

Write your name here

Surname

Other names

Pearson
Edexcel GCE

Centre Number

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Candidate Number

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Chemistry

Advanced

**Unit 4: General Principles of Chemistry I – Rates,
Equilibria and Further Organic Chemistry
(including synoptic assessment)**

Tuesday 13 June 2017 – Afternoon

Time: 1 hour 40 minutes

Paper Reference

6CH04/01

**You must have: Data Booklet
Scientific calculator**

Total Marks

Instructions

- Use **black** ink or **black** ball-point pen.
- **Fill in the boxes** at the top of this page with your name, centre number and candidate number.
- Answer **all** questions.
- Answer the questions in the spaces provided
– *there may be more space than you need.*

Information

- The total mark for this paper is 90.
- The marks for **each** question are shown in brackets
– *use this as a guide as to how much time to spend on each question.*
- Questions labelled with an **asterisk** (*) are ones where the quality of your written communication will be assessed
– *you should take particular care with your spelling, punctuation and grammar, as well as the clarity of expression, on these questions.*
- A Periodic Table is printed on the back cover of this paper.

Advice

- Read each question carefully before you start to answer it.
- Keep an eye on the time.
- Try to answer every question.
- Check your answers if you have time at the end.

Turn over ►

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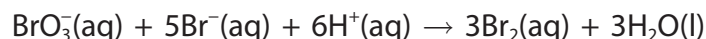



Pearson

SECTION A

Answer ALL the questions in this section. You should aim to spend no more than 20 minutes on this section. For each question, select one answer from A to D and put a cross in the box . If you change your mind, put a line through the box and then mark your new answer with a cross .

- 1 Bromate(V) ions react with bromide ions in the presence of a dilute acid.



The rate of this reaction can be determined by measuring the change in colour intensity or the change in conductivity of the solution.

Which changes will occur?

	Change in colour intensity	Change in conductivity
<input type="checkbox"/> A	decreases	decreases
<input type="checkbox"/> B	decreases	increases
<input type="checkbox"/> C	increases	decreases
<input type="checkbox"/> D	increases	increases

(Total for Question 1 = 1 mark)

- 2 Substance **A** decomposes in a first order reaction.

The half-life for this reaction is 48 s.

In an experiment, the initial amount of **A** is 1.00 mol.

The amount, in moles, of **A** remaining at 144 s is

- A 0.500
 B 0.333
 C 0.250
 D 0.125

(Total for Question 2 = 1 mark)

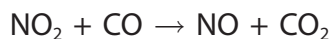
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3 Nitrogen dioxide, NO_2 , reacts with carbon monoxide, CO .



The rate equation is $\text{rate} = k[\text{NO}_2]^2$.

(a) The concentration of nitrogen dioxide was doubled and the concentration of carbon monoxide was halved, while the temperature remained constant.

The rate constant, k , will

(1)

- A stay the same.
- B double.
- C triple.
- D quadruple.

(b) Which is a possible mechanism for the reaction that is consistent with the rate equation?

(1)

- A $2\text{NO}_2 + 2\text{CO} \rightarrow \text{N}_2 + \text{O}_2 + 2\text{CO}_2$ fast
 $\text{N}_2 + \text{O}_2 \rightarrow 2\text{NO}$ slow
- B $2\text{NO}_2 + 2\text{CO} \rightarrow \text{N}_2 + \text{O}_2 + 2\text{CO}_2$ slow
 $\text{N}_2 + \text{O}_2 \rightarrow 2\text{NO}$ fast
- C $2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2$ fast
 $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$ slow
- D $2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2$ slow
 $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$ fast

(Total for Question 3 = 2 marks)

Use this space for any rough working. Anything you write in this space will gain no credit.



- 4 The decomposition of a concentrated solution of hydrogen peroxide is slow at room temperature.

What does this indicate about the values for the activation energy and the rate constant for this decomposition?

	Activation energy	Rate constant
<input type="checkbox"/> A	high	high
<input type="checkbox"/> B	high	low
<input type="checkbox"/> C	low	high
<input type="checkbox"/> D	low	low

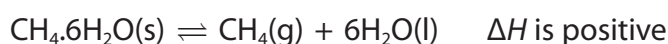
(Total for Question 4 = 1 mark)

- 5 Which process produces a **decrease** in the entropy of the system?

- A $\text{Mg(s)} + \text{H}_2\text{SO}_4\text{(aq)} \rightarrow \text{MgSO}_4\text{(aq)} + \text{H}_2\text{(g)}$
- B $\text{H}_2\text{O(s)} \rightarrow \text{H}_2\text{O(l)}$
- C $2\text{H}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{H}_2\text{O(g)}$
- D $\text{CaCO}_3\text{(s)} \rightarrow \text{CaO(s)} + \text{CO}_2\text{(g)}$

(Total for Question 5 = 1 mark)

- 6 Methane hydrate, $\text{CH}_4 \cdot 6\text{H}_2\text{O}$, decomposes to form methane and water.



Which conditions of temperature and pressure will give the highest equilibrium yield of methane?

	Temperature	Pressure
<input type="checkbox"/> A	high	high
<input type="checkbox"/> B	high	low
<input type="checkbox"/> C	low	high
<input type="checkbox"/> D	low	low

(Total for Question 6 = 1 mark)



7 Ethanoic acid, CH_3COOH , can react with methanoic acid, HCOOH .

$\text{p}K_{\text{a}}$ of ethanoic acid = 4.8

$\text{p}K_{\text{a}}$ of methanoic acid = 3.8

Which is a correct conjugate pair in the reaction between ethanoic acid and methanoic acid?

	Acid	Conjugate base
<input type="checkbox"/> A	HCOOH	HCOO^-
<input type="checkbox"/> B	HCOOH	HCOOH_2^+
<input type="checkbox"/> C	CH_3COOH	CH_3COO^-
<input type="checkbox"/> D	CH_3COOH	$\text{CH}_3\text{COOH}_2^+$

(Total for Question 7 = 1 mark)

8 What is the pH of water at 313 K?

$K_{\text{w}} = 2.92 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ at 313 K

- A 6.8
 B 7.0
 C 7.2
 D 13.5

(Total for Question 8 = 1 mark)

9 What is the pH of 0.1 mol dm^{-3} propanoic acid at 298 K?

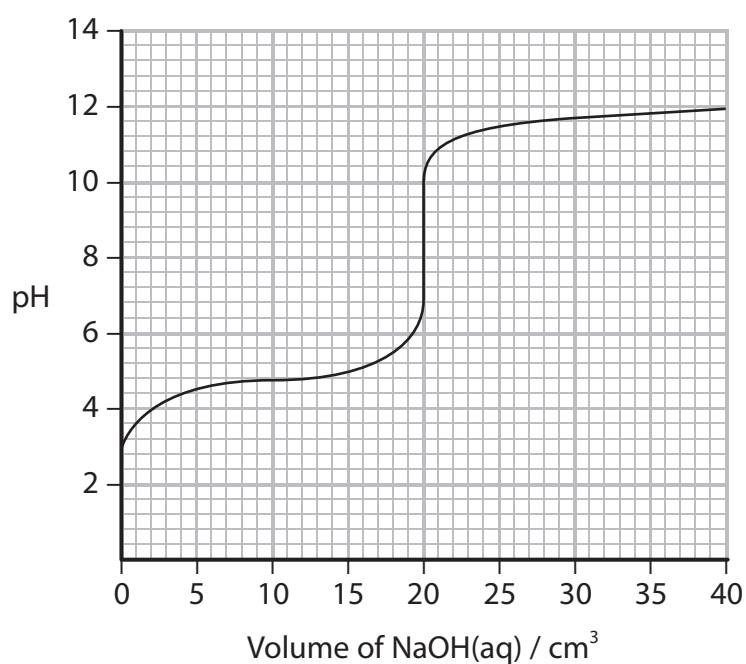
$K_{\text{a}} = 1.3 \times 10^{-5} \text{ mol dm}^{-3}$ at 298 K

- A 2.4
 B 2.9
 C 4.9
 D 5.9

(Total for Question 9 = 1 mark)



- 10 The titration curve shows the change in pH when $0.100 \text{ mol dm}^{-3}$ sodium hydroxide solution is added to 25.0 cm^3 of a weak acid, HA.



- (a) What is the pK_a value of the weak acid?

(1)

- A 2.9
 B 4.8
 C 7.0
 D 11.0

- (b) What is the concentration, in mol dm^{-3} , of the weak acid?

(1)

- A 0.040
 B 0.080
 C 0.100
 D 0.125



(c) Which is the best indicator to use in a titration between the weak acid and the sodium hydroxide solution?

(1)

- A methyl orange ($pK_{in} = 3.7$)
- B methyl red ($pK_{in} = 5.1$)
- C bromothymol blue ($pK_{in} = 7.0$)
- D phenol red ($pK_{in} = 7.9$)

(d) The following volumes of $0.100 \text{ mol dm}^{-3}$ sodium hydroxide solution were added to separate 25.0 cm^3 portions of the weak acid.

Which added volume, in cm^3 , will result in the best buffer solution?

(1)

- A 2
- B 10
- C 20
- D 30

(Total for Question 10 = 4 marks)

11 Which compound has the highest boiling temperature?

- A $\text{CH}_3\text{CH}_2\text{CHO}$ $M_r = 58$
- B CH_3COCH_3 $M_r = 58$
- C $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ $M_r = 60$
- D CH_3COOH $M_r = 60$

(Total for Question 11 = 1 mark)

12 Which compound reacts with iodine in an alkali to give a pale yellow precipitate with an antiseptic smell?

- A CH_3COCH_3
- B $\text{CH}_3\text{CH}_2\text{CHO}$
- C $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$
- D $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$

(Total for Question 12 = 1 mark)

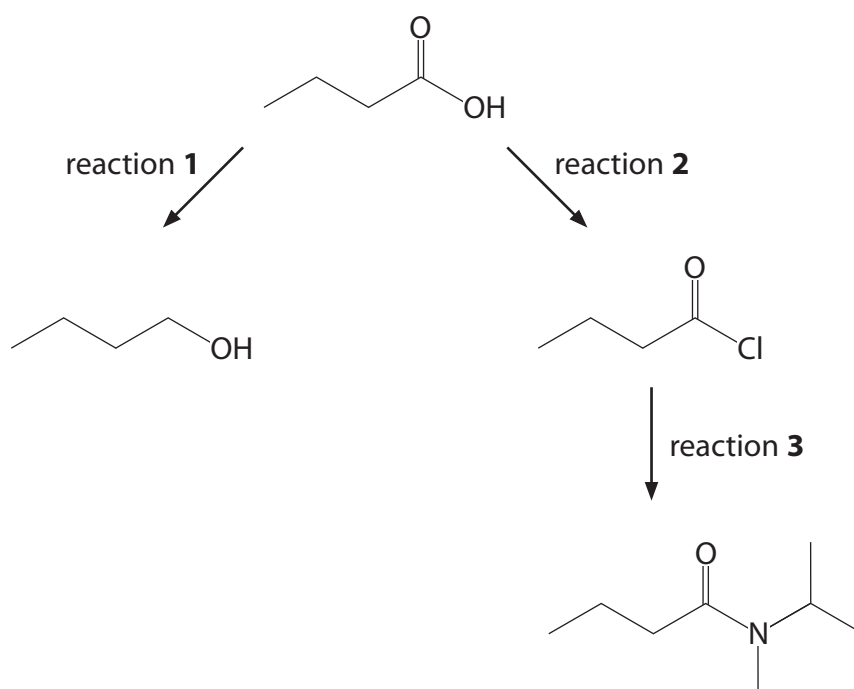


13 The reaction that produces propanoic acid is

- A heating $\text{CH}_3\text{CH}_2\text{CH}_3$ with acidified potassium dichromate(VI).
- B heating CH_3COCH_3 with acidified potassium dichromate(VI).
- C refluxing $\text{CH}_3\text{CH}_2\text{CN}$ with dilute hydrochloric acid.
- D refluxing $\text{CH}_3\text{CH}_2\text{CH}_2\text{CN}$ with dilute hydrochloric acid.

(Total for Question 13 = 1 mark)

14 Some reactions are shown in the scheme below.



(a) Which of these reagents is needed for reaction 1?

(1)

- A Lithium tetrahydridoaluminate(III) in dry ether
- B Hydrogen with a nickel catalyst
- C Sodium in ethanol
- D Zinc in dilute acid



(b) Which reagent is needed in reaction 2?

(1)

- A Aluminium chloride
- B Chlorine
- C Phosphorus(V) chloride
- D Sodium chloride

(c) Which reagent is needed in reaction 3?

(1)

- A $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$
- B $(\text{CH}_3)_2\text{CHCH}_2\text{NH}_2$
- C $\text{CH}_3\text{NHCH}(\text{CH}_3)_2$
- D $\text{CH}_3\text{CH}_2\text{N}(\text{CH}_3)_2$

(Total for Question 14 = 3 marks)

TOTAL FOR SECTION A = 20 MARKS

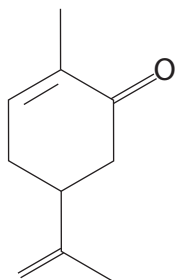


SECTION B

Answer ALL the questions. Write your answers in the spaces provided.

15 This question is about carbonyl compounds.

(a) Carvone exists as two optical isomers.



(i) Label the chiral carbon atom with an asterisk (*).

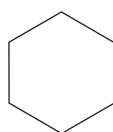
(1)

(ii) Give the molecular formula of carvone.

(1)

(iii) Complete the **skeletal** formula of the organic product formed when carvone reacts with excess bromine.

(2)



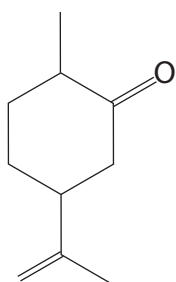
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(b) Dihydrocarvone has the structure shown.

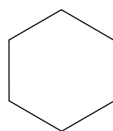


(i) State why dihydrocarvone does not exhibit geometric isomerism.

(1)

(ii) Complete the **skeletal** formula of the organic product formed when dihydrocarvone reacts with hydrogen cyanide in the presence of potassium cyanide.

(1)



(iii) State the number of different proton environments in a molecule of dihydrocarvone.

(1)

(iv) Suggest one of the main absorbance ranges in the infrared spectrum of dihydrocarvone in the region 2500 to 1500 cm^{-1} and identify the bond responsible.

(1)

Bond

Range cm^{-1}

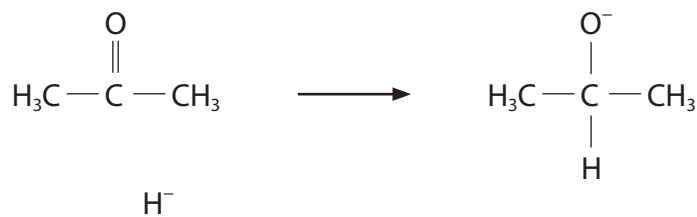


(c) Sodium tetrahydridoborate, NaBH_4 , acts as a source of H^- ions and is a reducing agent.

Complete the mechanism for the reduction of propanone to propan-2-ol.

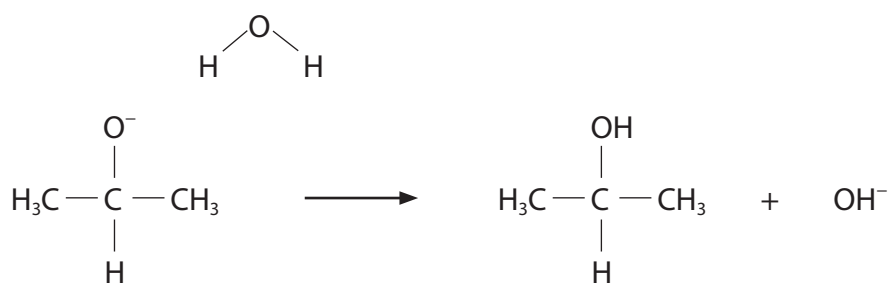
- (i) In **Step 1**, add the relevant dipole, a lone pair of electrons and curly arrows. (2)

Step 1

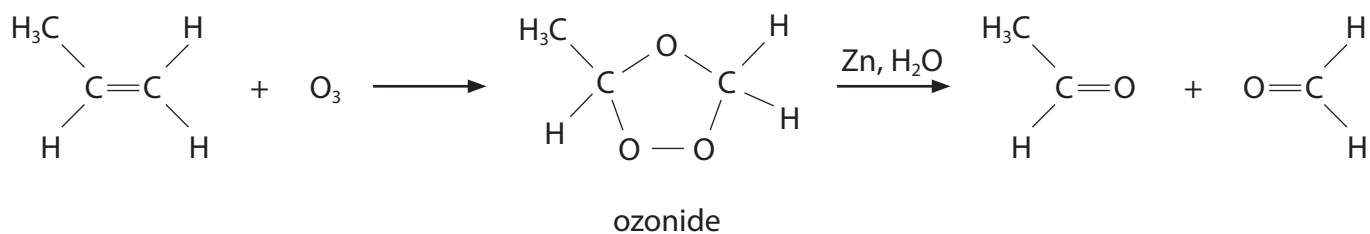


- (ii) In **Step 2**, add a relevant lone pair of electrons and curly arrows. (1)

Step 2



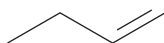
(d) When propene, C_3H_6 , reacts with ozone, O_3 , an ozonide is formed. The ozonide is then hydrolysed with water and zinc to form two carbonyl compounds.



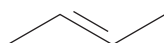
- (i) Show how the reaction with ozone and subsequent hydrolysis can be used to distinguish between but-1-ene and but-2-ene, by giving the **structures** of the carbonyl products formed in each case.

(2)

But-1-ene



But-2-ene



- (ii) Give the **structure** of an alkene that produces ethanal and butanone when it reacts with ozone, and the product is hydrolysed with water and zinc.

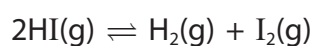
(1)

(Total for Question 15 = 14 marks)

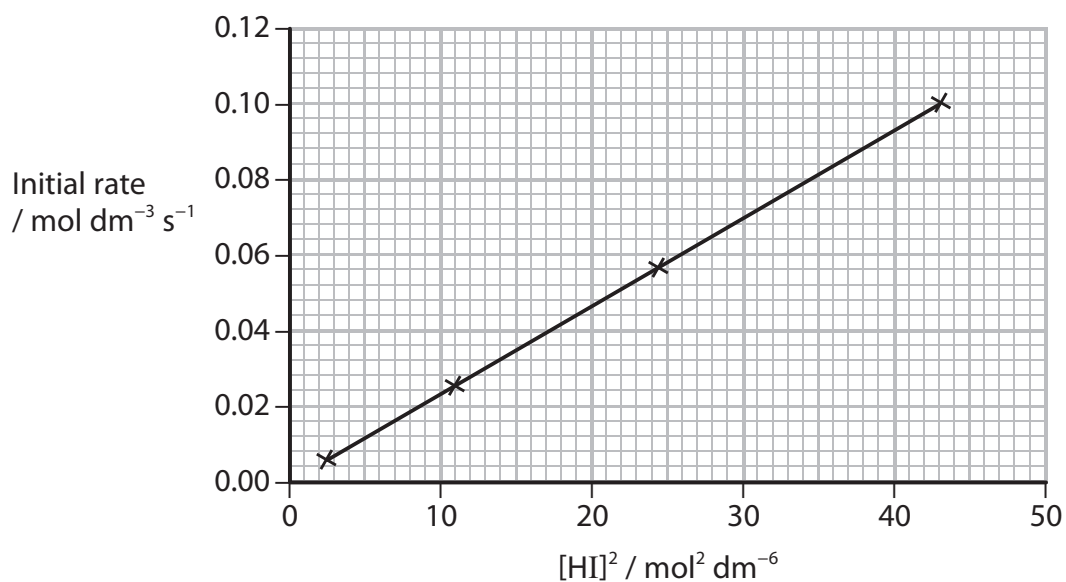


P 4 8 0 8 2 A 0 1 3 2 8

16 Hydrogen iodide partially decomposes into hydrogen and iodine.



(a) A graph of the initial rate of reaction against the square of the initial concentration of hydrogen iodide is shown.



(i) Deduce the order of reaction with respect to hydrogen iodide. Explain your reasoning.

(2)

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(ii) Write the rate equation for the reaction.

(1)

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- (iii) In one of the experiments, the initial concentration of hydrogen iodide was 1.00 mol dm^{-3} and the initial rate of reaction was $0.00620 \text{ mol dm}^{-3} \text{ s}^{-1}$.

Use the data to calculate the number of molecules decomposing in the first minute in 1.00 dm^3 of hydrogen iodide.

Assume that the rate of reaction remains constant for the first minute.

[Avogadro constant = $6.02 \times 10^{23} \text{ mol}^{-1}$]

(2)

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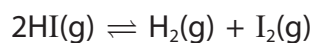
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P 4 8 0 8 2 A 0 1 5 2 8

*(b) The activation energy for the forward reaction is 184 kJ mol^{-1} .



At 700 K, the rate constant is $2.32 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

Calculate the rate constant at 800 K and give your answer to **three** significant figures.

You should **not** attempt to use any graphical method to answer this question.

The Arrhenius equation is

$$\ln k = -\frac{E_a}{R} \times \frac{1}{T} + A$$

[Gas constant, $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$ and A is a constant]

(5)

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(c) (i) Write the expression for the equilibrium constant, K_c , for the reaction.



(ii) Explain why K_c for this reaction has no units. (1)



(iii) In an experiment to determine K_c , 0.192 g of hydrogen iodide, in a 1 dm^3 vessel, was heated at 700 K until equilibrium was established.

0.00019 mol of iodine was present in the equilibrium mixture.

Calculate the value of K_c at 700 K.

(4)

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* (iv) The enthalpy change for the forward reaction is $+9.5 \text{ kJ mol}^{-1}$.

State and explain the effect of an increase in temperature on the entropy change of surroundings, $\Delta S_{\text{surroundings}}$, and hence on the value of K_c .

(3)

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(Total for Question 16 = 19 marks)

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17 Ethanol reacts with a carboxylic acid, **P**, to produce an ester, **Q**.

- (a) Carboxylic acid **P** contains 58.8% carbon and 9.8% hydrogen by mass.
The mass spectrum of compound **P** has the molecular ion peak at $m/e = 102$.

Use **all** these data to confirm that the molecular formula of **P** is $C_5H_{10}O_2$.

(3)

- (b) Draw the **displayed formulae** of the four possible structures of carboxylic acid **P**.

(2)

Carboxylic acid 1	Carboxylic acid 2
Carboxylic acid 3	Carboxylic acid 4



(c) The mass spectrum of carboxylic acid **P** has a major peak at $m/e = 43$.

Draw the structures of two species that could give this peak.

(2)

(d) Use your answers to (b) and (c) to identify which two of the carboxylic acids you have drawn in (b) could be carboxylic acid **P**.

(1)

(e) Draw the displayed formulae of the two possible ethyl esters that could be **Q**.

(2)



(f) Information from the high resolution proton nmr spectrum of ester **Q** is given.

Peak	Chemical shift, δ / ppm for TMS	Splitting pattern	Relative area below peak
A	0.96	doublet	6
B	1.26	triplet	3
C	2.10	split into 9	1
D	2.20	doublet	2
E	4.13	quartet	2

Use the data from the table to determine the **displayed** formula of ester **Q**.

Draw the formula below and on it label the protons responsible for the peaks A to E.

Explain the splitting pattern in peak B.

(5)

Displayed formula of **Q**

Explanation of splitting pattern in peak B

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(Total for Question 17 = 15 marks)

TOTAL FOR SECTION B = 48 MARKS



SECTION C

Answer ALL the questions. Write your answers in the spaces provided.

18 This question is about solutions, enthalpy changes and entropy changes.

- (a) (i) Draw a labelled Hess cycle and use it to calculate the enthalpy change of solution of barium chloride.

Show all of your working.

Hydration enthalpy of Ba^{2+}	$-1360 \text{ kJ mol}^{-1}$
Hydration enthalpy of Cl^-	-364 kJ mol^{-1}
Lattice energy of BaCl_2	$-2056 \text{ kJ mol}^{-1}$

(4)

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- (ii) Explain how you would expect the value of the enthalpy change of hydration of calcium ions to compare with that of barium ions.

(2)

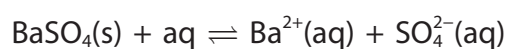
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- (b) Barium sulfate, BaSO_4 , dissolves to a very small extent in water and reaches equilibrium as shown in the equation.



The equilibrium constant for this reaction is

$$K_c = [\text{Ba}^{2+}(\text{aq})][\text{SO}_4^{2-}(\text{aq})]$$

- (i) Suggest why the concentration of solid barium sulfate, $[\text{BaSO}_4(\text{s})]$, is not included in the expression for K_c .

(1)

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.....

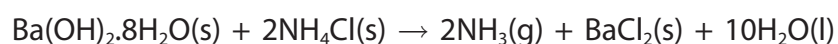
- (ii) The value for K_c is $1.00 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$ at 298 K.

Calculate the maximum mass, in g, of barium sulfate that will dissolve in 50.0 cm^3 of water at 298 K.

(3)



(c) Hydrated barium hydroxide reacts with ammonium chloride as shown.

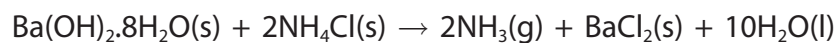


(i) Use the Data Booklet to complete the table below.

(2)

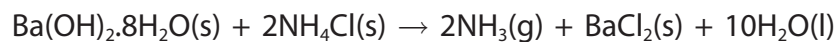
	Ba(OH) ₂ ·8H ₂ O(s)	NH ₄ Cl(s)	NH ₃ (g)	BaCl ₂ (s)	H ₂ O(l)
ΔH_f^\ominus /kJ mol ⁻¹	-3345	-314.4	-46.1		
S^\ominus /J mol ⁻¹ K ⁻¹	427	94.6	192.3		

(ii) Use data from the table to calculate the standard enthalpy change, in kJ mol⁻¹, for this reaction.



(2)

(iii) Use data from the table to calculate the standard entropy change of the system, in J mol⁻¹ K⁻¹, for the same reaction.



(2)

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(iv) Use your answers to (c)(ii) and (c)(iii) to calculate ΔS_{total} for the reaction at 298 K. (3)

*(v) It is possible that hydrated barium chloride, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, forms instead of anhydrous barium chloride, BaCl_2 , in this reaction.

Predict any effect on ΔS_{system} if hydrated barium chloride forms instead of anhydrous barium chloride.

Hence explain whether it is possible to predict the effect on the total entropy change of the reaction if hydrated barium chloride forms instead of anhydrous barium chloride. (3)

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TOTAL FOR SECTION C = 22 MARKS
TOTAL FOR PAPER = 90 MARKS

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