



National
Qualifications

X813/77/02

Chemistry
Section 1 — Questions

Duration — 3 hours

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

- According to the aufbau principle, electrons fill the atomic orbitals of potassium in the order
 - 1s 2s 2p 3s 3p 3d
 - 1s 2s 2p 3s 3d 3p
 - 1s 2s 2p 3s 3p 4s
 - 1s 2s 2p 3s 3d 4s.
- Which of the following is **not** a possible quantum number for an outer electron in an atom of oxygen, in its ground state?
 - $l = 0$
 - $l = 1$
 - $m_l = 0$
 - $m_l = 1$
- The number of unpaired electrons in a chromium atom, in its ground state, is
 - 1
 - 4
 - 5
 - 6.

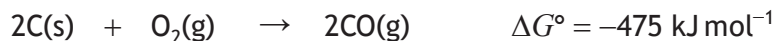
4.

Substance	K_a
X	1.85×10^{-11}
Y	1.57×10^{-10}
Z	1.61×10^{-5}

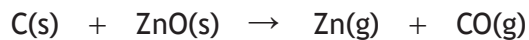
Based on information in the table,

- X is less basic than Y
- X is more acidic than Z
- Y is more basic than Z
- Y is less acidic than X.

5. At 1400 K



For the reaction



the standard free energy change, ΔG° , in kJ mol^{-1} , at 1400 K is

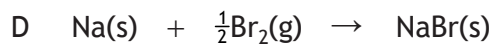
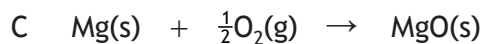
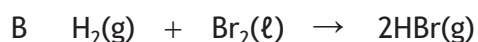
A -67.5

B $+67.5$

C -135

D $+135$

6. Which of the following represents the enthalpy of formation of a compound?



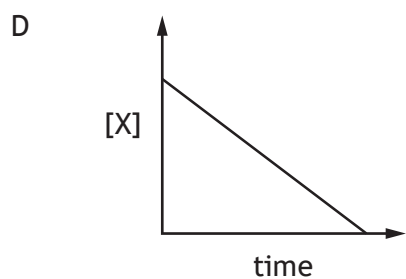
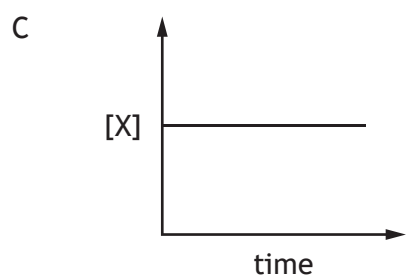
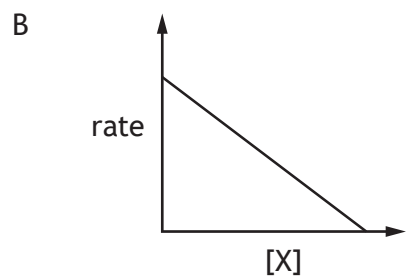
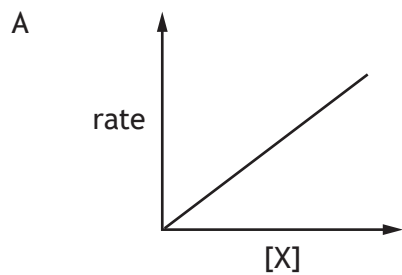
7. Kinetic data for the reaction between bromate ions and bromide ions in the presence of hydrogen ions is shown below.

Experiment	$[\text{BrO}_3^-]$ (mol l^{-1})	$[\text{Br}^-]$ (mol l^{-1})	$[\text{H}^+]$ (mol l^{-1})	Initial rate ($\text{mol l}^{-1} \text{s}^{-1}$)
1	0.1	0.1	0.1	8.0×10^{-4}
2	0.2	0.1	0.1	1.6×10^{-3}
3	0.2	0.2	0.1	3.2×10^{-3}
4	0.1	0.1	0.2	3.2×10^{-3}

Which line in the table shows the order of reaction for each reactant?

	BrO_3^-	Br^-	H^+
A	1	1	0
B	1	1	2
C	1	2	2
D	2	2	0

8. Which of the following graphs would be obtained for a reaction that is zero order with respect to reactant X?



9. For the reaction



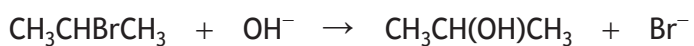
the rate equation is

$$\text{rate} = k[P]^2[Q].$$

Which of the following shows a possible mechanism for this reaction?

- A $P + 2Q \rightarrow X$ slow
 $X + P \rightarrow R$ fast
- B $2P + Q \rightarrow X$ slow
 $X + Q \rightarrow R$ fast
- C $P + 2Q \rightarrow X$ fast
 $X + P \rightarrow R$ slow
- D $2P + Q \rightarrow X$ fast
 $X + Q \rightarrow R$ slow

10. For the reaction

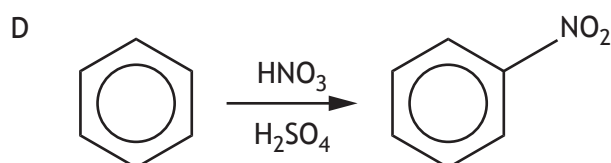
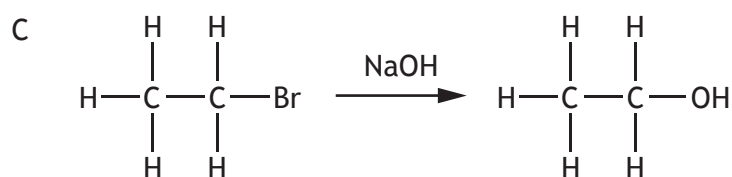
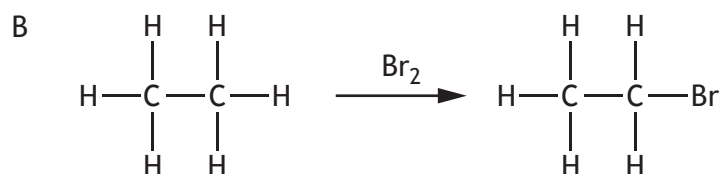
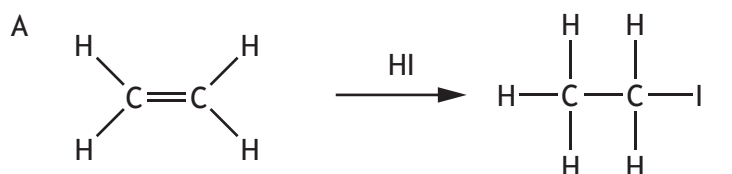


which line in the table is correct?

	OH^-	$\text{CH}_3\text{CH(OH)CH}_3$
A	nucleophile	secondary
B	electrophile	secondary
C	nucleophile	tertiary
D	electrophile	tertiary

[Turn over

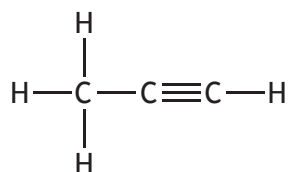
11. Which of the following reactions involves homolytic fission?



12. Which of the following has the fewest sigma bonds?

- A Hexane
- B Hex-1-ene
- C Hex-1-yne
- D Cyclohexane

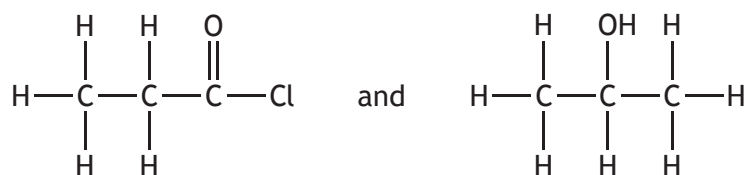
13. Propyne undergoes addition reactions.



Assuming the reaction between propyne and hydrogen chloride, HCl, follows Markovnikov's rule, a possible product could be

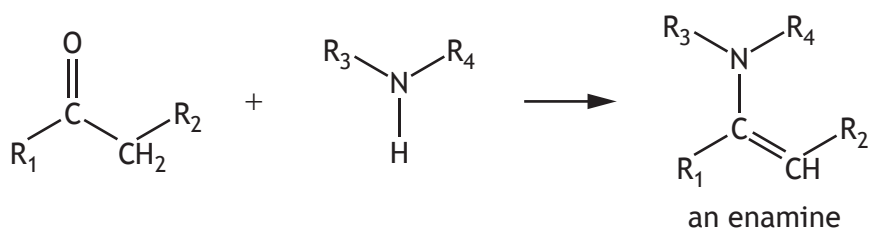
- A 1-chloropropane
- B 2-chloropropane
- C 1-chloropropene
- D 2-chloropropene.

14. An ester is formed by a condensation reaction between

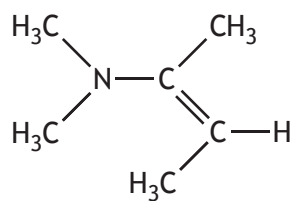


What are the products of this reaction?

- A $(\text{CH}_3)_2\text{CHCOOCH}_2\text{CH}_3 + \text{H}_2\text{O}$
 B $\text{CH}_3\text{CH}_2\text{COOCH}(\text{CH}_3)_2 + \text{H}_2\text{O}$
 C $\text{CH}_3\text{CH}_2\text{COOCH}(\text{CH}_3)_2 + \text{HCl}$
 D $(\text{CH}_3)_2\text{CHCOOCH}_2\text{CH}_3 + \text{HCl}$
15. Secondary amines react with some carbonyl compounds to form unsaturated amines known as enamines.



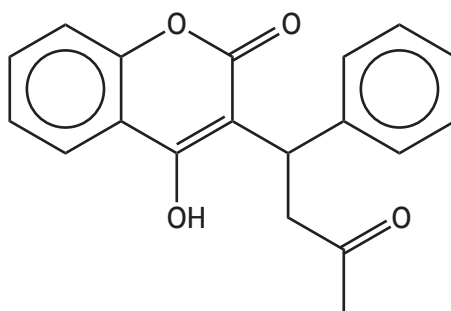
Which carbonyl compound would react with $(\text{CH}_3)_2\text{NH}$ to form the enamine with the following structure?



- A Propanal
 B Propanone
 C Butanal
 D Butanone

[Turn over

16.

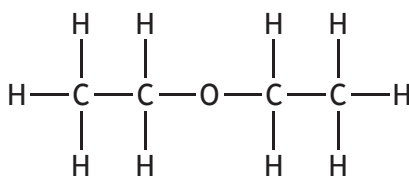


warfarin

Which of the following functional groups is **not** present in warfarin?

- A Carbonyl
- B Carboxyl
- C Hydroxyl
- D Phenyl

17. Which line in the table is correct for a high resolution ^1H NMR spectrum of ethoxyethane?

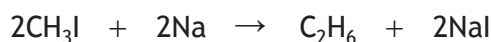


	Number of ^1H environments	Observed splitting patterns
A	2	triplet, quartet
B	2	doublet, triplet
C	4	doublet, triplet
D	4	triplet, quartet

18. Which of the following amines is likely to have the lowest boiling point?

- A $\text{C}_4\text{H}_9\text{NH}_2$
- B $\text{C}_3\text{H}_7\text{NHCH}_3$
- C $\text{C}_2\text{H}_5\text{NHC}_2\text{H}_5$
- D $\text{C}_2\text{H}_5\text{N}(\text{CH}_3)_2$

19. Ethane can be prepared by adding iodomethane to sodium.



When a mixture of iodomethane and iodoethane is used, the only alkane(s) produced will be

- A propane
 - B ethane and butane
 - C ethane, propane and butane
 - D methane, ethane, propane and butane.
20. Which of the following will react with lithium aluminium hydride but **not** react with Tollens' reagent?
- A CH_3COCH_3
 - B $\text{CH}_3\text{CH}_2\text{CHO}$
 - C $\text{CH}_3\text{OCH}_2\text{CH}_3$
 - D $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
21. Two substances were analysed and found to have the empirical formula CH_3O . From this information it can be concluded that the substances
- A are isomers of each other
 - B have the same molecular mass
 - C have the same functional groups
 - D have the same percentage by mass of carbon.

[Turn over

22. The wavelength associated with a spectral line of hydrogen can be determined using the following relationship.

$$\frac{1}{\lambda} = R \left(\frac{1}{(n_1)^2} - \frac{1}{(n_2)^2} \right)$$

Where,

λ is wavelength in m

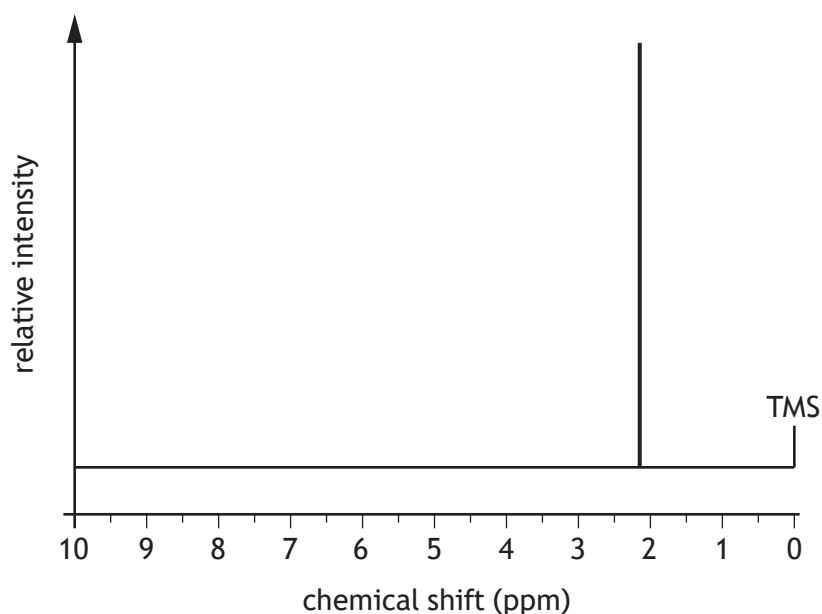
R is Rydberg constant ($1.1 \times 10^7 \text{ m}^{-1}$)

n_1 is the energy level to which the electron falls

n_2 is the energy level from which the electron falls.

When an electron falls from the ninth energy level to the second energy level, the wavelength, in m, associated with the spectral line is

- A 6.55×10^{-7}
 B 3.83×10^{-7}
 C 2.34×10^{-7}
 D 1.86×10^{-7}
23. The low resolution ^1H NMR spectrum for an organic compound is shown below.



Which of the following compounds gave this spectrum?

- A Propane
 B Propanal
 C Propanone
 D Propan-1-ol

24. Which of the following contains the greatest number of negatively charged ions?

- A 400 cm³ of 0.10 mol l⁻¹ Zn(NO₃)₂(aq)
- B 500 cm³ of 0.10 mol l⁻¹ Na₂SO₄(aq)
- C 250 cm³ of 0.12 mol l⁻¹ BaCl₂(aq)
- D 300 cm³ of 0.15 mol l⁻¹ KI(aq)

25. The covalent bond in a halogen molecule can be broken to produce halogen atoms when exposed to light of appropriate energy.

The bond enthalpy is the energy required to break one mole of bonds in a diatomic molecule.

Which halogen would require a minimum of 3.22×10^{-22} kJ to break one covalent bond?

- A Fluorine
- B Chlorine
- C Bromine
- D Iodine

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

FOR OFFICIAL USE



National
Qualifications

Mark

X813/77/01

Chemistry
Section 1 — Answer grid
and Section 2

Duration — 3 hours



* X 8 1 3 7 7 0 1 *

Fill in these boxes and read what is printed below.

Full name of centre

Town

Forename(s)

Surname

Number of seat

Date of birth

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.



* X 8 1 3 7 7 0 1 0 1 *

SECTION 2 — 85 marks

Attempt ALL questions

1. Fireworks contain metal compounds and produce coloured light when ignited.

(a) Explain, in terms of electrons, how coloured light is produced when fireworks are ignited.

1

(b) A firework produced coloured light with energy of 193 kJ mol^{-1} .

(i) Calculate the wavelength, in nm, of this coloured light.

2

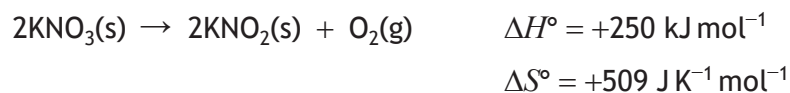
(ii) Identify the metal most likely to produce this coloured light.

1



1. (continued)

- (c) Fireworks also contain potassium nitrate, which decomposes when heated to produce oxygen.



This reaction obeys the second law of thermodynamics.

- (i) State the second law of thermodynamics.

1

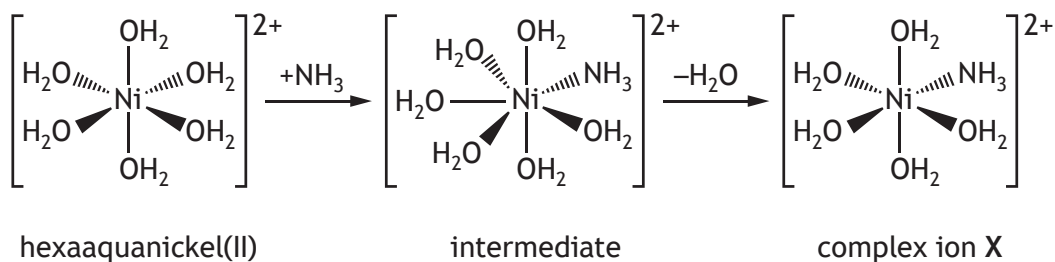
- (ii) Calculate the temperature, in K, above which this reaction becomes feasible.

2



* X 8 1 3 7 7 0 1 0 6 *

2. Hexaaquanickel(II) can react with ammonia forming complex ion X.
A proposed mechanism for this reaction is shown.



- (a) State the shape of the hexaaquanickel(II) ion.

1

- (b) The intermediate has a pentagonal bipyramidal arrangement of bonds around the nickel.

State the co-ordination number of nickel in the intermediate.

1

- (c) Complex ion X is formed when a water molecule is removed from the intermediate.

- (i) Name complex ion X.

1

- (ii) State why ammonia and water are classed as monodentate ligands.

1



* X 8 1 3 7 7 0 1 0 8 *

2. (continued)

- (d) In an experiment to determine the rate equation for this reaction, some of the data obtained by a student is shown below.

$[\text{Ni}(\text{OH}_2)_6]^{2+}$ (mol l ⁻¹)	$[\text{NH}_3]$ (mol l ⁻¹)	Initial rate (mol l ⁻¹ s ⁻¹)
0.10	0.25	1.3×10^2

The student proposed the following rate equation.

$$\text{rate} = k [\text{Ni}(\text{OH}_2)_6]^{2+} [\text{NH}_3]$$

- (i) Determine the overall order for this reaction.

1

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

2



* X 8 1 3 7 7 0 1 0 9 *

3. Benzene is a colourless, aromatic compound containing a conjugated system of pi (π) bonds.



benzene

- (a) (i) State the type of hybridised orbitals found in benzene.

1

- (ii) Explain how a pi bond is formed.

1

- (iii) Colour arises in some aromatic compounds due to absorption of visible light.

Explain why the conjugated system in benzene results in absorption of ultraviolet light and not visible light.

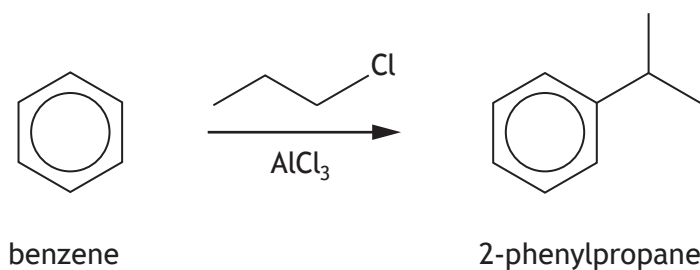
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* X 8 1 3 7 7 0 1 1 0 *

3. (continued)

(b) Benzene can react with 1-chloropropane to form 2-phenylpropane.



- (i) Name the type of chemical reaction taking place. 1
- (ii) Write the molecular formula for 2-phenylpropane. 1
- (iii) The reaction is thought to proceed via the carbocation rearrangement shown below.



Suggest why this rearrangement takes place. 1

[Turn over



4. Limestone contains calcium carbonate and can be used to produce slaked lime, a component of cement.

The calcium carbonate content of limestone can be determined by volumetric analysis.

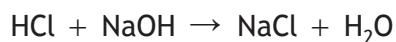
- (a) State why a back titration is necessary for this volumetric analysis.

1

- (b) 1.30 g of limestone was reacted with 25.0 cm³ of 1.50 mol l⁻¹ hydrochloric acid. The resulting solution was transferred to a 100 cm³ volumetric flask and made up to the mark with deionised water.



25.0 cm³ samples of this solution were then titrated against 0.300 mol l⁻¹ sodium hydroxide.



Titration	Titre volume (cm ³)
1	10.1
2	10.7
3	10.2

- (i) Calculate the number of moles of hydrochloric acid that reacted with the calcium carbonate in the limestone.

2



4. (b) (continued)

- (ii) Only limestone with a calcium carbonate content greater than 95% can be used to produce slaked lime.

Determine whether this limestone sample could be used to produce slaked lime.

(Clearly show your working for the calculation.)

2

[Turn over]



* X 8 1 3 7 7 0 1 1 3 *

4. (continued)

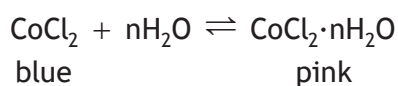
- (c) Using your knowledge of chemistry, discuss possible sources of error in this volumetric analysis and how the accuracy of the final percentage could be checked.

3



* X 8 1 3 7 7 0 1 1 4 *

5. Cobalt chloride changes colour in the presence of water.



- (a) (i) Write the electronic configuration, in terms of s, p and d orbitals, for the cobalt ion in blue CoCl_2 .

1

- (ii) Determine the oxidation number for the cobalt ion in pink $\text{CoCl}_2 \cdot n\text{H}_2\text{O}$.

1

- (b) In a gravimetric analysis to determine the value of n , a weighed sample of $\text{CoCl}_2 \cdot n\text{H}_2\text{O}$ was converted into CoCl_2 .

- (i) Describe fully an experimental procedure that could be used to carry out this gravimetric analysis.

2



5. (b) (continued)

- (ii) In the gravimetric analysis, 0.372 g of $\text{CoCl}_2 \cdot n\text{H}_2\text{O}$ was converted into 0.204 g of CoCl_2 .

Calculate the value of n .

(Clearly show your working for the calculation.)

2

- (c) The concentration of cobalt ions in a cobalt chloride solution can be determined by complexometric titration.

- (i) Suggest a suitable complexometric reagent that could be used in this titration.

1

- (ii) Suggest another analytical technique that could be used to determine the concentration of cobalt ions in a cobalt chloride solution.

1



* X 8 1 3 7 7 0 1 1 7 *

6. A sample of compound X was analysed to determine its structural formula.

MARKS

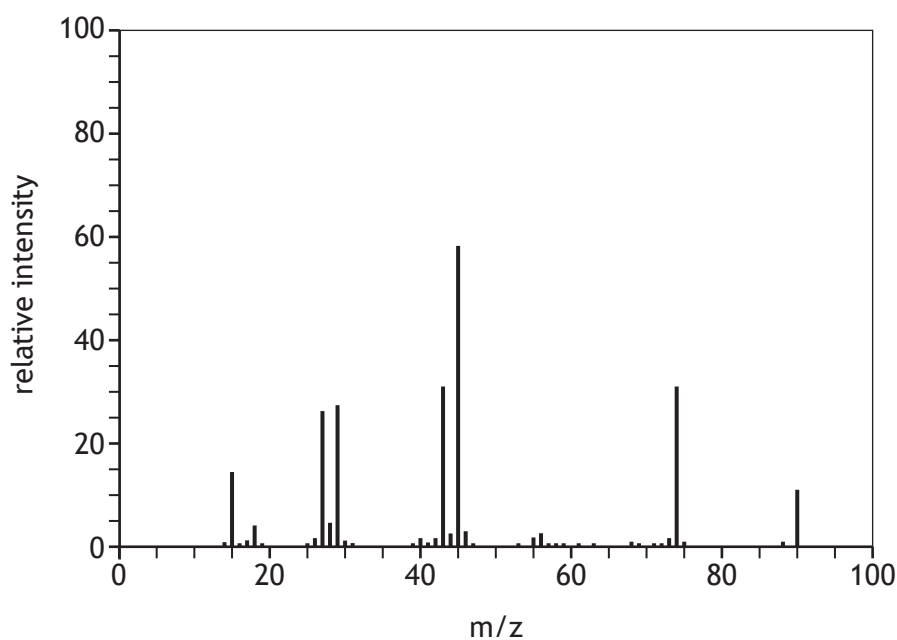
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- (a) Elemental microanalysis showed that compound X has a composition, by mass, of 40.0% carbon and 6.70% hydrogen.

Show, by calculation, that the empirical formula of X is CH_2O .

1

- (b) A simplified mass spectrum of compound X is shown below.



- (i) Write the molecular formula of compound X.

1



* X 8 1 3 7 7 0 1 1 8 *

6. (b) (continued)

- (ii) Suggest a possible ion fragment that may be responsible for the peak at m/z 45.

1

- (c) Compound X was found to rotate plane polarised light.
Considering all the evidence, draw a structural formula for compound X.

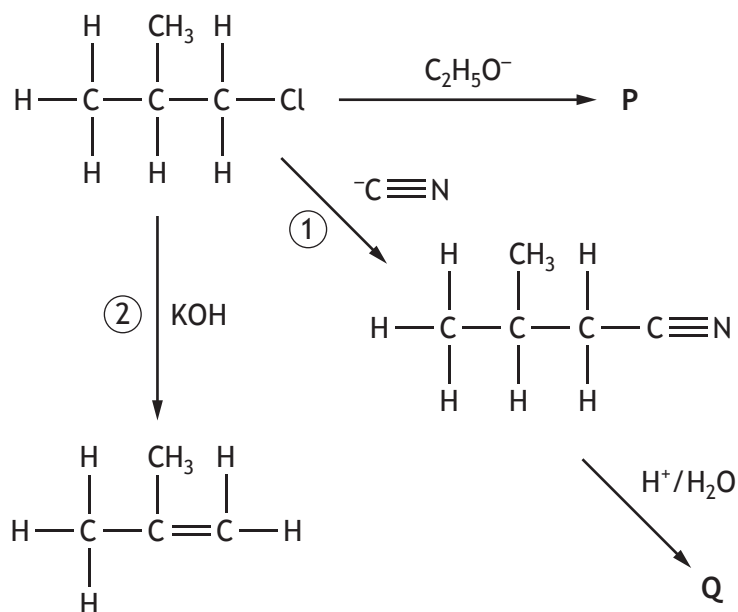
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[Turn over



* X 8 1 3 7 7 0 1 1 9 *

7. Haloalkanes are useful starting materials in organic chemistry.



(a) Draw a structural formula for P.

1

(b) State the class of compound to which Q belongs.

1



* X 8 1 3 7 7 0 1 2 0 *

7. (continued)

- (c) Using structural formulae and curly arrow notation, outline the most likely mechanism for the formation of the nitrile in reaction ①.

2

- (d) (i) Suggest a solvent for use in reaction ②.

1

- (ii) Assuming the percentage yield for reaction ② was 60.4%, calculate the volume of methylpropene produced from 1.85 g of 1-chloromethylpropane.

Take the molar volume of methylpropene to be 23.0 l mol^{-1} .

3



* X 8 1 3 7 7 0 1 2 1 *

8. A buffer solution was prepared by dissolving sodium ethanoate in dilute ethanoic acid.

(a) Write a formula for the conjugate base present in this buffer solution.

1

(b) 250 cm³ of buffer solution was prepared by dissolving 4.10 g of sodium ethanoate (*GFM* = 82.0 g) in 0.500 mol l⁻¹ ethanoic acid.

(i) Calculate the pH of this buffer solution.

3

(ii) Explain why the pH of this buffer solution remains approximately constant when a small volume of water is added.

1



8. (continued)

- (c) Buffer capacity is a measure of how resistant a buffer solution is to pH changes. It can be defined as the number of moles of hydroxide ions required to raise the pH of a buffer solution by one pH unit.

A student prepared two different buffer solutions, both pH 5.

Describe an experimental procedure that could be carried out to determine which of the two solutions has the larger buffer capacity.

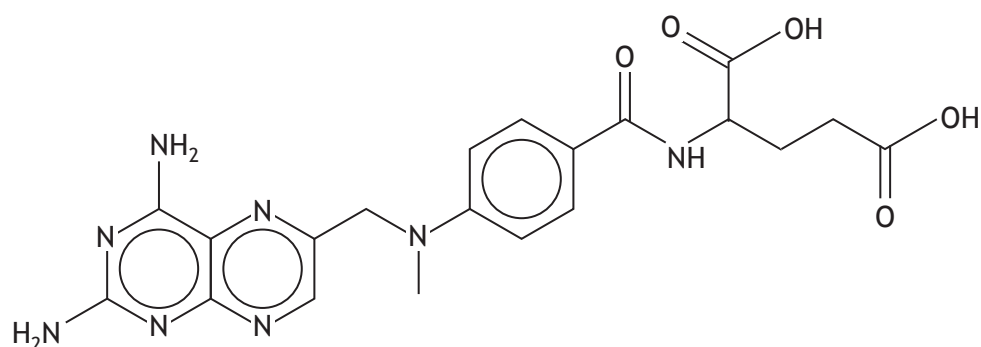
2

[Turn over]



* X 8 1 3 7 7 0 1 2 3 *

9. Methotrexate is a drug commonly used to treat cancer in dogs. It binds to the active site of an enzyme, blocking the production of folic acid required for the synthesis of DNA.



methotrexate

- (a) State what is meant by the term drug. 1
- (b) State the classification of drug used to describe methotrexate. 1
- (c) One treatment for dogs involves a dose of 0.68 mg per kg of bodyweight. Calculate the concentration of methotrexate, in ppm, required to produce a 2.3 cm³ dose to treat an 8.4 kg dog. 1



9. (continued)

- (d) Isomerism is an important concept in the research and development of the chemical synthesis of drug molecules.

Using your knowledge of chemistry, discuss isomerism and its role in chemical synthesis and drug action.

3

[Turn over]



* X 8 1 3 7 7 0 1 2 5 *

10. The gram formula mass of some liquids can be determined using the following relationship.

$$PV = nRT$$

Where,

P is pressure in kilopascals, kPa

V is volume in litres, l

n is number of moles

R is 8.31 joules per kelvin per mole, $\text{J K}^{-1} \text{mol}^{-1}$

T is temperature in kelvin, K

In an experiment, 0.518 g of a liquid carbonyl compound was boiled producing 259 cm^3 of gas at a temperature of 353 K and a pressure of 101 kPa.

- (a) (i) Use the data to calculate the gram formula mass of the liquid carbonyl compound.

2

(Clearly show your working for the calculation.)

- (ii) Using your answer to (a) (i), suggest a liquid carbonyl compound used in this experiment.

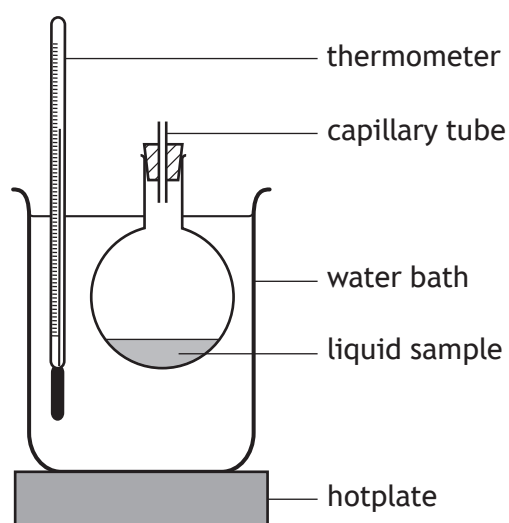
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* X 8 1 3 7 7 0 1 2 6 *

10. (continued)

(b) The diagram shows the apparatus used in the experiment.



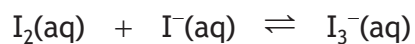
Suggest why this apparatus would not be suitable to determine the gram formula mass when the liquid sample is butanoic acid.

1

[Turn over



11. Iodine solutions are prepared by dissolving iodine in aqueous potassium iodide. The following equilibrium is established.



- (a) (i) Write an expression for the equilibrium constant, K , for this reaction.

1

- (ii) A solution of iodine was prepared by dissolving iodine in 0.239 mol l^{-1} aqueous potassium iodide.

The following data was obtained by analysing the equilibrium mixture.

$$[\text{I}_2(\text{aq})] = 1.21 \times 10^{-3} \text{ mol l}^{-1}$$

$$[\text{I}_3^-(\text{aq})] = 0.116 \text{ mol l}^{-1}$$

Calculate the equilibrium constant, K , for this reaction.

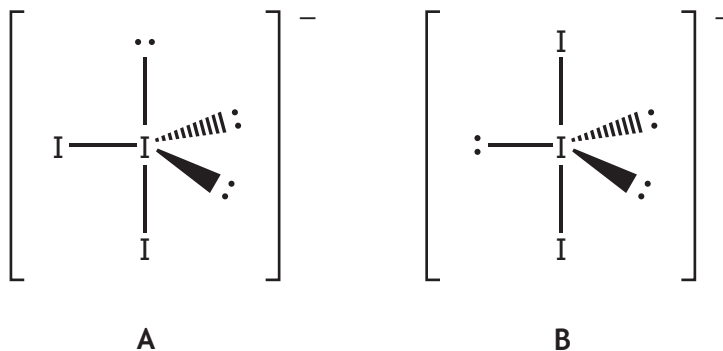
2



* X 8 1 3 7 7 0 1 2 8 *

11. (continued)

- (b) Structures **A** and **B** show two possible arrangements of the electron pairs around the central iodine atom in a triiodide ion, I_3^- .



•• denotes a non-bonding electron pair.

Explain fully why the electron pairs around the central iodine atom adopt structure **B** rather than structure **A**.

2

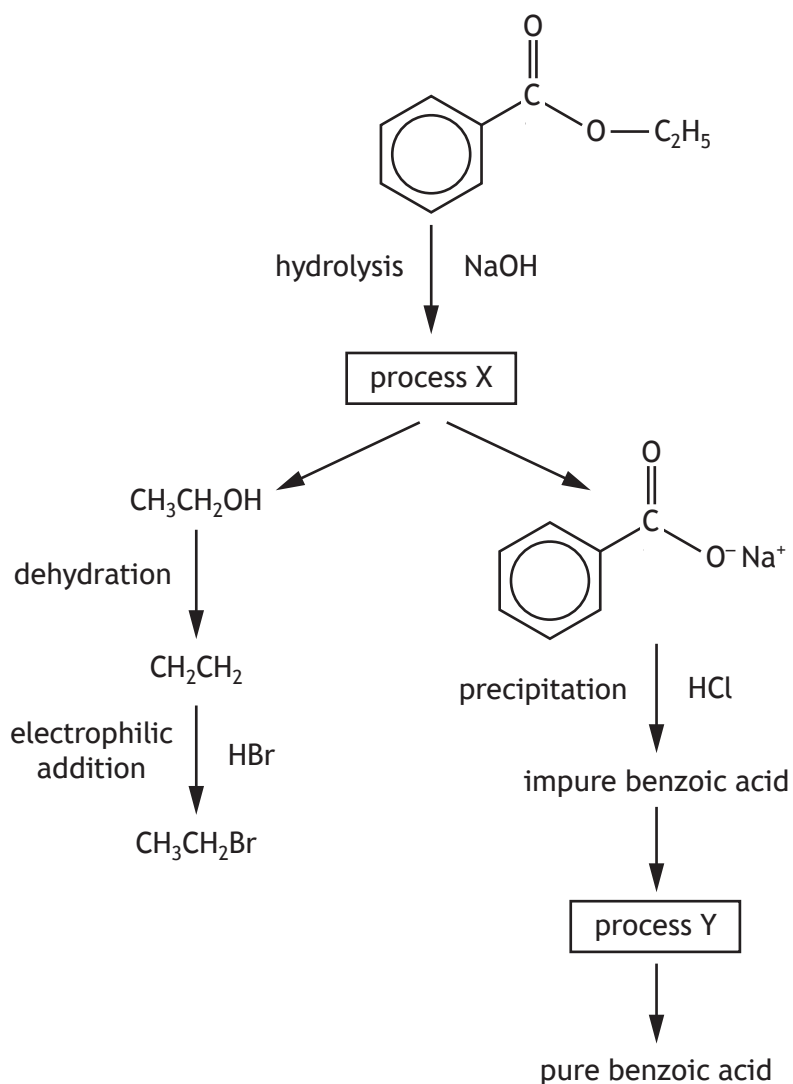
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* X 8 1 3 7 7 0 1 2 9 *

12. The following reaction scheme starts with ethyl benzoate.

MARKS
DO NOT
WRITE IN
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MARGIN



(a) Draw the skeletal formula for ethyl benzoate.

1

(b) Suggest why the hydrolysis reaction mixture was heated under reflux.

1



* X 8 1 3 7 7 0 1 3 0 *

12. (continued)

- | | |
|---|---|
| (c) Name process X. | 1 |
| (d) State another name for the dehydration reaction. | 1 |
| (e) Identify the electrophile in the electrophilic addition reaction. | 1 |
| (f) The impure precipitate of benzoic acid is produced by acidifying the alkaline sodium benzoate solution. | |
| (i) Explain fully why an aqueous solution of sodium benzoate is alkaline. | 2 |
| (ii) Name a technique that would be used to separate the impure precipitate from the reaction mixture. | 1 |
| (g) Name process Y. | 1 |



12. (continued)

(h) The purity of the benzoic acid produced in process Y can be assessed using mixed melting point analysis.

(i) State what should be mixed with this sample of benzoic acid in a mixed melting point analysis.

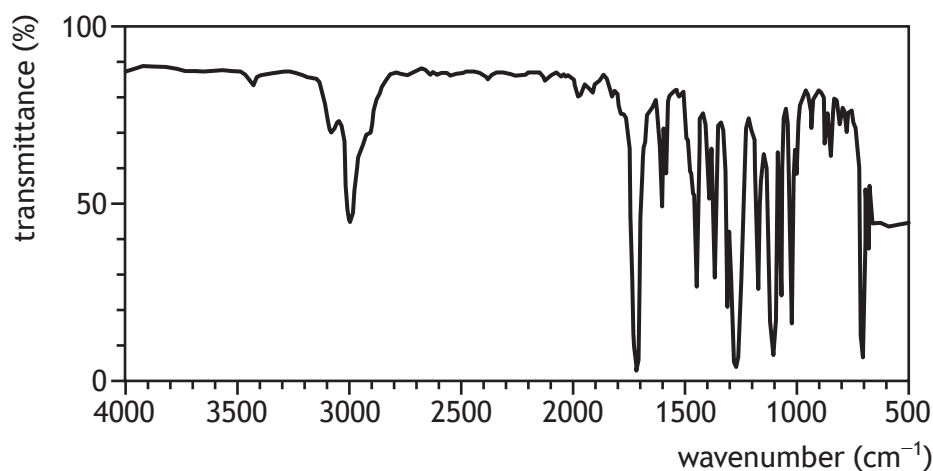
1

(ii) Explain how the results of a mixed melting point analysis would be used to assess the purity of this sample of benzoic acid.

2

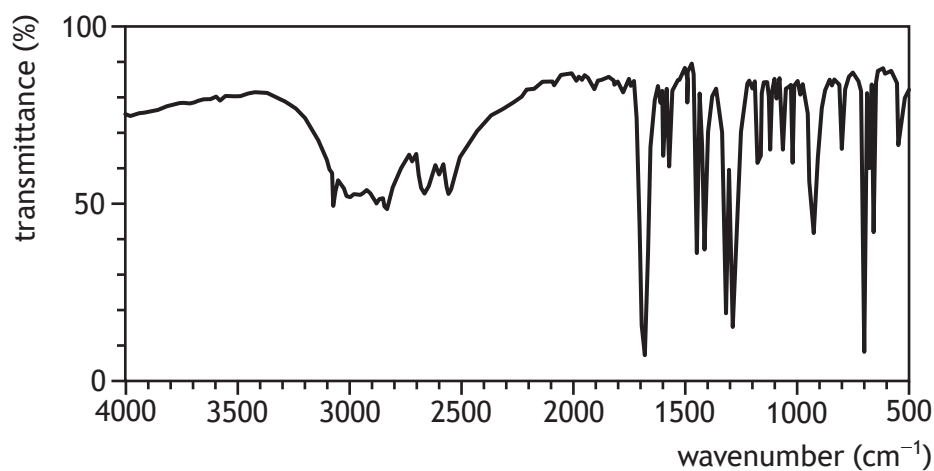
(i) Infrared spectra for three of the compounds in the reaction scheme are shown.

Spectrum A

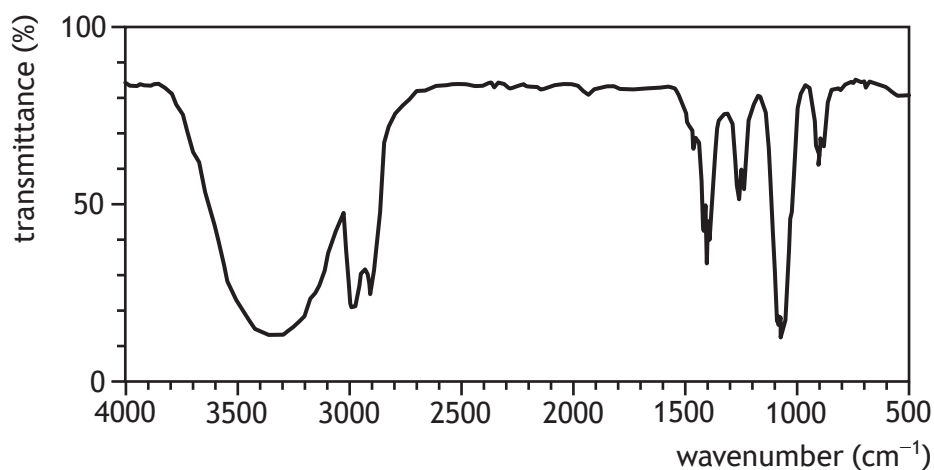


12. (i) (continued)

Spectrum B



Spectrum C



Identify the spectrum for ethanol and give a reason for your answer.

2

[END OF QUESTION PAPER]

