Cambridge International AS & A Level

Cambridge International Examinations
Cambridge International Advanced Subsidiary and Advanced Level

CANDIDATE NAME	

CENTRE NUMBER		CANDIDATE NUMBER	

8488148240

CHEMISTRY **9701/42**

Paper 4 A Level Structured Questions **February/March 2017**

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 **24** printed pages.

IB17 03_9701_42/6RP

CAMBRIDGE
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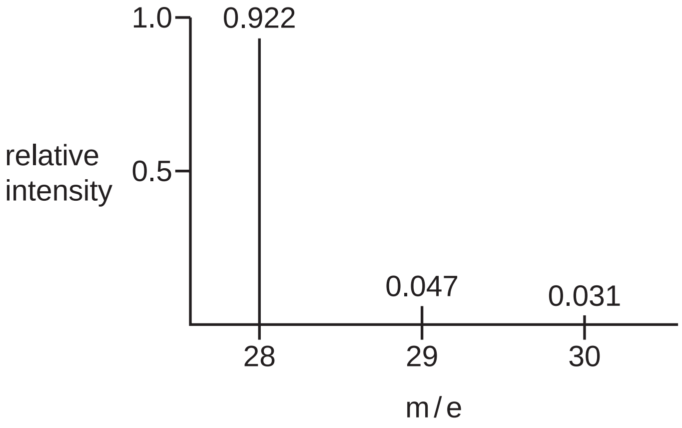
[Turn over

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

1 **(a)** **(i)** The mass spectrum of silicon is shown.



Calculate the A_r of silicon. Give your answer to **two** decimal places.

A_r = ... [1]

(ii) Silicon forms a low boiling point chloride which reacts with water.

Write an equation to show the reaction of the chloride with water.

.... [1]

(iii) Draw a three-dimensional diagram showing the shape of the chloride. Give the C*l*–Si–C*l* bond angle.

[2]

(iv) Silicon reacts with oxygen to form a high melting point oxide.

- Suggest the formula of the oxide. ....
- Suggest, in terms of structure, why the oxide has a high melting point whereas the chloride has a low boiling point.

....

....

....
[2]

(b) Element **A** is in the same period as silicon. Element **A** reacts with dilute nitric acid to form a nitrate. This nitrate decomposes on heating to form an oxide.

(i) Write an equation for the decomposition of the nitrate.

.... [2]

(ii) The oxide of element **A** has a high melting point.

Suggest the structure and bonding present in the oxide of **A**.

.... [1]

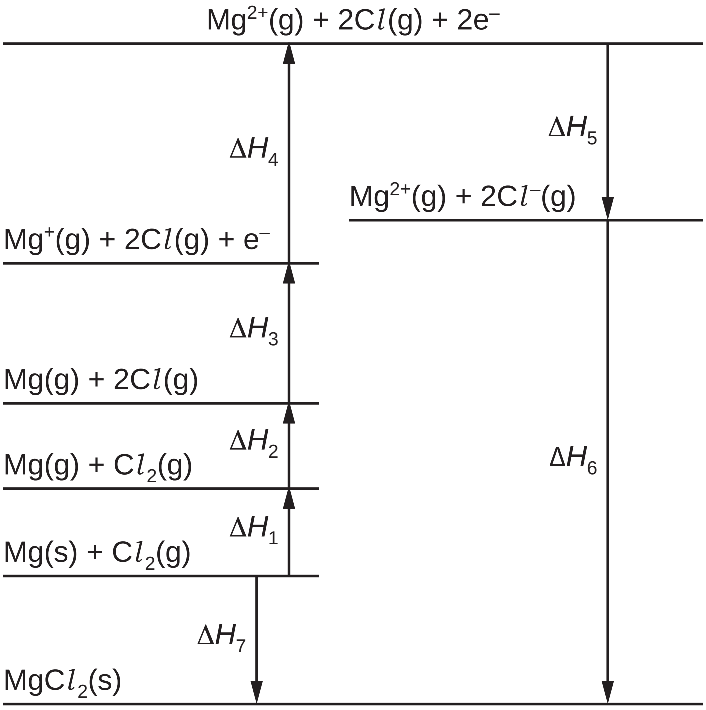
[Total: 9]

2 **(a)** Complete the table using ticks (✓) to indicate whether the sign of each type of energy change, under standard conditions, is always positive, always negative or could be either positive or negative.

energy change	always positive	always negative	either positive or negative
electron affinity			
enthalpy change of atomisation			
ionisation energy			
lattice energy			

[2]

(b) The Born-Haber cycle for magnesium chloride is shown.



(i) Explain why ΔH_4 is greater than ΔH_3.

....

.... [1]

(ii) What names are given to the enthalpy changes ΔH_6 and ΔH_7?

ΔH_6 ....

ΔH_7 ....

[1]

(c) Chlorine is in Group 17.

Suggest the trend in the first electron affinity of the elements in Group 17. Explain your answer.

....

....

.... [2]

(d) The equation for the formation of magnesium oxide from its elements is shown.

$$\text{Mg(s)} + \tfrac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{MgO(s)} \qquad \Delta H^{\ominus} = -602\,\text{kJ mol}^{-1}$$

substance	$S^{\ominus}$ / J K^{-1} mol^{-1}
Mg(s)	32.7
O_2(g)	205
MgO(s)	26.9

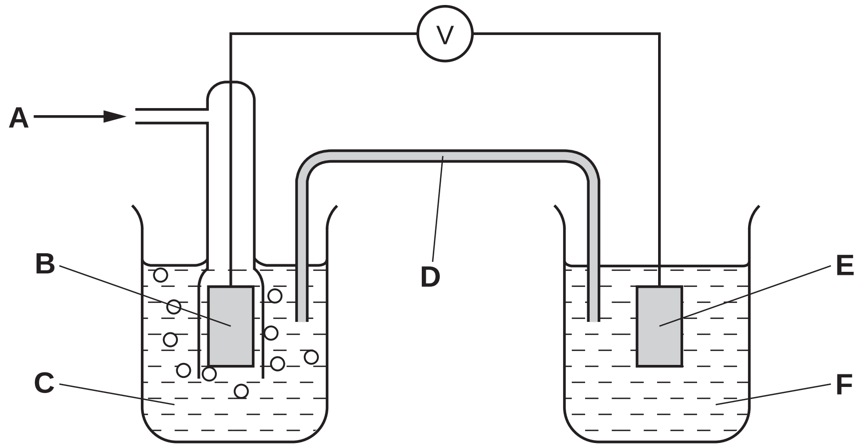
Use the equation and the data given in the table to calculate $\Delta G^{\ominus}$ for the reaction at 25 °C.

$\Delta G^{\ominus}$ = ... units ....

[4]

[Total: 10]

3 **(a)** The diagram shows the apparatus used to measure the standard electrode potential, $E^{\ominus}$, of $Fe^{3+}(aq) / Fe^{2+}(aq)$.



(i) Identify what the letters **A** to **F** represent.

A ....

B ....

C ....

D ....

E ....

F ....

[3]

(ii) Label the diagram to show

- which is the positive electrode,
- the direction of electron flow in the external circuit.

Use the *Data Booklet* to help you.

[1]

(b) In another experiment, an $Fe^{3+}(aq) / Fe^{2+}(aq)$ half-cell was connected to a $Cu^{2+}(aq) / Cu(s)$ half-cell.

Determine the standard cell potential, $E^{\ominus}_{cell}$, when these two half-cells are connected by a wire and the circuit is completed.
Use the *Data Booklet* to help you.

$E^{\ominus}_{cell}$ = ... V [1]

(c) **(i)** The $E^{\ominus}$ of $Ni^{2+}(aq) / Ni(s)$ is –0.25 V.

State and explain how the electrode potential changes if the concentration of $Ni^{2+}(aq)$ is decreased.

....

....

.... [1]

(ii) The $E^{\ominus}$ of $Cr^{3+}(aq) / Cr^{2+}(aq)$ is –0.41 V.

Calculate the electrode potential when $[Cr^{3+}(aq)]$ is 0.60 mol dm^{-3} and $[Cr^{2+}(aq)]$ is 0.15 mol dm^{-3}. Use the Nernst equation.

$$E = E^{\ominus} + \frac{0.059}{z} \log \frac{[\text{oxidised species}]}{[\text{reduced species}]}$$

E = ... V [2]

[Total: 8]

4 **(a)** Chlorine dioxide undergoes the following reaction in aqueous solution.

$$2ClO_2 + 2OH^- \rightarrow ClO_2^- + ClO_3^- + H_2O$$

The initial rate of the reaction was measured at different initial concentrations of ClO_2 and OH^-. The table shows the results obtained.

experiment	$[ClO_2]$ / mol dm^{-3}	$[OH^-]$ / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	1.25×10^{-2}	1.30×10^{-3}	2.33×10^{-4}
2	2.50×10^{-2}	1.30×10^{-3}	9.34×10^{-4}
3	2.50×10^{-2}	2.60×10^{-3}	1.87×10^{-3}

(i) Use the data in the table to determine the rate equation, showing the order with respect to each reactant. Show your reasoning.

....

....

....

....

....

....

rate equation = ...

[3]

(ii) Calculate the value of the rate constant, *k*, using the data from experiment 2. State its units.

k = ... units .... [2]

(b) **(i)** Explain the difference between heterogeneous and homogeneous catalysts.

....

....

.... [1]

(ii) Complete the table using ticks (✓) to indicate whether the catalyst used in the reaction is heterogeneous or homogeneous.

catalysed reaction	heterogeneous	homogeneous
manufacture of ammonia in the Haber process		
removal of nitrogen oxides from car exhausts		
oxidation of sulfur dioxide in the atmosphere		

[2]

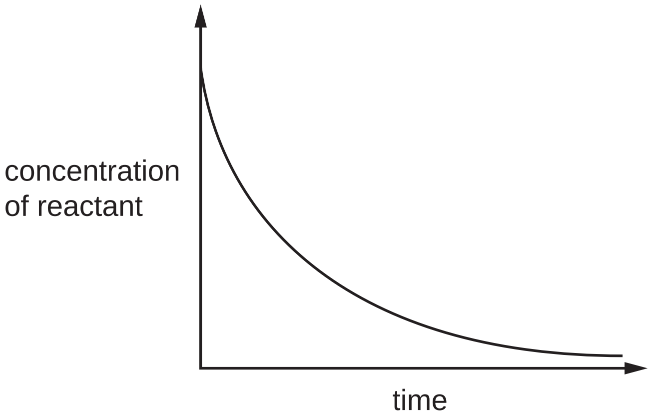
(c) Some reactions are catalysed by one of the products of the reaction. This is called autocatalysis. An example of autocatalysis is the reaction between acidified manganate(VII) ions, MnO_4^-, and ethanedioic acid, $(CO_2H)_2$. Mn^{2+} ions catalyse this reaction. The reaction is slow in the absence of a catalyst.

(i) Balance the equation for this reaction.

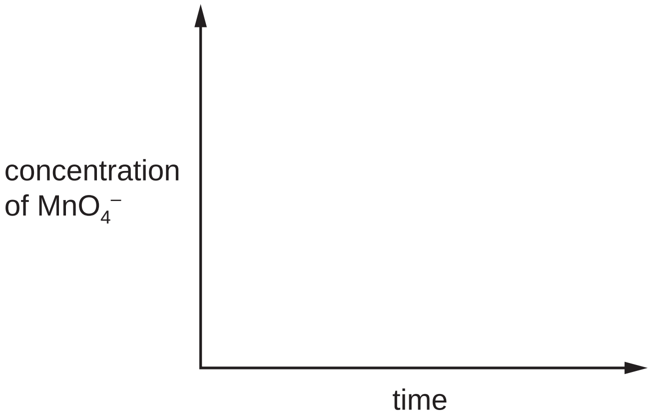
$$......MnO_4^- + ...H^+ + ...(CO_2H)_2 \rightarrow ......Mn^{2+} + ...CO_2 + ...H_2O$$

[2]

(ii) The graph shown is a concentration-time graph for a typical reaction.



On the axes below, sketch the curve you would expect for the autocatalysed reaction in **(i)**.



[2]

(d) **(i)** Describe, with the aid of a reaction pathway diagram, the effect of a catalyst on a reversible reaction. Suggest why catalysts are used in industrial processes.

....

....

....
[3]

(ii) The reaction for the Haber process to produce ammonia is shown.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H^\ominus = -92\,kJ\,mol^{-1}$$

At 500 °C, when pressure is measured in atmospheres, the numerical value of K_p for this equilibrium is 1.45×10^{-5}.

- Write the expression for K_p for this equilibrium.

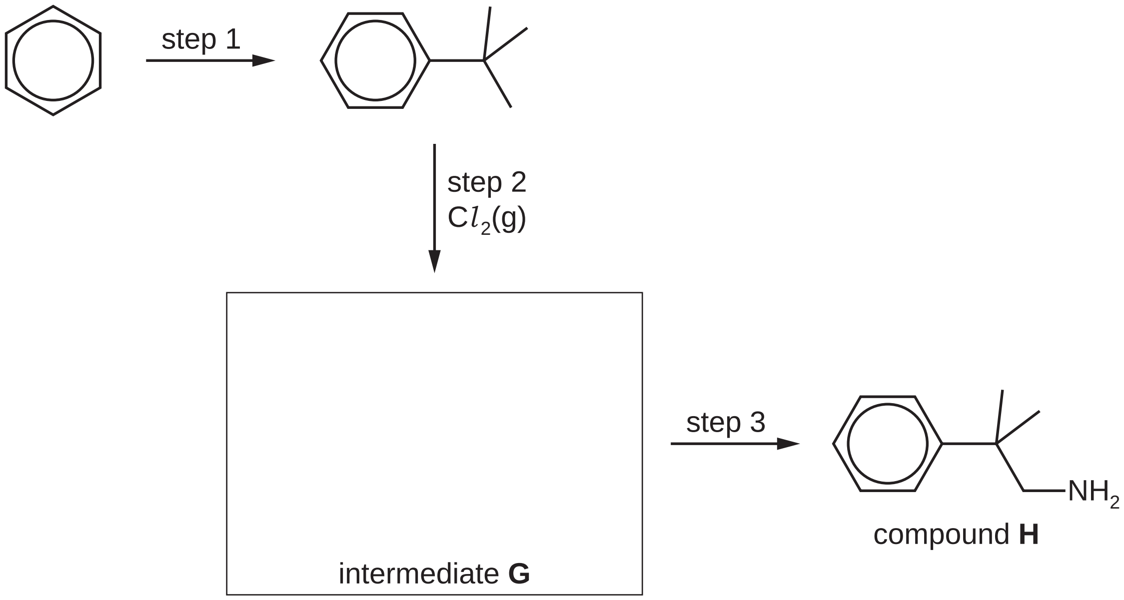
K_p =

- Calculate the partial pressure of NH_3 at equilibrium at 500 °C, when the partial pressure of N_2 is 20 atm and that of H_2 is 60 atm.

p_{NH_3} = ... atm
[2]

[Total: 17]

5 **(a)** Compound **H** can be synthesised from benzene as shown.



intermediate **G**

compound **H**

(i) State the reagents and conditions needed for step 1.

reagents ....

conditions .... [2]

(ii) Step 2 takes place in the presence of chlorine gas.

State the conditions for this reaction.

.... [1]

(iii) Draw the structure of intermediate **G** in the box. [1]

(iv) State the reagents and conditions needed for step 3.

reagents ....

conditions .... [2]

(b) Write an equation to show how compound **H**, $C_{10}H_{13}NH_2$, behaves as a base.

.... [1]

(c) Compare the relative basicities of ammonia, phenylamine and compound **H**. Explain your answer.

....

....

.... [2]

[Total: 9]

6 **(a)** **(i)** Draw the shape of one of the d orbitals.

[1]

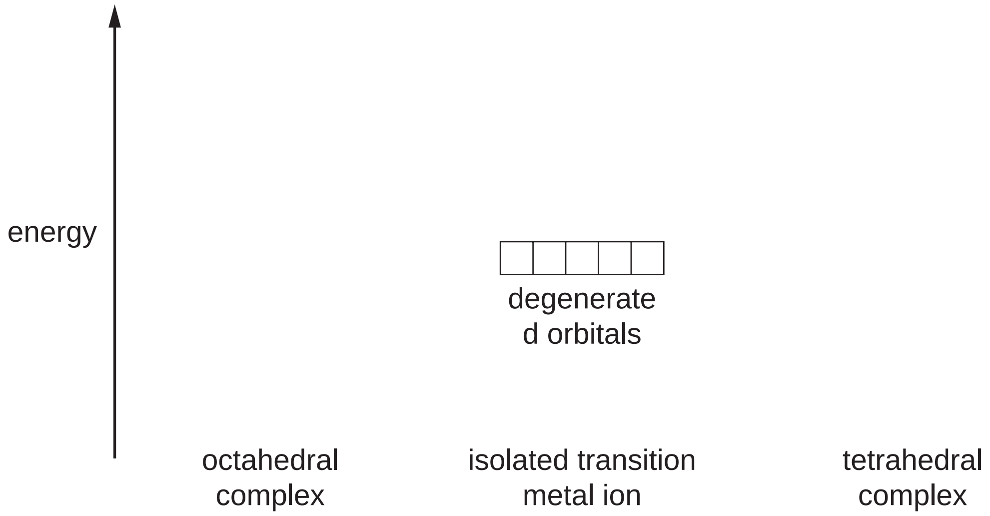
(ii) Complete the following electronic configurations.

Ni $1s^2 2s^2 2p^6 3s^2 3p^6$ ....

Ni^{3+} $1s^2 2s^2 2p^6 3s^2 3p^6$ ....

[1]

(b) **(i)** Complete the diagram to show how the presence of ligands around an isolated transition metal ion affects the **energy** of the d orbitals.



[1]

(ii) Explain why transition metal complexes are coloured.

....

....

....

.... [2]

(iii) $[Cu(H_2O)_6]^{2+}$ is pale blue but $[Cu(NH_3)_4(H_2O)_2]^{2+}$ is deep purple-blue.

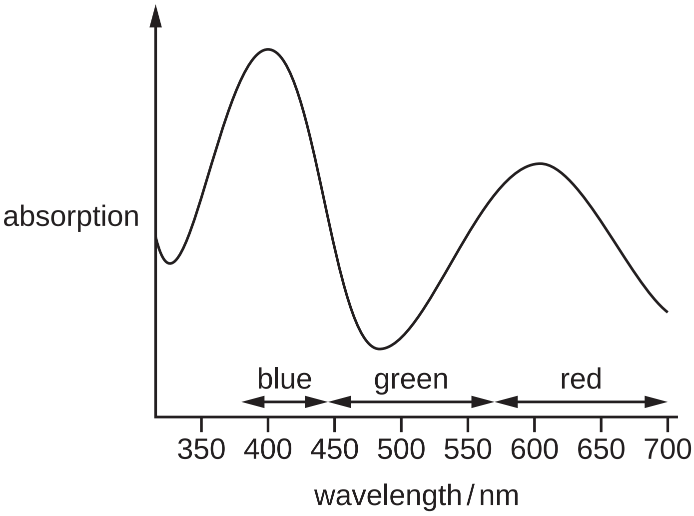
Suggest a reason for this.

....

....

.... [1]

(c) The diagram shows the visible spectrum of a solution of $[V(H_2O)_6]^{3+}$.



State and explain what colour the solution is.

colour of solution ....

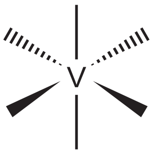
explanation ....

.... [2]

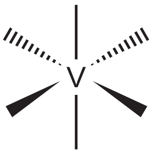
(d) **(i)** In the presence of chloride ions, $[V(H_2O)_6]^{3+}$ reacts to form a mixture of isomeric octahedral complexes.

$$[V(H_2O)_6]^{3+} + 2Cl^- \rightleftharpoons [V(H_2O)_4Cl_2]^+ + 2H_2O$$

Complete the three-dimensional diagrams to show the **two** isomers of $[V(H_2O)_4Cl_2]^+$.



isomer 1



isomer 2

[2]

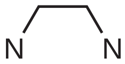
(ii) State the type of isomerism shown by isomer 1 and isomer 2 in **(i)**.

.... [1]

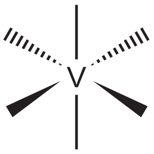
(e) **(i)** The complex $[V(H_2O)_6]^{3+}$ also reacts with ethane-1,2-diamine (*en*), $H_2NCH_2CH_2NH_2$, to form a mixture of isomeric octahedral complexes.

$$[V(H_2O)_6]^{3+} + 3en \rightleftharpoons [V(en)_3]^{3+} + 6H_2O$$

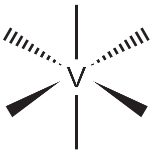
Complete the three-dimensional diagrams to show the **two** isomers of $[V(en)_3]^{3+}$.

You may use 

to represent *en*.



isomer 1



isomer 2

[2]

(ii) State the type of isomerism shown by isomer 1 and isomer 2 in **(i)**.

.... [1]

(f) The reaction of $[Ni(H_2O)_6]^{2+}$ with aqueous ammonia produces the complex $[Ni(NH_3)_6]^{2+}$.

$$[Ni(H_2O)_6]^{2+}(aq) + 6NH_3(aq) \rightleftharpoons [Ni(NH_3)_6]^{2+}(aq) + 6H_2O(l)$$

(i) Write the expression for K_{stab} for $[Ni(NH_3)_6]^{2+}$.

K_{stab} =

[1]

(ii) $[Ni(H_2O)_6]^{2+}$ also reacts with *en* to form $[Ni(en)_3]^{2+}$.
The values of the stability constants for the two complexes are shown.

K_{stab} $[Ni(NH_3)_6]^{2+} = 4.8 \times 10^7\,mol^{-6}\,dm^{18}$

K_{stab} $[Ni(en)_3]^{2+} = 2.0 \times 10^{18}\,mol^{-3}\,dm^9$

A solution containing equal numbers of moles of ammonia and *en* is added to $[Ni(H_2O)_6]^{2+}$.

State which complex is produced in the larger amount. Explain your answer.

....

....

.... [1]

(iii) Adding a limited amount of *en* to $[Ni(H_2O)_6]^{2+}$ forms the complex $[Ni(H_2O)_2(en)_2]^{2+}$.

Suggest the number of possible stereoisomers of $[Ni(H_2O)_2(en)_2]^{2+}$. Explain your answer.
You are advised to include three-dimensional diagrams in your answer.

....

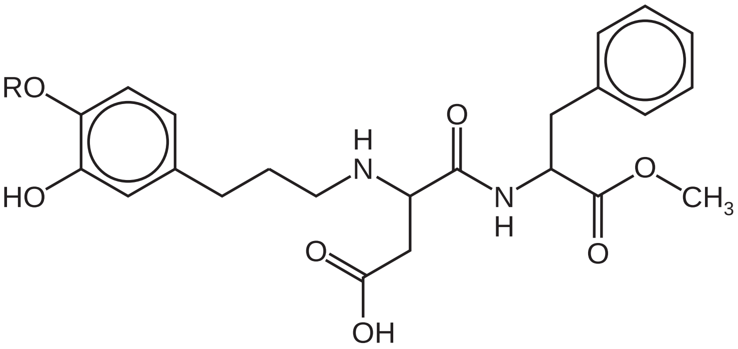
....

....

.... [2]

[Total: 18]

7 The compound *Advantame* is a sweetener that tastes approximately 25 000 times sweeter than sucrose.

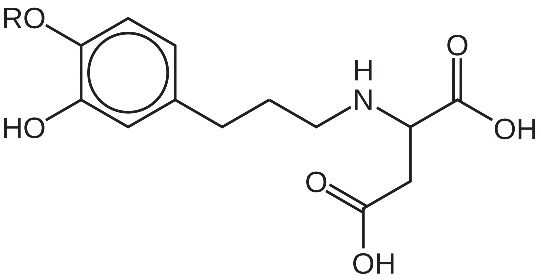


Advantame

(a) *Advantame* is optically active.

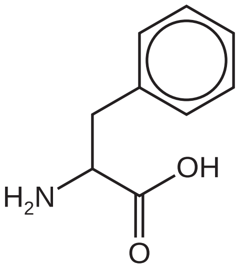
On the diagram of *Advantame*, circle all the chiral carbon atoms. [1]

(b) The decomposition of *Advantame* produces three molecules, **J**, **K** and **L**. The RO– group in *Advantame* is unreactive.



J

+



K

+

L

(i) Suggest possible reagents and conditions for this decomposition.

.... [1]

(ii) Name the *type of reaction* occurring.

.... [1]

(iii) Draw the structure of **L** in the box above. [1]

(c) **(i)** Aqueous bromine was added dropwise to a solution of **J** until the bromine was in excess.

State what you would observe.

....

.... [1]

(ii) **J** has the molecular formula $C_{14}H_{19}O_6N$.

Use this formula to write an equation for the reaction of excess aqueous sodium hydroxide with **one** mole of **J**.

.... [2]

(d) **(i)** State what you would observe when an excess of aqueous bromine is added to a solution of **K**.

.... [1]

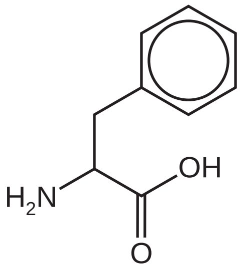
(ii) **K** can be polymerised.

Draw the structure of the polymer showing **two** repeat units. The linkage between the monomer units should be fully displayed.

[2]

(e) Use the *Data Booklet* to help you answer this question.

The carbon-13 NMR spectrum of **K** was recorded.



K

(i) State how many different carbon environments are present in **K**.

.... [1]

(ii) The chemical shifts, δ, due to two of the carbon atoms x and y present in **K** are given in the table.

carbon atom	δ / ppm
x	130
y	170

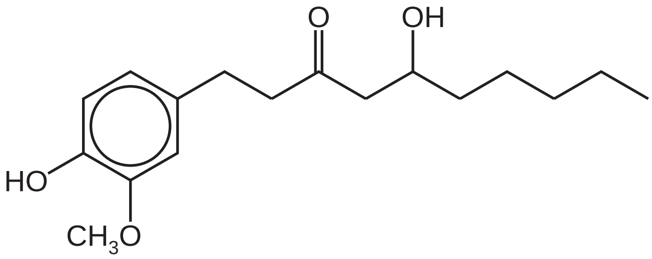
On the structure of **K**, circle **and** label **two** carbon atoms which could correspond to x and y. [1]

[Total: 12]

Question 8 starts on the next page.

8 The root of the ginger plant contains compounds with medicinal and flavouring properties. Three of the more important compounds are gingerol, shogaol and zingerone.

(a) The structure of gingerol is shown. The CH_3O– group in gingerol is unreactive.



gingerol

Gingerol reacts with acidified potassium dichromate(VI).

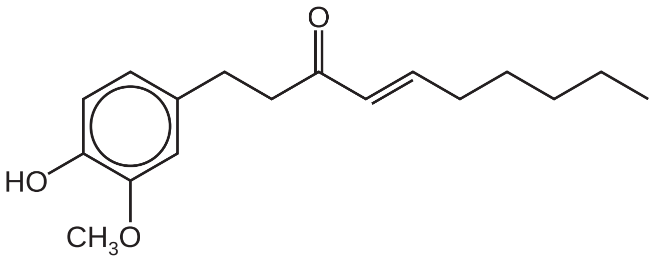
State the *type of reaction* and the functional group change which occurs during this reaction.

type of reaction ....

functional group change

from .... to .... [1]

(b) The structure of shogaol is shown.



shogaol

(i) State the *type of reaction* needed to convert gingerol into shogaol.

.... [1]

(ii) State the reagents and conditions needed to convert gingerol into shogaol.

reagents ....

conditions ....
[1]

(iii) Shogaol reacts with hot, concentrated acidified manganate(VII) ions to form two organic products, **Q** and **R**.

Draw the structures of **Q** and **R**.

Q

R

[2]

(c) Zingerone is formed from gingerol.

Some reactions of zingerone are shown.

Complete the table to identify the functional groups in zingerone.

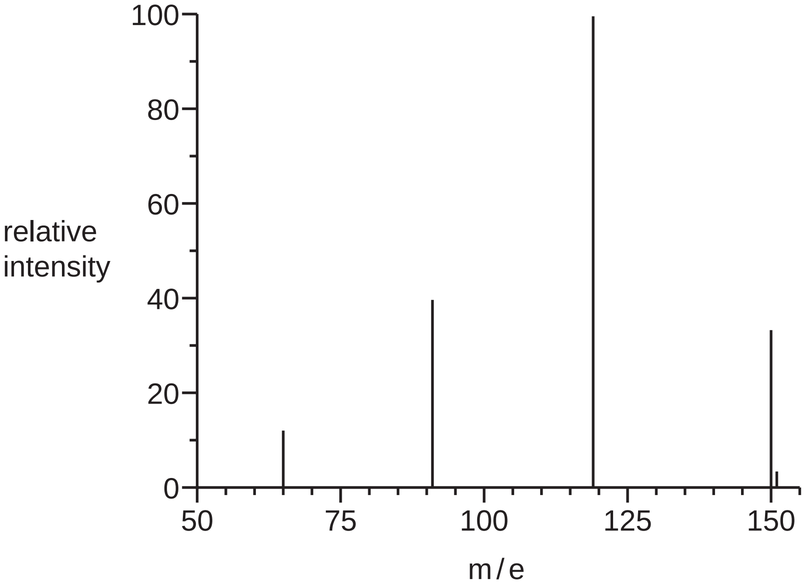
reagent and conditions	observation	functional group in zingerone indicated by the observation
benzenediazonium chloride, 5 °C, alkaline solution	red ppt.	
2,4-dinitrophenylhydrazine	orange ppt.	
warm with Tollens' reagent	no change	

[2]

[Total: 7]

9 This question is about compound **T**, $C_xH_yO_z$.

(a) Part of the mass spectrum of **T** is shown.
The peak heights of the M and M+1 peaks are 33.9 and 3.4 respectively.



(i) Calculate x, the number of carbon atoms present in **T**.

x = ... [2]

(ii) Deduce the molecular formula of **T**.

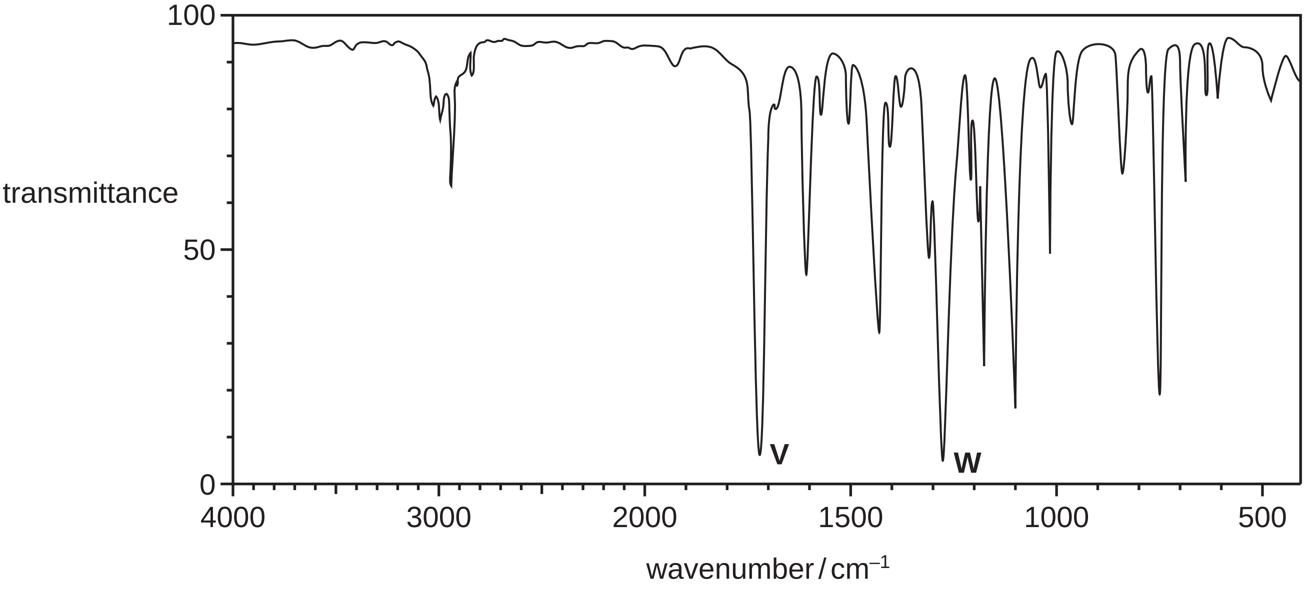
.... [1]

(iii) The mass spectrum has a peak at m / e = 119.

Identify the fragment lost from **T** to produce this peak.

.... [1]

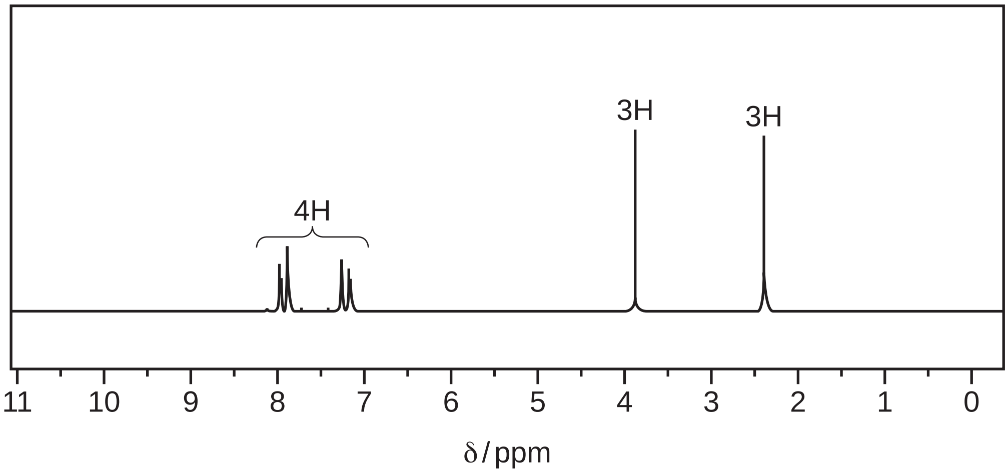
(b) The infra-red spectrum of **T** is shown.



Identify the type of bond responsible for each of the peaks **V** and **W**.
Use the *Data Booklet* to help you.

V .... **W** .... [1]

(c) The proton NMR spectrum of **T** in $CDCl_3$ is shown.



(i) Complete the table for the proton NMR spectrum of **T**.
Use the *Data Booklet* to help you.

δ / ppm	type of proton
3.9	
7.2–7.9	

[1]

(ii) The peak at $\delta = 2.4$ ppm is due to a proton attached to a saturated carbon atom.

State the **two** possible types of proton.

1. ....

2. ....
[1]

(iii) Adding D_2O to **T** does **not** change its proton NMR spectrum.

What does this tell you about the functional groups present in **T**?

.... [1]

(d) Use the information to draw **two** possible structures of **T** which are functional group isomers of each other.

[2]

[Total: 10]
