PROSPERITY ACADEMY

A2 CHEMISTRY 9701

Crash Course

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ANALYTICAL CHEMISTRY

COMPLETE NOTES

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Nuclear Magnetic Resonance :-

^1H - NMR :-

- When radio waves are passed through an organic sample, in the presence of an external magnetic field, the ^1H atoms in it absorb specific frequencies due to their chemical environment and undergo resonance

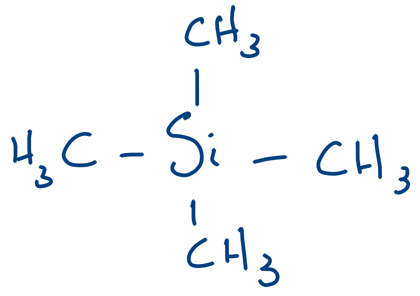
- If an electron donating group is present near the Hydrogen, it will experience a weaker magnetic field, and hence a lower frequency will be absorbed to achieve resonance. (e.g alkyl)

- If an electron withdrawing group is present near the Hydrogen, it will experience a stronger magnetic field, and hence a higher frequency will be absorbed to achieve resonance (e.g. OH, Cl, C=O)

- The frequency of radiowaves absorbed is typically around a 100 MHz, while the difference in frequencies absorbed by hydrogens in different chemical environments is around 100 Hz

→ It would be very difficult to spot the difference between 100000100 and 100000000

- We use TMS (Tetramethylsilane) to solve this problem. All frequencies are noted relative to it



$\mathrm{H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}-CH_3}$

- It has 12 H atoms in the same environment, so it produces a strong noticeable absorption
- TMS absorbs frequency that does not coincide with the frequencies our organic compound will absorb
- Chemically inert, does not react with anything

$$-\delta = \frac{f_{sample} - f_{TMS}}{f_{TMS}} \times 10^6$$ → This is what we use to identify groups

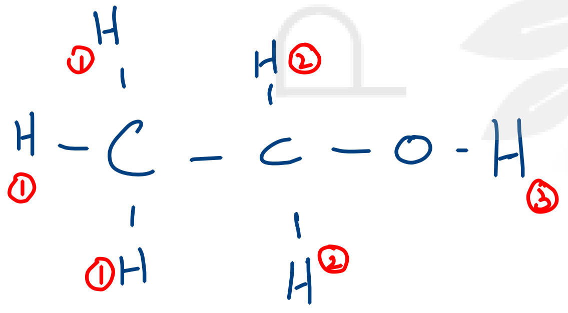
- $\delta = 0$ is due to TMS so ignore it if given

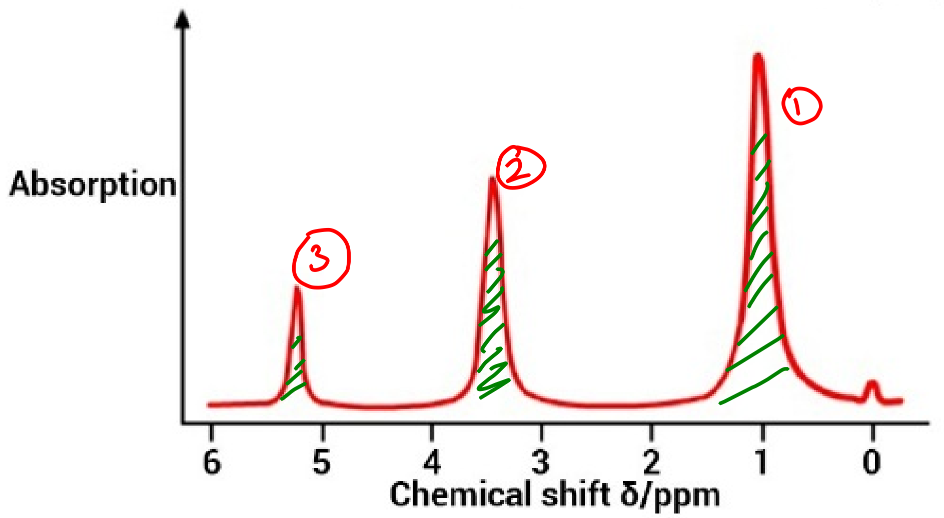
Deuterated solvent

- H_2O or ethanol cannot be used as solvent as they have hydrogens. We use $CDCl_3$ which contains D: $^2H_1$ and does not absorb in the range where ^1H absorb

Low Resolution NMR Spectrum:-

Let's consider ethanol:-



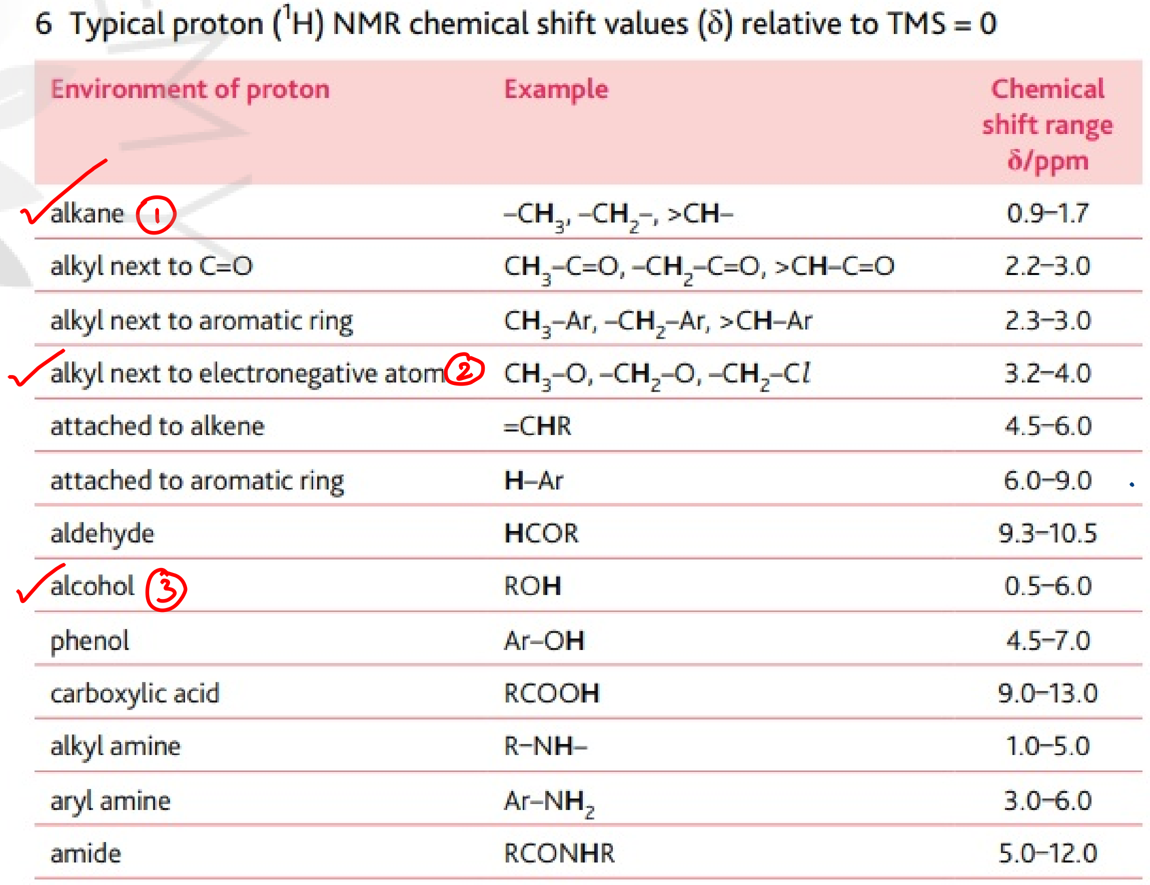


1 : 2 : 3

- The number of peaks corresponds to different hydrogen environments

- The ratio of area under curve gives us number of hydrogens in each environment

- As you can see OH and NH_2 are hard to identify so we use D_2O → upon addition of D_2O the absorption of OH and NH_2 disappears so we can confirm

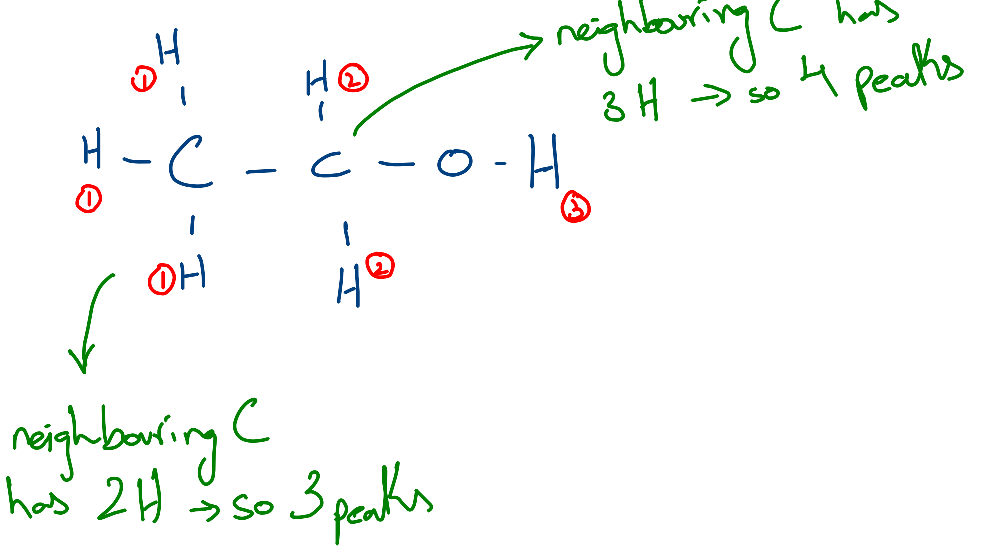


6 Typical proton (^{1}H) NMR chemical shift values (δ) relative to TMS = 0

Environment of proton	Example	Chemical shift range δ/ppm
✓ alkane ①	$-CH_3$, $-CH_2-$, $>CH-$	0.9–1.7
alkyl next to C=O	$CH_3-C=O$, $-CH_2-C=O$, $>CH-C=O$	2.2–3.0
alkyl next to aromatic ring	CH_3-Ar, $-CH_2-Ar$, $>CH-Ar$	2.3–3.0
✓ alkyl next to electronegative atom ②	CH_3-O, $-CH_2-O$, $-CH_2-Cl$	3.2–4.0
attached to alkene	=CHR	4.5–6.0
attached to aromatic ring	H–Ar	6.0–9.0
aldehyde	HCOR	9.3–10.5
✓ alcohol ③	ROH	0.5–6.0
phenol	Ar–OH	4.5–7.0
carboxylic acid	RCOOH	9.0–13.0
alkyl amine	R–NH–	1.0–5.0
aryl amine	$Ar-NH_2$	3.0–6.0
amide	RCONHR	5.0–12.0

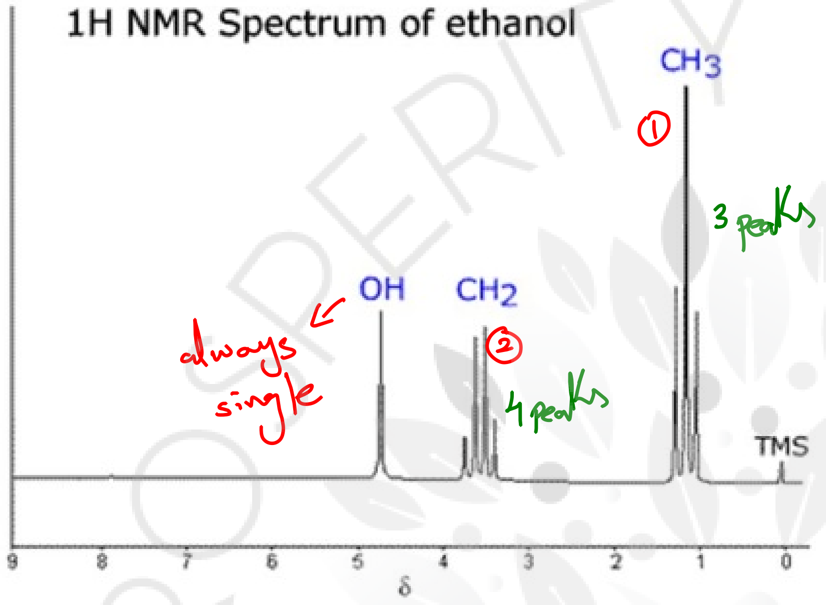
High Resolution NMR Spectrum:-

Considering ethanol again:-



neighbouring C has 3 H → so 4 peaks

neighbouring C has 2H → so 3 peaks



- In high resolution, the peaks show splitting

If there are n hydrogens on the adjacent carbon, the peaks split into n+1

OH group peak never splits or causes splitting

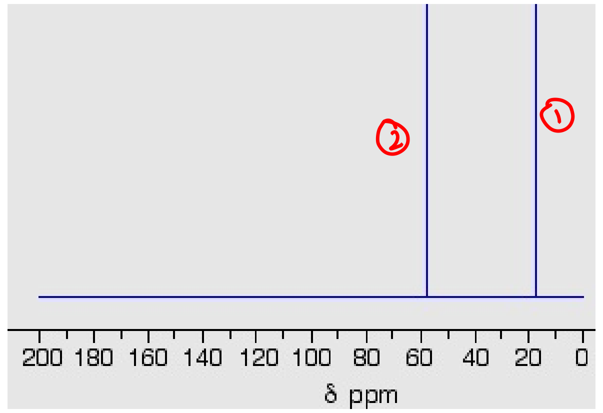
Carbon - 13 NMR :-

- ^{12}C don't absorb radio waves but 1.1% Carbon atoms in any sample are C-13 and they absorb radio waves.

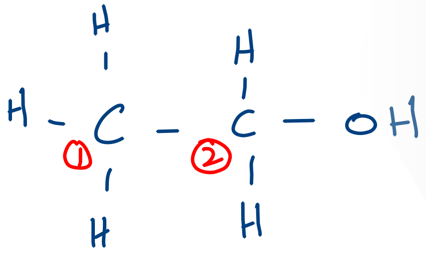
- The number of peaks = number of different Carbon environments.

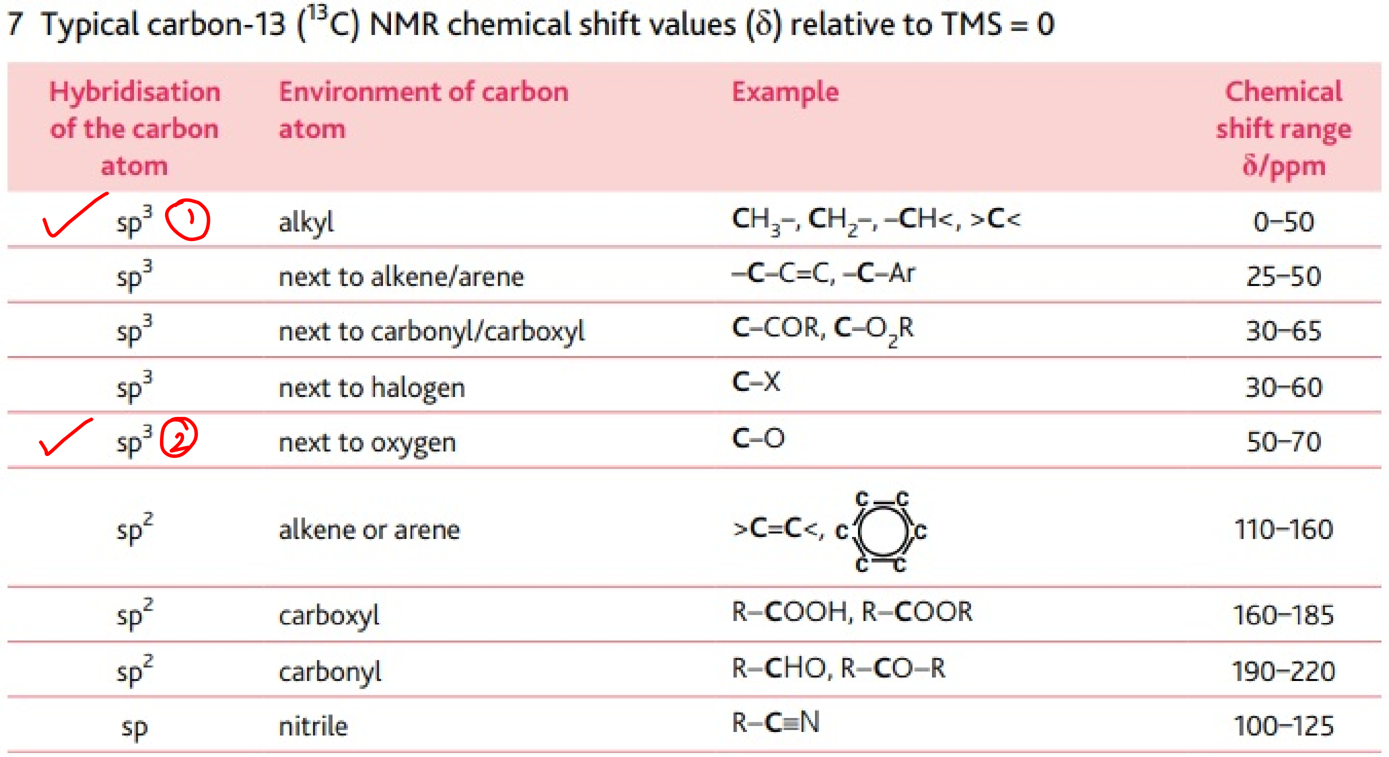
- Nothing else :)

C-13 NMR of ethanol →



- 2 peaks = 2 C environments





7 Typical carbon-13 (^{13}C) NMR chemical shift values (δ) relative to TMS = 0

Hybridisation of the carbon atom	Environment of carbon atom	Example	Chemical shift range δ/ppm
✓ sp^3 ①	alkyl	CH_3–, CH_2–, –CH<, >C<	0–50
sp^3	next to alkene/arene	–**C**–C=C, –**C**–Ar	25–50
sp^3	next to carbonyl/carboxyl	**C**–COR, **C**–O_2R	30–65
sp^3	next to halogen	**C**–X	30–60
✓ sp^3 ②	next to oxygen	**C**–O	50–70
sp^2	alkene or arene	>**C**=**C**<,	110–160
sp^2	carboxyl	R–**C**OOH, R–**C**OOR	160–185
sp^2	carbonyl	R–**C**HO, R–**C**O–R	190–220
sp	nitrile	R–**C**≡N	100–125

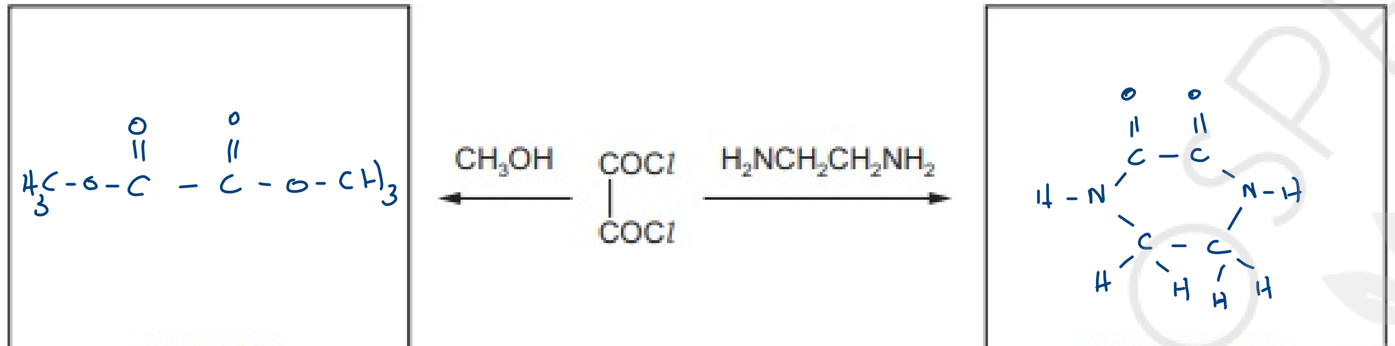
(b) Ethanedioic acid can be converted into ethanedioyl chloride:

$$HO_2CCO_2H \rightarrow ClOCCOCl$$

(i) State a suitable reagent for this reaction.

PCl_5 [1]

(ii) For the reactions of ethanedioyl chloride below, suggest the structures of compounds **J** and **K** and draw them in the boxes.



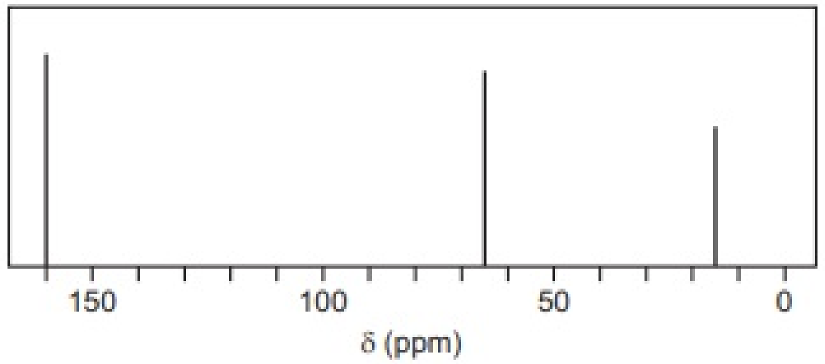
J ($C_4H_6O_4$)

K ($C_4H_6N_2O_2$)

[2]

(c) When ethanedioyl chloride is reacted with silver ethanedioate, AgO_2CCO_2Ag, in ethoxyethane at –30 °C, an oxide of carbon, **L**, is formed. The molecule of **L** has no overall dipole and has molecular formula C_4O_6.

The carbon-13 NMR spectrum of a solution of **L** in ethoxyethane, $CH_3CH_2OCH_2CH_3$, is shown below.



(i) Use the *Data Booklet* to state in the boxes below the δ values for the peaks in the spectrum which are due to the carbon atoms in ethoxyethane.

	② CH_3	① CH_2	O	① CH_2	② CH_3
δ values	15	65		65	15

[2]

(ii) Explain what the rest of the carbon-13 NMR spectrum indicates about the structure of **L**.

Only one type of environment in L [1]

(d) When pure **L** is reacted with an excess of CH_3OH, a mixture of three compounds is formed.

L (C_4O_6)	and	CH_3OH	→	**M** ($C_2H_2O_4$)	and	**N** ($C_3H_4O_4$)	and	**O** ($C_4H_6O_4$)
				carboxylic acid		ester		ester

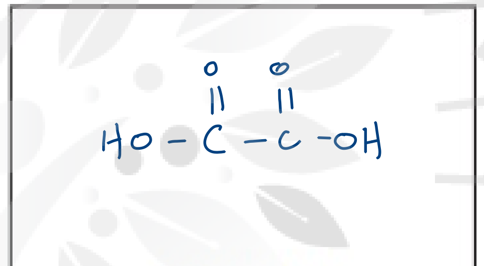
M is formed as one of the products when either **N** or **O** is heated with aqueous acid.

The table gives information of the peaks recorded in the carbon-13 NMR spectra of **M**, **N** and **O**.

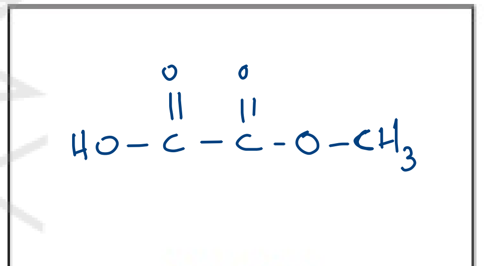
compound	peaks recorded in carbon-13 NMR spectrum
M	δ 162 COO
N	δ 53 δ 160 δ 162
O	δ 53 δ 160

53 = C next to C=O
C next to O
160/162 = COO

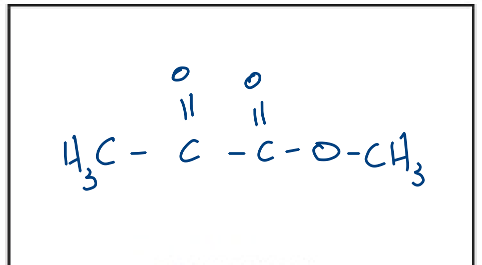
(i) Suggest the structures of **M**, **N** and **O**.



M, ($C_2H_2O_4$)



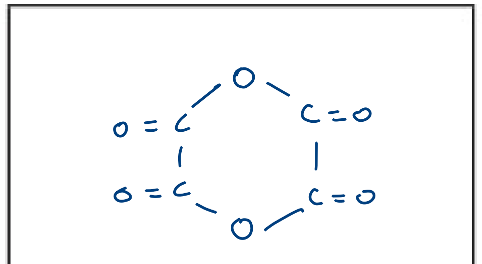
N, ($C_3H_4O_4$)



O, ($C_4H_6O_4$)

[3]

(ii) Suggest a structure for **L** that fits all the data given in **(c)** and **(d)**.



L, (C_4O_6)

[1]

8 Compound **F** is a carboxylic acid.

(a) Compound **F** contains 31.4% oxygen by mass and its mass spectrum has a molecular ion peak at $m/e = 102$.

M peak

Use all of this information to show that the molecular formula of compound **F** is $C_5H_{10}O_2$.
Show all your working.

$$\frac{31.4}{100} \times 102 = 32.028 \rightarrow \text{so } 2 \text{ O atoms}$$

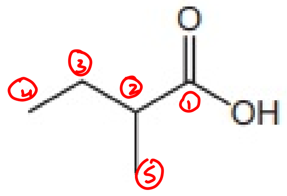
$$102 - 32 = 70 - \underset{\substack{\downarrow \\ 5C}}{5(12)} = 10 \rightarrow \text{Hydrogen}$$

[1]

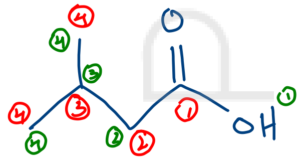
(b) There are **four** possible structural isomers of $C_5H_{10}O_2$ that are carboxylic acids.

(i) The first isomer has been drawn.

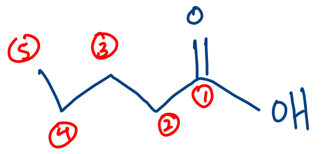
Draw the skeletal formulae of the three **other** structural isomers.



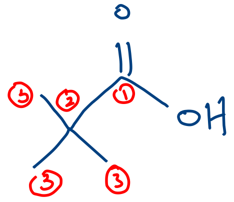
isomer 1



isomer 2



isomer 3



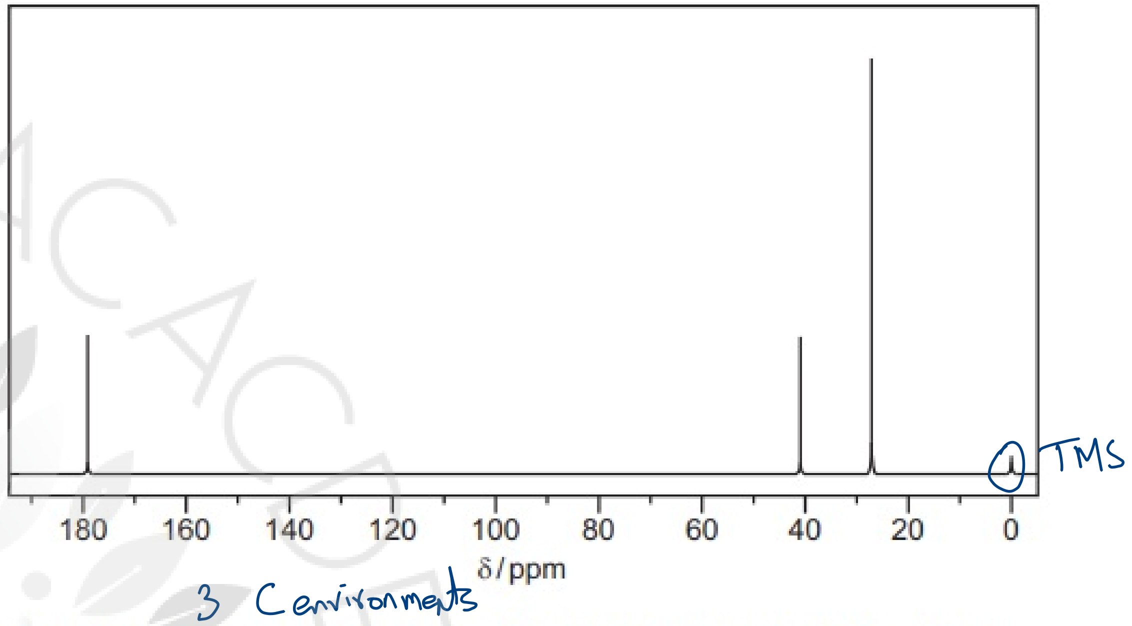
isomer 4

[2]

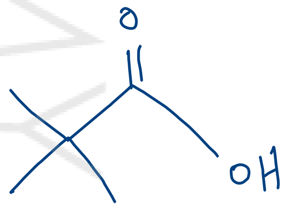
(ii) State the systematic name of isomer 1.

2-methyl butanoic acid [1]

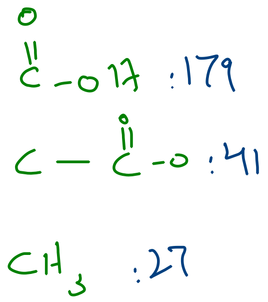
(c) **F** is one of the four structural isomers in **(b)(i)**. A carbon-13 NMR spectrum of **F** is shown.



(i) Use the spectrum to identify isomer **F**. Draw its structure in the box below.



F



$$\overset{O}{\overset{\|}{C}}-OH \ : 179$$

$$C - \overset{O}{\overset{\|}{C}}-O \ : 41$$

$$CH_3 \ : 27$$

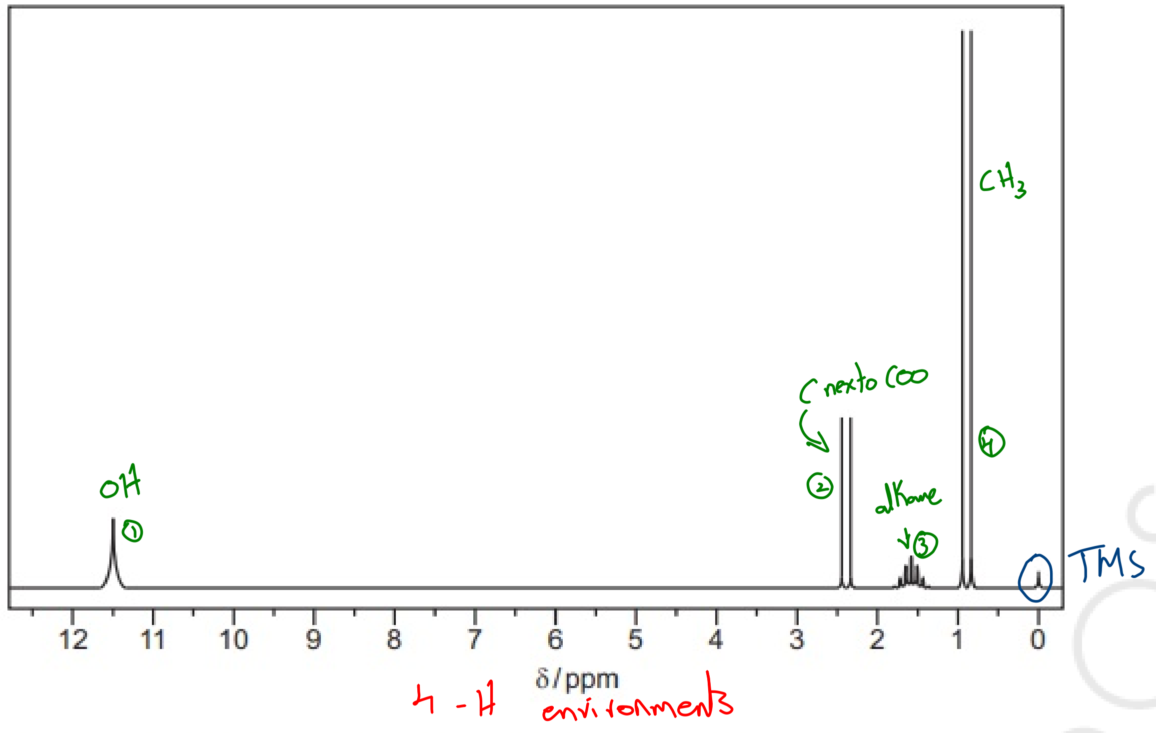
[1]

(ii) Use the *Data Booklet* and your knowledge of carbon-13 NMR spectroscopy to identify the environments and hybridisations of the carbon atoms responsible for each of the three absorptions.

δ / ppm	environment of the carbon atom	hybridisation of the carbon atom
27	alkyl (CH_3-)	sp^3
41	next to carboxyl ($C-COOR$)	sp^3
179	carboxyl ($R-COO$)	sp^2

[2]

(d) **G** is another of the four structural isomers in **(b)(i)**. The proton NMR spectrum of **G** is shown.



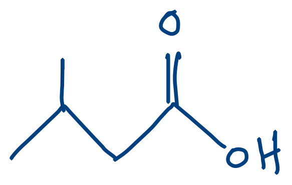
(i) Use the *Data Booklet* and the spectrum to complete the table below.

The actual chemical shifts for the four absorptions in **G** and the splitting pattern at δ = 1.6 ppm have been added for you.

δ / ppm	type of proton	number of protons	splitting pattern
0.9	alkane (CH_3)	6	doublet
1.6	alkane (CH)	1	multiplet
2.4	alkyl next to C=O	2	doublet
11.5	alcohol (OH)	1	singlet

[4]

(ii) Deduce which isomer is **G** and draw its structure in the box.



G

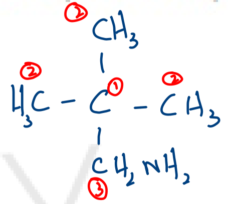
[1]

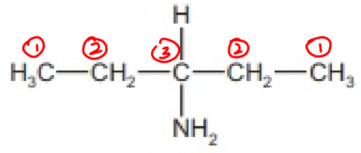
(e) Name or give the formula of a suitable solvent for obtaining a proton NMR spectrum.

$CDCl_3$ [1]

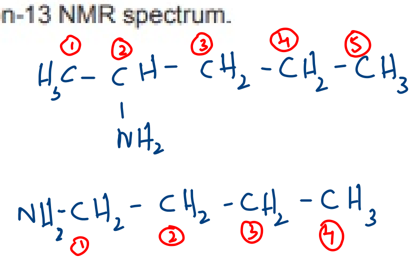
[Total: 13]

(c) Compound **H** is a primary amine which has three peaks in its carbon-13 NMR spectrum.



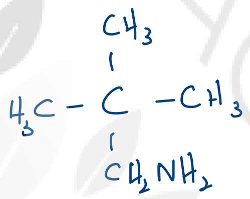


compound **H**



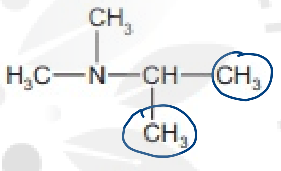
(i) An isomer of **H** is another primary amine **J** which also has three peaks in its carbon-13 NMR spectrum.

Use this information to suggest the structure of **J**.



[1]

(ii) Another isomer of **H** is the tertiary amine **K**. It has three peaks in its proton NMR spectrum. One of the peaks is a doublet.



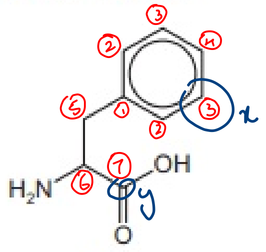
K

Circle the protons responsible for the doublet. [1]

[Total: 12]

(e) Use the *Data Booklet* to help you answer this question.

The carbon-13 NMR spectrum of **K** was recorded.



K

(i) State how many different carbon environments are present in **K**.

7 [1]

(ii) The chemical shifts, δ, due to two of the carbon atoms x and y present in **K** are given in the table.

carbon atom	δ / ppm
x	130
y	170

On the structure of **K**, circle **and** label **two** carbon atoms which could correspond to x and y.

[1]

5 Compound **F** contains the elements carbon, hydrogen and oxygen only. All carbon-carbon bonds in **F** are single bonds. The structure of **F** was analysed by mass spectrometry and infra-red and NMR spectroscopy.

(a) The mass spectrum shows that the m/e value for the M peak is 90.

The ratio of the heights of the M and M+1 peaks is 22.1 : 0.7.

(i) Use the ratio of the heights of the M and M+1 peaks to calculate the number of carbon atoms in a molecule of **F**.

22.1 : 0.7
100 : 1.1n

n = 2.88

number of carbon atoms = 3 [2]

(ii) Suggest the molecular formula of **F**.

90 - 3(12) = 54
54 - 3(16) = 6

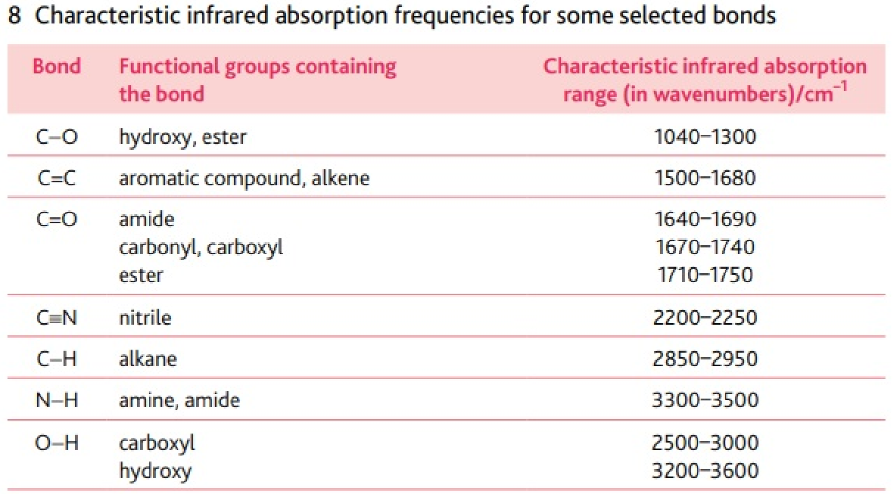
molecular formula = $C_3H_6O_3$ [1]

(b) The infra-red spectrum of **F** was obtained.

Use the *Data Booklet* and your knowledge of infra-red spectroscopy to identify the type of bond and the functional group responsible for these **three** absorptions.

absorption / cm^{-1}	appearance of the peak	type of bond	functional group
3350	broad and strong	O-H	alcohol
2680	very broad and strong	O-H	carboxyl
1725	strong	C=O	carboxyl

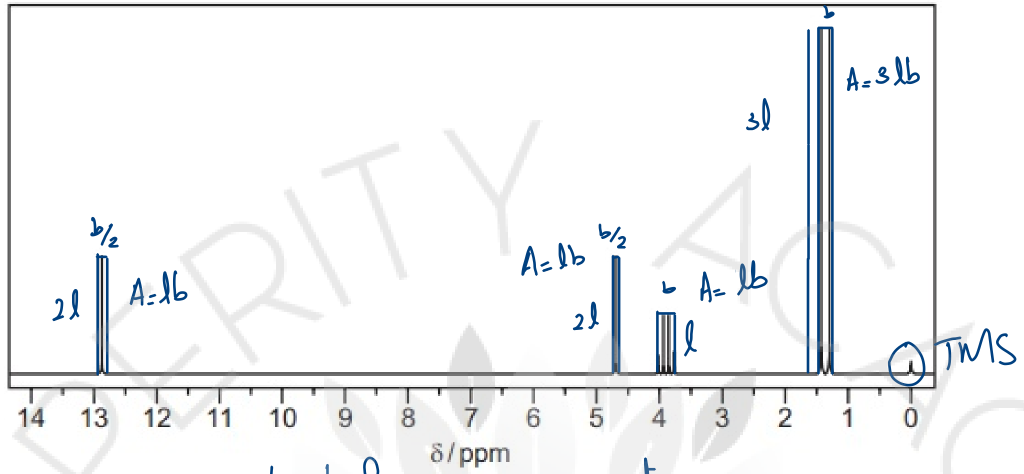
[2]



8 Characteristic infrared absorption frequencies for some selected bonds

Bond	Functional groups containing the bond	Characteristic infrared absorption range (in wavenumbers)/cm^{-1}
C–O	hydroxy, ester	1040–1300
C=C	aromatic compound, alkene	1500–1680
C=O	amide carbonyl, carboxyl ester	1640–1690 1670–1740 1710–1750
C≡N	nitrile	2200–2250
C–H	alkane	2850–2950
N–H	amine, amide	3300–3500
O–H	carboxyl hydroxy	2500–3000 3200–3600

(c) **F** was dissolved in deuterated trichloromethane, $CDCl_3$, and the proton NMR spectrum of this solution obtained.



4- hydrogen environments

(i) Use the *Data Booklet* and your answer to **(a)(ii)** to complete Table 1 for the proton NMR spectrum of **F**.
The actual chemical shifts for the four absorptions in **F** have been added for you.

Table 1

δ / ppm	type of proton	relative peak area
1.4	alKane	3
3.9	alKyl next to electronegative element	1
4.7	Alcohol	1
12.9	Carboxylic	1

[4]

(ii) Describe and explain the splitting pattern for the absorption at δ = 1.4.

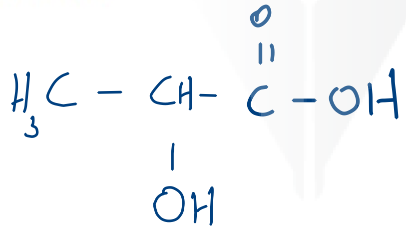
it is a doublet, the neighbouring C atom must have a single H atom [1]

(iii) **F** was dissolved in D_2O and the proton NMR spectrum of this new solution obtained.
Two of the absorptions in Table 1 were not present in this spectrum.

Which absorptions were **not** present?

4.7 and 12.9 [1]

(iv) Suggest the structure of **F**.

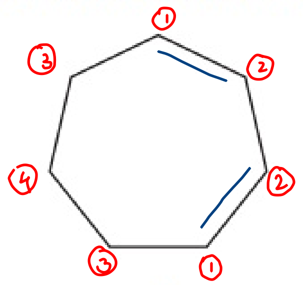


$H_3C-CH(OH)-C(=O)-OH$

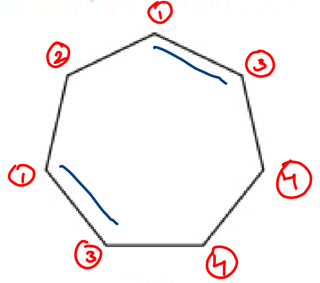
[1]

(d) Molecules of cycloheptadiene, C_7H_{10}, consist of a seven-membered ring with two carbon-carbon double bonds.

(i) Complete the skeletal formulae of two isomers of cycloheptadiene.



P



Q

[1]

The isomers **P** and **Q** were analysed using carbon-13 NMR spectroscopy.

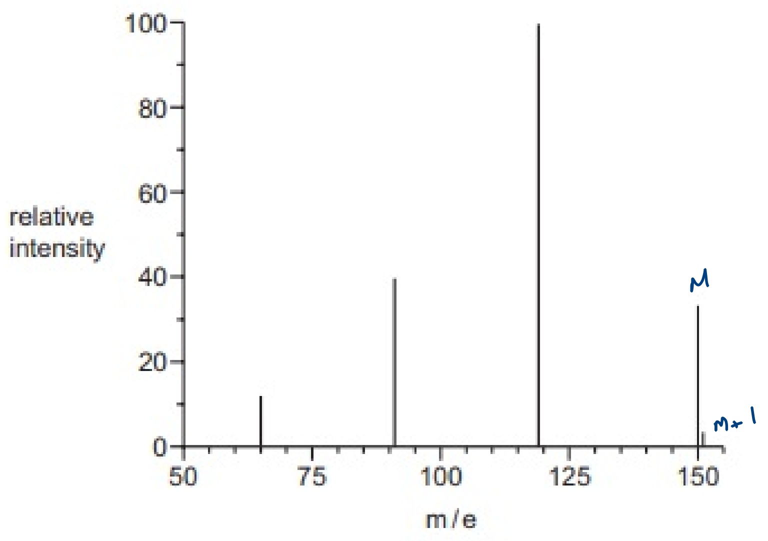
(ii) Predict the number of peaks that will be seen in the carbon-13 NMR spectra of **P** and **Q**.

isomer	number of peaks
P	4
Q	4

[2]

9 This question is about compound **T**, $C_xH_yO_2$.

(a) Part of the mass spectrum of **T** is shown.
The peak heights of the M and M+1 peaks are 33.9 and 3.4 respectively.



(i) Calculate x, the number of carbon atoms present in **T**.

$100 : 1.1n$

$33.9 : 3.4$

$n = 9$

x = 9 [2]

(ii) Deduce the molecular formula of **T**.

$C_9H_{10}O_2$ [1]

(iii) The mass spectrum has a peak at m / e = 119. $150 - 119 = 31 \rightarrow CH_3O$

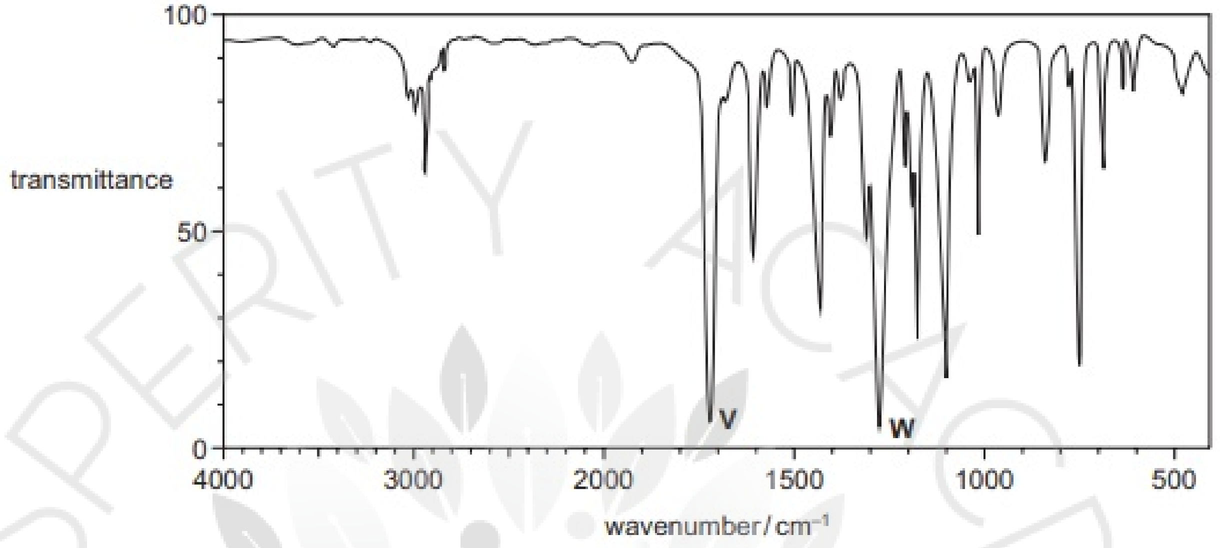
Identify the fragment lost from **T** to produce this peak.

CH_3O [1]

$150 - \overset{\uparrow C}{9}(12) = 42$

$42 - \underset{\downarrow O}{2}(16) = 10 \rightarrow H$

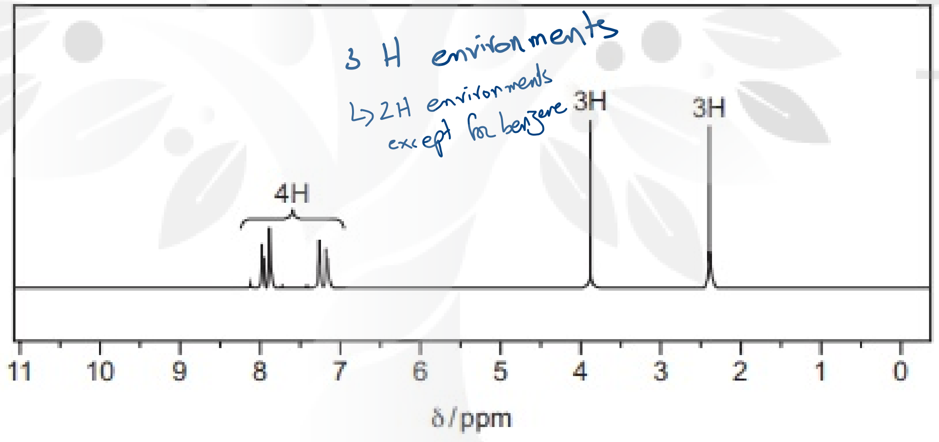
(b) The infra-red spectrum of **T** is shown.



Identify the type of bond responsible for each of the peaks **V** and **W**.
Use the *Data Booklet* to help you.

V $C=O$ **W** $C-O$ [1]

(c) The proton NMR spectrum of T in $CDCl_3$ is shown.



(i) Complete the table for the proton NMR spectrum of **T**.
Use the *Data Booklet* to help you.

δ / ppm	type of proton
3.9	alkyl next to electronegative element
7.2–7.9	H attached to aromatic ring

[1]

(ii) The peak at δ = 2.4 ppm is due to a proton attached to a saturated carbon atom.

State the **two** possible types of proton.

1. alkyl next to aromatic ring
2. alkyl next to C=O

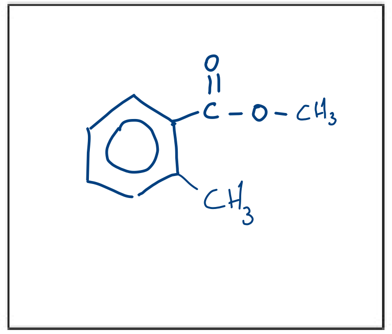
[1]

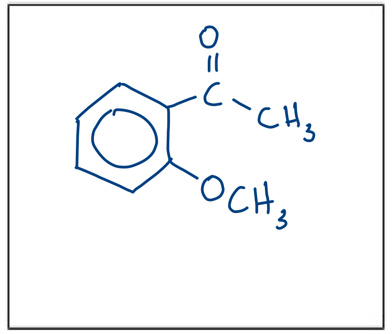
(iii) Adding D_2O to **T** does **not** change its proton NMR spectrum.

What does this tell you about the functional groups present in **T**?

it does not have OH or NH [1]

(d) Use the information to draw **two** possible structures of **T** which are <u>functional group isomers</u> of each other.

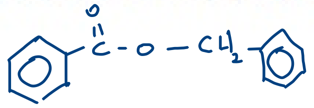




[2]

9 **(a)** Two molecules of compound **F** react together under suitable conditions to form compound **G**.
Some information about compounds **F** and **G** is given.

- The mass spectrum of **F** has a peak due to the molecular ion at m/e = 106, and a peak at m/e = 107 with an abundance 8% of the 106 peak.
- The mass spectrum of **G** has a peak due to the molecular ion at m/e = 212, and major peaks at m/e = 91 and m/e = 105.
- Both **F** and **G** contain oxygen and are neutral compounds which are insoluble in water.
- The ¹H NMR spectrum of **F** includes a singlet peak at δ = 10.0 due to one proton. aldehyde
- The ¹H NMR spectrum of **G** includes a singlet peak at δ = 5.1 due to two protons.
- When **G** is heated with dilute sulfuric acid, benzoic acid, $C_6H_5CO_2H$, and phenylmethanol, $C_6H_5CH_2OH$, are produced.



Use this information to answer **(i)**–**(vi)**.

(i) Explain how the mass spectrum of **F** shows that a molecule of **F** contains seven carbon atoms. Show your working.

100 : 1.1n
100 : 8

n = 7.27 ≈ 7C

[1]

(ii) Suggest the molecular formula of the fragment of **G** at m/e = 91.

$C_7H_7^+$ [1]

(iii) Suggest the molecular formulae of **F** and **G**.

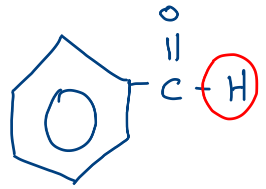
F C_7H_6O

G $C_{14}H_{12}O_2$

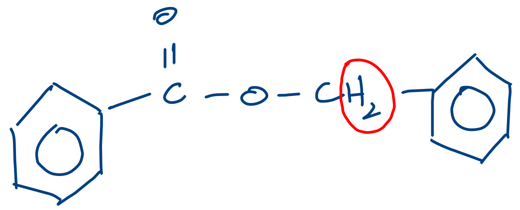
[2]

(iv) Suggest structures for compounds **F** and **G**.

F



G



[2]

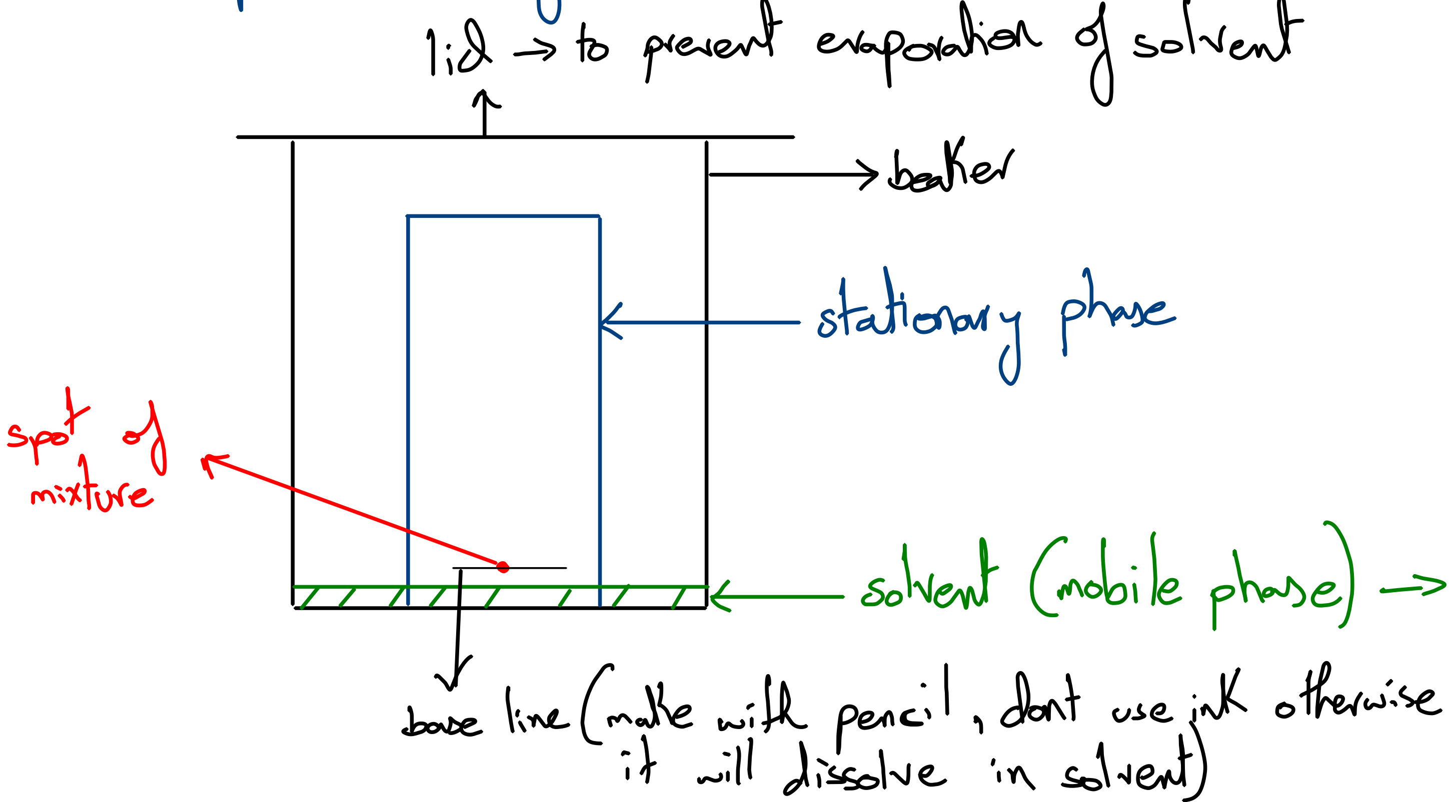
(v) On the structures you have drawn in **(iv)**, circle the protons responsible for the ¹H NMR peaks at δ = 10.0 in **F** and δ = 5.1 in **G**. [1]

Chromatography:-

- Technique used to separate a mixture of substances into their components
- Chromatography has a stationary phase → a solid or liquid that does not move
- And it also has a mobile phase → a liquid or gas that moves and carries the components
- The mobile phase moves through the stationary phase and the components are separated due to some properties.

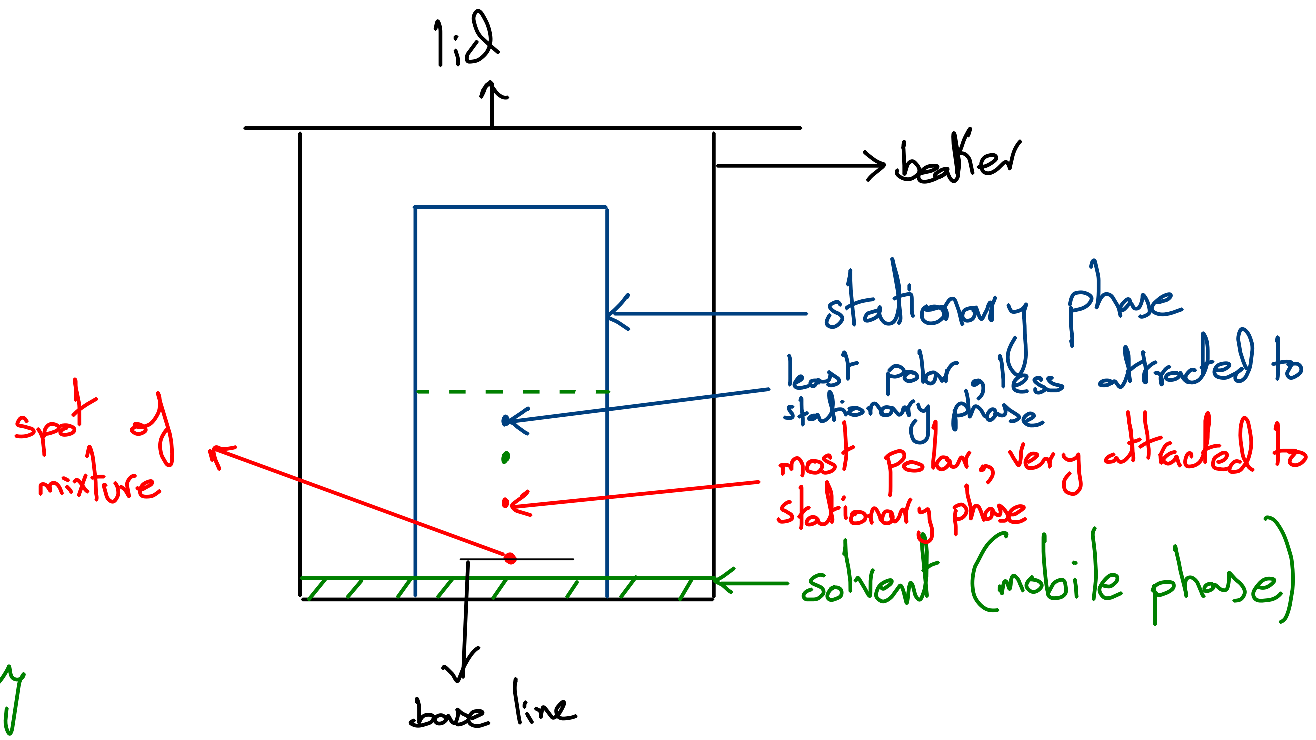
1) Thin Layer Chromatography (TLC):-

- stationary phase:- Thin layer of aluminium or silica gel → polar Al_2O_3 or SiO_2
- mobile phase:- any solvent that can dissolve the mixture → non polar



→ Keep below spot/base line otherwise it will dissolve spot of mixture completely

After some time →

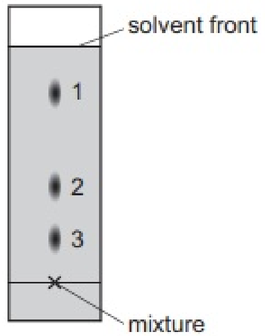


Retention/Retardation factor
↑
- Each component has a specific R_f value → a mixture is separated using TLC and then the R_f value is measured and compared to standardized R_f values to identify component.

$$R_f = \frac{\text{distance travelled by component}}{\text{distance travelled by solvent}}$$

- Doing TLC for amino acids requires Ninhydrin as locating agent to make them visible.

(b) A mixture of three different compounds, **J**, **K** and **L**, was analysed by thin layer chromatography using a polar stationary phase and a non-polar mobile phase. The three compounds all have similar molecular masses. The resulting chromatogram is shown.



(i) Identify which spot corresponds to each compound.

compound	spot
J CH_3COCO_2H	2
K HO_2CCO_2H	3
L $CH_3CH_2COCH_2CH_3$	1

[1]

(ii) Explain your answers to **(b)(i)**.

Compound K is most polar, J is less polar than K and L is non polar. Polar solutes will form stronger attractive forces to stationary polar phase

[1]

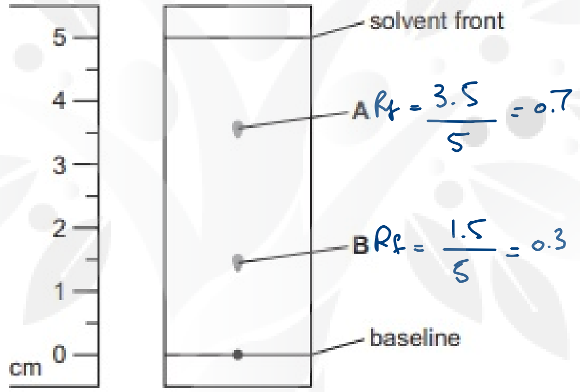
(iii) What is meant by the term *R_f value*?

$$R_f = \frac{\text{distance moved by compound}}{\text{distance moved by solvent}}$$

[1]

7 **(a)** Amino acids can be separated by thin-layer chromatography. A mixture of amino acids is analysed using this technique.

The chromatogram obtained is shown, drawn to scale. The table shows some R_f values for different amino acids in the solvent used.



A $R_f = \frac{3.5}{5} = 0.7$

B $R_f = \frac{1.5}{5} = 0.3$

amino acid	R_f value
alanine	0.40
B glutamic acid	0.29
leucine A	0.71
valine	0.61

(i) Use the chromatogram and the R_f values to deduce the amino acid responsible for spot **A** and spot **B**.

amino acid responsible for spot **A** leucine

amino acid responsible for spot **B** glutamic acid

[1]

(ii) A second chromatogram of the same mixture is taken using a **more polar** solvent. → attract amino acids strongly

Predict the effect on the R_f values of the amino acids. Explain your reasoning.

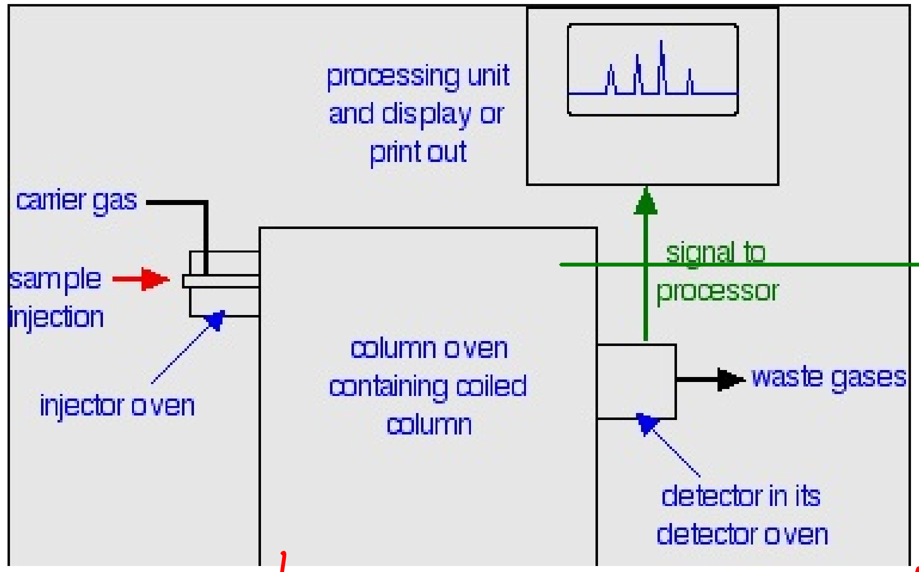
R_f values will be greater as amino acids will make stronger bonds to polar solvent and therefore travel more.

[1]

$$R_f = \frac{\text{distance moved by component}\uparrow}{\text{distance moved by solvent}}$$

2) Gas Liquid Chromatography (GLC):-

- stationary phase: high boiling point liquid adsorbed onto solid
- mobile phase: Gas like Helium



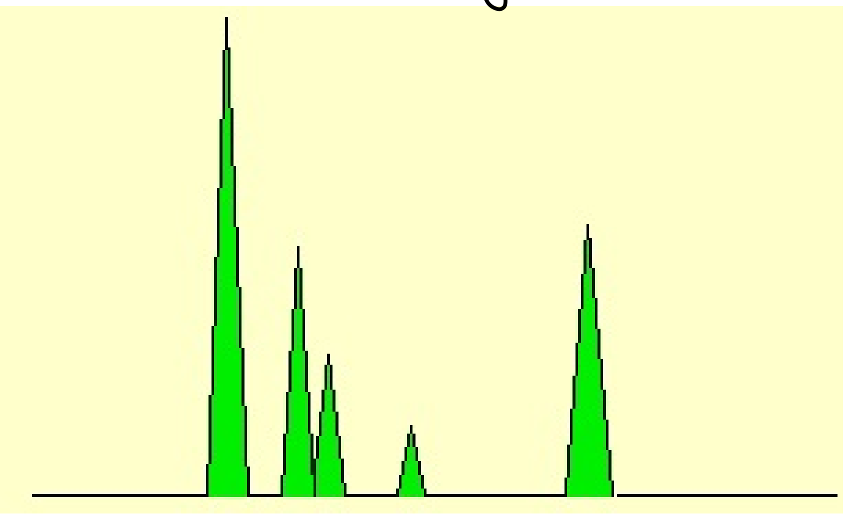
→ sample and gas move through coils of tube coated with high boiling point liquid

↑ solid stationary phase

↓ liquid stationary phase

↳ oven is hot enough to form all sample to gas

Gas liquid Chromatogram:-



- Area under graph represents amount of each compound

The components are separated by:

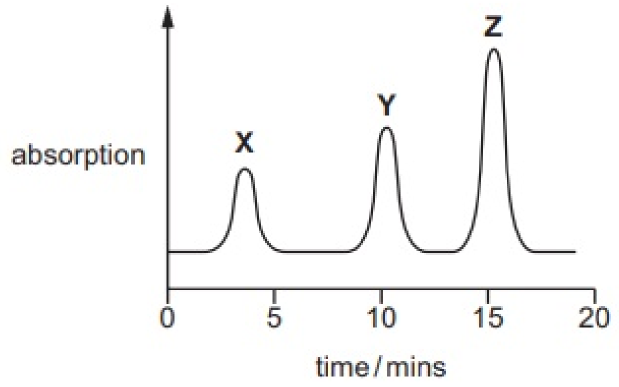
1) Different boiling points:- High boiling point components might condense into liquid in the tubes and take longer to travel

2) Depending on the polarity of the stationary phase, some components may attract it strongly and take longer to travel.

Different components can be identified by standardized R_t (Retention times). Retention time is the time taken by a particular component to produce a maximum peak at the display from the time when it was injected.

1 **(a)** An aldehyde, an alkane and a carboxylic acid, all of similar volatility, are mixed together. The mixture is then analysed in a gas chromatograph.

The gas chromatogram produced is shown.



The separation of the compounds depends on their relative solubilities in the stationary phase. The stationary phase is a liquid alcohol. polar

(i) Complete the table to suggest which compound in the mixture is responsible for each peak **X**, **Y** and **Z**. Explain your answer by reference to the intermolecular forces of the compounds.

peak	organic compound	explanation
X	Alkane	they have temporary dipoles only
Y	aldehyde	they have temporary and permanent dipoles
Z	Carboxylic acid	they have hydrogen bonding

[2]

(ii) A student calculates the areas underneath the three peaks in the chromatogram.

peak	**X**	**Y**	**Z**
area / mm²	19	32	47

The area underneath each peak is proportional to the mass of the respective compound.

Calculate the percentage **by mass** in the original mixture of the compound responsible for peak **Z**.

$$\frac{47}{47+32+19} \times 100 =$$

% of mixture responsible for peak **Z** = 48% [1]

(b) (i) The mass spectrum of a halogenoalkane containing one chlorine atom **or** bromine atom will show an additional peak at M+2.

State the isotopes of chlorine and bromine responsible for M+2 peaks.

chlorine ^{37}Cl bromine ^{81}Br

[1]

(ii) The mass spectrum of bromochloromethane, CH_2BrCl, has a molecular ion peak, M, at an *m*/*e* value of 128. It also has M+2 and M+4 peaks.

Suggest the identity of the molecular ions that give rise to these peaks.

M peak $[CH_2{}^{79}Br\,{}^{35}Cl]^+$

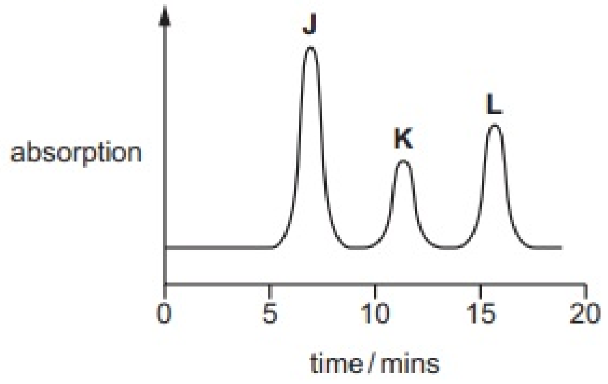
M+2 peak $[CH_2{}^{81}Br\,{}^{35}Cl]^+$

M+4 peak $[CH_2{}^{81}Br\,{}^{37}Cl]^+$

[2]

1 **(a)** An alkene, a carboxylic acid and a ketone, all of similar volatility, are mixed together. The mixture is then analysed by gas chromatography.

The gas chromatogram produced is shown.



The separation of the three compounds depends on their relative solubilities in the liquid stationary phase. The liquid stationary phase is an alkane. non polar

(i) Complete the table to suggest which compound in the mixture is responsible for each peak **J**, **K** and **L**. Explain your answer by reference to the intermolecular forces of each compound.

peak	organic compound	explanation
J	carboxylic acid	most polar
K	Ketone	polarity between J and L
L	alkene	most non polar

[2]

A student calculates the areas underneath the three peaks in the chromatogram.

peak	**J**	**K**	**L**
area / mm^2	46	18	28

(ii) The area underneath each peak is proportional to the mass of the respective compound.

Calculate the percentage **by mass** in the original mixture of the compound responsible for peak **K**.

$$\frac{18}{28+18+46} \times 100 = 19.6\%$$

% of mixture responsible for peak **K** = 19.6% [1]