

Week 44

A-Level Chemistry

Homework bundle for this week

本周作业合集

exercises.lol

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29. An introduction to A Level organic chemistry Starter Quiz · 课前小测

A-Level Chemistry

Name: _____ Score: _____

1. Aromatic compounds are built on a:
 - ☐ benzene ring (six carbons)
 - ☐ single C=C bond
 - ☐ long straight chain
 - ☐ metal ion
2. Electrophilic substitution is when:
 - ☐ an electrophile replaces a hydrogen atom on a benzene ring
 - ☐ a nucleophile adds across a double bond
 - ☐ two molecules join with no loss
 - ☐ a radical removes an electron
3. Each carbon in benzene is:
 - ☐ sp^2 hybridised, forming a flat ring of sigma bonds
 - ☐ sp^3 hybridised and tetrahedral
 - ☐ sp hybridised and linear
 - ☐ not bonded to hydrogen
4. Two enantiomers differ in that they:
 - ☐ rotate plane-polarised light in opposite directions (and may differ in biological effect)
 - ☐ have different melting points
 - ☐ have different molecular formulas
 - ☐ react completely differently
5. When naming an aromatic compound, you:
 - ☐ use the benzene ring as the parent and number the substituents
 - ☐ ignore the ring
 - ☐ never use numbers
 - ☐ name only the longest chain
6. A compound containing a benzene ring is described as _____.

7. Benzene is a flat, regular hexagon.

☐ True ☐ False

8. A single pure enantiomer is optically active (it rotates plane-polarised light).

☐ True ☐ False

9. Benzene has the molecular formula C_6H_6 .

☐ True ☐ False

10. Reduction adds hydrogen (or removes oxygen) to a molecule.

☐ True ☐ False

A-Level Chemistry

1. **benzene ring (six carbons)**

Aromatic compounds contain a benzene ring; new families also include the amide group.

2. **an electrophile replaces a hydrogen atom on a benzene ring**

Benzene reacts by electrophilic substitution, keeping its stable ring while swapping an H for the electrophile.

3. **sp^2 hybridised, forming a flat ring of sigma bonds**

sp^2 carbons give the flat hexagon; the leftover p-orbitals form the delocalised π system.

4. **rotate plane-polarised light in opposite directions (and may differ in biological effect)**

Enantiomers are otherwise identical; they rotate plane-polarised light oppositely and can act differently in the body.

5. **use the benzene ring as the parent and number the substituents**

e.g. 3-nitrobenzoic acid puts a $-NO_2$ on carbon 3 of the ring.

6. **aromatic**

Aliphatic compounds have no benzene ring.

7. **True**

Its sp^2 σ framework and delocalised π system make it planar and symmetrical.

8. **True**

A pure enantiomer rotates the plane of polarised light; only a racemic mixture cancels out.

9. **True**

Six carbons in a ring, each with one hydrogen.

10. **True**

The opposite of oxidation.

29.1 Formulas, functional groups and naming

Name: _____ Class: _____ Date: _____

Total: 21 marks

KEY WORDS benzene 苯 • functional group 官能团 • aromatic 芳香 • benzene ring 苯环
 • systematic nomenclature 系统命名法

Objective

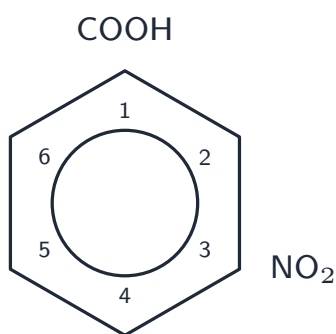
Build the skills to answer exam questions on **naming organic compounds** 有机化合物命名 — functional groups, the four kinds of formula, and **systematic nomenclature** 系统命名法 of aliphatic and **aromatic** 芳香 molecules.

You must be able to:

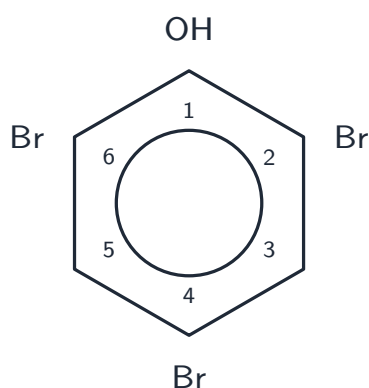
- identify the functional group that dictates a compound's properties
- interpret general, structural, displayed and skeletal formulas
- name aliphatic molecules (up to six carbons, incl. single rings)
- name simple aromatic molecules with one benzene ring (e.g. 3-nitrobenzoic acid)

1 Worked examples

■ Naming an aromatic compound

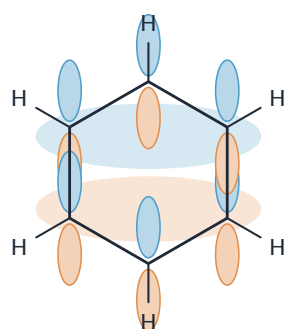


3-nitrobenzoic acid



2,4,6-tribromophenol

Number the ring from the principal group (carbon 1); the substituent positions give the name



one **delocalised** π system
above and below the ring

sp^2 σ framework;
all six C-C bonds equal

The delocalised benzene ring

Name $C_6H_4(NO_2)(COOH)$ with the groups on carbons 1 and 3.

- the $-COOH$ is the principal group $\rightarrow$ parent is **benzoic acid**, its carbon is **C1**
- the $-NO_2$ is on **C3** $\rightarrow$ prefix **3-nitro**
- name: **3-nitrobenzoic acid**

Skeletal vs displayed. A skeletal formula shows each bond as a line, with carbons at the ends/bends and hydrogens on carbon left out; a displayed formula shows every atom and bond.

2 Practice

2.1 State what is meant by a **functional group**.

[1]

2.2 Name the compound: a benzene ring with an $-OH$ on C1 and $-Br$ on C2, C4 and C6.

[1]

3 Exam-style questions

3.1 The skeletal formula of a compound has 5 line-ends and bends in a chain with a terminal $-COOH$. Which feature does a skeletal formula leave out? [1]

- **A** the functional group
- **B** carbon atoms
- **C** hydrogen atoms bonded to carbon
- **D** the longest chain

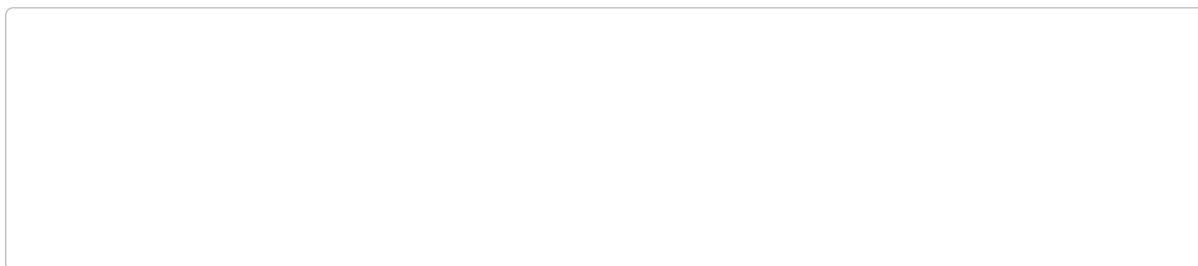
3.2 Which is the correct systematic name for the molecule with an -NH_2 on C2 of a 4-carbon carboxylic acid? [1]

- **A** 2-aminobutanoic acid
 - **B** butan-2-amine
 - **C** 2-aminobutanal
 - **D** aminobutanoic acid
-

3.3 Give the systematic name of: [3]

- (a) a benzene ring carrying one -CH_3 and one -NO_2 on adjacent carbons (methyl on C1)
- (b) the cyclic alcohol cyclohexanol
- (c) propanenitrile, $\text{CH}_3\text{CH}_2\text{CN}$
-
-
-

3.4 Draw the **skeletal** formula of 3-nitrobenzoic acid. [2]



3.5 A compound **W** has the skeletal structure of a five-carbon chain with a methyl branch on carbon 2, a C=C between carbons 3 and 4, and an OH on carbon 1. Its molecular formula is C₆H₁₂O.

(a) Give the systematic name of **W**, and explain how the position numbers are chosen. [3]

(b) Give the empirical formula and the general formula of the homologous series to which **W**'s alcohol group belongs. [2]

(c) Draw the displayed formula of **W**. [3]

(d) Name **two** functional groups present in **W**, and for each state one reagent that would react with it. [4]

Solutions

2.1 an atom or group of atoms that gives a molecule its characteristic chemical (and physical) properties.

2.2 2,4,6-tribromophenol.

3.1 C. A skeletal formula omits the hydrogen atoms bonded to carbon (and the carbons are shown only as line-ends/bends).

3.2 A. 2-aminobutanoic acid — the -COOH is C1, the -NH_2 is on C2.

3.3 (a) 2-methylnitrobenzene / 1-methyl-2-nitrobenzene

(b) cyclohexanol

(c) propanenitrile.

3.4 a benzene hexagon with -COOH drawn at C1 and -NO_2 at C3.

3.5 (a) 2-methylpent-3-en-1-ol. The chain is numbered from the end that gives the **principal functional group** — here the alcohol — the lowest number, so the OH carbon is C1; the double bond and the methyl branch are then numbered from that same end.

(b) Empirical formula $\text{C}_6\text{H}_{12}\text{O}$ — the ratio 6:12:1 has no common factor, so it equals the molecular formula; the alcohols have the general formula $\text{C}_n\text{H}_{2n+1}\text{OH}$.

(c) Every atom and every bond shown, with $\text{HOCH}_2\text{-CH}(\text{CH}_3)\text{-CH}=\text{CH-CH}_3$.

(d) Alcohol (hydroxyl) — reacts with sodium (effervescence of hydrogen), or with acidified potassium dichromate(VI). Alkene ($\text{C}=\text{C}$) — reacts with bromine water, decolourising it, or adds hydrogen over a nickel catalyst.

- 8 (a) Describe the difference in reactivity between ethanoyl chloride and chlorobenzene with water.

Explain your answer.

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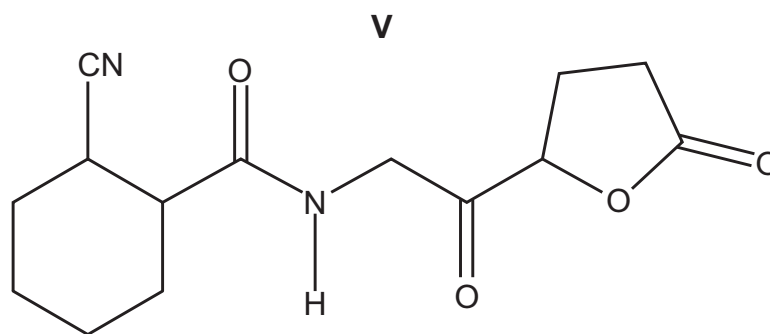
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.....

..... [2]

- (b) The structure of compound **V** is shown.



- (i) Name all the functional groups in **V**.

.....

.....

..... [2]

- (ii) Deduce the number of possible optical isomers for **V**.

..... [1]

- (iii) Suggest **one** reason, other than better biological activity and lower dosage required, why it is beneficial to synthesise a single optical isomer of **V** for use as a drug.

.....

.....

..... [1]

(c) A sample of **V** is hydrolysed with an excess of hot aqueous alkali.

The products are isolated from the reaction mixture at pH 12.

Draw the structures of the **two** organic products of the **complete** alkaline hydrolysis of **V** in Fig. 8.1.

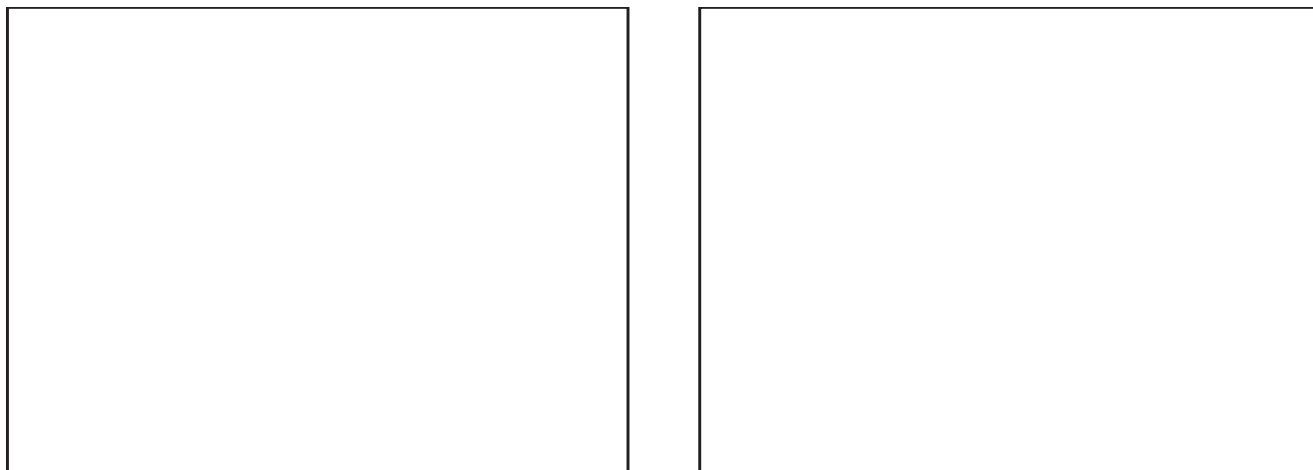


Fig. 8.1

[3]

- (d) A polypeptide formed from four amino acids, **A**, **B**, **C** and **D**, is completely hydrolysed and then analysed by gas–liquid chromatography.

The chromatogram produced is shown in Fig. 8.2.

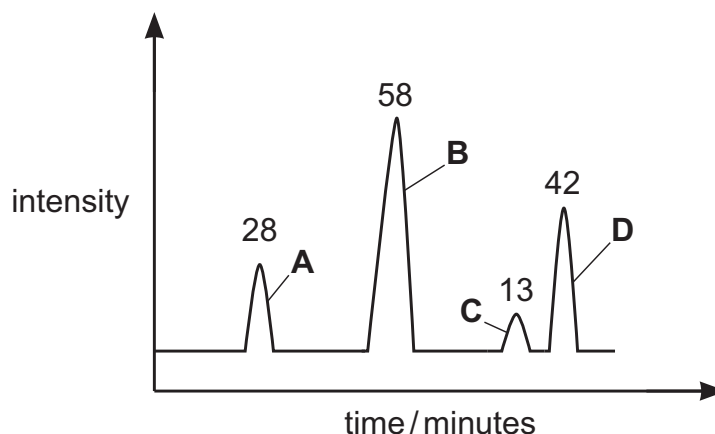


Fig. 8.2

The number above each peak represents the area under the peak.

The area under each peak is proportional to the mass of the respective amino acid in the mixture.

- (i) Calculate the percentage by mass of amino acid **A** in the original mixture.

percentage by mass of amino acid **A** = [1]

- (ii) The retention time for amino acid **D** is the longest.

Explain why **D** has a longer retention time than the **other** amino acids **A**, **B** and **C**.

.....
.....
.....
..... [1]

[Total: 11]

Important values, constants and standards

molar gas constant	$R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$
Faraday constant	$F = 9.65 \times 10^4 \text{ C mol}^{-1}$
Avogadro constant	$L = 6.02 \times 10^{23} \text{ mol}^{-1}$
electronic charge	$e = -1.60 \times 10^{-19} \text{ C}$
molar volume of gas	$V_m = 22.4 \text{ dm}^3 \text{ mol}^{-1}$ at s.t.p. (101 kPa and 273 K) $V_m = 24.0 \text{ dm}^3 \text{ mol}^{-1}$ at room conditions
ionic product of water	$K_w = 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ (at 298 K (25 °C))
specific heat capacity of water	$c = 4.18 \text{ kJ kg}^{-1} \text{ K}^{-1}$ (4.18 J g ⁻¹ K ⁻¹)

29.2 Characteristic organic reactions

Name: _____ Class: _____ Date: _____

Total: 21 marks

KEY WORDS electrophilic substitution 亲电取代 • addition-elimination 加成消去

• characteristic organic reactions 有机反应类型 • free radicals 自由基 • electrophiles 亲电试剂

Objective

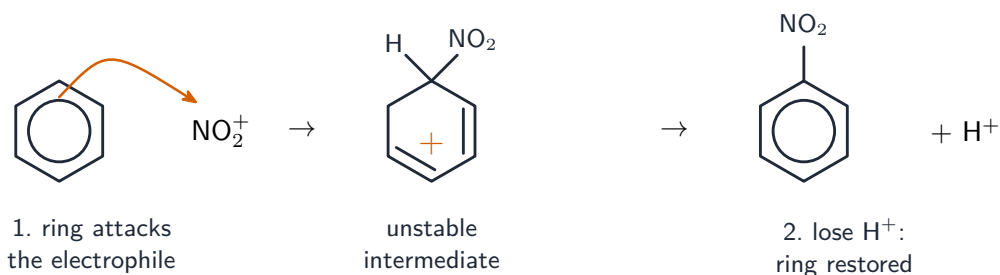
Build the skills to answer exam questions on **characteristic organic reactions** 有机反应类型 — classifying a reaction by its type and the kind of reagent involved.

You must be able to:

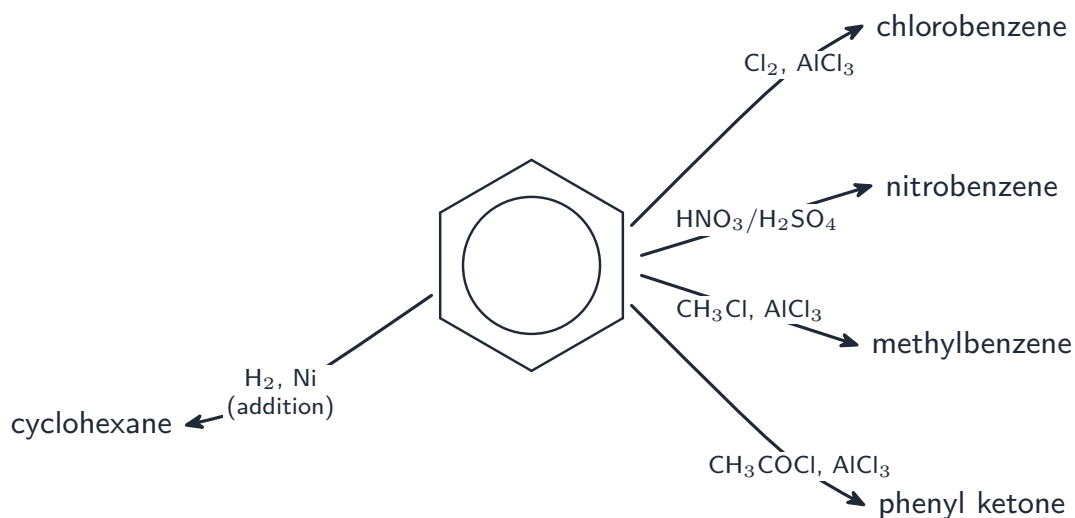
- classify reactions as addition, substitution, elimination, hydrolysis, condensation, oxidation, reduction or polymerisation
- classify reagents as **electrophiles** 亲电试剂, **nucleophiles** 亲核试剂 or **free radicals** 自由基
- describe the two new mechanism types: **electrophilic substitution** and **addition-elimination**

1 Worked examples

■ Naming the reaction type



Electrophilic substitution: an electrophile replaces a ring hydrogen — the characteristic reaction of benzene



Characteristic reactions of the benzene ring

- **electrophilic substitution** — an electrophile replaces an H on a benzene ring (e.g. nitration).
- **nucleophilic substitution** — a nucleophile replaces a leaving group (e.g. OH^- + halogenoalkane).
- **addition** — a π bond opens and two groups add on (e.g. Br_2 + alkene).
- **addition-elimination** — a group adds, then a small molecule leaves (e.g. 2,4-DNPH, acyl chlorides).

Reagent types: electrophile = electron-pair **acceptor**; nucleophile = electron-pair **donor**; radical = species with an unpaired electron.

2 Practice

2.1 State what is meant by an **electrophile**.

[1]

2.2 Classify the reaction of bromine with ethene (an alkene).

[1]

3 Exam-style questions

3.1 The reaction of OH^- with bromoethane is best classified as: [1]

- A electrophilic addition
 - B nucleophilic substitution
 - C electrophilic substitution
 - D free-radical substitution
-

3.2 Which species is a nucleophile? [1]

- A NO_2^+
 - B H^+
 - C $:\text{NH}_3$
 - D $\text{Cl}^\bullet$
-

3.3 For each reaction, name the **type** and the **reagent class**: [3]

(a) $\text{benzene} + \text{NO}_2^+ \rightarrow \text{nitrobenzene} + \text{H}^+$

(b) $\text{ethene} + \text{Br}_2 \rightarrow \text{1,2-dibromoethane}$

(c) $\text{an ester} + \text{water} \rightarrow \text{a carboxylic acid} + \text{an alcohol}$

3.4 Explain why benzene undergoes **substitution** rather than **addition**, unlike an alkene. [2]

3.5 Four reactions of propene and its derivatives are shown.

- **I** $\text{CH}_3\text{CH}=\text{CH}_2 + \text{Br}_2 \rightarrow \text{CH}_3\text{CHBrCH}_2\text{Br}$
- **II** $\text{CH}_3\text{CHBrCH}_3 + \text{KOH}(\text{aq}) \rightarrow \text{CH}_3\text{CH}(\text{OH})\text{CH}_3 + \text{KBr}$
- **III** $\text{CH}_3\text{CHBrCH}_3 + \text{KOH}$ in ethanol $\rightarrow \text{CH}_3\text{CH}=\text{CH}_2 + \text{KBr} + \text{H}_2\text{O}$
- **IV** $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3 + [\text{O}] \rightarrow \text{CH}_3\text{COCH}_3 + \text{H}_2\text{O}$

(a) Classify each reaction by type.

[4]

(b) For **I**, name the attacking species and explain how a non-polar bromine molecule comes to attack an alkene.

[3]

(c) Reactions **II** and **III** use the same reagent on the same compound but give different products. Explain what decides which happens.

[2]

(d) Name a suitable oxidising agent for **IV**, and state what you would see. Explain why the product cannot be oxidised further.

[3]

Solutions

2.1 an electron-pair acceptor / a species that is attracted to a region of high electron density.

2.2 electrophilic addition.

3.1 B. OH^- is a nucleophile and it replaces the bromine — nucleophilic substitution.

3.2 C. $:\text{NH}_3$ has a lone pair to donate — a nucleophile.

3.3 (a) electrophilic substitution; electrophile

(b) (electrophilic) addition; electrophile

(c) hydrolysis (substitution); water/nucleophile.

3.4 benzene's delocalised π system is very stable; substitution keeps the stable ring intact, whereas addition would destroy the delocalisation, so substitution is favoured.

3.5 (a) **I** electrophilic addition; **II** nucleophilic substitution; **III** elimination; **IV** oxidation.

(b) The **electrophile** is bromine, Br_2 , acting as $\text{Br}^{\delta+}-\text{Br}^{\delta-}$. The high electron density of the π bond repels the electrons in the approaching Br_2 , inducing a dipole; the now $\delta+$ bromine atom is attacked by the π electrons.

(c) The **solvent and conditions**: aqueous KOH favours substitution, giving the alcohol; hot KOH in ethanol favours elimination, giving the alkene.

(d) Acidified potassium dichromate(VI), $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$; the solution turns from orange to green as $\text{Cr}_2\text{O}_7^{2-}$ is reduced to Cr^{3+} . Propanone is a **ketone** — its carbonyl carbon carries no hydrogen, so further oxidation would need a C–C bond to break, which this reagent cannot do.

- 8 (a) Describe the difference in reactivity between ethanoyl chloride and chlorobenzene with water.

Explain your answer.

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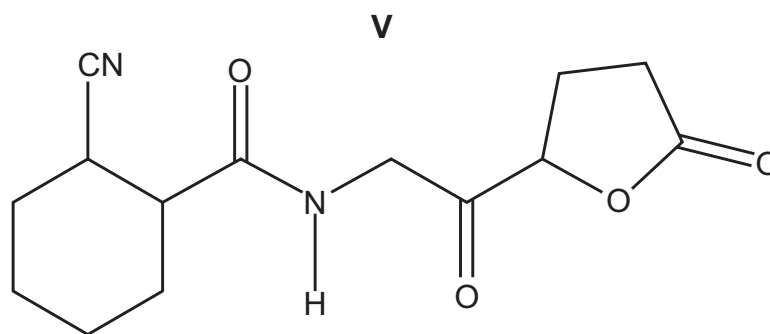
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..... [2]

- (b) The structure of compound **V** is shown.



- (i) Name all the functional groups in **V**.

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- (iii) Suggest **one** reason, other than better biological activity and lower dosage required, why it is beneficial to synthesise a single optical isomer of **V** for use as a drug.

.....

.....

..... [1]

(c) A sample of **V** is hydrolysed with an excess of hot aqueous alkali.

The products are isolated from the reaction mixture at pH 12.

Draw the structures of the **two** organic products of the **complete** alkaline hydrolysis of **V** in Fig. 8.1.

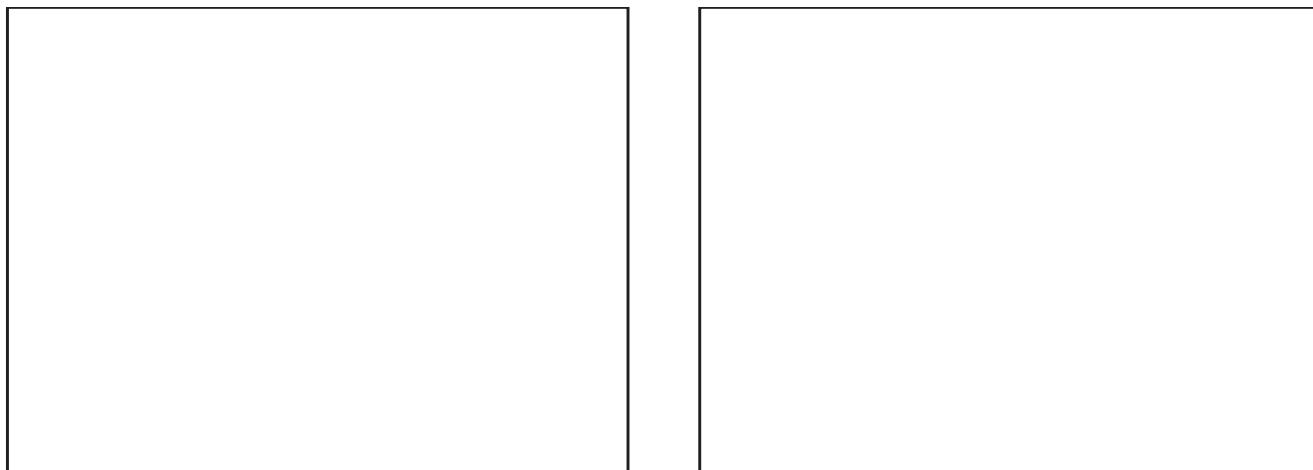


Fig. 8.1

[3]

- (d) A polypeptide formed from four amino acids, **A**, **B**, **C** and **D**, is completely hydrolysed and then analysed by gas–liquid chromatography.

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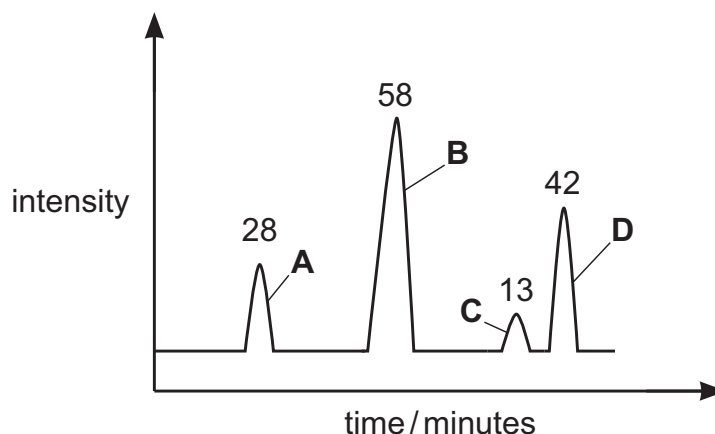


Fig. 8.2

The number above each peak represents the area under the peak.

The area under each peak is proportional to the mass of the respective amino acid in the mixture.

- (i) Calculate the percentage by mass of amino acid **A** in the original mixture.

percentage by mass of amino acid **A** = [1]

- (ii) The retention time for amino acid **D** is the longest.

Explain why **D** has a longer retention time than the **other** amino acids **A**, **B** and **C**.

.....
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..... [1]

[Total: 11]

Important values, constants and standards

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specific heat capacity of water	$c = 4.18 \text{ kJ kg}^{-1} \text{ K}^{-1}$ (4.18 J g ⁻¹ K ⁻¹)

The Periodic Table of Elements

Group																			
1	2													13	14	15	16	17	18

29.3 Shape and bonding of benzene

Name: _____ Class: _____ Date: _____

Total: 21 marks

KEY WORDS delocalised 离域 • benzene 苯 • hybridisation 杂化
• enthalpy change of hydrogenation 氢化焓变

Objective

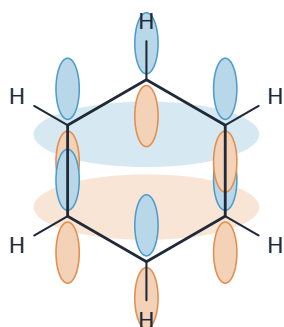
Build the skills to answer exam questions on the **shape and bonding of benzene** 苯的形状与成键 — sp^2 hybridisation, σ and π bonds, **delocalisation** 离域, and the evidence for it.

You must be able to:

- describe benzene as a planar regular hexagon of sp^2 carbons
- explain the σ framework and the delocalised π system
- use enthalpy of hydrogenation as evidence for delocalisation

1 Worked examples

■ Bonding and stability



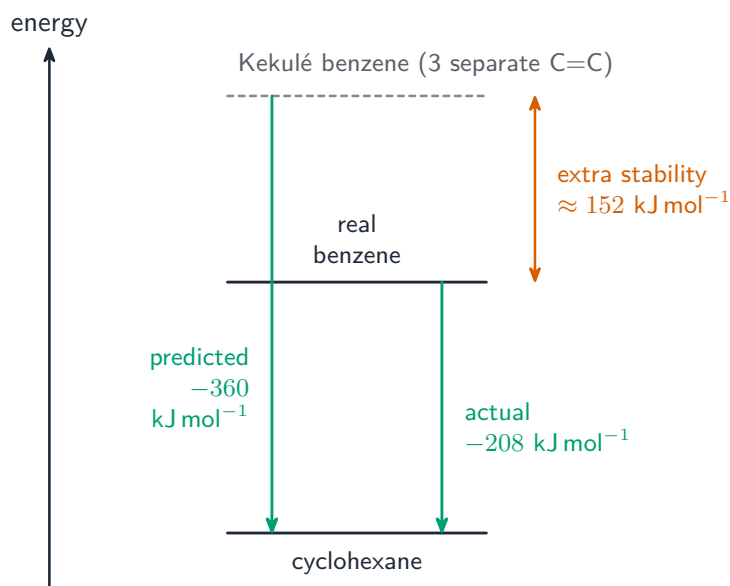
one **delocalised** π system
above and below the ring

sp^2 σ framework;
all six C-C bonds equal

Each carbon is sp^2 : three σ bonds make the flat hexagon; the leftover p orbitals overlap into one delocalised π system

- each C is sp^2 : three σ bonds (to 2 C + 1 H) in the plane.
- each C keeps one electron in a **p orbital**; these overlap sideways all round → one **delocalised** π ring above and below the plane.
- all six C-C bonds are **equal length** (between single and double); the ring is very stable.

■ Evidence: enthalpy of hydrogenation



Real benzene releases only 208 kJ mol⁻¹ vs the Kekulé prediction 360 = 3 × cyclohexene → ~152 more stable

The shortfall ($360 - 208 = 152 \text{ kJ mol}^{-1}$) is the extra stability from delocalisation.

2 Practice

2.1 State the hybridisation of each carbon atom in benzene.

[1]

2.2 State what the equal C–C bond lengths in benzene tell you about its bonding.

[1]

3 Exam-style questions

3.1 The π system in benzene is formed by the overlap of:

[1]

- A sp^2 hybrid orbitals
- B s orbitals
- C p orbitals at right angles to the ring
- D sp^3 hybrid orbitals

3.2 Hydrogenation of cyclohexene releases 120 kJ mol^{-1} . The Kekulé model of benzene would predict a hydrogenation enthalpy of about: [1]

- **A** -120 kJ mol^{-1}
 - **B** -208 kJ mol^{-1}
 - **C** -240 kJ mol^{-1}
 - **D** -360 kJ mol^{-1}
-

3.3 Describe the bonding in benzene, referring to sp^2 hybridisation, the σ framework and the delocalised π system. [3]

3.4 The real enthalpy of hydrogenation of benzene is -208 kJ mol^{-1} ; the Kekulé prediction is -360 kJ mol^{-1} . State and explain what this difference shows. [2]

3.5 Benzene is a planar molecule with all six C–C bonds of the same length, 0.139 nm. (C–C in ethane is 0.154 nm; C=C in ethene is 0.134 nm.)

(a) Describe the bonding in benzene in terms of sp^2 hybridisation, σ bonds and π bonds.[4]

(b) Explain how the bond-length data support the delocalised model rather than the Kekulé structure. [2]

(c) The enthalpy change of hydrogenation of cyclohexene is -120 kJ mol^{-1} , and of benzene -208 kJ mol^{-1} . Explain what these values show, with a calculation. [3]

(d) Explain why benzene undergoes substitution rather than addition. [3]

Solutions

2.1 sp^2 .

2.2 the bonding is delocalised / identical round the ring (not alternating single and double bonds).

3.1 C. The p orbitals at right angles to the ring overlap sideways to form the delocalised π system.

3.2 D. Three $\text{C}=\text{C} \times 120 = -360 \text{ kJ mol}^{-1}$.

3.3 each carbon is sp^2 hybridised, forming three σ bonds (to two C and one H) in a planar hexagon; each carbon has one electron in a p orbital perpendicular to the ring; these p orbitals overlap sideways all round to give one delocalised π system above and below the plane.

3.4 benzene is about 152 kJ mol^{-1} more stable than the Kekulé model predicts; this extra stability is due to delocalisation of the π electrons.

3.5 (a) Each carbon uses three sp^2 hybrid orbitals, in a plane at 120° ; these overlap end-on to form σ bonds to two carbons and one hydrogen, giving the planar hexagonal ring; each carbon keeps one electron in an unhybridised p orbital perpendicular to the ring; these six p orbitals overlap sideways all round the ring, forming a π system **delocalised** above and below the plane.

(b) Kekulé's structure needs alternating single (0.154 nm) and double (0.134 nm) bonds; the measured 0.139 nm is the same for all six and lies **between** the two, which is what a delocalised, evenly shared π system predicts.

(c) Three isolated $\text{C}=\text{C}$ bonds would give $3 \times (-120) = -360 \text{ kJ mol}^{-1}$; benzene releases only -208 , i.e. 152 kJ mol^{-1} **less**; so real benzene lies 152 kJ mol^{-1} lower in energy than the Kekulé model — the delocalisation (resonance) energy.

(d) Addition would destroy the delocalised π system and lose that stabilisation; substitution replaces a hydrogen and leaves the ring intact; so the substitution route is energetically far more favourable.

9 Compound **X** is made from benzene by the route shown in Fig. 9.1.

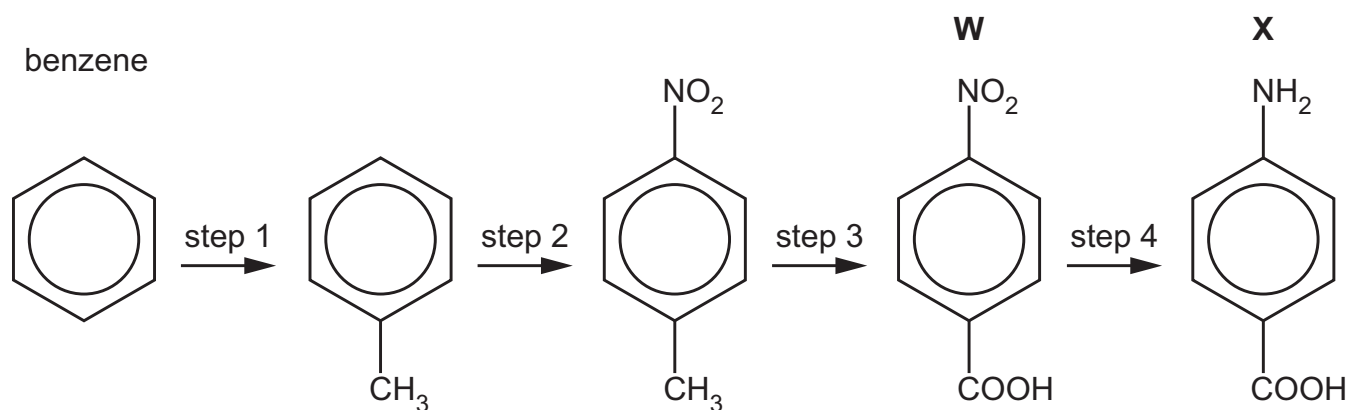


Fig. 9.1

(a) Describe the bonding in benzene, C₆H₆.

Your answer should include:

- the hybridisation of the six carbon atoms
- the types of bond between the carbon atoms
- the orbitals that overlap to produce the bonds between the carbon atoms
- the type of bond between the carbon atoms and the hydrogen atoms
- the orbitals that overlap to produce the bonds between the carbon atoms and the hydrogen atoms.

.....

.....

.....

.....

.....

.....

..... [3]

(b) Describe the reagents and conditions required for step 1 in Fig. 9.1.

.....

..... [1]

(c) In step 1 of Fig. 9.1 benzene reacts with $^+\text{CH}_3$.

Complete Fig. 9.2 to show the mechanism for this reaction, including:

- the movement of electron pairs using curly arrows
- the structure of the intermediate involved.

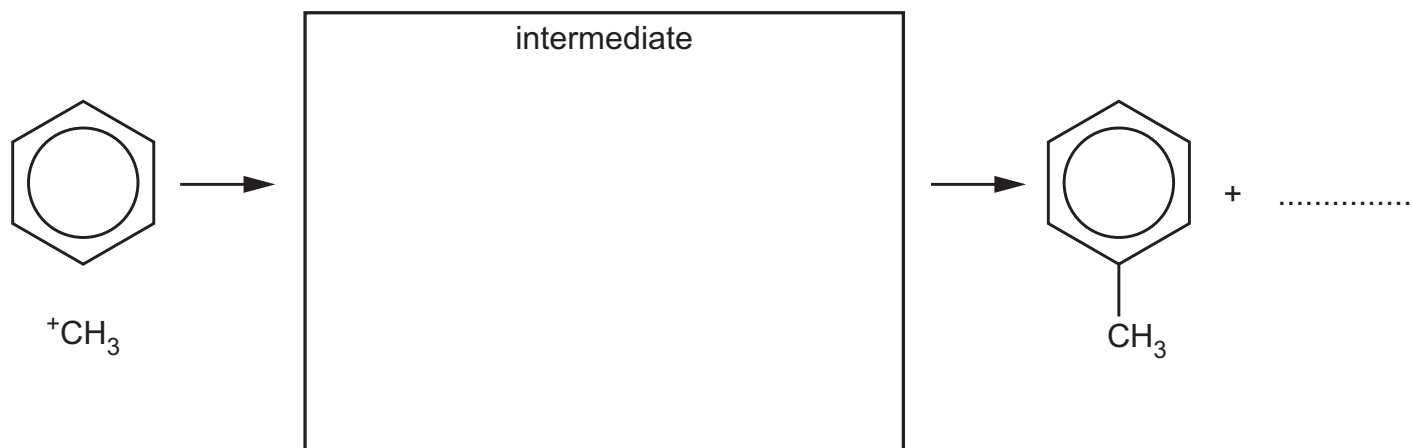


Fig. 9.2

[3]

(d) Describe the reagents and conditions required for step 2 of Fig. 9.1.

.....
..... [2]

(e) Identify the reagents required for step 3 of Fig. 9.1. Compound **W** is the product of this step.

..... [1]

(f) Name compound **W**.

..... [1]

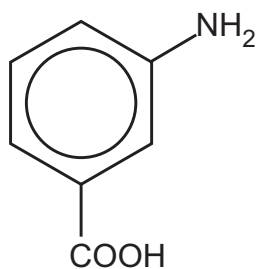
(g) The reagents commonly used for step 4 will **not** reduce the $-\text{COOH}$ group.

Identify the reagents and conditions required for step 4 of Fig. 9.1.

..... [1]

(h) Benzene can also be used as a starting material to make compound **Y**.

compound **Y**



Describe how the route described in Fig. 9.1 (repeated below) can be changed to give compound **Y** instead of compound **X**.

Explain your answer.

.....
.....
.....
..... [2]

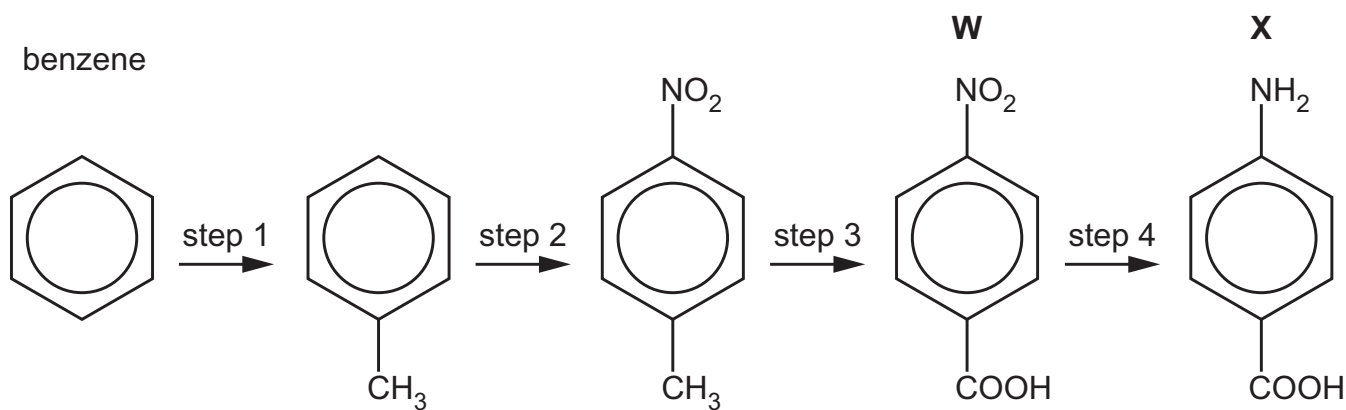


Fig. 9.1

[Total: 14]

Important values, constants and standards

molar gas constant	$R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$
Faraday constant	$F = 9.65 \times 10^4 \text{ C mol}^{-1}$
Avogadro constant	$L = 6.02 \times 10^{23} \text{ mol}^{-1}$
electronic charge	$e = -1.60 \times 10^{-19} \text{ C}$
molar volume of gas	$V_m = 22.4 \text{ dm}^3 \text{ mol}^{-1}$ at s.t.p. (101 kPa and 273 K) $V_m = 24.0 \text{ dm}^3 \text{ mol}^{-1}$ at room conditions
ionic product of water	$K_w = 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ (at 298 K (25 °C))
specific heat capacity of water	$c = 4.18 \text{ kJ kg}^{-1} \text{ K}^{-1}$ (4.18 J g ⁻¹ K ⁻¹)

5 (a) Describe and explain the shape of benzene.

In your answer, include:

- the shape and bond angle in the ring
- the hybridisation of the carbon atoms
- how orbital overlap forms σ and π bonds between the carbon atoms in the ring.

.....

.....

.....

.....

.....

.....

.....

.....

..... [4]

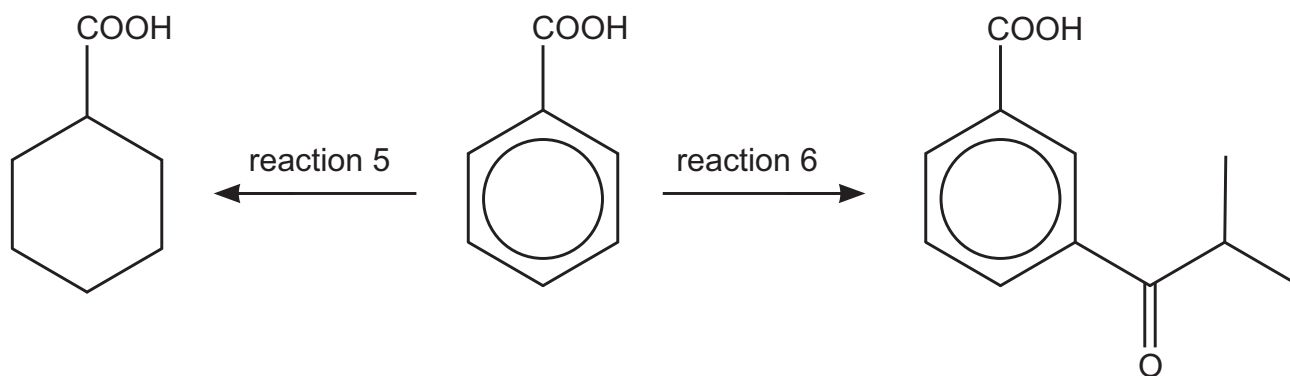
(b) Fig. 5.1 shows two reactions of benzoic acid.

Fig. 5.1

(i) Suggest reagents and conditions for reaction 5 and for reaction 6 in Fig. 5.1.

reaction 5

reaction 6

[2]

(ii) State the type of reaction for reaction 5 in Fig. 5.1.

..... [1]

(c) In the electrophilic substitution of arenes, different substituents can direct to different ring positions.

(i) Describe the directing effect of the $-\text{CH}_2\text{CH}_3$ group.

Explain your answer.

.....
..... [1]

(ii) The alkylation of arenes uses a mixture of $\text{CH}_3\text{CH}_2\text{Br}$ and FeBr_3 to generate the CH_3CH_2^+ electrophile.

Write an equation for the formation of the CH_3CH_2^+ electrophile.

..... [1]

(iii) Complete the mechanism in Fig. 5.2.

Include all relevant curly arrows and charges. Draw the structure of the organic intermediate.

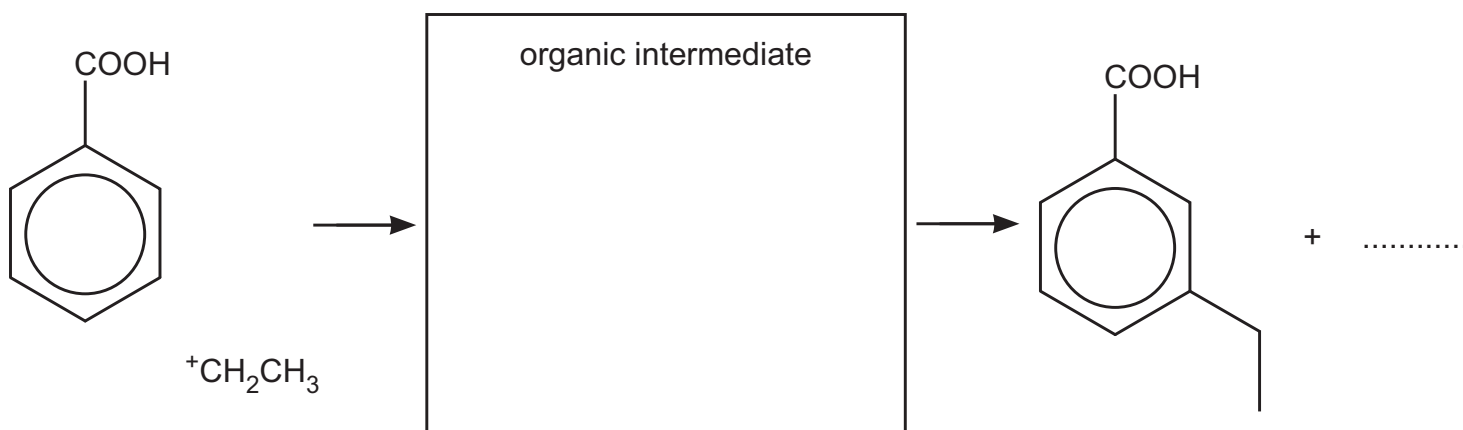


Fig. 5.2

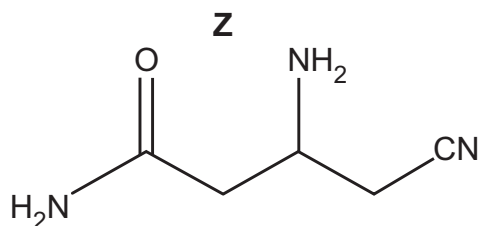
[3]

(iv) Write an equation to show how FeBr_3 is regenerated after the reaction in Fig. 5.2.

..... [1]

[Total: 13]

6 (a) Compound **Z** is used in organic synthesis.



Complete Table 6.1 to show the number of sp , sp^2 and sp^3 hybridised carbon atoms present in one molecule of **Z**.

Table 6.1

type of hybridisation	sp	sp^2	sp^3
number of carbon atoms			

[1]

(b) **Z** can undergo different reactions, as shown in Fig. 6.1.

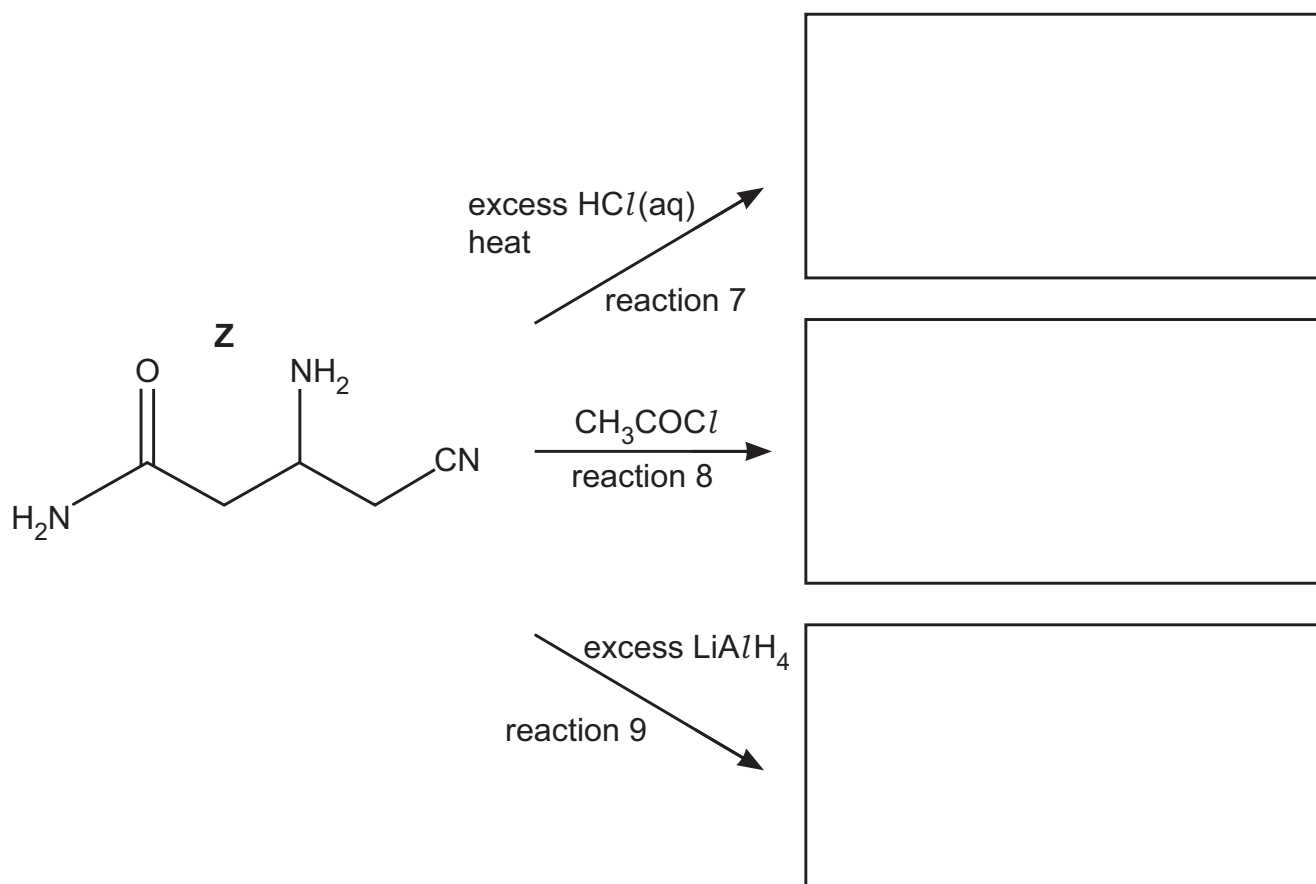


Fig. 6.1

(i) Name the **two** types of reaction occurring in reaction 7 in Fig. 6.1.

..... and [1]

(ii) Draw the structures of the organic products of reactions 7, 8 and 9 in Fig. 6.1.

[4]

(c) Compound **Z** is dissolved in D₂O and analysed by carbon-13 NMR and proton (¹H) NMR spectroscopy.

(i) Predict the number of peaks in the carbon-13 NMR spectrum of **Z**.

..... [1]

(ii) The proton (¹H) NMR spectrum of **Z** in D₂O gives three peaks for the proton environments, labelled **a**, **b** and **c**, as shown on Fig. 6.2.

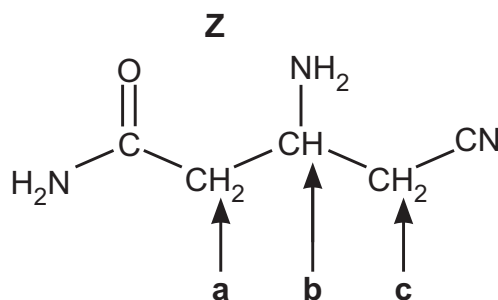


Fig. 6.2

Complete Table 6.2 for the proton (¹H) NMR spectrum of **Z** in D₂O.

Table 6.2

proton environment	a	b	c
name of splitting pattern			
chemical shift range, δ /ppm			

[2]

Table 6.3

environment of proton	example	chemical shift range, δ /ppm
alkane	$-\text{CH}_3$, $-\text{CH}_2-$, $>\text{CH}-$	0.9–1.7
alkyl next to C=O	$\text{CH}_3-\text{C}=\text{O}$, $-\text{CH}_2-\text{C}=\text{O}$, $>\text{CH}-\text{C}=\text{O}$	2.2–3.0
alkyl next to nitrile	$-\text{CH}_2-\text{CN}$	2.0–3.0
alkyl next to electronegative atom	CH_3-O , $-\text{CH}_2-\text{O}$, $-\text{CH}_2-\text{N}$	3.2–4.0
attached to alkene	$=\text{CHR}$	4.5–6.0
alkyl amine	$\text{R}-\text{NH}-$	1.0–5.0
amide	RCONHR	5.0–12.0

[Total: 9]

29.4 Optical isomerism

Name: _____ Class: _____ Date: _____

Total: 29 marks

KEY WORDS optically active 旋光活性 • enantiomers 对映体 • plane-polarised light 平面偏振光
• racemic mixture 外消旋混合物 • chirality 手性

Objective

Build the skills to answer exam questions on **optical isomerism** 旋光异构 — **chiral centres** 手性中心, **enantiomers** 对映体, **plane-polarised light** 平面偏振光 and **racemic mixtures** 外消旋混合物.

You must be able to:

- identify a chiral centre (4 different groups on one carbon)
- describe how enantiomers differ (rotation of plane-polarised light; biological activity)
- explain why a racemic mixture is optically inactive

1 Worked examples

■ Chirality and optical activity

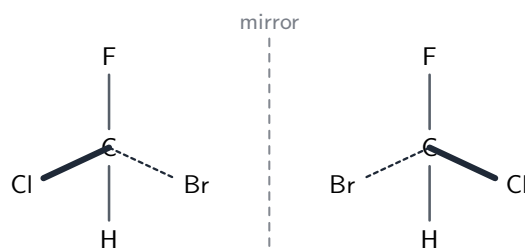


enantiomer 2 (mirror image)



a 50:50 **racemic mixture** gives no net rotation (the two cancel)

The two enantiomers rotate plane-polarised light in opposite directions; a 50:50 racemic mixture gives no net rotation



enantiomers: mirror images that cannot be superimposed
(the central carbon has 4 different groups)

Optical isomers are non-superimposable mirror images

- a **chiral centre** is a carbon with **four different** groups → two non-superimposable mirror images (enantiomers).
- enantiomers are identical in all properties **except**: they rotate plane-polarised light in **opposite** directions, and may have different biological effects.
- a **racemic mixture** (50:50) shows **no** net rotation — the two opposite rotations cancel.

Drugs: one enantiomer may cure while the other harms — so makers use a chiral catalyst or separate the enantiomers.

■ Finding a chiral centre, and what optical activity actually means

A **chiral centre** 手性中心 is a carbon with **four different groups** attached. Such a molecule is **not superimposable on its mirror image**, and the two mirror images are **enantiomers** 对映异构体.

Testing for chirality — go carbon by carbon. At each carbon, list its four attachments; if any two are identical, that carbon is not chiral. Watch for the trap where two groups look different but are the same, for example two CH_3 groups written at different angles.

What differs between enantiomers, and what does not:

- **Identical:** melting point, boiling point, density, solubility, and every ordinary chemical reaction with a non-chiral reagent.
- **Different:** they rotate the plane of **plane-polarised light** by equal amounts in **opposite directions**, and they react differently with other **chiral** molecules — which is why one enantiomer of a drug can be therapeutic and the other inactive or harmful.

A **racemic mixture** 外消旋混合物 is an equal mixture of both enantiomers. It shows **no optical rotation**, because the two rotations cancel exactly.

Why a mechanism predicts which you get — the examinable link:

- $\text{S}_{\text{N}}2$: the nucleophile attacks from the opposite side to the leaving group, so the configuration is **inverted** and a single enantiomer gives a single, opposite enantiomer.

- S_N1 : the intermediate is a **planar carbocation**, so the nucleophile attacks either face with equal probability, giving a **racemic mixture**.
- Adding HCN to an aldehyde or unsymmetrical ketone likewise attacks a planar $C=O$ from both faces, so the hydroxynitrile is racemic.

Worked example. $CH_3CH(OH)COOH$ (lactic acid): identify the chiral centre and state what a 50:50 mixture of its enantiomers would do to plane-polarised light.

1. The middle carbon carries $-H$, $-OH$, $-CH_3$ and $-COOH$: four different groups, so it is the chiral centre.
2. A 50:50 mixture is racemic, so the equal and opposite rotations cancel and there is **no net rotation**.

2 Practice

2.1 State what feature a molecule must have to show optical isomerism. [1]

2.2 State why a racemic mixture does not rotate plane-polarised light. [1]

2.3 State the two features that make a molecule optically active. [2]

2.4 Explain why a racemic mixture shows no optical rotation. [2]

2.5 State one property in which two enantiomers differ, and one in which they are identical. [2]

3 Exam-style questions

3.1 A chiral carbon atom is bonded to: [1]

- A four identical groups
 - B two identical and two different groups
 - C four different groups
 - D three different groups and one H, with a double bond
-

3.2 Two enantiomers of a molecule always have the **same**: [1]

- A rotation of plane-polarised light
 - B boiling point
 - C effect in the body
 - D direction of optical rotation
-

3.3 The molecule $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$ (lactic acid) is optically active.

(a) Mark the chiral centre and state how many enantiomers it has. [2]

(b) State the two ways in which the enantiomers differ. [2]

3.4 Explain why drug manufacturers often want a single enantiomer rather than a racemic mixture. [2]

3.5 2-bromobutane, $\text{CH}_3\text{CHBrCH}_2\text{CH}_3$, is hydrolysed by aqueous sodium hydroxide.

(a) Identify the chiral centre in 2-bromobutane and explain your choice. [2]

(b) Draw the two enantiomers of 2-bromobutane as three-dimensional structures. [2]

(c) A single enantiomer of 2-bromobutane is hydrolysed by an $\text{S}_{\text{N}}2$ mechanism. State what is observed about the optical activity of the product and explain why. [3]

(d) A tertiary halogenoalkane hydrolyses by $\text{S}_{\text{N}}1$. Explain why the product is optically inactive. [3]

(e) HCN is added to butanone. Explain why the hydroxynitrile formed is a racemic mixture. [3]

Solutions

2.1 a chiral centre — a carbon atom bonded to four different groups.

2.2 the two enantiomers are present in equal amounts, so their equal and opposite rotations cancel.

2.3 A carbon atom with four different groups attached; the molecule is not superimposable on its mirror image.

2.4 It contains equal amounts of the two enantiomers, which rotate the plane of polarised light by equal amounts in opposite directions, so the rotations cancel.

2.5 They differ in the direction in which they rotate plane-polarised light; they are identical in all ordinary physical properties such as boiling point, and in reactions with non-chiral reagents.

3.1 C. A chiral carbon has four different groups attached.

3.2 B. Enantiomers share all physical properties such as boiling point; only the direction of optical rotation and biological activity differ.

3.3 (a) the central carbon (bonded to -OH , -COOH , -CH_3 and -H) is the chiral centre; it has 2 enantiomers.

(b) they rotate plane-polarised light in opposite directions; they may have different biological effects.

3.4 the two enantiomers can behave very differently in the body — one may be effective or safe while the other is inactive or harmful; so the maker wants only the beneficial single enantiomer.

3.5 (a) Carbon 2; it carries -H , -Br , -CH_3 and $\text{-CH}_2\text{CH}_3$, which are four different groups.

(b) Two tetrahedral structures drawn as mirror images, using wedges and dashes, which cannot be superimposed on each other.

(c) The product is optically active; in $\text{S}_{\text{N}}2$ the hydroxide attacks from the side opposite the bromine, so the configuration is inverted and a single enantiomer of the alcohol is formed rather than a mixture.

(d) The mechanism goes through a carbocation intermediate which is planar, with the positive carbon having three groups in a plane; the nucleophile attacks either face with equal probability, giving equal amounts of the two enantiomers, so the product is racemic and optically inactive.

(e) The carbonyl carbon in butanone is planar; the cyanide ion attacks from either face with equal probability, giving equal amounts of the two enantiomers of the hydroxynitrile, whose rotations cancel.

- 8 Asparagine and aspartic acid are two naturally occurring amino acids. Their structures and isoelectric points are shown in Table 8.1.

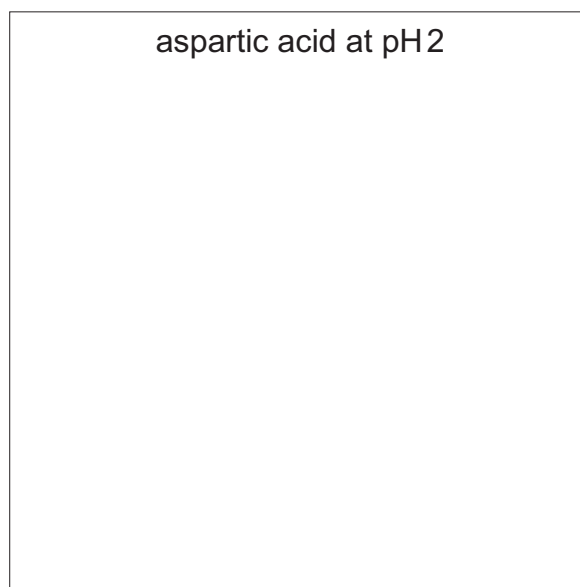
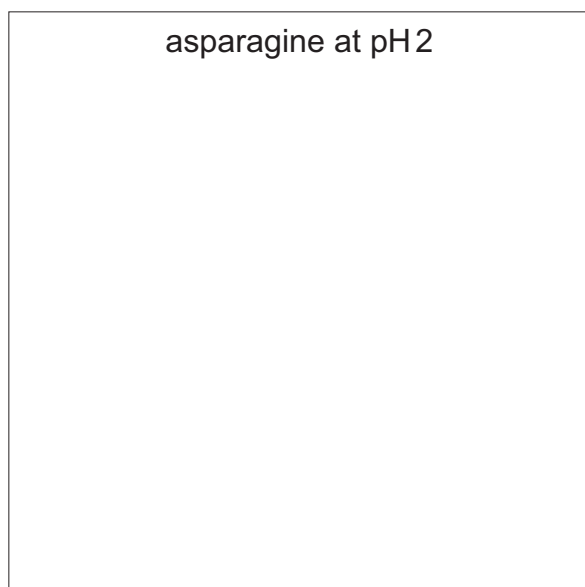
Table 8.1

amino acid	structure	isoelectric point
asparagine	$\text{HOOCCH}(\text{NH}_2)\text{CH}_2\text{CONH}_2$	5.41
aspartic acid	$\text{HOOCCH}(\text{NH}_2)\text{CH}_2\text{COOH}$	2.77

- (a) Define isoelectric point.

.....
..... [1]

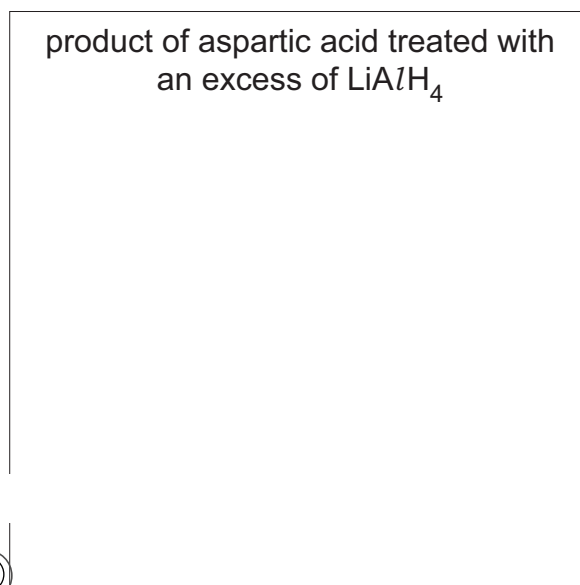
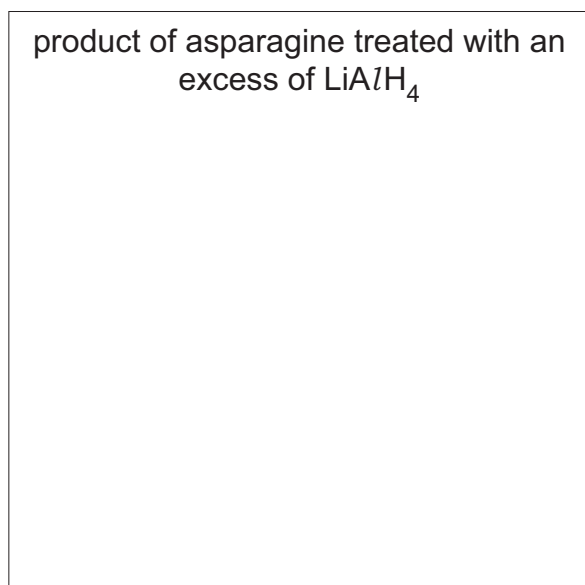
- (b) Draw the structures of asparagine and aspartic acid at pH 2.



[2]

- (c) Asparagine and aspartic acid are treated separately with an excess of LiAlH_4 .

Draw the structures of the organic products of these reactions.



- (d) Propanedioic acid, $\text{HOOCCH}_2\text{COOH}$, is treated with an excess of thionyl chloride, SOCl_2 . Propanedioyl chloride, $\text{ClOCCH}_2\text{COCl}$, is formed.

(i) Write an equation for this reaction.

..... [1]

- (ii) Propanedioyl chloride reacts with an excess of asparagine to form compound **G** with molecular formula $\text{C}_{11}\text{H}_{16}\text{N}_4\text{O}_8$.

Each molecule of compound **G** has four amide groups.

Draw the structure of compound **G**.

Compound **G**, $\text{C}_{11}\text{H}_{16}\text{N}_4\text{O}_8$

[2]

- (e) Asparagine is hydrolysed with an excess of hot NaOH(aq) .

Draw the structure of the organic product of this reaction.

[2]

- (f) A polymer can form from asparagine, $\text{HOOCCH}(\text{NH}_2)\text{CH}_2\text{CONH}_2$, as the only monomer.

Draw a length of the polymer chain containing **three** monomer residues.

Clearly label the repeat unit of the polymer on your diagram.

[3]

(g) Aspartic acid exists in two optically active forms.

- (i)** Plane polarised light is passed through pure samples of these two optically active forms in solutions of the same concentration.

Describe **two** similarities and **one** difference in their effect on the plane polarised light.

similarities

.....

difference

.....

[2]

- (ii)** Give the term used to describe a mixture of equal amounts of the two optically active forms.

..... [1]

[Total: 16]

Question 9 starts on page 20.



- 8 (a) Describe the difference in reactivity between ethanoyl chloride and chlorobenzene with water.

Explain your answer.

.....

.....

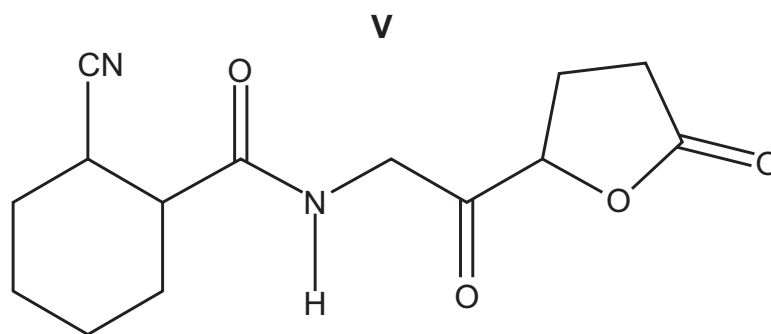
.....

.....

.....

..... [2]

- (b) The structure of compound **V** is shown.



- (i) Name all the functional groups in **V**.

.....

.....

..... [2]

- (ii) Deduce the number of possible optical isomers for **V**.

..... [1]

- (iii) Suggest **one** reason, other than better biological activity and lower dosage required, why it is beneficial to synthesise a single optical isomer of **V** for use as a drug.

.....

.....

..... [1]

(c) A sample of **V** is hydrolysed with an excess of hot aqueous alkali.

The products are isolated from the reaction mixture at pH 12.

Draw the structures of the **two** organic products of the **complete** alkaline hydrolysis of **V** in Fig. 8.1.

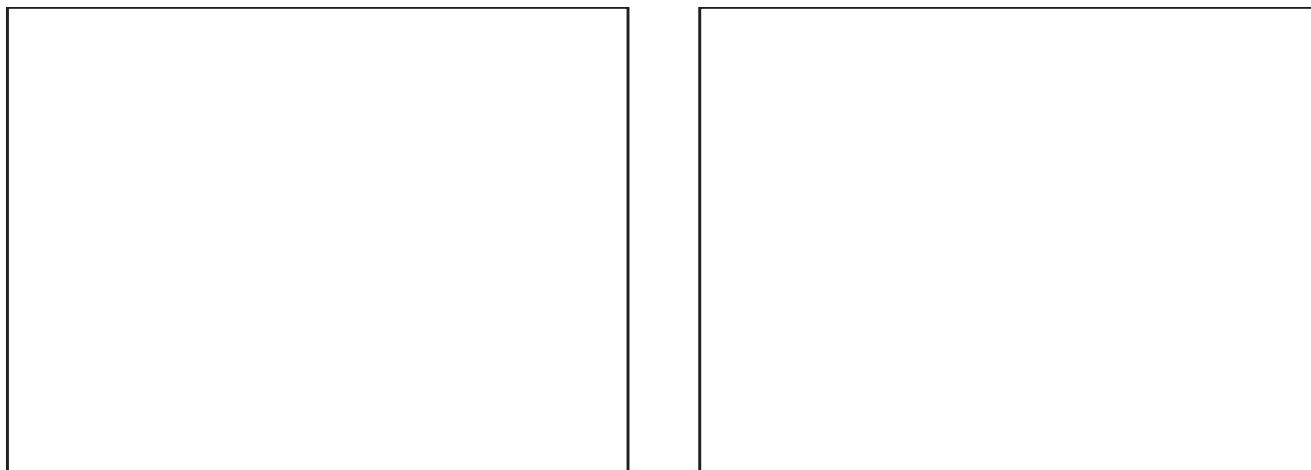


Fig. 8.1

[3]

- (d) A polypeptide formed from four amino acids, **A**, **B**, **C** and **D**, is completely hydrolysed and then analysed by gas–liquid chromatography.

The chromatogram produced is shown in Fig. 8.2.

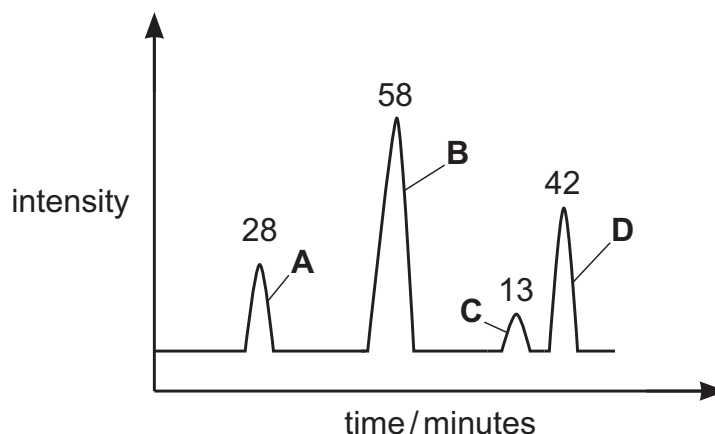


Fig. 8.2

The number above each peak represents the area under the peak.

The area under each peak is proportional to the mass of the respective amino acid in the mixture.

- (i) Calculate the percentage by mass of amino acid **A** in the original mixture.

percentage by mass of amino acid **A** = [1]

- (ii) The retention time for amino acid **D** is the longest.

Explain why **D** has a longer retention time than the **other** amino acids **A**, **B** and **C**.

.....
.....
.....
..... [1]

[Total: 11]

Important values, constants and standards

molar gas constant	$R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$
Faraday constant	$F = 9.65 \times 10^4 \text{ C mol}^{-1}$
Avogadro constant	$L = 6.02 \times 10^{23} \text{ mol}^{-1}$
electronic charge	$e = -1.60 \times 10^{-19} \text{ C}$
molar volume of gas	$V_m = 22.4 \text{ dm}^3 \text{ mol}^{-1}$ at s.t.p. (101 kPa and 273 K) $V_m = 24.0 \text{ dm}^3 \text{ mol}^{-1}$ at room conditions
ionic product of water	$K_w = 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ (at 298 K (25 °C))
specific heat capacity of water	$c = 4.18 \text{ kJ kg}^{-1} \text{ K}^{-1}$ (4.18 J g ⁻¹ K ⁻¹)

