



WEST BENGAL STATE UNIVERSITY

B.Sc. Honours 4th Semester Examination, 2022

CEMACOR08T-CHEMISTRY (CC8)

PHYSICAL CHEMISTRY-III

Time Allotted: 2 Hours

Full Marks: 40

*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.*

Answer any three questions taking one from each unit

Unit-I

1. (a) Consider a one component system. Explain the variation of the slope of μ vs. T plot at constant pressure as we go from **solid** \rightarrow **liquid** \rightarrow **gas**. 4
- (b) The melting point of pure phenol is **40.5°C**. A solution containing 0.18 gm acetanilide in 13.0 gm phenol freezes at **39.5°C**. Calculate the cryoscopic constant of phenol. Why the concentration is expressed in molality instead of molarity? 3+1
- (c) What do you mean by the abnormal colligative properties? What is Van't Hoff factor? Consider a **0.6%** aqueous solution of NaCl. It is experimentally observed that the solution freezes at **-0.3°C**. Calculate the Van't Hoff factor and degree of dissociation of NaCl in the aforesaid solution. 2+1+3
2. (a) State Gibbs phase rule of a thermodynamic system at equilibrium. Find out the number of Phase(s), Component(s) and Degree(s) of Freedom of the following systems at equilibrium. 2+3
 - (i) $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$; (ii) $\text{NH}_4\text{Cl}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{HCl}(\text{g})$
- (b) State Raoult's law and Henry's law. Show that Henry's law follows from Raoult's law for dilute solutions. 2+2
- (c) Consider the Maxwell's equation for a single phase given by $\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$. 2+3

Derive Clapeyron equation from this relation. Show that

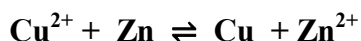
$$\left(\frac{\partial P}{\partial T}\right)_{\text{solid} \rightarrow \text{gas}} > \left(\frac{\partial P}{\partial T}\right)_{\text{liquid} \rightarrow \text{gas}}$$

Unit-II

3. (a) What do you mean by activity and activity coefficient of an ionic solution? Discuss how the electrophoretic and relaxation effects play the role to reduce the ionic mobility in Debye-Hückel theory. 2+4



- (b) Calculate the equilibrium constant for the reaction given by



[Given: $E_{\text{Cu}^{2+}/\text{Cu}}^0 = 0.337 \text{ V}$; $E_{\text{Zn}^{2+}/\text{Zn}}^0 = -0.763 \text{ V}$ at 25°C].

- (c) Discuss the principle of determination of pH of a solution by using quinhydrone electrode. 3
4. (a) What do you mean by reversible and irreversible electrochemical cells? Explain with an example. 2+2
- (b) Determine the standard equilibrium constant of the following reaction at 298 K. 4
- $$2\text{Fe}^{3+} + \text{Sn}^{2+} \rightarrow 2\text{Fe}^{2+} + \text{Sn}^{4+}$$
- [$E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 = 0.771 \text{ V}$; $E_{\text{Sn}^{4+}/\text{Sn}^{2+}}^0 = 0.150 \text{ V}$]
- (c) What is the principle underlying potentiometric titrations? Explain how can we determine the pH of a solution using Quinhydrone electrode. 1+3
- (d) State whether the statement is true or false: 2
- “In order to minimize Liquid Junction Potentials, one must use a salt bridge containing a salt such that $t_+ = t_-$.”

Unit-III

5. (a) Find the value of the commutator, $[L_x, L_y]$. 4
- (b) Show that $Y_1^{-1}(\theta, \phi)$ is normalized and orthogonal to $Y_0^0(\theta, \phi)$. 4
- Given: $Y_1^{-1}(\theta, \phi) = (3/8)^{1/2} \sin \theta e^{-i\phi}$ and $Y_0^0(\theta, \phi) = (1/4\pi)^{1/2}$
- (c) Write down the electronic Hamiltonian of H_2^+ . 2
- (d) Draw the radial probability density with respect to distance from the nucleus for 2s orbital of hydrogen atom. 2
6. (a) Write down the time-independent Schrödinger equation for H-atom in polar coordinates with the meaning of the symbols. 2
- (b) Find out the average distance of the electron of a hydrogen atom in 1s orbitals. 3
- [Given: $\psi_{1s} = \left(\frac{1}{\pi a_0^3} \right)^{1/2} \cdot e^{-r/a_0}$]
- (c) Write the Hamiltonian operator for the hydrogen molecule stating the meaning of the symbols. 2
- (d) Explain the concepts of molecular orbital theory and valence bond theory. State the strengths and limitations of valence bond approach to molecular bonding. 3+2

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WEST BENGAL STATE UNIVERSITY

B.Sc. Honours 4th Semester Examination, 2022

CEMACOR09T-CHEMISTRY (CC9)

INORGANIC CHEMISTRY-III

Time Allotted: 2 Hours

Full Marks: 40

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Answer any *three* questions taking *one* from each unit

Unit-I

1. (a) Define the following with example: 1×4 = 4
Alloy, Mineral, Ore and Slag
- (b) What does roasting mean in metallurgy? 2
- (c) Describe briefly the extraction of Ti metal from its ore by Kroll process. 4

2. (a) What do you mean by parting process? Describe briefly how Gold metal can be obtained from the mixture by parting process. 1+3
- (b) Consult the Ellingham diagram and determine if there are conditions under which Aluminium might be able to reduce MgO? 3
- (c) In some modern process of hydrometallurgy, the beneficiation and conservation are carried out in one step. Give examples. 3

Unit-II

3. (a) Compare and Contrast the properties of B and Al considering the following points: 5
(i) Elemental states
(ii) Hydrides
(iii) Halides.
- (b) The fluorocarbons are remarkably chemically inert. — Comment. 2
- (c) Depict the structural features of Diborane. Explain the reactivity of Diborane as a Lewis acid with reference to ammonia and amines. 3
- (d) Give example of a three dimensional silicate and on the basis of its structure mention its use. 3
- (e) Cyanogen is a pseudohalogen. — Justify. 2
- (f) Suggest a method of preparation of XeO₂F₂ and also draw its structure. 2
- (g) What happens when 3
(i) Ferric chloride solution is added gradually to a sodium thiosulphate solution.
(ii) Silver nitrate is added to a concentrated solution of ammonium persulphate.



4. (a) Predict and explain the order of the 'tendency of polymerisation' of the following oxyanions: 3
 SO_4^{2-} , ClO_4^- , PO_4^{3-} , SiO_4^{4-}
- (b) Amongst inert gases, Xenon is most suitable to form chemical compounds — Explain. 2
- (c) Discuss the structure and bonding of $(\text{SN})_x$ [$x = 4$]. 3
- (d) State two evidences of chemical reaction to establish that SCN^- is a pseudohalide. 2
- (e) Write down the structures of trimeta-phosphoric acid and tripoly-phosphoric acid. Hence, comment on the basicities of the two acids. 2
- (f) Why fluorocarbons are very stable and not easily oxidisable? 2
- (g) What are interhalogens? On the basis of hybridization, mention the structures of different types of interhalogen compounds. 3
- (h) Give the structure of cyclic trimetasilicate ion. Give an example to show that hydrazine behaves as a reducing agent. 3

Unit-III

5. (a) How would you show that the thiocyanate ion acts as an ambidentate ligand? 2
- (b) Write down the structures of different isomeric forms of $[\text{Cr}(\text{ox})_3]^{3-}$. 2
- (c) How many isomers are possible for $[\text{Co}(\text{NH}_3)(\text{OH})_2\text{Cl}_3]^{2-}$? 2
- (d) How will you distinguish between the following pairs of isomers? 2+2
 (i) $[\text{Co}(\text{NH}_3)_6] [\text{Cr}(\text{NO}_2)_6]$ and $[\text{Cr}(\text{NH}_3)_6] [\text{Co}(\text{NO}_2)_6]$
 (ii) $[\text{Cr}(\text{NH}_3)_6] [\text{Cr}(\text{NO}_2)_6]$ and $[\text{Cr}(\text{NH}_3)_4(\text{NO}_2)_2] [\text{Cr}(\text{NH}_3)_2(\text{NO}_2)_4]$
6. (a) Molar conductance at a dilution of 1024 litres of $\text{PtCl}_4 \cdot 2\text{NH}_3$; $\text{PtCl}_4 \cdot 3\text{NH}_3$; $\text{PtCl}_4 \cdot 6\text{NH}_3$ are 7, 97 and $520 \text{ Ohm}^{-1}\text{cm}^2$ respectively. Rationalise these data in the light of Werner's theory. 3
- (b) Acetyl acetone is a potential ligand that forms a square planar complexes with Cu(II). Draw the structure of the complex and predict the formal charge on the complex. 2
- (c) Metal chelates are more stable than non-chelated complexes. — Comment. 3
- (d) Write the IUPAC name of $[(\text{SCN})_3(\text{H}_2\text{O})_2\text{Cr}-\text{OH}-\text{Co}(\text{NH}_3)_5](\text{SO}_4)$ and the formula of pentaammineazidocobalt(III) sulphate. 2

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WEST BENGAL STATE UNIVERSITY

B.Sc. Honours 4th Semester Examination, 2022

CEMACOR10T-CHEMISTRY (CC10)

ORGANIC CHEMISTRY-IV

Time Allotted: 2 Hours

Full Marks: 40

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Answer any four questions taking one from each unit

Unit-I

1. (a) How would you chemically distinguish the following pair of compounds? 2
 (i) Benzyl cyanide and benzyl isocyanide
 (ii) N-methylaniline and N, N-dimethylaniline.
 (b) Explain the products [A] and [B] with proper mechanism of the reaction. 2

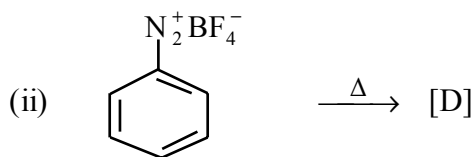
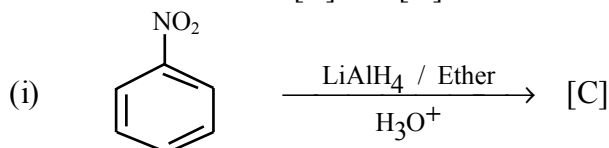
$$\text{CH}_3\text{CH}_2\text{NO}_2 \xrightarrow[\text{NaOH}]{\text{aqueous}} [\text{A}] \xrightarrow[\text{room temperature}]{50\% \text{ H}_2\text{SO}_4} [\text{B}]$$

 (c) How can you prepare N-methylaniline from aniline? 2

2. (a) Suggest the product(s) and give the mechanism for the following reaction: 2

$$\text{Et}_2\text{NH} \xrightarrow[\Delta]{\text{HCHO} / \text{HCOOH}} \text{Product(s)}$$

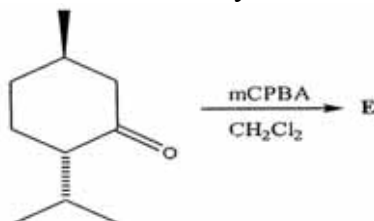
 (b) Give the structures of [C] and [D]: 2



- (c) How can you convert aniline to 1,3,5-tribromobenzene? 2

Unit-II

3. (a) Draw the structure of **E** with the proper configuration of the stereogenic centres and give plausible mechanistic steps. Discuss the effect of stereoelectronic factors for the determination of regio and stereoselectivity. 4



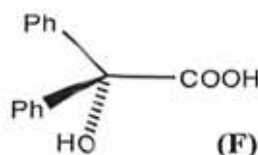


(b) Carry out the following conversions:

(i) Phthalic anhydride \longrightarrow anthranilic acid

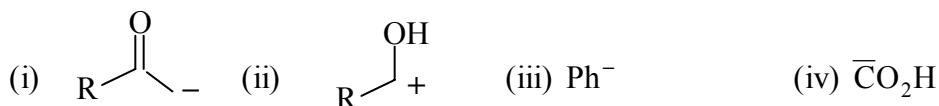


4. (a) Outline two methods for the preparation of phenyl acetate. Rationalise the products in the reaction of phenyl acetate and anhydrous AlCl_3 (Friedel-Crafts conditions) with plausible mechanism. Explain the role of solvents and temperature in the control of product ratio. 4
- (b) Convert benzoyl chloride to phenylacetic acid in one-step. Suggest plausible mechanism with a comment on the intermediate. 2
- (c) Convert benzoin to the α -hydroxyacid (**F**) in two steps and suggest plausible mechanism for step two only. 2

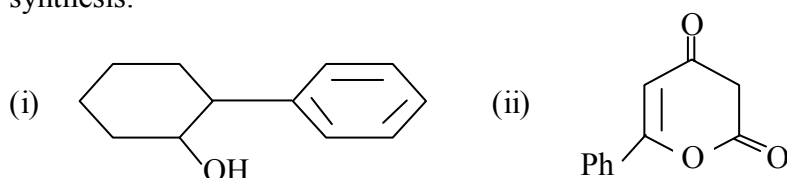


Unit-III

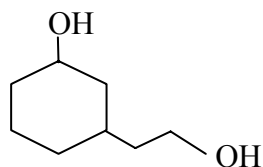
5. (a) Give the synthetic equivalent for the following species: 2



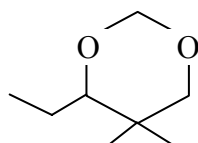
- (b) Show the retrosynthetic analysis of the following compounds and then carry out the synthesis: $1\frac{1}{2}+1\frac{1}{2}$



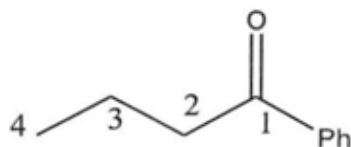
- (c) Plan a retrosynthesis followed by the synthesis of the following by FGI approach. 3



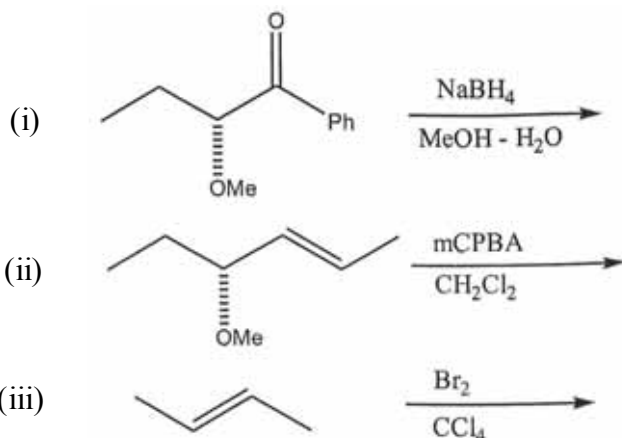
- (d) Propose a synthesis of the following compound: 2



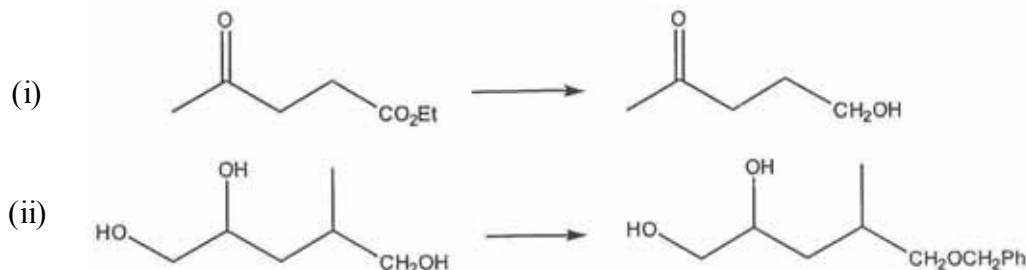
6. (a) Depict the disconnections, as indicated for the retrosynthesis of the following ketone and then draw the synthons and the corresponding synthetic equivalents. Also, classify all the synthons as logical / illogical and donor / acceptor terminology. 4



- (i) FGI followed by C – C disconnection
 (ii) 1,2 C – C disconnection
 (iii) 2,3 C – C disconnection
 (iv) 3,4 C – C disconnection.
- (b) Predict the product(s) in the reactions given below and comment whether these are stereoselective or stereospecific reactions. 3



- (c) Carry out the following conversions using protection / deprotection strategy. 3



Unit-IV

7. (a) Sketch and label the possible bending vibrational modes in CH_2Cl_2 . 2
- (b) What are the radiation sources of IR spectrometer and UV spectrometer? 2
- (c) What are the significance of the terms: (i) absorbance and (ii) vacuum UV? 2
- (d) Describe Fermi coupling. Which region in IR spectrum is known as fingerprint region? Describe its significance. 2
- (e) Distinguish the following pair of compounds using spectroscopy: 3
- (i) (IR spectroscopy)
- (ii) *cis* and *trans* stilbene (UV spectroscopy)
- (iii) $\text{CH}_3 - \text{CH}_2 - \text{C} \equiv \text{CH}$ and $\text{H}_3\text{C} - \text{C} \equiv \text{C} - \text{CH}_3$ (^1H NMR)
- (f) Aromatic protons are more deshielded than ethylenic protons, although both the types of protons are attached to sp^2 hybridised C-atom. — Explain. 2



(g) An organic compound having molecular formula $C_8H_7NO_3$ shows a strong IR bond at 1690 cm^{-1} and three signals at

δ 8.5 (doublet)

δ 7.9 (doublet)

δ 2.5 (singlet)

in its ^1H NMR spectra. Establish the structure of the compound.

8. (a) In IR spectroscopy ethylacetoacetate shows the peaks at 1715 cm^{-1} , 1690 cm^{-1} , 2900 cm^{-1} and 3500 cm^{-1} . How will you explain it? 2
- (b) Define the following terms: 2
- (i) Hypochromic effect, (ii) Hypsochromic effect
- (c) How would you distinguish 4-nitro-N,N-dimethylaniline and acidified 4-nitro-N,N-dimethylaniline by UV spectroscopy? 2
- (d) Predict and label the chemical shifts in δ_{ppm} and the splitting pattern of the nonequivalent Hs of butanone. Express the difference of chemical shift value in Hz between the upfield and downfield Hs in butanone. 3
- (e) The compound (X) is obtained as major product after the mononitration of toluene. Compound X on reduction with Sn and concentrated HCl gives compound Y. Compare the ^1H -NMR spectra of X and Y. 2
- (f) What are the two probable products (enone) in the aldol condensation of acetone? How would you distinguish them by UV, IR and ^1H -NMR spectroscopy? 3
- (g) Why is tetramethylsilane (TMS) preferred as an internal standard in ^1H -NMR experiment? 2

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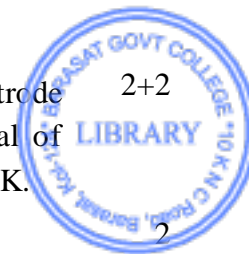
Answer any three questions taking one from each unit

Unit-I

1. (a) Using the concept of chemical potential, derive thermodynamically the relation between the elevation of boiling point of a solvent and molality of the solution. Clearly mention the assumptions and approximations used in the derivation. 3+1
- (b) Liquid carbon dioxide cannot exist at normal atmospheric pressure, whatever be the temperature. — Justify. 2
- (c) The heat of fusion of ice is 6.0 kJmol^{-1} . Calculate the freezing point of water in a solution containing a non-volatile nonelectrolyte solute where the mole fraction of water is 0.8. 3
- (d) State the degrees of freedom for an azeotrope in two component liquid-vapour equilibrium. Explain why an azeotropic mixture is not considered to be a compound. 1+1
- (e) Consider the phase transition $\text{H}_2\text{O(l)} \rightleftharpoons \text{H}_2\text{O(v)}$ and depict with a graphical representation, the variation of chemical potential of H_2O against temperature at constant pressure in the vicinity of its boiling point. 3
2. (a) Derive Duhem-Margules equation for binary solution stating clearly the assumptions. 3
- (b) Show that the expression of osmotic pressure of a dilute solution is similar to that of an ideal gas. State the assumptions and approximations involved. 3+1
- (c) What do you understand by phase (P), component (C) and degrees of freedom (F) of a thermodynamic system? 3
- (d) A mixture of 100 g water and 80 g of Phenol separates into two layers at 60°C . One layer, L_1 , consists of 44.9% water by mass, the other layer L_2 , consists of 83.2% water by mass. Calculate the total number of moles in L_1 and L_2 . 4
[Given: molar mass of Phenol is 94.4 g mol^{-1}]

Unit-II

3. (a) What are the factors on which the Debye-Hückel constant (A) depends? 2
- (b) Discuss the principle of standardization of a given Mohr's salt solution by standard potassium dichromate solution. Show the plot of E_{cell} (volt) vs. N_{oxidant} , where N_{oxidant} is the number of drops of oxidant. Also calculate $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0$. 3+2+1



- (c) For AgI $K_{sp} = 1 \times 10^{-16}$ at 298 K. What will be the potential of $\text{Ag}^+ | \text{Ag(s)}$ electrode in a saturated solution of AgI? Also calculate the standard reduction potential of $\text{Ag(s)} | \text{AgI(s)} | \text{I}^-$ electrode at 298 K. Given: E^0 of $\text{Ag}^+ | \text{Ag(s)} = 0.80 \text{ V}$ at 298 K. 2+2
- (d) How does molar polarisation vary with temperature for polar molecules? 2
4. (a) Show schematically the plots of $\log f_{\pm}$ versus \sqrt{C} (where C is the molar concentration) for the dilute aqueous solutions of two strong electrolytes AlCl_3 and Na_2SO_4 in the same graph at 298 K and hence show that their slopes are in the ratio $3:\sqrt{2}$. 3
- (b) Given that standard potentials of the Cu^{2+}/Cu and Cu^+/Cu couples are $+0.340 \text{ V}$ and $+0.552 \text{ V}$, respectively. Evaluate standard potential (E^0) of ($\text{Cu}^{2+}/\text{Cu}^+$) system. 3
- (c) Set up a reversible cell without transference for the process: 1+1+1
 $\text{CuSO}_4(a_1) \rightarrow \text{CuSO}_4(a_2) ; (a_2 < a_1)$
 What is liquid junction potential? How it can be eliminated?
- (d) Explain how the pH of a solution can be determined by the use of a glass electrode. 3
- (e) If the dipole moment for Chlorobenzene is 1.57 D then find that for m -dichlorobenzene. 2

Unit-III

5. (a) Evaluate the following commutators and comment on the results. 2+2
 (i) $[L_x, L_z]$ (ii) $[L_z, L^2]$
- (b) (i) Define an orbital. 1+2+1
 (ii) Find the number of radial nodes in the wave functions of the following orbitals:
 $2p$ and $3s$
 (iii) What is the physical significance of a node?
- (c) Calculate the probability of finding a $1s$ electron of hydrogen within a distance $2a_0$ from the nucleus. What is the probability beyond $2a_0$? 3+1
6. (a) What is Born-Oppenheimer approximation? 2
- (b) Suppose an atom has two electrons in two different orbitals. What will be the values for the total spin quantum number S and the multiplicity? 2
- (c) Consider a trial function $\psi = x(a-x)$ for a particle in a one-dimensional box of length a . Show that this function satisfies the boundary conditions. Apply the variation method to get an upper bound to the ground state energy of the particle and compare the result with true value. 4
- (d) Under what conditions the mixing between two atomic orbitals would result in a molecular orbital with better combination in LCAO-MO method? Explain qualitatively with suitable examples. 4

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Unit-I

1. (a) Explain why, metal oxides are generally unstable at high temperature from Ellingham diagram? 2
- (b) Describe the principle and reactions related to the extraction of Aluminium by electrolytic reduction. 3
- (c) What is the role of Cryolite in the extraction of Aluminium? 2
- (d) What is 'leaching'? Name two basic leaching reactors. 3
2. (a) Write the difference between calcination and roasting. 2
- (b) The choice of flux depends upon the impurities present in the ore. — Comment. 2
- (c) What is Hydrometallurgy? How are Gold and Silver extracted by this method? Write the reactions. 3
- (d) Which factor influences refining of Ni by Mond process? 2
- (e) Which method is used for refining Zr and Ti by removal of oxygen and nitrogen? 1

Unit-II

3. (a) Give a comparative account of the chemistry of O, S, Se and Te with respect to their oxidation states and stability of hydrides. 5
- (b) Discuss the structure and bonding of polyphosphazenes. 3
- (c) Catenation power of carbon is higher than that of boron and nitrogen. — Explain. 2
- (d) What are silicones? Discuss their polymeric nature. 3
- (e) Give examples to show that hydroxylamine possesses both oxidizing and reducing properties. 2
- (f) How would you isolate Argon from air? State one use of it. 2
- (g) Write down the formula and structure of a dithionic acid. Explain why it is not considered as a member of the polythionic acid group having the general formula $H_2S_nO_6$. 3



4. (a) How does Be differ from other alkaline earth metals? 2
 (b) Explain why boron nitride is called 'inorganic graphite'? 2
 (c) Write the structure of N_2O_5 and comment on its stability and decomposition products. 4
 (d) Complete the following reactions: 4

$$B_3N_3H_6 + HCl \rightarrow$$

$$(NPCl_2)_3 + CH_3MgI \rightarrow$$

 (e) What is clathrates? Give example. 2
 (f) Me_3P acts as a stronger base than Me_3N in their reaction with B_2H_6 — Explain. 3
 (g) Give a convenient route for the synthesis of $XeOF_4$ with equations. Why it cannot be stored in glass/quartz vessel? 2+1

Unit-III

5. (a) Distinguish between ambidentate and flexidentate ligands with proper example. 2
 (b) What are chelates? Mention one application of it in qualitative and quantitative analysis. 3
 (c) $[Pt(NH_3)_2Cl_2]$ has two isomeric forms. Suggest a chemical method to elucidate the structure of the isomers. 3
 (d) Write the IUPAC name of $[(CO)_3Fe(CO)_3Fe(CO)_3]$ and the formula of μ -amido- μ -hydroxooctaminedicobalt(III) ion. 2
6. (a) Give the IUPAC names of $[Co(NH_3)_4(NO_2)Cl]$, $[Pt(NH_3)_4][PtCl_4]$. 2
 (b) Which ligands satisfy the primary and secondary valency in $[Co(NH_3)_5Cl]Cl_2$? 3
 (c) Explain why, $K_4[Fe(CN)_6]$ is non-toxic whereas KCN is toxic? 2
 (d) Draw the possible geometrical isomers of $[Co(en)(NH_3)_2BrCl]^+$ and hence predict which of them would be optically active. 3

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B.Sc. Honours 4th Semester Examination, 2021

CEMACOR10T-CHEMISTRY (CC10)

ORGANIC CHEMISTRY-IV

Time Allotted: 2 Hours

Full Marks: 40

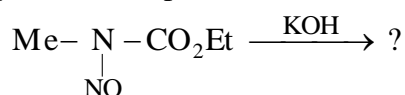
*The figures in the margin indicate full marks.
Candidates should answer in their own words and adhere to the word limit as practicable.
All symbols are of usual significance.*

Answer any four questions taking one from each unit

Unit-I

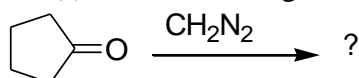
1. (a) Why ammonolysis on the corresponding alkyl bromides (RBr) cannot be used for the preparation of $t\text{BuNH}_2$ and $\text{Me}_3\text{CCH}_2\text{NH}_2$? How would you prepare these amines from carboxylic acids (RCO_2H)? 3

- (b) Give the product with plausible mechanism: 3

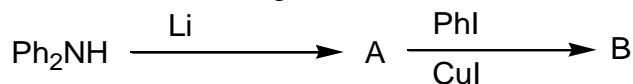


2. (a) Explain why benzene diazonium chloride couples with phenol in alkaline medium but not with anisole under the same reaction conditions. 2

- (b) Give the product(s) of the following reaction with plausible mechanism: 2



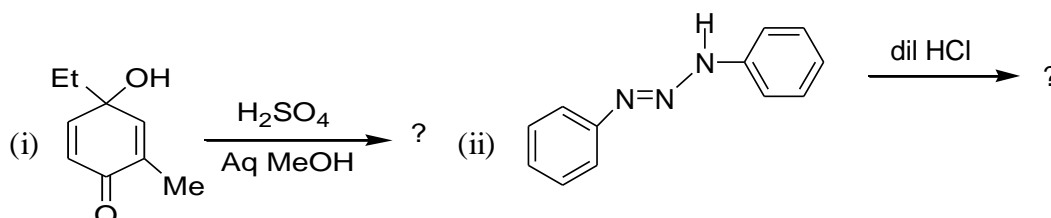
- (c) Identify A and B in the following: 2



Unit-II

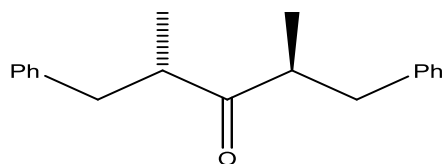
3. (a) In the Arndt-Eistert synthesis two equivalent of diazomethane is recommended. — Explain. 2

- (b) Identify the product(s) in the following with plausible mechanism. 2+2

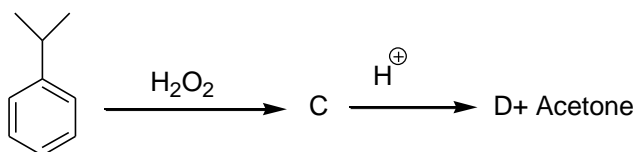




- (c) Derive the product(s) of Baeyer-Villiger rearrangement on the following enantiomerically pure ketone. Suggest mechanism and comment on the stereochemistry of the product(s).

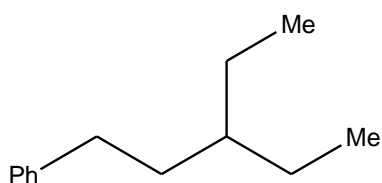


4. (a) Carry out the following conversion and suggest plausible mechanism (any *two*). 2+2
- Acetophenone to 2-phenylpropanal
 - Phenol to catechol
 - p*-Hydroxyacetophenone to paracetamol.
- (b) The isomeric pinacols $\text{Ph}_2\text{C}(\text{OH})\text{C}(\text{OH})\text{Me}_2$ and $\text{PhMeC}(\text{OH})\text{C}(\text{OH})\text{PhMe}$ undergo acid-catalyzed rearrangement to afford a common product. — Explain. 2
- (c) Identify C and D with proper mechanistic explanation. 2

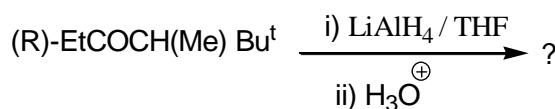


Unit-III

5. (a) Draw the scheme for retro-synthetic analysis of the following hydrocarbon using FGA strategy. Also, depict the synthetic pathway of it. 3

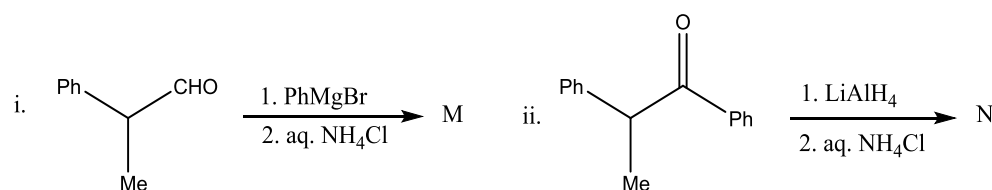


- (b) Predict the major product of the following reaction with reason. 3



- (c) Explain with suitable examples: Synthons and illogical electrophile. 2+2

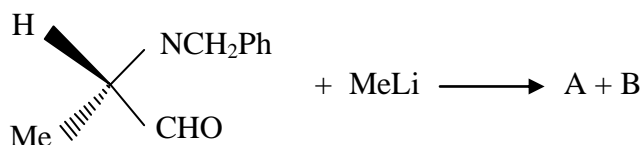
6. (a) Draw the structure of the major products (M and N) in the following reactions. Establish the stereoisomeric relationship between M and N and rationalize the results. 4



- (b) What do you mean by high dilution technique for the synthesis of large ring compounds? — Explain. 2
- (c) What do you mean by chemo-selective reaction? Give an example. 2

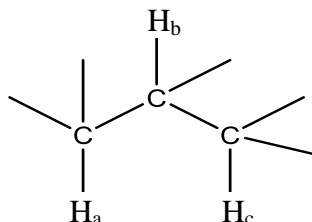


(d) Write the products with proper stereochemistry. Justify your answer.

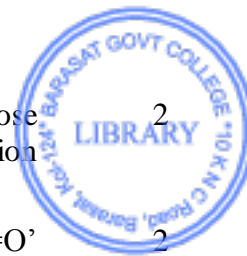


Unit-IV

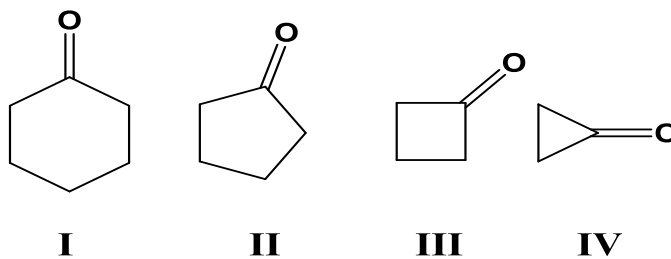
7. (a) Distinguish the following pair of compounds on the basis of their IR spectra: 2+2
 (any *two*)
- (i) Acetone and hexamethyl acetone
 - (ii) Salicylic acid and *p*-hydroxy benzoic acid
 - (iii) Phenyl acetate and methyl benzoate.
- (b) The UV spectrum of mesityl oxide shows absorption bands at 321 and 230 nm in hexane. Assign them in terms of electronic transition. Depict the changes of this spectrum if the experiment is carried out in 95% ethanol solvent. Justify your answer. 3
- (c) An organic compound of molecular formula $\text{C}_6\text{H}_{12}\text{O}$ shows a peak at 1715 cm^{-1} in its IR spectrum. The ^1H NMR spectrum of the compound displays two singlets at δ 0.9 and 2.2 in the ratio of 3:1. Deduce the structure of the compound and explain the spectral data. 3
- (d) "Two protons are chemically equivalent but magnetically non-equivalent". Justify the statement with an example. 2
- (e) Predict the number(s) of ^1H -NMR peak of chlorocyclopropane and justify. 2
- (f) Esters of *o*-chlorobenzoic acid show two C=O stretching frequencies. — Explain. 2
8. (a) Distinguish the following pairs by UV spectroscopy (any *two*): 3
- (i) *p*-cresol and anisole
 - (ii) mesityl oxide and $\text{CH}_2 = \text{C}(\text{Me})\text{CH}_2\text{COMe}$
 - (iii) aniline and cyclohexylamine.
- (b) Predict the organic compound of molecular formula $\text{C}_9\text{H}_{10}\text{O}_2$ from the following spectral data. 3
 IR: 1740 cm^{-1} ; ^1H NMR: δ 1.96 (3H, s), 5.00 (2H, s) and 7.20 (5H, m).
- (c) The stretching absorption maxima for C–H and C–D are approximately 2900 cm^{-1} and 2200 cm^{-1} respectively. Explain why. 2
- (d) Draw the splitting pattern for H_b in the ^1H -NMR spectrum of the fragment given below, where 2
- (i) $J_{ba} = 12\text{ Hz}$ and $J_{bc} = 6\text{ Hz}$
 - (ii) $J_{ba} = 12\text{ Hz}$ and $J_{bc} = 12\text{ Hz}$.



(e) Define the terms (i) up-field (ii) downfield shifts as used in NMR spectroscopy. 2



- (f) The UV absorption maxima of aniline in aqueous solution are different from those of benzene, but the positions of UV absorption maxima of aniline in acidic solution ($\text{pH} \approx 1$) are almost identical with benzene. — Explain.
- (g) Arrange the following compounds according to their increasing order of 'C=O' stretching frequency and give reason.



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WEST BENGAL STATE UNIVERSITY

B.Sc. Honours 4th Semester Examination, 2020

CEMACOR08T-CHEMISTRY (CC8)

PHYSICAL CHEMISTRY

Time Allotted: 2 Hours

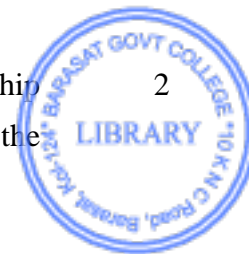
Full Marks: 40

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Answer any three questions taking one from each unit

Unit-I

1. (a) Using the concept of chemical potential (μ) derive thermodynamically a relation between the osmotic pressure of a binary solution and its molar concentration. Clearly mention the assumptions and approximations used in your derivation. 4+2
- (b) Starting from a suitable form of Duhem-Margules equation, derive the condition that for an azeotrope the mole fraction of each component in the liquid phase is equal to that in the vapor phase. 3
- (c) The vapor pressure of benzaldehyde is 400 torr at 154 °C and its normal boiling point is 179 °C. Calculate the molar enthalpy of vaporization of benzaldehyde. Mention the assumption(s), if any, in your calculation. 2+1
- (d) The intermolecular attraction between the molecules of all components (solute and solvent) in an ideal solution must be identical in nature. Justify or criticize. 2
2. (a) Draw the chemical potential versus temperature diagram at constant pressure for a pure substance in the three states of matter with proper explanation. Comment on the relative magnitudes of ΔT_f and ΔT_b from the plot. Mention the assumptions in your answer (ΔT_f is the depression of freezing point, ΔT_b is the elevation of boiling point). 2+1+1
- (b) (i) For an ideal solution plot the variation of the quantity p_1/p_1^0 as a function of x_2 . 1+2+2
- (ii) Sketch the plot of p_1/p_1^0 as a function of molality of the solute if water is the solvent.
- (iii) How is the plot of p_1/p_1^0 with molality affected when the solvent is changed to toluene?
(x_2 = mole fraction of solute, p_1^0 = vapor pressure of pure solvent, p_1 = partial vapor pressure of solvent in solution).
- (c) Using the Clausius-Clapeyron equation show that the slope of the solid-gas coexistence curve is greater than the slope of the liquid-gas coexistence curve at the triple point. 3



- (d) The vapor pressure of benzene is expressed by the following empirical relationship $\ln(p/\text{torr}) = 17.63 - \frac{3884\text{K}}{T}$. Find the boiling point of benzene when the atmospheric pressure is 500 torr. 2

Unit-II

3. (a) (i) Derive the expression $\left[\frac{\partial(E^0/T)}{\partial(1/T)} \right]_p = -\frac{\Delta H^0}{nF}$, where the terms have usual significance. 3+1
- (ii) Justify whether the standard emf (E^0) of a cell is an intensive or extensive property.
- (b) A cell is represented by $\text{Pb} | \text{PbI}_2(\text{s}) | \text{KI}(\text{aq}) | \text{AgI}(\text{s}) | \text{Ag}$ 4
Write down the cell reaction. If the cell has an e.m.f of 0.2078 V at 25 °C and $\left(\frac{\partial E}{\partial T} \right)_p = -1.88 \times 10^{-4} \text{V/K}$, calculate ΔG and ΔS for the cell reaction.
- (c) Write down the Debye Huckel Limiting Law explaining all the terms. Calculate the mean ionic activity coefficient of a 2-1 electrolyte at a molality of 0.01 aqueous solution at 15 °C [$A = 0.50$ at 15 °C] 1+2
- (d) Why does Clausius-Mossotti equation fail in case of polar molecules? How is it modified in the form of the Debye equation? 3
4. (a) For the concentration cell 2+2
 $\text{Ag} | \text{AgCl}(\text{s}) | \text{HCl}(a_1) | \text{HCl}(a_2) | \text{AgCl}(\text{s}) | \text{Ag}$
- (i) Write the various processes at the two electrodes and at the liquid junction
- (ii) Derive the expression for ΔG and e.m.f of the cell
- (b) How does molar polarization vary with temperature? Explain using proper equation. Find the C.G.S unit of $\frac{\mu^2}{kT}$. 2+1
- (c) The thermodynamic dissociation constant for acetic acid, HAc, is 1.75×10^{-5} at 25 °C. 3
Calculate using the Debye-Huckel theory, the degree of dissociation of 0.001 M acid in 0.05 M $\text{Ca}(\text{NO}_3)_2$.
- (d) The molar orientation polarization of chloroform decreases sharply with increasing temperature but that of carbon tetrachloride remains almost invariant with temperature. Explain with the help of an appropriate equation. 2
- (e) Calculate the equilibrium constant for the formation of I_3^- from $\text{I}_2(\text{aq})$ and I^- at 25 °C using the following data 2



**Unit-III**

5. (a) The operator for the z-component of angular momentum in spherical polar coordinates is given as $\hat{L}_z = -i\hbar \frac{\partial}{\partial \varphi}$ where $0 \leq \varphi \leq 2\pi$ and $Y_{l,m}(\theta, \varphi)$ is an eigenfunction of the operator. 1+3+2
- (i) Construct a suitable eigen value equation giving proper justification for your answer.
- (ii) Solve the eigen value equation applying the technique of separation of variables to find a suitable solution for the φ -part.
- (iii) Verify if the solution gives quantized values for L_z .
- (b) What are the relative merits and demerits of VB method as compared to the LCAO-MO method? 2
- (c) The radial wavefunctions for the 1s and 2s orbitals of H-atom are given below. Without using any explicit formula justify the number and location of nodes in the two wavefunctions and indicate the same graphically. 3+1

$$R_{1s} = 2a_0^{-3/2} e^{-r/a_0}$$

$$R_{2s} = (2a_0)^{-3/2} (2 - \frac{r}{a_0}) e^{-r/2a_0}$$

(a_0 is Bohr radius).

Find the SI units of the functions R_{1s} and R_{2s} .

6. (a) Using the results $\hat{L}^2 Y_{l,m} = \lambda \hbar^2 Y_{l,m}$ and $\hat{L}_z Y_{l,m} = m \hbar^2 Y_{l,m}$ find the maximum allowed limit for the value of m (m and λ are pure integers). 3
- (b) (i) If we measure L_y of a particle whose state function is an eigen function of \hat{L}^2 with eigen value $12\hbar^2$, what possible outcomes for the measurement do you expect? Give proper justification for your answer. 3+1
- (ii) What possible outcome do you expect if L_z is also measured at the same time? Justify.
- (c) (i) Using the expression for ψ_{1s} find an expression for the average distance $\langle r \rangle$ of a 1s electron from the nucleus for a hydrogen-like atom. 3+(1+1)
- (ii) Using your expression for $\langle r \rangle$ calculate the average distance of a 1s electron from the nucleus for H-atom and He^+ ion and state the significance of your result.

Given: $\psi_{1s} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$, $\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$, Bohr radius, $a_0 = 0.529 \text{ \AA}$, $Z = \text{atomic number}$.

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WEST BENGAL STATE UNIVERSITY
B.Sc. Honours 4th Semester Examination, 2020

CEMACOR09T-CHEMISTRY (CC9)

Time Allotted: 2 Hours

Full Marks: 40

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Candidates should answer in their own words and adhere to the word limit as practicable.
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Answer any *three* questions taking *one* from each unit

Unit-I

1. (a) Describe the principle of refining of nickel by Mond's process. 4
- (b) Copper can be extracted by hydrometallurgy but not zinc. Explain. 3
- (c) Which metals are produced and refined by van Arkel de Boer process? Give a brief description of the method used. 1+2
2. (a) Outline the principle of refining of metal by zone refining. 4
- (b) Which metals are generally extracted by electrolytic reduction and why? 2
- (c) Which metals are generally extracted together by Parting process? 1
- (d) What is the role of graphite rod in the electrometallurgy of aluminium? 3

Unit-II

3. (a) What product is expected when Xe reacts with PtF_6 in vapour state? 2
- (b) Why the chemistry of Li is anomalous in comparison to sodium and potassium? 3
- (c) Why is $\text{B}_3\text{N}_3\text{H}_6$ called 'inorganic benzene'? State the hybridization of B and N in the compound. State one difference between this compound and benzene regarding chemical behaviour. 2+2+1
- (d) Discuss the structure of S_4N_4 . How the compound is prepared? 2+1
- (e) Why is AlCl_3 covalent but AlF_3 ionic? 2
- (f) Compare the properties of elements N, P, As, Sb, Bi in respect of their (i) hydrides and (ii) halides. 5
4. (a) What are interhalogens? Classify different binary interhalogens and give examples of each type. Comment on their hydrolysis products and structures. 6



- (b) Compare the catenation properties of C, Si and Ge with explanation.
- (c) 'Freons deplete the ozone layer of upper atmosphere' — Explain with equations.
- (d) 'The acidity of aqueous solution of boric acid increases in presence of glycerol' — Explain.
- (e) Discuss the structure and bonding of the following compounds: 2+2
- (i) XeO₃ (ii) XeF₂

Unit-III

5. (a) Give IUPAC names of: 2
- (i) Na₄(Fe(CN)₅NOS]
- (ii) [PtCl(NH₂CH₃)₂(NH₃)]Cl
- (b) Draw the structures of the possible isomers of [Pt(NO₂)(py)(NH₃)(NH₂OH)NO₂]. 3
- (c) What is ambidentate ligand? Give examples. 3
- (d) Give evidence to show that [Co(NH₃)₅Cl]SO₄ and [Co(NH₃)₅SO₄]Cl exist as ionization isomers. 2
6. (a) Give examples of each of the following types of ligand with name and formula: 2
- (i) bridging ligand
- (ii) bidentate ligand.
- (b) Write the IUPAC names of: 2
- (i) [Pt(py)₄][PtCl₄]
- (ii) [CoN₃(NH₃)₅]SO₄
- (c) What do you mean by chelate effect? Explain why it is called an entropy effect. 2+2
- (d) Show the structure of Cu(SO₄)·5H₂O. 1
- (e) Give one example of 'Electronic Isomerism'. 1

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WEST BENGAL STATE UNIVERSITY

B.Sc. Honours 4th Semester Examination, 2020

CEMACOR10T-CHEMISTRY (CC10)

Time Allotted: 2 Hours

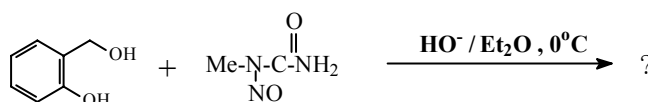
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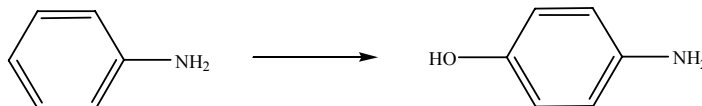
Answer any four questions taking one from each unit

Unit-I

1. (a) Nitriles undergo both acidic and alkaline hydrolysis but isonitriles are hydrolysed only by acids. Explain with mechanism. 2
- (b) Give the product with plausible mechanism explanation of the following reaction. 2



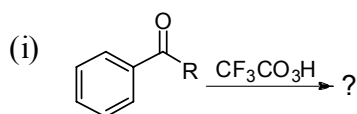
- (c) Carry out the following conversions. 2



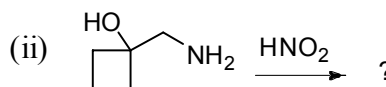
2. (a) Compare the reactions of aniline, N-methyl aniline and N,N-dimethylaniline towards benzenesulfonyl chloride and aq. KOH. How can you utilize this reaction for the separation of primary, secondary and tertiary amines? 2
- (b) How can you chemically distinguish between 4-nitro toluene and PhCH₂NO₂? 2
- (c) How can you convert aniline into 1, 2, 3-tribromobenzene? 2

Unit-II

3. (a) Identify the products in the following and show the plausible mechanism involved. 2+2



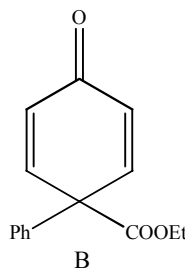
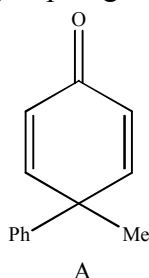
Case I: R= ^tBu
Case II: R= Me





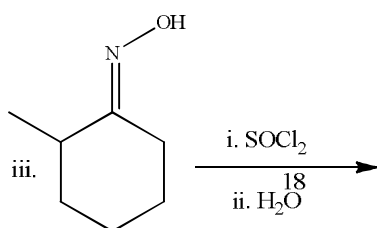
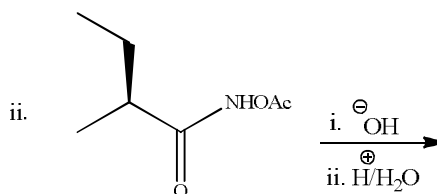
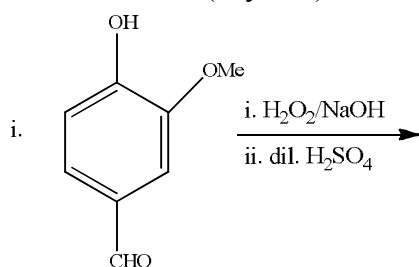
(b) Explain the following observations.

- (i) In the dienone-phenol rearrangement of compound A the phenyl group migrates but in the dienone-phenol rearrangement of compound B the $-\text{COOEt}$ group migrates.

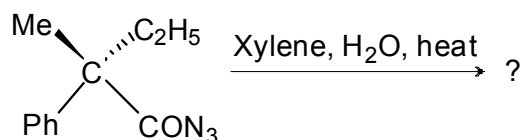


- (ii) In the Hofmann degradation of RCONH_2 a small amount of $\text{CO}(\text{NHR})_2$ and RNHCONHCOR are produced along with R-NH_2 .

4. (a) Predict the products in the following reactions and formulate plausible mechanism for their formation. (any *two*). 2+2



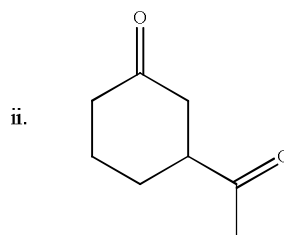
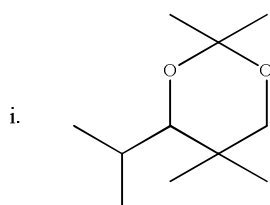
- (b) Predict the product (with proper stereochemistry) in the following reaction with suitable mechanistic explanation. 2



- (c) Two isomeric α -halo ketones **A** and **B** on treatment with NaOMe (separately) gave the same product $\text{PhCH}_2\text{CH}_2\text{CO}_2\text{Me}$. Identify **A** and **B**. 2

Unit-III

5. (a) Analyse the following molecules retro synthetically and suggest plausible synthetic route to them. $2\frac{1}{2} + 2\frac{1}{2}$

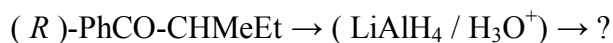




(b) Give synthetic equivalent for the following species.



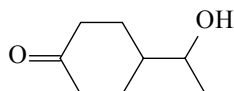
(c) Predict the major product of the following reaction with proper stereochemistry.



(d) Which combination of reagents is appropriate for the following transformation? 1



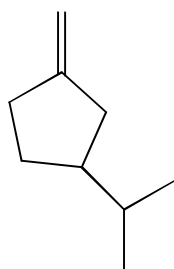
6. (a) Synthesize the following compound using Diels-Alder reaction one of the key step. 2



(b) Explain with proper example: Illogical Nucleophile, Functional Group Addition. 3

(c) Show disconnection of hexane-2,4-dione in terms of consonant and dissonant polarities. 2

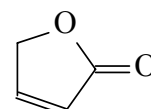
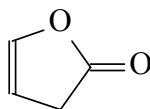
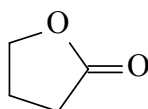
(d) Outline a synthesis of the following molecule showing logical retro synthetic analysis. 3



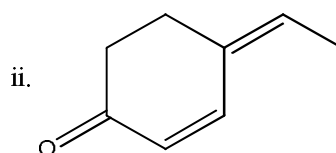
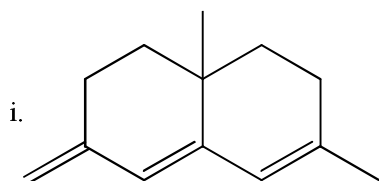
Unit-IV

7. (a) Concentrated solutions of $\text{C}_2\text{H}_5\text{OH}$ and $\text{HOCH}_2\text{CH}_2\text{OH}$ have broad O-H bands near 3350 cm^{-1} . On dilution with CCl_4 , the spectrum of ethylene glycol does not change but that of the alcohol shows a sharp peak at 3600 cm^{-1} replacing the band at 3350 cm^{-1} . Provide a suitable explanation in support of this observation. 3

(b) Arrange the following compounds in order of increasing carbonyl stretching frequencies with proper explanation. 2



(c) Calculate λ_{max} values for the following compounds using Woodward Fieser rule. 2+2





4

(d) Compound B ($C_3H_6Cl_2$) displays the following spectroscopic data.

UV : $\lambda_{max}(\epsilon_{max})$: Transparent above 210 nm

IR (cm^{-1}) : 2950, 1270, 690.

1H -NMR : δ (ppm) 1.25 (d, 3H, J 7 Hz), 3.6 (m, 1H), 3.2 (dd, 2H, J 7 Hz, 11 Hz).

Deduce the structure of compound B and explain the spectroscopic data as far as practicable.

(e) Toluene is oxidised to benzaldehyde. What changes would you expect in PMR spectral feature for the product with respect to that of the starting material? 2

(f) Mention one solvent, other than $CDCl_3$, that acts as NMR-solvent. 1

8. (a) $PhCOCH_3$ gives two isomeric oximes. Both of them are separately treated with conc. H_2SO_4 to give the products **A** and **B** respectively. Identify the products on the basis of IR spectroscopy. 3

(b) An organic compound of molecular formula, $C_9H_{10}O_2$ showed three peaks in the PMR spectrum as given below: δ 1.96, singlet, 3H; δ 5.0, singlet, 2H and δ 7.2, singlet, 5H. One of the intense IR bands of this compound appears at 1740 cm^{-1} . Deduce the structure of the compound and explain the spectral data. 3

(c) Account for the following observations. 2+2+2

(i) Although sp carbon is more electronegative than sp^2 carbon, alkenyl protons appear at higher δ value than alkynyl protons in 1H -NMR spectrum.

(ii) Stretching of aldehydic C-H appears as a doublet and at higher wave number than alkenyl C-H.

(iii) Homoannular dienes absorb at higher wavelength than heteroannular dienes.

(d) 'C=C' stretching frequency of cyclobutene is at 1566 cm^{-1} but that of 1-methylcyclobutene is at 1641 cm^{-1} . Account for this observation. 2

(e) What is bathochromic shift in UV spectroscopy? Explain with a suitable example. 2

N.B. : Students have to complete submission of their Answer Scripts through E-mail / Whatsapp to their own respective colleges on the same day / date of examination within 1 hour after end of exam. University / College authorities will not be held responsible for wrong submission (at in proper address). Students are strongly advised not to submit multiple copies of the same answer script.

—x—