Please check the examination details below before entering your candidate information

Candidate surname	Other names

Pearson Edexcel
International
Advanced Level

Centre Number | | | | | |

Candidate Number | | | | |

Thursday 10 January 2019

Afternoon (Time: 1 hour 40 minutes) | Paper Reference **WCH04/01**

Chemistry

Advanced

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

Candidates must have: Scientific calculator
Data Booklet

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.
- Show all your working in calculations and include units where appropriate.
- 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 Propanone reacts with iodine in acidic solution according to the equation

$$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + H^+(aq) + I^-(aq)$$

Which method would **not** be suitable for obtaining the rate of this reaction?

☒ **A** Colorimetry.

☒ **B** Measuring the increase in pH of the solution.

☒ **C** Measuring the increase in the infrared absorption for the C–I bond.

☒ **D** Quenching followed by titrating with sodium thiosulfate.

(Total for Question 1 = 1 mark)

2 For the reaction

$$2HgCl_2(aq) + C_2O_4^{2-}(aq) \rightarrow 2Cl^-(aq) + 2CO_2(g) + Hg_2Cl_2(s)$$

the rate equation is

$$\text{rate} = k[HgCl_2(aq)][C_2O_4^{2-}(aq)]^2$$

The concentrations of both $HgCl_2$ and $C_2O_4^{2-}$ are increased by a factor of three.
The rate of reaction increases by a factor of

☒ **A** 3

☒ **B** 9

☒ **C** 12

☒ **D** 27

(Total for Question 2 = 1 mark)

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3 To determine the activation energy, E_a, for a reaction, a graph was plotted of $\ln k$ against $1/T$, where k is the rate constant.

The Arrhenius equation is

$$\ln k = -\frac{E_a}{RT} + \text{constant}$$

The gradient of the graph is equal to

☒ **A** $-E_a$

☒ **B** $-\frac{E_a}{R}$

☒ **C** $-\frac{E_a}{T}$

☒ **D** $-\frac{E_a}{RT}$

(Total for Question 3 = 1 mark)

4 Which is correct for standard molar entropy?

	Highest entropy	Medium entropy	Lowest entropy
☒ **A**	Hydrogen	Nitrogen	Iron
☒ **B**	Nitrogen	Iron	Hydrogen
☒ **C**	Nitrogen	Hydrogen	Iron
☒ **D**	Iron	Nitrogen	Hydrogen

(Total for Question 4 = 1 mark)

5 The Haber process is used to make ammonia from nitrogen and hydrogen at 450°C.

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

When the temperature of the system is increased,

☒ **A** K_p decreases.

☒ **B** K_p increases.

☒ **C** K_p stays the same.

☒ **D** K_p increases and then decreases.

(Total for Question 5 = 1 mark)

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6 When magnesium hydroxide dissolves in water, the following equilibrium is established.

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$$

The expression for the equilibrium constant, K_c, is

☒ **A** $[Mg^{2+}(aq)] \times 2[OH^-(aq)]$

☒ **B** $[Mg^{2+}(aq)] \times [OH^-(aq)]^2$

☒ **C** $\dfrac{[Mg^{2+}(aq)] \times 2[OH^-(aq)]}{[Mg(OH)_2(s)]}$

☒ **D** $\dfrac{[Mg^{2+}(aq)] \times [OH^-(aq)]^2}{[Mg(OH)_2(s)]}$

(Total for Question 6 = 1 mark)

7 Energy is given out when one mole of gaseous magnesium ions is hydrated.

$$Mg^{2+}(g) + aq \rightarrow Mg^{2+}(aq)$$

This is more exothermic than the corresponding value for barium ions, Ba^{2+}, because the

☒ **A** ionic radius of Mg^{2+} is less than that of Ba^{2+}.

☒ **B** ionisation energy of magnesium is greater than that of barium.

☒ **C** lattice energy of magnesium oxide is more exothermic than that of barium oxide.

☒ **D** solubility of magnesium hydroxide in water is less than that of barium hydroxide.

(Total for Question 7 = 1 mark)

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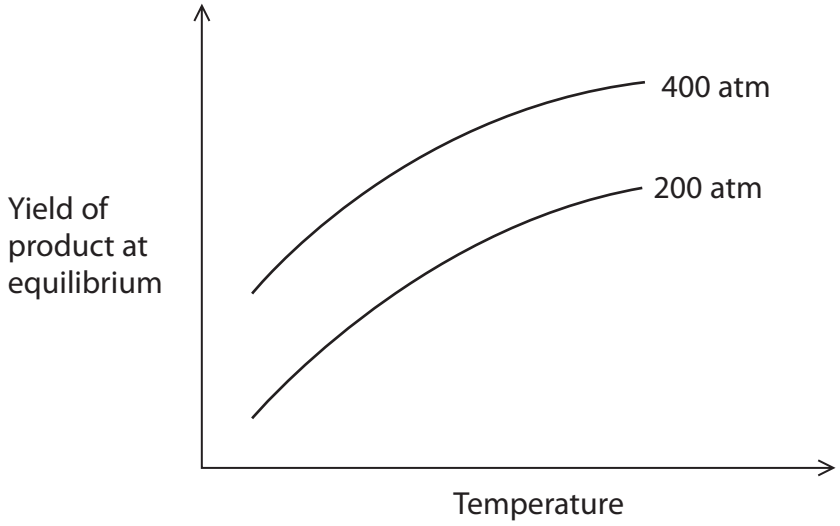
8 The graph shows the yield of product in a gaseous equilibrium at different temperatures and pressures.



The forward reaction is

☒ **A** exothermic, and there are more moles of gas on the right-hand side.

☒ **B** endothermic, and there are more moles of gas on the right-hand side.

☒ **C** exothermic, and there are fewer moles of gas on the right-hand side.

☒ **D** endothermic, and there are fewer moles of gas on the right-hand side.

(Total for Question 8 = 1 mark)

9 An aqueous solution contains 4.0 g of sodium hydroxide in 250 cm^3 of solution.

[$K_w = 1.00 \times 10^{-14}$ mol^2 dm^{-6} Molar mass of NaOH = 40 g mol^{-1}]

The pH of the solution is

☒ **A** 13.0

☒ **B** 13.4

☒ **C** 13.6

☒ **D** 13.9

(Total for Question 9 = 1 mark)

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10 A solution containing HCN and KCN is a buffer. When a small amount of acid is added, the solution acts as a buffer because

☒ **A** hydrogen ions in the acid combine with cyanide ions to make HCN.

☒ **B** hydrogen ions in the acid combine with HCN to make H_2CN^+.

☒ **C** HCN dissociates to make more CN^- ions.

☒ **D** the hydrogen ions in the acid prevent dissociation of the HCN.

(Total for Question 10 = 1 mark)

11 When 0.1 mol of hydrogen and 0.1 mol of iodine were allowed to react according to the equation

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

30% of the hydrogen was found to have been converted at equilibrium.

The number of moles of each gas present at equilibrium is

	Hydrogen	Iodine	Hydrogen iodide
☒ **A**	0.03	0.03	0.07
☒ **B**	0.03	0.03	0.14
☒ **C**	0.07	0.07	0.03
☒ **D**	0.07	0.07	0.06

(Total for Question 11 = 1 mark)

12 Which compound can show both geometric **and** optical isomerism?

☒ **A** $(CH_3)_2C{=}CHCH(CH_3)CH_2CH_3$

☒ **B** $CH_3CH_2CH{=}CHCH(CH_3)CH_2CH_3$

☒ **C** $(CH_3)_2C{=}C(CH_2CH_3)_2$

☒ **D** $CH_3CH_2CH{=}CHCH_2CH(CH_3)_2$

(Total for Question 12 = 1 mark)

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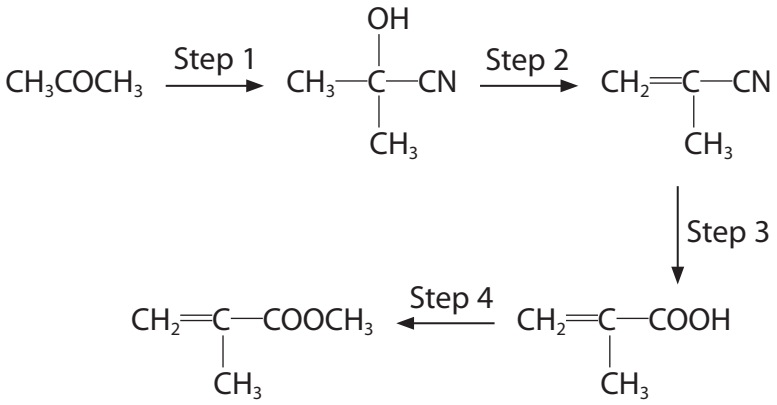
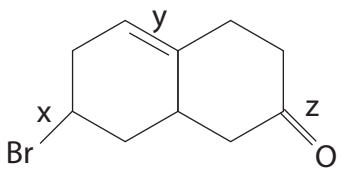
13 Which set of reagents is **not** suitable for the step indicated?



- ☒ **A** Step 1: HCN and KCN
- ☒ **B** Step 2: hot ethanolic KOH
- ☒ **C** Step 3: warm aqueous H_2SO_4
- ☒ **D** Step 4: CH_3OH with an acid catalyst

(Total for Question 13 = 1 mark)

14 The molecule shown has three functional groups labelled x, y and z.



Which of the functional groups can undergo nucleophilic attack?

- ☒ **A** x, y and z
- ☒ **B** x and z only
- ☒ **C** x only
- ☒ **D** z only

(Total for Question 14 = 1 mark)

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15 What is the formula of the pale yellow solid formed when propanone reacts with iodine in the presence of sodium hydroxide?

☒ **A** NaI

☒ **B** CH_3COCH_2I

☒ **C** CH_3I

☒ **D** CHI_3

(Total for Question 15 = 1 mark)

16 Butanone can be distinguished from butanoic acid by the addition of

☒ **A** Fehling's solution and warming.

☒ **B** Tollens' reagent and warming.

☒ **C** 2,4-dinitrophenylhydrazine solution.

☒ **D** acidified potassium dichromate(VI) solution and refluxing.

(Total for Question 16 = 1 mark)

17 Which could be used to make $CH_3CONHCH_3$?

☒ **A** CH_3COOCH_3 and NH_3

☒ **B** CH_3CONH_2 and CH_3NH_2

☒ **C** $CH_3COO^-Na^+$ and CH_3NH_2

☒ **D** CH_3COCl and CH_3NH_2

(Total for Question 17 = 1 mark)

18 Which reaction may be used to make a carboxylic acid in a single step?

☒ **A** Hydrolysis of an ester with hydrochloric acid.

☒ **B** Hydrolysis of an ester with sodium hydroxide.

☒ **C** Reaction of acidified potassium manganate(VII) with an alkene.

☒ **D** Reaction of an acyl chloride with ammonia.

(Total for Question 18 = 1 mark)

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19 The mass spectrum of ethanoyl chloride would **not** be expected to have a peak at the *m* / *e* value of

☒ **A** 35.5

☒ **B** 37

☒ **C** 43

☒ **D** 78

(Total for Question 19 = 1 mark)

20 A ketone which would not be expected to have a peak in its mass spectrum at *m* / *e* = 57 is

☒ **A** butanone, $CH_3CH_2COCH_3$

☒ **B** 3-methylbutanone, $(CH_3)_2CHCOCH_3$

☒ **C** pentan-3-one, $CH_3CH_2COCH_2CH_3$

☒ **D** hexan-3-one, $CH_3CH_2CH_2COCH_2CH_3$

(Total for Question 20 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

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SECTION B

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

21 Methanol has been proposed as a carbon-neutral fuel because it can be synthesised from carbon dioxide, as shown in the equation

$$CO_2(g) + 3H_2(g) \rightarrow CH_3OH(g) + H_2O(g)$$

(a) Standard enthalpy change of formation and standard molar entropy data for the reactants and products are shown in the table.

	$CO_2(g)$	$H_2(g)$	$CH_3OH(g)$	$H_2O(g)$
$\Delta H_f^{\ominus}$ / kJ mol^{-1}	−394	0	−201	−242
$S^{\ominus}$ / J K^{-1} mol^{-1}	214	131	238	189

(i) Calculate the standard enthalpy change for this reaction.

(2)

(ii) Calculate the standard entropy change in the system, ΔS_{system}, for this reaction.

(2)

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(iii) Calculate the total entropy change, ΔS_{total}, for this reaction at 298K.

(3)

(iv) Calculate the highest temperature at which the reaction is feasible.

(2)

(v) State why the industrial process is carried out at a higher temperature than you have calculated.

(1)

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.....

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(b) (i) Write the equation for the complete combustion of methanol in the gas phase.
State symbols are not required.

(1)

*(ii) Suggest why this combustion reaction in the gas phase is likely to be thermodynamically feasible at **all** temperatures.
Calculations are not required.

(3)

(c) Give **two** reasons why methanol, synthesised from carbon dioxide and hydrogen, may **not** be a completely carbon-neutral fuel.

(2)

(Total for Question 21 = 16 marks)

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22 This question is about three colourless liquids butanal, pentane and propenoic acid. The bottles have lost their labels.

(a) Propenoic acid is the simplest carboxylic acid containing a carbon to carbon double bond.

(i) Draw the **displayed** formula of propenoic acid showing **all** the bonds.

(1)

(ii) Propenoic acid reacts with methanol at a temperature of 100 °C in the presence of an acid catalyst.

Name the product of this reaction and draw its **skeletal** formula.

(2)

(iii) Under appropriate conditions, propenoic acid will react with lithium tetrahydridoaluminate(III) ($LiAlH_4$).

Identify the conditions necessary for this reaction and give the **structural** formula of the expected product.

(2)

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(iv) The polymerisation of propenoic acid forms poly(propenoic acid), which is used in the manufacture of superabsorbents.

Draw the structure of poly(propenoic acid) showing two repeat units.

(1)

(b) The three liquids can be identified by their boiling temperatures.

(i) Complete the table with the boiling temperatures of butanal and pentane in °C and the number of electrons in propenoic acid. Use the Data Booklet where necessary.

(2)

	butanal	pentane	propenoic acid
Boiling temperature / °C			141
Number of electrons	40	42	

*(ii) Explain the differences in boiling temperature of these three compounds using the information in the table and their structures.
A detailed explanation of the forces involved is **not** required.

(3)

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(c) Chemical tests can also be used to identify two of the liquids, and hence, by elimination, the third.

Give **two** chemical tests and the expected positive results.
The use of indicators will **not** be accepted as a chemical test.

(4)

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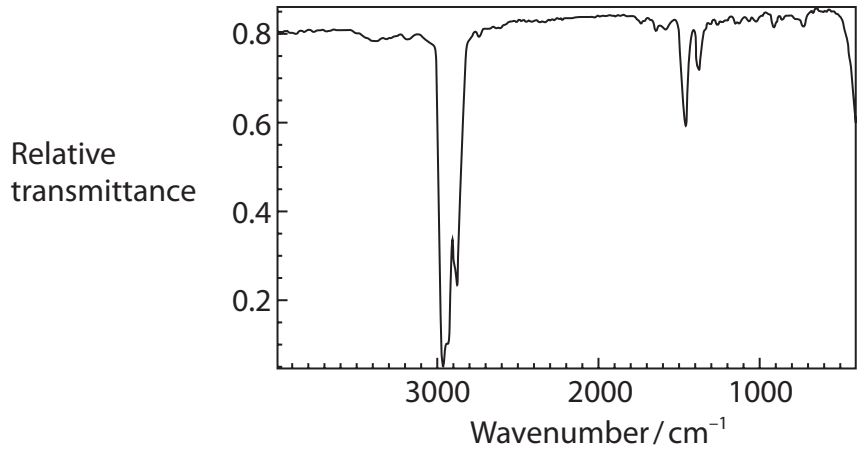
(d) The three liquids can also be identified using infrared spectroscopy.

(i) Spectrum **A** contains very few peaks.

Identify which of the three liquids gives this spectrum and explain why it has fewer peaks than the other spectra.

(2)



Spectrum **A**

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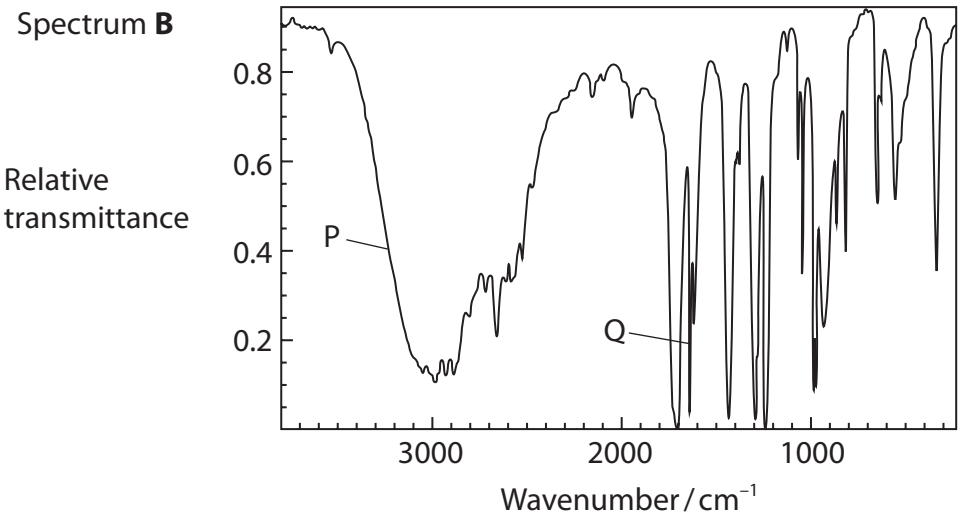
(ii) Spectra **B** and **C** are the infrared spectra of the other two liquids.

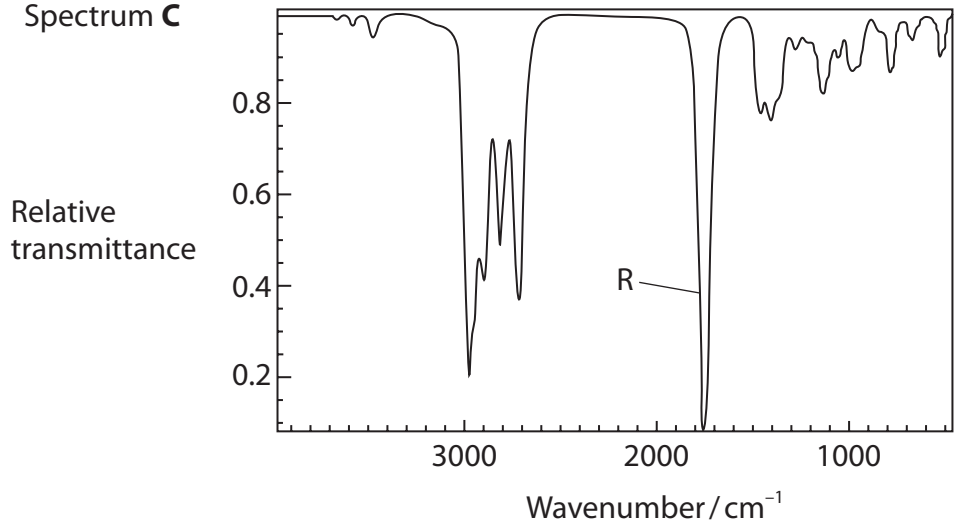
Using information from the Data Booklet, identify the **bonds** responsible for the peaks labelled P, Q and R.
Hence state which spectrum is given by which liquid.

(3)

Spectrum **B**



Spectrum **C**



P .....

Q .....

R .....

Spectrum B .....

Spectrum C .....

(Total for Question 22 = 20 marks)

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23 Compound **X** can be formed by a dimerisation reaction where two molecules of ethanal link together, as shown in the equation.

$$2CH_3CHO \rightarrow CH_3CH(OH)CH_2CHO$$
Compound **X**

(a) Give the name of compound **X**.

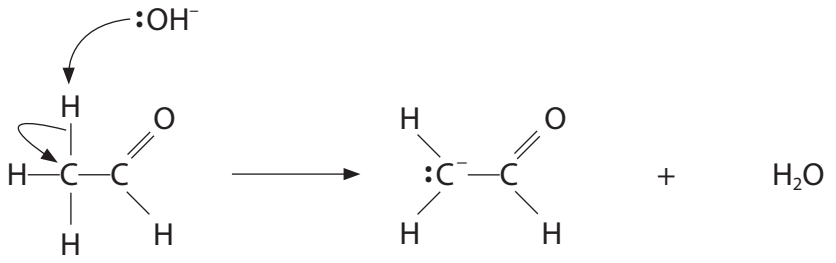
(1)

.....

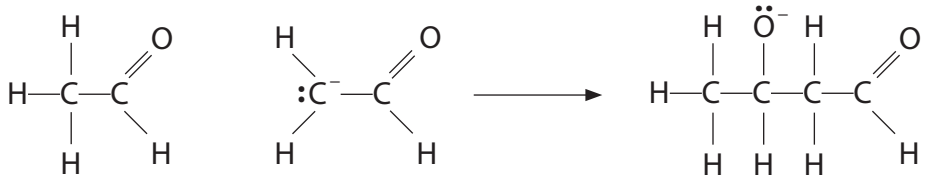
(b) The following three-step mechanism has been suggested for this reaction.

Steps **2** and **3** of this mechanism have some similarities to the reaction of aldehydes with hydrogen cyanide in the presence of potassium cyanide.

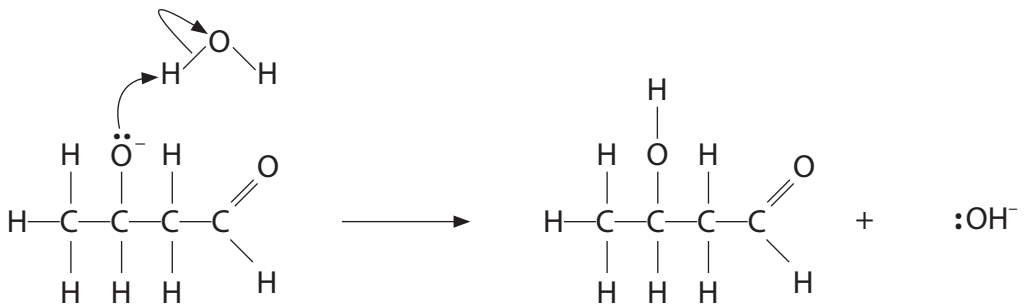
Step **1**



Step **2**



Step **3**



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(i) Deduce the role of ethanal in Step **1**.

(1)

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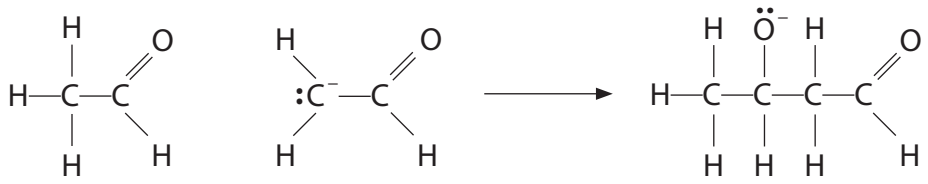
(ii) Complete Step **2** of the mechanism showing the relevant curly arrows.

(2)

Step **2**



(iii) Deduce the type and mechanism of the **overall** reaction.

(2)

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(iv) State the overall role of the hydroxide ion, OH^-, in the suggested mechanism. Justify your answer.

(2)

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(v) Explain why the sample of **X** produced by the reaction in (b) does **not** rotate the plane of plane-polarised light.

(2)

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(c) At low concentrations of hydroxide ions, OH^-, the rate equation for this reaction is

$$\text{rate} = k[CH_3CHO][OH^-]$$

When the concentration of ethanal was 0.20 mol dm^{-3} and the concentration of sodium hydroxide was 0.040 mol dm^{-3}, the rate of the reaction at 298 K was 8.8×10^{-3} mol dm^{-3} s^{-1}.

(i) Calculate a value for the rate constant at this temperature. Include units in your answer.

(2)

(ii) Give a reason why the rate equation suggests that Step **1** is the rate-determining step for this reaction.

(1)

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(Total for Question 23 = 13 marks)

TOTAL FOR SECTION B = 49 MARKS

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SECTION C

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

24 Ammonia is manufactured from nitrogen and hydrogen.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

*(a)(i) In an experiment, 1 mol of nitrogen and 3 mol of hydrogen were placed in a sealed vessel.

At a temperature of 450 K and a pressure of 2 atm, the system reached equilibrium when 20% of the nitrogen had been converted into ammonia.

Calculate the value of the equilibrium constant K_p for this reaction at 450 K, giving units in your answer.

(6)

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(ii) Give the equation that relates K_p to ΔS_{total} and use your equation and your answer to (a)(i) to calculate the total entropy change for the reaction at 450 K.

[$R = 8.31\ J\,mol^{-1}\,K^{-1}$]

(2)

(b) Ammonia is a weak base which reacts with hydrochloric acid according to the equation

$$NH_3(aq) + HCl(aq) \rightarrow NH_4Cl(aq)$$

25.0 cm^3 of aqueous ammonia with a concentration of 1.00 mol dm^{-3} was placed in a conical flask.

It was titrated with hydrochloric acid with a concentration of 0.625 mol dm^{-3}.

(i) Calculate the volume of the acid required to react exactly with the aqueous ammonia.

(2)

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(ii) Aqueous ammonium chloride is acidic.
Write an ionic equation to show the acidic behaviour of the ammonium ion.
State symbols are not required.

(1)

(iii) Write an expression for K_a for this dissociation.

(1)

(iv) When all of the ammonia has just reacted with hydrochloric acid the concentration of the ammonium chloride solution is 0.385 mol dm^{-3}.
Calculate the pH of this solution.

[$K_a = 5.6 \times 10^{-10}$ mol dm^{-3}]

(3)

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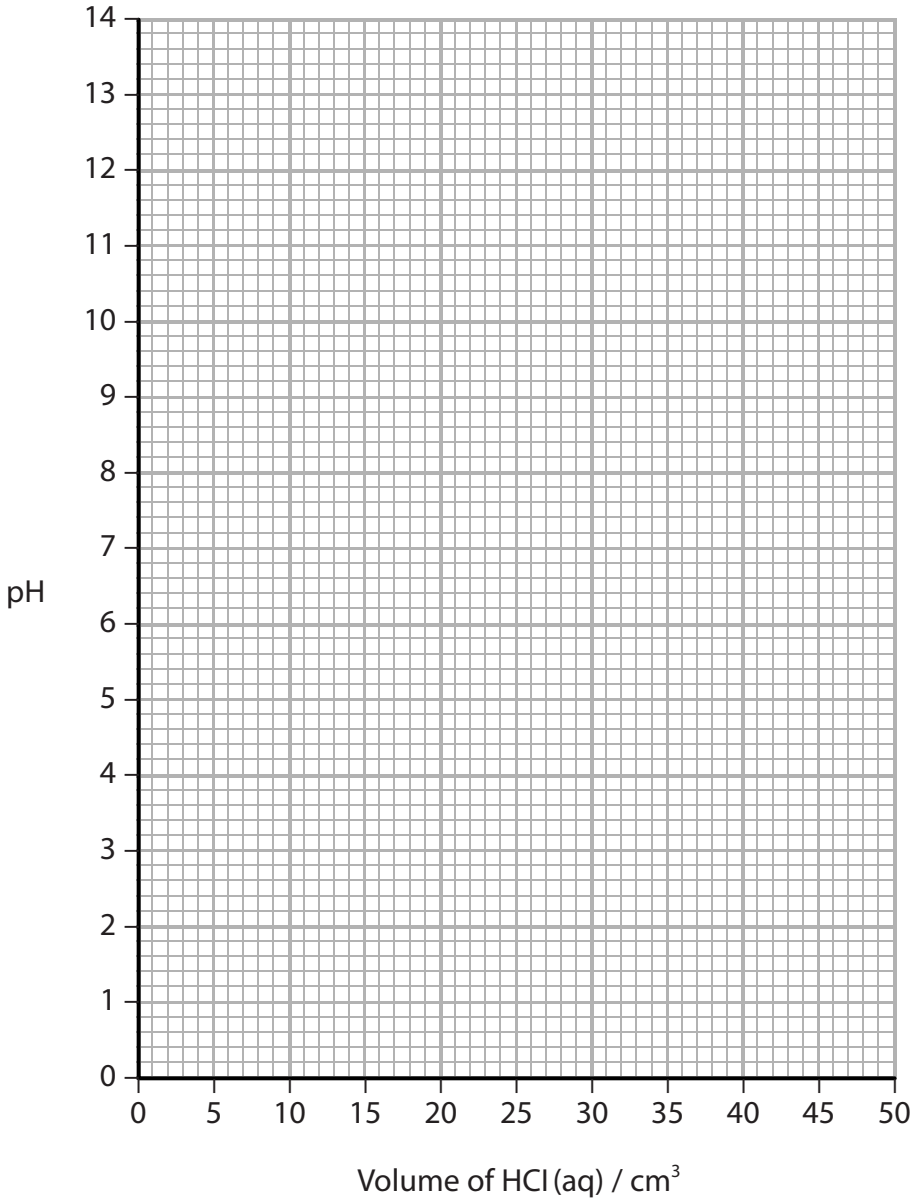
(v) Using your answers to (b)(i) and (b)(iv), draw the titration curve showing the change in pH when 50.0 cm^3 of 0.625 mol dm^{-3} hydrochloric acid solution is added to 25.0 cm^3 of 1.00 mol dm^{-3} ammonia solution.

The pH of 1.00 mol dm^{-3} ammonia solution is 11.6.

(4)



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(vi) Explain, by referring to the Data Booklet, whether or not thymol blue (base) would be a suitable indicator for this titration.

(2)

(Total for Question 24 = 21 marks)

TOTAL FOR SECTION C = 21 MARKS
TOTAL FOR PAPER = 90 MARKS

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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									(13)	(14)	(15)	(16)	(17)	
6.9 Li lithium 3	9.0 Be beryllium 4		relative atomic mass atomic symbol name atomic (proton) number									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 radium 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

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
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

* Lanthanide series

* Actinide series

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