

R-4502

Sub. Code

536201

M.Sc. DEGREE EXAMINATION, APRIL 2021

Second Semester

Chemistry

INORGANIC CHEMISTRY – II

(CBCS – 2019 onwards)

Time : 3 Hours

Maximum : 75 Marks

Part A

(10 × 2 = 20)

Answer **all** questions.

1. What are isopolyanions? Give suitable examples.
2. List out the difference between homogeneous and heterogeneous catalysis.
3. What are cages? Write any two examples.
4. Define Wade's rule.
5. List out the difference between the complementary and non-complementary reaction.
6. What is mean by acid hydrolysis reaction? Give suitable example.
7. Define 18-electron rule.
8. Draw the structure of $\text{Os}_3(\text{CO})_{12}$ and $\text{Ru}_4(\text{CO})_{12}$.
9. What are the differences between the fission and fusion reactions?
10. Write any two industrial applications of radioactive isotopes.

Part B**(5 × 5 = 25)**Answer **all** questions, choosing either (a) or (b).

11. (a) Discuss the structure and preparation of sulphur-nitrogen compounds.

Or

- (b) Discuss the preparation, chemical reactivity and structure of borazine compounds.
12. (a) Classify the following species as closo, nido, arachno or hypho.
- (i) 2-CB₅H₉
 - (ii) 1, 2-C₂B₆H₁₁
 - (iii) B₉H₁₁S
 - (iv) B₈H₁₂
 - (v) B₉H₁₂NH⁻

Or

- (b) Discuss about the di and trinuclear clusters.
13. (a) List out the various factors affecting the rate of substitution reaction.

Or

- (b) Discuss the substitution reaction of S_N1 and S_N2 reaction mechanism.
14. (a) Give the classification of metal carbonyls on the basis of metal carbon bond.

Or

- (b) Discuss the synthesis and structure of Fe(CO)₅.

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

Or

- (b) Write notes on nuclear cross sections.

Part C (3 × 10 = 30)

Answer any **three** questions.

16. Discuss the preparation, reactivity and structure of phosphazine compounds.
17. (a) Write short note on isolobal analogy. (5)
(b) Discuss about metal organic frameworks and their applications. (5)
18. Explain with suitable examples of inner sphere and outer sphere electron transfer reaction mechanism.
19. Discuss the preparation and structure of the following metal carbonyls.
(a) $\text{Fe}_2(\text{CO})_9$
(b) $\text{Ni}(\text{CO})_4$ (5 + 5)
20. Describe in detail the major difference between the shell and the liquid drop models of the nucleus bringing out the salient features of both.
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R-4503

Sub. Code

536202

M.Sc. DEGREE EXAMINATION, APRIL 2021

Second Semester

Chemistry

ORGANIC CHEMISTRY – II

(CBCS – 2019 onwards)

Time : 3 Hours

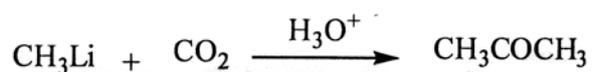
Maximum : 75 Marks

Part A

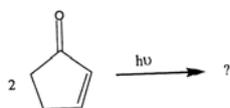
(10 × 2 = 20)

Answer **all** questions.

1. Write the mechanism of the following product



2. What is Knoevenagel condensation?
3. Define Wallach rearrangement with one example.
4. What is Curtius rearrangement?
5. What is Felkin-Ahn model?
6. Define Axial Chirality.
7. Predict the stereochemistry of the product in the following reaction:



8. Define McMurry coupling.
9. What is sigmatropic reaction?
10. Define cheletropic elimination.

Part B

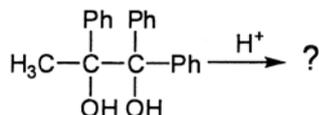
(5 × 5 = 25)

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

11. (a) Explain in details about the organolithium reagent used for the synthesis of organic compounds.

Or

- (b) Write short note on Peterson olefination.
12. (a) Predict the product and give the mechanism of the following reaction:



Or

- (b) What is Wittig rearrangement? Give the mechanism.
 13. (a) Write short note on Cram-Chelate model.
- Or
- (b) What is ansa compound? Explain.
 14. (a) Write note on Paterno-Buchi reaction.

Or

- (b) Discuss about the mechanism and application of di-pi methane rearrangement.

15. (a) Set up an orbital correlation diagram for photochemical electrocyclic reaction of butadiene.

Or

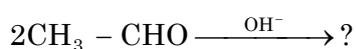
- (b) Establish, what way the $\pi^4S + \pi^2S$ cycloaddition is an allowed process by using correlation diagram and Frontier molecular orbital approach method.

Part C

(3 × 10 = 30)

Answer any **three** questions.

16. Complete the following reaction with suitable mechanisms:



17. Discuss briefly Sommelet-Hauser rearrangement mechanism.
18. Discuss about the stereochemistry of allenes and binaphthyls.
19. Write short notes on
- (a) Sandmeyer reaction
 - (b) Barton deoxygenation.
20. Describe the FMO method to stereochemical course of 1,5 -sigmatropic reaction is thermally or photochemically allowed process.

R-4504

Sub. Code

536203

M.Sc. DEGREE EXAMINATION, APRIL 2021

Second Semester

Chemistry

PHYSICAL CHEMISTRY – II

(CBCS – 2019 onwards)

Time : 3 Hours

Maximum : 75 Marks

Part A

(10 × 2 = 20)

Answer **all** the questions.

1. Write the zero point energy of one dimensional simple harmonic oscillator.
2. Write the Hamiltonian for helium atom.
3. What is enzyme catalysis reaction? Give one example.
4. Give one example for acid and base catalysed reactions.
5. Write the mutual exclusion rule for molecules with centre of symmetry.
6. Write the selection rules for I.R. Spectra.
7. What is meant by partial molar free energy?
8. Define the term fugacity.

9. Write the Freundlich adsorption isotherm equation.
10. Adsorption process must always be exothermic –Justify this statement.

Part B (5 × 5 = 25)

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

11. (a) Solve the schrodinger equation for a particle in 3-dimensional box.

Or

- (b) Discuss briefly the perturbation theory.

12. (a) Explain briefly the vibrational modes of ammonia molecule using group theory.

Or

- (b) Discuss the selection rules for Raman spectra.

13. (a) Write a note on explosion reactions.

Or

- (b) Discuss briefly the mechanism of enzyme inhibition reactions.

14. (a) Explain the variation of chemical potential with respect to temperature and pressure.

Or

- (b) Derive Gibbs-Duhem equation.

15. (a) Explain the Langmuir-Hinshelwood mechanism of surface reactions.

Or

- (b) Discuss the basic concepts of semiconductor catalysis and its applications.

Part C

(3 × 10 = 30)

Answer any **three** questions.

16. Solve the schrodinger equation to Rigid rotor and find the energy and wave function values.
 17. Derive the Michaelis-menton equation and explain its importances.
 18. Explain the importances of Debye-Huckel theory..
 19. Discuss the applications of SALC procedure to butadiene molecule.
 20. Write a note on BET adsorption isotherm equation and explain its applications.
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R-4505

Sub. Code

536052

M.Sc. DEGREE EXAMINATION, APRIL 2021

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 imidazole from glyoxal.
2. Predict the products (A-D) of the following reaction:
$$\text{Caffeine} \xrightarrow{\text{Cl}_2} \text{A} \xrightarrow[\text{NaOH}]{\text{CH}_3\text{OH}} \text{B} \xrightarrow[\text{Boil}]{\text{dil HCl}} \text{C} + \text{D}$$
3. Which method followed to determine the number of rings on steroids?
4. Define axial haloketone rule with an example.
5. Write the Herzig-Meyer's method to estimate the number of methyl group in alkaloids.
6. Define Isoprene rule.

14. (a) Elucidate the structure of Cephalosporin C (Synthesis not necessary).

Or

- (b) Write the physiological action of vitamin B₁₂ and vitamin E.
15. (a) Discuss classification of amino acids.

Or

- (b) Distinguish between catabolism and anabolism.

Part C (3 × 10 = 30)

Answer any **three** questions.

16. Discuss briefly the synthesis and chemical reactions of pyrimidines.
17. Discuss the differences between ORD and CD.
18. Write the structural determination of Abietic acid (synthesis not necessary).
19. Identify the Ascorbic acid (Vit. C) contain γ - or δ - lactone ring structure to use the Weerman test.
20. What is the purpose of TCA cycle? Explain.

R5372

Sub. Code

536053

M.Sc. DEGREE EXAMINATION, APRIL – 2021

Fourth Semester

Chemistry

SPECTROSCOPIC METHODS OF ANALYSIS

(CBCS – 2019 onwards)

Time : 3 Hours

Maximum : 75 Marks

Part A

(10 × 2 = 20)

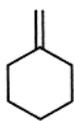
Answer **all** questions.

1. Arrange the following compounds in their decreasing C=C IR stretching frequency. Justify your answer.

(a)



(b)



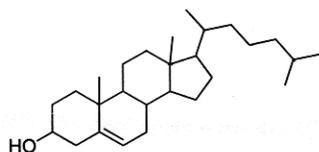
(c)



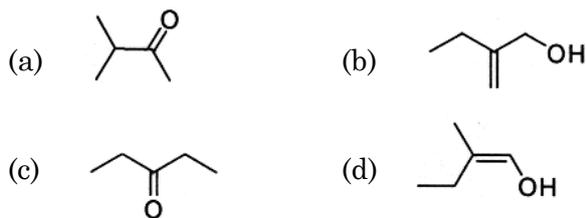
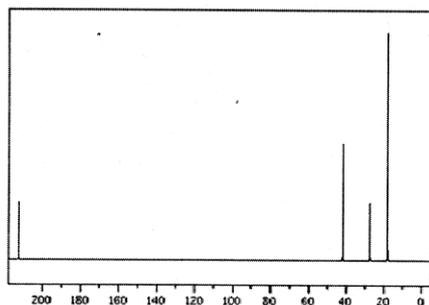
(d)



2. What is Hook's law?
3. In the ^1H NMR why do sp hybridized protons appear at lower chemical shift value than the sp^2 protons?
4. Predict the number of signals obtained in the broad band decoupled ^{13}C NMR of the following compound:



5. The ^{19}F NMR spectrum of SiF_6^{2-} in aqueous solution gives one main peak and two satellite peaks. Explain.
6. Write a short note on Zeeman splitting.
7. The ESI mass spectrum of cyclohexanone has m/z at 42, 55, 70 and 98. Identify each of these fragments.
8. In the following compounds which would have the largest quadrupole splitting for the starred atom: Justify
 high spin *cis* $^*\text{Fe}(\text{NH}_3)_4\text{Cl}_2$ or high spin *trans* $^*\text{Fe}(\text{NH}_3)_4\text{Cl}_2$
9. Predict the structure of an organic compound with the following data:
 Molecular formula: $\text{C}_6\text{H}_8\text{O}_2$; ^1H NMR δ ppm: 1.33, t, 3H; 2.10, s, 3 H; 4.22, q, 2H.
10. A compound has a strong absorption near 1720 cm^{-1} , but no absorptions above 3000 cm^{-1} in its infrared spectrum. It has a parent ion at $m/z = 86$ in its mass spectrum and its ^{13}C NMR spectrum is given. Which of the structures below is consistent with these data?



Part B

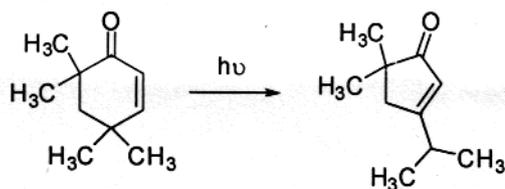
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Answer **all** questions, choosing either (a) or (b).

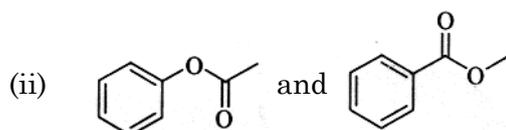
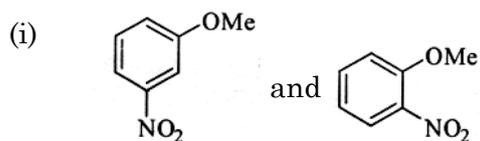
11. (a) Account for the two strong bands for nitro group in the IR spectrum? How will you distinguish aliphatic and aromatic nitro compounds using IR?

Or

- (b) Predict the UV maximum for the reactant and product of the following photochemical reaction:



12. (a) How will you distinguish each of the following pairs of compounds using ^1H NMR spectroscopy?



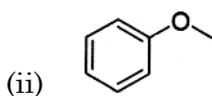
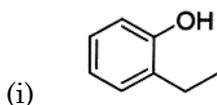
Or

- (b) Write a note on shift reagents and selective decoupling.

13. (a) Explain the mechanism of spin-spin coupling with the help of a hypothetical molecule H-X where X is having spin of 1/2.

Or

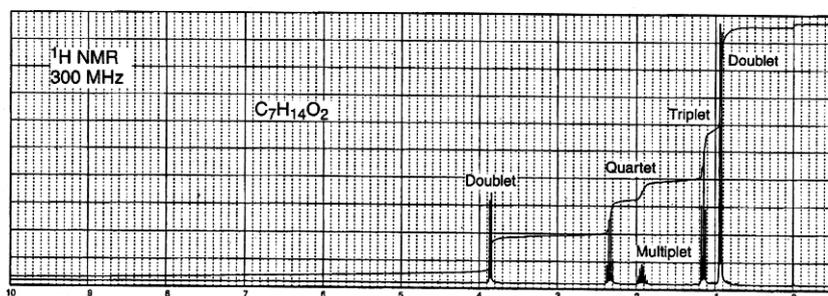
- (b) Explain the ESR spectra of bis-salicylaldimnecopper(II).
14. (a) Identify the fragmentation pattern of the following compounds in the mass spectrum.



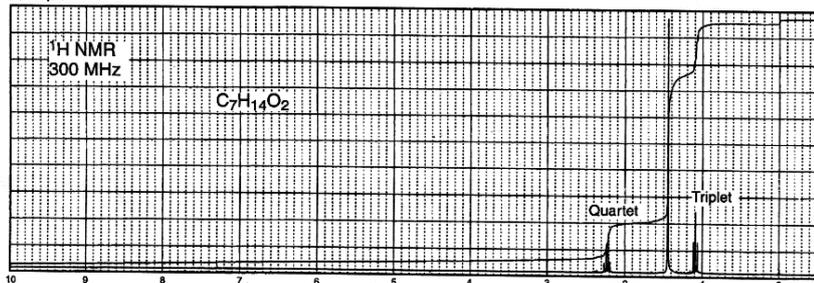
Or

- (b) Explain the magnetic and quadrupole splitting in a ferromagnetic ^{57}Fe compound.
15. (a) Following are the ^1H NMR of the three isomeric esters with molecular formula $\text{C}_7\text{H}_{14}\text{O}_2$, all derived from propanoic acid. Identify the structure of each.

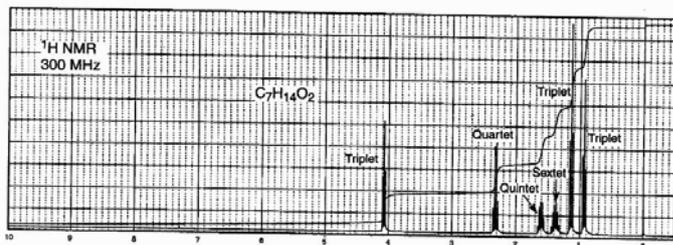
compound 1:



compound 2:



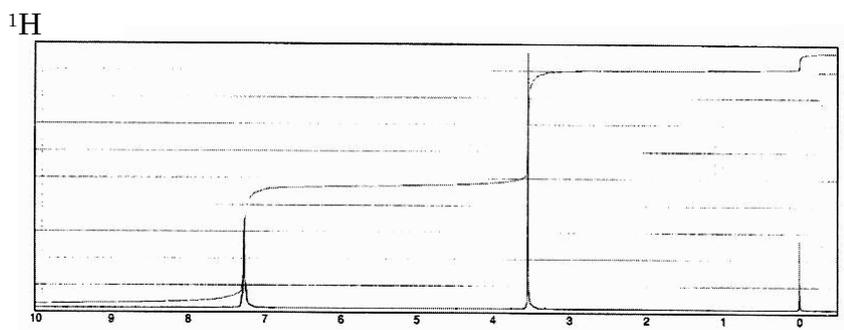
compound 3:



Or

- (b) The proton NMR spectrum for a compound with formula C_9H_8O is shown below. The carbon NMR spectrum has five peaks. The IR spectrum has strong band at 1746 cm^{-1} . The DEPT-135 and DEPT-90 spectral results are tabulated. Draw the structure of this compound.

^{13}C (ppm)	DEPT- 135	DEPT-90
44	Negative	No peak
125	Positive	Positive
127	Positive	Positive
138	No peak	No peak
215	No peak	No peak

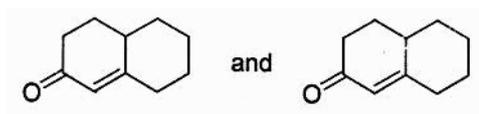


Part C

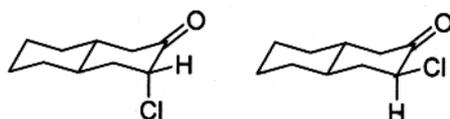
(3 × 10 = 30)

Answer any **three** questions.

16. (a) Explain the IR and Raman spectra of NO₃⁻ and CO₂. (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.

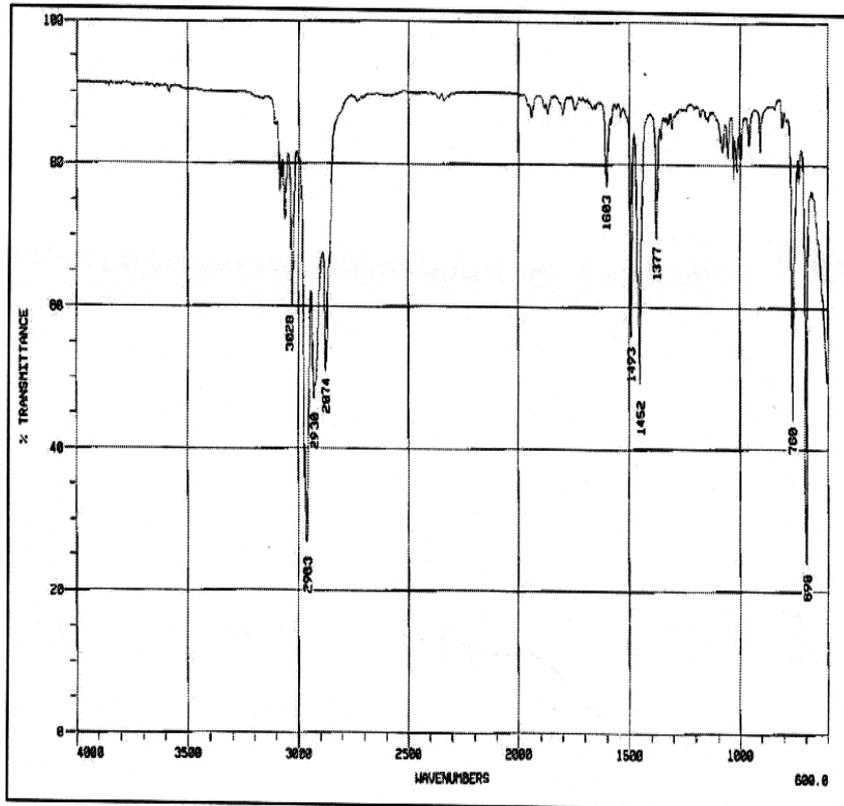


- (c) How will you distinguish the following two compounds using IR spectroscopy?



17. Explain the features of C,H-COSY, HMBC and INADEQUATE spectra. (4+4+2)

18. (a) Explain how ^{31}P NMR spectroscopy is helpful in the determining the structure of P_4S_3 . (4)
- (b) Explain hyperfine splitting and Cramer's degeneracy. (6)
19. Discuss the principle and applications of HRMS and ESI-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: $m/z = 134$ (M, 100 %); $m/z = 135$ (M+1, 10.8 %);
 IR: $m/z = 136$ (M+2, 0.2 %).



^1H and ^{13}C NMR

