Write your name here

Surname	Other names

Pearson Edexcel
International Advanced Level

Centre Number | | | | | |

Candidate Number | | | | |

Chemistry

Advanced

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

Monday 11 January 2016 – Afternoon
Time: 1 hour 40 minutes

Paper Reference
WCH04/01

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 ▶

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6/6/6/6/3/3/

P 4 6 9 4 0 A 0 1 2 8

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 The equation for the reaction between bromate(V) ions and bromide ions in acid solution is

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

The rate equation for this reaction is

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

When the concentrations of all of the reactants are doubled, the rate increases by a factor of

☒ **A** 2

☒ **B** 4

☒ **C** 8

☒ **D** 16

(Total for Question 1 = 1 mark)

2 The decomposition of hydrogen peroxide is catalysed by iodide ions.

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

The rate equation for this reaction is

$$\text{rate} = k[H_2O_2][I^-]$$

This is consistent with a reaction mechanism in which

☒ **A** there is only one step.

☒ **B** the catalyst is used up.

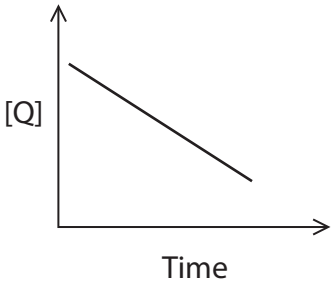
☒ **C** the slowest step is the reaction of two molecules of hydrogen peroxide with an iodide ion.

☒ **D** the slowest step is the reaction of one molecule of hydrogen peroxide with an iodide ion.

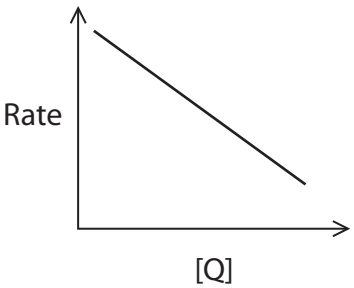
(Total for Question 2 = 1 mark)

3 Which of the following sketch graphs shows a reaction that is zero order with respect to reactant Q?

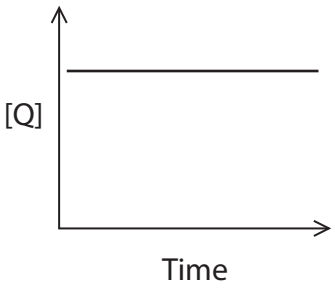
☒ **A**



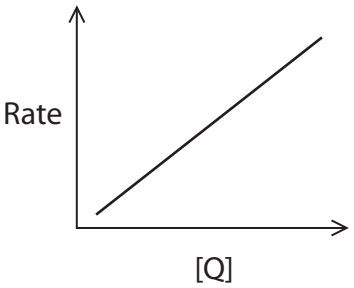
☒ **B**



☒ **C**



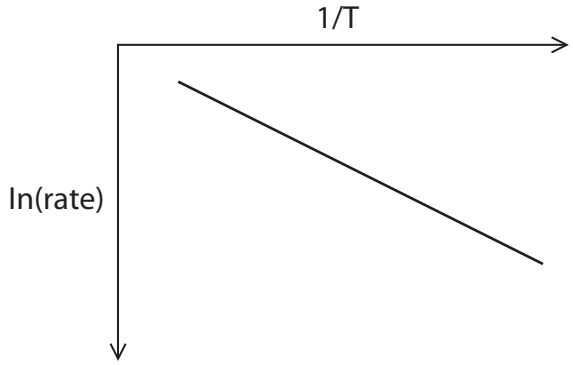
☒ **D**



(Total for Question 3 = 1 mark)

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

4 Typical results of a rate experiment are shown in the sketch graph below.



The activation energy, E_a, of a reaction is related to the rate by the equation

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

For the graph above, E_a is equal to

☒ **A** (–gradient) / R

☒ **B** (–gradient) / RT

☒ **C** (–gradient) × R

☒ **D** (–gradient) × RT

(Total for Question 4 = 1 mark)

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

5 The equation for the manufacture of ethanol by the reaction of ethene and steam with a catalyst of phosphoric(V) acid is

$$C_2H_4(g) + H_2O(g) \rightleftharpoons C_2H_5OH(g) \quad \Delta H = -45 \text{ kJ mol}^{-1}$$

(a) The highest equilibrium yield of ethanol is obtained at

(1)

☒ **A** high temperature and high pressure.

☒ **B** low temperature and low pressure.

☒ **C** low temperature and high pressure.

☒ **D** high temperature and low pressure.

(b) The units of the equilibrium constant, K_c, for this reaction are

(1)

☒ **A** mol dm^{-3}

☒ **B** dm^3 mol^{-1}

☒ **C** mol^2 dm^{-6}

☒ **D** dm^6 mol^{-2}

(c) The equilibrium constant for this reaction increases when

(1)

☒ **A** the pressure is increased.

☒ **B** more catalyst is added.

☒ **C** the temperature is decreased.

☒ **D** ethanol is removed from the reaction mixture.

(Total for Question 5 = 3 marks)

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

6 In which of the following reactions is there a **decrease** in the entropy of the system?

☒ **A** $Ca(OH)_2(aq) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l)$

☒ **B** $Ca(OH)_2(s) \rightarrow CaO(s) + H_2O(l)$

☒ **C** $CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$

☒ **D** $Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(aq) + H_2(g)$

(Total for Question 6 = 1 mark)

7 Which of the following statements is always true for an exothermic reaction?

☒ **A** $\Delta S_{surroundings}$ doubles when the temperature in kelvin doubles.

☒ **B** $\Delta S_{surroundings}$ doubles when the natural log of the temperature in kelvin, ln*T*, doubles.

☒ **C** The equilibrium constant, *K*, doubles when ΔS_{total} doubles.

☒ **D** The natural log of the equilibrium constant, ln*K*, doubles when ΔS_{total} doubles.

(Total for Question 7 = 1 mark)

8 When one mole of magnesium chloride dissolves in water, the enthalpy change, $\Delta H_{solution}$, is more negative than the corresponding change for sodium chloride.

One explanation for this difference is that

☒ **A** the lattice enthalpy for magnesium chloride is more negative than the lattice enthalpy for sodium chloride.

☒ **B** the $\Delta H_{hydration}$ of magnesium ions is more negative than $\Delta H_{hydration}$ of sodium ions.

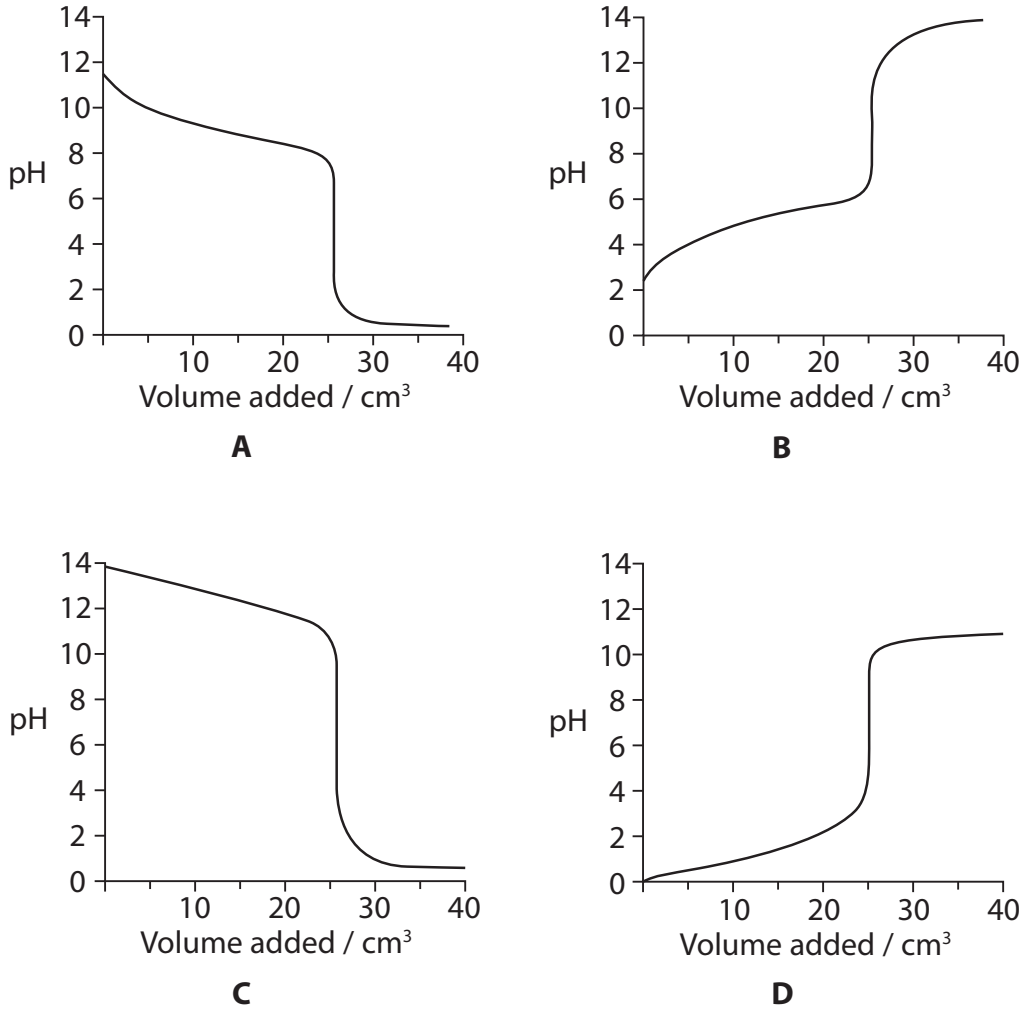
☒ **C** the $\Delta H_{formation}$ of magnesium chloride is more negative than $\Delta H_{formation}$ of sodium chloride.

☒ **D** magnesium chloride has more covalent character than sodium chloride.

(Total for Question 8 = 1 mark)

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

9 Titrations were carried out using aqueous solutions with concentration 1.0 mol dm^{-3}.
The titration curves below were obtained.



(a) Which curve would be obtained for the titration in which hydrochloric acid is added to aqueous ammonia?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(b) For which titration would methyl orange **not** be a suitable indicator?
Use the data on page 19 of the Data Booklet.

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(Total for Question 9 = 2 marks)

10 The pH of three solutions with concentration 1.0 mol dm^{-3} was measured.

Solution 1 NH_3

Solution 2 CH_3COONa

Solution 3 NH_4Cl

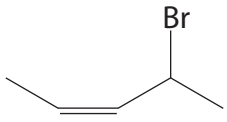
Which of the following shows the three solutions in order of **increasing** pH?

- ☒ **A** 1, 2, 3
- ☒ **B** 3, 2, 1
- ☒ **C** 3, 1, 2
- ☒ **D** 2, 3, 1

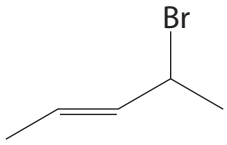
(Total for Question 10 = 1 mark)

11 Which formula shows an *E* isomer which also contains a chiral carbon atom?

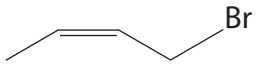
☒ **A**



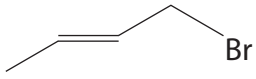
☒ **B**



☒ **C**



☒ **D**



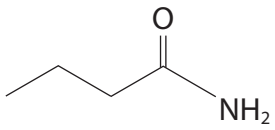
(Total for Question 11 = 1 mark)

12 Two polar compounds are separated using HPLC. The retention times (the average time spent in the column) are **not** affected by the

- ☒ **A** pressure used.
- ☒ **B** particle size of the stationary phase.
- ☒ **C** polarity of the stationary phase.
- ☒ **D** concentration of the polar compounds.

(Total for Question 12 = 1 mark)

13 This question is about four organic compounds.

1


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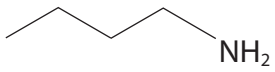

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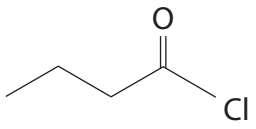

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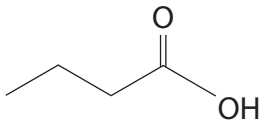


(a) Which compounds react with methanol under suitable conditions to form methyl butanoate?

(1)

☒ **A** 1 and 3 only

☒ **B** 1 and 4 only

☒ **C** 3 and 4 only

☒ **D** 2, 3 and 4 only

(b) Which compound reacts with water to form two different acids?

(1)

☒ **A** 1

☒ **B** 2

☒ **C** 3

☒ **D** 4

(c) Which compounds react together to form an amide?

(1)

☒ **A** 1 and 4

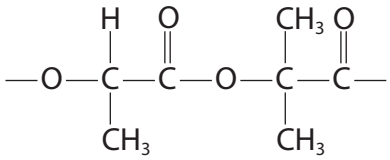
☒ **B** 3 and 4

☒ **C** 2 and 4

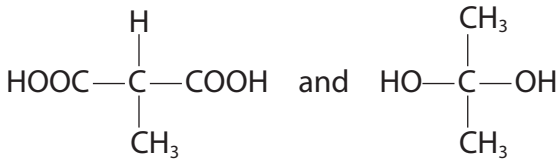
☒ **D** 2 and 3

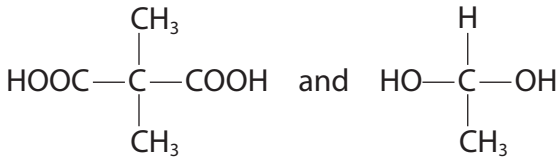
(Total for Question 13 = 3 marks)

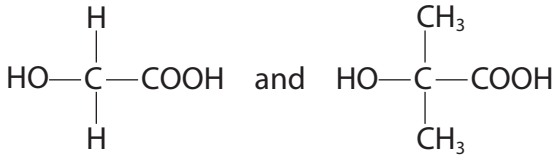
14 A polymer has the repeat unit

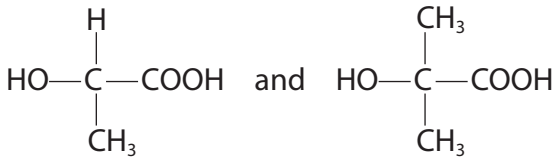


It could be made from the monomers

☒ **A** 

☒ **B** 

☒ **C** 

☒ **D** 

(Total for Question 14 = 1 mark)

15 Which of the following isomers has the highest boiling temperature?

☒ **A** $CH_3CH_2CH_2COOH$

☒ **B** $CH_3CH_2COOCH_3$

☒ **C** $HCOOCH_2CH_2CH_3$

☒ **D** $HCOOCH(CH_3)_2$

(Total for Question 15 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

SECTION B

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

16 Bromine reacts with methanoic acid as shown below.

$$HCOOH(aq) + Br_2(aq) \rightarrow 2H^+(aq) + 2Br^-(aq) + CO_2(g)$$

The kinetics of the reaction can be investigated by various methods.

(a) For two different named substances, identify a method of following the progress of the reaction. The methods given should be different for each substance and should **not** involve taking samples from the reaction mixture.

(2)

Substance 1

.....

Method

.....

Substance 2

.....

Method

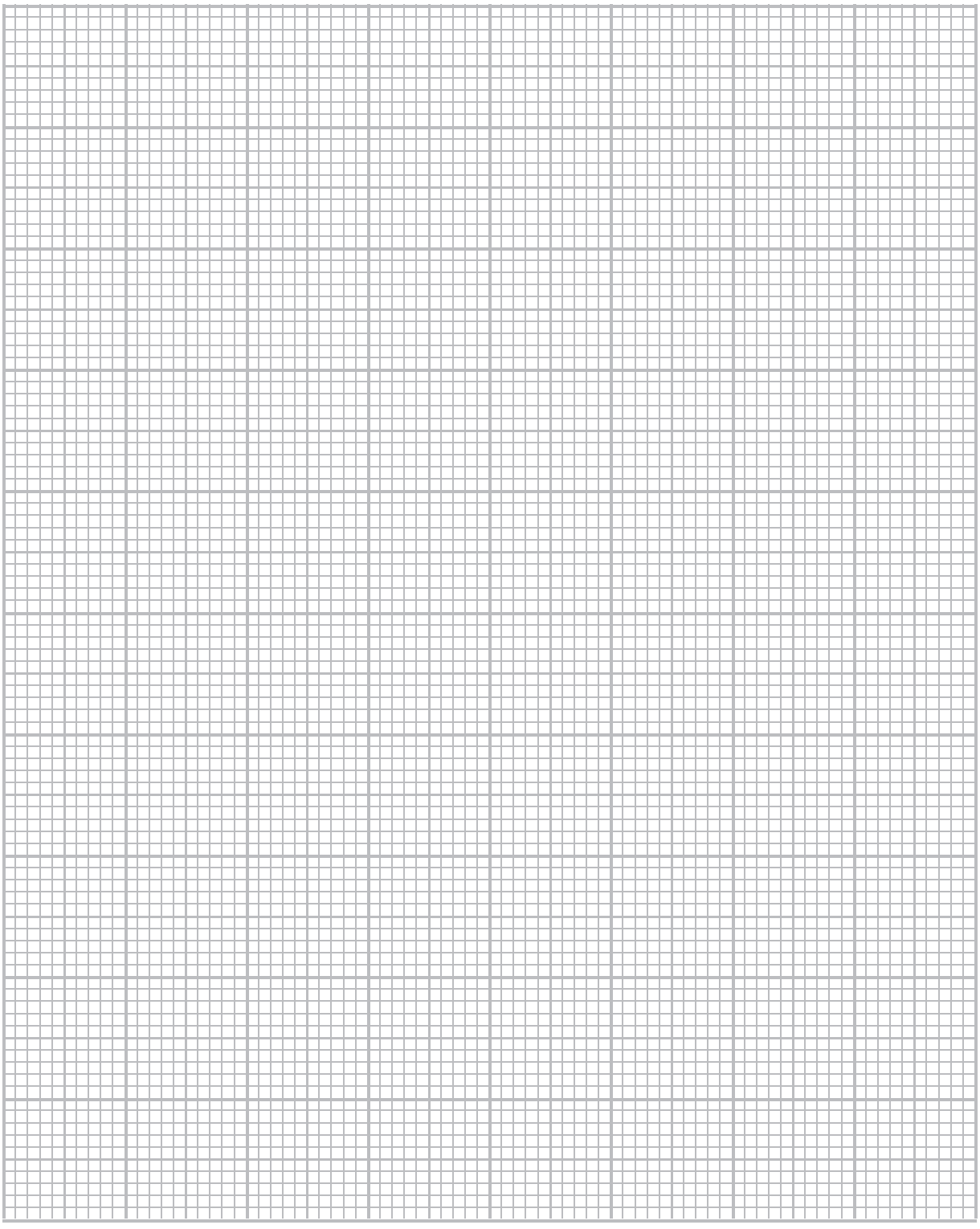
.....

(b) In an investigation of the kinetics of the reaction, a large excess of methanoic acid was used.

(i) Use the data shown on page 12 to plot a graph that can be used to determine the order of reaction with respect to bromine.

(2)

Time / s	0	60	120	180	240	300	420	600	700
$[Br_2(aq)]$ / mol dm^{-3}	0.0100	0.0082	0.0066	0.0053	0.0043	0.0034	0.0021	0.0011	0.0007



(ii) Use the graph to confirm that the reaction is first order with respect to bromine.

Show on the graph the measurements you use to confirm this and explain how the order is deduced.

(3)

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(iii) Under the conditions of the experiment, the order of reaction with respect to methanoic acid appears to be zero.

Explain why this is the case.

(1)

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.....

(iv) Further experiments show that the reaction is actually first order with respect to methanoic acid.

Write the rate equation for the reaction.

(1)

(v) The initial rate of the reaction carried out in part (b)(i) was found to be 4.54×10^{-5} mol dm^{-3} s^{-1}.

The initial concentration of methanoic acid was 0.500 mol dm^{-3} and that of bromine was 0.0100 mol dm^{-3}.

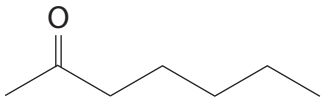
Use these values, and your rate equation in part (b)(iv), to calculate the rate constant for the reaction.

Give the units of the rate constant.

(2)

(Total for Question 16 = 11 marks)

17 A naturally occurring ketone, compound **A**, contributes to the smell and flavour of some blue cheeses.



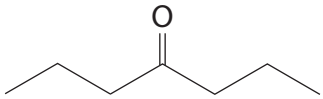
Compound **A**

(a) Give the systematic name of **A**.

(1)

.....

(b) Compound **B** is an isomer of **A** with the same functional group.



Compound **B**

Describe a simple **chemical** test which would distinguish **A** from **B**.
State the result of the test for each of the compounds.

(2)

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.....

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.....

.....

.....

(c) Give **two** chemical tests for **B** which, when used together, would confirm that **B** contains a carbonyl group and is not an aldehyde. For each test, state the result and what is deduced.

(4)

Test 1

.....

.....

.....

.....

Test 2

.....

.....

.....

.....

(d) Give the **displayed** or **structural** formula of the compound which forms when **A** is reduced. State the name or formula of a suitable reducing agent.

(2)

Formula

Reducing agent .....

(e) (i) Hydrogen cyanide reacts with **A** in the presence of CN^- ions.

Write a mechanism for this reaction, using the skeletal formula of **A** below.

(3)

*(ii) By considering the reaction mechanism, explain why the solution produced in this reaction does **not** rotate the plane of plane-polarized light.

(3)

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(Total for Question 17 = 15 marks)

18 Methanol is synthesised by the following reaction.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

A mixture of 39.5 mol of carbon monoxide and 77.5 mol of hydrogen was allowed to reach equilibrium at 500 K and 50 atm pressure. Under these conditions, the equilibrium mixture contained 38.5 mol of methanol.

(a) Write the expression for the equilibrium constant in terms of pressure, K_p, for this reaction.

(1)

*(b) Complete the table below.

Hence calculate the value of K_p under these conditions.
Give your answer to **three** significant figures and include the units.

(5)

	CO	H_2	CH_3OH	Total mol
mol at start	39.5	77.5	0	
mol at equilibrium			38.5	

*(c) When the reaction is carried out at 700 K and 50 atm pressure, the value of K_p is smaller.

Use this information to deduce the sign of $\Delta S_{surroundings}$ for the forward reaction.
Justify your answer.

(2)

.....

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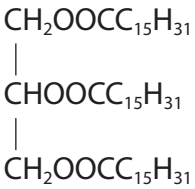
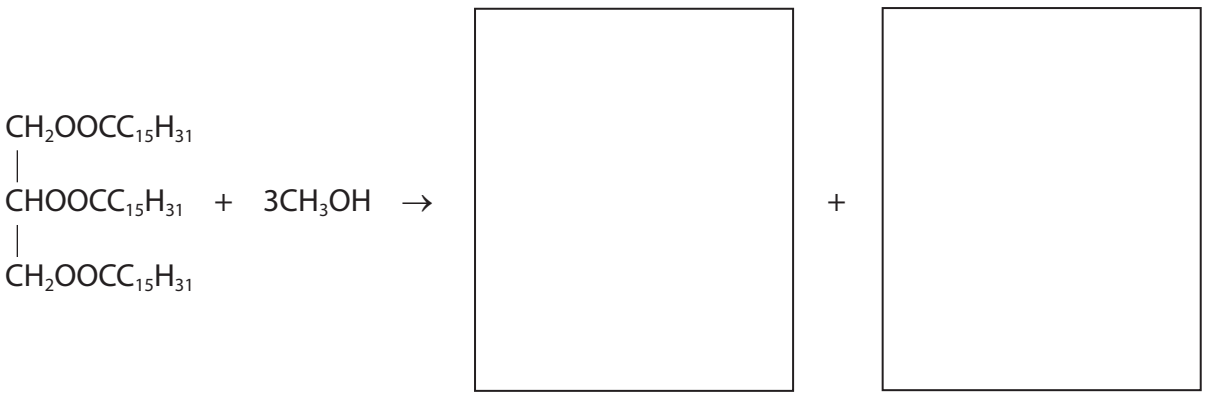
.....

(d) One industrial use of methanol is in the production of bio-diesel from vegetable oils.
A component of these oils is shown below.



Complete the equation for the reaction of methanol with this compound.

(2)



(Total for Question 18 = 10 marks)

19 Propanoic acid is a weak Brønsted-Lowry acid.

(a) Define the term Brønsted-Lowry acid.

(1)

.....

(b) What is the pH of a 0.100 mol dm^{-3} solution of hydrochloric acid?
How would the pH of any weak acid of the same concentration differ from the pH of hydrochloric acid?

(1)

.....

.....

.....

(c) Methanoic acid was mixed with propanoic acid.

(i) Use your Data Booklet to decide which acid is stronger.
Justify your answer.

(1)

.....

.....

.....

(ii) Hence complete the following equation.

(1)

$HCOOH + C_2H_5COOH \rightleftharpoons$ ..... + ...

(d) Calculate the pH of a solution of 0.050 mol dm^{-3} sodium hydroxide.

[$K_w = 1.0 \times 10^{-14}$ mol^2 dm^{-6}]

(2)

(e) A buffer was made by mixing 20 cm^3 of 0.050 mol dm^{-3} sodium hydroxide and 20 cm^3 of 0.25 mol dm^{-3} propanoic acid.

(i) Write the equation for the reaction between sodium hydroxide and propanoic acid. State symbols are not required.

(1)

(ii) Calculate the pH of this buffer solution. Show your working. Refer to your Data Booklet where needed.

(5)

(iii) Explain how this solution acts as a buffer when a small amount of **alkali** is added. Include any relevant equations in your explanation.

(3)

(Total for Question 19 = 15 marks)

TOTAL FOR SECTION B = 51 MARKS

SECTION C

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

20 Nitrogen monoxide, NO, reacts with oxygen as shown below.

$$NO(g) + \tfrac{1}{2}O_2(g) \rightarrow NO_2(g) \qquad \Delta H^{\ominus} = -57 \text{ kJ mol}^{-1}$$

(a) (i) Calculate the standard entropy change of the system, $\Delta S^{\ominus}_{system}$.

The standard molar entropy of $\tfrac{1}{2}O_2(g)$ is 102.5 J mol^{-1} K^{-1}.

Use other standard molar entropy values from your Data Booklet.

Include a sign and units in your answer.

(2)

(ii) Calculate the entropy change of the surroundings, $\Delta S^{\ominus}_{surroundings}$ at 298 K and hence the total entropy change, $\Delta S^{\ominus}_{total}$ at this temperature.

Include a sign and units in your answers.

(2)

(iii) Calculate the temperature at which the reaction ceases to be spontaneous.

(2)

(b) Nitrogen monoxide and carbon monoxide are formed in car engines. To prevent these pollutant gases being released into the atmosphere, car exhausts are fitted with a catalyst and the reaction below occurs.

$$CO(g) + NO(g) \rightarrow CO_2(g) + \tfrac{1}{2}N_2(g)$$

At the temperature of the car exhaust, ΔS_{total} for this reaction is positive.

Suggest why this reaction needs a catalyst.

(1)

.....

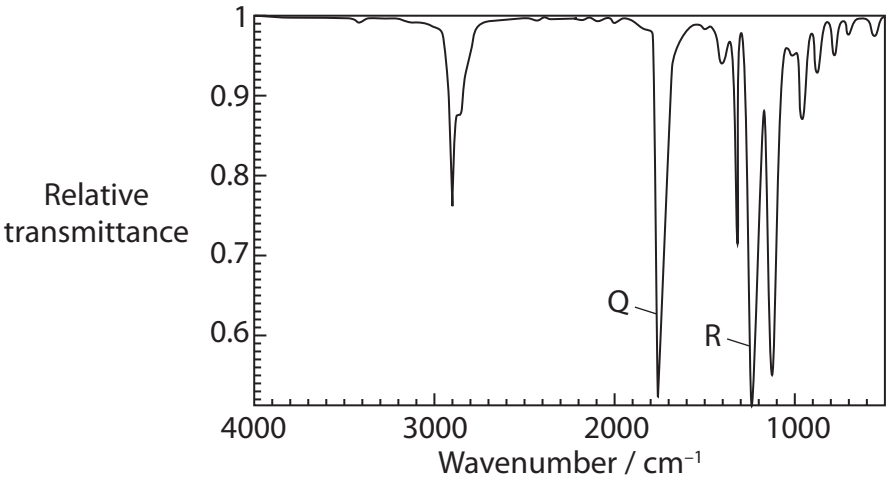
.....

.....

(Total for Question 20 = 7 marks)

21 An organic compound, **X**, has the molecular formula $C_6H_{12}O_2$ and contains **one** functional group.

(a) The infrared spectrum of **X** is shown below.



Identify the **bonds** responsible for the peaks labelled Q and R in the spectrum by referring to your Data Booklet. Hence deduce the functional group present in **X**.

(2)

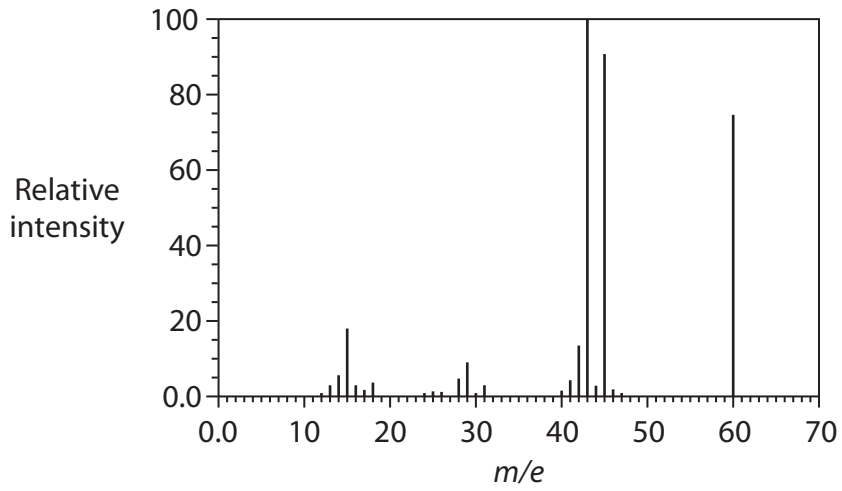
Q .....

R .....

Functional Group .....

(b) When **X** is heated under reflux with dilute sulfuric acid, two organic products, **Y** and **Z**, are formed.

The mass spectrum of **Y** is shown below.



(i) **Y** reacts with sodium carbonate solution producing carbon dioxide.
Use this information, together with the mass spectrum, to identify **Y**.

Explain your reasoning.

(3)

(ii) **Z** has molecular formula $C_4H_{10}O$. **Z** reacts with sodium, producing a gas. When **Z** is warmed with a mixture of potassium dichromate(VI) and sulfuric acid, no reaction occurs.

Deduce the structural formula of **Z**. Explain your reasoning and give the equation for the reaction with sodium producing a gas.

(3)

Equation for reaction of **Z** with sodium:

(iii) Use your answers to part (a), part (b)(i) and (b)(ii) to deduce the **displayed** formula of **X**.

(1)

(iv) Evidence for the structure of **X** comes from its proton nmr spectra.

Use the formula you have deduced in (b)(iii) to predict the number of peaks and their relative areas in the **low** resolution nmr spectrum of **X**.

State the splitting pattern of each peak in the **high** resolution nmr spectrum.

Justify your answers.

(3)

(Total for Question 21 = 12 marks)

TOTAL FOR SECTION C = 19 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 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