Write your name here

Surname	Other names

Edexcel GCE

Centre Number	Candidate Number

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

Candidates may use a calculator.

Total Marks

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 ▶

P39308A

7/7/5/5/3/

P 3 9 3 0 8 A 0 1 2 4

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.

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$

(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)

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

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

☒ **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)

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

☒ **A** $CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$

☒ **B** $CH_3COOH + PCl_5 \rightarrow CH_3COOCl + PCl_3 + HCl$

☒ **C** $CH_3COOH + PCl_5 \rightarrow CH_3COCl + PCl_3 + HOCl$

☒ **D** $2CH_3COOH + PCl_5 \rightarrow (CH_3CO)_2O + PCl_3 + H_2O + Cl_2$

(Total for Question 5 = 1 mark)

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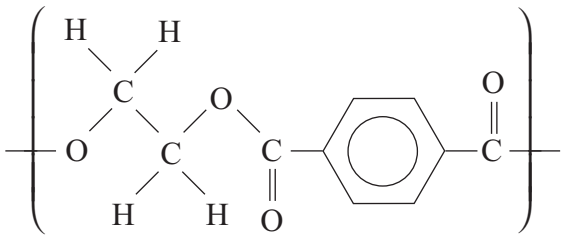
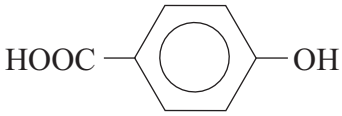
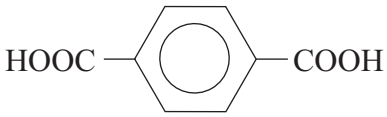
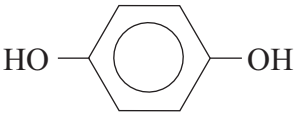
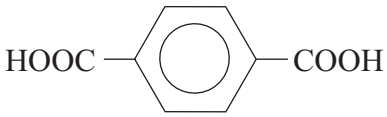
6 An example of a polyester is



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

(1)

	Monomer One	Monomer Two
☒ **A**		$HO(CH_2)_2OH$
☒ **B**		$HO(CH_2)_2OH$
☒ **C**		$HOOC(CH_2)_2COOH$
☒ **D**		$HOOC(CH_2)_2COOH$

(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** $HSO_4^- + H_3O^+ \rightarrow H_2SO_4 + H_2O$

☒ **B** $HSO_4^- + Ba^{2+} \rightarrow BaSO_4 + H^+$

☒ **C** $HSO_4^- + H_2O \rightarrow SO_4^{2-} + H_3O^+$

☒ **D** $HSO_4^- + CO_3^{2-} \rightarrow SO_4^{2-} + HCO_3^-$

(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.

$$SO_2(g) + 2H_2S(g) \rightarrow 3S(s) + 2H_2O(g) \qquad \Delta H = -107.4 \text{ kJ mol}^{-1}$$

Substance	Standard molar entropy, $S^{\ominus}$ / J mol^{-1} K^{-1}
$SO_2(g)$	248
$H_2S(g)$	206
$H_2O(g)$	189
S(s)	32

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

(1)

☒ **A** −186

☒ **B** +186

☒ **C** −233

☒ **D** +233

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

(1)

☒ **A** 107.4 × 1000 / 25

☒ **B** −107.4 × 1000 / 25

☒ **C** 107.4 × 1000 / 298

☒ **D** −107.4 × 1000 / 298

(Total for Question 8 = 2 marks)

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

$$RX + OH^- \rightarrow ROH + X^-$$

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

☒ **A** Rate $\propto$ [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

$$\text{rate} = k[NO]^2[H_2]$$

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 rate = $k[X][Y]^2[Z]$. 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 mol dm^{-3} 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** mol^{-3} dm^9 s^{-1}

☒ **B** mol^3 dm^9 s^{-1}

☒ **C** mol^{-3} dm^{-9} s^{-1}

☒ **D** mol^3 dm^{-9} 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.

A $CH_3CH_2CH_2CH_2CHO$

B $CH_3CH_2CH_2CH_2COOH$

C $CH_3COCH_2CH_2CH_3$

D $CH_3CH_2CH_2CH_2COCl$

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 $CH_3CH_2CONHCH_3$, you could use

☒ **A** $CH_3CH_2COOCH_3 + NH_3$

☒ **B** $CH_3CH_2COCl + CH_3NH_2$

☒ **C** $CH_3CH_2COO^-Na^+ + CH_3NH_2$

☒ **D** $CH_3CH_2CONH_2 + CH_3NH_2$

(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, $CH_3COOH(aq)$. 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.

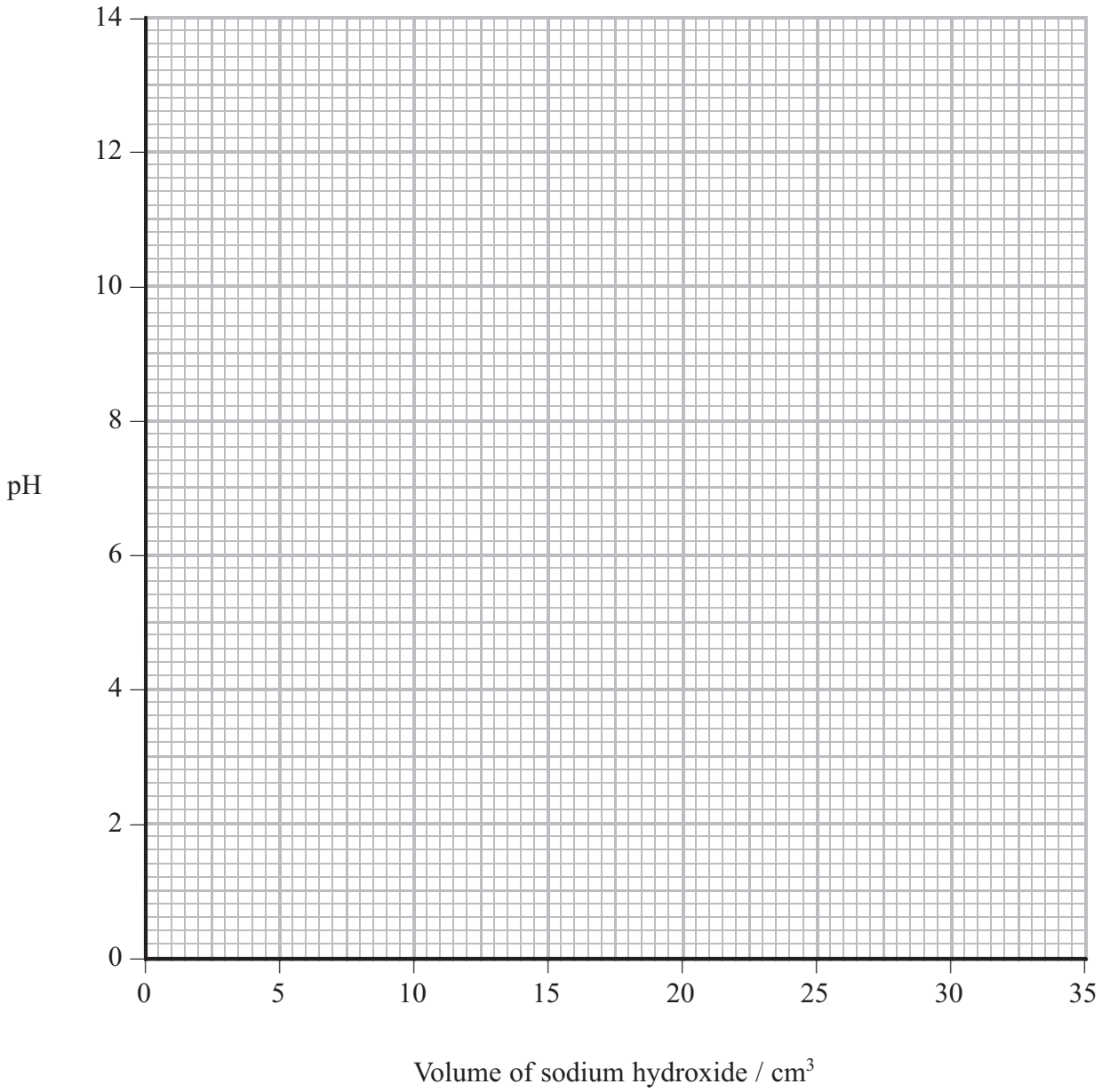
(1)

(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 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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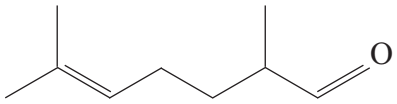
(Total for Question 14 = 18 marks)

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.

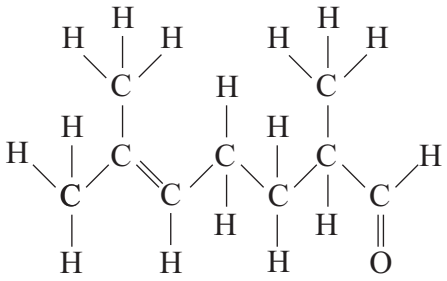
(2)

m/e = 57.....

m/e = 83.....

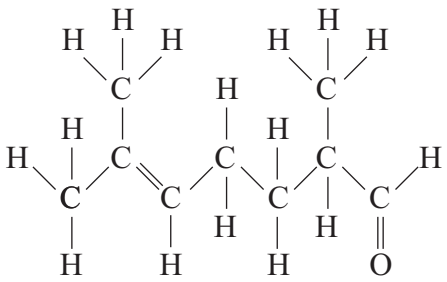
(e) (i) On the displayed formula below, circle the hydrogen atom that has a triplet peak in the proton nmr spectrum of melonal.

(1)



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

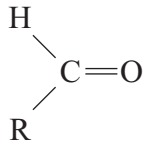
(1)



(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)

(Total for Question 15 = 19 marks)

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

$$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + HI(aq)$$

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)

.....

.....

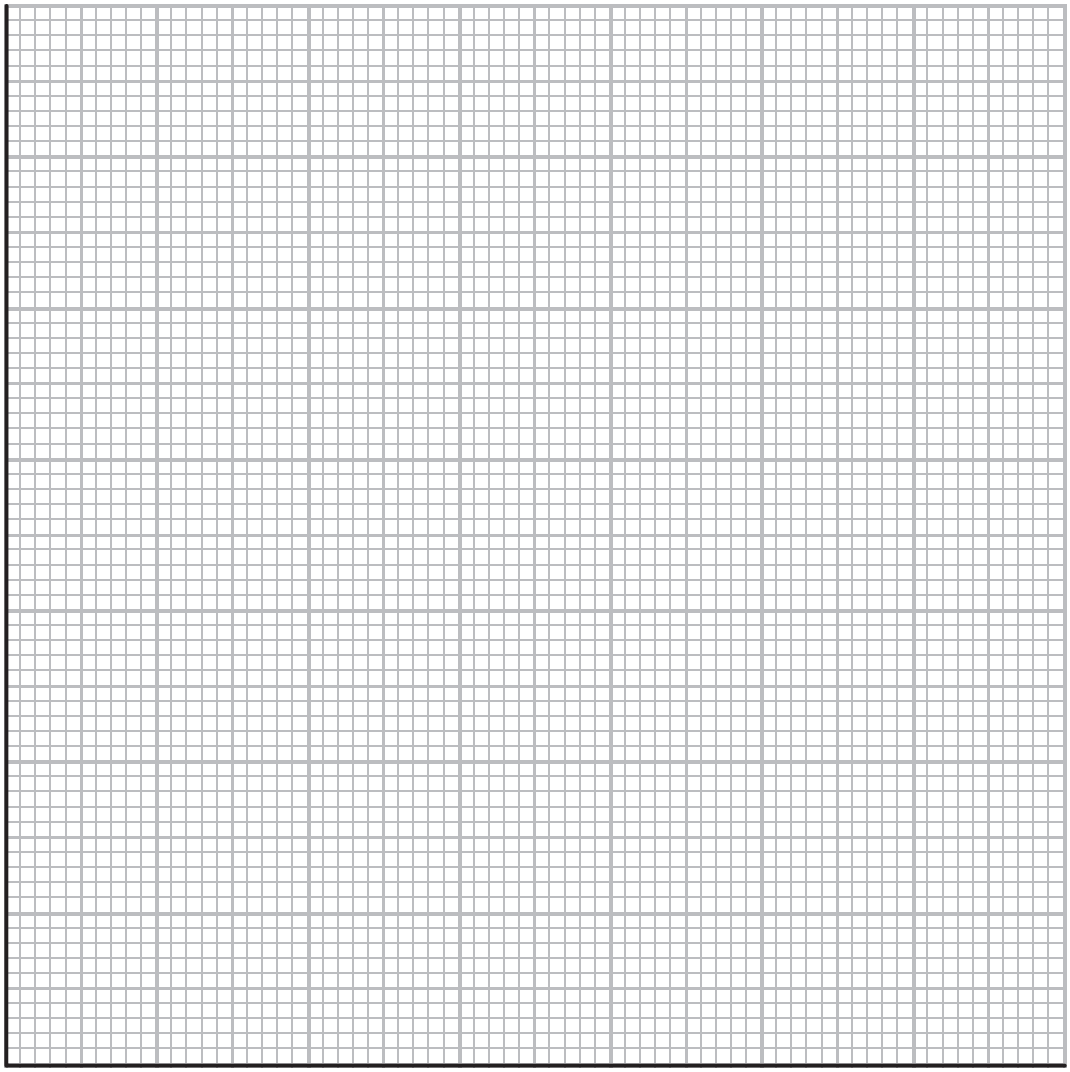
.....

.....

(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	$[I_2(aq)]$ / 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}



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 $CH_3CH_2COOCH_3$ can be formed from the reaction between propanoic acid and methanol with an acid catalyst.

$$CH_3CH_2COOH + CH_3OH \rightleftharpoons CH_3CH_2COOCH_3 + H_2O$$

(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)

	CH_3CH_2COOH	CH_3OH	$CH_3CH_2COOCH_3$	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.

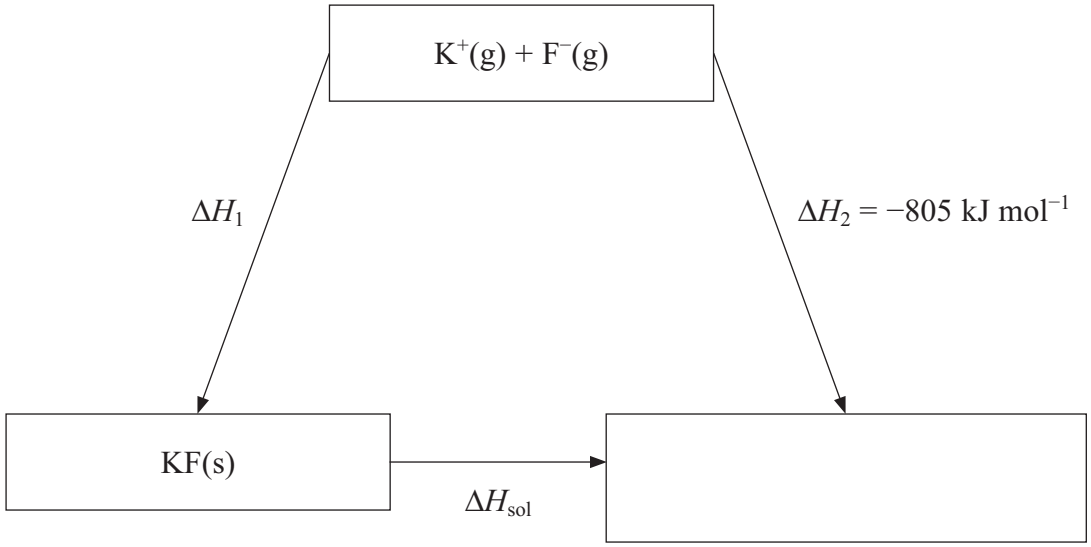
18 This question is about the solubility of some Group 1 halides.

(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)

(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)

ΔH_{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 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

The Periodic Table of Elements

1	2											3	4	5	6	7	0 (8) (18)
							1.0 H hydrogen 1										4.0 He helium 2
(1)	(2)		Key: relative atomic mass / atomic symbol / name / atomic (proton) number									(13)	(14)	(15)	(16)	(17)	
6.9 Li lithium 3	9.0 Be beryllium 4											10.8 B boron 5	12.0 C carbon 6	14.0 N nitrogen 7	16.0 O oxygen 8	19.0 F fluorine 9	20.2 Ne neon 10
23.0 Na sodium 11	24.3 Mg magnesium 12	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	27.0 Al aluminium 13	28.1 Si silicon 14	31.0 P phosphorus 15	32.1 S sulfur 16	35.5 Cl chlorine 17	39.9 Ar argon 18
39.1 K potassium 19	40.1 Ca calcium 20	45.0 Sc scandium 21	47.9 Ti titanium 22	50.9 V vanadium 23	52.0 Cr chromium 24	54.9 Mn manganese 25	55.8 Fe iron 26	58.9 Co cobalt 27	58.7 Ni nickel 28	63.5 Cu copper 29	65.4 Zn zinc 30	69.7 Ga gallium 31	72.6 Ge germanium 32	74.9 As arsenic 33	79.0 Se selenium 34	79.9 Br bromine 35	83.8 Kr krypton 36
85.5 Rb rubidium 37	87.6 Sr strontium 38	88.9 Y yttrium 39	91.2 Zr zirconium 40	92.9 Nb niobium 41	95.9 Mo molybdenum 42	[98] Tc technetium 43	101.1 Ru ruthenium 44	102.9 Rh rhodium 45	106.4 Pd palladium 46	107.9 Ag silver 47	112.4 Cd cadmium 48	114.8 In indium 49	118.7 Sn tin 50	121.8 Sb antimony 51	127.6 Te tellurium 52	126.9 I iodine 53	131.3 Xe xenon 54
132.9 Cs caesium 55	137.3 Ba barium 56	138.9 La* lanthanum 57	178.5 Hf hafnium 72	180.9 Ta tantalum 73	183.8 W tungsten 74	186.2 Re rhenium 75	190.2 Os osmium 76	192.2 Ir iridium 77	195.1 Pt platinum 78	197.0 Au gold 79	200.6 Hg mercury 80	204.4 Tl thallium 81	207.2 Pb lead 82	209.0 Bi bismuth 83	[209] Po polonium 84	[210] At astatine 85	[222] Rn radon 86
[223] Fr francium 87	[226] Ra radius 88	[227] Ac* actinium 89	[261] Rf rutherfordium 104	[262] Db dubnium 105	[266] Sg seaborgium 106	[264] Bh bohrium 107	[277] Hs hassium 108	[268] Mt meitnerium 109	[271] Ds darmstadtium 110	[272] Rg roentgenium 111							

Elements with atomic numbers 112-116 have been reported but not fully authenticated

* Lanthanide series	140 Ce cerium 58	141 Pr praseodymium 59	144 Nd neodymium 60	[147] Pm promethium 61	150 Sm samarium 62	152 Eu europium 63	157 Gd gadolinium 64	159 Tb terbium 65	163 Dy dysprosium 66	165 Ho holmium 67	167 Er erbium 68	169 Tm thulium 69	173 Yb ytterbium 70	175 Lu lutetium 71
* Actinide series	232 Th thorium 90	[231] Pa protactinium 91	238 U uranium 92	[237] Np neptunium 93	[242] Pu plutonium 94	[243] Am americium 95	[247] Cm curium 96	[245] Bk berkelium 97	[251] Cf californium 98	[254] Es einsteinium 99	[253] Fm fermium 100	[256] Md mendelevium 101	[254] No nobelium 102	[257] Lr lawrencium 103