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CHEMISTRY

9701/04

Paper 4 A Level Structured Questions

For Examination from 2016

SPECIMEN PAPER

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, candidate number and name on all the work you hand in.

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.

DO NOT WRITE IN ANY BARCODES.

Answer **all** questions.

Electronic calculators may be used.

You may lose marks if you do not show your working or if you do not use appropriate units.

A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.

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

This document consists of **21** printed pages and **1** blank page.

Answer **all** the questions in the spaces provided.

- 1 (a) (i) Describe and explain the trend observed in the thermal stability of the carbonates of the Group 2 elements.

.....
.....
.....
..... [3]

- (ii) By quoting suitable data from the *Data Booklet* suggest how the thermal stabilities of zinc carbonate and lead carbonate might compare to that of calcium carbonate.

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

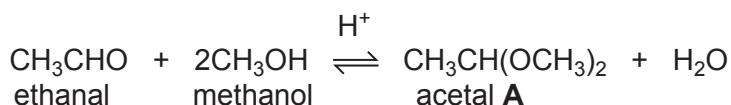
- (b) Describe and explain qualitatively the trend in the solubilities of the hydroxides of the Group 2 elements.

.....
.....
.....
.....
..... [4]

[Total: 9]

Question 2 begins on the next page.

- 2 Acetals are compounds formed when aldehydes are reacted with an alcohol in the presence of an acid catalyst. The reaction between ethanal and methanol was studied in the inert solvent dioxan.



- (a) In an experiment, the concentrations of the reactants and products were measured. The results are shown in the table below.

| | $[\text{CH}_3\text{CHO}] / \text{mol dm}^{-3}$ | $[\text{CH}_3\text{OH}] / \text{mol dm}^{-3}$ | $[\text{H}^+] / \text{mol dm}^{-3}$ | $[\text{acetal A}] / \text{mol dm}^{-3}$ | $[\text{H}_2\text{O}] / \text{mol dm}^{-3}$ |
|----------------|--|---|-------------------------------------|--|---|
| at start | 0.20 | 0.10 | 0.05 | 0.00 | 0.00 |
| at equilibrium | $(0.20-x)$ | | | x | |
| at equilibrium | | | | 0.025 | |

- (i) Complete the second row of the table in terms of x , the concentration of acetal **A** at equilibrium. The first one has been done for you. [3]
- (ii) Using the [acetal **A**] as given, $0.025 \text{ mol dm}^{-3}$, calculate the equilibrium concentrations of the other reactants and products and write them in the third row of the table. [4]
- (iii) Write the expression for the equilibrium constant for this reaction, K_c , stating its units.

$$K_c =$$

units = [2]

- (iv) Use your values in the third row of the table to calculate the value of K_c .

$$K_c = [1]$$

- (b) When the initial rate of this reaction was measured at various starting concentrations of the three reactants, the following results were obtained.

| experiment number | $[\text{CH}_3\text{CHO}] / \text{mol dm}^{-3}$ | $[\text{CH}_3\text{OH}] / \text{mol dm}^{-3}$ | $[\text{H}^+] / \text{mol dm}^{-3}$ | relative rate |
|-------------------|--|---|-------------------------------------|---------------|
| 1 | 0.20 | 0.10 | 0.05 | 1.00 |
| 2 | 0.25 | 0.10 | 0.05 | 1.25 |
| 3 | 0.25 | 0.16 | 0.05 | 2.00 |
| 4 | 0.20 | 0.16 | 0.10 | 3.20 |

- (i) Use the data in the table to determine the order with respect to each reactant.

order with respect to $[\text{CH}_3\text{CHO}]$

order with respect to $[\text{CH}_3\text{OH}]$

order with respect to $[\text{H}^+]$

[3]

- (ii) Use your results from (i) to write the rate equation for the reaction.

..... [1]

- (iii) State the units of the rate constant in the rate equation.

..... [1]

- (iv) Calculate the relative rate of reaction for a mixture in which the starting concentrations of all three reactants are 0.20 mol dm^{-3} .

relative rate = [1]

[Total: 16]

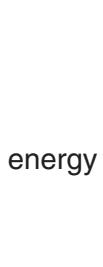
- 3 (a) Complete the electronic structure for

Fe [Ar]

Fe³⁺ [Ar] [1]

- (b) In an isolated atom the five d orbitals have the same energy. When a transition element ion is in an octahedral complex the d orbitals are split into two groups.

- (i) Draw an orbital energy diagram to show this, indicating the number of orbitals in each group.



[2]

- (ii) Use your diagram in (i) to explain why transition element complexes are often coloured.

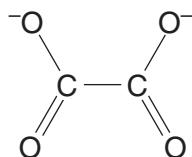
.....
.....
.....
..... [3]

- (iii) Use your diagram in (i) to explain why the colour of a complex of a given transition element often changes when the ligands around it are changed.

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

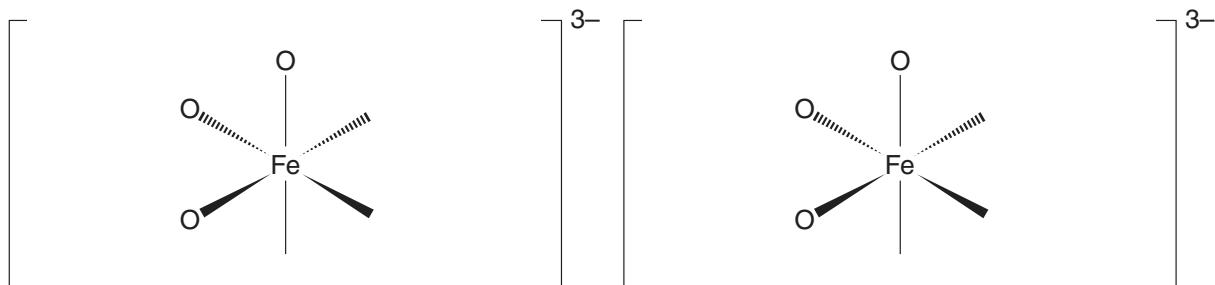
- (c) Heating a solution containing potassium ethanedioate, iron(II) ethanedioate and hydrogen peroxide produces the light green complex $\text{K}_3\text{Fe}(\text{C}_2\text{O}_4)_3$, which contains the ion $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$.

The structure of the ethanedioate ion is as follows.



- Calculate the oxidation number of carbon in this ion. [1]
- Calculate the oxidation number of iron in $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ [1]
- The iron atom in the $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ ion is surrounded octahedrally by six oxygen atoms. The ion shows stereoisomerism.

Complete the two diagrams of the ion showing both stereoisomers.



[2]

- In sunlight, the complex decomposes into potassium ethanedioate, iron(II) ethanedioate and carbon dioxide.

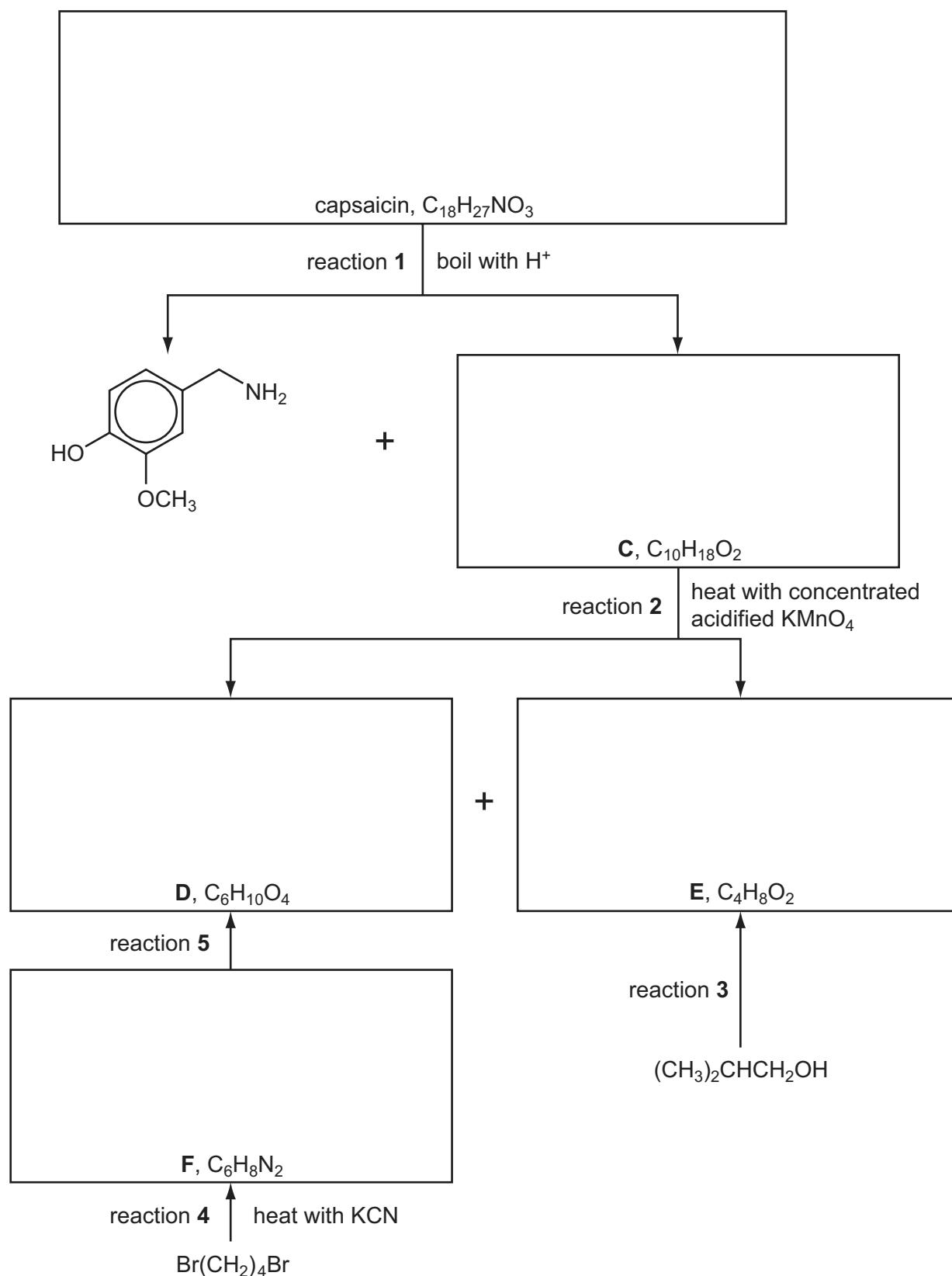
Balance the equation for this decomposition.



[1]

[Total: 13]

- 4 The compound responsible for the hot taste of chilli peppers is capsaicin. Its molecular structure can be deduced by the following reaction scheme.



Compounds **C**, **D** and **E** all react with $Na_2CO_3(aq)$.

Answer the following questions.

- (a) Suggest reagents and conditions for reaction 3.

..... [1]

- (b) What type of reaction is reaction 4?

..... [1]

- (c) Suggest reagents and conditions for reaction 5.

..... [1]

- (d) Name the functional group in C that has reacted with hot, concentrated, acidified KMnO_4 .

..... [1]

- (e) Suggest the name of the functional group in capsaicin that has reacted in reaction 1.

..... [1]

- (f) Work out structures for compounds C–F and capsaicin, and draw their structural formulae in the boxes on page 8. [5]

[Total: 10]

5 (a) State the functional groups positively identified by the following.

(i) $\text{Br}_2(\text{aq})$

..... [1]

(ii) $\text{Na}(\text{s})$

..... [1]

(iii) $\text{I}_2(\text{aq}) + \text{OH}^-(\text{aq})$

..... [1]

(iv) 2,4-dinitrophenylhydrazine

..... [1]

Compound **G** has the molecular formula $\text{C}_7\text{H}_{14}\text{O}$. Treating **G** with hot, concentrated, acidified $\text{KMnO}_4(\text{aq})$ produces two compounds, **H**, $\text{C}_4\text{H}_8\text{O}$, and **J**, $\text{C}_3\text{H}_4\text{O}_3$. The four reagents in (a) were used to test these three compounds and the results are shown in the table below.

| test reagent | result of test with | | |
|--|---------------------|--------------------|--------------------|
| | compound G | compound H | compound J |
| $\text{Br}_2(\text{aq})$ | decolourises | no reaction | no reaction |
| $\text{Na}(\text{s})$ | fizzes | no reaction | fizzes |
| $\text{I}_2(\text{aq}) + \text{OH}^-(\text{aq})$ | no reaction | yellow precipitate | yellow precipitate |
| 2,4-dinitrophenylhydrazine | no reaction | orange precipitate | orange precipitate |

(b) Based on the results of the tests in the table, suggest structures for compounds **H** and **J**.

H, $\text{C}_4\text{H}_8\text{O}$

J, $\text{C}_3\text{H}_4\text{O}_3$

[2]

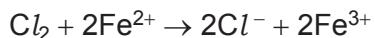
(c) Compound **G** exists as two stereoisomers.

Draw the structural formula of **each** of the two isomers, and state the type of stereoisomerism involved.

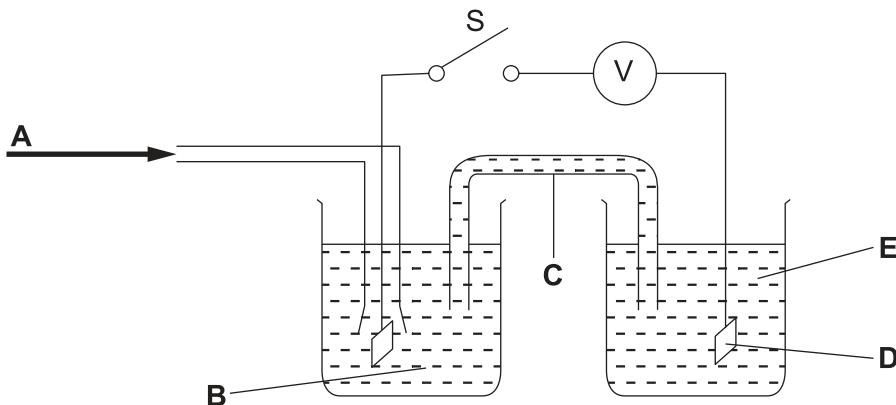
type of stereoisomerism [3]

[Total: 9]

- 6 Chlorine gas and iron(II) ions react together in aqueous solution as follows.



- (a) The diagram below shows the apparatus needed to measure the $E_{\text{cell}}^{\ominus}$ for the above reaction.



- (i) In the spaces below, identify what the five letters A–E in the above diagram represent.

A

B

C

D

E

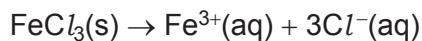
[5]

- (ii) Use the *Data Booklet* to calculate the $E_{\text{cell}}^{\ominus}$ for this reaction, and hence decide which direction (left to right, or right to left) electrons would flow through the voltmeter V when switch S is closed.

$$E_{\text{cell}}^{\ominus} = \dots \text{ V}$$

direction of electron flow [2]

- (b) Iron(III) chloride readily dissolves in water.



- (i) Use the following data to calculate the standard enthalpy change for this process.

| species | $\Delta H_f^\ominus \text{ kJ mol}^{-1}$ |
|-----------------------------|--|
| $\text{FeCl}_3(\text{s})$ | -399.5 |
| $\text{Fe}^{3+}(\text{aq})$ | -48.5 |
| $\text{Cl}^-(\text{aq})$ | -167.2 |

$$\Delta H^\ominus = \dots \text{ kJ mol}^{-1} [2]$$

- (ii) A solution of iron(III) chloride is used to dissolve unwanted copper from printed circuit boards.

When a copper-coated printed circuit board is immersed in $\text{FeCl}_3(\text{aq})$, the solution turns pale blue.

Suggest an equation for the reaction between copper and iron(III) chloride and use the *Data Booklet* to calculate the E^\ominus for the reaction.

equation

$$E^\ominus = \dots \text{ V} [2]$$

[Total: 11]

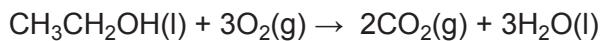
- 7 (a) The table lists the equations for five processes.

For each process, predict the sign of ΔS .

| process | sign of ΔS |
|--|--------------------|
| $\text{NaBr(s)} + \text{(aq)} \rightarrow \text{NaBr(aq)}$ | |
| $\text{H}_2\text{O(l)} \rightarrow \text{H}_2\text{O(g)}$ | |
| $2\text{H}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{H}_2\text{O(g)}$ | |
| $\text{CoCl}_2\text{(s)} + 6\text{H}_2\text{O(l)} \rightarrow \text{CoCl}_2\cdot 6\text{H}_2\text{O(s)}$ | |

[2]

- (b) Ethanol can be combusted as shown in the equation.



Standard entropies are shown in the table.

| substance | $\text{CH}_3\text{CH}_2\text{OH(l)}$ | $\text{O}_2\text{(g)}$ | $\text{CO}_2\text{(g)}$ | $\text{H}_2\text{O(l)}$ |
|--|--------------------------------------|------------------------|-------------------------|-------------------------|
| $S^\ominus, \text{ J K}^{-1} \text{ mol}^{-1}$ | 161 | 205 | 214 | 70 |

Calculate the standard entropy change, ΔS^\ominus , for this reaction.

$$\Delta S^\ominus = \dots \text{ J K}^{-1} \text{ mol}^{-1} [2]$$

- (c) The combustion of ethanol is an exothermic reaction.

This reaction occurs spontaneously at low temperatures but does **not** occur at very high temperatures. Explain why.

.....

.....

.....

.....

[2]

- (d) The decomposition of calcium carbonate is an endothermic reaction.



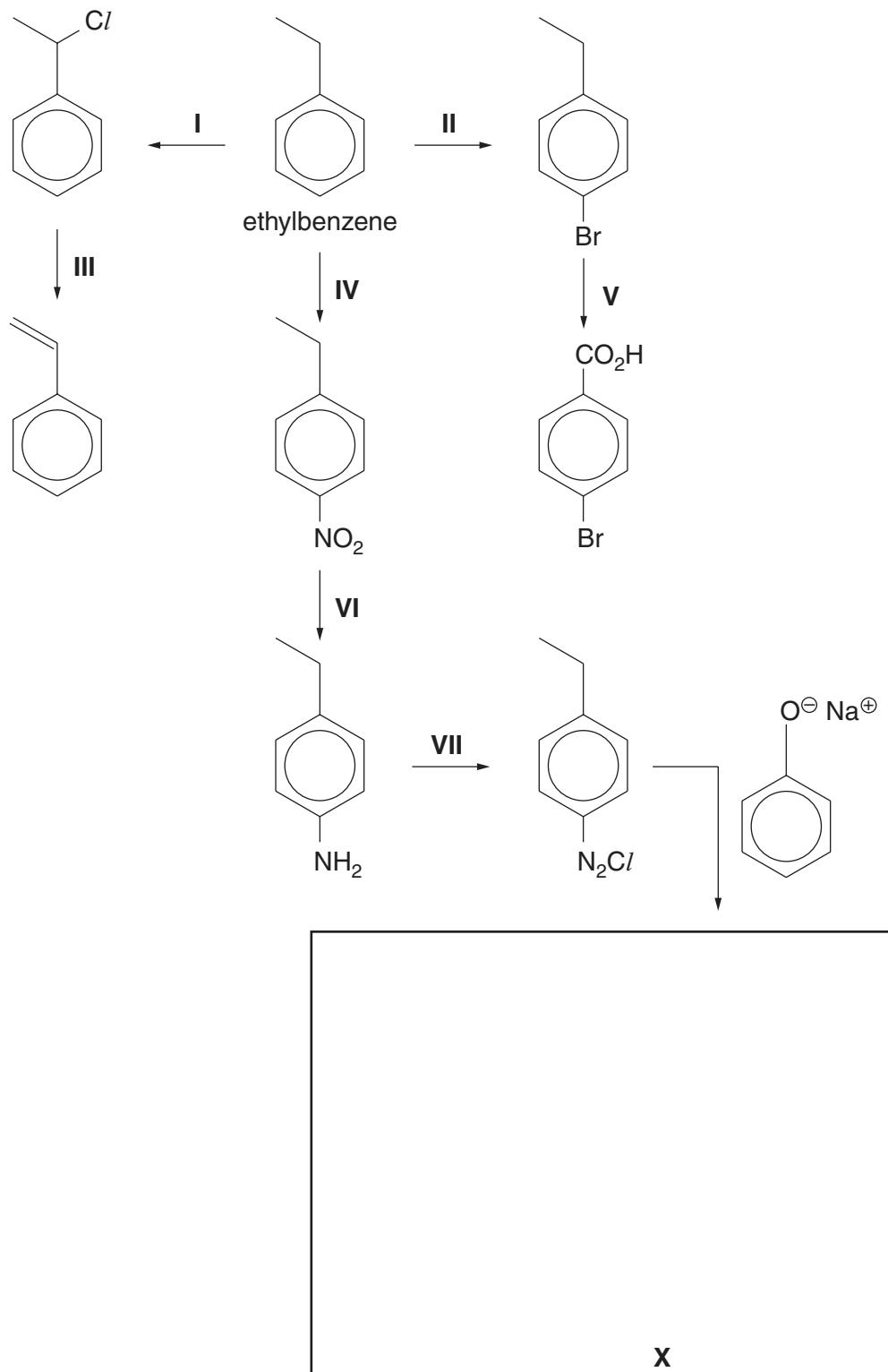
$\Delta H = +178 \text{ kJ mol}^{-1}$ and $\Delta S = +159 \text{ J K}^{-1} \text{ mol}^{-1}$

Calculate the **minimum** temperature at which this reaction becomes feasible.
Show all your working.

[3]

[Total: 9]

- 8 The following chart shows some reactions of ethylbenzene and compounds produced from it.



- (a) Draw the structure of compound X in the box above.

[1]

(b) Suggest reagents and conditions for each of the reactions.

reaction I

reaction II

reaction III

reaction IV

reaction V

reaction VI

reaction VII

[Total: 9]

- 9 (a) A chemist analysed a mixture and separated compound Y using gas chromatography (GC), and measured its retention time.

State what is meant by *retention time*.

.....
.....

[1]

- (b) Compound Y was analysed using two techniques with the following results.

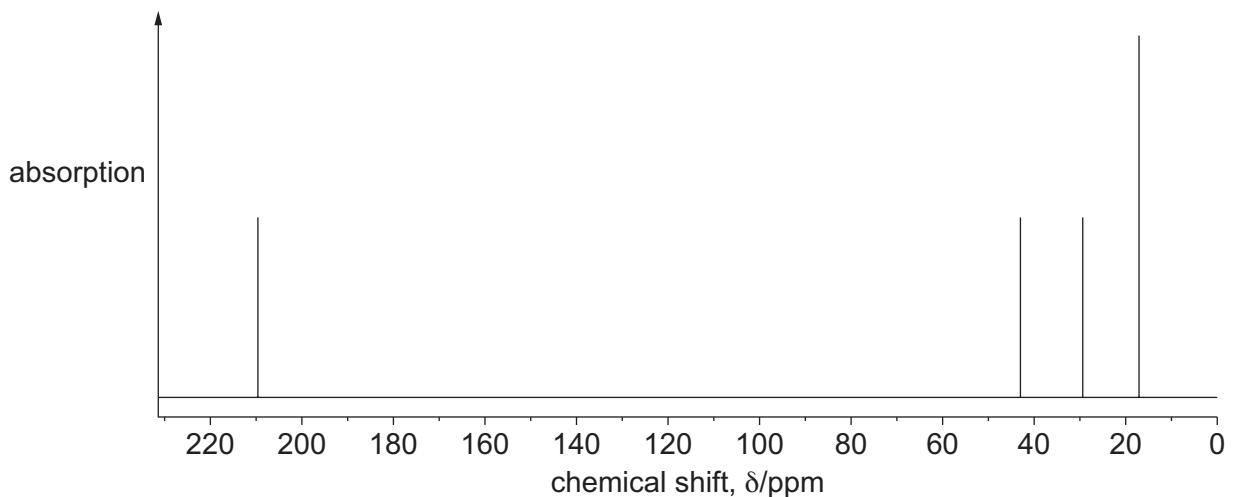
The mass spectrum showed that,

- the M peak was at m/e 86,
- the ratio of heights of the M and M+1 peaks was 23.5 : 1.3.

- (i) Use these data about the ratio of peak heights to show that there are five carbons in Y.

[1]

A carbon-13 NMR spectrum of Y is shown.

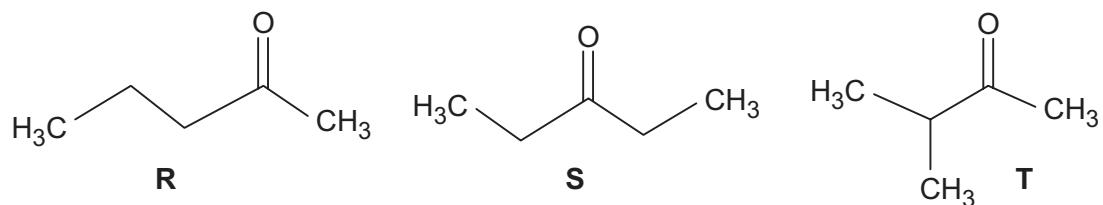


- (ii) Use this spectrum to describe the main features of Y. Use of the *Data Booklet* may be helpful.

.....
.....
.....

[3]

(iii) Y is one of three isomeric ketones R, S or T.



Use the carbon-13 NMR spectrum to identify Y as either R, S or T.

Explain how you ruled out the **other two** isomers.

.....
.....
.....
.....
..... [3]

[Total: 8]

10 Polypeptides are made by the condensation polymerisation of amino acids.

- (a) Explain what is meant by the term *condensation polymerisation*.

..... [1]

- (b) Polypeptide molecules coil and fold, producing proteins with complex three-dimensional shapes. This is referred to as the secondary and tertiary structures of a protein.

Complete the table by placing a tick (✓) in the correct column to indicate which level of protein structure (secondary or tertiary) can contain **each** bonding type.

| bonding type | secondary structure | tertiary structure |
|------------------|---------------------|--------------------|
| hydrogen bonding | | |
| ionic bonding | | |
| van der Waals' | | |

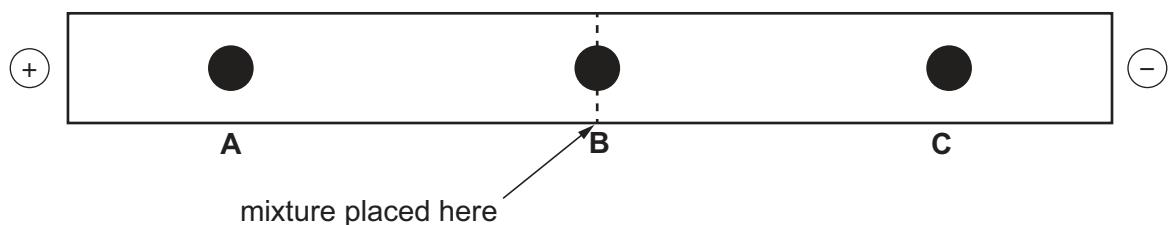
[2]

(c) Electrophoresis is a technique that can be used to separate amino acids present in a mixture.

- (i) State **one** factor that will determine the direction of travel of an amino acid during electrophoresis.

..... [1]

- (ii) A mixture of three amino acids, **A**, **B** and **C**, was analysed by this technique at pH 7. Use the *Data Booklet* to suggest the possible identity of each of these three amino acids, **A**, **B** and **C**.



| amino acid | identity of amino acid |
|------------|------------------------|
| A | |
| B | |
| C | |

[2]

[Total: 6]

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