synthesis of the organometallic involved. 2



Show the mechanism of the reaction and predict the product composition with proper justification. 3