R6598	Sub. Code
	536201

M.Sc. DEGREE EXAMINATION, APRIL – 2022

Second Semester

Chemistry

INORGANIC CHEMSTRY - II

(CBCS – 2019 onwards)

Time : 3 Hours Maximum : 75 Marks

Part A $(10 \times 2 = 20)$

Answer **all** questions.

1. Write any two preparation methods for alkaline earth metals.

2. What are heterogeneous catalysis? Give one example.

3. What is mean by metal organic framework? Write any two examples.

4. What are closo, nido and arachno boranes?

5. What is base hydrolysis? Write one example.

6. What is anation reaction?

7. Calculate the number of bridged and terminal CO ligands present in $OS_3 (CO)_{12}$ and $Ru_4 (CO)_{12}$ complexes.

8. What is mononuclear carbonyls? Give two examples.

9. What are the differences between the fission and fusion reactions?

10. Write any two industrial applications of radioisotopes.

Part B (5 × 5 = 25)

Answer **all** questions, choosing either (a) or (b).

11. (a) Explain with suitable examples of isopoly and heteropoly anions.

Or

(b) Discuss the preparation, chemical reactivity and structure of borazine compounds.

12. (a) Classify the following species as colso, nido, arachno or hypho. (i) B_6H_{12} (ii) $B_6H_{11}^+$ (iii) B_4H_8 (iv) B_4H_{10} (v) B_9H_9NH

Or

(b) Write short note on isolobal analogy.

13. (a) Discuss the theories of trans effect.

Or

(b) List out the various factors affecting the rate of substitution reaction.

14. (a) Discuss the nature of bonding and structure of $Ni(CO)_4$.

Or

(b) Explain how IR spectra useful for the structural determination of metal carbonyls.

15. (a) Define terms, Q values, cross section and threshold energy of nuclear reaction.

Or

(b) What are the characteristics of nuclear reactions? How do they differ from chemical reaction?

Part C

$(3 \times 10 = 30)$

Answer any **three** questions.

16. Discuss the preparation, reactivity and structure of phosphazine compounds.

17. Discuss elaborately about the di, tri, tetra and hexanuclear clusters.

18. What is mean by acid hydrolysis? Discuss the reaction mechanism of acid hydrolysis of Co(III) amine complexes and how various factors affecting the rate of the reaction.

19. Discuss the preparation and structure of the following metal carbonyls. (a) $Fe_2(CO)_9$ (b) $Cr(CO)_6$ (5 + 5)

20. Explain in details about the various types of nuclear reactions.

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R6599	Sub. Code 536202

M.Sc. DEGREE EXAMINATION, APRIL – 2022

Second Semester

Chemistry

ORGANIC CHEMISTRY – II

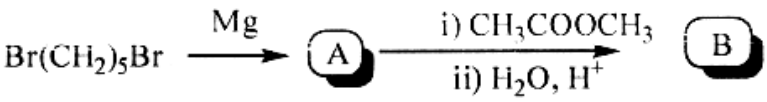
(CBCS – 2019 onwards)

Time : 3 Hours Maximum : 75 Marks

Part A (10 × 2 = 20)

Answer **all** questions.

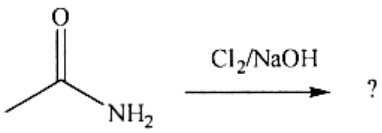
1. Predict the product(s) A & B of the following reaction :



2. Define Peterson olefination.

3. Define "Pinacole-pinacolone" rearrangement.

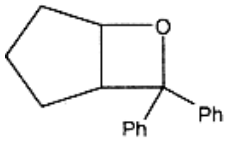
4. Predict the product of the following reaction :



5. What is configuration in stereochemistry?

6. What is ansa compound?

7. Suggest a photochemical reaction to prepare the following compound :



8. Define "Ullmann reaction".

9. What is pericyclic reaction?

10. Define Ene reaction.

Part B $(5 \times 5 = 25)$

Answer **all** questions, choosing either (a) or (b).

11. (a) Write the preparation and application of organozinc reagent.

Or

(b) Write the mechanism of "Dieckmann" condensation.

12. (a) Write short note on Wagner-Meerwein rearrangement.

Or

(b) What is Curtius rearrangement? Give the mechanism.

13. (a) Discuss the Zimmerman-Traxler transition states.

Or

(b) Write the stereochemistry of allenes.

14. (a) Explain the mechanism of oxetane formation.

Or

(b) Distinguish between thermal and photochemical reactions.

15. (a) Construct a correlation diagram for the conrotatory ring opening of cyclobutene and express your conclusions.

Or

(b) Write short note on chelotropic elimination.

Part C $(3 \times 10 = 30)$

Answer any **three** questions.

16. Write short note on the following : (5 + 5)

(a) Darzen reaction

(b) Julia Olefination.

17. What is Backmann rearrangement? How will you prove that the migrating group in trans to the leaving group?

18. Describe briefly the stereochemistry of biphenyls and spiranes.

19. Explain and illustrate Norrish Type I and Type II reactions of ketones.

20. Account for the stereochemistry of the 1, 3-sigmatropic rearrangement shown on thermally or photochemically allowed process by using the FMO approach method.

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R6600

Sub. Code
536203

M.Sc DEGREE EXAMINATION, APRIL – 2022

Second Semester

Chemistry

PHYSICAL CHEMISTRY — II

(CBCS – 2019 onwards)

Time : 3 Hours Maximum : 75 Marks

Part A (10 × 2 = 20)

Answer **all** questions.

1. What is the zero point energy of a particle in a one dimensional box of infinite height?

2. Calculate the degeneracies of a particle in a 3-dimensional box having energy equal to $6h^2/8ma^2$.

3. Give an example for homogeneous and heterogeneous catalysis reaction.

4. What is meant by turnover number of the enzyme?

5. Define the term entropy.

6. Write the Debye Huckel onsager equation and mention its uses.

7. Write the mutual exclusion rule.

8. Define the condition for I-R and Raman active molecules.

9. What are adsorption isotherms?

10. Define the term contract angle.

Part B (5 × 5 = 25)

Answer **all** questions, choosing either (a) or (b).

11. (a) Discuss briefly about the shapes of orbital and shape quantisation.

Or

(b) Explain the energy and wave function equations of one dimensional simple harmonic oscillator.

12. (a) Explain the selection rules for I-R spector.

Or

(b) Discuss briefly the selection rules for $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions in formaldehyde.

13. (a) Discuss the mechanism of acid-base catalysed reactions.

Or

(b) Describe the stopped flow method for studying the first reactions.

14. (a) Derive Gibbs-Duhem equation.

Or

(b) Discuss any two applications of Debye-Huckel theory.

15. (a) How can B.E.T. equation be used for the determination of surface area of an adsorbent?

Or

(b) Derive Langmuir adsorption isotherm equation.

Part C

$(3 \times 10 = 30)$

Answer any **three** questions.

16. Discuss an expression for energy and wave function equations of a particle in one-dimensional box using schrodinger equation.

17. Discuss the applications of SALC procedure to ethylene molecule.

18. Derive Michaelis-Menton equation for enzyme catalysed reactions.

19. Deduce debye-Huckel limiting law expression and mention its applications.

20. Derive Gibbs adsorption isotherm equation.

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R6601	Sub. Code
	536052

M.Sc. DEGREE EXAMINATION, APRIL – 2022

Second Semester

Chemistry

NATURAL PRODUCTS AND INTRODUCTORY BIOCHEMISTRY

(CBCS – 2019 onwards)

Time : 3 Hours Maximum : 75 Marks

Part A (10 × 2 = 20)

Answer **all** questions.

1. Write the synthesis of oxazole from α-acylaminoketone.

2. Write the synthesis of cyanidin chloride (by Robinson et al., 1928)

3. Predict the product of the following reaction:

$$\text{Oestron} \xrightarrow[\text{Zn dust}]{\text{Distiiled with}} ?$$

4. Define circular birefringence.

5. Draw the structure of Lysergic acid and indicate its chiral centers.

6. Write the products (A&B) of the following reaction:

$$\text{camphor} \xrightarrow[\text{HCl}]{\text{Amyl nitrile}} \text{A} \xrightarrow{OH^-} \text{B}$$

7. Suggest the product of the following reaction:

$$\text{Penicillin} \xrightarrow{HCl/H_2O}$$

8. Draw the structure of 'Cephalosporin C' and indicate its chiral centers. How many stereoisomers are possible?

9. Define proteins.

10. What do you mean by oxidative phosphorylation?

Part B $(5 \times 5 = 25)$

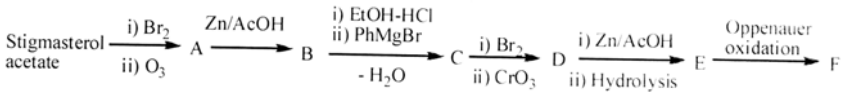
Answer **all** questions, choosing either (a) or (b).

11. (a) Write the synthesis and reactions of imidazole.

Or

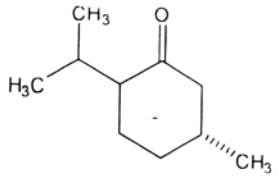
(b) Write the synthesis of anthocyanins.

12. (a) Write the structures of the lettered compounds A-F:



Or

(b) Menthone exhibits a positive $n-\pi^*$ Cotton effect in methanol near 300 nm and a negative $n-\pi^*$ cotton effect in isooctane. Explain the conformations of the (–) menthone in these solvents.



13. (a) Write the biosynthesis of alkaloids.

Or

(b) Discuss the structure of zingiberene.

14. (a) Outline a Vigneaud *et al* (1946) synthesis of benzylpenicillin.

Or

(b) Discuss the physiological action of riboflavin and thiamin.

15. (a) Write the basic structure and function of nucleic acid.

Or

(b) Discuss the regulatory steps in glycolysis.

Part C $(3 \times 10 = 30)$

Answer any **three** questions.

16. Write the synthesis and properties of indole.

17. Outline a synthesis of Testosterone from Cholesterol.

18. Discuss the structural elucidation of Morphine (synthesis not necessary).

19. Write down the synthesis of D-Chloramphenicol from benzaldehyde and β-nitroethanol.

20. Discuss briefly the structure and classification of carbohydrates.

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R6602	Sub. Code 536053

M.Sc. DEGREE EXAMINATION, APRIL – 2022

Fourth Semester

Chemistry

SPECTROSCOPIC METHODS OF ANALYSIS

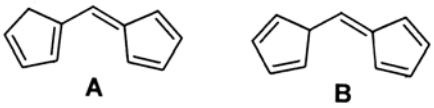
(CBCS – 2019 onwards)

Time : 3 Hours Maximum : 75 Marks

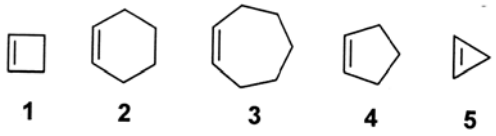
Part A (10 × 2 = 20)

Answer **all** questions.

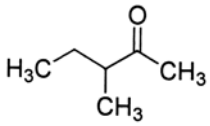
1. Which of the following molecules would absorb at a shorter wavelength in the UV spectrum? Explain your answer.



2. Arrange the following compounds according to their increasing C=C IR stretching frequency. Justify your answer.



3. Predict the number of signals and the multiplicity of each proton in the ^{1}H NMR of the following compound:



4. What is ring current effect? How does it influence the ^{1}H and ^{13}C chemical shifts?

5. Explain the ^{1}H NMR spectrum of diborane.

6. Comment on hyperfine coupling constant.

7. Write down the fragmentation process of the following compound in the mass spectra.

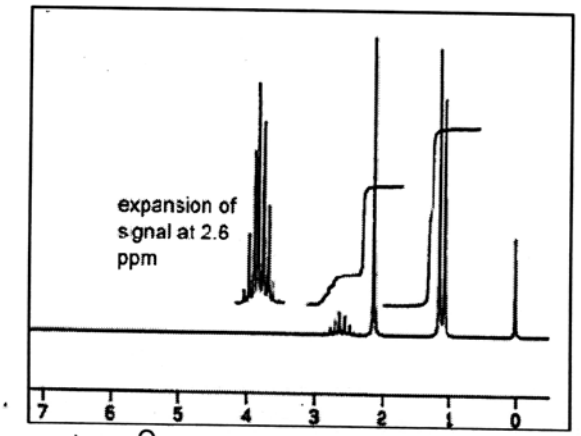
8. In the following compounds which would have the largest quadrupole splitting for the starred atom: Justify

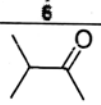
   cis$^{*}Fe(CO)_4Cl_2$ or trans$^{*}Fe(CO)_4Cl_2$

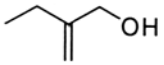
9. Predict the structure of a compound with the following data:

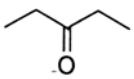
   Molecular formula: C_3H_6Br ^{1}H NMR δ (ppm): 2.35, qui, 2 H; 3.55, t, 4 H

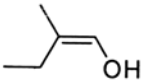
10. A compound has a strong absorption near 1720 cm^{-1} in its IR spectrum and a parent ion at *m*/*z* 86 in its mass spectrum. Its ^1H NMR spectrum is given. Which of the structures below is consistent with these data?



(i) 

(ii) 

(iii) 

(iv) 

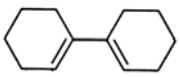
Part B (5 × 5 = 25)

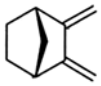
Answer **all** questions, choosing either (a) or (b).

11. (a) How will you distinguish primary, secondary and tertiary amines using IR spectroscopy?

Or

(b) Predict the λ_{max} of the following compounds:





12. (a) How do the following factors affect the chemical shift of ^{1}H and ^{13}C?

(i) Electronegativity

(ii) Hybridization.

Or

(b) Explain the utility of deutaration and shift reagents in simplifying complex NMR spectra.

13. (a) Explain the usefulness of double resonance technique in the ^{1}H NMR spectrum of $Al(BH4)_3$.

Or

(b) Explain the EPR spectrum of an octahedral Mn(II) complex.

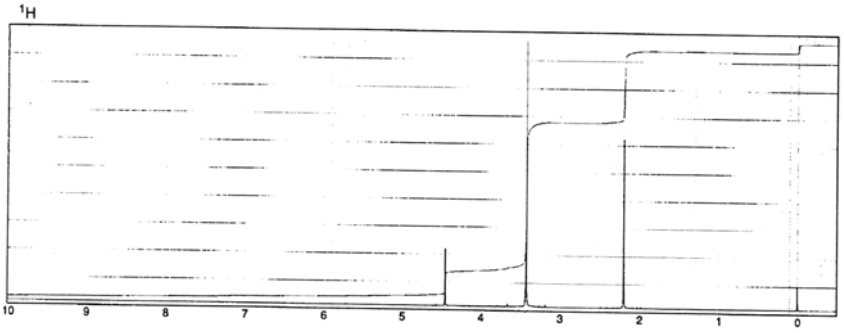
14. (a) Explain the significances of McLafferty rearrangement and retro Diels-Alder reaction in mass spectroscopy.

Or

(b) Draw the structure for SnF_4 and explain why quadrupole splitting is observed in this compound but not in $SnCl_4$.

15. (a) The proton NMR spectrum for a compound with formula $C_5H_{10}O_3$ is shown below. The carbon NMR spectrum has four peaks. The IR spectrum has strong band at 1728 cm^{-1}. The DEPT-135 and DEPT-90 spectral results are tabulated. Draw the structure of this compound.

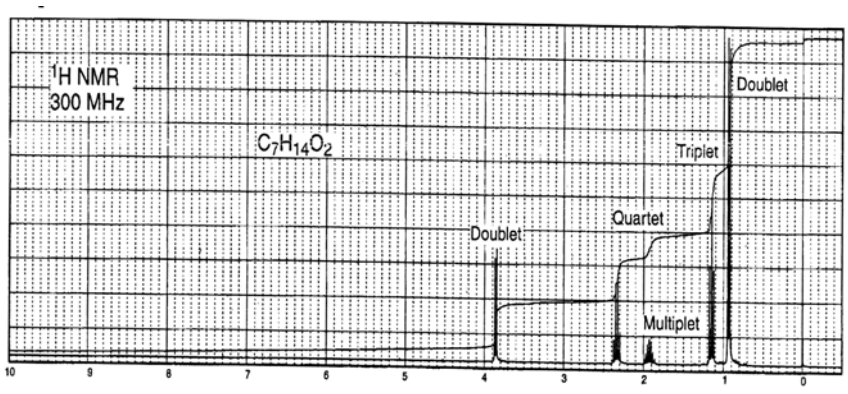
^{13}C	DEPT-135	DEPT-90
25 ppm	Positive	No peak
55	Positive	No peak
104	Positive	Positive
204	No peak	No peak



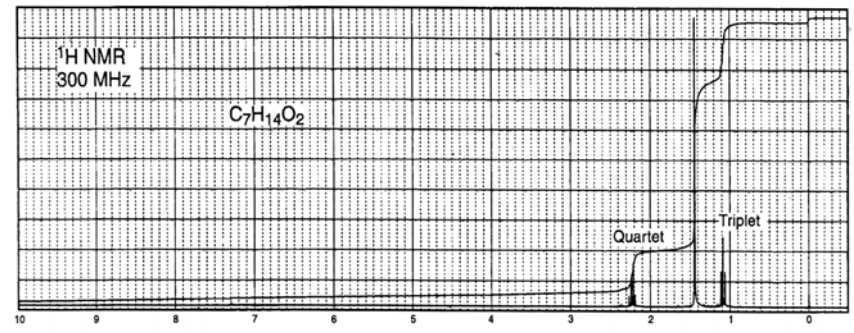
Or

(b) Following are the ^{1}H NMR of three isomeric esters with molecular formula $C_7H_{14}O_2$, all derived from propanoic acid. Identify the structure of each.

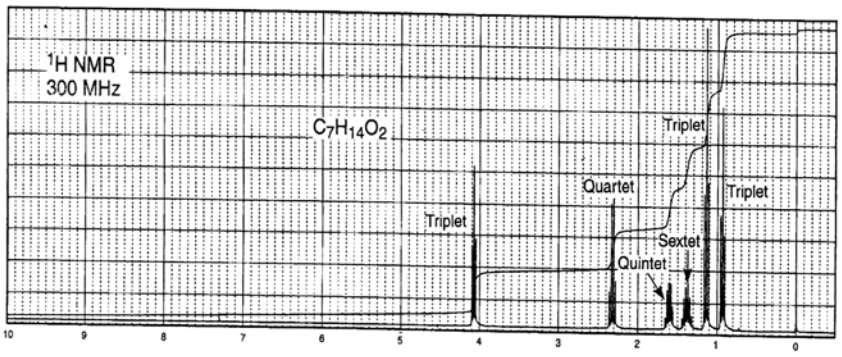
Compound 1:



Compound 2:



Compound 3:

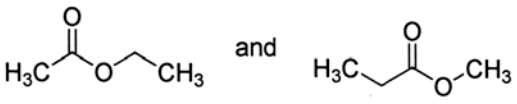


Part C $(3 \times 10 = 30)$

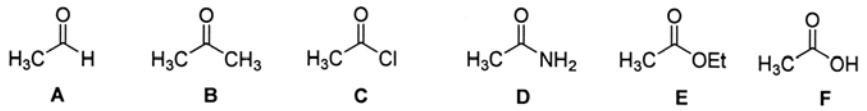
Answer any **three** questions.

16. (a) Explain the IR and Raman spectra of NO_3^- and H_2O. (4+3+3)

(b) Predict and explain whether UV visible spectroscopy can be used to distinguish between the following pairs of compounds. Where possible, support your answer with calculations.



(c) Arrange the following compounds in their decreasing C=O IR frequencies and justify your answer:



A B C D E F

17. Explain the features of DEPT, NOESY and H, H-COSY NMR spectra. (4+3+3)

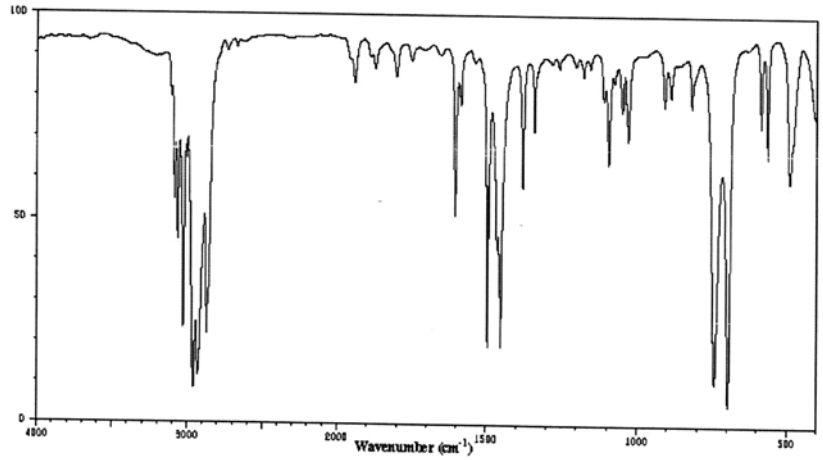
18. Explain how NMR spectroscopy is useful in studying the fluxional behaviour of molecules considering $(\pi\text{-}C_5H_5)Fe(CO)_2C_5H_5$ as an example.

19. Discuss the principle and applications of HRMS and MALDI-MS. (5+5)

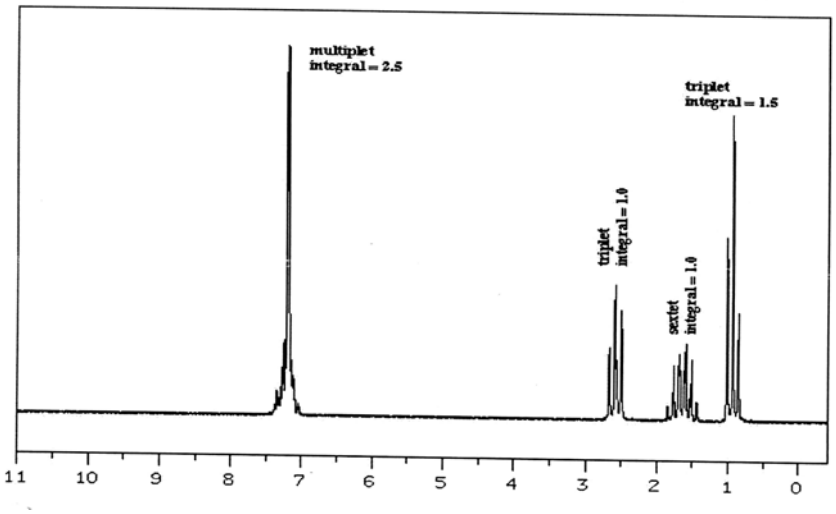
20. Deduce the plausible molecular formula using the given mass data, calculate the double bond equivalence and arrive at the structure of the compound using the other spectral data given:

Mass: m/z = 120 (M, 48.0 %); m/z = 121 (M+1, 9.9 %); m/z = 122 (M+2, 0.2 %)

IR:



^{1}H NMR:


multiplet
integral = 2.5
triplet
integral = 1.0
sextet
integral = 1.0
triplet
integral = 1.5
11
10
9
8
7
6
5
4
3
2
1
0

R6602