X273/13/02

NATIONAL QUALIFICATIONS 2013

FRIDAY, 31 MAY
1.00 PM – 3.30 PM

CHEMISTRY
ADVANCED HIGHER (REVISED)

Reference may be made to the Chemistry Higher and Advanced Higher Data Booklet.

SECTION A – 30 marks

Instructions for completion of **SECTION A** are given on page two.

For this section of the examination you must use an **HB pencil.**

SECTION B – 70 marks

All questions should be attempted.

Answers must be written clearly and legibly in ink.

SECTION A

Read carefully

1 Check that the answer sheet provided is for **Chemistry Advanced Higher (Revised) (Section A)**.

2 For this section of the examination you must use an **HB pencil** and, where necessary, an eraser.

3 Check that the answer sheet you have been given has **your name**, **date of birth**, **SCN** (Scottish Candidate Number) and **Centre Name** printed on it.

Do not change any of these details.

4 If any of this information is wrong, tell the Invigilator immediately.

5 If this information is correct, **print** your name and seat number in the boxes provided.

6 The answer to each question is **either** A, B, C or D. Decide what your answer is, then, using your pencil, put a horizontal line in the space provided (see sample question below).

7 There is **only one correct** answer to each question.

8 Any rough working should be done on the question paper or the rough working sheet, **not** on your answer sheet.

9 At the end of the exam, put the **answer sheet for Section A inside the front cover of your answer book**.

Sample Question

To show that the ink in a ball-pen consists of a mixture of dyes, the method of separation would be

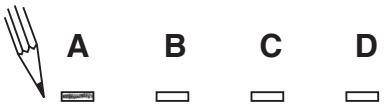
A chromatography

B fractional distillation

C fractional crystallisation

D filtration.

The correct answer is **A**—chromatography. The answer **A** has been clearly marked in **pencil** with a horizontal line (see below).



Changing an answer

If you decide to change your answer, carefully erase your first answer and using your pencil, fill in the answer you want. The answer below has been changed to **D**.

1. Which equation can be used to represent the second ionisation energy of the diatomic element, X?

A $X_2(g) \rightarrow X_2^{2+}(g) + 2e^-$

B $\frac{1}{2}X_2(g) \rightarrow X^{2+}(g) + 2e^-$

C $X^+(g) \rightarrow X^{2+}(g) + e^-$

D $X(g) \rightarrow X^{2+}(g) + 2e^-$

2. Which of the following lists electromagnetic radiation bands in order of increasing frequency?

A Ultraviolet, visible, infra-red, radio

B Radio, infra-red, visible, ultraviolet

C Radio, microwave, ultraviolet, visible

D Visible, ultraviolet, X-ray, microwave

3. Using information from the Data Booklet which one of the following metal salts will emit radiation of the highest frequency when placed in a Bunsen flame?

A Copper(II) sulfate

B Potassium chloride

C Barium chloride

D Lithium sulfate

4. Which of the following indicators transmits only the lower frequencies of the visible spectrum at low pH?

	Indicator	*Colour in acid*	*Colour in alkali*
A		Violet	Red
B		Green	Blue
C		Yellow	Violet
D		Red	Yellow

5. When electrons occupy degenerate orbitals, they do so in such a way as to maximise the number of parallel spins. This statement is known as

A Hund's rule

B the aufbau principle

C the Pauli exclusion principle

D Valence Shell Electron Pair Repulsion (VSEPR) theory.

6. Which of the following represents the configuration of the highest energy electrons in an atom of a Group III element in the ground state?

A $3s^2 3p^1$

B $3s^2 3p^3$

C $4s^2 3d^1$

D $4s^2 4p^3$

7. Which of the following analytical techniques would be most suitable to determine quantitatively the concentration of sodium ions in a urine sample?

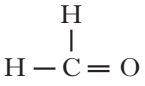
A Mass spectrometry

B Infra-red spectroscopy

C Atomic emission spectroscopy

D Proton nuclear magnetic resonance spectroscopy

8. Which of the following molecules has the greatest number of non-bonding electron pairs (lone pairs)?

A


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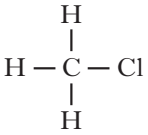
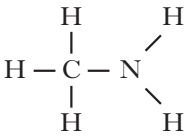
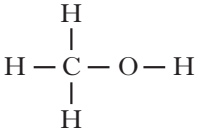


C


D


[Turn over

9. The following diagram represents a square-planar structure.

Where ▬ and ▬ represent bonding electron pairs

and ⊙⊙ represents a non-bonding electron pair (lone pair).

Which of the following species could have the structure shown above?

A SF_4

B NH_4^+

C XeF_4

D AlH_4^-

10. In which of the following reactions does the oxidation state of copper neither increase nor decrease?

A $Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$

B $CuSO_4 + 4NH_3 \rightarrow [Cu(NH_3)_4]SO_4$

C $FeCl_2 + CuCl_2 \rightarrow FeCl_3 + CuCl$

D $Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2$

11. $100\,cm^3$ of $0{\cdot}500\,mol\,l^{-1}$ $AgNO_3(aq)$ is reacted with excess $CaCl_2(aq)$.

What mass of precipitate forms?

A 7·17 g

B 8·95 g

C 12·6 g

D 14·3 g

12. What volume of $0{\cdot}2\,mol\,l^{-1}$ potassium sulfate is required to make, by dilution with water, one litre of a solution with a **potassium** ion concentration of $0{\cdot}1\,mol\,l^{-1}$?

A $100\,cm^3$

B $250\,cm^3$

C $400\,cm^3$

D $500\,cm^3$

13. Phosphoric acid is a weak acid and undergoes partial dissociation according to the equation

$$H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+$$

The position of equilibrium would be shifted to the right by the addition of

A a catalyst

B sulfuric acid

C sodium hydroxide

D sodium dihydrogenphosphate.

14. Caffeine can be extracted from coffee dissolved in water using the solvent dichloromethane (CH_2Cl_2).

$$\text{caffeine(aq)} \rightleftharpoons \text{caffeine}(CH_2Cl_2)$$

Which of the following, when increased, will change the value of the equilibrium constant for this process?

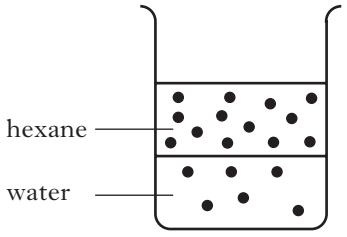
A Temperature

B Mass of coffee

C Volume of water

D Volume of dichloromethane

15. Substance **X** is distributed between equal volumes of two immiscible liquids as shown in the diagram. The number of dots represents the relative distribution of **X** in the two liquids at equilibrium.



$$\mathbf{X}(aq) \rightleftharpoons \mathbf{X}(hexane)$$

The value of the equilibrium constant for this system is

A 0·46

B 0·50

C 2·00

D 2·17.

16. Which of the following decreases when an aqueous solution of ethanoic acid is diluted?

A pH

B pKa

C $[H^+]$

D The degree of dissociation

17. Iodide ions are oxidised by acidified nitrite ions according to the equation

$2NO_2^- + 2I^- + 4H^+ \rightarrow 2NO + I_2 + 2H_2O$

Addition of sodium ethanoate to the reaction mixture slows down the formation of iodine.

The most likely explanation for this effect is that ethanoate ions

A remove iodine

B reduce the concentration of iodide ions

C react with nitrite ions

D react with hydrogen ions.

18. Which of the following indicators should be used in the titration of potassium hydroxide solution with ethanoic acid solution?

A Phenolphthalein, pH range 8·0 – 9·8

B Bromothymol blue, pH range 6·0 – 7·6

C Methyl red, pH range 4·2 – 6·2

D Methyl orange, pH range 3·1 – 4·4

19. Which of the following always increases in a spontaneous process?

A The free energy

B The total entropy

C The total enthalpy

D The surrounding temperature

20. One mole of which of the following chlorides would have the greatest entropy at **750 °C**?

A Sodium chloride

B Calcium chloride

C Potassium chloride

D Magnesium chloride

21. Which of the following techniques could be used to purify an impure sample of solid benzoic acid?

A Refluxing

B Distillation

C Recrystallisation

D Thin layer chromatography

22. The conversion of butanoic acid into butan-1-ol is an example of

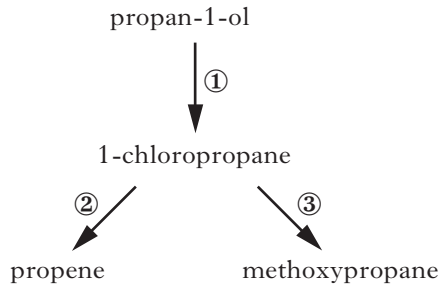
A elimination

B substitution

C oxidation

D reduction.

23.



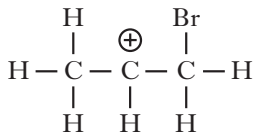
Which line in the table is correct for the types of reaction taking place at ① , ② and ③?

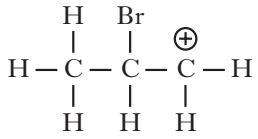
	Reaction ①	Reaction ②	Reaction ③
A	substitution	elimination	substitution
B	substitution	reduction	substitution
C	addition	reduction	condensation
D	addition	elimination	substitution

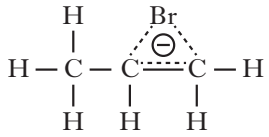
[Turn over

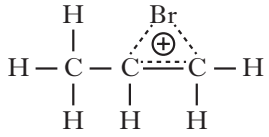
24. Bromine reacts with propene to produce 1,2-dibromopropane.

A possible intermediate in the reaction is

A 

B 

C 

D 

25. Which of the following compounds would be expected to have the highest boiling point?

A Pentanal

B Pentan-2-ol

C Pentan-2-one

D Ethoxypropane

26. The Williamson synthesis for the preparation of unsymmetrical ethers (ROR′) starting with an alcohol and a haloalkane is summarised in the general equations:

Step 1: $ROH + Na \rightarrow RO^{-}Na^{+} + \frac{1}{2}H_2$

Step 2: $RO^{-}Na^{+} + R'X \rightarrow ROR' + Na^{+}X^{-}$

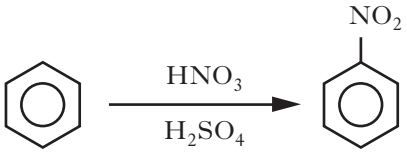
Using propan-2-ol and 2-chlorobutane, the unsymmetrical ether formed would be

A $CH_3CH_2CH_2OCH(CH_3)CH_2CH_3$

B $CH_3CH_2CH_2OCH_2CH_2CH_2CH_3$

C $CH_3CH(CH_3)OCH_2CH_2CH_2CH_3$

D $CH_3CH(CH_3)OCH(CH_3)CH_2CH_3$

27. 

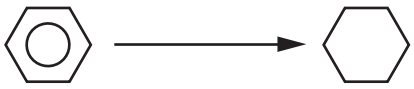
Which species initially attacks the benzene molecule in the above reaction?

A NO_2

B NO_3^{-}

C NO_2^{+}

D HSO_4^{-}

28. 

The above reaction is an example of

A addition

B oxidation

C elimination

D substitution.

29. Most medicines work by binding to receptors.

Receptors are usually

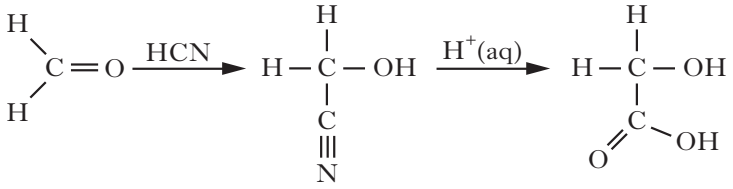
A nucleophiles

B electrophiles

C free radicals

D protein molecules.

30. Carbonyl groups in aldehydes and ketones react with HCN and the product can then be hydrolysed forming a 2-hydroxycarboxylic acid as shown in the equation below.



methanal 2-hydroxyethanoic acid

When the final product is 2-hydroxy,2-methylbutanoic acid, the starting carbonyl compound is

A propanal

B propanone

C butanal

D butanone.

[*END OF SECTION A*]

Candidates are reminded that the answer sheet for Section A MUST be placed INSIDE the front cover of your answer book.

[Turn over for SECTION B on *Page eight*

SECTION B

Marks

70 marks are available in this section of the paper.

All answers must be written clearly and legibly in ink.

1. The electronic configuration of a carbon atom is $1s^2 2s^2 2p^2$.

(*a*) The electrons in the 2p orbitals are said to be "degenerate".

What is meant by the term "degenerate"? **1**

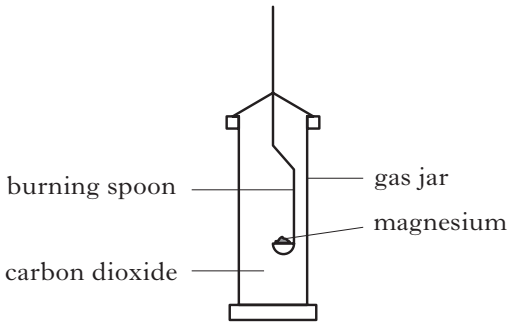
(*b*) Draw the electronic configuration of a carbon atom in orbital box notation. **1**

(*c*) Explain what is thought to take place when carbon atoms form four equivalent single bonds in methane. **2**

(4)

2. Burning magnesium continues to burn when placed in a gas jar of carbon dioxide according to the equation

$$2Mg(s) + CO_2(g) \rightarrow 2MgO(s) + C(s)$$



substance	$S°/JK^{-1}\,mol^{-1}$
Mg(s)	33·0
$CO_2(g)$	214
MgO(s)	27·0
C(s)	5·70

(*a*) Using the values from the table above, calculate $\Delta S°$ for the reaction. **1**

(*b*) Using the information below and your answer to (*a*), calculate $\Delta G°$ for the burning of magnesium in carbon dioxide.

$Mg(s) + \frac{1}{2}O_2(g) \rightarrow MgO(s)$ $\quad \Delta H° = -493\ kJ\ mol^{-1}$

$C(s) + O_2(g) \rightarrow CO_2(g)$ $\quad \Delta H° = -394\ kJ\ mol^{-1}$ **3**

(4)

Marks

3. A student measured the pH of water at various temperatures using a pH meter and obtained the following results.

Temperature/ °C	pH
20	7·08
30	6·92
50	6·63

The student was unsure whether the results were accurate or if the pH meter was faulty.

Using your knowledge of chemistry, discuss possible reasons for the results obtained. **(3)**

[Turn over

Marks

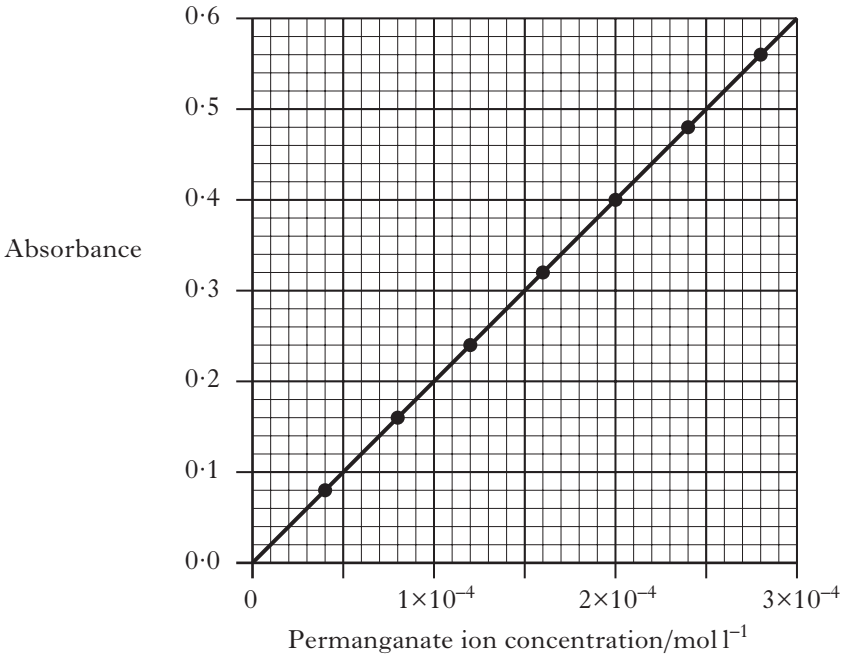
4. The manganese content of a steel paperclip can be determined by oxidising the manganese firstly into manganese(II) ions and then to the purple permanganate ion. Colorimetry is then used to find the concentration of the permanganate ion, from which the percentage manganese in the steel paperclip can be determined.

(*a*) What data must be collected to allow the calibration graph to be drawn? **1**

(*b*) Which colour of filter or wavelength of light should be used in this procedure? **1**

(*c*) In a determination, the manganese in 0·245 g of steel was oxidised to permanganate ions and the solution made up to 100 cm^3 in a standard flask. The absorbance of the solution was measured as 0·26.

Use this information and the following calibration graph to calculate the percentage of manganese in this sample of steel.



3

(*d*) Colorimetry is not used to determine potassium content because potassium ions are not coloured. The concentration of potassium ions in a compound can be determined using atomic absorption spectroscopy at a wavelength 405 nm.

Calculate the energy, in kJ mol^{-1}, of this radiation. **2**

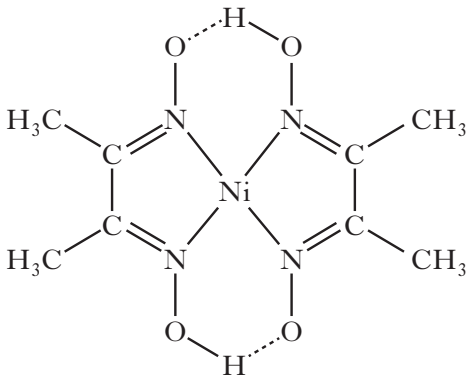
(7)

[Turn over for Question 5 on *Page twelve*

Marks

5. Nickel(II) ions react quantitatively with dimethylglyoxime ($C_4H_8O_2N_2$) forming a complex which precipitates out as a red solid. The equation for the reaction and the structure of the complex are shown below.

$$Ni^{2+} + 2C_4H_8O_2N_2 \rightarrow Ni(C_4H_7O_2N_2)_2 + 2H^+$$



Relative formula mass = 288·7

(*a*) What is the coordination number of nickel in the complex? **1**

(*b*) When 0·968 g of an impure sample of nickel(II) sulfate, $NiSO_4.7H_2O$, was dissolved in water and reacted with dimethylglyoxime. 0·942 g of the red precipitate was formed.

Calculate the percentage, by mass, of nickel in the impure sample of nickel(II) sulfate. **2**

(*c*) The formulae of two very common ions of nickel are $[Ni(H_2O)_6]^{2+}$ and $[Ni(NH_3)_6]^{2+}$.

(i) Name the complex ion $[Ni(H_2O)_6]^{2+}$. **1**

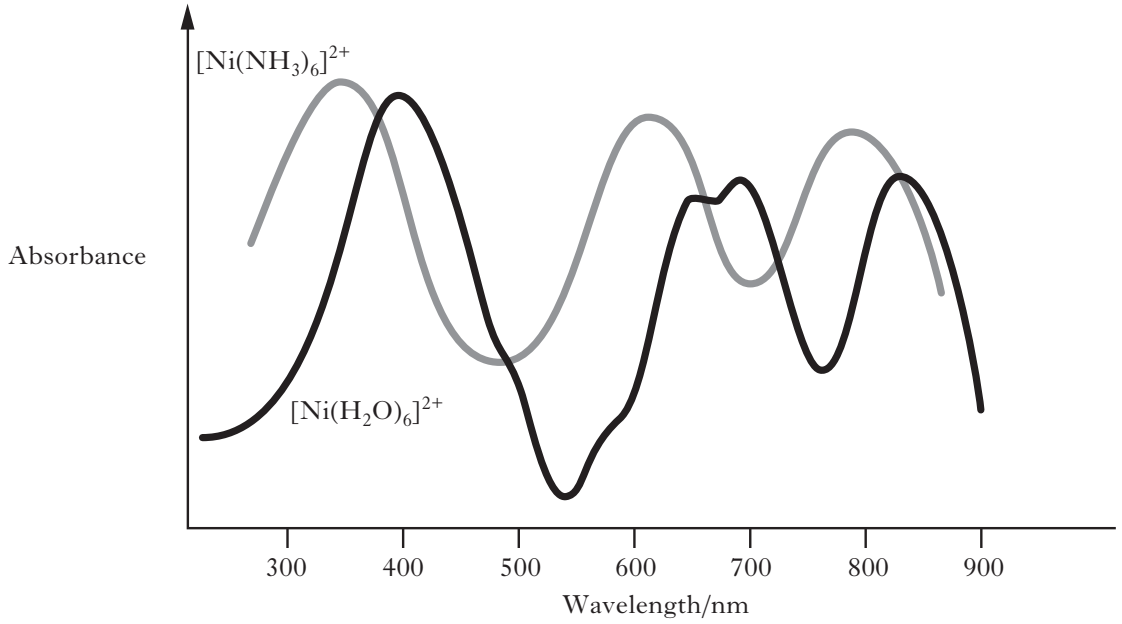
(ii) In terms of s, p and d orbitals, write down the electronic configuration of the nickel ion in $[Ni(H_2O)_6]^{2+}$. **1**

(*d*) The relative ability of a ligand to split the d-orbitals when forming a complex ion is given in the spectrochemical series. Three ligands from this series and their relative ability to split the d-orbitals are shown below.

$$NH_3 > H_2O > Cl^-$$

The absorption spectra for $[Ni(H_2O)_6]^{2+}$and $[Ni(NH_3)_6]^{2+}$ are shown on the following page.

5. (*d*) (continued)



(i) Why is $[Ni(H_2O)_6]^{2+}(Cl^-)_2(aq)$ likely to be green? **1**

(ii) Explain why the peaks in the absorption spectrum of $[Ni(NH_3)_6]^{2+}$ are at shorter wavelengths. **2**

(iii) Predict the colour of $[Ni(NH_3)_6]^{2+}(Cl^-)_2(aq)$. **1**

(9)

6. Propanoic acid is a weak acid. Sodium propanoate is a salt which can be formed from it. Both propanoic acid and sodium propanoate can be used as mould inhibitors.

(*a*) Calculate the pH of 0·10 mol l^{-1} propanoic acid solution. **2**

(*b*) 0·20 moles of sodium propanoate are added to 100 cm^3 of the 0·10 mol l^{-1} solution of propanoic acid.

Calculate the pH of the buffer solution formed. **2**

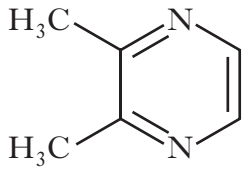
(4)

[Turn over

Marks

7. The dominant flavours of chocolate are due to molecules called substituted pyrazines. These are produced when sugars and amino acids react during the roasting of cocoa beans.

An example is 2,3-dimethylpyrazine

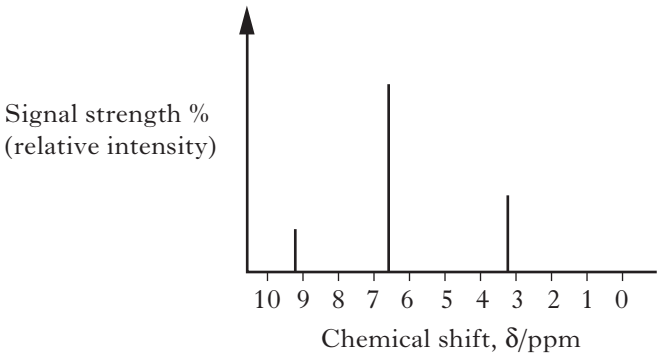


This compound is responsible for the nutty flavour of chocolate. Other substances responsible for the distinctive smell of chocolate are aldehydes including phenylethanal, 2-methylbutanal and 3-methylbutanal.

(*a*) Write the molecular formula for 2,3-dimethylpyrazine. **1**

(*b*) Draw a skeletal formula for 2-methylbutanal and circle the asymmetric carbon present. **2**

(*c*) The low resolution proton NMR spectrum shown is that of one of the aldehydes in chocolate.



Explain which of the three aldehydes above would give this proton NMR spectrum. **2**

(*d*) Anandamide is another substance also found in small quantities in chocolate, that plays a role in appetite, memory, fertility and pain depression. It binds to the same receptors as the cannabinoid drugs and enhances some of the body's natural responses.

What general term is used for a substance that behaves in this way? **1**

(6)

Marks

8. A kinetics study was carried out on the reaction between a haloalkane, C_4H_9Br, and aqueous sodium hydroxide.

$$C_4H_9Br + NaOH \rightarrow C_4H_9OH + NaBr$$

The following results were obtained.

$[C_4H_9Br]$/mol l^{-1}	[NaOH]/mol l^{-1}	Initial Rate/mol $l^{-1}s^{-1}$
$8{\cdot}0 \times 10^{-4}$	0·10	0·15
$1{\cdot}6 \times 10^{-3}$	0·10	0·30
$1{\cdot}6 \times 10^{-3}$	0·20	0·30
$3{\cdot}2 \times 10^{-3}$	0·40	0·60

(*a*) What is the order of reaction with respect to

(i) the haloalkane

(ii) the sodium hydroxide? **1**

(*b*) Write the rate equation for the reaction. **1**

(*c*) Calculate a value for the rate constant, k, including the appropriate units. **2**

(*d*) There are four structural isomers of C_4H_9Br.

Explain which isomer is likely to have been used. **2**

(*e*) Outline the mechanism for this reaction using curly arrow notation. **3**

(9)

9. (*a*) State one of the characteristics of a primary standard. **1**

(*b*) As part of an AH Chemistry investigation, a student had to prepare a standard solution of sodium carbonate.

Outline how the student would prepare this standard solution from pure sodium carbonate. **2**

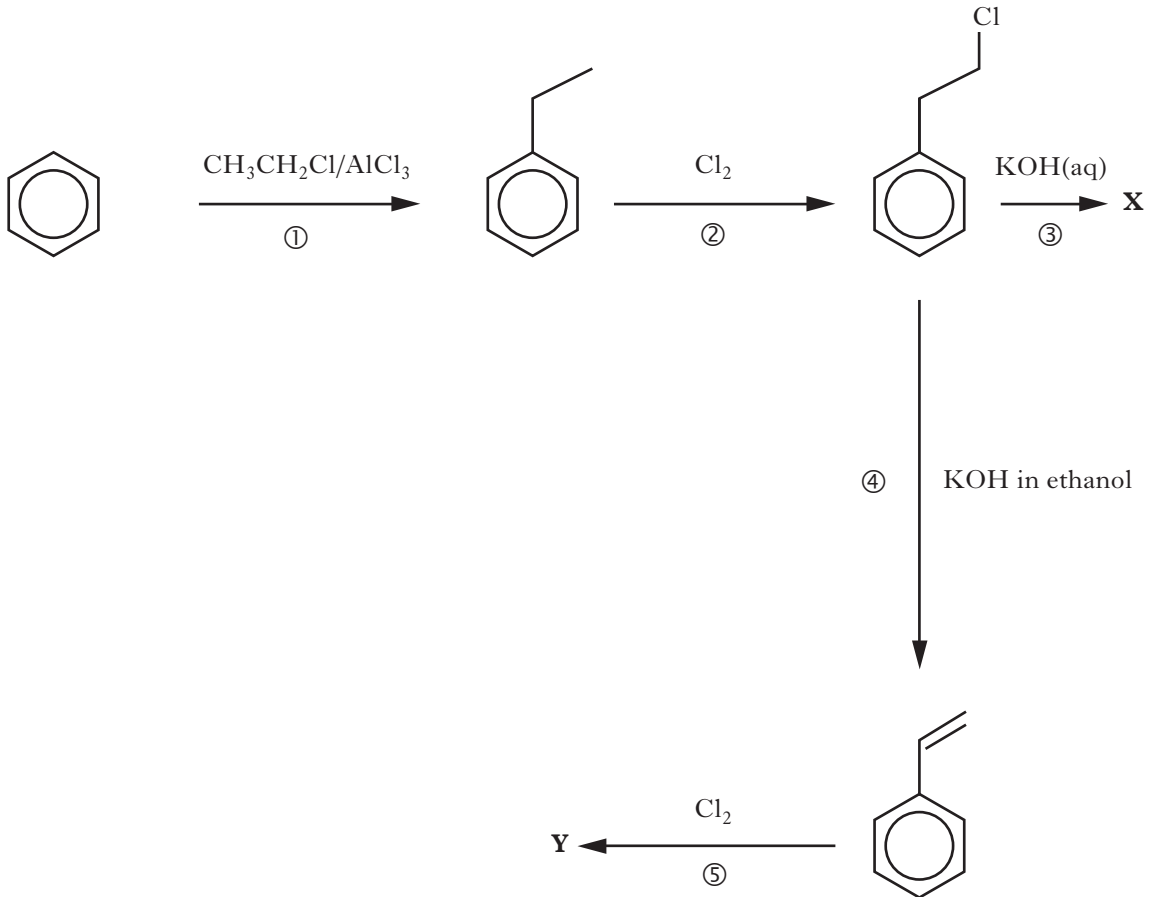
(*c*) Outline how 250 cm^3 of 0·20 mol l^{-1} sodium carbonate solution would be prepared from a standard 1·00 mol l^{-1} sodium carbonate solution. **2**

(5)

[Turn over

Marks

10. A student devised the following reaction sequence.



(*a*) What type of reaction is taking place in step ①? **1**

(*b*) During step ②, chlorine firstly undergoes homolytic fission.
Explain what this means. **1**

(*c*) Draw a structural formula for product **X**. **1**

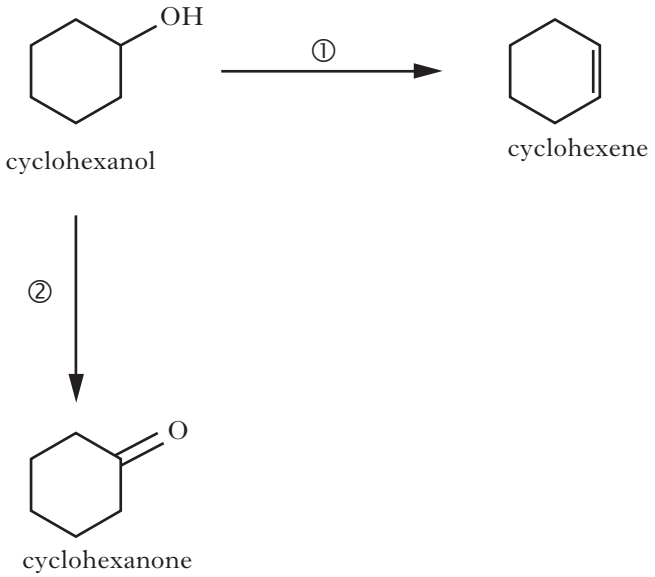
(*d*) What type of reaction is taking place in step ④? **1**

(*e*) Draw a structural formula for product **Y**. **1**

(5)

Marks

11. Cyclohexanol can be converted into cyclohexene or cyclohexanone using different reagents as outlined below.



(*a*) Suggest a dehydrating agent that could be used to convert cyclohexanol into cyclohexene in reaction ①. **1**

(*b*) In an experiment, a student obtained 3·14 g of cyclohexene from 4·36 g of cyclohexanol.

(i) Calculate the percentage yield. **3**

(ii) Give a reason why the yield is not 100%. **1**

(*c*) **Using your knowledge of chemistry**, comment on how it could be established that the product of reaction ②, is cyclohexanone. **3**

(8)

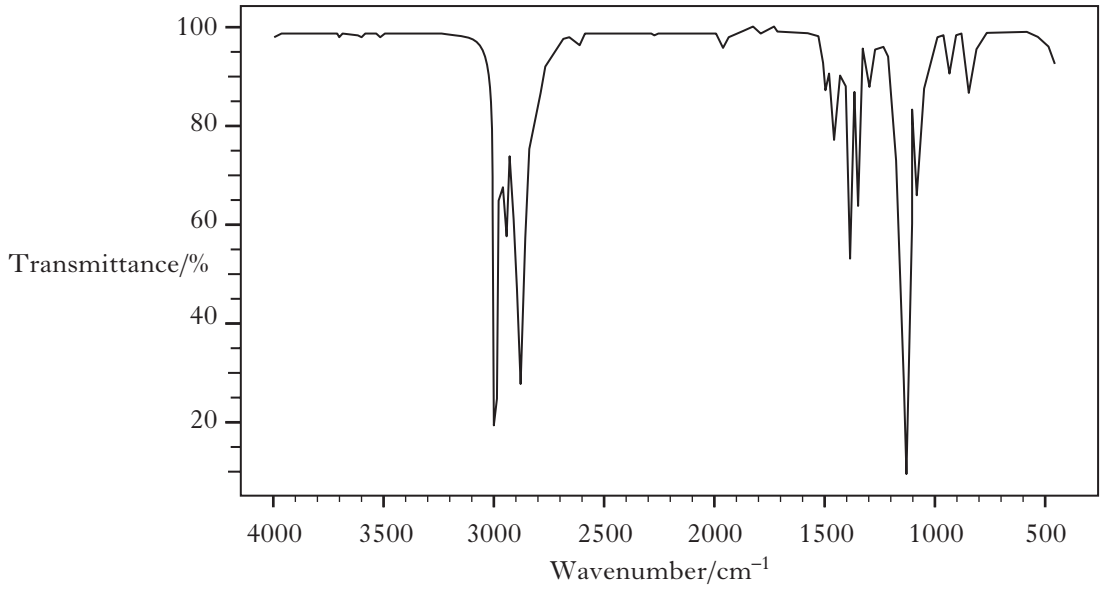
[Turn over for Question 12 on *Page eighteen*

Marks

12. 5·00 g of an organic compound **A** was burned completely producing 11·89 g of CO_2 and 6·08 g of H_2O as the only products.

(*a*) **Using the information above**, calculate the empirical formula of compound **A**. **3**

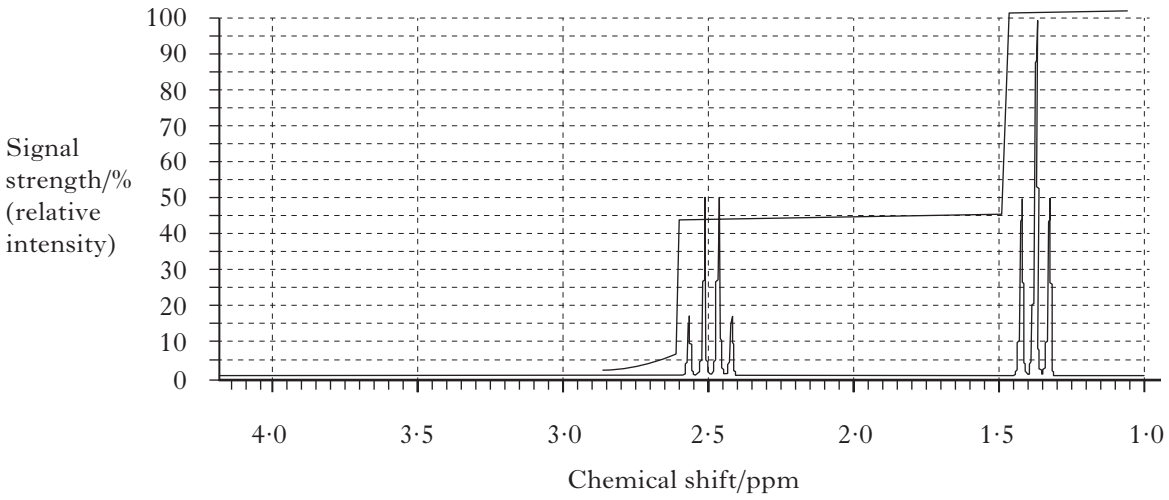
(*b*) The infra-red spectrum of compound **A** is shown below.



Which bond is responsible for the peak at 1140 cm^{-1}? **1**

(*c*) The mass spectrum of compound **A** shows the molecular ion to have a mass/charge ratio of 74. Deduce the molecular formula of compound **A**. **1**

(*d*) The high resolution proton NMR spectrum of compound **A** is shown below.



Using all the above information, deduce a structural formula for compound **A**. **1**

(6)

[*END OF QUESTION PAPER*]

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