

PGIIS-N 1513 B-2K13
M.Sc. IIIrd Semester Degree Examination
Chemistry
(Organic Chemistry-III(Spectroscopy))
Paper - HCT-3.1
(New)

Time : 3 Hours

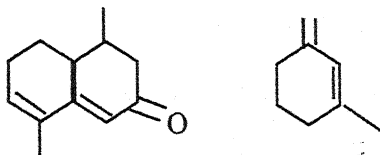
Maximum Marks : 80

Instructions:

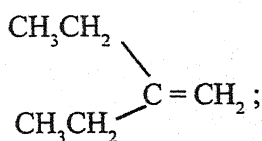
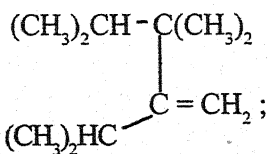
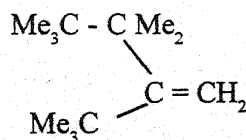
1. All questions are **compulsory**
2. All questions carry **equal** marks.

1. Answer any **eight** of the following (8×2=16)

- a) Calculate the λ_{\max} for an absorption band in the UV-vis spectrum of the following compound"



- b) Aniline absorbs at 230 nm (ϵ 8600) however, in acidic solution the main absorption band is seen at 203 nm (ϵ 7500) and is comparable with benzene. Why?
- c) Account for the observed $\text{C}=\text{C}$ frequencies in the IR spectra of the following compounds

1652 Cm^{-1} 1639 Cm^{-1} 1621 Cm^{-1}

- d) Why strong bands in IR corresponds to weak bands in Raman and vice-versa?
- e) In the ^1H NMR spectrum of cyclo hexane two signals are observed at low temperature. Why?
- f) Why TMS is used as an internal standard in ^1H NMR spectroscopy?

- g) The CMR spectrum of one of the butyl acetate isomer ($C_4H_9OCOCH_3$) showed signals at δ : 22, 28, 80 and 170. What is its structure?
- h) Predict the chemical shift position for the alkyne carbons in 1-hexyne.
- i) What is meta stable peak in mass spectrometry? Mention its importance.
- j) The mass spectrum of butyro phenone shows peaks at M/z 162, 120, 105 and 85. Interpret these peaks.

2. a) Discuss the effect of solvents of varying polarity on the UV-vis absorption of α, β -unsaturated carbonyl compounds.
- b) How will you distinguish the inter and intra-molecular hydrogen bonding using I.R. Spectroscopy? Explain with examples.
- c) An organic compound with a molecular formula C_7H_5OCl has the following spectral data.

IR (Cm^{-1}) : 3070, 2900, 1730, 1595 and 830.

1H NMR (δ): 9.0(s, 1H), 7.6(d, 2H), 8.2(d, 2H)

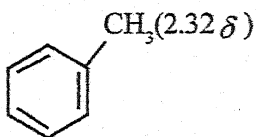
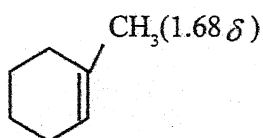
Mass (M/z) : 140(M^+), 142 (M^++2).

Deduce the structure of a compound and interpret the spectral data.

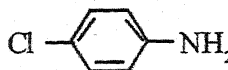
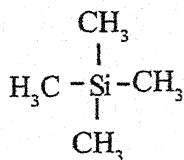
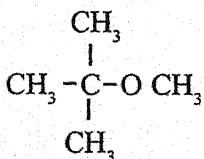
OR

- c) i) Esters of O-chloro benzoic acid show two $C=O$ stretching frequencies . Explain.
- ii) Explain how does an auxochrome exerts bathochromic shift on a chromophore? (5+5+6=15)

3. a) How do you explain the chemical shift data of the following compounds:



- b) Comment on the number of signals, their splitting if any and give the approximate chemical shift values for the following compounds.



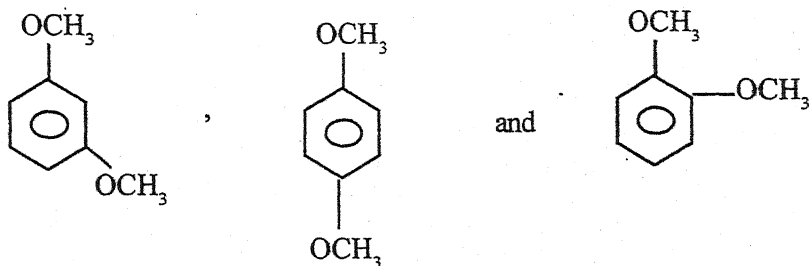
- c) Write short note on-
- Lanthanide shift reagents
 - Spin decoupling and its applications

OR

Why only two geometric isomers are possible for a compound with two double bonds molecular formula: $[\text{Me}_2\text{C}=\text{CHCH}_2\text{CH}_2\text{C}(\text{Me})=\text{CH}-\text{CHO}]$?

Assign E-Z nomenclature to the isomers. On irradiation of the C-3 methyl group of one isomer enhancement about 20% of the signal due to 'H' at C-2 was observed while no such enhancement was observed in the other isomer. What is the stereo structure of this isomer? (5+5+6=16)

4. a) How will you differentiate among the following isomers on the basis of their proton decoupled CMR spectra.



- Explain HETCOR spectroscopy with suitable example.
- What is Broad band decoupling in ^{13}C NMR? Mention its merits and demerits over off-resonance decoupling.

OR

- c) The off-resonance decoupled ^{13}C NMR spectrum of an organic compound with a molecular formula $\text{C}_6\text{H}_{10}\text{O}$ showed the following signals, δ : 20(9), 27(9), 31(9), 124(s), 154(d) and 197(s) with relative intensities 3:4:3:4:2:1. Deduce its structure. (5+5+6=16)

- Explain the differences observed in the EI and CI mass spectra of n-butyl propanoate.
 - Comment on the typical fragmentation of benzyl methyl ether. How alkyl benzyl amines fragment?

- c) The molecular ion of 2-methyl-3-phenyl butane (M^+ ; $M/z = 148$) fragments to give a base peak at $m/z = 105$. The isomeric compound 2,2-dimethyl-1-phenyl propane, however, gives the base peak at $M/z = 57$. With another significant peak at $M/z = 91$. Explain.

OR

An organic compound with a molecular formula C_6H_8O showed the following spectral data.

UV(λ_{max}) : 225 nm ($\epsilon = 10,000$), 318 nm ($\epsilon = 40$)

IR : A strong band at 1690 cm^{-1}

$^1\text{H NMR}(\delta)$: 7.0 (m, 1H), 5.9 (d, 1H), 2.6 (f, 2H), 2.3 (quint, 2H), 2.8 (9, 2H)

Mass (M/z) : 96 (M^+), 68 (base peak)

Propose a structure for this molecule.

(5+5+6=16)

PGIIS-N 1516 B-2K13
M.Sc. IIIrd Semester (CBCS) Degree Examination
Chemistry
(Physical Chemistry-III)
Paper - HCT-3.2
(New)

Time : 3 Hours

Maximum Marks : 80

Instructions to Candidates:

1. All questions are compulsory
2. All questions carry **equal** marks

1. Answer any **Eight** questions**(8×2=16)**

- a) What are γ space and μ space
- b) Calculate the value of $4!$ using and without using Stirling's equation and compare the results.
- c) What is residual entropy of a crystal
- d) What is degeneracy? Explain
- e) Write down the schrodinger's wave equation for H atom.
- f) What are Ferro and Ferri Magnetic solids
- g) Distinguish between intrinsic and extrinsic defects
- h) Differentiate between ideal and nonideal solutions
- i) What is microscopic reversibility? Explain
- j) Define degree of solvation

2. a) Derive classical maxwell-Boitz mean distribution law

(5)

- b) Show that $S = Kh\Omega$ calculate the molar residual entropy of a crystal in which molecules can adopt 5 orientation of equal energy of O_k .

(5)

- c) What are partition functions? Derive the expressions for vibrational partition function of a diatomic molecule. (6)

or

- c) Derive the expression for the distribution of n_i number of particles among various ϵ_i energy levels on the basis of Fermi - Dirac quantum statistics (6)

3. a) Explain 1st order perturbation theory (5)
b) Discuss the Hartree-Fock self consistent field theory (5)
c) Give the concept of Rigid Rotor with reference of CHCl_3 (6)

or

- c) Give an account of
i) Correlation diagrams
ii) Non crossing rule (6)

4. a) Discuss the principle and classifications of solid state reactions (5)
b) Give an account of electronics properties of solids based on band theory (5)
c) Classify the solids based on their magnetic behaviour. (6)

or

- c) Write a note on
i) Optical reflectance
ii) photoelectric effect (6)

5. a) Discuss excess thermodynamic functions for non ideal solutions (5)
b) Write the principle of microscopic reversibility and derive the onsager reciprocity relations (5)
c) Give an account of electrokinetic phenomena of colloids (6)

or

- c) Explain a method for determination of surface tension of colloids (6)

PGIIS-N 1518 B-2K13**M.Sc. IIIrd Semester (CBCS) Degree Examination****Chemistry****(Inorganic Chemistry-III)****Paper - SCT-3.2****(New)**

Time : 3 Hours

Maximum Marks : 80

Instructions to candidates:

1. Answer *all* the questions.
2. All questions carry *equal* marks.

1. Answer any **eight** questions: **(8×2=16)**
 - a) Write optical and electromagnetic properties of Ceramics.
 - b) Give the composition of portland cement. Mention its properties.
 - c) Explain why the storage of iron in a non toxic form is a necessary feature of metabolism
 - d) List out the essential elements in the order of their abundance and mention their functions.
 - e) Write the impact of toxic chemicals on enzymes.
 - f) Explain the terms: nuclear fusion and nuclear fission. Give examples.
 - g) What are breeder reactors? Mention their advantages and disadvantages.
 - h) Distinguish between secular and transient equilibrium.
 - i) State photo chemical laws.
 - j) Metal complexes used as sensitizers. Explain.
2.
 - a) Explain the manufacture of steel by Bessemer converter method and discuss the reactions involved in it. **(5)**
 - b) What is glass? Explain the structure of glass. How glass is manufactured by tank furnace method. **(5)**
 - c) Discuss the nuclear waste management with respect to storage and disposal procedures. **(6)**

OR

What is thermal pollution? "Metallurgical industries are major sources of thermal pollution" - Justify.

3. a) Discuss the sources and biochemical effects of As and Pb. (5)
- b) Give the structural representation of the mode of dioxygen binding in hemerythrin and hemocyanin. Comment on their mechanism of binding to oxygen. (5)
- c) What are the chemical barriers in the reduction of N_2 and NH_3 ? How does nature overcome these barriers. Discuss in vitro N_2 fixation. (6)

OR

What are cytochromes? What are their functions? Discuss their structural features.

4. a) Draw a schematic diagram of nuclear reactor and label the components. Explain its characteristic features. (5)
- b) Describe the construction and operation of ionization chamber. Explain its uses. (5)
- c) Discuss the parent daughter decay growth relationship with reference to
- i. Parent shorter lived than daughter ($\tau_p < \tau_d$)
- ii. Parent and daughter nearly the same half life ($\tau_p \approx \tau_d$). (6)

OR

Describe the nuclear power reactors in India. Explain the applications, advantages and disadvantages of nuclear reactors.

5. a) Explain the photo redox reactions? Give examples. Discuss their applications. (5)
- b) Discuss the energy dissipation by radioactive and non-radioactive processes. (5)
- c) What is charge transfer spectra? Discuss the ligand-metal and metal-ligand charge transfer spectra with examples. (6)

OR

With suitable examples, explain the photo racemization and photo isomerisation reactions.

PGIIS-O 1520 B-2K13
M.Sc. IIIrd Semester Degree Examination
Chemistry
(Environmental Chemistry)
Paper - CHEMT 3.30
(Old)

Time :3 Hours

Maximum Marks : 80

Instructions to Candidates:-

Answer all the questions.

1. Answer the following : (8×2=16)
- a) What are the sources of N_2O_5 and N_2O_3 in the atmosphere?
 - b) Enumerate the water quality parameters. Indicate the permissible limits of more relevant parameters.
 - c) Define the term chlorine demand.
 - d) Write the sources and sinks of carbon monoxide.
 - e) Give the principle involved in the determination content of mercury water sample.
 - f) Distinguish between pollutant and contaminant.
 - g) What are the macro and micro nutrients in the soil?
 - h) What is the significance of determining COD & BOD?
2. a) Name the important biogeochemical cycles. Describe the oxygen cycle. (5)
- b) Discuss various mechanisms of reactions that result in smog. (5)
- c) Write a note on Chernobyl disaster. (6)

OR

Explain any two methods of determining Nox in air sample.

3. a) Describe about different sources, sinks and control of SOX in air sample. (5)
b) Explain the procedure for the determination of chlorine demand in water (5)
c) Discuss methods for domestic waste water treatment. (6)

OR

Write a note on Minamata disease.

4. a) Discuss the principle involved in Spectroscopic determination of SO_2 in air sample. (5)
b) Explain the distribution of temperature with height in the atmosphere with the help of diagram identifying different regions in the atmosphere. (5)
c) What is acid rain? How is it caused? Explain its impact on the environment suggest remedial measures to control it. (6)

OR

Give the classification of solid waste and discuss the different modes of solid waste disposal.

5. a) Describe a procedure for the determination of oil and grease in polluted water. (5)
b) Discuss the reactions of Ozone in the atmosphere and explain as to why depletion of Ozone layer is an important environmental issue (5)
c) Describe the principle involved in the determination of fluoride content of polluted water and explain the effects of fluoride on human life and suggest methods for its removal from water bodies. (6)

OR

Discuss the role of fertilizers, pesticides and Urban waste in soil pollution. How can soil pollution from these sources be controlled?

PGIIS-O 1525 B-2K13**M.Sc. IIIrd Semester (Non-CBCS) Degree Examination****Chemistry****(Applied Chemistry(Physical))****Paper - CHEMT 3.43**

Time : 3 Hours

Maximum Marks : 80

Instructions to candidates:

- 1) *All questions are compulsory.*
- 2) *All questions carry equal marks.*

1. Answer the following: (2×8=16)
 - a) State and explain Born-Oppenheimer approximation
 - b) Write the selection rules of microwave spectroscopy
 - c) Write the principle of electro gravimetric analysis
 - d) Explain two applications of coulometry
 - e) How the analytical data generated from photoelectron spectroscopy?
 - f) What are ν' and ν'' progressions
 - g) Define Half wave potential and diffusion current.
 - h) State and explain principle underlying potentiometer.
2.
 - a) Write a note on calculation of bond lengths in diatomic molecules (5)
 - b) Write a note on Fortrate diagram (5)
 - c) Explain about overtones and hot bands (6)

or

 - c) What are PQR branches in IR spectroscopy (6)
3.
 - a) Write the applications of Raman Spectroscopy (5)
 - b) Give an outline on vibrational - rotational Raman spectra. (5)

- c) Explain electrogravimetric for estimating quantity of metal from its salt solution. (6)

or

- c) Explain a note on cyclic voltametry and explain its application in electrochemical analysis (6)
4. a) Write down the Ilkovic equation and explain the terms included in it. (5)
- b) What is principle involved in chromopotentiometry? How it is differentiate from classical potentiometric technique (5)
- c) Write the schematic diagram of Depolarograph and explain the parts involved in it. (6)

or

- c) Write the applications of vibrational spectroscopy (6)
5. a) Explain the basic principle, instrumentation and applications of DSC (5)
- b) Write principle, methodology and applications of coulometry at controlled potential and at constant current. (5)
- c) Explain the following
- i) X-ray photoelectron spectroscopy
- ii) Thermogravimetry (6)

or

- c) Explain the applications of polarography in qualitative and quantitative analysis (6)
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PGIIS-O 1525 B-2K13**M.Sc. IIIrd Semester (Non-CBCS) Degree Examination****Chemistry****(Applied Chemistry(Physical))****Paper - CHEMT 3.43**

Time : 3 Hours

Maximum Marks : 80

Instructions to candidates:

- 1) *All questions are compulsory.*
- 2) *All questions carry equal marks.*

1. Answer the following: (2×8=16)
 - a) State and explain Born-Oppenheimer approximation
 - b) Write the selection rules of microwave spectroscopy
 - c) Write the principle of electro gravimetric analysis
 - d) Explain two applications of coulometry
 - e) How the analytical data generated from photoelectron spectroscopy?
 - f) What are ν' and ν'' progressions
 - g) Define Half wave potential and diffusion current.
 - h) State and explain principle underlying potentiometer.
2.
 - a) Write a note on calculation of bond lengths in diatomic molecules (5)
 - b) Write a note on Fortrate diagram (5)
 - c) Explain about overtones and hot bands (6)

or

 - c) What are PQR branches in IR spectroscopy (6)
3.
 - a) Write the applications of Raman Spectroscopy (5)
 - b) Give an outline on vibrational - rotational Raman spectra. (5)

- c) Explain electrogravimetric for estimating quantity of metal from its salt solution. (6)

or

- c) Explain a note on cyclic voltametry and explain its application in electrochemical analysis (6)

4. a) Write down the Ilkovic equation and explain the terms included in it. (5)
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or

- c) Write the applications of vibrational spectroscopy (6)
5. a) Explain the basic principle, instrumentation and applications of DSC (5)
- b) Write principle, methodology and applications of coulometry at controlled potential and at constant current. (5)
- c) Explain the following
- i) X-ray photoelectron spectroscopy
 - ii) Thermogravimetry (6)

or

- c) Explain the applications of polarography in qualitative and quantitative analysis (6)

PGIIS-O 1521 B-2K13**M.Sc. IIIrd Semester Degree Examination****Chemistry****(Applied Chemistry (Inorganic))****Paper - CHEMT 3.41****(Old)**

Time : 3 Hours

Maximum Marks : 80

Instructions:

1. Answer *all* the questions.
2. All questions carry *equal* marks.

1. Answer the following. (8×2=16)
 - a) Explain why generally Mossbauer spectra is recorded for solid samples and preferably at low temperature.
 - b) IR spectroscopic technique can be used to identify cis-trans isomers:- justify
 - c) What is ambidentate ligand? Give an example
 - d) Explain how NMR spectroscopy applicable to Geometric isomerism
 - e) What is polarographic maxima?
 - f) Distinguish DJA from DSC
 - g) What is diffusion current value of cadmium if $C=3\times 10^{-3}$ moles/litre C Given: $m = 3\text{mg/sec}$, $D = 0.72\times 10^{-5}\text{cm}^2/\text{sec}$, $t = 4$ sec and $n = 2$?
 - h) Calculate the EJR frequency of an unpaired electron in a magnetic field of 3000 gauss (0.3 Tesla)
2.
 - a) With illustrative examples, discuss the applications to IR spectroscopic technique in structural elucidation of metal complexes. (5)
 - b) What is g - value? Discuss the factors influencing g - value (5)
 - c) What is chemical shift? Sketch and explain the NMR spectra of B_2H_6 (6)

OR

With suitable examples explain. How NMR technique can be used in the study of linkage isomerism.

3. a) Discuss the theory and applications of DSC. (5)
b) Sketch and comment on the Mossbauer spectra of $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$ (5)
c) Outline the principle and methodology of conductometric titrations (6)

OR

What is half wave potential? Obtain an expression for halfwave potential and explain the terms involved in it.

4. a) Explain the principles involved in the electrodeposition of copper by electro gravimetry (5)
b) Compare and contract chrono - potentiometry and chrono amperometric techniques. (5)
c) Sketch a typical cyclic voltammogram for a typical reversible redox system, and explain its salient features. (6)

OR

Explain the principles involved in stripping voltammetry.

5. a) Discuss any two applications of TGA and DTA techniques. (5)
b) With suitable examples explain the theory and applications of radiometric titrations. (5)
c) Explain the factors influencing the nature of TGA curves. (6)

OR

Write notes on

- i) Radio tracers
ii) Isotopic delection methods. (6)
-

PGIIS-O 1515 B-2K13**M.Sc. IIIrd Semester (Non-CBCS) Degree Examination****Chemistry****(Spectroscopy, Group theory & Diffraction Studies)****Paper - CHEMT 3.10****(Old)**

Time : 3 Hours

Maximum Marks : 80

Instructions to Candidates:

- 1) All questions are *compulsory*.
- 2) All questions carry *equal marks*.

1. Answer the following:**(2×8=16)**

- a) Explain the fact that H_2 and CH_4 do not give rise to rotation spectra while HCl and CH_3Cl do.
- b) Why microwave spectra are difficult to be observed in case of liquids and solids?
- c) Assign the frequencies and force constants to proper functional group $-C-C-$, $-C=C-$, value given: 4.5×10^5 k dynes cm^{-1} , 2130 cm^{-1} , 15.6×10^5 k dynes cm^{-1} , 1200 cm^{-1} .
- d) Water can't be used as a solvent for IR spectroscopy. Why?
- e) What is ionization interference in AAS?
- f) Explain the term chemical shift with respect to NMR spectroscopy.
- g) The UV spectrum of acetone shows two peaks at $\lambda_{max} = 189$ nm and 273 nm. Identify the electronic transition for each.
- h) What is the nitrogen rule?

2.
 - a) The moment of inertia of CS_2 molecule is found to be 2.56×10^{-38} g cm^2 . Calculate the C-S bond length.
 - b) Give a brief account on the classification of polyatomic molecule on the basis of moment of inertia.
 - c) Give the limitations of Beer's Law and its applications for quantitative analysis.

OR

- c) What are symmetry operations and symmetry elements? Give the symmetry elements present in C_{2v} and C_{2h} point groups. (5+5+6=16)
3. a) Deduce an expression for spectral frequencies for the vibration-rotation spectra of diatomic molecules.
- b) Which of the following transitions allowed? Give reasons: $n - \pi^*$, $\pi - \pi^*$ and $\sigma - \sigma^*$.
- c) Outline the working of a simple mass spectrometer by means of a diagram. Give the function of each component of the system.

OR

- c) Write a note on 'chemical exchange' phenomena in NMR. (5+5+6=16)
4. a) What do you understand by harmonic vibrations? Outline the general equation for vibrational energy of an anharmonic oscillator.
- b) Discuss the effect of conjugation on UV-V is spectra with suitable examples.
- c) Give an account of spin-spin interaction and J-coupling observed in NMR spectroscopy.

OR

- c) In the case of ^{13}C NMR spectroscopy, the intensities of the spectral lines are not related to the number of nuclei. Discuss with one example. (5+5+6=16)
5. a) Describe the electron diffraction experiment.
- b) Illustrate how IR spectroscopy can be used in the study of
- i) Hydrogen bonding
 - ii) Cis trans isomers and
 - iii) Mesomeric effect.
- c) Give the theoretical account of electron coupled spin-spin interaction in NMR spectra of molecules.

OR

- c) Write the brief notes on
- i) Zero fields splitting
 - ii) Spin Hamiltonian. (5+5+6=16)
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PGIIS-O 1526 B-2K13**M.Sc. IIIrd Semester (Non-CBCS) Degree Examination****Chemistry****(Applied Chemistry (Analytical))****Paper - IV, CHEMT 3.44****(Old)**

Time : 3 Hours

Maximum Marks : 80

Instructions to Candidates:*Answer all the questions*

1. Answer the following : (8×2=16)
- a) What is the short wavelength region in x-ray tube?
 - b) Why is flame emission spectroscopy temperature dependant where as A A S is not?
 - c) How are x-rays generated?
 - d) Define the terms plane polarized light and optical rotatory dispersion.
 - e) What is the role of ionization suppressors in A A S.
 - f) Mention any two complexes in nature and indicate their significance
 - g) Define the terms stability constant and instability constant
 - h) State the principle of photometric titrations
2. a) Explain the principle of mass absorption Coefficient in x-ray absorption method. (5)
- b) Explain the utility of ^1H NMR and ^{13}C NMR in the study of metal complexes. (5)
- c) Write the experimental procedure of internal standard addition method of quantitative analysis in flame emission spectroscopy (6)

OR

Illustrate the applications of UV-Visible spectroscopy in the study of structure of inorganic complexes.

3. a) Discuss any two methods of background correction in A A S. (5)
- b) Discuss the theory of x-ray photo electron spectroscopy (electron spectroscopy) for chemical analysis. (5)
- c) Explain the applications of Anger electron spectroscopy. (6)

OR

Illustrate the applications of complexes in metallurgy and industry

4. a) Describe a method of determining stability constant of complexes by UV-visible spectroscopy. (5)
- b) Write a note on direct current organ plasma (5)
- c) Write the block diagram of modern ESCA instrument label the components and describe their working in brief. (6)

OR

Give a brief account of ORD and CD curves. Illustrate your answers with suitable examples.

5. a) Write a note on plate diffusion (cup-plate method) technique of studying antibacterial activity of complexes. (5)
- b) Discuss fluorescent screen and photographic film method of detecting x-rays (5)
- c) Write a note on sampling of surfaces and surface contamination (6)

OR

Discuss some quantitative applications of emission spectroscopy.

PGIS-O 1014 B-2K13
M.Sc. Ist Semester (Non-CBCS) Degree Examination
Chemistry
(Physical Chemistry - I)
Paper - CHEMT-1.33
(Old)

Time : 3 Hours

Maximum Marks :80

Instructions to Candidates:

- 1) All questions carry equal marks.
- 2) All questions are compulsory.

1.
 - a) State and explain heisenberg's uncertainty principle (8×2=16)
 - b) What are eigen functions & eigen values
 - c) Define activity and activity coefficients.
 - d) What is meant by corrossion? Give example
 - e) Distinguish between ideal and non-ideal solutions
 - f) Explain electric properties of ceramic materials
 - g) What do you mean by reaction coordinate
 - h) What is the effect of temperature and catalyst on energy of action?
2.
 - a) Discuss the postulates of quantum mechanics (5).
 - b) Explain Black body radiation (5)
 - c) Formulate the schrodinger wave equation to a particle in one dimensional box and solve for its energy. (6)

OR

- c) Discuss importance of buffers in biological systems (6)

3. a) Describe the methods employed to control the corrosion of metals (5)
b) Derive Henderson-Hasselbalch equation (5)
c) Explain relationship between fugacity and pressure (6)
4. a) Discuss primary salt effect (5)
b) Give the comparison between collision theory and transition state theory (5)
c) Derive the rate expression on the basis of transition state theory (6)

OR

- c) Give an account of RRKM theory of unimolecular reaction rates (6)
5. a) State and explain the Fluorescence & phosphorescence (5)
b) Discuss the classification of composite materials (5)
c) Explain how co-precipitation acts as a precursor to solid state reactions (6)

OR

- c) Write a note on Maxwell's relations (6)
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PGIIS-O 1517 B-2K13
M.Sc. IIIrd Semester Degree Examination
Chemistry
(Bio-Inorganic, Bio-Organic and Bio-Physical Chemistry)
Paper - CHEMT - 3.20
(Old)

Time : 3 Hours

Maximum Marks : 80

Instructions to candidates:

- 1) All questions are **compulsory**.
- 2) All questions carry **equal** marks.

1. Answer the following:

(8×2=16)

- a) What is the role of zinc and iron ions in biological system.
- b) Give the structure and any two functions of ferridoxin.
- c) Mention the biological importance of thiamine hydrochloride.
- d) List the important functions of prostaglandins.
- e) What do you mean by enzymes? How they are classified
- f) What are biopolymers? Give examples.
- g) How ions transport through cell - membranes?
- h) Mention the important functions of RNA in living system.

2. a) What are metallo enzymes? Discuss the enzyme action of any one.

b) Explain the structure and functions of iron - sulfur proteins.

c) What is nitrogen fixation? Explain with mechanism, how it is earned out in - vitro.

OR

Discuss the structure and functions of hemoglobin.

(5+5+6=16)

3. a) Discuss the constitution of ascorbic acid.
- b) Explain the mechanism of action of enzyme.
- c) Outline the synthesis of biotin.

OR

Explain the functions of

- a) prostaglandin E_2
- b) Chymotrypsin.

(5+5+6=16)

4. a) Explain how molecular weight of biopolymers determined by sedimentation velocity technique.
- b) What is nerve conduction? Explain with proper reasoning.
- c) Discuss the biological cell membrane and its functions.

OR

With suitable mechanism describe the biochemical conversion of ADP into ATP.

(5+5+6=16)

5. a) How transport and storage of dioxygen occur in living system? Explain.
- b) Write a note on occurrence and classification of vitamins.
- c) Outline the synthesis of riboflavin.

OR

Discuss the following:

- a) Electrophoresis.
- b) Standard free energy change in biochemical reactions.

(5+5+6=16)

PGIIS-O 1524 B-2K13

M.Sc. IIIrd Semester Degree Examination

Organic Chemistry

(Applied Chemistry (Organic))

Paper - CHEMT-3.42

(Old)

Time : 3 Hours

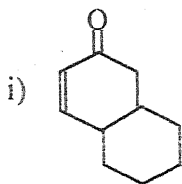
Maximum Marks :80

Instructions to Candidates:

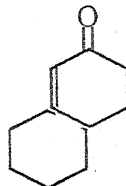
- i) All questions are compulsory
- ii) All questions carry equal marks.

1. Answer eight of the following:

(8×2=16)

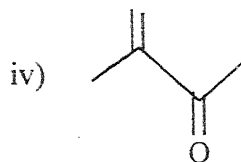
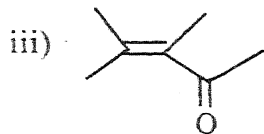
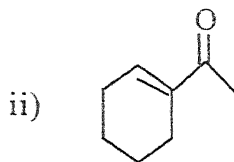
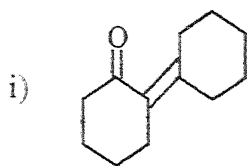
a) Calculate the λ_{\max} of the following:

ii)



- b) 2-Hydroxy-3-nitroacetophenone shows two carbonyl stretching frequencies. Justify.
- c) Define the chemical shift.
- d) Give the structure of pyrethrin.
- e) Mention the applications of congo-red.
- f) Give the synthesis of crystal violet.
- g) Draw the partial structure of PVC and give two important properties.
- h) Illustrate bulk polymerization.

2. a) Assign the observed λ_{\max} values 221, 237, 249, and 258 nm to the following ketones and justify your answer.



- b) Describe the applications of IR in the study of H-bonding in the following compounds.

i) Ethanol,

ii) 2-chlorophenol,

iii) Cyclohexane-1,3-diol

iv) 2-Hydroxy acetophenone.

- c) Deduce the Structure of the compound with the following spectral data:

Molecular formula: $C_7H_4NO_4Cl$

UV-Vis : 280nm.

IR (Cm^{-1}): 3200, 2700(br), 1720, 1600, 1540

1H NMR(δ): 9.8(br,s, 1H, D_2O exchangeable)

7.9(d, 1H, $J=7.5$ Hz)

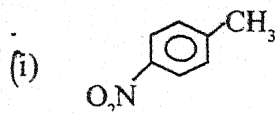
8.4(dd, 1H, $J=7.5$ and 2.1 Hz),

8.64(d, 1H, $J=2.1$ Hz)

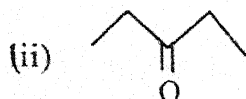
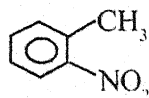
MS(M/Z): 203, 201(3:1), 186, 184(3:1), 159, 157(3:1), 122, 113, 111(3:1).

OR

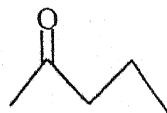
Distinguish the following pairs of compounds by their mass spectral fragmentation.



and



and



(5+5+6=16)

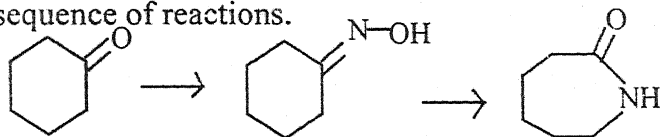
3. a) Give the general principles involved in the analysis of dyes with suitable examples.
 b) Outline the synthesis of the following.
 i) Methyl orange
 ii) Rosaniline
 c) Give the synthesis of the following and their applications:
 i) Melachite green
 ii) Phenolphthalein

OR

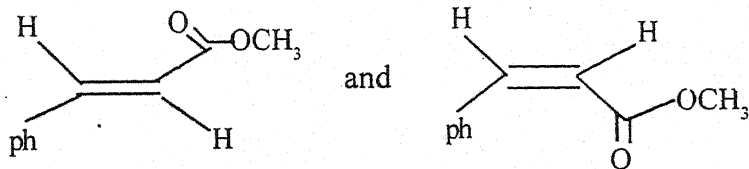
- iii) Fast Violet
 iv) Tinopal. (5+5+6=16)
4. a) Explain the glass-transition temperature with suitable example.
 b) Give the partial structure and applications of the following:
 i) Nylon-66
 ii) Teflon.
 c) Explain the following
 i) Ziegler-Natta catalyst.
 ii) Emulsion polymerization

OR

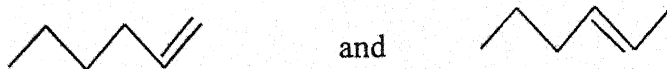
- i) Mechanism and stereochemistry of free radical polymerization
 ii) Block copolymerization. (5+5+6=16)
5. a) Account for the changes observed both in IR and UV-Vis spectra in the following sequence of reactions.



- b) Give the synthesis of the following
 i) DDT ii) Nicotine
 c) How do you distinguish the following pairs by:
 i) $^1\text{H NMR}$:



- ii) MS:



OR

- Give the synthesis of Buna-S rubber and explain its properties. (5+5+6=16)

PGIIS-N 1519 B-2K13
M.Sc. IIIrd Semester Degree Examination
Organic Chemistry
(Heterocyclic chemistry)
Paper - SCT 3.2
(New)

Time :3 Hours

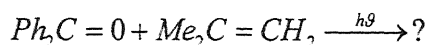
Maximum Marks : 80

Instructions to candidates:

- 1) All questions are **compulsory**.
- 2) All questions carry **equal** marks.

1. Answer any **eight** of the following.**(8×2=16)**

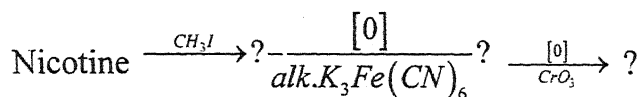
a) Predict the product in the following



b) How do you convert oxirane to thirane?

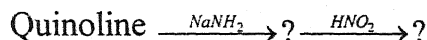
c) Draw the structure of LSD and mention its uses.

d) Write the products in the following reaction.



e) Give a method for the synthesis of phthalazine.

f) Sketch the products in the following:



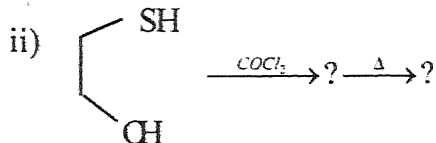
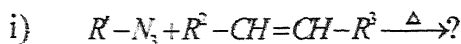
g) How would you establish the presence of phenanthrene nucleus in morphine?

h) Reserpine acid gives δ - lactone on heating with acetic anhydride. What does it indicate?i) How do you establish the presence of -OCH₃ group in reserpine?

j) How do you show that strychnine has indole nucleus?

2. a) Formulate the synthesis and give the reactions of oxaziranes.

- b) Out line the reactions of diazepines
- c) Predict the products in the following and outline their mechanisms.



OR

Describe the ring opening reactions of oxiranes.

(5+5+6=16)

3. a) Discuss the stereochemistry of the ring junction in reserpine.
- b) Give an account of biological significance of:
- i) Tryptophan
- ii) Serotonin.
- c) Name and draw the structures of bases present in RNA and DNA.

OR

Write the relationship between pyridoxine, pyridoxamine and pyridoxal with their inter conversions

(5+5+6=16)

4. a) Explain the Gabriels synthesis of pyrimidine and with the help of resonance structures show the preferred positions for electrophilic and nucleophilic reactions.
- b) Describe the synthesis and important reactions of quinoxaline.
- c) Give an account of the following:
- i) Skraup's synthesis of quinoline.
- ii) Bischler - Napiralski's cyclization of isoquinoline.

OR

How do you achieve the following.

- i) pyridine \rightarrow 4- nitropyridine.
- ii) Isatin \rightarrow 2- phenylquinolin - 4 - carboxylic acid.

(5+5+6=16)

5. a) Outline the synthesis of yohimbine.
- b) How the following inter conversions can be brought about.
- i) Morphine \rightarrow codeine
 - ii) morphine \rightarrow Thebaine.
- c) Discuss the various reactions that led to the structure elucidation of papaverine.

OR

Give the steps involved in the synthesis of quinine.

(5+5+6=16)

PGIIS-N 1519-A B-2K13
M.Sc. IIIrd Semester Degree Examination
Organic Chemistry
(Natural Products)
Paper - SCT 3.1
(New)

Time : 3 Hours

Maximum Marks : 80

Instructions to candidates:

- 1) All questions are **compulsory**.
- 2) All questions carry **equal** marks.

1. Answer any **eight** of the following. **(8×2=16)**

- a) What are $L-\alpha$ - aminoacids and how are they different from peptides?
- b) Write Hudson's ~~lactone~~ *lactone* rule.
- c) what are steroidal hormones? Give their general structure.
- d) Write Salkowski and Liebermann-Burchard reaction for cholesterol.
- e) How are alkaloids classified?
- f) What is Tilden's reagent? Give its application in terpenoid chemistry.
- g) What are vitamins and provitamins. Give examples.
- h) What are nucleosides and nucleotides? Give examples.
- i) Write a reaction which proves the presence of β - ionone in vitamin - A.
- j) what are prostaglandins? Write the structure of prostaglandin - E_2

2.
 - a) Discuss various reactions leading to the establishment of ring size of maltose.
 - b) Give an account on the tertiary structure of proteins.
 - c) Write note on important derivatives of carbohydrates with respect to acetals and ketals.

OR

How is sequence of aminoacids in a polypeptide chain determined by sanger's method?
(5+5+6=16)

3.
 - a) Discuss various reactions which ascertain the presence of.
 - i) hydroxyl group.
 - ii) double bond and
 - iii) cyclopenteno phenan threne ring system in cholesterol.

- b) Sketch the synthesis of estrone.
- c) convert Diosgenin into progesterone.

OR

Write a note on photo products of ergosterol.

(5+5+6=16)

- 4.
- a) How are camphoric acid and camphoronic acid obtained from camphor? Discuss the degradation reactions which led to the structure of camphoronic acid.
 - b) Elucidate the structure of Nicotine with the help of suitable degradation reactions.
 - c) Write the reaction of abietic acid which yields retene. Elucidate the structure of retene and give its synthesis.

OR

Discuss Hofmann's exhaustive methylation and Emde method in structure elucidation of alkaloids.

(5+5+6=16)

- 5.
- a) Describe the biological importance of vitamin - A and ascorbic acid.
 - b) Discuss the reactions which prove the attachment of ribose moiety to phosphate moiety at its 3' and 2'-positions in ribose nucleoside.
 - c) Give the synthesis of some key intermediates used in the synthesis of prostaglandins.

OR

Give an account on genetic code sequencing in nucleic acids.

(5+5+6=16)

PGIIS-N 1527-A B-2K13

M.Sc. IIIrd Semester Degree Examination

Organic Chemistry

(Spectroscopy)

Paper - HCT-3.1

(New)

Time : 3 Hours

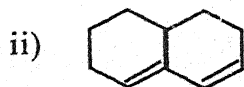
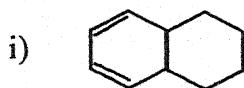
Maximum Marks :80

Instructions to Candidates:

- i) All questions are **compulsory**
- ii) All questions carry **equal marks**.

1. Answer any **eight** of the following: (8×2=16)

- a) Indicate the various allowed electronic transitions for acetone.
- b) Write the mathematical form of Beer-Lambert's law and elaborate the terms.
- c) In the proton NMR spectrum of cyclohexane two signals are observed at low temperature. Why?
- d) Sketch the mass spectral profile of the molecular ion peaks of:
 - i) Methyl chloride
 - ii) Dichloro methane
- e) Highlight the phenomenon of NOE.
- f) Write the magnetic spin quantum numbers (I) for ^{15}N , ^{19}F , ^{31}P and ^{13}C .
- g) State the Stevenson rule.
- h) Predict the λ_{max} for:



- i) Calculate the chemical Shift values for C-Z and C-3 of Z-3-methyl-2-pentene.
 - j) What is molecular ion peak and base ion peak in mass spectrometry?
2. a) Write an account of the Woodward-Fieser rules to empirically calculate the λ_{max} of α, β -unsaturated carbonyl compounds.
- b) Discuss the effect of ring size on the double bond stretching frequency of cycloalkanes.
- c) Give an account of the complementarity of IR and Raman spectroscopy.

OR

Describe the various sampling techniques employed during the recording of IR spectrum. (5+5+6=16)

3. a) Write the Karplus equation and draw the Karplus curve. Give a detailed account of the usefulness of the curves.
- b) Discuss the use of contact shift reagents employed to simplify complex ^1H NMR spectra.
- c) Outline the anisotropic effects prevalent while recording the ^1H NMR spectro of
- i) Aromatics
 - ii) Alkynes.

OR

Highlight:

- i) Use of D_2O to identify labile protons in ^1H NMR
- ii) CIDNP (5+5+6=16)

4. a) Give an account of broad band and off resonance decoupling
- b) Describe the use of DEPT techniques in ^{13}C NMR studies.
- c) Citing suitable example, discuss 2D-homonuclear correlation - experiments (^1H - ^1H COSY). Illustrate appropriately 'Cross peaks' and 'diagonal peaks'.

OR

Sketch the ^1H - ^{13}C HETCOR 2D-spectrum of chloroacetaldehyde and illustrate its usefulness. (5+5+6=16)

5. a) Discuss the McLafferty and McLafferty+1 rearrangements with suitable examples.
- b) How do you differentiate between 3-methyl cyclohexene and 4-methyl-cyclohexene by mass spectral fragmentation.
- c) Write short notes on the following methods:
- i) CI
 - ii) DI and SI.

OR

Deduce the structure of a compound from the following data and assign the values.

Molecular Formula: C_8H_7BrO

UV-Vis(λ_{max}): 261 nm.

IR(cm^{-1}): 1684, 1587, 1395, 1264, 1078 and 1010.

1H NMR(δ): 7.82(d, 2H, $J=7.5Hz$), 7.60(d, 2H, $J=7.5Hz$) and 2.60(s, 3H).

^{13}C NMR(δ): 197(s), 136(s), 130(d), 128(d) and 26(9).

MS(m/z): 200, 198, 185, 183, (base peak), 157, 155, 77, 75, and 43. (5+5+6=16)

PGIIS-N 1514 B-2K13

M.Sc. IIIrd Semester Degree Examination

Organic Chemistry

(Reaction Mechanism)

Paper - HCT - 3.2

(New)

Time : 3 Hours

Maximum Marks : 80

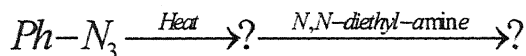
Instructions to candidates:

1. All questions are **compulsory**.
2. All questions carry **equal marks**.

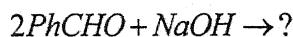
1. Answer any **eight** of the following:

(8×2=16)

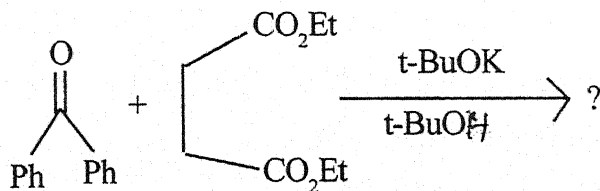
- a) Explain stability of carbocations by taking suitable examples.
- b) What are free radicals? How they are detected?
- c) What are the products formed in the following reaction?



- d) Explain the nucleophilic substitution at allylic carbon using suitable example.
- e) Illustrate chugay reaction with an example.
- f) Formulate the product and name the reaction.

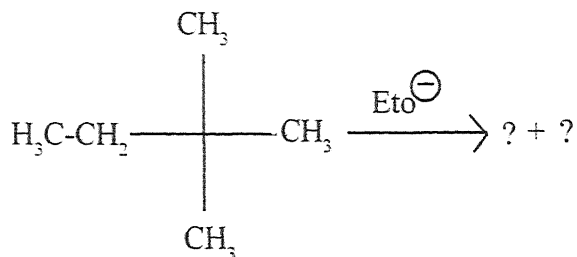


- g) Explain the addition of Phenylhydrazine to a ketone.
- h) With suitable mechanism, suggest the product formed in the following reaction:



- i) What is Kolbe reaction? Give an example.

j) Suggest the product(s) formed in the reaction given below:



2. a) Discuss the importance of phosphorus ylides in organic synthesis.
b) Write a note on formation 'structure and stability of carbocations.
c) Discuss stork-enamine reaction. Give its synthetic utility.

OR

Discuss the addition of triplet and singlet carbene to an alkene. (5+5+6=16)

3. a) Explain the participation of sulfur group as an neighbouring group taking suitable example.
b) Write a note on trans annular rearrangement.
c) How the nucleophilic substitution takes place at trigonal carbon?

OR

Describe the neighbouring group participation of alkyl and cyclo-alkyl groups. (5+5+6=16)

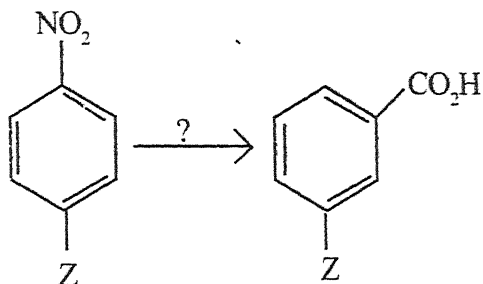
4. a) Explain the mechanism of Barton reaction.
b) Write a note on stereochemistry of elimination reaction in non-cyclic systems.
c) Explain the importance of Cram's rule taking suitable example.

OR

Discuss briefly the following reactions:

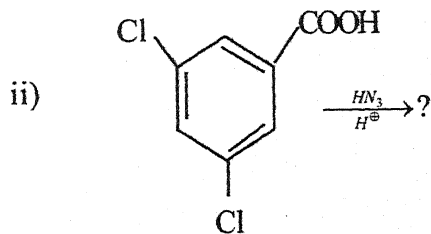
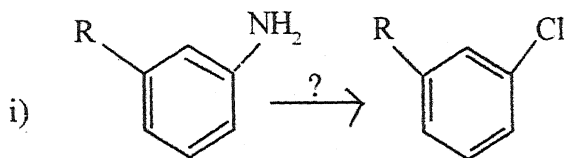
- i. Cope reaction.
ii. Meerwein-Ponndorf-Verley reaction. (5+5+6=16)
5. a) What is Perkin reaction? Give its mechanism.
b) Explain the synthetic utility of Fries rearrangement.

- c) How the following conversion is achieved? Provide suitable reagent, reaction conditions and mechanism.



OR

Answer the following reactions and suggest suitable mechanism.



(5+5+6=16)