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UNIVERSITY EXAMINATIONS
2022/2023ACADEMIC YEAR

FORTH YEAR FIRST SEMESTER
MAIN EXAMINATIONS

FOR THE DEGREE OF BSC (CHEMISTRY)

COURSE CODE: SCH 411

COURSE TITLE: SPECTROSCOPY AND SEPARATION

DATE: 19/04/2023 **TIME: 2:00-4:00pm**

INSTRUCTIONS TO CANDIDATES
Time: 2 Hours

Answer question ONE and any other TWO of the remaining

QUESTION ONE [30 MARKS]

a) Define the following terms: **[5 marks]**

i) Spectroscopy.

ii) Transmittance.

iii) Fermi resonance.

iv) Electromagnetic radiation.

v) Combination bands.

b) Mention two (2) reasons why wave number is used in the measurement of IR absorption instead of wavelength. **[2 marks]**

c) Calculate the number of vibration modes of the following compounds. **[2 marks]**

i) NH_3

ii) C_2H_2

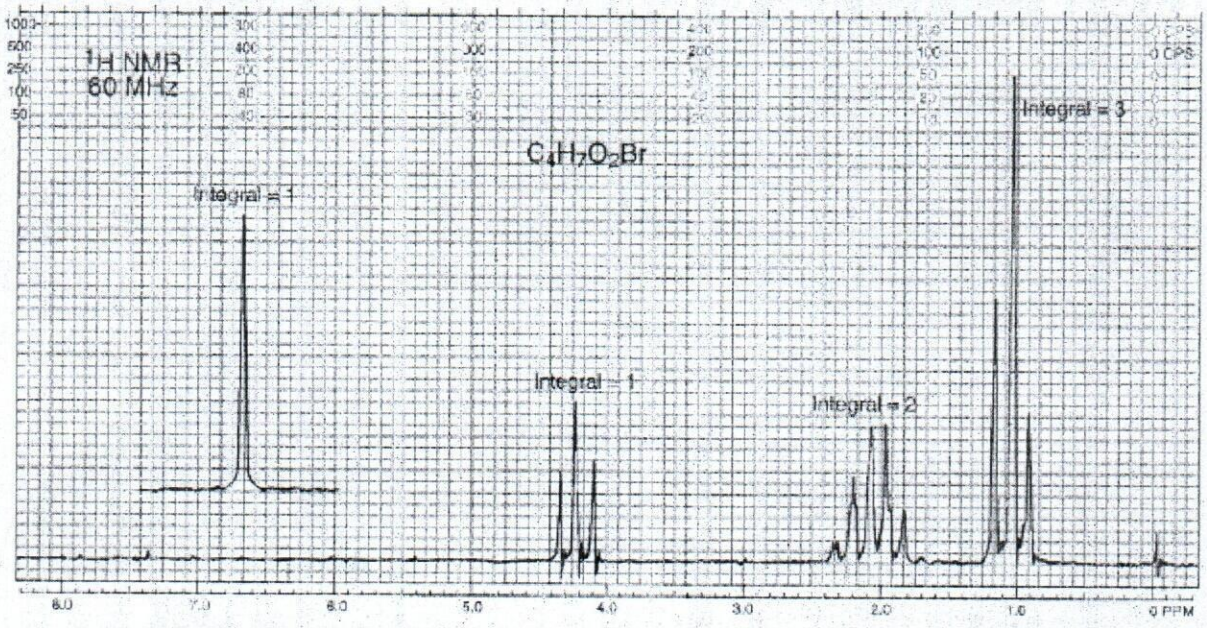
d) Give the relationship between the strength of the magnetic field, energy and the resonance frequency of NMR. **[1 mark]**

e) State three (3) rules that govern the splitting patterns in the proton NMR spectra of organic compounds. **[3 marks]**

f) Name the variables that characterize NMR with their appropriate units. **[2 marks]**

g) List four (4) features of proton NMR responsible for giving insight into the structure compound. **[2 marks]**

h) The following compound is a carboxylic acid that contain bromine atom: $C_4H_7O_2Br$. The peak at 10.97 ppm was moved onto the chart for clarity.



i. Propose the structure of the carboxylic acid **[3 marks]**

ii. Assign peaks of the protons that give rise to the structure you proposed in (i) above **[2 marks]**

i) Gas chromatography (GC) is an analytical methodology, which was devised by Nobel Laureate, Martin, et al. in 1952. It is widely commercialized and used in various industries, capable of both of quantitative and qualitative analysis.

i. Explain the working principle of partition GC. **[3 marks]**

ii. List four (4) characteristics of carrier gas used in GC. **[2 marks]**

iii. Explain the function of guard column in HPLC and why it is not in GC sytems **[3 marks]**

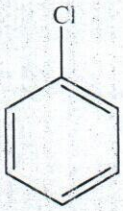
QUESTION TWO [20 MARKS]

a. Predict the elution order of the following solutes in reversed phase HPLC

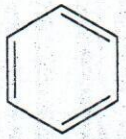
[4 marks]

i

ii



iii



iv

b. Derivatization is the process of chemically modifying a compound to produce a new compound which has properties that are suitable for analysis.

c. Give four reasons why derivatization is necessary in gas chromatography

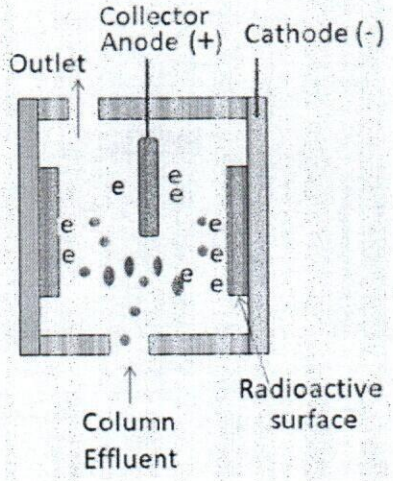
[2 marks]

d. With help of equations, explain the following derivatization techniques.

a) Silylation **[2.5 marks]**

b) Acylation **[2.5 marks]**

e. The figure below is diagram for electron capture detector (ECD), study it and answer the questions that follows.



i. Explain basis of its operations **[5 marks]**

ii. Name four species that are separated by this detector **[2 marks]**

iii. Name two advantages of using this detector **[2 mark]**

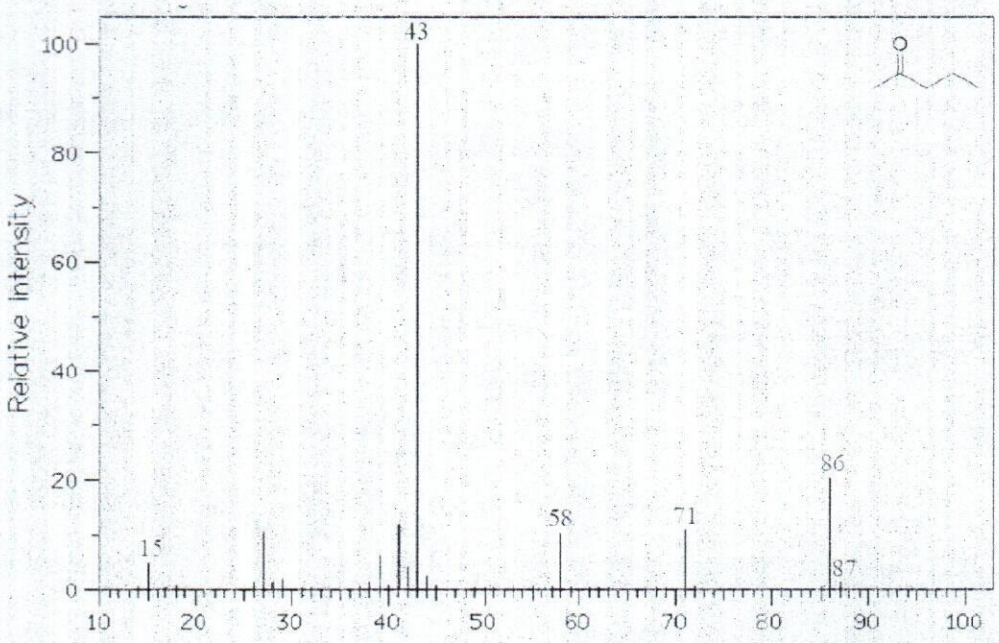
QUESTION THREE [20 MARKS]

a. Differentiate between the following terms as use in chromatography.

i. Normal phase and Reverse phase. **[2 marks]**

ii. Isocratic elution and gradient elution. **[2 marks]**

b. Using the mass spectrum of 2-pentanone ($C_5H_{10}O$) shown below, answer the questions that follow about its fragmentation.

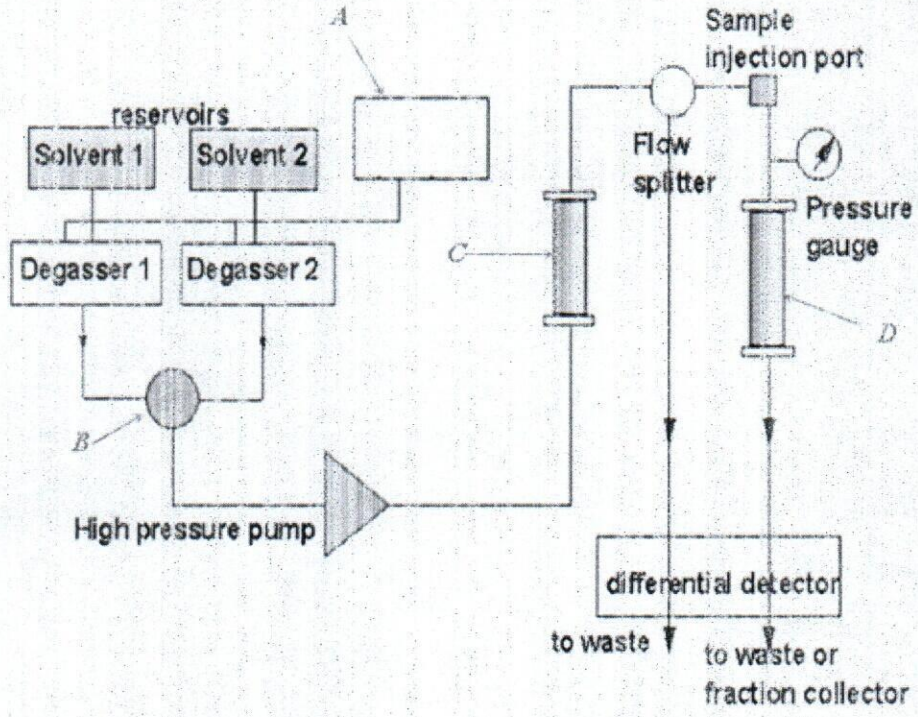


i. Draw a valid resonance structure of the molecular ion (m/z = 86). Explain the source of the small peak at m/z = 87. **[3 marks]**

ii. Important decomposition pathways for the molecular ion of carbonyl-containing compound such as 2-pentanone involves α-cleavage. Beginning with both viable α-cleavage decomposition pathways, draw fragmentation mechanisms that lead to ions with m/z values of 71, 43, 15. Make sure your mechanisms account for two different ions with m/z values of 43. **[4 marks]**

iii. The other major decomposition pathway arises from a McLafferty rearrangement of the molecular ion followed by the loss of an ethylene gas molecule. Show an electron-pushing mechanism for this decomposition which will rationalize the peak with a value of m/z = 58. **[3 marks]**

c. The flow diagram below represents HPLC system. Study it and answer the questions that follow.

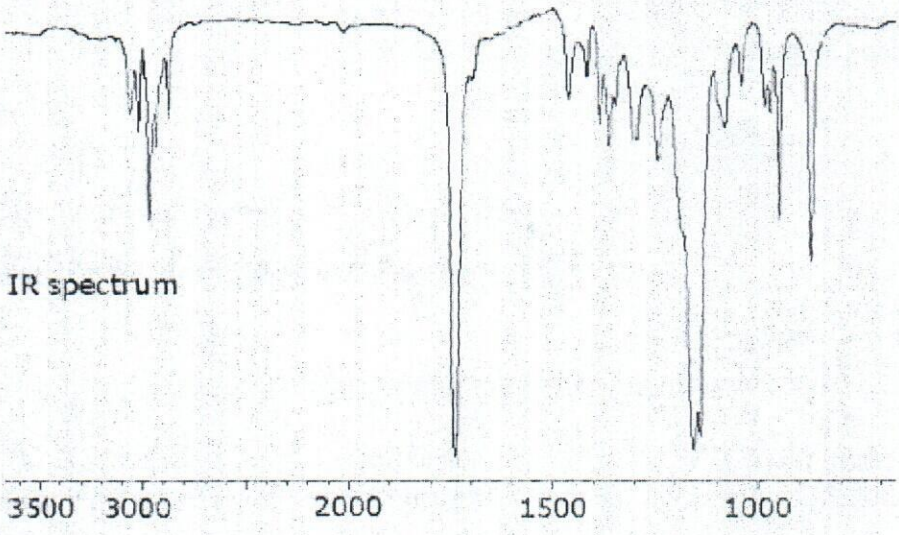


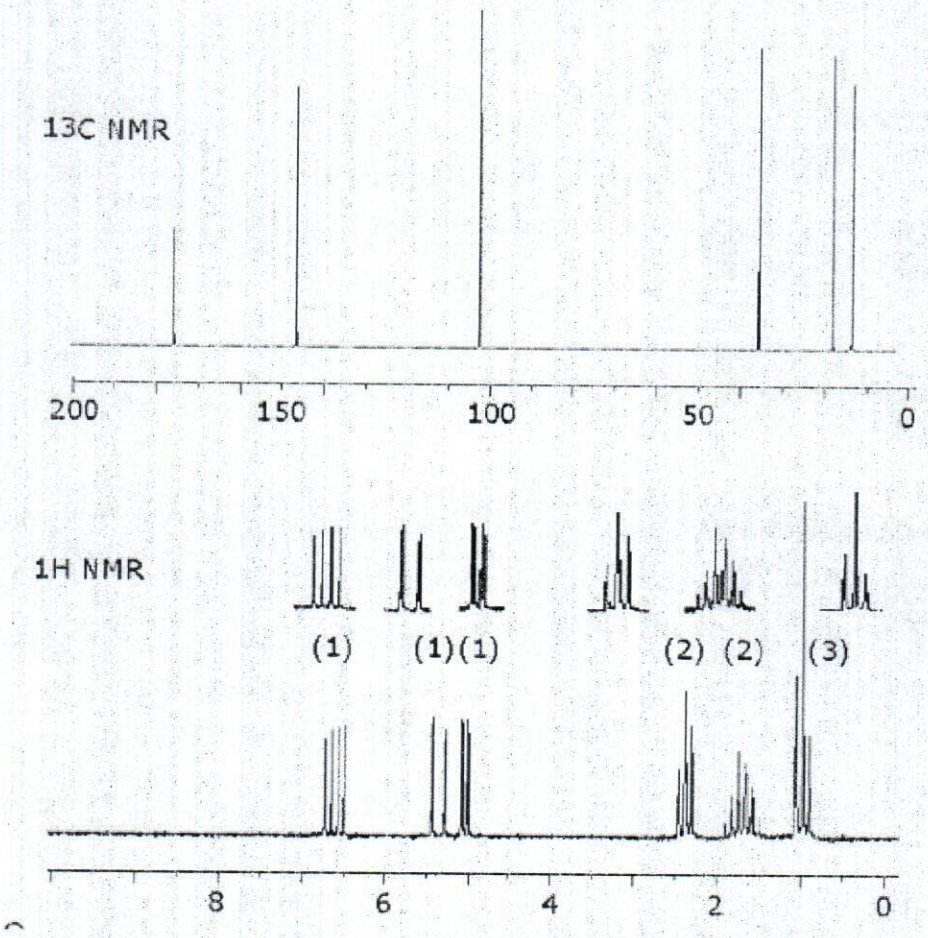
i. Name and state the function of part **A, B, C** and **D**. **[4 mars]**

ii. Explain importance of having degassing unit in HPLC system. **[2 marks]**

QUESTION FOUR [20 MARKS]

Study the IR, ^{13}C NMR and ^{1}H NMR spectra for an unknown compound with the formula $C_6H_{10}O_2$, then answer the question on the next page.





i. Determine degrees of unsaturation in this compound and explain its significance **[4 marks]**

ii. In the IR, what does the signal at about 1740 suggest? **[2 marks]**

iii. In the ^{13}C NMR, what does the chemical shift of the signal at about 105 suggest? **[2 marks]**

iv. In the ^{1}H NMR, what does the chemical shift of the signal at about 5.2 suggest? **[2 marks]**

v. In the ^{1}H NMR, what does the integration of the signal at about 2.3 suggest? **[2 marks]**

vi. In the ^{1}H NMR, what does the splitting pattern of the signal at about 1.0 suggest? **[2 marks]**

vii. Deduce the structure of this unknown compound **[6 marks]**

APPENDICES

Approximate IR Absorption Frequencies

Bond	Frequency (cm^{-1})	Intensity
O–H (alcohol)	3650–3200	Strong, broad
O–H (carboxylic acid)	3300–2500	Strong, very broad
N–H	3500–3300	Medium, broad
C–H	3300–2700	Medium
C≡N	2260–2220	Medium
C≡C	2260–2100	Medium to weak
C=O	1780–1650	Strong
C–O	1250–1050	Strong

Approximate ^{1}H NMR Chemical Shifts

Hydrogen	δ (ppm)
CH_3	0.8–1.0
CH_2	1.2–1.5
CH	1.4–1.7
C=C–CH_x	1.7–2.3
O=C–CH_x	2.0–2.7
Ph–CH_x	2.3–3.0
≡C–H	2.5
R_2N–CH_x	2.0–2.7
I–CH_x	3.2
Br–CH_x	3.4
Cl–CH_x	3.5
F–CH_x	4.4
O–CH_x	3.2–3.8
C=CH	4.5–7.5
Ar–H	6.8–8.5
O=CH	9.0–10.0
ROH	1.0–5.5
ArOH	4.0–12.0
RNH_x	0.5–5.0
$CONH_x$	5.0–10.0
RCOOH	10–13

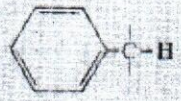
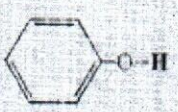
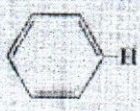
Approximate ^{13}C NMR Chemical Shifts

Carbon	δ (ppm)
Alkanes	
Methyl	0–30
Methylene	15–55
Methine	25–55
Quaternary	30–40
Alkenes	
C=C	80–145
Alkynes	
C≡C	70–90
Aromatics	110–170
Benzene	128.7
Alcohols, Ethers	
C–O	50–90
Amines	
C–N	40–60
Halogens	
C–F	70–80
C–Cl	25–50
C–Br	10–40
C–I	–20–10
Carbonyls, C=O	
R_2C=O	190–220
RXC=O (X = O or N)	150–180

A SIMPLIFIED CORRELATION CHART

Type of Vibration			Frequency (cm^{-1})	Intensity	Page Reference
C–H	Alkanes	(stretch)	3000–2850	s	29
	$-CH_3$	(bend)	1450 and 1375	m	
	$-CH_2-$	(bend)	1465	m	
	Alkenes	(stretch)	3100–3000	m	31
		(out-of-plane bend)	1000–650	s	
	Aromatics	(stretch)	3150–3050	s	41
		(out-of-plane bend)	900–690	s	
	Alkyne	(stretch)	ca. 3300	s	33
	Aldehyde		2900–2800	w	54
			2800–2700	w	
C–C	Alkane		Not interpretatively useful		
C=C	Alkene		1680–1600	m–w	31
	Aromatic		1600 and 1475	m–w	41
C≡C	Alkyne		2250–2100	m–w	33
C=O	Aldehyde		1740–1720	s	54
	Ketone		1725–1705	s	56
	Carboxylic acid		1725–1700	s	60
	Ester		1750–1730	s	62
	Amide		1680–1630	s	68
	Anhydride		1810 and 1760	s	71
	Acid chloride		1800	s	70
C–O	Alcohols, ethers, esters, carboxylic acids, anhydrides		1300–1000	s	45, 48, 60, 62, and 71
O–H	Alcohols, phenols				
	Free		3650–3600	m	47
	H-bonded		3400–3200	m	47
	Carboxylic acids		3400–2400	m	61
N–H	Primary and secondary amines and amides				
	(stretch)		3500–3100	m	72
	(bend)		1640–1550	m–s	72
C–N	Amines		1350–1000	m–s	72
C=N	Imines and oximes		1690–1640	w–s	75
C≡N	Nitriles		2260–2240	m	75
X=C=Y	Allenes, ketenes, isocyanates, isothiocyanates		2270–1940	m–s	75
N–O	Nitro ($R-NO_2$)		1550 and 1350	s	77
S–H	Mercaptans		2550	w	79
S–O	Sulfoxides		1050	s	79
	Sulfones, sulfonyl chlorides, sulfates, sulfonamides		1375–1300 and 1350–1140	s	80
C–X	Fluoride		1400–1000	s	83
	Chloride		785–540	s	83
	Bromide, iodide		<667	s	83

APPROXIMATE CHEMICAL SHIFT RANGES (PPM) FOR SELECTED TYPES OF PROTONS[a]

$R-CH_3$		0.7 – 1.3
$R-CH_2-R$		1.2 – 1.4
R_3CH		1.4 – 1.7
$R-C(-C)=C-C-H$		1.6 – 2.6
$R-C(=O)-C-H$, $H-C(=O)-C-H$		2.1 – 2.4
$RO-C(=O)-C-H$, $HO-C(=O)-C-H$		2.1 – 2.5
$N\equiv C-C-H$		2.1 – 3.0
		2.3 – 2.7
$R-C\equiv C-H$		1.7 – 2.7
$R-S-H$	var	1.0 – 4.0[b]
$R-N(-)-H$	var	0.5 – 4.0[b]
$R-O-H$	var	0.5 – 5.0[b]
	var	4.0 – 7.0[b]
	var	3.0 – 5.0[b]
$R-C(=O)-N(-)-H$	var	5.0 – 9.0[b]
$R-N(-)-C-H$		2.2 – 2.9
$R-S-C-H$		2.0 – 3.0
$I-C-H$		2.0 – 4.0
$Br-C-H$		2.7 – 4.1
$Cl-C-H$		3.1 – 4.1
$R-S(=O)(=O)-O-C-H$		ca. 3.0
$RO-C-H$, $HO-C-H$		3.2 – 3.8
$R-C(=O)-O-C-H$		3.5 – 4.8
O_2N-C-H		4.1 – 4.3
$F-C-H$		4.2 – 4.8
$R-C(-C)=C-H$		4.5 – 6.5
		6.5 – 8.0
$R-C(=O)-H$		9.0 – 10.0
$R-C(=O)-OH$		11.0 – 12.0