West Bengal State University

B.A./B.Sc./B.Com. (Honours, Major, General) Examinations, 2014

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.

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

CEMAT-11-IA

Answer *four* questions, taking *one* from each Unit.

UNIT - I

1. a) Which set of orbitals is defined by the quantum numbers $n = 3$ and $l = 2$? How many orbitals are there in this set ? 1 + 1

b) Give the radial wave-functions of the 3*s* hydrogenic orbital. How many radial nodes are there ? Define nodal plane. $1\frac{1}{2} + 1 + 1\frac{1}{2}$

c) What are magic numbers ? Explain their importances. 2

d) Give short notes on the following : $2 \times 2\frac{1}{2}$

(i) Radio carbon dating

(ii) Use of isotopes in tracer techniques.

2. a) The radius of third Bohr orbit of hydrogen atom is 476 pm. Calculate the radius of the fourth orbit. 2

b) Find out the spectroscopic ground term symbols for d^4 and d^8 systems. $1\frac{1}{2} + 1\frac{1}{2}$

c) What do you understand by 'Exchange energy' ? 2

d) Out of $2s$ and $2p$ hydrogenic orbitals which orbital gives the electron a greater probability of close approach to the nucleus ? $1\frac{1}{2}$

e) The first ionisation potential of rubidium is 96·4 kcal/mole. What will be the lowest frequency of light that can ionise a rubidium atom ? 3

f) What are the hazards of radiation ? $1\frac{1}{2}$

Unit - II

3. a) 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). 4

b) (i) Electron affinity of Li is 60 $kJmol^{-1}$ whereas that of Be is around zero. Explain. 2

(ii) Why does Thallium form stable chloride in univalent state though it is included in Group 13 ? 2

c) Who proposed that 'electronegativity is determined by the electric field at the surface of an atom' ? Give his name. Write the theory expressed by him and the expression followed therein. 4

4. a) Arrange the atomic radii of the following elements in increasing order.

(i) O^{2-}

(ii) F^{-}

(iii) Mg^{2+}

(iv) Al^{3+}.

Justify your answer. 1 + 2

b) Calculate the Z_{eff} faced by a 3*s* and 3*d* electron in Managanese atom.

(Z = 25) 2 + 2

c) Lanthanides behave identically with respect to chemical properties while actinides differ to some extent in this regard. Give reason. 3

d) The second electron attachment enthalpy of oxygen is positive — yet oxygen forms most compounds in oxidation state-2. Explain. 2

CEMAT-11-IB

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

Unit - I

5. a) State the basis of prediction of structure of ionic crystals by radius-ratio rule. Calculate the limiting radius ratio for tetrahedral coordination. 1 + 3

b) What is polarizability ? Which would be more polarizable an F^- ion or an I^- ion ? 3

c) The dipole moment of NH_3 is 1·49 D while that of NF_3 is only 0·2D. Explain. 2

d) What is lattice energy ? Calculate the lattice energy of sodium chloride (in kJ/mol) from the following data :

$A = 1{\cdot}75$, $r_0 = 2{\cdot}8$ Å, $n = 9$

$N_0 = 6{\cdot}02 \times 10^{23}$, $e = 4{\cdot}8 \times 10^{10}$ esu. $\varepsilon_0 = 8{\cdot}854 \times 10^{-12}$ Fm^{-1}. 1 + 3

6. a) State Bent's rule and predict the geometry of the following molecules with the help of Bent's rule and VSEPR theory. Also draw the correct structures :

(i) PF_2Cl_3

(ii) $XeOF_4$. 2 + 2 + 2

b) $N(SiH_3)_3$ is planar while $N(CH_3)_3$ is pyramidal. Explain using $d\pi - p\pi$ overlap. 4

c) What do you understand by Schottky defect ? Give example. 2 + 1

UNIT-II

7. a) Which is the strongest Lewis acid in the following series ? Explain.

BF_3, BCl_3, BI_3 2

b) The dissociation constant of an indicator acid is 1×10^{-6}. The undissociated acid has a red colour, the anionic form has yellow colour. What will be the colour at pH 4 and 8 ? 3

c) What are super acids ? Give one example. How the acidity of such solutions is expressed ? 1 + 1 + 2

d) Cl^- and CN^- ions are bases. What will be their preferences towards the following metal ions and why ?

(i) Na^+

(ii) Cu^{+2}

(iii) Cd^{+2}

(iv) Mg^{+2}. 2 + 1

8. a) Explain the following :

(i) $\left[CoF_6 \right]^{3-}$ is more stable than $\left[CoI_6 \right]^{3-}$

(ii) BF_3 is acidic while BH_3 is neutral. 4

b) Define buffer capacity. When does it become maximum ? 4

c) 'CF_3COOH is a very strong acid and $(CF_3)_3N$ had no basic character.' Explain. 2

d) What will be the effect on acidity if $CuSO_4$ is added to an aqueous solution of $(NH_4)_2SO_4$? 2

CEMAT-11-OA

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

UNIT - I

1. a) Draw all resonating structures of $\overset{\ominus}{C}H_2-\overset{\oplus}{N}\equiv N$ and justify which one is the most contributing structure. 2

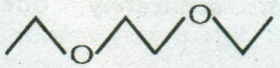
b) Calculate the DBE of the compound having molecular formula C_6H_7N. 1

c) Arrange with reason $\overset{\ominus}{I}, \overset{\ominus}{F}, \overset{\ominus}{Cl}, \overset{\ominus}{Br}$ in the increasing order of nucleophilicity in aqueous solution. 2

d) Which one will have lower dipole moment ? Give reason. 2

C_2H_5CN and C_2H_5NC.

e) Give IUPAC names of the following compounds :

(i) 

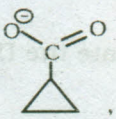
(ii) $(CH_3)_2CHCONH_2$. 2

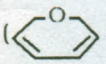
f) Show the HOMO of hexa – 1, 3, 5 – Friene in the excited state and LUMO of allyl anion in the ground state. 2

g) C = C bond energy is lower than that of 2 × C — C bond energy but C = N bond energy is greater than 2 × C — N bond energy. Explain. 2

2. a) Arrange the following in the order of increasing nucleophilicity. Give reasons. 3

$\overset{\ominus}{N}H_2$, $\ddot{N}H_3$, $\ddot{N}H_2 - \ddot{N}H_2$ and $Ph\ddot{N}H_2$

b) Compare the ' C = O' bond distances of  ,  and  with proper reason. 2

c) Explain why tetrahydrofuran is more water soluble than furan (). 2

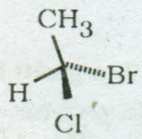
d) When silver nitrate is added to two isomeric compounds having molecular formula C_7H_7Br separately, one forms curdy white precipitate readily, other does not. Identify the compounds with proper explanation. 2

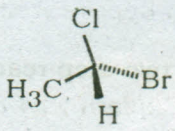
e) When $PhCH_2Br$ is added to a suspension of KF in benzene, no reaction occurs. However when a catalytic amount of 18-crown-6 ether is added, $PhCH_2F$ can be isolated in high yield. If LiF is substituted for KF, there is no reaction even in the presence of crown ether. Explain these observations. 3

f) Draw the orbital picture of singlet carbene. 1

UNIT - II

3. a) Consider the following two structures and state, with reason, whether they are enantiomer or two molecules of the same compound. 2





b) Show the symmetry elements present in

(i) (2R, 2R) – 2, 3 – dihydroxybutanedioic acid

(ii) eclipsed from of 2, 3 –dihydroxybutanedioic acid

(iii) staggered form of 2, 3-dihydroxybutanedioic acid. 3

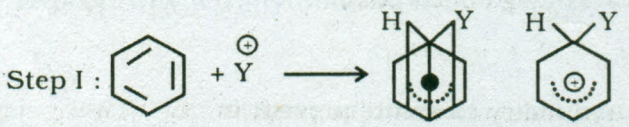
c) Draw the energy diagram for the conformations of *n*-butane arising out of rotation around C(2) — C(3) bond and label maxima, minima with appropriate conformation in Newman projection formula. 3

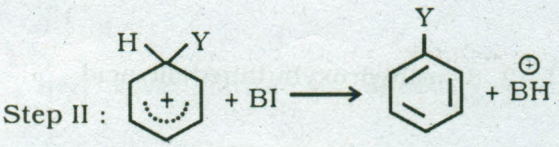
d) The addition of chlorine (1 mol) to 1,3-butadiene at 25°C produces 60 % 3,4-dichlorobut-1-ene and 40% 1,4-dichlorobut-2-ene. At 200°C, the yields are 30% and 70% respectively. Explain these observations with energy profile diagram. 4

4. a) Draw flying-wedge formula of (R)-2-chlorobutane. 1

b) Centres of stereogenicity is not always the centres of chirality. Explain with an appropriate example. 2

c) A two-step reaction with K_H/K_D ~7 is given below :





Draw and explain the energy profile for the reaction and indicate rate determining step. 3

d) Optically active most populated conformer of 2,3-dichlorobutane is dissymmetric but not asymmetric. Explain. 2

e) State Hammond's postulate with explanation. 2

f) Draw the stereochemical structure of (2E, 4Z)-2,4-hexadienoic acid. 1

g) Indicate the symmetry element(s) present in (E) 1,2-dichloroethene. 1

CEMAT - 11-OB

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

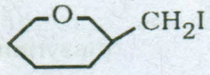
UNIT-I

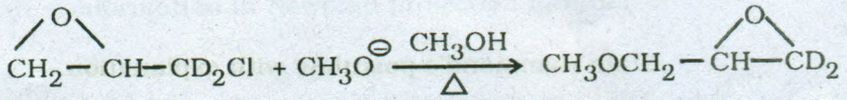
5. a) Explain the following observations :

(i) Neopentyl halides cannot be prepared by treating neopentyl alcohol with hydrogen halides. 2

(ii) $D_3CCH=CH_2$ cannot be prepared by acid catalysed dehydration of $D_3CCH_2CH_2OH$, but can be synthesised through pyrolysis of xanthate of the alcohol. Explain. 3

b) Propose mechanism for the following reactions : $2 \times 2 = 4$

(i) $HOCH_2CH_2CH_2CH=CH_2 \xrightarrow{I_2/NaHCO_3}$ 

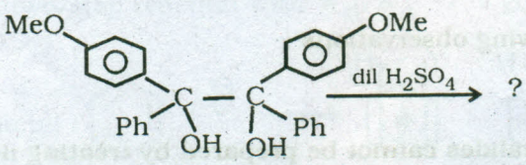
(ii) 

c) Explain the role of pyridine in the acetylation of alcohol by acetyl chloride. 2

d) Which of the following will react faster in S_N1 reaction ?

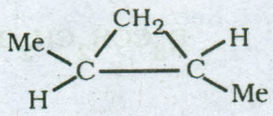
$ClCH_2-O-CH_2CH_3$ and $CH_3O-CH_2CH_2Cl$. 2

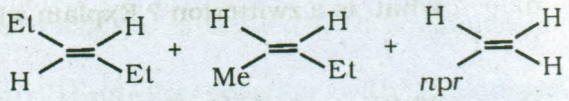
6. a) Optical rotation of a solution of NaI and (+)-2-iodopentane in acetone slowly goes to zero. Explain. 2

b) 

Write the product(s) of the reaction with mechanism. 3

c) Carry out the following conversion : 2

$MeO-C\equiv C-Me \longrightarrow$ 

d) 2-bromopentane $\xrightarrow[E^2]{EtOK}$ 

53% 18% 29%

Account for the relative yield of the above reaction. 3

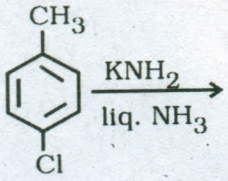
e) How many ozonides can be formed from $CH_3CH=CHCHMe_2$? Explain with mechanism. 3

UNIT-II

7. a) Both chlorobenzene and nitrobenzene undergo aromatic electrophilic substitution with deactivation, whereas chlorobenzene forms mainly ortho and para substituted products, nitrobenzene produces mainly meta substituted product. Explain. 3

b) What is activated aromatic nucleophilic substitution reaction ? Explain with an example. 3

c) Predict the product(s) of the following reaction with mechanism. 2



d) What is a zwitterion ? Explain with one example. 1

c) Which one of the following alkanes cannot be synthesised by Wurtz reaction in good yield and why ? How can this alkane be synthesised using Corey-House synthesis ?

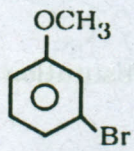
$(CH_3)_2CHCH_2CH_2CH(CH_3)_2$, $CH_3CH_2-C(CH_3)_2-CH_2CH_3$. 3

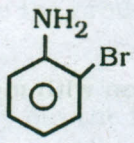
8. a) Which would you expect to be more reactive towards electrophilic substitution in the following pairs ? Give reason for your answer. 4

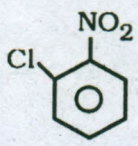
(i) $PhCF_3$ and PhF

(ii) $PhOCH_3$ and PhSMe.

b) Where would you expect electrophilic substitution to occur in the following substances ? 3

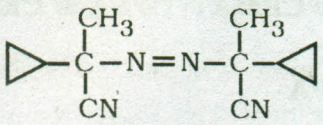
(i) 

(ii) 

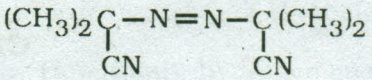
(iii) 

c) What happens when chlorobenzene is treated with sodamide in liquid NH_3 ? Write the product(s) of the reaction with mechanism and evidence. 3

d) The azo compound *A* decomposes 20 times faster than the compound *B*. Suggest a reason for this. 2



A



B