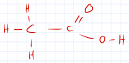
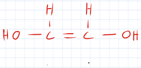
Analytical Chemistry





$C_2H_4O_2$

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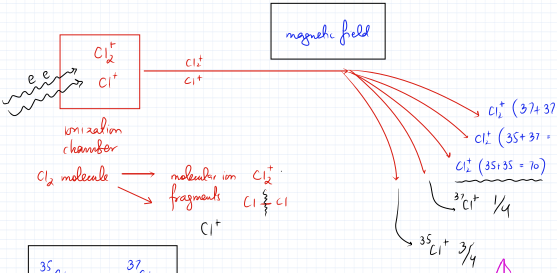
Fahad H. Ahmad

mass spectroscopy

number of Carbon atoms
M_r / molecular mass
some information about structure
number of Cl / Br atom


Cl_2^+
Cl^+
e
e
ionization chamber
magnetic field
Cl_2^+
Cl^+
Cl_2^+ (37+37 = 74)
Cl_2^+ (35+37 = 72)
Cl_2^+ (35+35 = 70)
$^{37}Cl^+$ 1/4
$^{35}Cl^+$ 3/4

deflection α $\frac{1}{mass}$

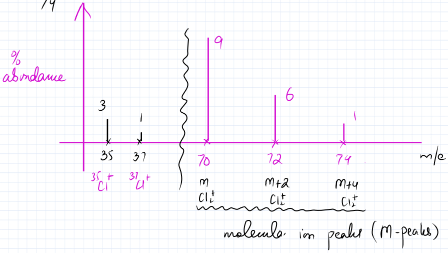
^{37}Cl and ^{37}Cl $\frac{1}{4} \times \frac{1}{4} = \boxed{1/16}$

$(^{35}Cl$ and $^{37}Cl)$ or $(^{37}Cl$ and $^{35}Cl) = \left(\frac{3}{4} \times \frac{1}{4}\right) + \left(\frac{1}{4} \times \frac{3}{4}\right) = \boxed{\frac{6}{16}}$

^{35}Cl and ^{35}Cl = $\frac{3}{4} \times \frac{3}{4} = \boxed{\frac{9}{16}}$

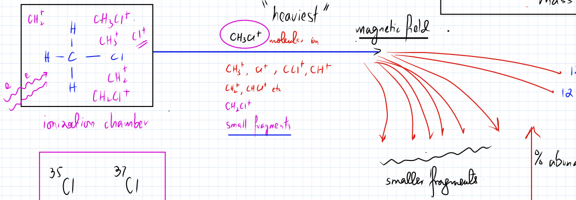
Cl_2 molecule → molecular ion Cl_2^+
→ fragments $Cl \wr Cl$
Cl^+

^{35}Cl	^{37}Cl
75%	25%
3/4	1/4



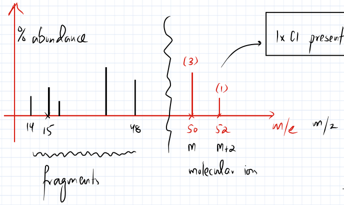
- if a molecule has 1 x Cl
  M : M+2
  3 : 1
- if a molecule has 2 x Cl
  M : M+2 : M+4 → tentatively
  9 : 6 : 1

deflection α $\frac{1}{mass}$


CH_2^+
CH_3Cl^+
CH_3^+
Cl^+
H
H – C — Cl
H
CH_2^+
CH_2Cl^+
e
e
ionization chamber
"heaviest"
CH_3Cl^+
molecular ion
magnetic field
CH_3^+, Cl^+, CCl^+, CH^+
CH_2^+, $CHCl^+$ etc
CH_2Cl^+
small fragments
smaller fragments

"heaviest"
CH_3Cl^+ molecular ion
12 + 1 x 3 + 37 = 52 1/4 M+2
12 + 1 x 3 + 35 = 50 3/4 M

^{35}Cl	^{37}Cl
75%	25%
3/4	1/4



1x Cl present

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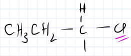
2 x Cl present



$CH_3CH_2-\overset{H}{\underset{Cl}{C}}-Cl$

ionization

molecular ion

$CH_3CH_2CHCl_2^+$

magnetic field

CH_3^+, CH_2^+, Cl^+

$CH_3CH_2^+$, C^+, $CHCl_2^+$

etc

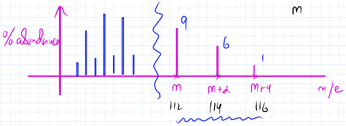
fragments

$CH_3CH_2CHCl_2^+$ molecular ion

42 + $\underline{37}$+$\underline{37}$ = 116 M+4 1/16 1/4 × 1/4

42 + $\underline{35}$+$\underline{37}$ = 114 M+2 6/16 (3/4 × 1/4)+(1/4 × 3/4)

42 + $\underline{35}$+$\underline{35}$ = 112 M 9/16 3/4 × 3/4



molecule has 2 × Cl

Br_2	^{79}Br	^{81}Br
	50%	50%
	1/2	1/2

e

e

Br_2

molecular ion

Br_2^+

Br^+

fragment

magnetic field

deflection ∝ $\frac{1}{mass}$

Br_2^+ (81+81=162) 1/2 × 1/2 = 1/4

Br_2^+ (79+81 = 160) (1/2 × 1/2)+(1/2 × 1/2) = 2/4

Br_2^+ (79+79 = 158) 1/2 × 1/2 = 1/4

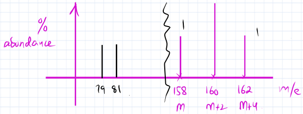
$^{81}Br^+$ 1/2

$^{79}Br^+$ 1/2

^{79}Br	^{81}Br
50%	50%
1/2	1/2

- if a molecule has 1× Br
  M : M+2
  1 : 1
- if a molecule has 2× Br
  M : M+2 : M+4
  1 : 2 : 1

tentatively



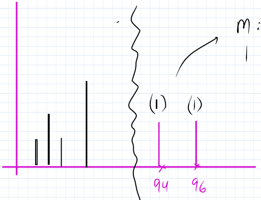
CH_3Br^+

CH_3^+ C^+

CH^+ Br^+

$CHBr^+$

	M	M+2
	12+3+$\underline{79}$	12+3+$\underline{81}$
	94	96
	1/2	1/2



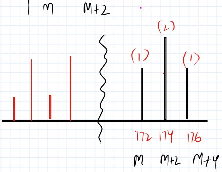
1× Br

M : M+2

1 : 1

$\boxed{CH_2Br_2^+}$

M	M+2	M+4
14+79+79	14+79+81	14+81+81
= 172	= 174	= 176
1/4	2/4	1/4
$\frac{1}{2}\times\frac{1}{2}$	$\left(\frac{1}{2}\times\frac{1}{2}\right)+\left(\frac{1}{2}\times\frac{1}{2}\right)$	$\frac{1}{2}\times\frac{1}{2}$
1/4	2/4	1/4



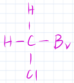
A molecule has 1 x Cl, 1 x Br

Br → 81 ½, 79 ½

Cl → 35, 37: ¾, ¼

$\boxed{\begin{array}{ccccc} M & : & M+2 & : & M+4 \\ 3 & : & 4 & : & 1 \end{array}}$

tentatively



$$\begin{array}{c} H \\ | \\ H-C-Br \\ | \\ Cl \end{array} \longrightarrow CH_2BrCl^+$$

$\boxed{\begin{array}{l} 14+\underline{79}+\underline{35} \\ 128 = M \\ \frac{1}{2}\times\frac{3}{4} = \frac{3}{8} \end{array}}$

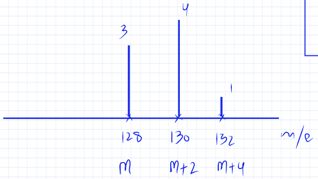
M

$\boxed{\begin{array}{l} 14+\underline{79}+\underline{37} \\ \text{or} \\ 14+\underline{81}+\underline{35} \\ 130 = M+2 \\ \left(\frac{1}{2}\times\frac{1}{4}\right)+\left(\frac{1}{2}\times\frac{3}{4}\right) \\ = \frac{4}{8} \end{array}}$

M+2

$\boxed{\begin{array}{l} 14+\underline{81}+\underline{37} \\ 132 = M+4 \\ \frac{1}{2}\times\frac{1}{4} = \frac{1}{8} \end{array}}$

M+4



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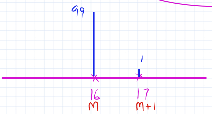
$\boxed{\begin{array}{l} \text{Number of Carbon atoms} = \frac{100}{1.1}\times\frac{M+1}{M} \\ M : M+1 \end{array}}$

M : 97 %
M+1 : 3 %

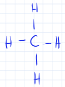
$\frac{100}{1.1}\times\frac{3}{97} = 3$

#C = $\frac{100}{1.1}\times\frac{1.5}{48.5} = 3C$

^{12}C	^{13}C
98.9 %	1.1 %



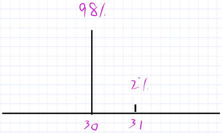
C = 1



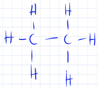
$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H \end{array}$$

M = $\underline{12}$+1+1+1+1 = 16   99%

M+1 = $\underline{13}$+1+1+1+1 = 17   1%



C = 2



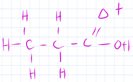
$$\begin{array}{c} H \quad H \\ | \quad\; | \\ H-C-C-H \\ | \quad\; | \\ H \quad H \end{array}$$

M = 12+12+6 = 30 $\frac{98.9}{100}\times\frac{98.9}{100} = 98\%$

M+1 = 13+12+6 = 31 $\left(\frac{98.9}{100}\times\frac{1.1}{100}\right)\times 2 = 2\%$

~~$M+2 = 13+13+6 = 32$ $\left(\frac{1.1}{100} \times \frac{1.1}{100}\right) = 0.012\%$~~

$C = 3$

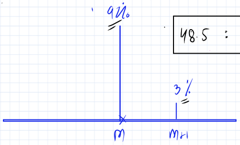


~~$M+3$ $13+13+13+32+6 = 77$~~

~~$M+2$ $13+13+12+32+6 = 76$~~

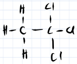
$M+1$ $13+12+12+32+6 = 75$ $\left(\frac{1.1}{100} \times \frac{98.9}{100} \times \frac{98.9}{100}\right) \times 3 = 3\%$

M $\underline{12}+\underline{12}+\underline{12}+32+6 = 74$ $\left(\frac{98.9}{100}\right)^3 = 97\%$



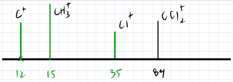
$\boxed{48.5 : 1.5}$

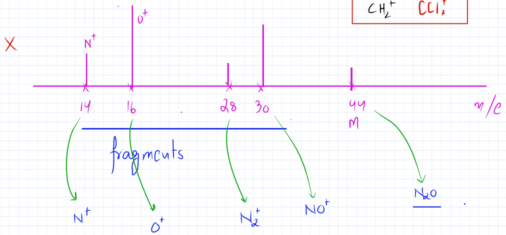
fragmentation



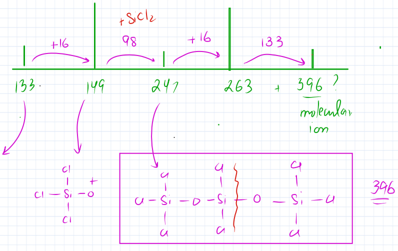
$CH_3CCl_3^+ \longrightarrow$

CH_3^+	CCl_3^+
C^+	Cl^+
CH_2^+	CCl_2^+

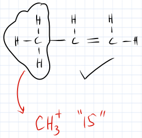


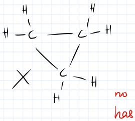


$\boxed{{}_{28}Si \quad {}_{35}Cl \quad {}_{16}O}$

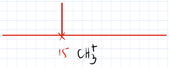


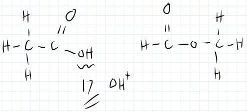
* $M = 42$ C_3H_6





no fragment that has mass of 15

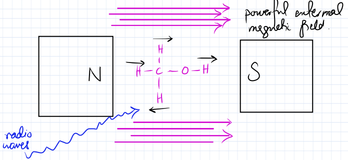


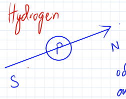


H - NMR (A2)

nuclear magnetic resonance

→ determining the chemical environment of H - protons


powerful external magnetic field
N
H
H - C - O - H
H
S
radio waves


Hydrogen
p
N
S

odd numbered nucleons

overall net magnetic dipole / spin

↑↑↓ dipoles don't cancel out

high energy state – opposing spin (magnetic dipole)

↕ ΔE

low energy state – alligned spin (magnetic dipole)

ΔE ∝ frequency (radiowaves)

only absorbs frequencies that match ΔE

even numbered nucleons

nucleons are paired

↑↓ no net magnetic dipole

$^{16}_{8}O$, $^{14}_{7}N$, $^{12}_{6}C$

not net magnetic dipole

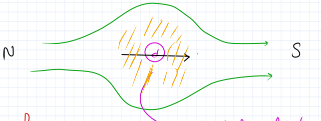
factors affecting ΔE / resonant frequency

1. External magnetic field (not important)

stronger magnetic field, more energy needed to go into opposing spin

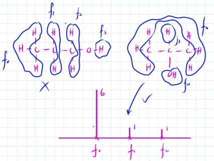
higher resonant frequency absorbed

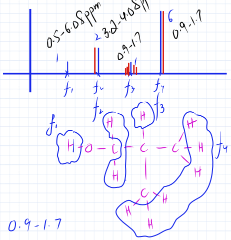
2. Chemical Environment / shielding (important)



e⁻ shield the nucleus / magnetic field gets deflected

easier to resonate, ΔE and resonant frequency changes


f₁
f₂
f₀
f₁
f₁
f₂
f₀
6
f₀
f₁
f₂


0.5-6.0 δ ppm
3.2-4.0 δ ppm
0.9-1.7
6
0.9-1.7
1
2
f₁
f₂
f₃
f₄
f₁
f₂
f₃
f₄
H - O - C - C - C

higher freq.

difficult to resonate

δ+ H — Cl f_0

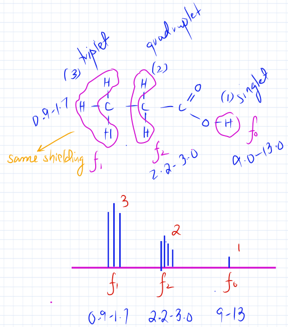
less shielded

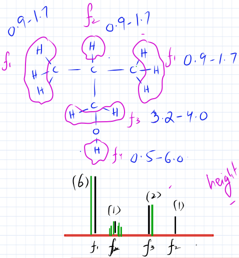
H — CH_3 f_1

more shielded

easier to resonate

lower freq

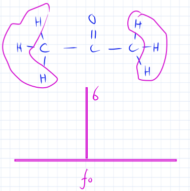

triplet
quadruplet
(3)
(2)
(1) singlet
0.9-1.7
same shielding
f₁
f₂
2.2-3.0
f₀
9.0-13.0
3
2
1
f₁
f₂
f₀
0.9-1.7
2.2-3.0
9-13


0.9-1.7
f₂ 0.9-1.7
f₁
f₁ 0.9-1.7
f₃ 3.2-4.0
f₄ 0.5-6.0
(6)
(1)
(2)
(1)
f₁
f₄
f₃
f₂

height = absorption = no of H atoms in same environment

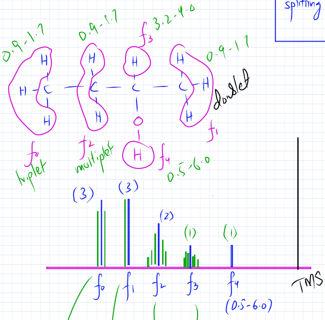
× no of chemical environments

× no of protons in the chemical environment splitting → neighboring protons



f_0

singlet
no H on neighboring carbon


0.9-1.7
0.9-1.7
f_3 3.2-4.0
0.9-1.7
doublet
f_1
f_0 triplet
f_2 multiplet
f_4 0.5-6.0
(3)
(3)
(2)
(1)
(1)
f_0
f_1
f_2
f_3
f_4
(0.5-6.0)
TMS

triplet
neighboring C has 2H

doublet
neighbor has 1×H

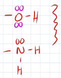
multiplet
neighbor has many H protons

singlet
neighbor has no H or O-H / NH_2

Splitting Pattern

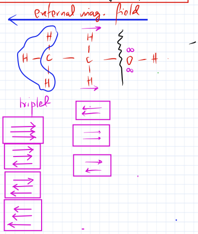
n+1 rule, if neighboring carbon has "n" protons so peak will split into n+1 peaks

neighbor C has		
	0×H	singlet
	1×H	doublet
	2×H	triplet
	3×H	quadruplet
	>3H	multiplet



are always singlets, they don't cause any splitting

external mag. field



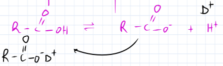
$D = {}^2_1H$

even no. nucleons, no spin/dipoles
no resonance

Heavy water $D_2O \rightleftharpoons D^+ + OD^-$

$R-O-H$ / $R-NH_2$

their protons replaced with D

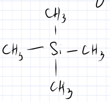


$R-C(=O)-OH \rightleftharpoons R-C(=O)-O^- + H^+$; D^+ ; $R-C(=O)-O^-D^+$

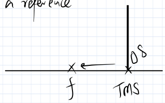
peaks disappear in D_2O

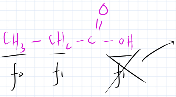
* $CDCl_3$ deutrated solvents
don't resonate, deutium $D: {}^2_1H$

* TMS tetramethyl Silane



as a reference



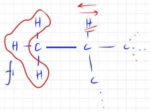

$CH_3-CH_2-C(=O)-OH$
f_0
f_1
~~f_1~~

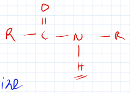
peak disappears when added to D_2O

NMR – no. of chemical environments
no. of protons in those chemical environments
no. of protons on neighboring / splitting pattern
chemical shift value → environment (databooklet)

* COOH, CHO, CONH → easy to identify using databooklet

* useful tip : C : H → benzene
1 : 1





amides are not basic
so they don't ionize
and their protons are not replaced by Deutium

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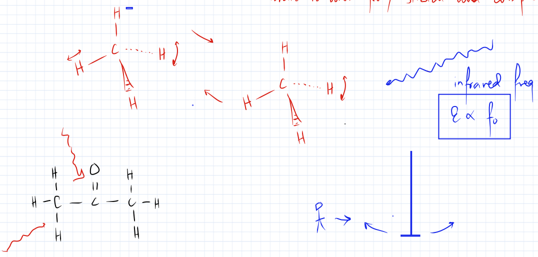
Infrared Spectroscopy (AS Chemistry)

vibrate to and fro / stretch and compressible


H
C
H
H
H
O
infrared freq.
$E \propto f_0$

bonds vibrate by absorbing a specific frequency from the infra red spectrum which is unique for each type of bond

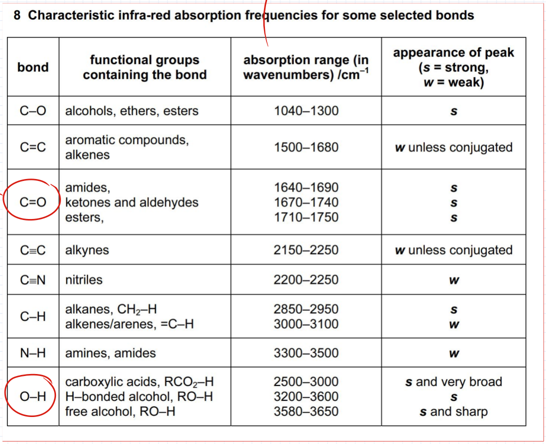
$C=O$ f_0
$C-H$ f_1
$C-C$ f_2

Usually a 1 or 2 mark question
at best you can identify 1 or 2 bonds in the molecule

$C=O$ and $O-H$ peaks are the easiest to identify.

wavenumber $= \frac{1}{\lambda} \propto$ frequency

Data Booklet

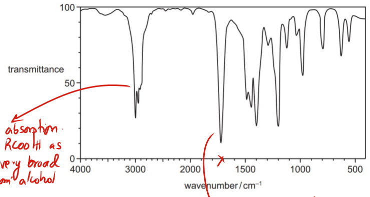


8 Characteristic infra-red absorption frequencies for some selected bonds

bond	functional groups containing the bond	absorption range (in wavenumbers) /cm^{-1}	appearance of peak (*s* = strong, *w* = weak)
C–O	alcohols, ethers, esters	1040–1300	*s*
C=C	aromatic compounds, alkenes	1500–1680	*w* unless conjugated
C=O	amides, ketones and aldehydes esters,	1640–1690 1670–1740 1710–1750	*s* *s* *s*
C≡C	alkynes	2150–2250	*w* unless conjugated
C≡N	nitriles	2200–2250	*w*
C–H	alkanes, CH_2–H alkenes/arenes, =C–H	2850–2950 3000–3100	*s* *w*
N–H	amines, amides	3300–3500	*w*
O–H	carboxylic acids, RCO_2–H H–bonded alcohol, RO–H free alcohol, RO–H	2500–3000 3200–3600 3580–3650	*s* and very broad *s* *s* and sharp

very easy to identify

The diagram shows the infra-red spectrum of Q.



not strong absorption.

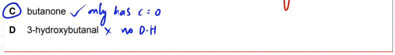
no O-H
- rule out O-H in RCOOH as it is strong and very broad
- rule out O-H from alcohol as absorption for them should be above 3200

absorption at 1700 cm^{-1} clearly indicates "C=O"

What could be Q?

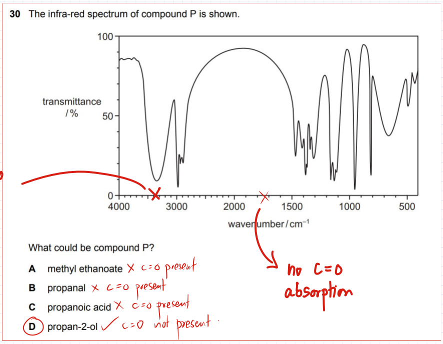
A butan-1-ol ✗ no O-H

B butanoic acid ✗ no O-H



[✓ C] butanone ✓ only has c=o

D 3-hydroxybutanal ✗ no O-H


100
transmittance / %
50
0
4000
3000
2000
1500
1000
500
wavenumber / cm^{-1}

30 The infra-red spectrum of compound P is shown.

absorption at 3200
O-H present

no C=O absorption

What could be compound P?

A methyl ethanoate ✗ c=o present

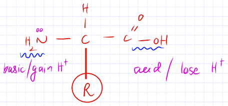
B propanal ✗ c=o present

C propanoic acid ✗ c=o present

[✓ D] propan-2-ol ✓ c=o not present.

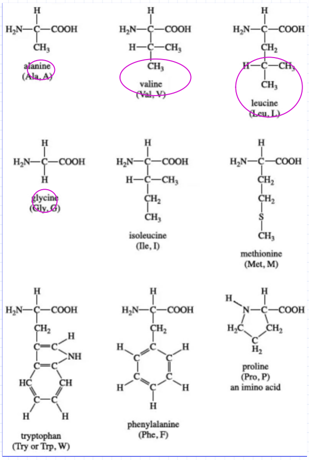
Electrophoresis

amino acid



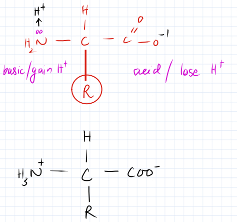
$$H_2\ddot{N}-\underset{R}{\overset{H}{C}}-C(=O)-OH$$

basic/gain H^+ acid / lose H^+


alanine (Ala, A)
valine (Val, V)
leucine (Leu, L)
glycine (Gly, G)
isoleucine (Ile, I)
methionine (Met, M)
tryptophan (Try or Trp, W)
phenylalanine (Phe, F)
proline (Pro, P) an imino acid

Zwitter ion

it has no overall charge but it has regions of both +ve and -ve charges

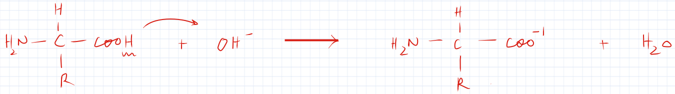


$$H^+ \rightarrow H_2\ddot{N}-\underset{R}{\overset{H}{C}}-C(=O)-O^{-1}$$

basic/gain H^+ acid / lose H^+

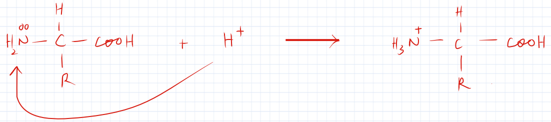
$$H_3\overset{+}{N}-\underset{R}{\overset{H}{C}}-COO^-$$

amino acid behaves as acid in basic solution



$$H_2N-\underset{R}{\overset{H}{C}}-COOH + OH^- \longrightarrow H_2N-\underset{R}{\overset{H}{C}}-COO^{-1} + H_2O$$

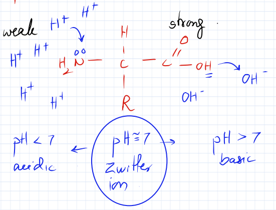
amino acid behaves as base in acidic solution



$$H_2\ddot{N}-\underset{R}{\overset{H}{C}}-COOH + H^+ \longrightarrow H_3\overset{+}{N}-\underset{R}{\overset{H}{C}}-COOH$$

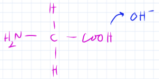
Isoelectric Point

the pH at which zwitter ions are formed


weak
H^+
strong
$H_2\ddot{N}-\underset{R}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-OH$
OH^-
pH < 7
acidic
pH ≅ 7
Zwitter ion
pH > 7
basic

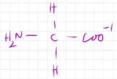
isoelectric point is around/near pH = 7. varies because of the difference in strength of acid and base group.

Glycine isoelectric pH = 6



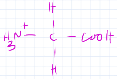
$$H_2N-\underset{H}{\overset{H}{C}}-COOH \quad \curvearrowright OH^-$$

draw glycine at pH 6.5 (higher than isoelectric point, for glycine this is basic)



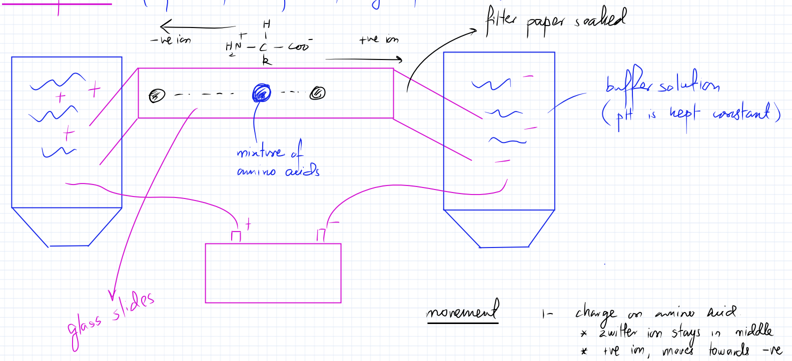
$$H_2N-\underset{H}{\overset{H}{C}}-COO^{-1}$$

draw glycine at pH 5.5 (lower than isoelectric point, for glycine this is acidic)



$$H_3N^+-\underset{H}{\overset{H}{C}}-COOH$$

electrophoresis (separation / identification / analysis of amino acids)


-ve ion
$H_2\overset{+}{N}-\underset{R}{\overset{H}{C}}-COO^-$
+ve ion
filter paper soaked
buffer solution
(pH is kept constant)
mixture of amino acids
glass slides
+
-

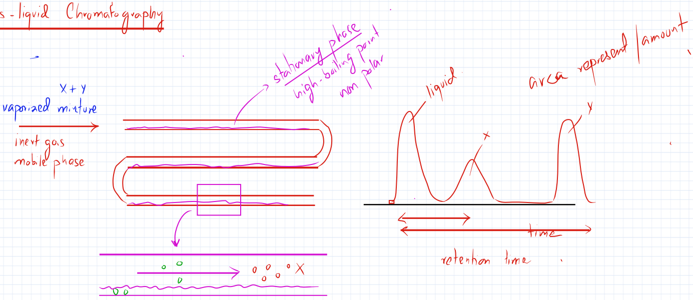
movement

1- charge on amino acid
- zwitter ion stays in middle
- +ve ion, moves towards -ve
- -ve ion, move towards +ve

2. Mr of amino acid

if Mr is less than it travels further and vice versa

Gas-liquid Chromatography


X + Y
vaporized mixture
inert gas
mobile phase
stationary phase
high-boiling point
non polar
X
liquid
x
y
area represent | amount
time
retention time

separation happens, due to difference in solubility of component, b/w stationary phase (and mobile phase)

high retention, substance is more soluble in stationary phase

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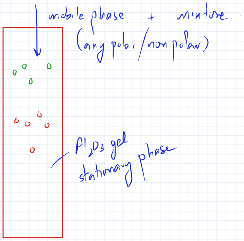
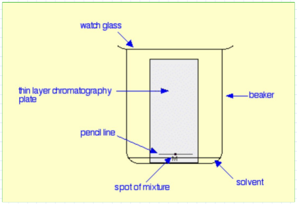
Thin layer Chromatography

adsorption.

if a substance forms weak bonds with stationary phase than it slows down


mobile phase + mixture
(any polar/non polar)
Al_2O_3 gel
stationary phase


watch glass
thin layer chromatography plate
pencil line
spot of mixture
beaker
solvent
M

$$R_f \text{ value} : \frac{\text{distance of dye}}{\text{distance of solvent}}$$

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