

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

PART-II
CHEMISTRY- Honours
Paper- III

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-23-IA & CEMAT-23-IB

and CEMAT-23-OA & CEMAT-23-OB]

Group - A

CEMAT-23-IA

Answer any four questions, taking one from each Unit.

UNIT - I

1. a) Discuss and compare the characteristics of H_2M ($M = S \text{ \& } Se$) in terms of (i) acidic behaviour and (ii) reducing character. 2 × 2 $\frac{1}{2}$
- b) The formula of telluric acid (H_6TeO_6) is different from selenic acid (H_2SeO_4). Justify. 2
- c) Why is NF_3 inert to hydrolysis but NCl_3 is not? 2
- d) $SnCl_2$ is a solid while $SnCl_4$ is a liquid, why? 2
- e) Why does Lithium behave as the most powerful reducing agent in aqueous solution? 2

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Group - A

CEMAT-23-IA

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UNIT - I

1. a) Discuss and compare the characteristics of H_2M ($M = S \text{ \& } Se$) in terms of (i) acidic behaviour and (ii) reducing character. $2 \times 2 \frac{1}{2}$
- b) The formula of telluric acid (H_6TeO_6) is different from selenic acid (H_2SeO_4). Justify. 2
- c) Why is NF_3 inert to hydrolysis but NCl_3 is not? 2
- d) $SnCl_2$ is a solid while $SnCl_4$ is a liquid, why? 2
- e) Why does Lithium behave as the most powerful reducing agent in aqueous solution? 2

2. a) Give a comparative study of oxy-acids of sulphur in terms of (i) Hybridization state of central element and (ii) Acidic strength. 3×2
- b) Compare the stability of $PbCl_2$ and $PbCl_4$ w.r. to inert pair effect. Draw the structure of anhydrous $SnCl_2$ in gas phase as well as in crystalline phase. $2 + 2$
- c) Elucidate noticeable properties that are developed when alkali metals or alkaline earth metals are dropped in liquid NH_3 . 3

Unit - II

3. a) Draw M.O. diagram of CN and predict the magnetic properties. 3
- b) Write down IUPAC — system name of
- $$\left[(NH_3)_3 Co \begin{array}{c} \diagup OH \\ - OH - \\ \diagdown OH \end{array} Co(NH_3)_3 \right]^{3+}$$
- c) Why are glass apparatus dried by cleaning with alcohol or acetone? Which one is more effective and why? 2
- d) Among the various geometrical isomers of $[Co(en)_2Cl_2]$, predict the optical isomers. 2
- e) Distinguish between $[Pt(NH_3)_4]Br_2$ and $[Pt(NH_3)_3Br]Cl$ by chemical test. What type of isomerism exists between them? $2 + 1$
4. a) What is the basic difference between semiconductors and superconductors? Mention two types of extrinsic semiconductors with examples. $2 + 2$
- b) What is ambidentate ligand? Give examples of two complexes where such ligands are used. $2 + 1$

r in terms of
length. 3 x 2
pair effect. Draw
as in crystalline
2 + 2
alkali metals or
3

- c) Predict which one between $K_3[FeF_6]$ and $K_3[Fe(CN)_6]$ is paramagnetic & inner metallic complex. 2
- d) Give the MO description of NO molecule. Though it contains one unpaired electron but it is stable. Moreover the bond in NO^+ is short and strong. Explain. 3

CEMAT-23-IB

Unit - I

order as well as
3

5. a) How many types of interhalogen compounds are formed by iodine and fluorine? Why are interhalogens more reactive than pure halogen molecules? 1 + 2 + 1
- b) Quantitative estimation of N_2H_4 is done using standard $KBrO_3$ in acid medium. Write the proper chemical reaction for such estimation and also indicate the colour at equivalence point. 3 + 1
- c) What are silicones? Write the proper structure of silicone produced when CH_3SiCl_3 is carefully hydrolysed under controlled heating. 1 + 2
- d) Why $XeOF_4$ cannot be stored in glass or quartz container? 1
6. a) Mention a convenient and less hazardous route to synthesize $XeOF_4$. Mention its reactions. 3
- b) What products are obtained when ICl is hydrolyzed under proper chemical conditions? 2
- c) Sodium thiosulphate solution is used as fixer for developing work in photography. Write the chemical reactions involved in the process. 2
- d) Why is $B_3N_3H_6$ called inorganic benzene? Mention the hybridization state of B and N in the compound. 2 + 2
- e) H_2O_2 behaves both as oxidant as well as reductant. Give one example for each case and establish involving half reactions. 2

2

al or acetone?

2

Cl_2]. predict the

2

$[NH_3)_4Br_2]Cl_2$ by

em? 2 + 1

tors and super-

conductors with

2 + 2

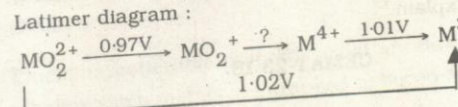
complexes where

2 + 1

Unit - II

7. a) Find the value of coefficients of the following redox reaction : 2

$$\text{As}_2\text{S}_5 + \text{HNO}_3 \longrightarrow x\text{H}_2\text{SO}_4 + y\text{NO}_2 + 2\text{H}_3\text{AsO}_4 + z\text{H}_2\text{O}$$
- b) Calculate E° for $\text{MO}_2^+ \longrightarrow \text{M}^{4+}$ in 1M acid medium from the following Latimer diagram :

$$\text{MO}_2^{2+} \xrightarrow{0.97\text{V}} \text{MO}_2^+ \xrightarrow{?} \text{M}^{4+} \xrightarrow{1.01\text{V}} \text{M}^{3+}$$

- c) Discuss the solubility product principle. Explain how the principle is applied to the precipitation of Cr^{3+} , Ni^{2+} , Mn^{2+} and Zn^{2+} cations. 4
- d) For the reaction $2\text{Cu}^+ \rightleftharpoons \text{Cu}^0 + \text{Cu}^{2+}$ in aqueous medium the value of $K_c = 1 \times 10^6$. Addition of slight excess of CN^- ion results $K_c \sim 1 \times 10^{30}$. Justify the result. 2
8. a) Calculate the emf of the cell :
 $\text{Pt}, \text{H}_2(1 \text{ atm}) | 0.1 \text{ N HCl} || 1 \text{ N KOH} | \text{H}_2(1 \text{ atm}), \text{Pt}$, provided 0.1 N HCl is 90% ionized and 1N KOH is 75% ionized. Also comment on the result. 3
- b) How does BDS act as redox indicator during titration of Fe^{2+} solution by standard $\text{K}_2\text{Cr}_2\text{O}_7$ solution in concentrated H_2SO_4 medium ?
- c) Give the disproportionation of chlorous acids and its salts in ion-electron balance method. 2
- d) A silver electrode is immersed in saturated Ag_2SO_4 solution. The potential difference between the Ag and normal H-electrode is found to be 0.711 volt at 25°C . Determine K_{sp} of Ag_2SO_4 . 5

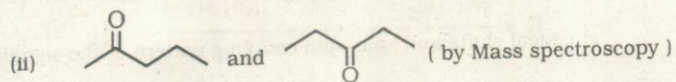
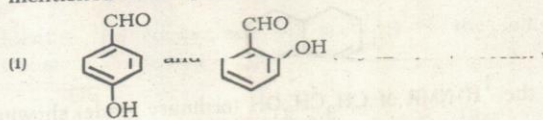
Group - B

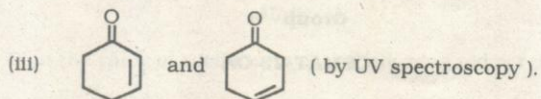
CEMAT-23-OA

Answer any two questions taking one from each Unit.

Unit - I

9. a) The UV spectrum of mesityl oxide shows absorption bands at 230 nm ($\epsilon=12600$) and 329 nm ($\epsilon=41$) in hexane. Assign them in terms of electronic transitions. How do the absorption bands change their positions in water as solvent? 3
- b) What do you mean by the following terms? (any two) 2 + 2
(ii) Fingerprint region
- c) Why is TMS used as reference compound of a compound? 2
Magnetically non-equivalent protons.
- d) Compare the $\text{C}=\text{O}$ stretching frequencies of acetone and hexamethyl acetone and explain. 2
- e) How would you distinguish between *o*-xylene and *p*-xylene by $^1\text{H-NMR}$ spectroscopy? 2
10. a) How would you distinguish between the members in each of the following pairs of compounds using the spectroscopic techniques mentioned within parenthesis? (any two) 2 x 2





b) Compound A (C_3H_8O) shows the following spectral pattern :

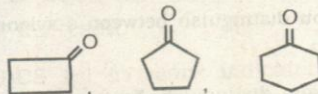
UV : transparent above 200 nm :

IR (cm^{-1}) : 3410, 2950, 1275, 1045.

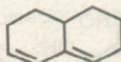
1.90 (2H, sextet), 1.0 (3H, triplet).

Deduce the structure of the compound A. 3

c) Arrange the following compounds in their increasing order of 'C = O' stretching frequency and rationalize ; 2



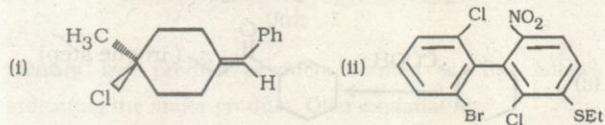
d) Calculate the λ_{max} of the following compound



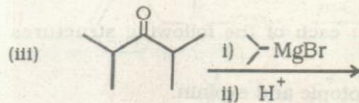
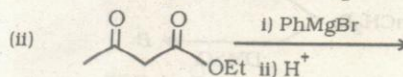
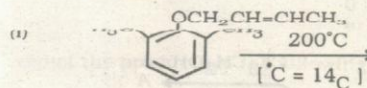
e) Draw the 1H -NMR of CH_3CH_2OH (ordinary grade) showing the relative chemical shifts and spin-spin coupling pattern of the signals. 2

UNIT-II

11. a) Find out (R/S) configuration for the following compounds. 2

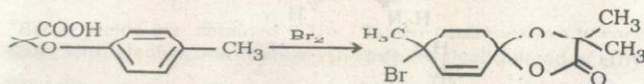


- b) Predict the product(s) in the following reactions and suggest mechanisms for their formation. 3 x 2

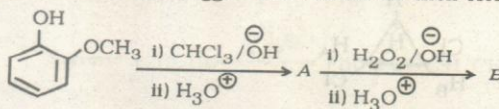


- c) How can you resolve (\pm) 2-aminopropanoic acid? 2

- d) Suggest a mechanism for the following reaction. 2



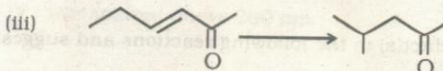
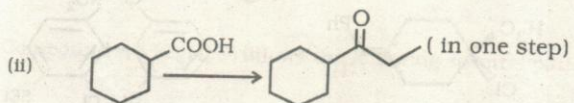
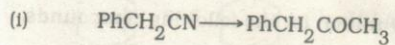
12. a) Identify the compounds (A) and (B) in the following sequence of transformations and suggest mechanism for their formation. 4



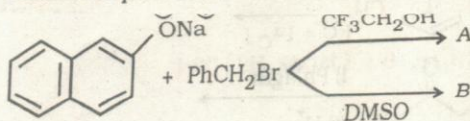
SUB.-B.Sc.(HN)-CEMA-6008

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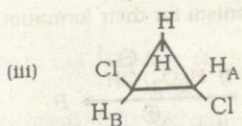
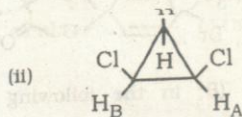
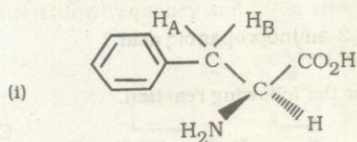
b) How can you carry out the following transformations ? 3



c) Predict the products : 1 + 1



d) Identify H_A and H_B in each of the following structures as homotopic, enantiotopic or diastereotopic and explain. 1 + 1 + 1

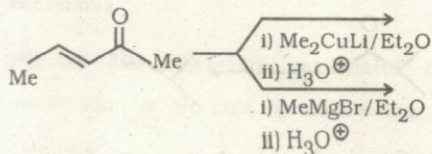


CEMAT-23-OB

Answer any two questions taking one from each unit.

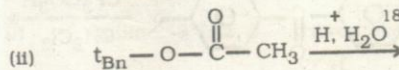
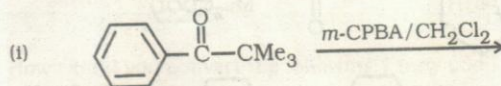
Unit - I

13. a) Identify the product/products formed in the following reactions, indicating the major product. Offer explanation. 3

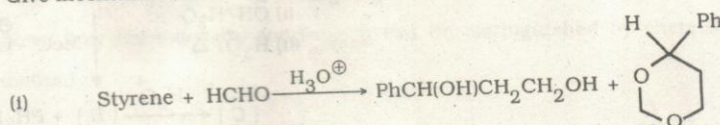


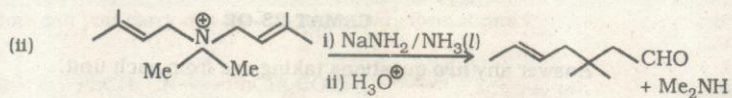
- b) Predict the products of the following reactions and give mechanisms :

$$2 \times 1 \frac{1}{2} = 3$$

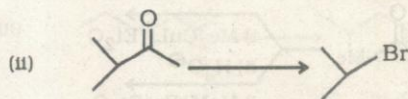
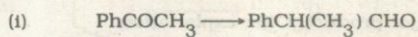


- c) Which of the following compounds will reduce Fehling's solution faster ? *p*-dimethylaminobenzaldehyde or $\text{Me}_2\text{N}(\text{CH}_2)_6\text{CHO}$. Explain. 2
- d) "Better yields are obtained if the Claisen condensation is carried out in ether with alcohol free sodium ethoxide catalyst instead of ethyl alcohol." Explain. 2
- e) Give mechanism of the following reactions : $2 \times 1 \frac{1}{2}$

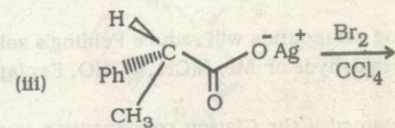
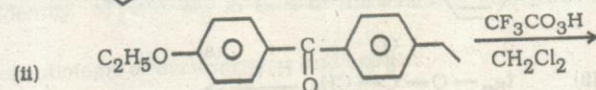
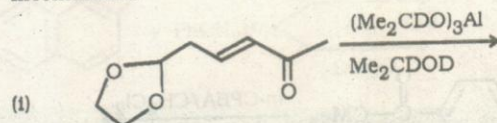




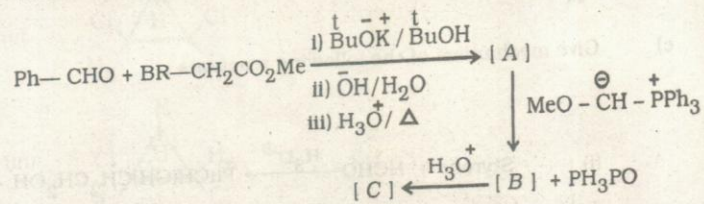
14. a) How can you achieve the following transformation? (any one) $2 \frac{1}{2}$



b) Indicate the product(s) of the following reactions and write their mechanisms. $3 \times 2 = 6$



c) Predict the products and explain their formation with mechanisms.



Unit - II

15. a) Explain the following observations : 2 + 2

- (i) Benzene diazonium chloride couples with phenol in alkaline medium but not with anisole (PhOCH_3) under the same reaction conditions.
- (ii) Phenols can be readily methylated by diazomethane but methylation of alcohols by diazomethane requires Lewis acid catalysis.

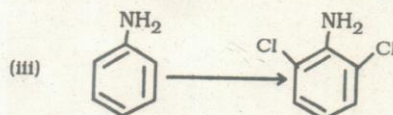
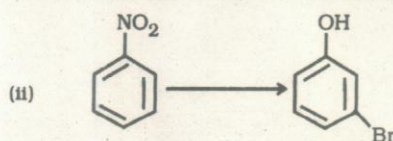
b) Give the product and mechanism of the following reaction : 2



Aq. KOH

c) How would you convert the following ? (any two) 2 + 2

(i) Aniline \rightarrow 1, 2, 3 - tribromobenzene.

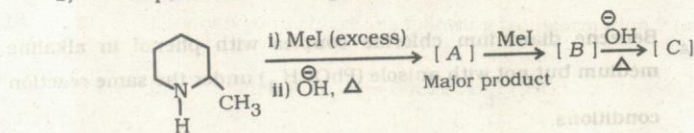


d) Show how the following compounds can be distinguished by chemical method. 2

Nitromethane and methyl nitrite.

16. a) Describe a convenient method for synthesizing diazoacetic ester. 2

b) Explain the following reaction sequence identifying [A], [B] and [C]. 3



c) Distinguish between the members of the following pairs by suitable chemical reactions. 2 + 2

(i) PhCH_2NO_2 and *p*-nitrotoluene

(ii) *Z*-benzaldoxime and *E*-benzaldoxime.

d) Describe a method to separate the mixture of amines (1° , 2° and 3°). 3

