

2018

M.Sc. Part-II Examination

CHEMISTRY

PAPER—VII

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

Illustrate the answers wherever necessary.

(Physical Special)

New Syllabus

F.M. - 100

Time : 4 Hrs.

Answer any *five* questions
taking at least *two* from each group (A and B) and
answer *five* questions from group C.

Old Syllabus

F.M. - 75

Time : 3 Hrs.

Answer any *five* questions
taking at least *two* from each group (A and B).

Group—A

1. (a) Write down the steps involved and the rate of each steps for unimolecular photophysical processes.

(Turn Over)

Deduce the expression,

$$\frac{\phi_P}{\phi_f} = \left(\frac{k_P}{k_f} \right) \cdot \left(\frac{k_{ISC}}{k_{ISC}^T + k_P} \right)$$

Here symbols have their usual significances. Assume for a photophysical process,

$$\phi_P + \phi_f + \phi_{ISC}^T \approx 1$$

and hence show that,

$$k_{ISC} = \frac{1}{\tau_f} \left(\frac{1 - \phi_f}{\phi_f} \right) \quad 3+4+3$$

(b) Write a note on P-type delayed emission. 5

2. (a) What is meant by static and dynamic quenching of a fluorophore? Give one example for each. 3

(b) Deduce the following form of stern-volmer equation,

$$\frac{\tau_0}{\tau} = 1 + K_{sv} [Q]$$

where τ_0 & τ are the fluorescence life time of the fluorophore in the absence and presence of quencher respectively. And all other symbols have their usual significances. 8

How do you obtain the stern-volmer quenching constant (K_{sv}) using half quenching method? 4

3. (a) What is meant by exciplex emission? Give one example. Write down the characteristics of exciplex emission. Explain the effect of solvent polarity on exciplex emission. 2+2+4

(b) "Inversion of population cannot be achieved for a two level system." — Justify or criticize the statement. 7

4. Write down the magnetic interaction Hamiltonian and spin wave functions for A – X spin system. Obtain the energy of all the spin state upto its 1st order correction and deduce the frequencies of all possible transitions. 1+2+8+4

Group—B

5. (a) Deduce the expression of Fermi-Golden rule. Comments on the final expression. 7

(b) Deduce the selection rule of Rotational transition. Recursion formula for Associated Legendre function is given below,

$$(2J+1)x P_J^{|M|}(x) = (J - |M| + 1)P_{J+1}^{|M|}(x) + (J + |M|)P_{J-1}^{|M|}(x)$$

(where symbols have their usual significances) 8

6. (a) ESR spectrum of methyl radical occurs at 330 mT in a spectrometer operating at 9248 MHz. Calculate the g value of the radical. 3

(b) Write short notes on :

(i) Zero-field splitting ;

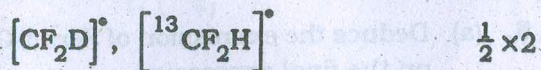
(ii) Hyperfine splitting. 2×2

(c) Why water and alcohol are not suitable solvents for ESR studies? 2

(d) Explain why the energy of α -spin ($m_s = +\frac{1}{2}$) of electron increases linearly whereas that of β -spin ($m_s = -\frac{1}{2}$) decreases with the increase in the external magnetic field.

3

(e) Predict the number of lines in the ESR spectrum of the following radicals :



7. (a) Some commercial EPR spectrometers use 7.89 mm microwave radiation. What magnetic field is needed to satisfy the resonance condition ?

3

(b) Predict the intensity distribution in the hyperfine lines of the ESR spectrum of the radical $\dot{\text{C}}\text{D}_3$.

4

(c) Showing all possible transitions explain the ESR spectrum of methyl radical.

3

(d) Explain the hyperfine splitting in the ESR spectrum of $(\text{CF}_3)\dot{\text{N}}\text{O}$ radical.

2

(e) Explain the ESR spectra of naphthalene diradical.

3

8. (a) What is Stark effect ? Derive an expression for the second order correction in the rotational energy of a molecule in an electrostatic field.

$$\text{Given : } \langle (J+1)M / \cos \theta / JM \rangle = \sqrt{\frac{(J+1)^2 - M^2}{(2J+1)(2J+3)}}$$

where M is the eigen value of J_4 .

2+8

(b) Derive expression for spherical top molecule in rotational spectra.

5

Group—C

9. Answer any five of the following :

5×5

(i) Write down the magnetic interaction Hamiltonian of a proton. Show that $|\alpha\rangle$ spin get stabilized and $|\beta\rangle$ spin get destabilized in presence of an external magnetic field.

(ii) Write a short note on the mode locking in LASER.

(iii) Write a note on uncertainty broadening in the spectral transition.

(iv) What is meant by fluorescence and phosphorescence emission ? Explain with example.

(v) What is excited state acidity constant of organic acid ? How do you obtain the excited state acidity constant of an organic acid using Fröster cycle ?

(vi) What is meant by induced absorption and induced emission?

(vii) Why do the spin lattice and spin-spin relaxation mechanism is so important in NMR spectroscopy?

(Organic Special)

New Syllabus

F.M. - 100

Time : 4 Hrs.

Answer any *five* questions taking at least *two* from each group (A and B) and answer *five* questions from group C.

Old Syllabus

F.M. - 75

Time : 3 Hrs.

Answer any *five* questions taking at least *two* from each group (A and B).

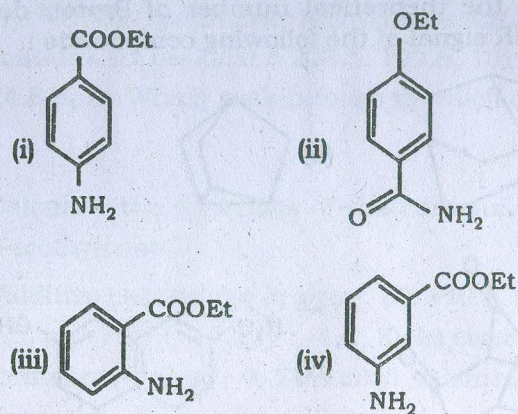
Group - A

1. (a) A compound shows following spectral data :

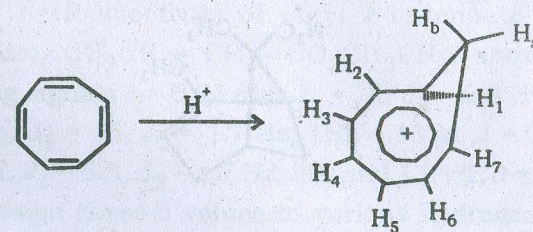
$^1\text{H NMR}$: δ 7.9 (d, $J = 8\text{Hz}$, 2H), 6.6 (d, $J = 8\text{Hz}$, 2H), 4.3 (q, $J = 6\text{Hz}$, 2H), 4.0 (br s, 2H, D_2O exchangeable), 1.4 (t, $J = 6\text{ Hz}$, 3H)

Mass : m/s 165, 137, 120, 92

Which of the compounds below most closely matches the $^1\text{H NMR}$ data? Justify your choice.

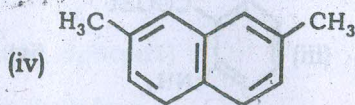
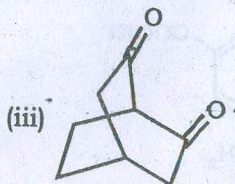
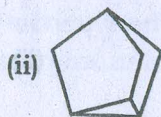
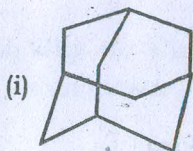


(b) Write the correct match of protons in Column A with the $^1\text{H NMR}$ chemical shifts in column B for the product of the following reaction :



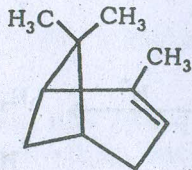
Column A		Column B (δ ppm)
H_a	i	-0.3
H_b	ii	5.1
$\text{H}_1, \text{H}_3, \text{H}_5, \text{H}_7$	ii	6.4
$\text{H}_2, \text{H}_4, \text{H}_6$	iv	8.5

- (c) Predict the theoretical number of Proton decoupled ^{13}C NMR signal of the following compounds :



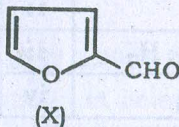
5

- (d) The chemical shifts (δ) of the methyl groups of following molecule are 1.63, 1.27 and 0.85 ppm. Assign these δ values to various methyl groups :



2

2. (a) The ^1H NMR spectrum of the following compound (X) shows the following signals $\delta = 9.70, 7.78, 7.32, 6.67$. Assign these δ values to various hydrogens and draw the ^1H NMR of the compound indicating splitting pattern :



4

- (b) The ^{13}C NMR spectrum for Acetylacetone ($\text{CH}_3\text{COCH}_2\text{COCH}_3$) contains six peaks at δ 203.5, 192.6, 101.1, 58.7, 30.9, 24.8 ppm. Which peak belongs to which carbon atom ?

3

- (c) Calculate the δ_{C} values of the carbons C2 and C3 of 3-methylpent-2-ene.

3

[Additive parameters in ppm : α : +10.6, β : +7.2 ; γ : -1.5, α : -7.9, β : -1.8, γ : -1.5, Z(cis) correction : -1.1, E (trans) correction : 0, Two alkyl substituent at C1 (two $\text{C}\alpha$) : -4.8 ; Base value 123.3 ppm]

- (d) 'The ^1H NMR spectrum of N, N-dimethylformamide is temperature dependent' — Explain.

2

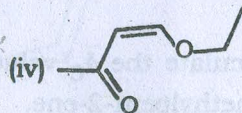
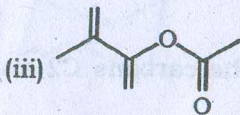
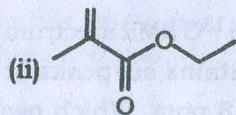
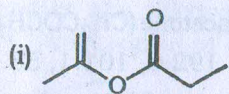
- (e) The ^1H NMR spectrum of ethyl 2-butenoate (ethyl crotonate), $\text{CH}_3\text{CH}=\text{CH}-\text{CO}_2\text{CH}_2\text{CH}_3$, shows the following signals $\delta = 6.95$ (dq, $J_1 = 16, J_2 = 6.8$ Hz, 1H), 5.81 (dq, $J_1 = 16, J_2 = 1.7$ Hz, 1H), 4.13 (q, $J = 7$, 2H), 1.88 (dd, $J_1 = 6.8, J_2 = 1.7$ Hz, 3H) and 1.24 (t, $J = 7$, 3H) ppm. Assign these δ values to various hydrogens and tell if the double bond is cis or trans substituted.

3

3. (a) Structure of the compound displaying following characteristic spectral data

IR : 1720 cm^{-1}

^1H NMR : δ 6.2 (br s, 1H), 5.5 (br s, 1H), 4.2 (q, 2H), 2.0 (s, 3H), 1.1 (t, 3H) is



Write the most suitable structure of the compound and justify your answer. 4

(b) What is Nuclear Overhauser Effect (NOE). Mention three factors on which NOE depends. 4

(c) What you mean by magnetic equivalent nuclei and chemical shift equivalent nuclei? Explain with example of each case. 3

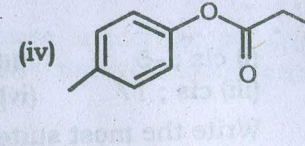
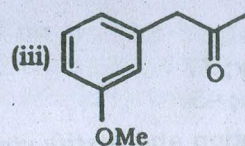
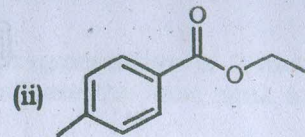
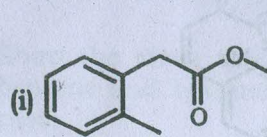
(d) Partial spectroscopy data is given below for an organic compound :

(i) 4 signals between δ 120-150 ppm in ^{13}C NMR spectrum.

(ii) 2 doublet between δ 6.8-8.5 ppm in ^1H NMR spectrum.

(iii) an absorption band at 1724 cm^{-1} in IR spectrum.

(e) The structure of the following compound follows :



OMe

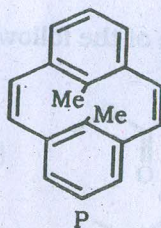
Write the most suitable structure of the compound and justify your answer. 4

4. (a) What were the initial difficulties encountered in the development of natural abundance ^{13}C NMR spectroscopy? How were these difficulties overcome by the introduction of pulsed NMR and Fourier Transform (FT-NMR)? Discuss briefly the principle of FT-NMR. 1+1+6

(b) What are the advantages of Fourier Transform (FT-NMR) technique over CW-NMR technique? 4

(c) Why a complex spectrum is simplified by using high field FT-NMR spectroscopy? 3

5. (a) The compound P undergoes a pericyclic reaction under photochemical condition to give compound Q. In compound Q, the relative stereochemistry and ^1H NMR chemical shift values of methyl groups (in δ ppm), respectively, are



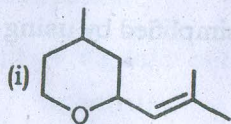
- (i) cis ; -5 (ii) trans ; 17
 (iii) cis ; 17 (iv) trans ; -5

Write the most suitable option and justify your answer 4

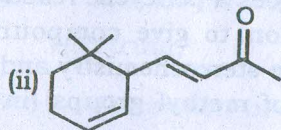
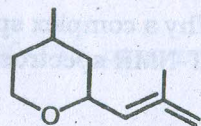
- (b) m-nitrobenzaldehyde shows ^1H NMR signals at about δ 10.12 (1H), 8.72 (1H), 8.5 (1H), 8.28 (1H) ppm. Assign these δ values to various hydrogens. Draw the spectrum of the above compound showing multiplicities of the signals. 5

- (c) How will you distinguish between inter and intramolecular hydrogen bonding on the basis of PMR spectroscopy. 2

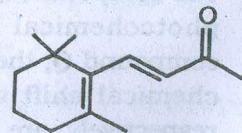
- (d) Distinguish between the following pairs on the basis of mass spectra fragmentations.



and



and



2+2

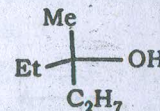
Group—B

6. (a) Show the Mass spectral fragmentation of 2-methyl-1-pentene and 1-hexene. Indicate the base peak in each case. 4

- (b) How on the basis of mass spectroscopy one can differentiate between 2-ethylcyclohexanone and 3-ethylcyclohexanone. 3

- (c) The molecular ion of 2-methyl-3-phenylbutane (M^+ m/z = 148) fragments to give a base peak at m/z = 105. The isomeric compound 2, 2-dimethyl-1-phenylpropane, however, gives the base peak at m/z = 57 with another significant peak at m/z = 91. Explain. 4

- (d) In the mass spectrum of the compound given below, during the α -cleavage, arrange the order of preferential loss of groups. 2



- (e) How one can use mass spectroscopy to distinguish between cyclohexane (C_6H_{12}) and dihydropyran ($\text{C}_5\text{H}_8\text{O}$)? 2

7. How would you carry out the following conversion ?

(i) Yohimbine to pseudo-yohimbine and vice versa.

(ii) Indole alkaloid to Quinoline alkaloid.

(iii) Caryophyllene to cloven.

(iv) Quinine to Quinidine.

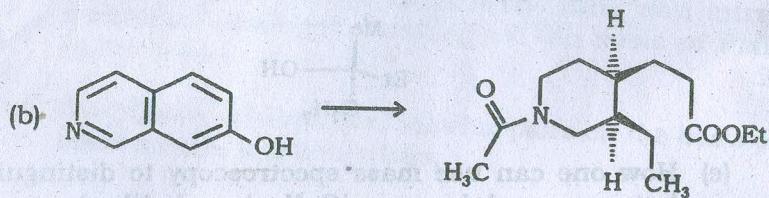
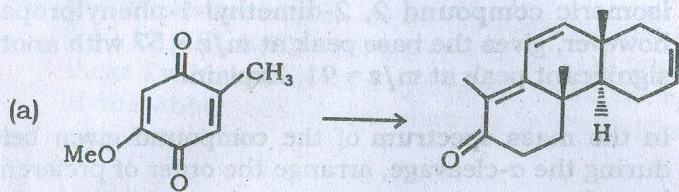
(3+3)+3+3+3

8. Derive suitable experiment to establish the absolute configuration of the following :

- (a) C₁₇-OH in yohimbine
 (b) Stereochemistry of the D/E ring junction in yohimbine.
 (c) Location of isopropyl grouping and the double bonds in abietic acid.

4+7+4

9. Complete the following synthesis :



(c) Meroquinine \longrightarrow 1, 2-diethylcyclohexane

10. (a) Complete the following conversions : (any two)

- (i) Acetyl coenzyme A \longrightarrow DMAPP
 (ii) Acetyl coenzyme A \longrightarrow IPP
 (iii) IPP \longrightarrow Geraniol.

3 \times 2

(b) Write down the synthesis of squalene starting from FPP.

5

(c) Write down the structure of any two :

(i) β -amyrin

(ii) taraxasterol

(iii) α -amyrin.

2 \times 2

Group—C

11. Answer any five questions from following :

5 \times 5

(a) Compound 'A', C₉H₁₁NO₂, exhibited the following spectral data. Suggest probable structure for the compound 'A'.

IR : ν_{\max} (cm⁻¹) 3415(s), 1690(s), 1620 and a series of bands below 900 cm⁻¹.

¹H NMR : δ 1.3 (3H, t, J = 7.0 Hz), 4.15 (2H, br. S ; disappeared on deuterium exchange), 4.30 (2H, q, J = 7.0 Hz), 6.6 and 7.8 (each 2H, d, J = 8.5 Hz).

¹³C NMR : δ_C 14.4 (q), 60.3 (t), 119.7 (d), 131.5 (d), 119.5 (S), 151.4 (S), 168.9 (S).

MS : m/z 165 (M⁺), 137, 120 (100%) and 92.

(b) A compound with molecular formula C₆H₁₂O₂ shows ¹H NMR signals :

¹H NMR : δ 1.1 (s, 6H), 2.1 (s, 3H), 2.6 (s, 2H), 3.9 (s, 1H).

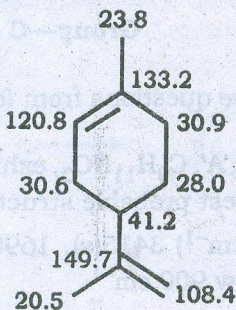
Propose a structure consistent with the given data.

- (c) A compound with molecular formula $C_9H_{12}O_3$ shows 1H NMR signals :

1H NMR : δ 7.2 (1H, dd, $J = 8$ Hz and 1.5 Hz), 6.8 (1H, d, 1.5 Hz), 6.7 (1H, d, $J = 8$ Hz), 4.9 (2H, s), 3.9 (3H, s), 3.85 (3H, s), 3.5 (1H, br s, exchangeable with D_2O).

Propose a structure consistent with the given data.

- (d) Draw the expected DEPT and ATP, spectra of the following compound :



- (e) What is spin decoupling in NMR spectroscopy ? How is it carried out ? Illustrate the phenomenon with pure ethanol.
- (f) Delineate the following biogenetic conversion :
GPP to abietic acid.
- (g) What is migratory insertion ? Show a migratory insertion with reference to transition metal complex.