**RAFFLES INSTITUTION**
**2022 YEAR 6 TERM 3 COMMON TEST**

**Higher 2**

| | |
|---|---|
| CANDIDATE NAME | |
| CLASS | INDEX NUMBER |

# CHEMISTRY 9729

**28 June 2022**

**2 hours 45 minutes**

Additional Materials: Multiple Choice Answer (OMR) Sheet
Data Booklet

**READ THESE INSTRUCTIONS FIRST**

Write your name, 6-digit exam index number and civics tutorial group in the spaces provided on the OMR sheet and the cover sheets on **pages 1 and 25**. Shade your 6-digit exam index number on the OMR sheet.

This paper consists of three sections, **A**, **B** and **C**.

**Section A (15 marks) consists of 15 multiple-choice questions.**

**Answer this section first**. The OMR sheet will be collected after the **first 30 minutes**.
For each question there are four possible answers **A**, **B**, **C** and **D**. Choose the **one** you consider correct and record your choice in **soft pencil** on the OMR sheet. Each correct answer will score one mark. A mark will not be deducted for a wrong answer. Any rough working should be done in the question paper.

**Section B (40 marks) consists of 3 structured questions.**

Answer **all** questions in the spaces provided in the question paper.
If additional space is required, you should use the pages at the end of the booklet for Section B (pages 23 – 24). The question number must be clearly shown.

**Section C (40 marks) consists of 4 free-response questions.**

Answer both **C1** and **C2**, and only **one** of **C3 EITHER** or **C3 OR**.
Answers to this section are to be written in the spaces provided in the question paper.
If additional space is required, you should use the pages at the end of the booklet for Section C (pages 40 – 41). The question number must be clearly shown.

Write in dark blue or black pen. You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

The use of an approved scientific calculator is expected, where appropriate.

The number of marks is given in brackets [ ] at the end of each question or part question.

| Question | Marks |
|---|---|
| B1 | / 10 |
| B2 | / 15 |
| B3 | / 15 |

## Section A (15 marks)

For each question, there are four possible answers, **A**, **B**, **C**, and **D**. Choose the **one** you consider to be correct.

**1** Iodate(V) ions react with iodide ions under acidic conditions.

$$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$$

25.0 $cm^3$ of 0.100 mol $dm^{-3}$ solution of iodate(V) ions was added to a solution containing excess iodide ions and sulfuric acid. The liberated iodine was then titrated with sodium thiosulfate solution.

If 20.00 $cm^3$ of sodium thiosulfate solution was required to react with the iodine produced, what was the concentration of the sodium thiosulfate solution in mol $dm^{-3}$?

**A** 0.125

**B** 0.250

**C** 0.375

**D** 0.750

**2** The reactivity of Group 2 metals with oxygen increases down the group.

Which statement best explains the trend?

**A** The ionic radius of the metal cations increases down the group.

**B** The reducing power of the elements increases down the group.

**C** The electronegativity of the elements decreases down the group.

**D** The magnitude of the lattice energy of the metal oxides decreases down the group.

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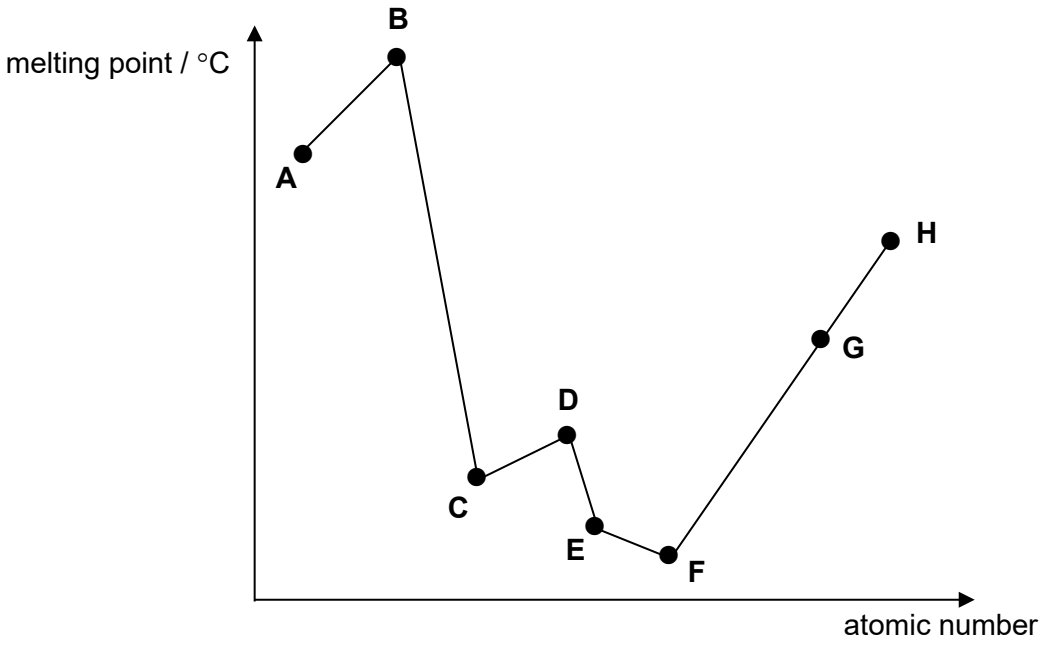
**3** *Use of the Data Booklet is relevant to this question.*

**A** to **H** are consecutive elements in the Periodic Table with atomic number ≤ 20. The graph below shows the variation in melting point for these eight elements.




Which of the following statements are correct?

1 The oxide of **B** dissolves in water to give an acidic solution while the oxide of **H** dissolves in water to give an alkaline solution.

2 **A** and **E** react together to form a product that dissolves in water to give an acidic solution.

3 Both **C** and **D** are solids at room temperature and each forms oxides with different oxidation states.

**A** 2 only

**B** 1 and 3 only

**C** 2 and 3 only

**D** 1, 2 and 3

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**4** The mechanism for the reaction between reactants A and B is shown below.

| | | |
|---|---|---|
| step 1 | $2A \rightleftharpoons C$ | fast |
| step 2 | $B + C \longrightarrow D$ | slow |
| step 3 | $B + D \longrightarrow A_2B_2$ | fast |

What conclusions can be drawn from the information given above?

1 The rate equation for the overall reaction is rate = $k$[B][C].

2 The overall equation is $2A + 2B \longrightarrow A_2B_2$.

3 The rate of formation of $A_2B_2$ is equal to the rate of depletion of B.

**A** 1 only
**B** 2 only
**C** 1 and 2
**D** 2 and 3

**5** *Use of the Data Booklet is relevant to this question.*

The following enthalpy changes are given.

$Mg(s) \longrightarrow Mg^{2+}(g) + 2e^-$ $\quad \Delta H = +2353$ kJ mol$^{-1}$
$O_2(g) + 4e^- \longrightarrow 2O^{2-}(g)$ $\quad \Delta H = +1794$ kJ mol$^{-1}$

Which statements are correct?

1 The enthalpy change of atomisation of magnesium is +167 kJ mol$^{-1}$.

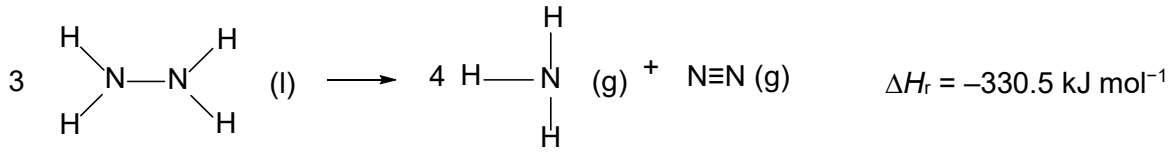
2 The enthalpy change of atomisation of oxygen is +496 kJ mol$^{-1}$.

3 The sum of the first and second electron affinities of oxygen is +897 kJ mol$^{-1}$.

**A** 1 only
**B** 1 and 3 only
**C** 2 and 3 only
**D** 1, 2 and 3

**6** *Use of the Data Booklet is relevant to this question.*

In monopropellant engines, hydrazine, $NH_2NH_2$, is decomposed as shown below.




What is the enthalpy change of vaporisation of hydrazine?

**A** +44.5 kJ mol$^{-1}$

**B** +133.5 kJ mol$^{-1}$

**C** +264.8 kJ mol$^{-1}$

**D** +1720 kJ mol$^{-1}$

**7** **X** and **Y** are acidic solutions with the same pH. When equal volumes of both solutions are separately diluted with the same volume of water, the pH of the resulting solution of **X** is higher than that of **Y**.

Which pair of acids fits the description above?

| | **X** | **Y** |
|---|---|---|
| **A** | HC*l* | $CH_3COOH$ |
| **B** | HC*l* | $H_2SO_4$ |
| **C** | $H_2SO_4$ | HC*l* |
| **D** | $CH_3COOH$ | HC*l* |

**8** Which of the following, when dissolved in 1 dm$^3$ of water, would give the lowest pH?

(p$K_a$ of $CH_3COOH$ = 4.76 and p$K_b$ of $NH_3$ = 4.75)

**A** $10^{-4}$ mol of HC*l*

**B** $10^{-4}$ mol of $CH_3COOH$

**C** 1 mol of HC*l* and 1 mol of $NH_3$

**D** 1.1 mol of $CH_3COOH$ and 0.1 mol of NaOH

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**9** The values of the solubility product, $K_{sp}$, of two calcium salts at 25 ºC are given below.

| | value of $K_{sp}$ |
|---|---|
| calcium fluoride, $CaF_2$ | $4.0 \times 10^{-11}$ |
| calcium carbonate, $CaCO_3$ | $3.4 \times 10^{-9}$ |

Which statement is correct?

**A** The solubility of calcium carbonate decreases with decreasing pH.

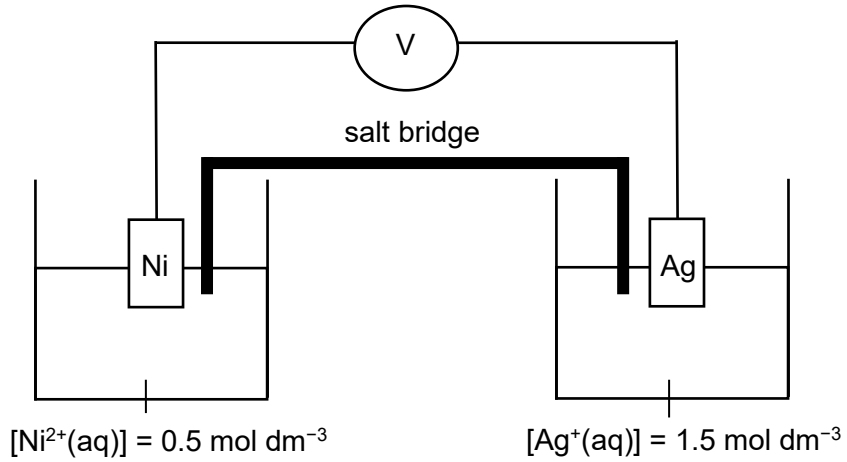
**B** Calcium fluoride has a higher molar solubility than calcium carbonate.

**C** Addition of sodium fluoride to a solution containing calcium fluoride decreases the solubility product of calcium fluoride.

**D** When solid calcium nitrate is added into a solution containing $F^-$ and $CO_3^{2-}$ ions, each of concentration 0.1 mol $dm^{-3}$, $CaCO_3$ precipitates out first.

**10** *Use of the Data Booklet is relevant to this question.*

The diagram below shows a cell at 25 °C.




Which set of information is correct for this cell?

| | $E_{cell}$ | direction of electron flow |
|---|---|---|
| **A** | less positive than +1.05 V | Ag to Ni |
| **B** | less positive than +1.05 V | Ni to Ag |
| **C** | more positive than +1.05 V | Ni to Ag |
| **D** | more positive than +1.05 V | Ag to Ni |

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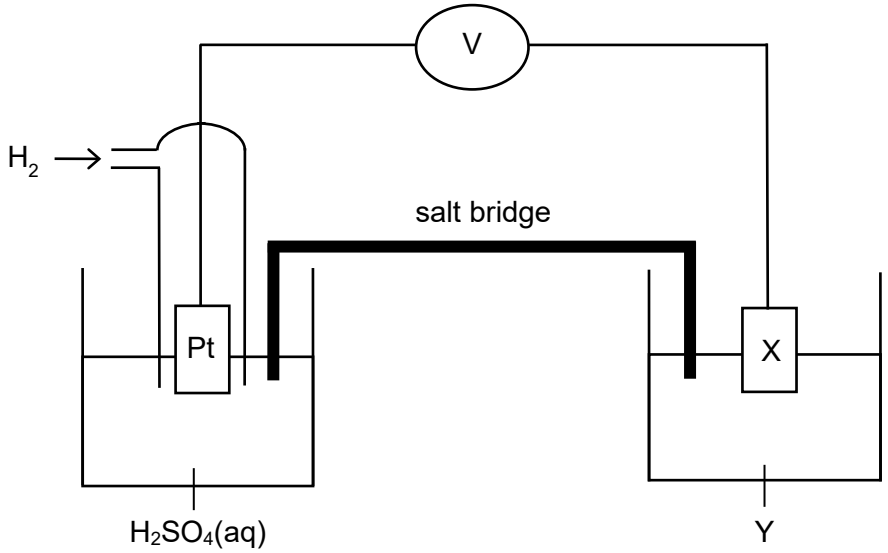
**11** The diagram shows the set-up needed to measure the standard electrode potential of a $Fe^{3+}/Fe^{2+}$ half-cell.




Which statement is correct?

**A** The pressure of $H_2$ is 1 bar.

**B** The experiment is conducted at 293 K.

**C** X is FeO(s) and Y is 1 mol $dm^{-3}$ $Fe(NO_3)_3$(aq).

**D** The concentration of $H_2SO_4$(aq) is 1 mol $dm^{-3}$.

**12** Compound **P**, $C_6H_{12}$, decolourises hot acidified $KMnO_4$, forming **Q** and **R** as the organic products. **Q** forms a yellow precipitate when warmed with alkaline aqueous iodine. **R** reacts with sodium carbonate to form a colourless gas.

Which statements about the compounds are correct?

1 **P** must exhibit cis-trans isomerism.

2 **P** decolourises aqueous bromine.

3 **Q** forms a silver mirror with Tollens' reagent.

4 **R** forms dense white fumes with $PCl_5$.

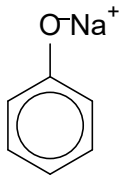
**A** 1 and 3 only

**B** 2 and 4 only

**C** 3 and 4 only

**D** 1, 2 and 4

**13** The compounds that were used to prepare four different solutions of equal concentrations are shown in the table below.

| solution | P | Q | R | S |
|---|---|---|---|---|
| compound | $CH_3CH_2O^-Na^+$ |  | $CH_3COO^-Na^+$ | $CH_3CH_2NH_3^+Cl^-$ |

Which sequence correctly shows the solutions in order of increasing pH?

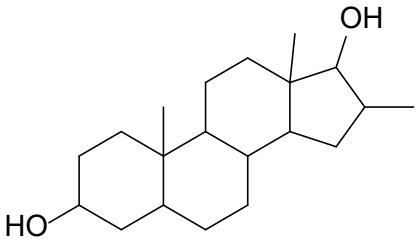
**A** P < Q < R < S

**B** R < Q < P < S

**C** S < R < Q < P

**D** S < P < Q < R

**14** Compound **X** is used in the synthesis of androstenone, a human pheromone.



**X**

Which statement about compound **X** is correct?

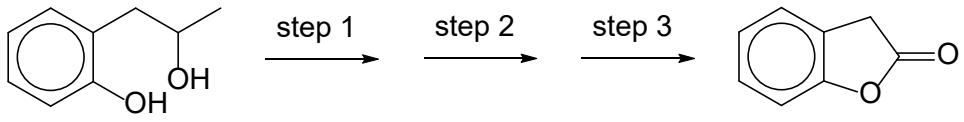
**A** When **X** reacts with $PCl_3$, dense white fumes are released.

**B** When excess Na is added to one mole of **X**, 48 $dm^3$ of $H_2$ is liberated at r.t.p.

**C** When **X** is heated with ethanolic KOH, a product with four $sp^2$ hybridised carbon atoms is formed.

**D** When **X** is heated with excess concentrated $H_2SO_4$, the product formed contains three fewer chiral carbons than **X**.

**15** The reaction scheme below shows the synthesis of compound **Z** from **Y**.




**Y** **Z**

Which row gives the correct reagents and conditions for the three steps?

| | step 1 | step 2 | step 3 |
|---|---|---|---|
| **A** | excess conc. $H_2SO_4$, heat | $KMnO_4$, $H_2SO_4$, heat | $PCl_5$ |
| **B** | $PCl_5$ | ethanolic KCN, heat | NaOH, heat |
| **C** | $I_2$, NaOH, heat | dilute $H_2SO_4$ | $PCl_5$ |
| **D** | $KMnO_4$, $H_2SO_4$, heat | $I_2$, NaOH, heat | $PCl_5$ |

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**[Turn Over**

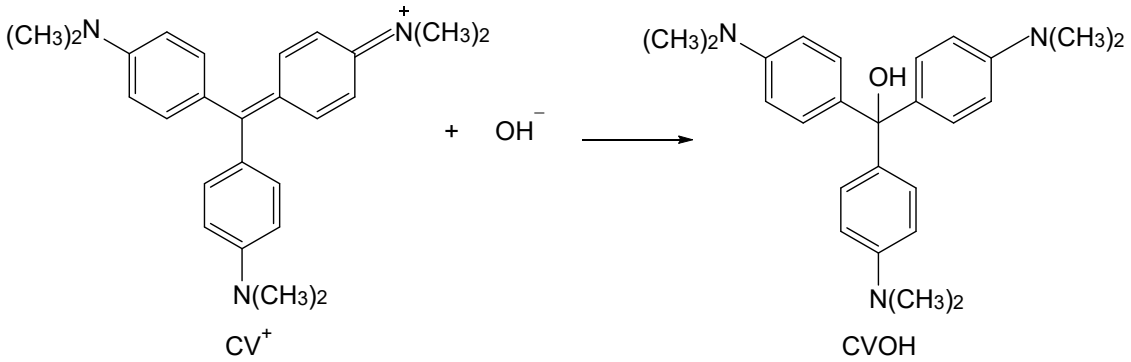
## Section B (40 marks)

This section consists of **3** questions.
Answer **all** the questions in this section in the spaces provided.

*For examiner's use*

**1** Crystal violet (abbreviated as $CV^+$) is a violet organic dye and a pH indicator. The structure of crystal violet is shown in reaction 1.

reaction 1




The multiple double bonds in $CV^+$ allow $\pi$ electrons in the benzene rings to be delocalised extensively within the structure. This extensive delocalisation of electrons is responsible for the violet colour of the $CV^+$ ion in solution.

When $CV^+$ reacts with $OH^-$, the addition of $OH^-$ to the "central" carbon atom disrupts the extensive delocalisation of electrons, and the product formed, CVOH, is colourless.

**(a)** State the hybridisation of the "central" carbon atom in $CV^+$ and in CVOH. Hence explain why the addition of $OH^-$ disrupts the extensive delocalisation of electrons.

hybridisation of "central" carbon atom in $CV^+$: ……..

hybridisation of "central" carbon atom in CVOH: ……..

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…….

……..[2]

**(b)** The rate equation for reaction 1 is shown below.

$$\text{rate} = k[CV^+]^x[OH^-]^y$$

The initial rate of the reaction between $CV^+$ with $OH^-$ ions can be investigated by the "clock" method, where the time taken for the violet colour of $CV^+$ to disappear is measured.

A teacher conducted an experiment by mixing the following:

- 25.0 $cm^3$ of $2.5 \times 10^{-5}$ mol $dm^{-3}$ $CV^+$ solution
- 5.0 $cm^3$ of 1.0 mol $dm^{-3}$ sodium hydroxide, NaOH
- 20.0 $cm^3$ of deionised water.

After 80 seconds, the violet colour of the solution completely faded.

*For examiner's use*

Using the information given, you are required to plan a series of experiments to graphically determine *y*, the order of reaction with respect to sodium hydroxide.

Your plan should ensure that the longest time taken for the violet colour to completely fade is 80 seconds.

You may assume that you are provided with:

- 200 $cm^3$ of $2.5 \times 10^{-5}$ mol $dm^{-3}$ $CV^+$ solution
- 200 $cm^3$ of 1.0 mol $dm^{-3}$ sodium hydroxide, NaOH
- deionised water
- a stopwatch
- the equipment normally found in a school or college laboratory.

In your plan you should include brief details of:

- the apparatus you would use
- the quantities of $CV^+$(aq), NaOH(aq) and deionised water you would use
- the procedure you would follow
- the measurements you would take to allow for a suitable graph to be drawn
- how the graph obtained would be used to determine *y*, the order of reaction with respect to sodium hydroxide.

You may find it useful to use $\frac{1}{\text{time}}$ to represent the reaction rate.

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For examiner's use

*For examiner's use*

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……[7]

**(c)** In a separate experiment to determine the order of reaction with respect to $CV^+$, a student suggested keeping the volume of NaOH used constant but varying the volume of $CV^+$, and then measuring the time taken for the violet colour to completely fade.

The student mistakenly thought that the rate of reaction is directly proportional to $\frac{1}{\text{time}}$. Explain why rate is **not** directly proportional to $\frac{1}{\text{time}}$, even though the total volume for each experiment was kept constant.

……

……[1]

[Total: 10]

*For examiner's use*

**2** Calcium carbonate, commonly known as limestone, has a wide range of uses, such as in construction materials.

**(a)** As calcium carbonate is sparingly soluble, the enthalpy change of solution of calcium carbonate, $\Delta H_{sol}$, is difficult to be determined experimentally. By using Hess' Law, a value for $\Delta H_{sol}$ can be determined.

Using the data in Table 2.1 and the *Data Booklet*, construct an energy cycle to calculate the enthalpy change of solution of calcium carbonate, $\Delta H_{sol}$.

**Table 2.1**

| | value / kJ mol$^{-1}$ |
|---|---|
| enthalpy change of formation of $CaCO_3(s)$ | −1207 |
| enthalpy change of atomisation of Ca(s) | +178 |
| enthalpy change of formation of $CO_3^{2-}(aq)$ | −675 |
| enthalpy change of hydration of $Ca^{2+}(g)$ | −1579 |

[3]

**(b)** With the aid of an equation, explain why a solution of calcium carbonate is basic.

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……..……..

……..……[2]

*For examiner's use*

**(c)** When water passes through mineral rocks containing $Ca^{2+}$ and $Mg^{2+}$, the ions dissolve to form hard water.

The total hardness of water is the sum of calcium and magnesium concentrations, expressed as $CaCO_3$-equivalent in mg $dm^{-3}$. The relative formula mass of $CaCO_3$ is 100.1.

Total hardness in mg $dm^{-3}$ $CaCO_3$-equivalent = $([Ca^{2+}] + [Mg^{2+}]) \times 100.1 \times 1000$

**(i)** Determine the total hardness of a solution containing $5.0 \times 10^{-4}$ mol $dm^{-3}$ $Mg^{2+}$ and $7.5 \times 10^{-4}$ mol $dm^{-3}$ $Ca^{2+}$.

[1]

The city of Guelph in Canada has one of the world's hardest natural water. A sample of water in Guelph has a total hardness of 500.5 mg $dm^{-3}$ $CaCO_3$-equivalent. When excess $Na_2CO_3$ was added to 1 $dm^3$ of the sample, 0.450 g of precipitate containing a mixture of $MgCO_3$ and $CaCO_3$ was formed.

**(ii)** Determine the concentration of $Ca^{2+}$ and the concentration of $Mg^{2+}$, in mol $dm^{-3}$, in the water sample.

[$M_r$: $MgCO_3$, 84.3 $CaCO_3$,100.1]

[2]

Table 2.2 shows the $K_{sp}$ values of the two metal carbonates.

*For examiner's use*

**Table 2.2**

| compound | numerical value of $K_{sp}$ at 25 °C |
|---|---|
| $MgCO_3$ | $6.82 \times 10^{-6}$ |
| $CaCO_3$ | $3.36 \times 10^{-9}$ |

**(iii)** A water sample from a neighbouring city contains 0.0015 mol $dm^{-3}$ $Ca^{2+}$ and 0.0030 mol $dm^{-3}$ $Mg^{2+}$. $Na_2CO_3$ was added in small amounts until the first trace of a white precipitate was seen. The solution was maintained at 25 °C.

Use the data in Table 2.2 to calculate the minimum concentration of carbonate ions present just before each precipitate is formed.

Hence identify the white precipitate.

[2]

For examiner's use

**(d)** A water sample in contact with limestone can be considered as a saturated solution of calcium carbonate.

Fig. 2.1 shows the variation of $K_{sp}$ of $CaCO_3$ with temperature.

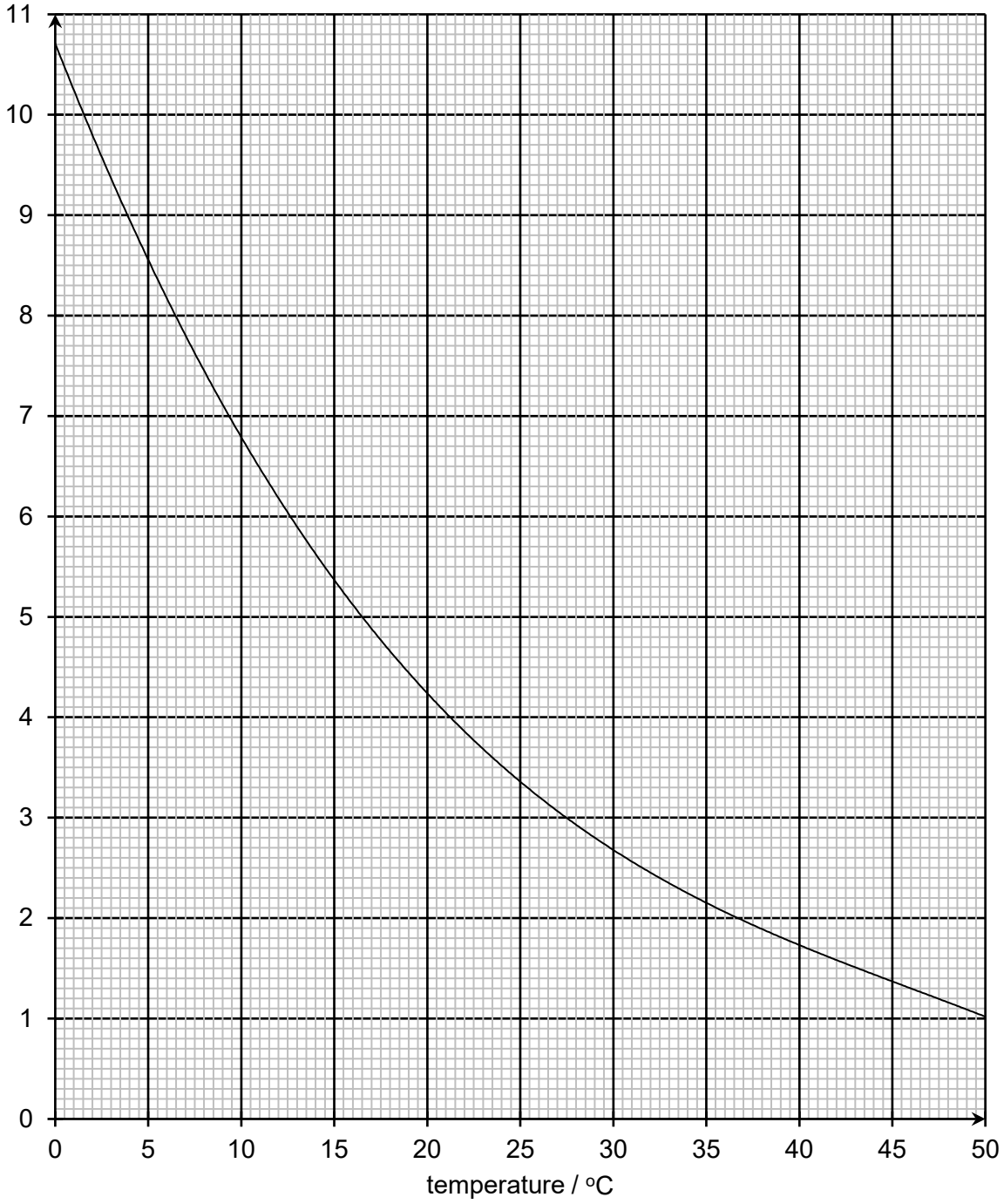


**Fig. 2.1**

**(i)** When this water sample was heated in a kettle, solid $CaCO_3$ was formed. With reference to Fig. 2.1, explain this observation.

……

……[1]

**(ii)** Determine the mass of solid $CaCO_3$ formed in the kettle when 1.5 $dm^3$ of the water sample was heated from 5 °C to 50 °C.

*For examiner's use*

[2]

**(iii)** Using Fig. 2.1, determine the sign of $\Delta S^{\ominus}$ for the dissolution of calcium carbonate.

You may assume that both $\Delta S^{\ominus}$ and $\Delta H^{\ominus}$ remain constant for the temperature range in Fig. 2.1.

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……[2]

[Total: 15]

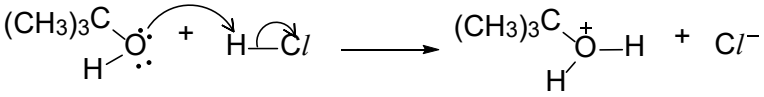
**3** 2-chloro-2-methylpropane, $(CH_3)_3CCl$, is produced industrially as a precursor to other organic compounds.

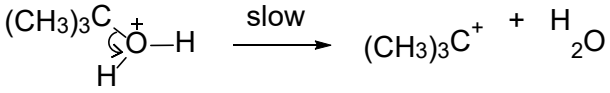
*For examiner's use*

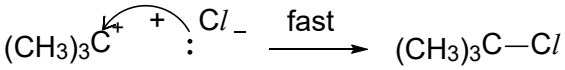
**(a)** $(CH_3)_3CCl$ can be prepared from 2-methylpropan-2-ol and concentrated hydrochloric acid.

$$(CH_3)_3COH + HCl \longrightarrow (CH_3)_3CCl + H_2O$$

The reaction mechanism is shown below.

step 1: 

step 2: 

step 3: 

**(i)** Define the term *Lewis base*.

……[1]

**(ii)** Identify the two different conjugate acid-base pairs in the reaction occurring in step 1.

base: …… conjugate acid: ……

acid: …… conjugate base: ……..……..

[1]

**(b)** $(CH_3)_3CCH_2OH$ can be synthesised from $(CH_3)_3CCl$ in three steps. Suggest the reagents and conditions for each step. Give the structures of the intermediate compounds.

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……..……[3]

*For examiner's use*

**(c)** $(CH_3)_3CCH_2OH$ reacts with HC*l* via a similar mechanism in **(a)**. However, the final product obtained is $(CH_3)_2CClCH_2CH_3$ instead of $(CH_3)_3CCH_2Cl$ as shown in Fig. 3.1.

In the mechanism, carbocation **X** is the intermediate formed after step 2. However, before step 3 occurs, carbocation **X** undergoes a rearrangement reaction to form carbocation **Y**.

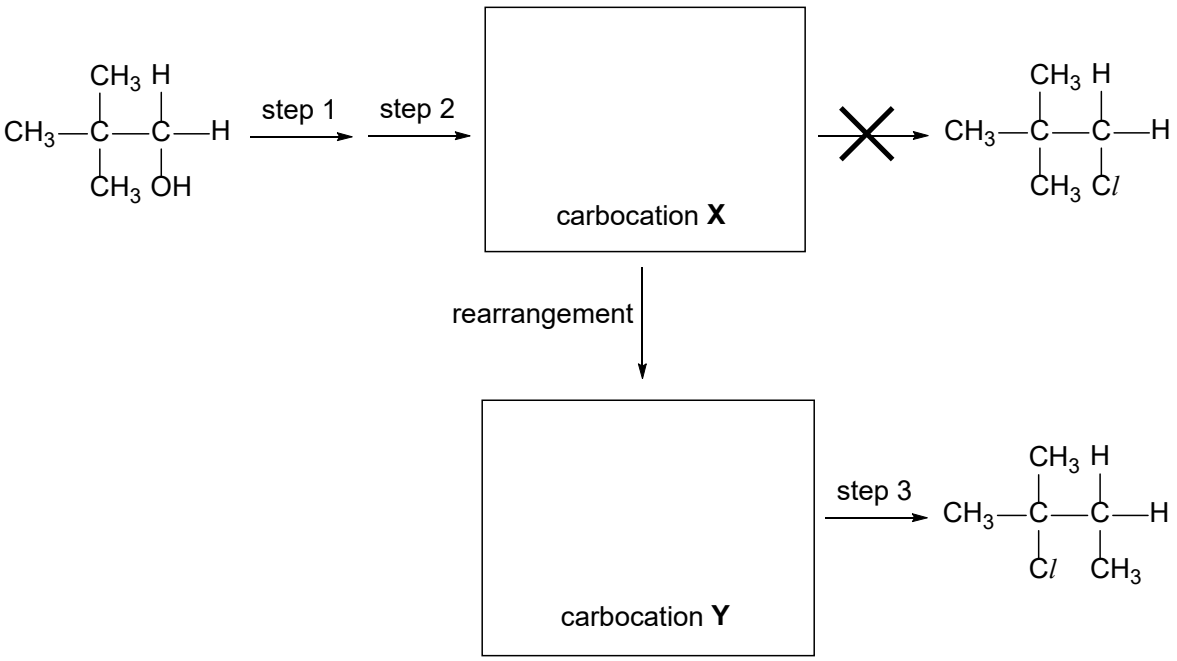


**Fig. 3.1**

**(i)** Draw the structures of carbocations **X** and **Y** in Fig. 3.1. [1]

**(ii)** On Fig. 3.1, draw a curly arrow on carbocation **X** to show the movement of an electron pair in the rearrangement reaction to form carbocation **Y**. [1]

**(iii)** With reference to your answer in **(c)(i)**, explain why carbocation **X** undergoes the rearrangement reaction.

……

……

……[1]

*For examiner's use*

**(d)** Equation 3.1 shows the reaction of 2-chlorobutane with sodium hydroxide.

equation 3.1 $CH_3CHClCH_2CH_3 + OH^- \longrightarrow CH_3CH(OH)CH_2CH_3 + Cl^-$

The rate equation for this reaction is found to be

$$\text{rate} = k[CH_3CHClCH_2CH_3][OH^-]$$

**(i)** Table 3.1 shows the kinetics data for the reaction at 60 °C.

Complete Table 3.1 for this reaction.

**Table 3.1**

| experiment | initial $[CH_3CHClCH_2CH_3]$ / mol $dm^{-3}$ | initial $[OH^-]$ / mol $dm^{-3}$ | initial rate / mol $dm^{-3}$ $s^{-1}$ |
|---|---|---|---|
| 1 | 0.010 | 0.010 | 0.00216 |
| 2 | 0.010 | 0.020 | |
| 3 | | 0.030 | 0.0259 |

[2]

**(ii)** Use the data from experiment 1 in Table 3.1 to calculate the rate constant, *k*, at 60 °C. Include units in your answer.

[1]

*For examiner's use*

**(iii)** Describe the mechanism for the hydrolysis of 2-chlorobutane shown in equation 3.1. Show all relevant charges, dipoles, lone pairs and curly arrows.

[2]

**(iv)** Compare the reactivities of 2-chlorobutane and butanoyl chloride, $CH_3CH_2CH_2COCl$, with water. Give reasons for your answer.

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……...[2]

[Total: 15]

**Additional answer space**

*For examiner's use*

If you use the following pages to complete the answer to any question in Section B, the question number must be clearly shown.

*For examiner's use*

H

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**Higher 2**

**C**

CANDIDATE NAME

CLASS

INDEX NUMBER

**For Examiner's Use Only**

| Section | | Marks |
|---|---|---|
| **A** | | **/ 15** |
| **B** | **B1** | **/ 10** |
| | **B2** | **/ 15** |
| | **B3** | **/ 15** |
| **C**<br>Answer **both C1** and **C2**.<br>**Circle the question (C3 EITHER or C3 OR)** you have answered. | **C1** | **/ 13** |
| | **C2** | **/ 17** |
| | **C3 EITHER** | **/ 10** |
| | **C3 OR** | **/ 10** |
| **Total** | | **/ 95** |
| **Percentage** | | **/ 100** |
| **Penalty** | | |
| **Overall** | | **/ 100** |
| **Grade** | | |

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## Section C (40 marks)

Answer both C1 and C2, and only one of C3 EITHER or C3 OR in this section.
Answers to this section are to be written in the spaces provided in the question paper.

*For examiner's use*

**1** *Use of the Data Booklet is relevant to this question.*

Chlorine is found abundantly in sea water as chloride ions and in arid regions as natural chlorate deposits.

**(a)** Group 2 chlorates(V) have a general formula of $M(ClO_3)_2$.

Upon heating, $M(ClO_3)_2$ decomposes to yield a metal chloride and a colourless gas which relights a glowing splint.

**(i)** Write a balanced equation for the decomposition of magnesium chlorate(V), $Mg(ClO_3)_2$. [1]

**(ii)** $Pb(ClO_3)_2$ decomposes in a similar way as $Mg(ClO_3)_2$.

Suggest whether $Mg(ClO_3)_2$ or $Pb(ClO_3)_2$ decomposes at a lower temperature. Explain your answer. [3]

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**[Turn Over**

**(b)** Chlorine is commercially manufactured by the electrolysis of concentrated sodium chloride (brine). The overall electrolytic process may be represented by the following equation.

*For examiner's use*

$$2NaCl + 2H_2O \xrightarrow{\text{electrolysis}} 2NaOH + Cl_2 + H_2$$

Sodium chlorate(V), $NaClO_3$, can be produced when the products from the electrolysis of brine are allowed to mix at 70–80 ºC, as shown in equation 1.1.

equation 1.1 $\quad 3Cl_2(g) + 6NaOH(aq) \longrightarrow NaClO_3(aq) + 5NaCl(aq) + 3H_2O(l)$

**(i)** State the type of reaction occurring in equation 1.1. Describe the change in oxidation state of chlorine which occurs during this reaction. [1]

The standard Gibbs free energy changes, $\Delta G^{\ominus}$, of some reactions involving different chlorine-containing species are shown in Table 1.1.

**Table 1.1**

| | half-equation | $\Delta G^{\ominus}$ / kJ mol$^{-1}$ |
|---|---|---|
| 1 | $2ClO_3^-(aq) + 12H^+(aq) + 10e^- \longrightarrow Cl_2(g) + 6H_2O(l)$ | –1420 |
| 2 | $Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$ | –262 |

**(ii)** The equation below gives the conversion of $ClO_3^-$ to $Cl^-$.

$$ClO_3^-(aq) + 6H^+(aq) + 6e^- \longrightarrow Cl^-(aq) + 3H_2O(l)$$

Using information from Table 1.1, draw an energy cycle, and calculate $\Delta G^{\ominus}$ for the conversion of $ClO_3^-$ to $Cl^-$. [2]

**(iii)** Hence, calculate $E^{\ominus}$ for the conversion of $ClO_3^-$ to $Cl^-$. [1]

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For examiner's use

For examiner's use

**(c)** A student designed a pH meter as shown in Fig. 1.1.

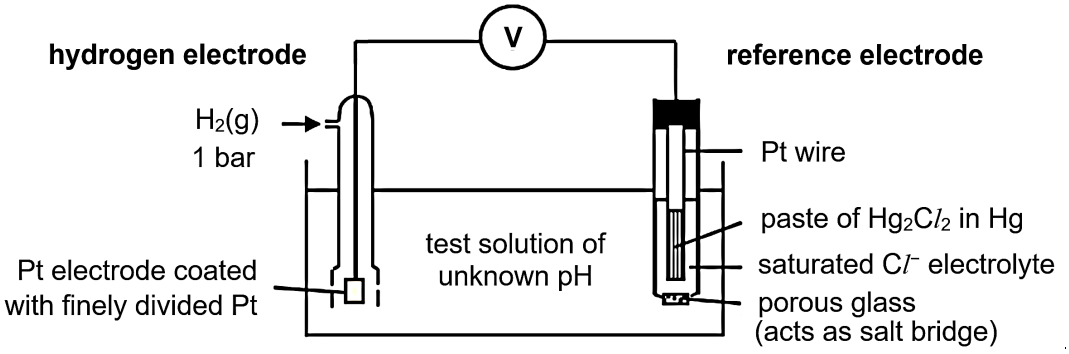


**Fig. 1.1**

When both electrodes are in contact with a test solution, an electric current flows through the wire, and $Hg_2Cl_2$ reacts to form liquid Hg and $Cl^-$ at the reference electrode.

Under standard conditions, the reduction potential of the reference electrode is +0.28 V.

**(i)** Write an overall balanced equation for the reaction in the pH meter. [1]

**(ii)** Explain how the cell potential will change when the pH meter is placed in a solution of a higher pH. [2]

**(iii)** The mathematical equation shown below can be used to calculate the concentration of $H^+$ ions detected by the pH meter.

$$E_{cell} = E^{\ominus}_{cell} - \frac{0.0592}{n} \log_{10} \left( \frac{[H^+]^2[Cl^-]^2}{P_{H_2}} \right)$$

where n is the amount of electrons (in mol) transferred in the overall equation in **(c)(i)**
$[H^+]$ is the molar concentration of $H^+$ ions detected
$[Cl^-]$ is the molar concentration of $Cl^-$ ions at the reference electrode
$P_{H_2}$ is the pressure, in bar, of hydrogen gas passed into the pH meter

The student used his pH meter to analyse a sample of nitric acid solution and he obtained a cell potential reading, $E_{cell}$, of +0.36 V.

Assuming that the concentration of $Cl^-$ is constant at 4.5 mol $dm^{-3}$, calculate the pH of the sample. [2]

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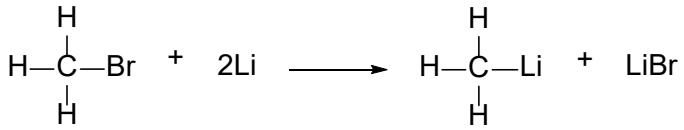
*For examiner's use*

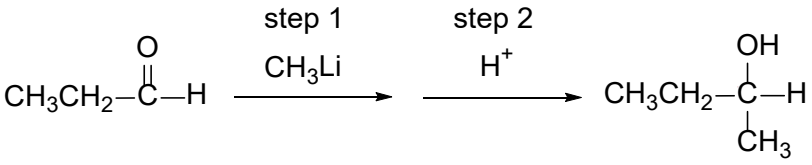
[Total: 13]

*For examiner's use*

**2** Besides forming ionic compounds, lithium also forms organolithium compounds which contain the C−Li covalent bond. Such compounds can be prepared by reacting lithium with an alkyl halide in an inert solvent. An example of the preparation of methyllithium, $CH_3Li$, is shown below.



When propanal is reacted with $CH_3Li$ followed by acidification, butan-2-ol is formed.




**(a)** **(i)** Using the concept of electronegativity, explain why the carbon in $CH_3Li$ is nucleophilic. [1]

**(ii)** Describe the mechanism for steps 1 and 2. Show relevant lone pairs and dipoles, and use curly arrows to indicate the movement of electron pairs.

You may use $:CH_3^-$ to represent $CH_3Li$. [3]

**(iii)** Predict, with reasoning, if the resultant solution would rotate plane polarised light. [2]

**(iv)** In a similar experiment, propanone was used in place of propanal. The rate of reaction was found to decrease substantially. Suggest reasons for the observation. [2]

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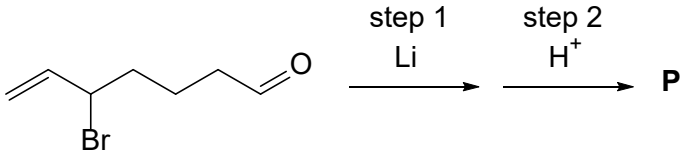
**(b)** Compound **P** ($C_7H_{12}O$) consists of a five-membered ring. **P** is formed when compound **N** is reacted with lithium in an inert solvent, followed by acidification.




**N**

s

**P** is reacted with HC*l*(g) to form **Q** ($C_7H_{13}OCl$).

When **Q** is reacted with hot acidified $KMnO_4$, **R** is formed. **R** reacts with 2,4-dinitrophenylhydrazine to give an orange precipitate, **S**.

When **Q** is heated with ethanolic KCN followed by heating with dilute $H_2SO_4$, **T** ($C_8H_{14}O_3$) is formed. Upon heating **Q** and **T** separately with alkaline aqueous iodine, only **Q** gives a yellow precipitate.

When heated with concentrated $H_2SO_4$, **T** produces a neutral compound **U** ($C_8H_{12}O_2$).

Suggest structures for **P** to **U**, explaining your reasoning. [9]

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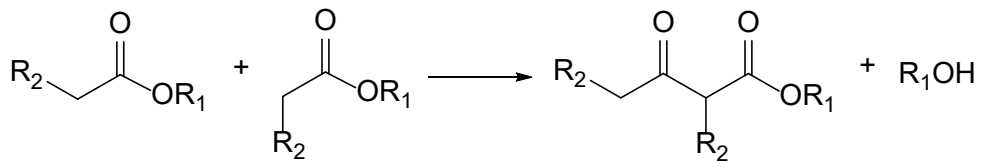
*For examiner's use*

[Total: 17]

For examiner's use

**3 EITHER**

**(a)** In the presence of a strong base, two ester molecules can react to form a β-keto ester, as shown in Fig. 3.1.




β-keto ester

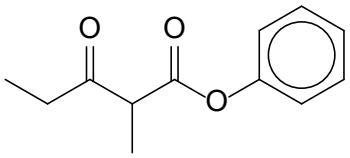
where $R_1$, $R_2$ = H, alkyl, aryl group

**Fig. 3.1**

**(i)** Suggest the type of reaction shown in Fig. 3.1. [1]

**(ii)** When ester **Y** is treated with a strong base, β-keto ester **Z** is formed via the same reaction shown in Fig. 3.1.

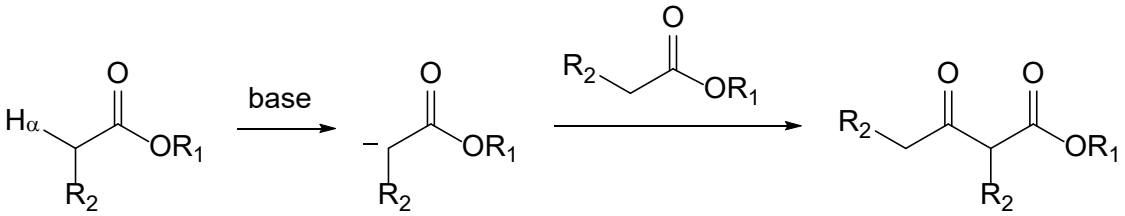
Suggest the structure of the ester **Y**. [1]




**Z**

Fig. 3.2 shows the steps involved in the reaction shown in Fig. 3.1.

In Fig. 3.2, the hydrogen, $H_\alpha$, bonded to a carbon that is adjacent to a carbonyl group is first removed by a base. The anion formed then reacts with another ester to form the β-keto ester.




anion

β-keto ester

**Fig. 3.2**

**(iii)** With reference to the structure of the anion, explain why $H_\alpha$ is acidic. [1]

Methyl benzoate, $C_6H_5COOCH_3$, has a pleasant smell and is often used in perfumery.

**(iv)** When treated with a strong base, $C_6H_5COOCH_3$ does not form a β-keto ester.

Explain why. [1]

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*For examiner's use*

**(v)** However, when $C_6H_5COOCH_3$ and $CH_3CH_2COOCH_3$ are reacted together in the presence of a strong base, a mixture of two β-keto esters is formed.

Suggest the structures of the β-keto esters formed. [2]

*For examiner's use*

**(b)** Compounds **S** and **T** are isomers of $C_6H_5COOCH_3$.

**S** does not form an orange precipitate with 2,4-dinitrophenylhydrazine. **S** reacts with hot acidified $KMnO_4$ to give 2-hydroxybenzoic acid as the only organic product.

**T** does not react with $PCl_5$. When reacted separately with hot acidified $KMnO_4$, **T** and $C_6H_5COOCH_3$ yield the same oxidation products.

Suggest the structures of **S** and **T**. [2]

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**(c)** With the aid of a suitable diagram, explain why 2-hydroxybenzoic acid is more acidic than 4-hydroxybenzoic acid. [2]

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[Total: 10]

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**[Turn Over**

**3 OR**

In an attempt to synthesise $CH_3CH_2NH_2$, a student heated $CH_3CH_2Br$ with $NH_3$ in ethanol. To his disappointment, he obtained a mixture of $CH_3CH_2NH_2$, $(CH_3CH_2)_2NH$, and $(CH_3CH_2)_3N$ instead of only $CH_3CH_2NH_2$.

*For examiner's use*

**(a)** Arrange the following compounds in the gaseous phase in order of increasing p$K_b$. Give reasons for your answer.

$CH_3CH_2NH_2$, $(CH_3CH_2)_2NH$ and $(CH_3CH_2)_3N$

[3]

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Upon further research, the student found a better method to obtain $CH_3CH_2NH_2$ via the reaction scheme as shown in Fig. 3.3.

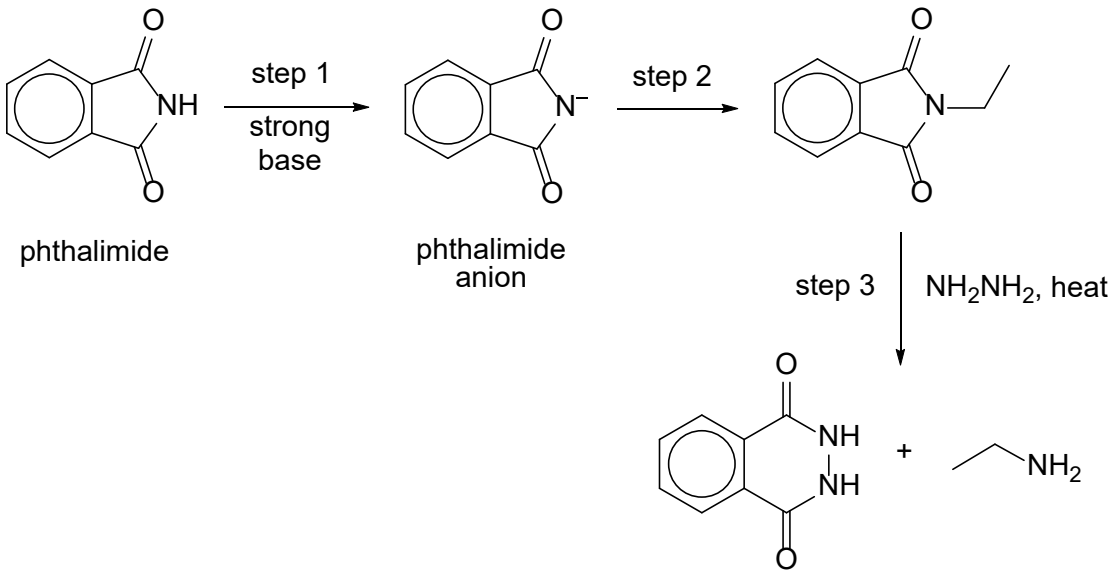


**Fig. 3.3**

*For examiner's use*

**(b)** **(i)** Unlike many other amides, phthalimide is acidic when treated with a strong base.

With reference to the structure of the phthalimide anion, explain why. [1]

**(ii)** State the reagents and conditions required for step 2. [1]

**(iii)** Suggest the type of reaction in step 3. [1]

**(iv)** The student prepared 50 $cm^3$ of 0.50 mol $dm^{-3}$ $CH_3CH_2NH_2$. Calculate the pH of the $CH_3CH_2NH_2$ solution.

($pK_b$ of $CH_3CH_2NH_2$ = 3.20) [2]

**(v)** To prepare a buffer solution of pH 10.0, the student added $x$ $cm^3$ of 0.20 mol $dm^{-3}$ aqueous HC*l* to the 50 $cm^3$ solution of 0.50 mol $dm^{-3}$ $CH_3CH_2NH_2$.

Calculate the value of $x$. [2]

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[Total: 10]

**Additional answer space**

*For examiner's use*

If you use the following pages to complete the answer to any question in Section C, the question number must be clearly shown.

*For examiner's use*