

B.Sc./Part-II/Hons./CEMA-III/2017



WEST BENGAL STATE UNIVERSITY

B.Sc. Honours PART-II Examinations, 2017

CHEMISTRY-HONOURS

PAPER-CEMA-III

Time Allotted: 4 Hours

Full Marks: 100

The figures in the margin indicate full marks.

Candidates should answer in their own words and adhere to the word limit as practicable.

All symbols are of usual significance.

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

Unit-I

1. (a) Compare the hydrides of group 15 elements with respect to their thermal stability and reducing property. 2+2
- (b) Explain with reasons (any *two*):- 2+2
- (i) AlCl_3 is covalent whereas AlF_3 is ionic.
- (ii) LiI is soluble in water but LiF is not.
- (iii) $(\text{CH}_3)_3\text{N}$ is basic but $(\text{SiH}_3)_3\text{N}$ has no basic character.
- (c) How does the acidity of the oxy-acids of chlorine varies with oxidation states? Give reasons. 3

- (d) What happens when a pinch of sodium bismuthate is added to a solution of Mn^{2+} in dilute nitric acid?
2. (a) Why phosphorus has higher tendency to catenate than nitrogen?
- (b) Explain why PbO_2 is an oxidising agent whereas SnO_2 , GeO_2 and SiO_2 are not.
- (c) What happens when—
 SO_2 is passed into an aqueous suspension of pyrolusite.
- (d) Why does PCl_5 conduct electricity in molten state? Explain.
- (e) H_3BO_3 is a weak acid but acts as a strong monobasic acid in presence of glycerol.
- (f) State with equation what happens when N_2O gas is passed over heated sodamide.
- (g) Draw the structure of H_3PO_2 .

Unit-II

3. (a) Discuss the role of dopant in p-type and n-type doped silicon semiconductors according to band theory. Give appropriate figures.
- (b) Draw the approximate MO energy level diagram for HF molecule. Discuss the polarity of HF molecule from the diagram.
- (c) O_2^+ and N_2^+ have almost the same bond lengths — Explain.
- (d) How will you distinguish between—
- (i) $[Co(NH_3)_5 Br]SO_4$ and $[Co(NH_3)_5 SO_4]Br$
- (ii) *cis*- $[Pt(NH_3)_2Cl_2]$ and *trans*- $[Pt(NH_3)_2Cl_2]$

4. (a) Give the IUPAC names of: 2
(i) $[\text{Co}(\text{en})_3][\text{Co}(\text{ox})_3]$, where en = ethylenediamine, ox = oxalate ion.
(ii) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]\text{Br}_2$.
- (b) Explain with the help of MO theory why BeH_2 is linear. 3
- (c) Draw the structures of the possible isomers of $[\text{Pt}(\text{NH}_3)(\text{PPh}_3)(\text{Cl})\text{Br}]$. 3
- (d) What is ambidentate ligand? Give one example of a complex where such ligand is present. 2
- (e) Neither germanium nor arsenic is conductor of electricity but germanium doped with arsenic is conductor of electricity. – Explain why. 2

CEMAT 23-IB

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

Unit-I

5. (a) Distinguish dithionic acid from polythionic acids with respect to two properties and their structures. 3
(b) Discuss the structure and bonding of tetrasulphur tetranitride. 2
(c) How will you prepare borazine? How does it hydrolyse in water? Give necessary equations. 2+2
(d) Discuss the photochemical reactions of ozone in upper atmosphere. 3
(e) Give the structure of the product of hydrolysis of trimethylchlorosilane. 1
6. (a) Comment on the structure and bonding in tri-cyclophosphazine. Comment on the states of hybridisation of 'N' and 'P' in the structure. 4
(b) Discuss the structure of XeF_6 and the state of hybridisation of 'Xe' in it. 3
(c) Discuss the structure and geometry of $(\text{ICl}_3)_2$. 2
(d) Why the interhalogens are more reactive than halogens? 2

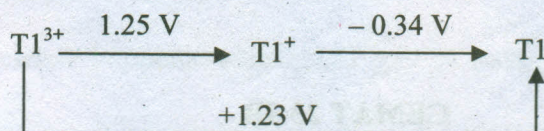
- (e) What are pseudohalides? Give example. Why these are called pseudohalides?

Unit-II

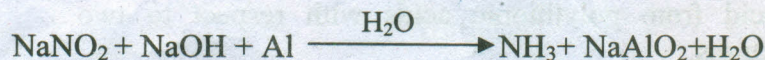
7. (a) Find the potential at equivalence point during the titration of 0.1 M Fe^{2+} with 0.1 M Ce^{4+} in aqueous solution.

Given $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 = 0.77 \text{ V}$ and $E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^0 = 1.57 \text{ V}$ at 25°C

- (b) What are the differences between 'standard potential' and 'formal potential'? Explain with example of your choice.
 (c) Construct the Frost diagram from the following Latimer diagram.



- (d) Aqueous Fe^{3+} oxidises I^- to liberate iodine. But the reaction is prevented in presence of excess ammonium bifluoride. Explain why?
 (e) Balance the reaction by ion electron method:

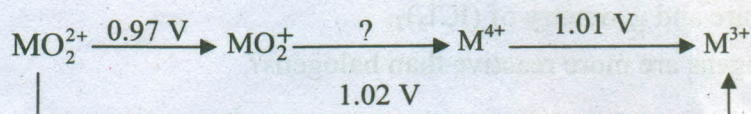


8. (a) Justify the oxidation of I^- to iodine by aqueous Cu^{2+} ion. Given the following redox potentials at 25°C :

$E_{\text{Cu}^{2+}/\text{Cu}^+}^0 = +0.15 \text{ V}$ and $E_{\frac{1}{2}\text{I}_2/\text{I}^-}^0 = +0.54 \text{ V}$.

Calculate the formal potential of the $\text{Cu}^{2+}/\text{Cu}^+$ System at 25°C at 0.1 M concentration of I^- (Given $K_{\text{sp}}(\text{CuI}) = 1 \times 10^{-12}$).

- (b) Calculate E^0 for $\text{MO}_2^+ \longrightarrow \text{M}^{4+}$ in 1M acid medium from the following Latimer diagram:



- (c) What is the minimum volume of water required to dissolve 1 g CaSO_4 at 298 K ? Given $K_{sp}(\text{CaSO}_4) = 9.1 \times 10^{-8}$. 2
- (d) Deduce the Nernst equation for the couple $\text{BrO}_3^-/\text{Br}^-$ in alkaline medium. 2

Group-B

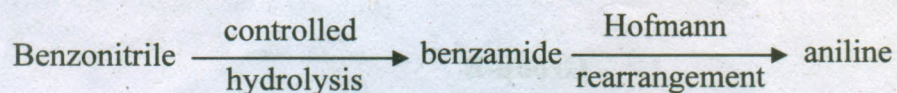
CEMAT-23-OA

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

Unit-I

9. (a) How would you distinguish between the members in each of the following pairs using the spectroscopic method given in the parentheses? $2 \times 3 = 6$
- (i) Methyl benzoate and phenyl acetate (IR spectroscopy);
 - (ii) Phenol and anisole (UV spectroscopy);
 - (iii) *E*- and *Z*-1-Bromo-2-chloroethene (^1H NMR spectroscopy).
- (b) A compound having the molecular formula $\text{C}_6\text{H}_{10}\text{O}$ has the following spectral data: 3
- ^1H NMR: δ_{ppm} 2.27 (3H, t); 2.30 (6H, s) and 6.09 (1H, s);
UV: λ_{max} (nm) 230 and 329 in hexane.
- Identify the compound with proper assignment of the given data.
- (c) Answer any *two* questions from the following: $2 \times 2 = 4$
- (i) Explain why on increasing solvent polarity, λ_{max} for $\pi \rightarrow \pi^*$ transition shifts to higher value for conjugated enones.
 - (ii) $\bar{\nu}_{\text{C}=\text{C}}$ has a value approximately 1640 cm^{-1} . Isobutene absorbs at that wave number; but 2, 3-dimethyl-2-butene fails to do so. Explain.
 - (iii) Draw the patterns of molecular ions bromobenzene and dibromobenzene in their mass spectra.

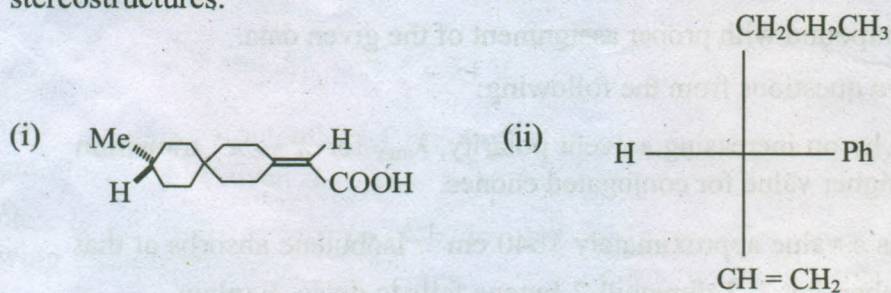
- 10.(a) Explain the terms hyperchromic and hypochromic shifts with the help of suitable examples. 3
- (b) How could you monitor the following reaction sequence by IR spectroscopy? 2



- (c) In the ^1H NMR spectrum, a particular proton appears 216 Hz downfield with respect to the TMS signal, when the operating frequency is 80 MHz. At which downfield frequency will it appear if the operating frequency is changed to 200 MHz? 2
- (d) Three signals at δ 4.0, 3.8 and 3.5 are observed in the ^1H -NMR spectrum of methyl methoxy acetate ($\text{C}_4\text{H}_8\text{O}_3$). Assign the signals for this structure and comment on the multiplicity of the signals. 4
- (e) What is molecular ion peak in mass spectra? Explain with a suitable example. 2

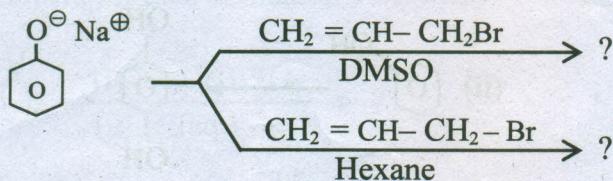
Unit-II

- 11.(a) Assign each chiral centre/axis as *R* or *S* present in the following stereostructures. 3

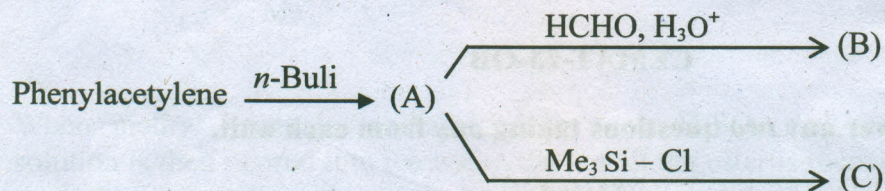


- (b) What happens when 1 mole of PhMgBr is separately reacted with (i) one mole of PhCHO , and (ii) 2 moles of PhCHO ? Show the product(s) with explanation of their formation. 3

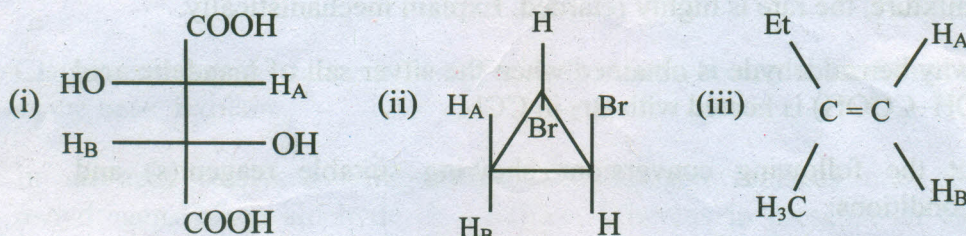
(c) Predict the products with plausible mechanism for the following reactions. 3



(d) Draw the structures for the products A, B and C. 3



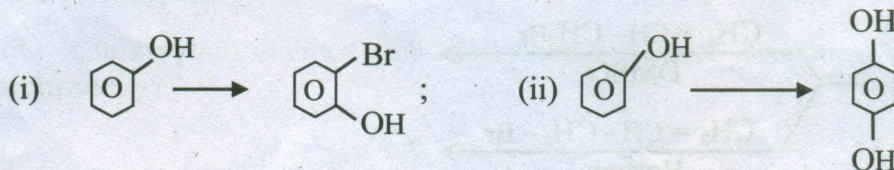
12.(a) Identify H_A and H_B in each of the following structures as homotopic, enantiotopic or diastereotopic and explain. 3



(b) Reimer-Tiemann reaction of *p*-cresol gives 2-hydroxy-4-methyl benzaldehyde along with a second product $C_7H_6OCl_2$ (A). Identify (A) and explain its formation as one of the products. 3

(c) Suggest a resolution process for the amino alcohol $ArCHOHCH_2NHCH_3$. 2

- (d) Carry out the following conversions mentioning the reagent(s) and reaction conditions: 4

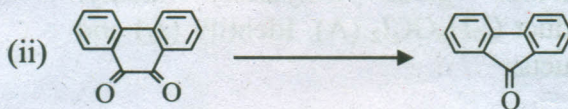


CEMAT-23-OB

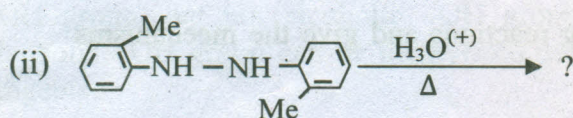
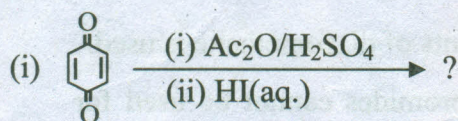
Answer any *two* questions taking *one* from each unit.

Unit-I

- 13.(a) Thioacetals and thioketals are not easily hydrolysable in dilute acid; but they can be easily hydrolysed by heating with aqueous HgCl_2 . Explain the role of Hg^{2+} . 2
- (b) In the LAH reduction of a ketone, if the crown ether 12-C-4 is added to the reaction mixture, the rate is highly retarded. Explain mechanistically. 2
- (c) Explain why benzaldehyde is obtained when the silver salt of mandelic acid (Ph-CHOH-COOH) is heated with Br_2 in CCl_4 . 2
- (d) Carry out the following conversions showing suitable reagent(s) and reaction conditions: 4



- (e) Predict the products in the following reactions and give plausible mechanism for their formation. (any one) 3



- 14.(a) When methyl benzoate is dissolved in conc. H_2SO_4 and the resulting solution is then poured into ice water, almost all the ester is recovered, while methyl mesitoate on same treatment yields quantitatively mesitoic acid. Explain. 3

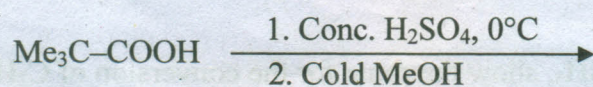
- (b) Suggest the structure of A and rationalize the second step mechanistically. 2



- (c) Claisen ester condensation of $\text{R}_2\text{CH-CO}_2\text{Et}$ cannot be achieved using $\ominus\text{OEt}$ as the base. Explain. 2

- (d) In an acid catalysed halogenation, the halogen replaces one of the α -hydrogens of an aldehyde or a ketone. Whereas in presence of excess halogen to a basic solution of an aldehyde or a ketone, the halogen replaces all of the α -hydrogens. Explain the above facts. 3

- (e) Identify the product(s) of the following reaction and offer justification. 3

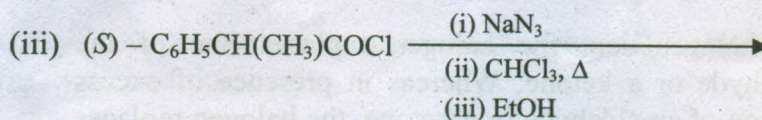
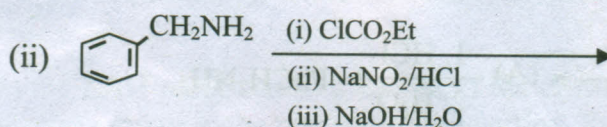
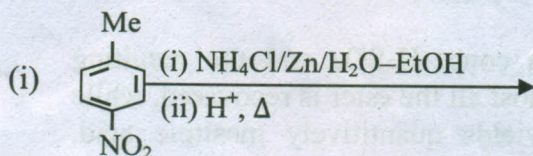


Unit-II

15.(a) Explain the following observations. 2×2 = 4

- (i) In the Arndt Eistert Synthesis, two equivalents of diazomethane is used.
- (ii) Ammonolysis of the corresponding allyl bromides cannot be used for the preparation of ^tBuNH₂ and Me₃CCH₂NH₂.

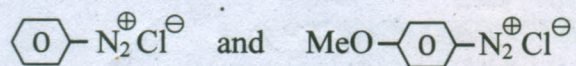
(b) Predict the product(s) of the following reactions and give the mechanisms for the key steps (*any two*). 3×2=6



(c) Starting from anisole how can you prepare *o*-nitroanisole as the major product? 2

16.(a) Using a protected form of NH₃, show the route for the conversion of C₂H₅Cl to C₂H₅NH₂ without any contamination with secondary or tertiary amines. 2

- (b) Which one of the two diazonium salts given below is hydrolysed at a faster rate when boiled in aqueous solution? Give reason(s). 2



- (c) Diazomethane alone can methylate carboxylic -OH group and phenolic -OH group, but not alcoholic -OH group - why? So suggest how an alcoholic -OH group can be methylated using diazomethane as one of the reagents. 2

- (d) State and explain the action of NaNO_2 and HCl on each of 1-nitropropane and 2-nitropropane. How are the products in the two cases distinguished? 2

- (e) Give a suitable route for each of the following conversions showing reagents and reaction conditions: $2 \times 2 = 4$

