Please check the examination details below before entering your candidate information

Candidate surname	Other names

Centre Number | Candidate Number

Pearson Edexcel International Advanced Level

Friday 20 October 2023

Morning (Time: 1 hour 45 minutes) | **Paper reference** **WCH14/01**

Chemistry

International Advanced Level
UNIT 4: Rates, Equilibria and Further Organic Chemistry

You must have:
Scientific calculator, Data Booklet, ruler

Total Marks

Instructions

- Use **black** ink or ball-point pen.
- If pencil is used for diagrams/sketches/graphs it must be dark (HB or B).
- **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.*
- In the question marked with an **asterisk (*)**, marks will be awarded for your ability to structure your answer logically, showing how the points that you make are related or follow on from each other where appropriate.
- 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.
- Try to answer every question.
- Check your answers if you have time at the end.

Turn over ▶

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 method would be most suitable to investigate the kinetics of the reactions shown?

(a) $(CH_3)_2C{=}CH_2(g) + HI(g) \rightarrow (CH_3)_3CI(g)$

(1)

☒ **A** colorimetry

☒ **B** measurement of change in volume

☒ **C** measurement of change in mass

☒ **D** quenching with ice-cold water followed by titrating with acid

(b) $HCOOCH_3(aq) + NaOH(aq) \rightarrow HCOONa(aq) + CH_3OH(aq)$

(1)

☒ **A** colorimetry

☒ **B** measurement of change in volume

☒ **C** measurement of change in mass

☒ **D** quenching with ice-cold water followed by titrating with acid

(Total for Question 1 = 2 marks)

2 The equation for the reaction of bromate(V) ions with bromide ions in acid solution is shown.

$$BrO_3^-(aq) + 5Br^-(aq) + 6H^+ \rightarrow 3Br_2(aq) + 3H_2O(l)$$

The rate equation for the reaction is

$$\text{rate} = k[BrO_3^-][Br^-][H^+]^2$$

The concentrations of all the reactants are doubled.
By what factor does the rate of reaction increase?

☒ **A** 2

☒ **B** 4

☒ **C** 8

☒ **D** 16

(Total for Question 2 = 1 mark)

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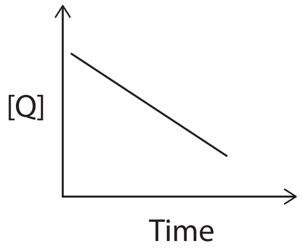
3 This question is about rates of chemical reactions.

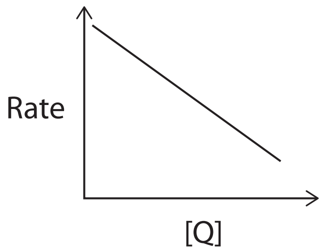
(a) Which graph shows a reaction that is zero order with respect to reactant Q?

(1)

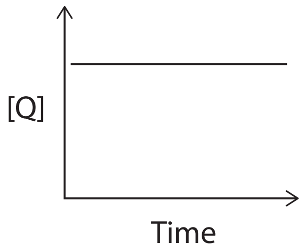
☒ **A**



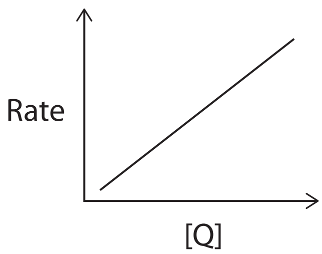
☒ **B**



☒ **C**



☒ **D**



(b) The equation for a gas phase reaction is shown.

$$A(g) \rightarrow B(g) + C(g)$$

The reaction is first order.
When the initial pressure of A is 2 atm the half-life of the reaction is 20 s.

What is the half-life of the reaction when the initial pressure of A is 4 atm?

(1)

☒ **A** 10 s

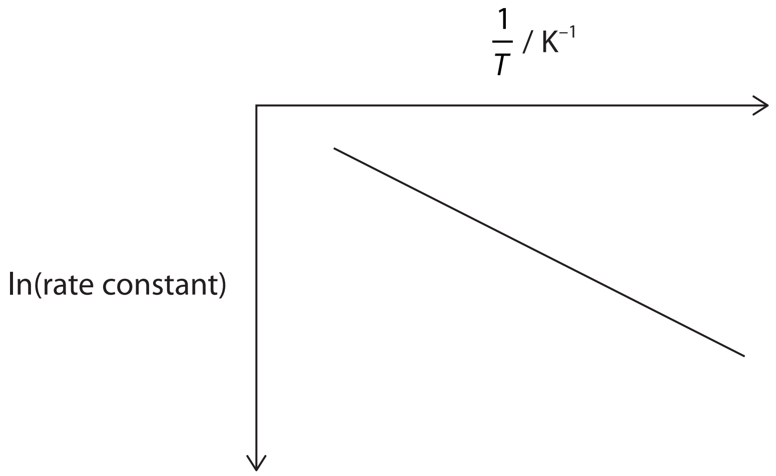
☒ **B** 20 s

☒ **C** 40 s

☒ **D** 400 s

(Total for Question 3 = 2 marks)

4 The graph shown can be used to obtain a value for the activation energy, E_a, of a reaction.



The activation energy is related to the rate constant by the equation

$$\ln(\text{rate constant}) = -\frac{E_a}{R} \times \frac{1}{T} + \text{constant}$$

From the graph, the E_a is equal to

- ☒ **A** $\frac{(-\text{gradient})}{R}$
- ☒ **B** $\frac{(-\text{gradient})}{RT}$
- ☒ **C** $(-\text{gradient}) \times R$
- ☒ **D** $(-\text{gradient}) \times RT$

(Total for Question 4 = 1 mark)

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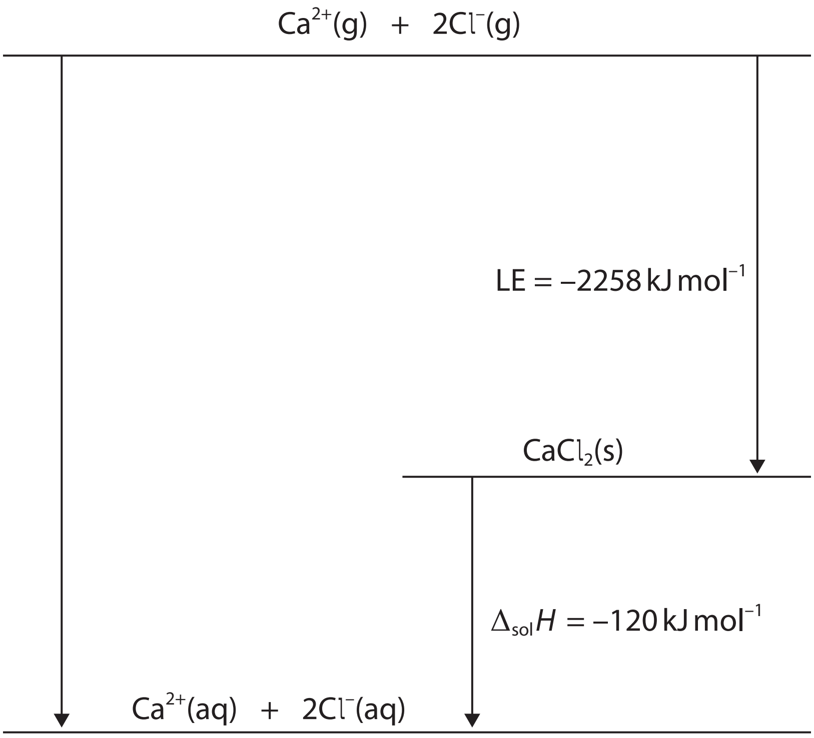
5 The energy cycle for dissolving calcium chloride in water is shown.



(a) The enthalpy change of hydration of the calcium ion is –1650 kJ mol^{-1}.

What is the enthalpy change of hydration, in kJ mol^{-1}, of the chloride ion?

(1)

☒ **A** –728

☒ **B** –364

☒ **C** +364

☒ **D** +728

(b) Why is the enthalpy change of hydration for magnesium ions more exothermic than that for calcium ions?

(1)

☒ **A** magnesium ions have a larger radius

☒ **B** magnesium ions form stronger ionic bonds

☒ **C** magnesium ions have a higher charge density

☒ **D** magnesium has higher first and second ionisation energies

(Total for Question 5 = 2 marks)

6 Heating copper(II) nitrate results in the equilibrium shown.

$$2Cu(NO_3)_2(s) \rightleftharpoons 2CuO(s) + 4NO_2(g) + O_2(g)$$

Which is the expression for K_p?

☒ **A** $K_p = \dfrac{2(pCuO) \times 4(pNO_2) \times (pO_2)}{2(pCu(NO_3)_2)}$

☒ **B** $K_p = \dfrac{(pCuO)^2 \times (pNO_2)^4 \times (pO_2)}{(pCu(NO_3)_2)^2}$

☒ **C** $K_p = 4(pNO_2) \times (pO_2)$

☒ **D** $K_p = (pNO_2)^4 \times (pO_2)$

(Total for Question 6 = 1 mark)

7 When concentrated hydrochloric acid is added to methanoic acid, an acid-base reaction occurs.

$$HCl + HCOOH \rightleftharpoons Cl^- + HCOOH_2^+$$

What are the Brønsted-Lowry acid-base conjugate pairs in this equilibrium?

	Acid 1	Conjugate base of Acid 1	Acid 2	Conjugate base of Acid 2
☒ **A**	HCl	HCOOH	$HCOOH_2^+$	Cl^-
☒ **B**	HCl	$HCOOH_2^+$	HCOOH	$HCOOH_2^+$
☒ **C**	HCl	Cl^-	HCOOH	$HCOOH_2^+$
☒ **D**	HCl	Cl^-	$HCOOH_2^+$	HCOOH

(Total for Question 7 = 1 mark)

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8 At 100 °C, pure water has a pH of 6, but at 25 °C it has a pH of 7.

This is because

☒ **A** the dissociation of water is endothermic, so the concentration of hydrogen ions is lower at 100 °C than at 25 °C

☒ **B** the dissociation of water is exothermic, so the concentration of hydrogen ions is lower at 100 °C than at 25 °C

☒ **C** the dissociation of water is endothermic, so the concentration of hydrogen ions is higher at 100 °C than at 25 °C

☒ **D** the dissociation of water is exothermic, so the concentration of hydrogen ions is higher at 100 °C than at 25 °C

(Total for Question 8 = 1 mark)

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9 Four beakers each contain equal volumes of four solutions.

Beaker **1** contains 0.01 mol dm^{-3} NaOH

Beaker **2** contains 0.01 mol dm^{-3} NH_3

Beaker **3** contains 0.1 mol dm^{-3} NaOH

Beaker **4** contains 0.1 mol dm^{-3} $Ba(OH)_2$

The pH of the four solutions was measured.
Which of the following gives the order of **decreasing** pH?

☒ **A** 1, 2, 3, 4

☒ **B** 2, 1, 3, 4

☒ **C** 3, 4, 1, 2

☒ **D** 4, 3, 1, 2

(Total for Question 9 = 1 mark)

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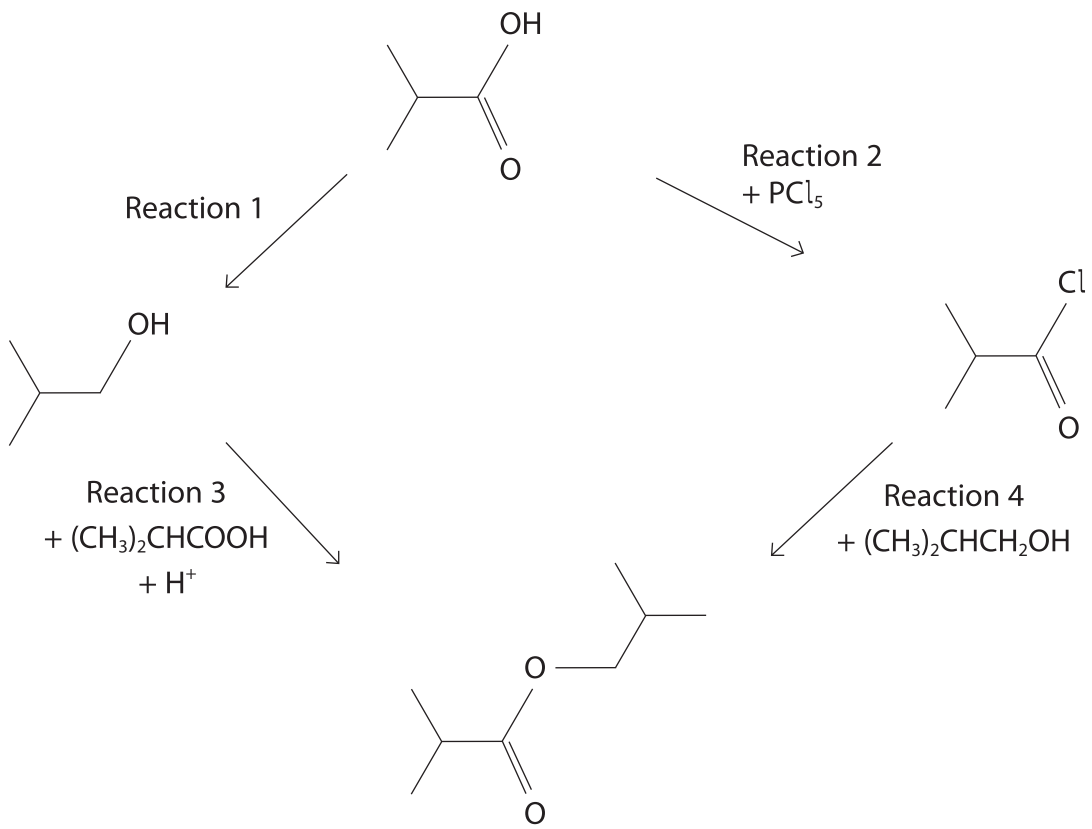
10 This question is about the reaction scheme shown.



(a) Which reagent is required for Reaction 1?

(1)

- ☒ **A** acidified potassium dichromate(VI)
- ☒ **B** concentrated sulfuric acid
- ☒ **C** hydrogen with a nickel catalyst
- ☒ **D** lithium tetrahydridoaluminate(III)

(b) Reaction 1 has a yield of 90%.
What mass of 2-methylpropanoic acid is required to produce 6.66 g of 2-methylpropan-1-ol?
[M_r values 2-methylpropanoic acid = 88 2-methylpropan-1-ol = 74]

(1)

- ☒ **A** 6.22 g
- ☒ **B** 7.13 g
- ☒ **C** 7.92 g
- ☒ **D** 8.80 g

(c) Which condition is essential for Reaction 2?

(1)

☒ **A** acid catalyst

☒ **B** anhydrous

☒ **C** high temperature

☒ **D** ether solvent

(d) Reactions 3 and 4 produce the same ester.

Which is an advantage of using Reaction 4 to produce this ester in the laboratory?

(1)

☒ **A** it can be carried out at room temperature

☒ **B** it requires a catalyst

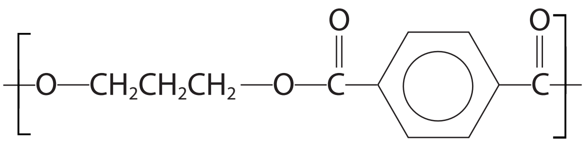
☒ **C** the atom economy is higher

☒ **D** hydrogen chloride is a product

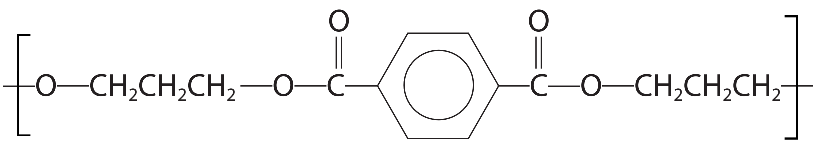
(Total for Question 10 = 4 marks)

11 Which diagram shows two repeat units of the polymer formed by the polymerisation of propane-1,3-diol and benzene-1,4-dicarboxylic acid?

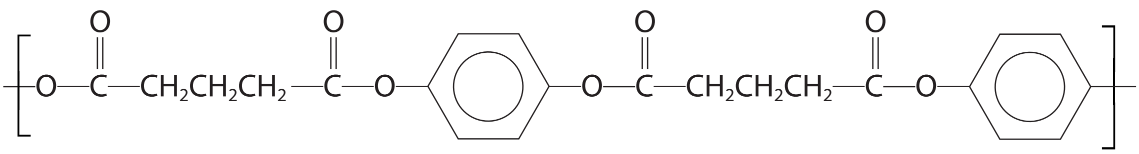
☒ **A**



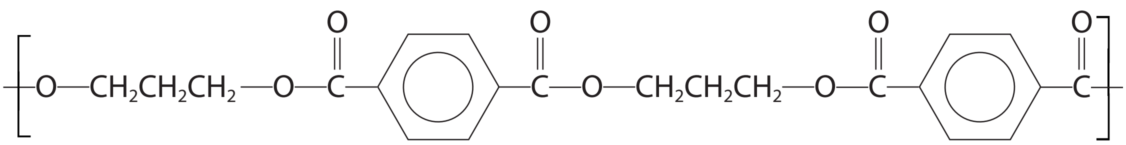
☒ **B**



☒ **C**



☒ **D**



(Total for Question 11 = 1 mark)

12 Polymer waste may be disposed of by incineration.

At a plant carrying out this process with poly(propene), a waste gas was produced that was thought to be either propane or carbon dioxide. These compounds have the same molecular ion peak in a low resolution mass spectrometer but can be separated at high resolution.

Atom	Relative atomic mass, A_r
^{1}H	1.0079
^{12}C	12.0000
^{16}O	15.9949

Which are the correct relative molecular masses?

	propane	carbon dioxide
☒ **A**	29.0395	27.9949
☒ **B**	27.9949	29.0395
☒ **C**	43.9898	44.0632
☒ **D**	44.0632	43.9898

(Total for Question 12 = 1 mark)

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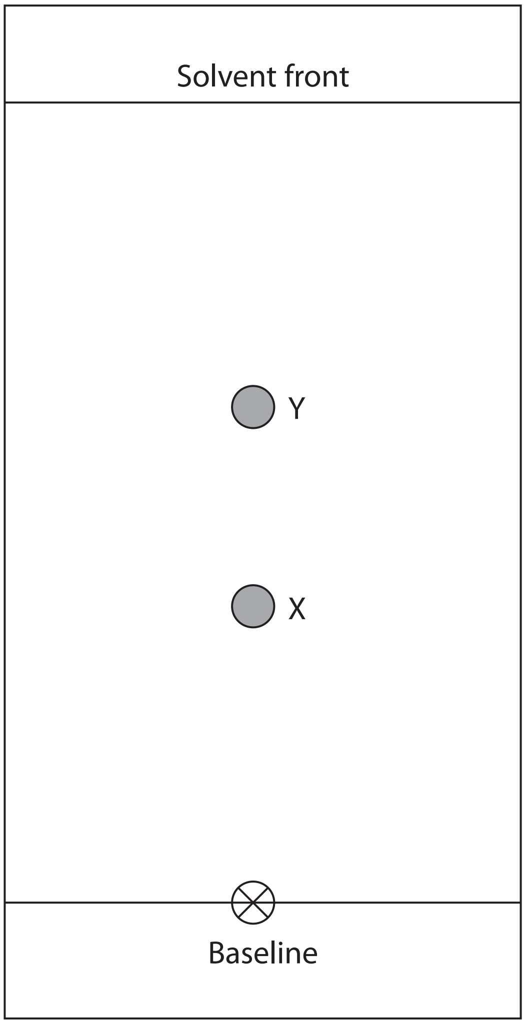
13 A thin-layer chromatogram of a mixture of two compounds, X and Y, is shown.



(a) What is the R_f value for compound X?

(1)

- ☒ **A** 0.33
- ☒ **B** 0.38
- ☒ **C** 0.60
- ☒ **D** 0.62

(b) Y travelled further than X. How do the attractions between Y and X to the stationary and mobile phases compare?

(1)

	Attraction between Y and the stationary phase	Attraction between Y and the mobile phase
☒ **A**	is stronger than the attraction between X and the stationary phase	is stronger than the attraction between X and the mobile phase
☒ **B**	is stronger than the attraction between X and the stationary phase	is weaker than the attraction between X and the mobile phase
☒ **C**	is weaker than the attraction between X and the stationary phase	is stronger than the attraction between X and the mobile phase
☒ **D**	is weaker than the attraction between X and the stationary phase	is weaker than the attraction between X and the mobile phase

(Total for Question 13 = 2 marks)

TOTAL FOR SECTION A = 20 MARKS

SECTION B

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

14 This question is about the nucleophilic addition reaction between ethanal and hydrogen cyanide in the presence of potassium cyanide as a catalyst.
The equation for the reaction is shown.

$$CH_3CHO + HCN \rightarrow CH_3CH(OH)CN$$

(a) (i) Give the IUPAC name of the organic product.

(1)

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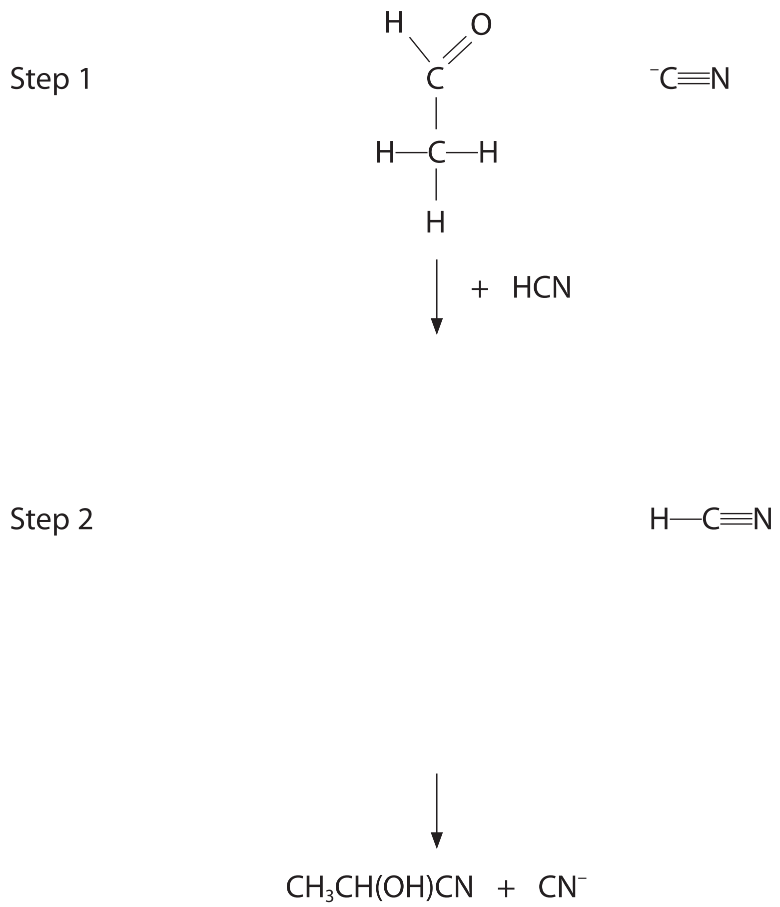
(ii) Complete the mechanism for this two-step reaction, showing the structure of the intermediate and including curly arrows, and relevant lone pairs and dipoles.

(4)



(a) (iii) Justify the use of the term 'nucleophilic addition' to describe the mechanism of this reaction.

(2)

(b) Explain why the product of the reaction is **not** optically active even though it contains a chiral carbon atom.

(2)

(Total for Question 14 = 9 marks)

15 A reaction vessel contained nitrogen monoxide and oxygen in a 2 : 1 molar ratio.
The mixture was allowed to come to equilibrium forming nitrogen dioxide.
The equation for the reaction is shown.

$$2NO + O_2 \rightleftharpoons 2NO_2$$

The volume of the vessel was 15 dm^3 and the reaction was carried out at a constant temperature and at a pressure of 200 000 Pa.

At equilibrium there was a total of 0.69625 mol of gas in the reaction vessel and the mass of oxygen was 7.000 g.

(a) (i) Calculate the number of moles of each substance at equilibrium.

(3)

(ii) Calculate the value of K_c under these conditions.
Include units in your answer.

(4)

(b) Calculate the temperature, in *K*, of the reaction mixture at equilibrium under these conditions.
Use the equation $pV = nRT$ and the data at the start of the question.

(3)

(c) Under a different set of conditions, the reaction was carried out to find the initial rate of reaction.

Experiment number	Initial [NO] / $mol\,dm^{-3}$	Initial [O_2] / $mol\,dm^{-3}$	Initial rate / $mol\,dm^{-3}\,s^{-1}$
1	6.50×10^{-2}	1.25×10^{-2}	6.87×10^{-4}

The rate equation for this reaction is

$$\text{rate} = k[NO]^2[O_2]$$

(i) Give the reason why colorimetry can be used to monitor the rate of the reaction.

(1)

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(ii) Use the data from Experiment 1 to find the value of the rate constant, *k*. Include units in your answer.

(2)

(iii) State why the reaction is unlikely to proceed in a single step.

(1)

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(iv) A student proposed the mechanism shown for this reaction.

$$2NO \rightleftharpoons N_2O_2 \qquad \text{slow}$$

$$N_2O_2 + O_2 \rightarrow 2NO_2 \qquad \text{fast}$$

Justify whether or not this mechanism is consistent with the overall equation for the reaction **and** with the rate equation.

(2)

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(Total for Question 15 = 16 marks)

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16 Iron, lead and zinc can be extracted using a blast furnace but aluminium cannot.

In a blast furnace, iron is extracted from iron(III) oxide, Fe_2O_3, at high temperature.

Some standard enthalpy changes of formation, $\Delta_f H^{\ominus}$, and standard molar entropies, $S^{\ominus}$, are shown.

Substance	Al(s)	Al_2O_3(s)	CO(g)	CO_2(g)	Fe(s)	Fe_2O_3(s)
$\Delta_f H^{\ominus}$ / kJ mol^{-1}	0	–1676	–111	–394	0	–824
$S^{\ominus}$ / J K^{-1} mol^{-1}	28.3	50.9	197.6	213.6	27.3	87.4

(a) The main reaction occurring in the blast furnace to form iron is shown.

$$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$$

This reaction is feasible at all temperatures.

(i) Calculate the standard entropy change of the system for this reaction.

(3)

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

(3)

(iii) Explain how your answers to (a)(i) and (a)(ii) show that this reaction is feasible at all temperatures.

(3)

(b) The main reduction reaction of aluminium oxide in a blast furnace is shown.

$$Al_2O_3 + 3CO \rightarrow 2Al + 3CO_2$$

(i) Calculate the temperature at which this reaction becomes feasible.

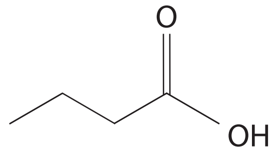
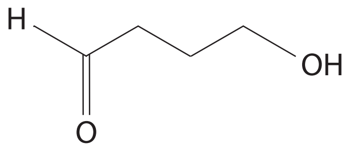
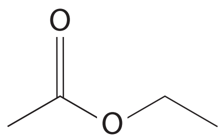
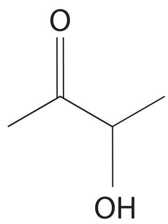
(4)

(ii) Suggest why aluminium is not extracted from its oxide using a blast furnace.

(1)

(Total for Question 16 = 14 marks)

17 This question is about four isomers with the molecular formula $C_4H_8O_2$.

Name	Skeletal formula
butanoic acid	
4-hydroxybutanal	
ethyl ethanoate	
3-hydroxybutanone	

*(a) These four isomers can be identified using three **chemical** tests.
Each test gives a positive result for only one isomer.
All three tests give a negative result for the fourth isomer.

Deduce the three **chemical** tests required. For each test

- identify the reagent
- give the positive observation in each test
- identify the functional group of the isomer that gives the positive result.

(6)

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(b) The four isomers can also be distinguished using NMR spectroscopy.

(i) State why it is **not** possible to distinguish any of these isomers from the number of peaks in their ^{13}C NMR spectra.

(1)

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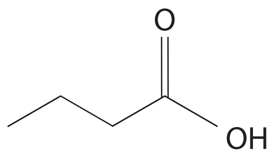
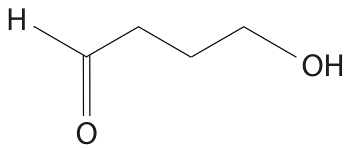
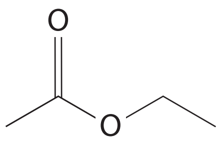
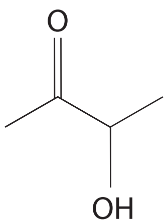
(ii) Complete the table below to give the number of peaks in a **low** resolution ^{1}H NMR spectrum of each isomer.

(3)

Name	Skeletal formula	Number of peaks
butanoic acid		
4-hydroxybutanal		
ethyl ethanoate		
3-hydroxybutanone		

(iii) One of the ^{1}H NMR spectra has a peak with a chemical shift, δ, greater than 10 ppm.
Identify the isomer, and the proton environment responsible for this peak.

(1)

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(iv) The high resolution ^{1}H NMR spectrum of one of the isomers contains a multiplet of five peaks (a quintet).
Explain, with reference to the structure of one of the isomers, the presence of the quintet.

(2)

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(Total for Question 17 = 13 marks)

TOTAL FOR SECTION B = 52 MARKS

SECTION C

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

18 Pentanoic acid, C_4H_9COOH, is a carboxylic acid with $K_a = 1.38 \times 10^{-5}\ mol\,dm^{-3}$.

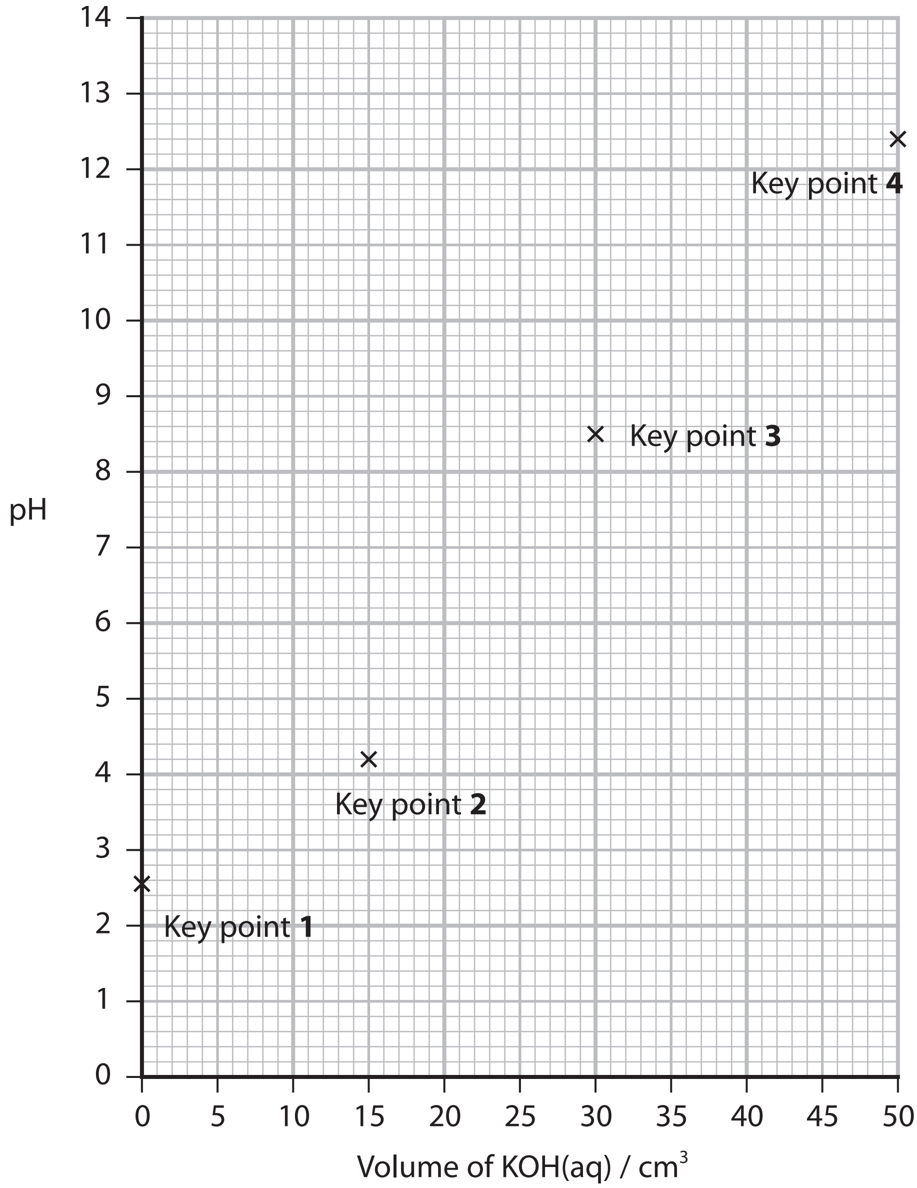
A student was asked to titrate $25.0\ cm^3$ of $0.120\ mol\,dm^{-3}$ pentanoic acid solution with $0.100\ mol\,dm^{-3}$ potassium hydroxide solution.

The equation for the reaction is shown.

$$C_4H_9COOH + KOH \rightarrow C_4H_9COO^-K^+ + H_2O$$

The teacher asked the student to sketch a graph showing the expected changes in pH as potassium hydroxide solution is added.

The student first identified four key points for the sketch graph, using four calculations and one chemical equation. These points are shown.



(a) (i) At Key point **1**, before any potassium hydroxide has been added, the pH = 2.9.
Use a calculation to justify this value.

(3)

....

....

(ii) The student deduced that the pH at Key point **4** must be less than 13.
Use a calculation to justify the student's deduction.
You are **not** required to calculate the exact pH of the solution.

(2)

....

....

(iii) The student deduced that the neutralisation point of the graph at Key point **3** would be at 30 cm^3.
Use a calculation to justify the student's deduction.

(2)

....

(iv) The student deduced that when equal amounts of pentanoic acid and potassium hydroxide have been mixed at Key point **3**, the pH would be greater than 7.
Justify the student's deduction.

(1)

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(v) The student deduced that at Key point **2**, 15.0 cm^3 of potassium hydroxide would have been added and the pH would be 4.9.
Justify the student's deductions using a calculation.

(2)

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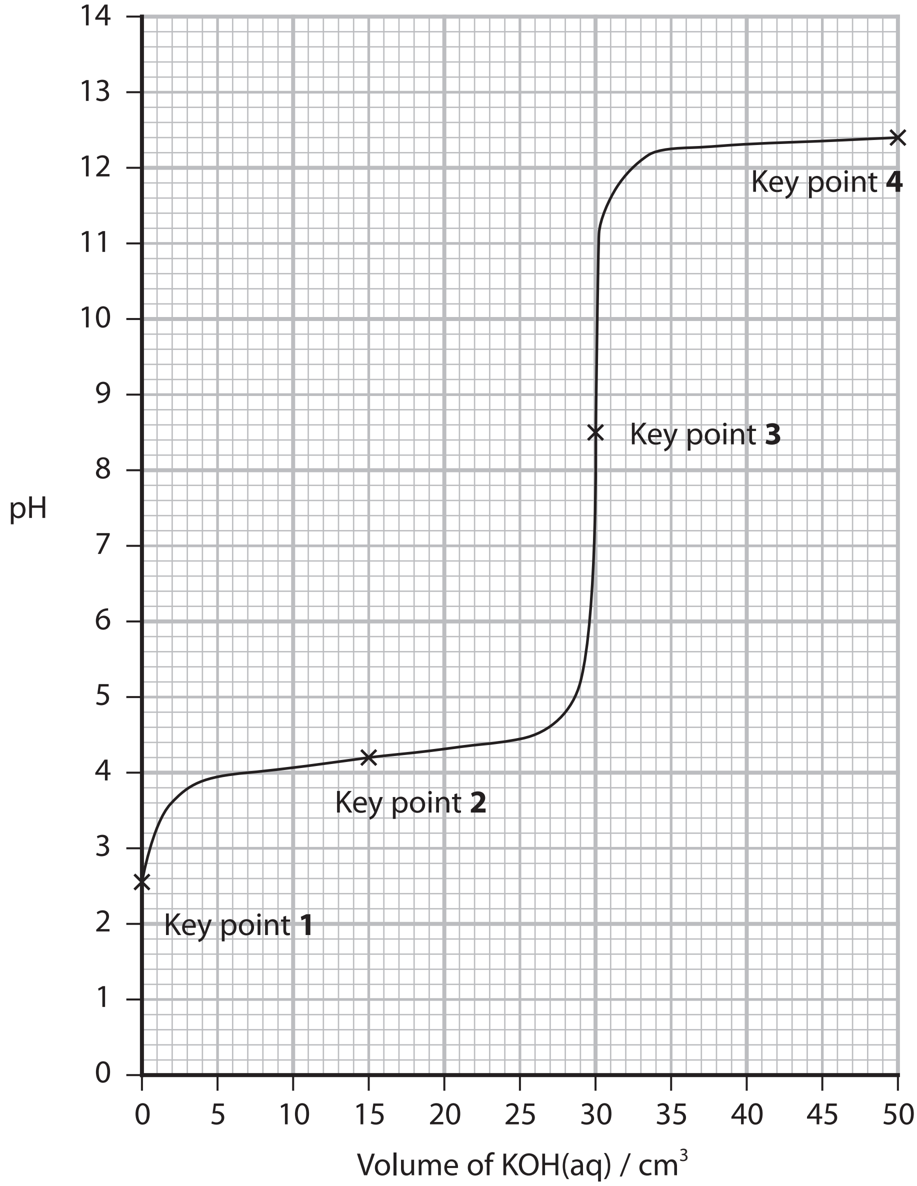
(b) The student then completed the sketch graph by linking these four points to show how the pH would change as potassium hydroxide was added.



Explain why the student drew the line so that in the section of the graph between 5 cm^3 and 25 cm^3 the pH changes very little as the potassium hydroxide is added. No calculation is required.

(3)

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(c) (i) The student carried out the titration using methyl orange as an indicator. The experiment did not give a satisfactory colour change at the neutralisation point, and the student continued adding potassium hydroxide until 50 cm^3 had been added.

Describe the colour of the solution during this titration experiment with particular reference to the key points on the sketch graph.

Use the Data Booklet.

(3)

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(ii) The student found a bottle labelled 'Acid-base indicator solution' in the store cupboard. The student, having checked with the teacher, used this as the indicator for the titration.

The initial yellow solution turned green at the neutralisation point of the titration.

Suggest the identity of the indicator solution including a justification for the colour observed at the neutralisation point.

Use the Data Booklet.

(2)

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(Total for Question 18 = 18 marks)

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

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The Periodic Table of Elements

Key

relative atomic mass
atomic symbol
name
atomic (proton) number

1 (1)	2 (2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	3 (13)	4 (14)	5 (15)	6 (16)	7 (17)	0 (8) (18)
							1.0 **H** hydrogen 1										4.0 **He** helium 2
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											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

* 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