

Write your name here

Surname

Other names

Centre Number

Candidate Number

Edexcel GCE

Chemistry

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

Wednesday 13 June 2012 – Morning

Time: 1 hour 40 minutes

Paper Reference

6CH04/01**You must have: Data Booklet**

Total Marks

Candidates may use a calculator.

Instructions

- Use **black** ink or 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 Which of the following interacts with the nuclei of hydrogen atoms in a nuclear magnetic resonance spectrometer?

- ☐ **A** Gamma rays
- ☐ **B** X-rays
- ☐ **C** Microwaves
- ☐ **D** Radio waves

(Total for Question 1 = 1 mark)

2 HPLC stands for

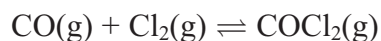
- ☐ **A** high pressure liquid column.
- ☐ **B** high performance liquid chromatography.
- ☐ **C** heterogeneous phase liquid chromatography.
- ☐ **D** homogenous phase liquid column.

(Total for Question 2 = 1 mark)

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



3 Consider the equilibrium below.



(a) An increase in pressure by a factor of 2 will

(1)

- ☐ A quadruple K_p .
- ☐ B double K_p .
- ☐ C have no effect on K_p .
- ☐ D halve K_p .

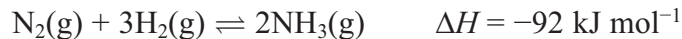
(b) The units of K_p are

(1)

- ☐ A atm^{-2}
- ☐ B atm^{-1}
- ☐ C atm
- ☐ D atm^2

(Total for Question 3 = 2 marks)

4 Which of these will **not** improve the **overall** yield of the Haber process?



- ☐ A Increasing the pressure.
- ☐ B Liquefying then removing the ammonia from the reaction.
- ☐ C Increasing the temperature.
- ☐ D Recycling unreacted nitrogen and hydrogen.

(Total for Question 4 = 1 mark)

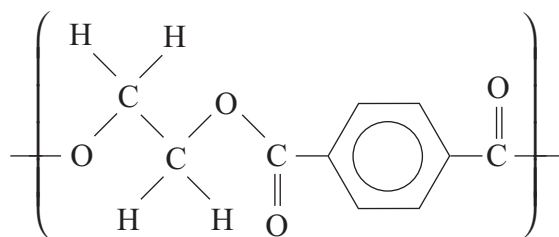
5 The equation for the reaction between ethanoic acid and phosphorus(V) chloride is

- ☐ A $\text{CH}_3\text{COOH} + \text{PCl}_5 \rightarrow \text{CH}_3\text{COCl} + \text{POCl}_3 + \text{HCl}$
- ☐ B $\text{CH}_3\text{COOH} + \text{PCl}_5 \rightarrow \text{CH}_3\text{COOCl} + \text{PCl}_3 + \text{HCl}$
- ☐ C $\text{CH}_3\text{COOH} + \text{PCl}_5 \rightarrow \text{CH}_3\text{COCl} + \text{PCl}_3 + \text{HOCl}$
- ☐ D $2\text{CH}_3\text{COOH} + \text{PCl}_5 \rightarrow (\text{CH}_3\text{CO})_2\text{O} + \text{PCl}_3 + \text{H}_2\text{O} + \text{Cl}_2$

(Total for Question 5 = 1 mark)



6 An example of a polyester is



(a) The two monomers needed to form this polymer are

(1)

	Monomer One	Monomer Two
<input type="checkbox"/> A		$\text{HO}(\text{CH}_2)_2\text{OH}$
<input type="checkbox"/> B		$\text{HO}(\text{CH}_2)_2\text{OH}$
<input type="checkbox"/> C		$\text{HOOC}(\text{CH}_2)_2\text{COOH}$
<input type="checkbox"/> D		$\text{HOOC}(\text{CH}_2)_2\text{COOH}$

(b) The type of reaction to form this polymer is

(1)

- ☐ A addition.
- ☐ B substitution.
- ☐ C condensation.
- ☐ D hydrolysis.

(Total for Question 6 = 2 marks)



7 In which of these reactions is the hydrogensulfate ion, HSO_4^- , behaving as a Brønsted-Lowry base?

- ☐ A $\text{HSO}_4^- + \text{H}_3\text{O}^+ \rightarrow \text{H}_2\text{SO}_4 + \text{H}_2\text{O}$
- ☐ B $\text{HSO}_4^- + \text{Ba}^{2+} \rightarrow \text{BaSO}_4 + \text{H}^+$
- ☐ C $\text{HSO}_4^- + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + \text{H}_3\text{O}^+$
- ☐ D $\text{HSO}_4^- + \text{CO}_3^{2-} \rightarrow \text{SO}_4^{2-} + \text{HCO}_3^-$

(Total for Question 7 = 1 mark)

8 The reaction below is carried out at 25 °C. Use the equation and the data to answer the questions that follow.



Substance	Standard molar entropy, S^\ominus / $\text{J mol}^{-1} \text{K}^{-1}$
$\text{SO}_2(\text{g})$	248
$\text{H}_2\text{S}(\text{g})$	206
$\text{H}_2\text{O}(\text{g})$	189
$\text{S}(\text{s})$	32

(a) The standard entropy change of the system, in $\text{J mol}^{-1} \text{K}^{-1}$, is

(1)

- ☐ A -186
- ☐ B +186
- ☐ C -233
- ☐ D +233

(b) The standard entropy change of the surroundings, in $\text{J mol}^{-1} \text{K}^{-1}$, is

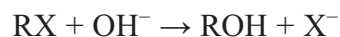
(1)

- ☐ A $107.4 \times 1000 / 25$
- ☐ B $-107.4 \times 1000 / 25$
- ☐ C $107.4 \times 1000 / 298$
- ☐ D $-107.4 \times 1000 / 298$

(Total for Question 8 = 2 marks)



- 9 A halogenoalkane, RX, reacts with hydroxide ions, OH⁻, to form an alcohol.



The rate equation for the reaction is $\text{rate} = k[\text{RX}]$. Which of these statements is **incorrect**?

- ☐ A Rate $\propto [\text{RX}]$.
- ☐ B RX is a primary halogenoalkane.
- ☐ C The reaction mechanism is S_N1.
- ☐ D A carbocation intermediate forms in the reaction.

(Total for Question 9 = 1 mark)

- 10 The rate equation for the reaction between hydrogen gas and nitrogen monoxide gas is

$$\text{rate} = k[\text{NO}]^2[\text{H}_2]$$

If the concentration of both reactants is doubled, the rate will increase by a factor of

- ☐ A 3
- ☐ B 4
- ☐ C 6
- ☐ D 8

(Total for Question 10 = 1 mark)

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



- 11 A reaction has the rate equation $\text{rate} = k[\text{X}][\text{Y}]^2[\text{Z}]$. The concentrations of each reactant are shown in the table below.

Reactant	Concentration / mol dm^{-3}
X	0.040
Y	0.20
Z	0.12

- (a) If the rate of reaction under these conditions has a value of $0.24 \text{ mol dm}^{-3} \text{ s}^{-1}$, then the numerical value of k is

(1)

- ☐ A 0.00080
- ☐ B 0.533
- ☐ C 1.875
- ☐ D 1250

- (b) The units for the rate constant, k , are

(1)

- ☐ A $\text{mol}^{-3} \text{ dm}^9 \text{ s}^{-1}$
- ☐ B $\text{mol}^3 \text{ dm}^9 \text{ s}^{-1}$
- ☐ C $\text{mol}^{-3} \text{ dm}^{-9} \text{ s}^{-1}$
- ☐ D $\text{mol}^3 \text{ dm}^{-9} \text{ s}^{-1}$

(Total for Question 11 = 2 marks)

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



12 This question is about the four organic substances shown below.



Which substance will

(a) give a positive result with both Brady's and Tollens' reagents?

(1)

☐ **A**

☐ **B**

☐ **C**

☐ **D**

(b) be formed by the oxidation of a secondary alcohol?

(1)

☐ **A**

☐ **B**

☐ **C**

☐ **D**

(c) form the most acidic solution when equal amounts are each mixed with 100 cm^3 of water?

(1)

☐ **A**

☐ **B**

☐ **C**

☐ **D**

(d) form steamy fumes in the reaction with PCl_5 ?

(1)

☐ **A**

☐ **B**

☐ **C**

☐ **D**

(Total for Question 12 = 4 marks)



13 In order to make $\text{CH}_3\text{CH}_2\text{CONHCH}_3$, you could use

- ☐ A $\text{CH}_3\text{CH}_2\text{COOCH}_3 + \text{NH}_3$
- ☐ B $\text{CH}_3\text{CH}_2\text{COCl} + \text{CH}_3\text{NH}_2$
- ☐ C $\text{CH}_3\text{CH}_2\text{COO}^-\text{Na}^+ + \text{CH}_3\text{NH}_2$
- ☐ D $\text{CH}_3\text{CH}_2\text{CONH}_2 + \text{CH}_3\text{NH}_2$

(Total for Question 13 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS



SECTION B

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

14 In a pH titration, 30 cm^3 of sodium hydroxide solution was added, in 1 cm^3 portions, to 20 cm^3 of ethanoic acid solution, $\text{CH}_3\text{COOH}(\text{aq})$. The concentration of both solutions was 0.50 mol dm^{-3} . After the addition of each 1 cm^3 , the pH was recorded using a pH meter.

(a) (i) Write the K_a expression for ethanoic acid.

(1)

(ii) Using your answer to (i), calculate the pH of the 0.50 mol dm^{-3} ethanoic acid solution before the titration starts. Refer to page 18 of the data booklet.

(2)

(iii) Deduce the volume of sodium hydroxide solution required to reach the end point.

(1)

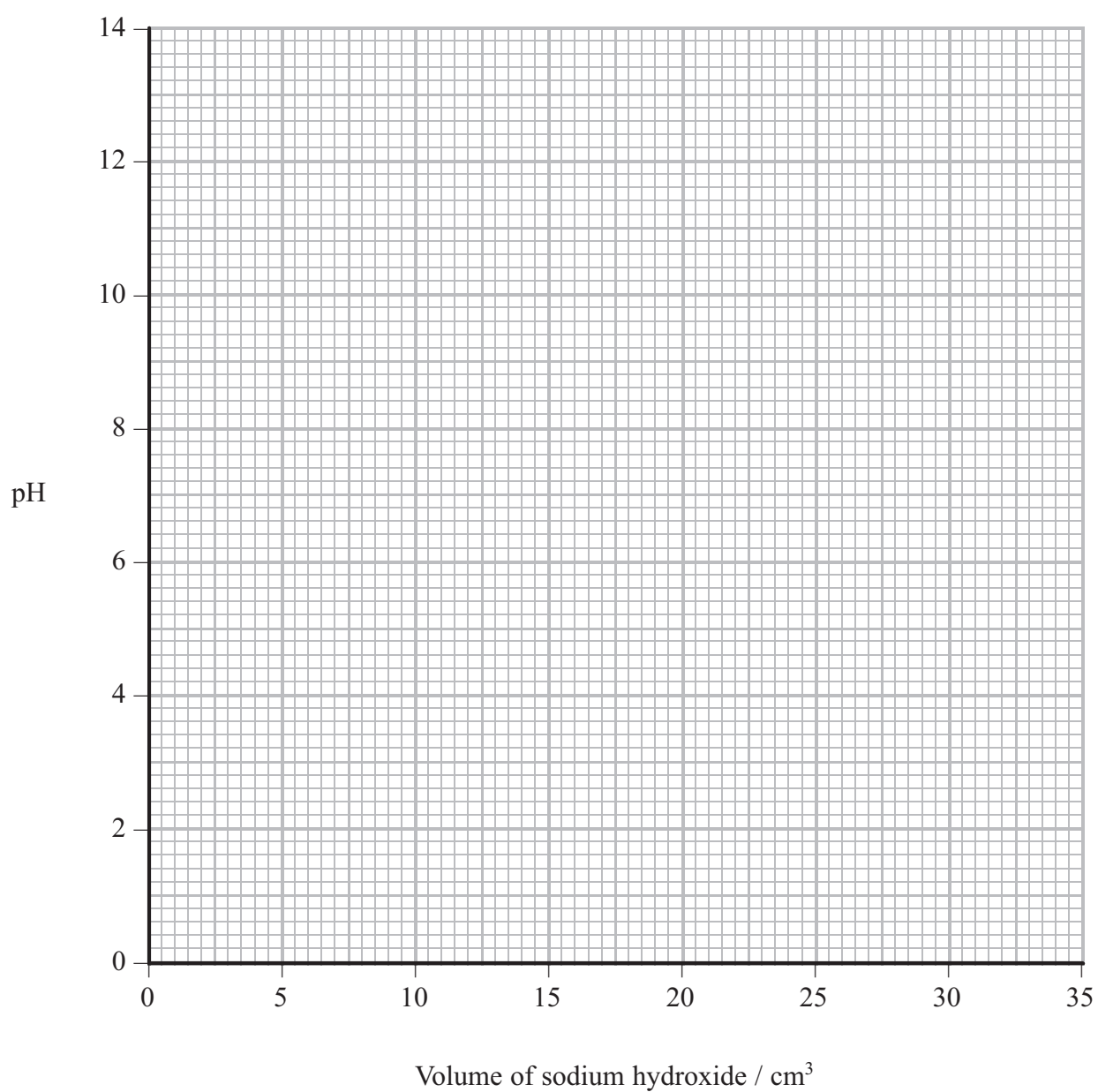
(iv) Calculate the pH of the solution after all of the sodium hydroxide is added.

(4)



- (v) On the axes below sketch a graph to show how the pH changes during the titration.

(3)



(b) An acidic buffer solution can be made by mixing together a solution of ethanoic acid and solid sodium ethanoate.

- (i) Calculate the mass of solid sodium ethanoate (molar mass = 82 g mol^{-1}) that would be added to 500 cm^3 of ethanoic acid, concentration 1.0 mol dm^{-3} , in order to make a buffer solution of $\text{pH} = 4.70$.

(4)

- *(ii) Explain how this buffer solution resists a change in pH when a few drops of sodium hydroxide are added.

(3)

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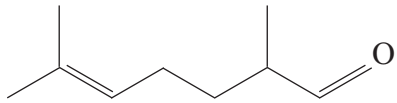
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(Total for Question 14 = 18 marks)



15 The molecule  is sometimes known as melonal as it smells similar to watermelon.

(a) Give the systematic name for melonal.

(2)

(b) (i) Melonal can be prepared by the oxidation of a compound, **X**. Suggest the formula of compound **X** and the names or formulae of the reagents needed to oxidize **X**.

(3)

Compound **X**

Reagents needed for oxidation

(ii) Briefly suggest a practical measure to maximise the yield of melonal in (b)(i). Justify your answer.

(2)

(c) Infrared spectra can be used to confirm the presence of functional groups in a molecule. Use page 5 of the data booklet to suggest the position of two absorptions and the identity of the bonds responsible which can confirm the presence of the two functional groups in melonal.

(2)

Wavenumber range / cm^{-1}	Bond	Functional group present in melonal



(d) The mass spectrum of melonal shows small peaks at $m/e = 57$ and $m/e = 83$.

Give the formula of each of the fragments most likely to have caused these peaks.

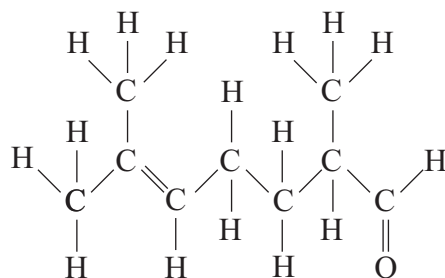
(2)

$m/e = 57$

$m/e = 83$

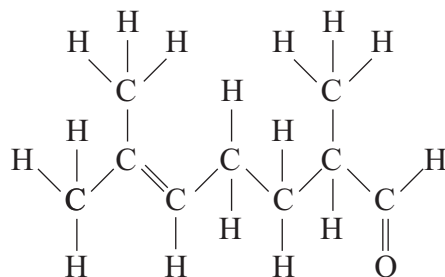
(e) (i) On the displayed formula below, circle the hydrogen atom that has a triplet peak in the proton nmr spectrum of melonal.

(1)



(ii) On the displayed formula below, circle the atom that gives rise to a peak at a chemical shift of $\delta = 9.65$ ppm in the proton nmr spectrum of melonal. Refer to page 7 of the data booklet.

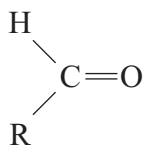
(1)



(f) Aldehydes react with HCN in the presence of CN^- ions.

- (i) Give the mechanism for this reaction, using the simplified displayed formula below.

(3)



- (ii) The product of this reaction has a chiral centre. Would you expect the reaction to produce a solution that rotates the plane of plane-polarized light? Explain your answer.

(3)

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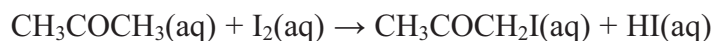
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(Total for Question 15 = 19 marks)



16 Iodine reacts with propanone in the presence of an acid catalyst.

An experiment was carried out to investigate the kinetics of this reaction by monitoring the concentration of iodine. The progress of the reaction was followed by mixing together the reagents, removing samples of the mixture every five minutes, quenching the reaction and then titrating to find the concentration of iodine at a given time.

(a) (i) Suggest a suitable reagent with which you could titrate the iodine.

(1)

(ii) State and explain how you would quench the reaction.

(2)

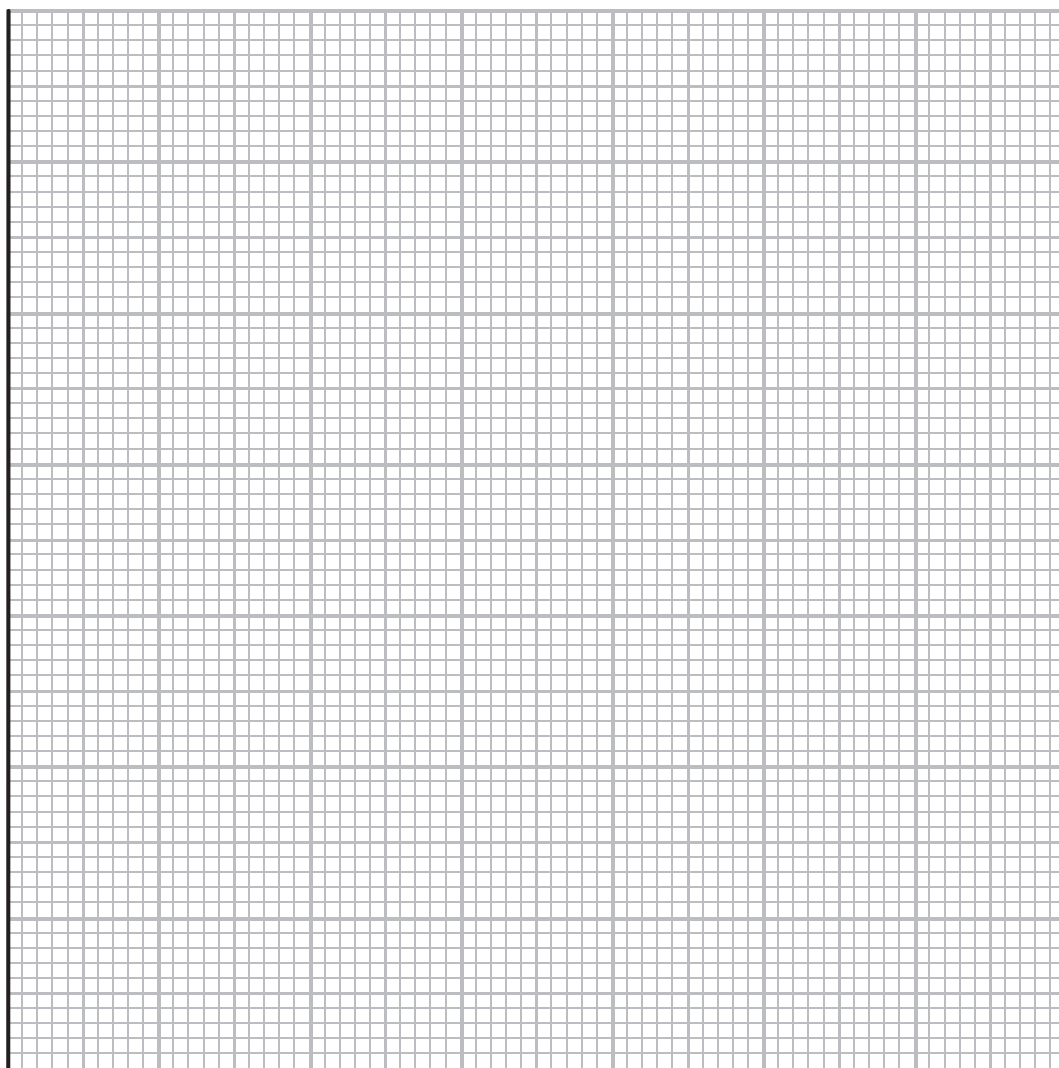
(b) (i) Data obtained from the experiment are shown in the table below. Use the data to plot a suitable graph to determine the order of the reaction with respect to iodine and state this order.

(3)

Time / mins	$[\text{I}_2(\text{aq})] / \text{mol dm}^{-3}$
5	9.74×10^{-4}
10	9.50×10^{-4}
15	9.25×10^{-4}
20	9.03×10^{-4}
25	8.80×10^{-4}
30	8.55×10^{-4}



$[\text{I}_2(\text{aq})] /$
 mol dm^{-3}



Time / minutes

Order with respect to iodine



(ii) Explain how you determined the order using your graph.

(2)

(c) State an alternative practical procedure that could be used to monitor the concentration of iodine.

(1)

(Total for Question 16 = 9 marks)



- 17 The ester $\text{CH}_3\text{CH}_2\text{COOCH}_3$ can be formed from the reaction between propanoic acid and methanol with an acid catalyst.



- (a) (i) Name the ester.

(1)

- (ii) The same product can be made using propanoyl chloride instead of propanoic acid. Suggest an additional hazard that could occur using this reagent and describe how you would minimise this risk.

(2)



- (b) Complete the table below to show the amounts of each substance present at equilibrium. Use your values to calculate the equilibrium constant, K_c , for the reaction.

(3)

	$\text{CH}_3\text{CH}_2\text{COOH}$	CH_3OH	$\text{CH}_3\text{CH}_2\text{COOCH}_3$	H_2O
Initial amounts / mol	0.52	0.37	0	1.2
Equilibrium amounts / mol			0.21	

(Total for Question 17 = 6 marks)

TOTAL FOR SECTION B = 52 MARKS



SECTION C

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

18 This question is about the solubility of some Group 1 halides.

- (a) Potassium fluoride is a soluble, white, crystalline solid used in etching glass. A Hess cycle can be used to calculate its enthalpy of solution, using data including enthalpies of hydration of ions.

Define the term **enthalpy of hydration** of an ion.

(2)

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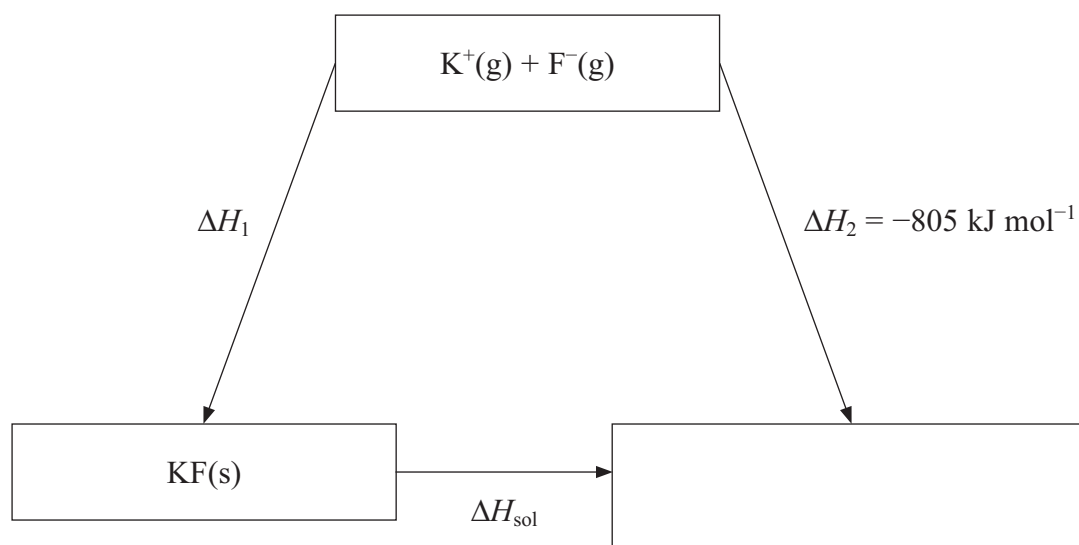
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- (b) Consider the Hess cycle below.



- (i) Complete the cycle by filling in the empty box.

(1)



- (ii) Apply Hess's Law to obtain an expression for ΔH_{sol} in terms of ΔH_1 and ΔH_2 . (1)

$$\Delta H_{\text{sol}} =$$

- (iii) Give the name of the energy change ΔH_1 . (1)

-
- (iv) Referring to page 12 of the data booklet and your answer to (ii), calculate the standard enthalpy of solution of potassium fluoride. (2)

- (c) The standard enthalpy of solution of sodium chloride is $+3 \text{ kJ mol}^{-1}$.

- (i) 1 g of sodium chloride was added to 250 cm^3 of water in a beaker and stirred with a thermometer graduated in intervals of 1°C . Describe and explain what would happen to the reading on the thermometer as the sodium chloride dissolves. No calculation is required. (3)



- *(ii) Explain, in terms of entropy changes, why sodium chloride dissolves in water under standard conditions. No calculation is required.

(4)

- *(d) Lithium iodide is generally much more soluble in organic solvents than lithium chloride. Explain this observation using values of lattice energies from your data booklet and your knowledge of the trend in ionic radii down Group 7.

(4)

(Total for Question 18 = 18 marks)

TOTAL FOR SECTION C = 18 MARKS
TOTAL FOR PAPER = 90 MARKS



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1								
2								
3								
4								
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* Lanthanide series