

X813/77/02

Chemistry Section 1 — Questions

THURSDAY, 1 MAY 9:00 AM – 12:00 NOON

Instructions for the completion of Section 1 are given on *page 02* of your question and answer booklet X813/77/01.

Record your answers on the answer grid on page 03 of your question and answer booklet.

You may refer to the Chemistry Data Booklet for Higher and Advanced Higher.

Before leaving the examination room you must give your question and answer booklet to the Invigilator; if you do not, you may lose all the marks for this paper.

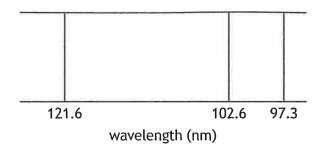




SECTION 1 — 25 marks

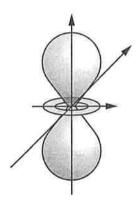
Attempt ALL questions

1. The diagram shows some lines in the hydrogen emission spectrum.



Each line in the emission spectrum

- A results from an excited electron dropping to a lower energy level
- B lies within the visible part of the electromagnetic spectrum
- C results from an electron moving to a higher energy level
- D represents an energy level within a hydrogen atom.
- 2.



The diagram above represents the shape of

- A any p orbital
- B a specific p orbital
- C any d orbital
- D a specific d orbital.

- 3. An ion, X^{3+} , contains 55 electrons. In which block of the periodic table would element X be found?
 - A s
 - Вр
 - C d
 - D f
- 4. Which line in the table is correct for a sulfur tetrafluoride, SF_4 , molecule?

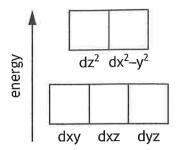
	Number of electron pairs around sulfur	Shape adopted by electron pairs around sulfur
Α	4	trigonal bipyramidal
В	5	trigonal bipyramidal
С	4	tetrahedral
D	5	tetrahedral

5. Which line in the table shows the changes that occur during the reaction below?

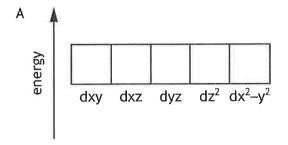
$$\begin{array}{ccc} [\mathsf{Cu}(\mathsf{OH}_2)_6]^{2+} & \to & [\mathsf{CuCl}_4]^{2-} \\ & & \text{blue} & & \text{green} \end{array}$$

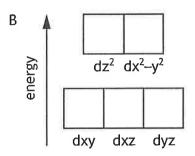
	Change in energy of light absorbed	Change in splitting of d orbitals
Α	increases	increases
В	increases	decreases
С	decreases	increases
D	decreases	decreases

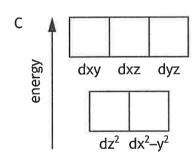
6. In transition metal complexes, the d subshell is split into orbitals of higher and lower energies due to repulsion between electrons in ligands and electrons in d orbitals.In an octahedral complex, the ligands lie along the axes. The splitting that occurs is shown.

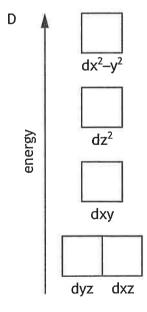


In tetrahedral complexes, the ligands lie between the axes. The likely energies of the d orbitals in a tetrahedral complex are









7. Which line in the table is correct for the oxidation numbers of sulfur?

	Oxidation number of sulfur in S ₈	Oxidation number of sulfur in Na ₂ S ₂ O ₃
Α	0	+2
В	0	+4
С	+8	+2
D	+8	+4

- 8. The Brønsted-Lowry definition of a base is a substance which acts as a
 - A proton donor to form a conjugate acid
 - B proton donor to form a conjugate base
 - C proton acceptor to form a conjugate acid
 - D proton acceptor to form a conjugate base.
- 9. The pH of a buffer solution prepared by mixing equal volumes of $0.100~\rm mol\,l^{-1}$ butanoic acid and $0.200~\rm mol\,l^{-1}$ sodium butanoate is
 - A 0.30
 - B 2.92
 - C 4.53
 - D 5.13
- 10. Which salt solution would have the lowest pH?
 - A NaCl
 - B Na₂CO₃
 - C Na₂SO₃
 - D CH₃COONa

11. Which line in the table correctly describes the properties of 0.1 mol l⁻¹ ethanoic acid when compared to 0.1 mol l⁻¹ hydrochloric acid?

	рН	pH Conductivity Rate	
Α	lower	higher	faster
В	higher	lower	slower
С	higher	lower	faster
D	lower	higher	slower

12. The reaction between nitrogen monoxide and hydrogen occurs by the following mechanism.

$$2NO + H_2 \xrightarrow{slow} N_2 + H_2O_2$$

$$H_2O_2 + H_2 \xrightarrow{fast} 2H_2O$$

The overall order of this reaction is

- A 2
- B 3
- C 4
- D 5

13. Which of the following equations correctly represents the standard enthalpy of formation of calcium nitrate at 298 K?

A Ca(s) +
$$2N(g) + 6O(g) \rightarrow Ca(NO_3)_2(s)$$

B Ca(g) + 2N(g) + 6O(g)
$$\rightarrow$$
 Ca(NO₃)₂(s)

C Ca(g) +
$$N_2(g)$$
 + $3O_2(g)$ \rightarrow Ca(NO_3)₂(s)

D Ca(s) +
$$N_2(g) + 3O_2(g) \rightarrow Ca(NO_3)_2(s)$$

14. Which of the following reactions will have a positive ΔS° value?

$$A \quad 2H_2(g) + C_2H_2(g) \rightarrow C_2H_6(g)$$

$$B \quad C_2H_4(g) \,+\, Br_2(\ell) \,\rightarrow\, C_2H_4Br_2(\ell)$$

C LiH(s) +
$$H_2O(\ell) \rightarrow LiOH(aq) + H_2(g)$$

D
$$Ca(OH)_2(aq) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(\ell)$$

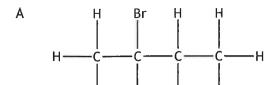
15. Pyridine has the following structure.



The number of $\boldsymbol{\sigma}$ bonds in a molecule of pyridine is

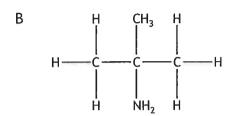
- A 3
- B 6
- C 11
- D 12
- 16. Which of the following statements is not true for both ethoxyethane and butan-1-ol?
 - A They can both be made by nucleophilic substitution from a haloalkane.
 - B They both have hydrogen bonds between their molecules.
 - C They both have the same gram formula mass.
 - D They are both flammable.

17. Which of the following shows two molecules that can both be classed as tertiary?



ĊΗ3

$$H \longrightarrow C \longrightarrow N \longrightarrow C \longrightarrow C \longrightarrow H$$
 $H \longrightarrow C_2H_5 \longrightarrow H$



$$H \longrightarrow C \longrightarrow C \longrightarrow N \longrightarrow C \longrightarrow H$$
 $H \longrightarrow H \longrightarrow H$
 $H \longrightarrow C \longrightarrow H$

18.

In this reaction

- A addition takes place
- B NO₃ acts as a nucleophile
- C NO₂⁺ acts as an electrophile
- D benzene acts as an electrophile.

19. Geometric isomers

- A are mirror images of each other
- B always contain a carbon-carbon double bond
- C have the same physical and chemical properties
- D have two different groups attached to each of the carbon atoms of the bond with restricted rotation.
- **20.** Which of the following aqueous solutions contains the greatest number of negatively charged ions?
 - A 200 cm 3 0.12 mol l $^{-1}$ FeCl $_{3}$ (aq)
 - B $300 \text{ cm}^3 0.15 \text{ mol l}^{-1} \text{ KI(aq)}$
 - C $400 \text{ cm}^3 0.10 \text{ mol l}^{-1} \text{ Zn(NO}_3)_2(\text{aq})$
 - D 500 cm³ 0.10 mol l⁻¹ Na₂SO₄(aq)
- 21. Which type of electromagnetic radiation is absorbed to produce a ¹H NMR spectrum?
 - A Radio waves
 - B Ultraviolet
 - C Infrared
 - D Visible

- **22.** Which of the following could be used as a primary standard in the standardisation of a solution of dilute hydrochloric acid?
 - A Sodium hydroxide
 - B Sodium carbonate
 - C Potassium dichromate
 - D Potassium hydrogen phthalate
- 23. The melting point of an impure substance was determined to be 132°C 135°C. After purification, the melting point was
 - A lower and over a wider range
 - B lower and over a narrower range
 - C higher and over a wider range
 - D higher and over a narrower range.
- 24. The concentration of an orange solution of carotene was determined by colorimetry.

An appropriate filter was selected and a blank determination carried out using the solvent only.

Which line in the table shows an appropriate filter and solvent for this colorimetric determination?

	Colour of filter	Solvent for blank determination	
Α	green-blue	water	
В	green-blue	hexane	
С	orange	water	
D	orange	hexane	

- 25. The process of recrystallisation is described by the following steps.
 - 1. Dissolve the impure sample in a minimum volume of hot solvent.
 - 2. Carry out hot filtration of the resulting mixture.
 - 3. Cool the filtrate slowly to allow crystals to form.
 - 4. Filter, wash and dry the pure crystals.

Which line in the table correctly identifies the steps at which the insoluble and soluble impurities are removed?

	Removal of insoluble impurities	Removal of soluble impurities
Α	2	1
В	3	2
С	2	4
D	4	2

[END OF SECTION 1. NOW ATTEMPT THE QUESTIONS IN SECTION 2 OF YOUR QUESTION AND ANSWER BOOKLET.]

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Mark

X813/77/01

Section 1 — Answer grid and Section 2

THURSDAY, 1 MAY 9:00 AM – 12:00 NOON



Fill in these boxes and read what is printed below.					
Full name of centre			Town	Town	
Forename(s)		Sur	name	Number of seat	
Date of birth	1			-	
Day	Month	Year	Scottish candidate number		

You may refer to the Chemistry Data Booklet for Higher and Advanced Higher.

Total marks — 110

SECTION 1 — 25 marks

Attempt ALL questions.

Instructions for the completion of Section 1 are given on page 02.

SECTION 2 — 85 marks

Attempt ALL questions.

Write your answers clearly in the spaces provided in this booklet. Additional space for answers and rough work is provided at the end of this booklet. If you use this space you must clearly identify the question number you are attempting. Any rough work must be written in this booklet. You should score through your rough work when you have written your final copy.

Use blue or black ink.

Before leaving the examination room you must give this booklet to the Invigilator; if you do not, you may lose all the marks for this paper.





- Aspartic acid can be used to date material from living things.
 Only one optical isomer of aspartic acid is found in living things. This is called L-aspartic acid.
 - (a) State what is meant by the term optical isomers.

1

(b) After living things die, L-aspartic acid converts to the other optical isomer, called D-aspartic acid. An equilibrium is established.

Draw a structural formula for the optical isomer, D-aspartic acid.

1

L-aspartic acid

D-aspartic acid

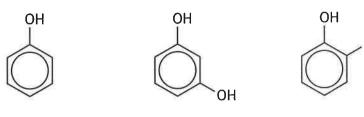
(c) Compare the effect that these isomers have on plane-polarised light.

1

(d) State the name given to an equilibrium mixture with equal concentrations of L-aspartic acid and D-aspartic acid.

1

2. Phenols are alcohols with at least one hydroxyl group bonded to a benzene ring. The structures of some phenols are shown.



phenol

3-hydroxyphenol

2-methylphenol

(a) The carbon atoms in the benzene ring are sp² hybridised giving rise to a π molecular orbital.

State how the π molecular orbital is formed.

(continued)

(b) Phenols are weak acids.

The table shows the $\mathrm{p}K_{\mathrm{a}}$ values of different phenols at 298 K.

Name of phenol	р <i>К</i> _а
phenol	9.99
3-hydroxyphenol	9.15
3,5-dihydroxyphenol	8.45
2-methylphenol	10.29
4-methylphenol	10.26
2-ethylphenol	10.20
4-ethylphenol	10.00

(i) From the information in the table, state one conclusion about the structure of phenols and acid strength.

1

(ii) Calculate the concentration of hydronium ions, H_3O^+ , in mol l^{-1} , in a 0.150 mol l^{-1} aqueous solution of 2-methylphenol.

3



2. (continued)

(c) 3-hydroxyphenol can be used to synthesise the indicator resazurin.

When used as a pH indicator, resazurin changes colour from violet to orange.

(i) Explain fully, in terms of the conjugation in the molecule, why resazurin changes colour from violet to orange.

resazurin

(ii) The K_{ln} value for resazurin = 7.9×10^{-6} . Calculate the pH range over which this colour change occurs.

3. Chloride ions are found in seawater.

A 50.0 cm³ sample of seawater was diluted with deionised water to 100 cm³ in a standard flask. 20.0 cm³ of the diluted seawater was transferred to a conical flask using a pipette.

Silver(I) nitrate solution was added to the sample to produce a precipitate of silver(I) chloride. When precipitation was complete, the mass of precipitate was determined.

(a) State the name of this type of quantitative analysis.

1

(b) Suggest what should be done to ensure the precipitation reaction has gone to completion.

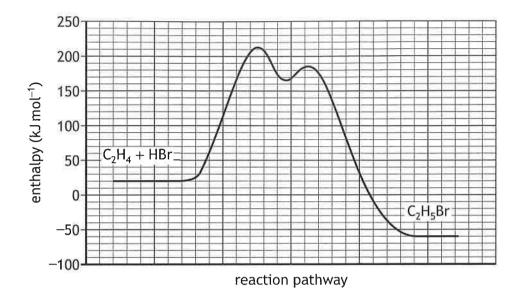
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(c) The mass of the precipitate was determined to be 0.779 g. Calculate the concentration of chloride ions, in gl^{-1} , in the undiluted seawater. 2



page 09

- 4. Alkenes can undergo addition reactions.
 - (a) The graph shows how enthalpy changes during the reaction of ethene with hydrogen bromide.



(i) (A) Draw a structural formula for the intermediate formed in this reaction.

(B) When the intermediate is formed there is a temporary increase in stability.

Draw an \boldsymbol{X} on the line of the graph above to suggest where the intermediate is formed.

(An additional graph, if required, can be found on page 31.)

1

4. (a) (continued)

MARKS DO NOT WRITE IN THIS MARGIN

- (ii) This reaction is feasible at room temperature and has a negative value for entropy change, ΔS .
 - (A) Explain why the second law of thermodynamics is obeyed even though the reaction decreases in entropy.

1

(B) Using information from the graph, calculate the enthalpy change, ΔH , in kJ mol⁻¹, for this reaction.

1

(C) The entropy change, ΔS , for this reaction is $-132 \, \mathrm{J \, K^{-1} \, mol^{-1}}$. Calculate the temperature, in K, above which this reaction will no longer be feasible.

2

- (b) Propene undergoes an addition reaction with hydrogen bromide to form two isomeric products.
 - (i) The product that obeys Markovnikov's rule is known as the major product.

Explain, in terms of the reaction intermediate, why more of this product forms.

1



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4. (b) (continued)

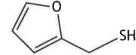
(ii) Propene can undergo other addition reactions that form two isomeric compounds. Some other unsaturated substances can also undergo addition reactions that produce a mixture of compounds including structural, geometric and optical isomers.

Using your knowledge of chemistry, discuss the mixture of compounds that could be produced in addition reactions and how these compounds could be isolated.

5. Coffee is a drink made from roasted coffee beans.

The taste of coffee comes from a mixture of aroma and flavour molecules. These molecules can be identified using different techniques.

(a) A distinctive aroma molecule produced during coffee roasting is 2-furanmethanethiol.



2-furanmethanethiol

(i) Write the molecular formula for 2-furanmethanethiol.

1

1

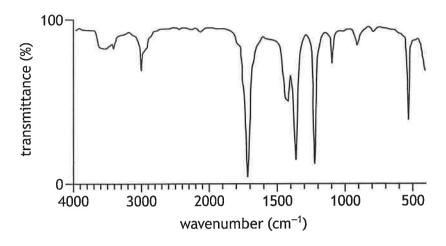
(ii) The mass spectrum of 2-furanmethanethiol has a peak at m/z 33.

Suggest a possible ion fragment that may be responsible for this peak.

5. (continued)

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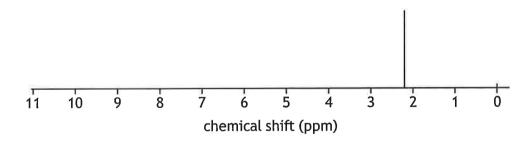
- (b) Compounds A and B are also found in roasted coffee beans and they have the molecular formula C_3H_6O .
 - (i) The infrared spectrum of A is given below.



Identify the bond responsible for the peak at 1710 cm⁻¹.

1

(ii) The low resolution ¹H NMR spectrum for compound **A** is given below.



(A) Draw a structural formula for compound A.

1

(B) Compound B contains the same functional group as compound A. Predict the number of peaks that would be found on the ¹H NMR spectrum of compound B.

MARKS DO NOT WRITE IN THIS MARGIN

2

1

5. (continued)

(c) Elemental analysis was carried out on a coffee flavour compound containing only carbon, hydrogen and oxygen.

Complete combustion of a 1.00 g sample of this compound produced 1.47 g of carbon dioxide and 0.60 g of water. No other product was formed.

(i) Calculate the masses of carbon and hydrogen in the original sample and therefore determine the mass, in g, of oxygen present.

(ii) Calculate the empirical formula of this compound.

5. (continued)

(d) Coffee contains the compound caffeine, which can be isolated by solvent extraction using dichloromethane.

A student carried out an investigation into the caffeine content of coffee.

Ground coffee was soaked in hot water to dissolve the caffeine. Dichloromethane was then added to extract the caffeine from this aqueous solution.

(i) Outline the steps that should have been carried out to extract the maximum mass of caffeine from the aqueous caffeine solution.

5. (d) (continued)

(ii) The solvent extraction relies on the following equilibrium.

In an experiment to determine the equilibrium constant, 100 cm³ of aqueous caffeine solution containing 0.150 g of caffeine was mixed with an equal volume of dichloromethane.

The mass of caffeine in the dichloromethane was found to be 0.136 g.

Calculate the value of the equilibrium constant for this extraction.

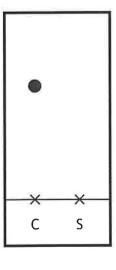
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(iii) The student carried out thin-layer chromatography on a sample of the extracted caffeine and determined that the sample was impure.

Complete the diagram of the thin-layer chromatogram showing a possible result for the impure sample.

1

(An additional diagram, if required, can be found on page 31.)



C = pure caffeine

S = student sample



- 6. Iron deficiency can be treated using iron tablets.
 - (a) The mass of iron in a tablet was determined by titration with a 0.010 mol l⁻¹ solution of potassium permanganate.
 - (i) Describe fully how a $0.010 \text{ mol } l^{-1}$ solution of potassium permanganate should be prepared in a 500 cm^3 volumetric flask by accurately diluting a $0.200 \text{ mol } l^{-1}$ solution.

2

(ii) $250 \ \text{cm}^3$ of an $\text{Fe}^{2+}(\text{aq})$ solution was prepared using five iron tablets.

 $25.0~\text{cm}^3$ samples of this solution were titrated with $0.010~\text{mol}\,\text{l}^{-1}$ acidified potassium permanganate solution.

$$MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(\ell) + 5Fe^{3+}(aq)$$

The average titre volume was 11.8 cm³.

Calculate the mass, in mg, of iron in one iron tablet.

- (a) (continued)
 - (iii) Dilute sulfuric acid is used to acidify potassium permanganate solutions. If dilute hydrochloric acid is used, chlorine gas is produced.

Suggest why chlorine gas is produced.

1

(b) When the tablet dissolves, a green solution containing hexaaquairon(II) ions, [Fe(OH₂)₆]²⁺, is formed.

(i) Explain fully why a solution of hexaaquairon(II) ions is green.

2

(ii) In an aqueous solution of hexaaquairon(II) ions, $[Fe(OH_2)_6]^{2+}$, the following equilibrium exists.

$$[Fe(OH_2)_6]^{2+} + H_2O \implies [FeOH(OH_2)_5]^+ + H_3O^+$$

This equation shows that water is amphoteric.

Explain, with reference to the equation, why water can be described as amphoteric.

1

Parkinson's disease is caused by a lack of dopamine in the brain.
 One of the main treatments for Parkinson's disease contains levodopa.

$$HO$$
 OH
 OH
 OH

levodopa

(a) Levodopa, $C_9H_{11}NO_4$, can be converted to dopamine, $C_8H_{11}NO_2$, as shown.

Identify compound X.

7. (continued)

MARKS | DO NOT WRITE IN

WRITE IN THIS MARGIN

- (b) Some levodopa can be broken down by an enzyme before it reaches the brain.
 - (i) An adult with a blood volume of 4.35 litres took a tablet containing 125 mg of levodopa.

Calculate the concentration, in mol l⁻¹, of levodopa remaining in the blood after 29.5% of it has been broken down.

The GFM of levodopa is 197 g.

2

(ii) To prevent levodopa being broken down, a drug called carbidopa can be given.

Carbidopa binds to the enzyme instead of levodopa.

carbidopa

(A) State the classification of drug used to describe carbidopa.

1

(B) Carbidopa can bind to enzymes through hydrogen bonds.

A hydrogen bond acceptor is an atom with a lone pair of electrons that can form a hydrogen bond.

Determine the number of hydrogen bond acceptors in carbidopa.

1



Camphorquinone is used in dentistry as part of a process to form a protective coating around teeth.

During the process camphorquinone undergoes homolytic fission to generate free radicals.

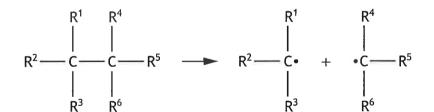
(a) Camphorquinone generates free radicals when exposed to radiation with a wavelength of 471 nm.

Calculate the energy, in kJ mol⁻¹, associated with this wavelength.

2

(b) (i) Complete the equation, using curly arrow notation, to show a carbon-carbon bond undergoing homolytic fission to create two free radicals.

(An additional equation, if required, can be found on page 32.)



(ii) State why homolytic fission is not commonly used in organic synthesis.

1

MARKS DO NOT WRITE IN THIS MARGIN

9. A student stated that orbital box notation is the most useful way of representing electrons and their arrangements.

Using your knowledge of chemistry, discuss how different ways of representing electrons allow chemists to explain chemical concepts and reactions.

3



- 10. Gold can be separated from rocks using a series of chemical reactions.
 - (a) In the first reaction a gold complex ion, $[Au(CN)_2]^-$, is formed.

$$2Au(s) + 4NaCN(aq) + \frac{1}{2}O_2(g) + H_2O(\ell) + 2OH^{-}(aq) \rightarrow 2[Au(CN)_2]^{-}(aq) + 4NaOH(aq)$$

- (i) Calculate the minimum volume of 0.0550% NaCN(aq) that would be required to react with 1.00 g of Au in this step.
- 2

- (ii) (A) The coordination number of gold in $[Au(CN)_2]^-$ is 2. State what is meant by the term coordination number.
- 1

- (B) When naming complex ions, the Latin term for gold ions, aurate, can be used.
 - State the name of the complex ion, $[Au(CN)_2]^-$.



10. (continued)

- (b) In the second reaction the complex ion, $[Au(CN)_2]^-$, is changed into gold metal, Au, which then precipitates from the solution.
 - (i) Name this type of reaction.

1

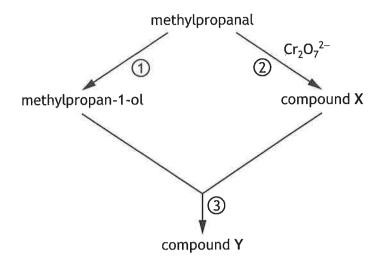
(ii) Describe the steps required to produce a pure, dry sample of gold metal from the reaction mixture.

2

(iii) Rock from one gold mine contains 21.5 ppm of gold.Calculate the mass of rock, in kg, that would produce 1.00 g of gold if the percentage yield for the entire process is 91.5%.

2

- Carbonyl compounds can take part in a variety of chemical reactions.
 - (a) The following reaction scheme involves methylpropanal.



- (i) Name a reagent that could be used to carry out step 1.
- 1

(ii) Name the type of reaction taking place in step (2).

- 1
- (iii) In step (3) methylpropan-1-ol and compound X react to produce compound Y.

Draw a structural formula for compound Y.

11. (continued)

(b) (i) Aldol reactions involve two molecules of aldehydes or ketones reacting together.

An aldol reaction can only take place if the aldehyde or ketone has an α -hydrogen atom. An α -hydrogen atom is bonded to a carbon atom next to the carbonyl group.

(A) Circle an α -hydrogen atom on the structure of pentanal shown below.

1

(An additional structure, if required, can be found on page 32.)

(B) Draw a structural formula for an isomer of pentanal that contains a carbonyl group but cannot take part in an aldol reaction.

1

11. (b) (continued)

(ii) (A) The aldol reaction between two molecules of ethanal is shown.

Draw a structural formula for the product formed in the aldol reaction between two molecules of propanone.

1

(B) When butanone takes part in an aldol reaction the two isomeric compounds shown below are formed.

4-hydroxy-3,4-dimethylhexan-2-one

compound Z

(I) Suggest why two isomers are formed.

1

(II) Name compound Z.

- Sulfur is formed in the reaction between sodium thiosulfate and hydrochloric acid.
 - (a) In an experiment to determine the rate equation for this reaction, a student obtained the following data.

Experiment	[Na ₂ S ₂ O ₃ (aq)] (mol l ⁻¹)	[HCl(aq)] (mol l ⁻¹)	Initial rate (mol l ⁻¹ s ⁻¹)
1	5.00 × 10 ⁻²	2.00×10^{-1}	6.55×10^{-3}
2	1.00 × 10 ⁻¹	2.00 × 10 ⁻¹	1.31 × 10 ⁻²
3	1.00×10^{-1}	4.00×10^{-1}	1.31 × 10 ⁻²

(i) Determine the order of reaction with respect to $Na_2S_2O_3$.

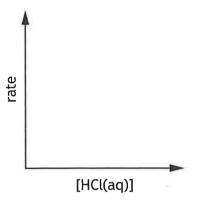
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(ii) The reaction is zero order with respect to HCl.

Complete the diagram below to show the effect of changing the concentration of HCl on the reaction rate.

(An additional diagram, if required, can be found on page 33.)



(iii) Write the overall rate equation for the reaction.

1

(iv) Calculate the value for the rate constant, k, including the appropriate units.

2

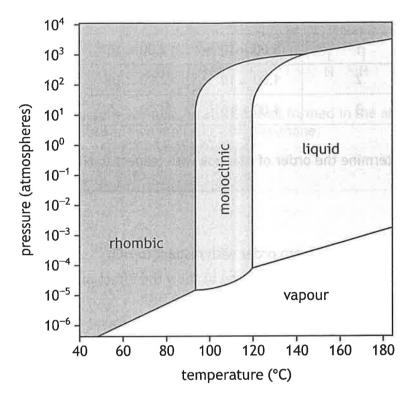
1

1

1

(b) Sulfur, S₈, can exist in four forms — liquid, vapour, and two solid forms (rhombic and monoclinic).

The phase diagram below shows the forms of S_8 that exist at different temperatures and pressures.



- (i) Determine the form in which S_8 exists at a temperature of 100°C and a pressure of 10^0 atmospheres.
- (ii) A triple point on a phase diagram shows the temperature and pressure at which three forms exist in equilibrium with each other.
 - (A) Circle the triple point on the phase diagram where rhombic, monoclinic and vapour forms exist in equilibrium with each other.(An additional diagram, if required, can be found on page 33.)
 - (B) Determine the three forms of S₈ that can never exist in equilibrium with each other.

[END OF QUESTION PAPER]

