Mark Scheme (Results)

October 2021

Pearson Edexcel International Advanced Level In Chemistry (WCH14)
Paper 01: Rates, Equilibria and Further Organic Chemistry

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General Marking Guidance

- All candidates must receive the same treatment. Examiners must mark the first candidate in exactly the same way as they mark the last.
- Mark schemes should be applied positively. Candidates must be rewarded for what they have shown they can do rather than penalised for omissions.
- Examiners should mark according to the mark scheme not according to their perception of where the grade boundaries may lie.
- There is no ceiling on achievement. All marks on the mark scheme should be used appropriately.
- All the marks on the mark scheme are designed to be awarded. Examiners should always award full marks if deserved, i.e. if the answer matches the mark scheme. Examiners should also be prepared to award zero marks if the candidate's response is not worthy of credit according to the mark scheme.
- Where some judgement is required, mark schemes will provide the principles by which marks will be awarded and exemplification may be limited.
- When examiners are in doubt regarding the application of the mark scheme to a candidate's response, the team leader must be consulted.
- Crossed out work should be marked UNLESS the candidate has replaced it with an alternative response.

Using the Mark Scheme

Examiners should look for qualities to reward rather than faults to penalise. This does NOT mean giving credit for incorrect or inadequate answers, but it does mean allowing candidates to be rewarded for answers showing correct application of principles and knowledge. Examiners should therefore read carefully and consider every response: even if it is not what is expected it may be worthy of credit.

The mark scheme gives examiners:
- an idea of the types of response expected
- how individual marks are to be awarded
- the total mark for each question
- examples of responses that should NOT receive credit.

/ means that the responses are alternatives and either answer should receive full credit.
( ) means that a phrase/word is not essential for the award of the mark, but helps the examiner to get the sense of the expected answer.
Phrases/words in **bold** indicate that the meaning of the phrase or the actual word is **essential** to the answer.
ecf/TE/cq (error carried forward) means that a wrong answer given in an earlier part of a question is used correctly in answer to a later part of the same question.

Candidates must make their meaning clear to the examiner to gain the mark. Make sure that the answer makes sense. Do not give credit for correct words/phrases which are put together in a meaningless manner. Answers must be in the correct context.

Quality of Written Communication

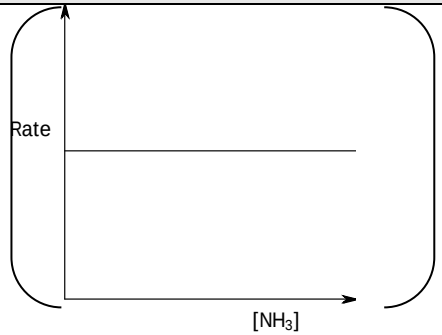
Questions which involve the writing of continuous prose will expect candidates to:
- write legibly, with accurate use of spelling, grammar and punctuation in order to make the meaning clear
- select and use a form and style of writing appropriate to purpose and to complex subject matter
- organise information clearly and coherently, using specialist vocabulary when appropriate.

Full marks will be awarded if the candidate has demonstrated the above abilities.
Questions where QWC is likely to be particularly important are indicated (QWC) in the mark scheme, but this does not preclude others.

Section A (Multiple Choice)

Question number	Answer	Mark
1(a)	**The only correct answer is A** (rate = k) ***B*** *is incorrect because this is a first order rate equation* ***C*** *is incorrect because this is a second order rate equation* ***D*** *is incorrect because this shows overall order four and refers to the reverse reaction*	**(1)**

Question number	Answer	Mark
1(b)	**The only correct answer is C** (mol dm^{-3} s^{-1}) ***A*** *is incorrect because rate constants always have units* ***B*** *is incorrect because these are the units of a first order rate constant* ***D*** *is incorrect because these are the units of a second order rate constant*	**(1)**

Question number	Answer	Mark
1(c)	**The only correct answer is A**  ***B*** *is incorrect because this graph shows a first order reaction* ***C*** *is incorrect because this graph shows a first order reaction* ***D*** *is incorrect because this graph shows no reaction occurring*	**(1)**

Question number	Answer	Mark
2	**The only correct answer is D** (increased, unchanged) ***A*** *is incorrect because the average energy of the particles in a system increases with temperature and activation energy is not affected by temperature* ***B*** *is incorrect because the average energy of the particles in a system increases with temperature* ***C*** *is incorrect because activation energy is not affected by temperature*	**(1)**

Question number	Answer	Mark
3	**The only correct answer is D** (the entropy change of the system, ΔS_{system}, is positive) ***A*** *is incorrect because this is a statement not an explanation* ***B*** *is incorrect because activation energy affects rate not direction of change* ***C*** *is incorrect because the overall enthalpy of reaction is still endothermic*	**(1)**

Question number	Answer	Mark
4	**The only correct answer is B** (positive, negative) ***A*** *is incorrect because endothermic reactions have negative* $\Delta S_{surroundings}$ ***C*** *is incorrect because when there are more gas molecules in the products than the reactants* ΔS_{system} *is positive and endothermic reactions have negative* $\Delta S_{surroundings}$ ***D*** *is incorrect because when there are more gas molecules in the products than the reactants* ΔS_{system} *is positive*	**(1)**

Question number	Answer	Mark
5	**The only correct answer is D**(changes when the temperature changes and when the substance changes state) ***A*** *is incorrect because standard molar entropy is affected by change of state and change in temperature* ***B*** *is incorrect because standard molar entropy is affected by change of state* ***C*** *is incorrect because standard molar entropy is affected change in temperature*	**(1)**

Question number	Answer	Mark
6(a)	**The only correct answer is C** $\left(K_c = \frac{[CO][H_2]}{[H_2O]} \right)$ ***A*** *is incorrect because the concentration of steam has been omitted* ***B*** *is incorrect because the concentration of steam has been omitted and carbon is not in the gas phase* ***D*** *is incorrect because carbon is not in the gas phase*	**(1)**

Question number	Answer	Mark
6(b)	**The only correct answer is B** (increases, decreases) ***A*** *is incorrect because the reverse reaction is exothermic so K_c decreases* ***C*** *is incorrect because the forward reaction is endothermic so K_c increases and the reverse reaction is exothermic so K_c decreases* ***D*** *is incorrect because the forward reaction is endothermic so K_c increases*	**(1)**

Question number	Answer	Mark
7(a)	**The only correct answer is B** (y/2) ***A*** *is incorrect because the electron affinity of an element refers to a single atom of that element* ***C*** *is incorrect because this includes the atomisation energy of two atoms of chlorine* ***D*** *is incorrect because this includes the atomisation energy of chlorine*	**(1)**

Question number	Answer	Mark
7(b)	**The only correct answer is A**(LE= $u - (v + w + x + y)$) ***B*** *is incorrect because this expression gives −LE* ***C*** *is incorrect because the electron affinity (x2) term and the enthalpy of formation have the wrong sign* ***D*** *is incorrect because this is the reverse of C which itself is incorrect.*	**(1)**

Question number	Answer	Mark
7(c)	**The only correct answer is C** (the sum of the first and second ionisation energies of magnesium) ***A*** *is incorrect because x includes the second ionisation energy* ***B*** *is incorrect because x includes the first ionisation energy* ***D*** *is incorrect because xdoes not include the atomisation energy of Mg*	**(1)**

Question number	Answer	Mark
8	**The only correct answer is C** ($CH_2ClCOOH$ and $CH_3COOH_2^+$) ***A*** *is incorrect because ethanoic acid accepts a proton in this system so is a base* ***B*** *is incorrect because ethanoic acid accepts a proton in this system so is a base* ***D*** *is incorrect because CH_2ClCOO^- is a base*	**(1)**

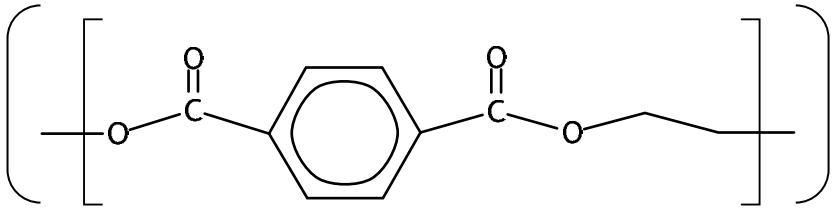
Question number	Answer	Mark
9	**The only correct answer is C** (12.3) ***A*** *is incorrect because the concentration of hydroxide ions has been halved instead of doubled* ***B*** *is incorrect because the concentration of hydroxide ions has been taken as 0.01 mol dm^{-3}* ***D*** *is incorrect because this has been calculated using 0.1 mol dm^{-3} as the concentration of calcium hydroxide*	**(1)**

Question number	Answer	Mark
10	**The only correct answer is B**(optical isomerism only) ***A*** *is incorrect because one of the carbon atoms of the double bond has two methyl groups* ***C*** *is incorrect because one of the carbon atoms of the double bond has two methyl groups and there is a chiral carbon* ***D*** *is incorrect because there is a chiral carbon*	**(1)**

Question number	Answer	Mark
11	**The only correct answer is D**(permanent dipole forces, hydrogen bonds) ***A*** *is incorrect because pure ethanal does not form hydrogen bonds* ***B*** *is incorrect because permanent dipole forces are less important than hydrogen bonding in the solubility of ethanal in water* ***C*** *is incorrect because pure ethanal does not form hydrogen bonds and permanent dipole forces are less important than hydrogen bonding in the solubility of ethanal in water*	**(1)**

Question number	Answer	Mark
12	**The only correct answer is A** (2,4-dinitrophenylhydrazine) ***B*** *is incorrect because the precipitate is copper(I) oxide for all aldehydes* ***C*** *is incorrect because no precipitate is formed* ***D*** *is incorrect because the precipitate is silver for all aldehydes*	**(1)**

Question number	Answer	Mark
13	**The only correct answer is C**(ethyl butanoate) ***A*** *is incorrect because hydrolysis would give ethanoic acid* ***B*** *is incorrect because hydrolysis would give butan-1-ol* ***D*** *is incorrect because hydrolysis would give propanoic acid*	**(1)**

Question number	Answer	Mark
14	**The only correct answer is A**  ***B*** *is incorrect because this structure has —C_2H_4— groups at both ends* ***C*** *is incorrect because this structure has —C_2H_4— groups at both ends and the ester groups are reversed* ***D*** *is incorrect because this structure has the ester groups reversed*	**(1)**

Question number	Answer	Mark
15	**The only correct answer is B** (acids only ;acids and bases) ***A*** *is incorrect because bases also speed up hydrolysis* ***C*** *is incorrect because bases do not speed up esterification and acids also speed up hydrolysis* ***D*** *is incorrect because bases do not speed up esterification*	**(1)**

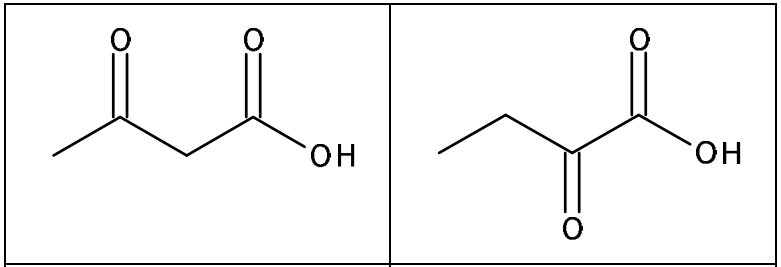
TOTAL FOR SECTION A = 20 MARKS

Section B

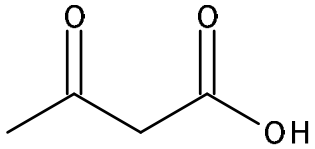
Question number	Answer	Additional guidance	Mark
16(a)(i)	• otherwise the mass of water from the combustion cannot be measured	Allow any indication that the measurement of water is affected Allow indication that the values of H and O obtained will be affected Ignore just reference to 'the products' Do not award (presence of water) affects the reaction of O_2 with X Do not award water reacts with X Do not award water dissolves CO_2	**1**

Question number	Answer	Additional guidance	Mark
16(a)(ii)	• moles of CO_2 **and** H_2O **(1)** • masses of C and H **(1)** • mass of O **(1)** • moles of C, H and O **(1)** • **ratio** (1.33:2:1), (integer ratio) **and** empirical formula **(1)**	Example of calculation mol CO_2 = 4.31 ÷ 44 = 0.097955 mol H_2O = 1.32 ÷ 18 = 0.073333 mass of C = 0.097955 x 12 = 1.1755 g mass of H = 0.073333 x 2 = 0.1467 g mass of O = 2.50 − (1.1755 + 0.1467) = 1.1778 g | | C | H | O | | mol | 0.0980 x 1 = 0.0980 | 0.0733 x 2 = 0.147 | 1.178/16 = 0.0736 | | ratio | 1.33 | 2 | 1 | | integers | 4 | 6 | 3 | $C_4H_6O_3$ No TE if oxygen mass not calculated In M1 and M2 mol CO_2 and mass of carbon scores (1) mol H_2O and mass of hydrogen scores (1)	**5**

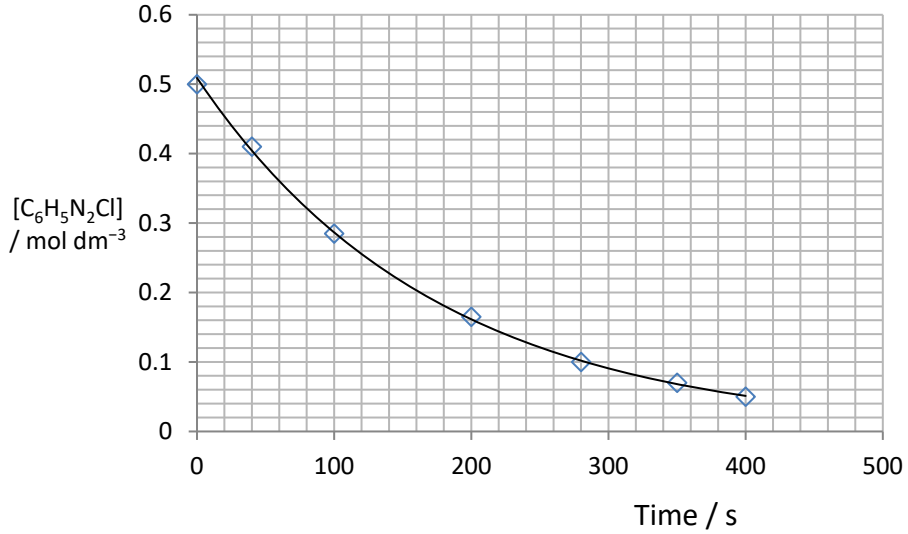
	Allow inductive calculation • balanced equation **(1)** • Formula mass ($C_4H_6O_3$) **(1)** • Product masses from equation **(1)** • Mass of CO_2 from 2.5 g of X **(1)** • Mass of H_2O from 2.5 g of X **(1)**	Example of inductive calculation $C_4H_6O_3 + 4O_2 \rightarrow 4CO_2 + 3H_2O$ Formula mass (4x12 + 6 + 3 x 16) = 102 (g) CO_2 = 4 x 44 = 176 (g) and H_2O = 3 x 18 = 54 (g) 2.5 x 176 ÷ 102 = 2.5 (g) 2.5 x 54 ÷ 102 = 1.32 (g) Correct answer with any correct method scores (5) Correct answer with no working scores (0) TE at each stage Ignore SF except 1 SF	

Question number	Answer	Additional guidance	Mark
16(b)(i)	An answer that makes reference to the following • two structures **(2)**	 A B Allow displayed or structural formulae or any combination of skeletal, displayed and structural Penalise incorrect horizontal –OH connectivity once Ignore names even if incorrect	**6**
	• ^{13}C spectrum shows four different (types of) carbon atom (so molecular formula same as empirical formula) **(1)**	Accept X has four carbon environments Allow ^{13}C spectrum shows X has four types of carbon atom Ignore just 'X has four carbon atoms'	
	• reaction with Brady's reagent indicates a carbonyl compound **(1)**	Ignore just 'X is a ketone' / C=O present Do not award 'acyl'	
	• no reaction with Tollens' reagent indicates a ketone (group) / not an aldehyde **(1)**		
	• reaction with $NaHCO_3$ (forming CO_2) indicates (carboxylic) **acid** **(1)**	Accept COOH (group)	

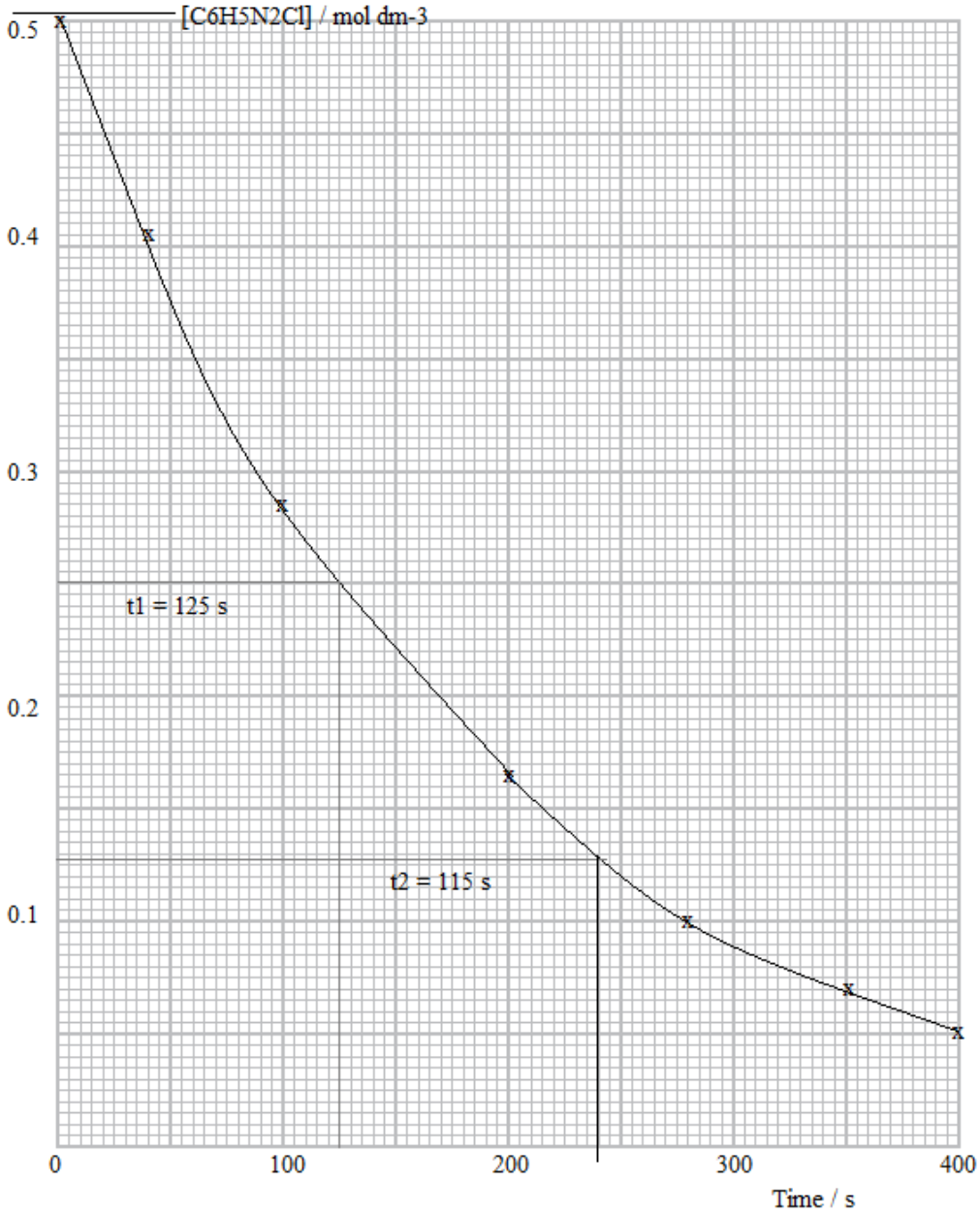
Question number	Answer	Additional guidance	Mark
16(b)(ii)	An answer that makes reference to the following • reagents for iodoform test **(1)** • result for methyl ketone **(1)** • result for ethyl ketone **(1)**	 iodine / I_2 **and** sodium hydroxide /NaOH / potassium hydroxide KOH Accept NaI / KI **and** NaOCl Allow iodine **and** OH^- / alkali Ignore 'iodoform test' (pale) yellow precipitate Allow yellow solid / ppt /ppte /antiseptic smell No change / precipitate Allow no reaction / (pale) yellow precipitate does not form M2 and M3 dependent on M1 or a near miss or just 'iodoform test' If result not linked to structure max (2) e.g NaOH and I_2 give yellow ppt (positive) and no reaction (negative) scores (2) If no reagent or an incorrect reagent given then both observation marks correct scores (1) Do not award use of physical methods	**3**

Question number	Answer	Additional guidance	Mark
16(c)	An answer that makes reference to the following • structure of **X** **(1)** • (three) peaks indicate three proton environments **(1)** • peak heights / areas indicate environments contain 3, 2 and 1 protons **(1)** • all singlets / no splitting so no adjacent proton environments **(1)** • identification of proton environments from chemical shifts **(1)**	 Answers may refer to the diagram Allow number of peaks shows number of proton environments Allow if the protons in each environment are clearly labelled e.g. each set circled Ignore just 'peak areas are 3:2:1' peak at δ about 11.1 is COO**H** peak at δ about1.9 is C**H**$_3$CO peak at δ about 2.5 is -OCC**H**$_2$COOH Allow 'alkane proton' / **H**-C-C Allow both 1.9 and 2.5 identified as **H**-C-C=O Do not award reference to the functional group rather than the proton M2, M3 and M5 may be awarded without referring to the structure M2 and M3 are standalone	**5**

(Total for Question 16 = 20 marks)

Question number	Answer	Additional guidance	Mark
17(a)(i)	An answer that makes reference to the following • sensible choice scale (to cover at least half the grid in both directions) **and** labelled axes with units on both axes **(1)** • All points given in table correctly plotted TE on **linear** axes used **(1)** • any sensible (reasonably) smooth best fit curve **(1)**	Example of graph Allow line  Allow any curve with all points within one square of the line Do not award a **clearly** point-to-point line Non-linear scale scores max (1) for M2 only Do not penalise punctuation errors, e.g. (mol dm^{-3}) for / mol dm^{-3} Allow seconds / sec / secs for 's'	**3**

Question number	Answer	Additional guidance	Mark
17(a)(ii)	• half-life / $t_{½}$ = 120 (s)	Allow 110 − 130 (s) for a correct curve Allow a value in this range given in (a)(iii) Do not award this mark unless there is some evidence of working on the graph in (a)(i) TE on the line drawn in (a)(i)	**1**

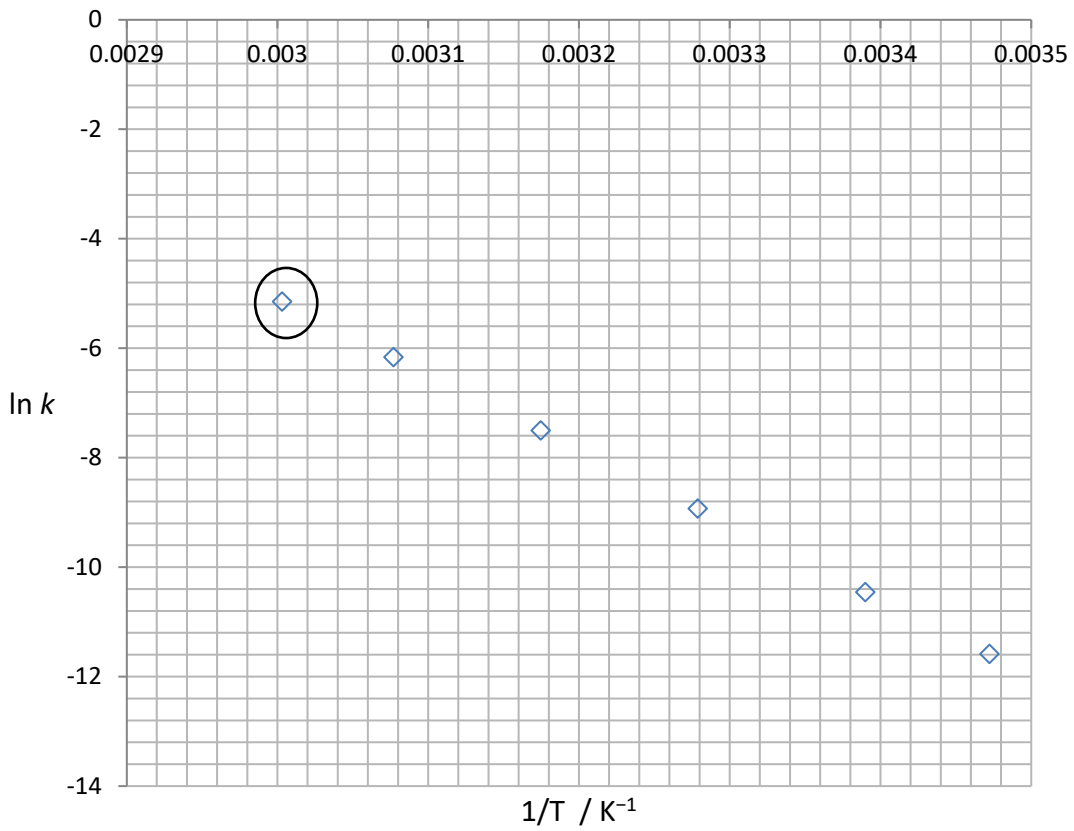


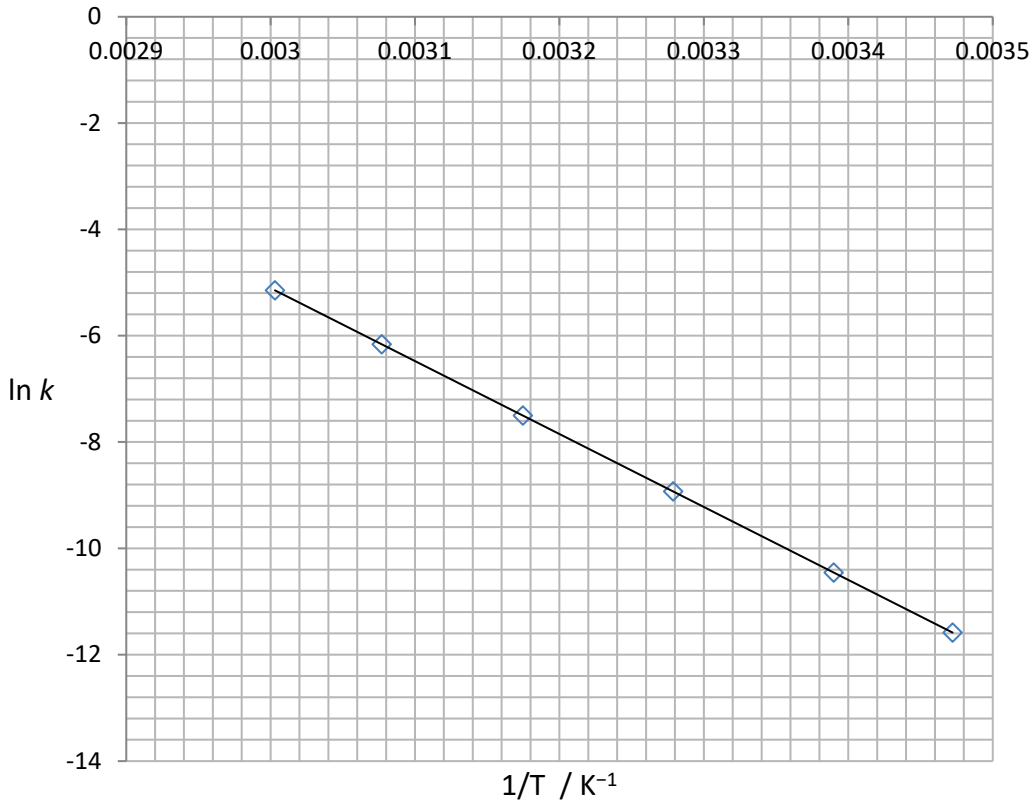
Example of graph using grid on the question paper

Accept use of one value of $t_{½}$

Question number	Answer	Additional guidance	Mark
17(a)(iii)	• rearrangement of expression **(1)** • calculation of value **and** units **(1)**	Example of calculation $k = \ln 2 \div t_{½}$ $= 0.693 \div 120 = 5.7762 \times 10^{-3} / 0.0057762\ s^{-1}$ Ignore SF except 1 SF TE on value from 17(a)(ii) No TE on incorrectly rearranged expression $t_{½} = 110$ gives $k = 6.3013 \times 10^{-3} / 0.0063013\ s^{-1}$ $t_{½} = 125$ gives $k = 5.5452 \times 10^{-3} / 0.0055452\ s^{-1}$ $t_{½} = 130$ gives $k = 5.3319 \times 10^{-3} / 0.0053319\ s^{-1}$	**2**

Question number	Answer	Additional guidance	Mark
17(b)(i)	• calculation of $\ln k$ **(1)** • calculation of $1/T$ **(1)**	Example of calculation $\ln 5.776 \times 10^{-3} = -5.154$ $1 \div 333 = 3.003 \times 10^{-3} / 0.003003\ (K^{-1})$ TE on 17(a)(iii) Plotted point can score both calculation marks Ignore incorrect or omitted units Ignore SF	**2**

Question number	Answer	Additional guidance	Mark
17(b)(ii)	• circled point correctly plotted on graph	Example of graph  TE on 17(b)(i)	**1**

Question number	Answer	Additional guidance	Mark
17(b)(iii)	An answer that makes reference to the following • best-fit line drawn **(1)**	Example of graph with BFL  Do not award BFL mark unless line goes through **all** the points given in the question. **Mark scheme continues on next page**	**3**

	• measures increase in ln*k* and increase in 1/T and used in correct expression **(1)** • final answer with sign **and** units **(1)**	Example of calculation Gradient = $\frac{-10.5-(-6.4)}{0.0034-0.0031}$ −13667 / −13700 / −14000 K ALLOW (−)13200—14200 on correct BFL or no BFL shown TE on BFL drawn No TE on incorrect gradient e.g. inverse grad can score BFL mark only Ignore SF except 1 SF	

Question number	Answer	Additional guidance	Mark
17(b)(iv)	• identification and rearrangement of relationship **(1)** • evaluation of activation energy **(1)** • sign and units **(1)**	Example of calculation Grad = $-E_a/R$ and $-E_a$ = Grad x R $-E_a$ = −13667 x R = −13667 x 8.31 =|113572| E_a = (+)113570 J mol^{-1} / (+)114000 J mol^{-1} Or E_a = (+)113.570 kJ mol^{-1} / (+)114 kJ mol^{-1} Allow (+)110000 J mol^{-1} — 118000 J mol^{-1} (from allowed range in (b)(iii) TE on (b)(iii) Sign on final value must be consistent with sign of gradient Ignore SF except 1 SF	**3**

(Total for Question 17 = 15 marks)

<table>
<tr><th>Question number</th><th>Answer</th><th>Additional guidance</th><th>Mark</th></tr>
<tr>
<td>*18</td>
<td>
This question assesses the student's ability to show a coherent and logically structured answer with linkages and fully sustained reasoning.

Marks are awarded for indicative content and for how the answer is structured and shows lines of reasoning.

The following table shows how the marks should be awarded for indicative content.
<table>
<tr><th>Number of indicative marking points seen in answer</th><th>Number of marks awarded for indicative marking points</th></tr>
<tr><td>6</td><td>4</td></tr>
<tr><td>5-4</td><td>3</td></tr>
<tr><td>3-2</td><td>2</td></tr>
<tr><td>1</td><td>1</td></tr>
<tr><td>0</td><td>0</td></tr>
</table>
The following table shows how the marks should be awarded for structure and lines of reasoning
<table>
<tr><th></th><th>Number of marks awarded for structure of answer and sustained lines of reasoning</th></tr>
<tr><td>Answer shows a coherent logical structure with linkages and fully sustained lines of reasoning demonstrated throughout</td><td>2</td></tr>
<tr><td>Answer is partially structured with some linkages and lines of reasoning</td><td>1</td></tr>
<tr><td>Answer has no linkages between points and is unstructured</td><td>0</td></tr>
</table>
</td>
<td>
Guidance on how the mark scheme should be applied.

The mark for indicative content should be added to the mark for lines of reasoning. For example, a response with five indicative marking points that is partially structured with some linkages and lines of reasoning scores 4 marks (3 marks for indicative content and 1 mark for partial structure and some linkages and lines of reasoning).

If there were no linkages between the points, then the same indicative marking points would yield an overall score of 3 marks (3 marks for indicative content and no marks for linkages).

In general it would be expected that
5 or 6 indicative points would get 2 reasoning marks
3 or 4 indicative points would get 1 reasoning mark
0, 1 or 2 indicative points would get zero reasoning marks

If there is any incorrect chemistry, deduct mark(s) from the reasoning. If no reasoning mark(s) awarded do not deduct mark(s).

Comment: Look for the indicative marking points first, then consider the mark for the structure of the answer and sustained line of reasoning
</td>
<td>6</td>
</tr>
</table>

M5

***18 cont**	**Indicative content** • **IP1**the rate equation for primary halogenoalkanes • **IP2** the rate equation for tertiary halogenoalkanes • **IP3** primary halogenoalkanes react by S_N2 • **IP4** and tertiary halogenoalkanes react by S_N1 • **IP5** for primary halogenoalkanes the slow step / RDS is when the compound reacts with hydroxide ions via a transition state • **IP6** for tertiary halogenoalkanes the slow step / RDS is when the compound forms a carbocation (in a step that only involves the halogenoalkane) Rate equations 2 IPs Identifying mechanism types 2 IPs Identifying rate determining / slow steps with transition state and carbocation 2 IPs	Rate = k[RX][OH^-] for primary Rate = k[RX] for tertiary Allow other symbols for the halogenoalkanes Rate equations are required for IP1 and IP2 Allow equation indicating slow step $RX + OH^- \longrightarrow [HO\text{---}R\text{---}X]^-$ **and** slow /rate determining step ($\longrightarrow ROH + X^-$) Allow equation indicating slow step $RX \longrightarrow R^+ + X^-$ **and** slow /rate determining step Ignore curly arrows even if incorrect Ignore detailed mechanisms even if incorrect If S_N2 and S_N1 given the wrong way round deduct one indicative point	

(Total for Question 18 = 6 marks)

Question number	Answer	Additional guidance	Mark
19(a)(i)	• $K_p = \frac{p(C_2H_5OH)}{p(C_2H_4) \times p(H_2O)}$	Allow p_x etc; upper case P / pp Do not award square brackets Do not award omission of '*p*' Ignore correct state symbols Ignore omission of times sign	1

Question number	Answer	Additional guidance	Mark
19(a)(ii)	• calculation of moles at equilibrium **(1)** • calculation of mole fractions at equilibrium **(1)** • calculation of partial pressures at equilibrium **(1)** • substitution of values into equation **(1)** • calculation of K_p **and** units of atm^{-1} **(1)**	Example of calculation $K_p = \frac{14.516}{17.742^2}$ = 0.046116 / 4.6116 x 10^{-2} atm^{-1} TE on expression in (a)(i) and at each stage Ignore SF except 1 SF Correct answer with some working scores (5)	5

	C_2H_4	H_2O	C_2H_5OH
Initial mol	1.00	1.00	0
Equil[m] mol	0.55	0.55	0.45
Mole Fraction	$\frac{0.55}{1.55} = 0.3548$	$\frac{0.55}{1.55}$	$\frac{0.45}{1.55} = 0.2903$
Partial Pressure	$\frac{50 \times 0.55}{1.55}$	$\frac{50 \times 0.55}{1.55}$	$\frac{50 \times 0.45}{1.55}$
Partial Pressure values	17.742	17.742	14.516

Question number	Answer	Additional guidance	Mark
19(b)	An answer that makes reference to the following • high pressure favours the formation of ethanol **and** because 2 mol (of gas) form 1 mol **(1)** • high temperature lowers the formation of ethanol **and** because the (forward) reaction is exothermic **(1)** • high temperature is needed because otherwise the rate of reaction is too slow **Or** unconverted reactants can be recycled to increase the overall yield **(1)**	Allow reverse arguments Accept increases yield (of ethanol) Allow reaction shifts to the right Allow fewer moles on RHS Do not award change in pressure changes K_p Accept decreases yield (of ethanol) Allow reaction shifts to the left Accepts because the back reaction is endothermic M1 & M2 both first statements without explanation scores 1 out of 2 Ignore just 'increasing / high temperature increases rate'	**3**

(Total for Question 19 = 9 marks)

Total for Section B = 50 marks

Section C

Question number	Answer	Additional guidance	Mark
20(a)(i)	• correct equation	Examples of equations: $HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$ Or $HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$ Allow $HSO_4^- + H_2O \rightleftharpoons H^+ + SO_4^{2-}$ Or $HSO_4^- \rightleftharpoons H_3O^+ + SO_4^{2-}$ Accept $\rightarrow$ for $\rightleftharpoons$ Ignore state symbols even if incorrect.	**1**

Question number	Answer	Additional guidance	Mark
20(a)(ii)	• expression for K_a **(1)** • calculation of K_a from pK_a and $[H^+]$ from pH **(1)** • rearrangement of expression for K_a and substitution of values and calculation of $[NaHSO_4]$ in mol dm^{-3} **(1)** • calculation of $M_r(NaHSO_4)$ **(1)** • calculation of $[NaHSO_4]$ in g dm^{-3} **(1)**	Example of calculation: $K_a = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]}$ or $K_a = \frac{[H^+]^2}{[HSO_4^-]}$ M1 is scored if implied in the calculation but if given must be correct Comment: Do not penalise SO_4^- for SO_4^{2-} $K_a = 10^{-1.92}$ (= 0.012023) **and** $[H^+] = 10^{-1.13}$ (= 0.074131) $[HSO_4^-] = \frac{0.074131^2}{0.012023}$ = 0.45709 (mol dm^{-3})* $M_r(NaHSO_4)$ = 120.1 Allow 120 $[NaHSO_4]$ = 120.1 x 0.45709 = 54.896(g dm^{-3})* (54.851 if 120 used) * These are obtained using unrounded intermediate values If $M_r(HSO_4^-)$ = 97.1 is used 44.383 (g dm^{-3}) scores M5 Accept $[HSO_4^-] - [H^+] = 0.45709$ $[HSO_4^-] = 0.45709 + 0.074131$ = 0.53122 (mol dm^{-3}) = 63.799 (g dm^{-3}) TE at each stage Ignore SF except 1 SF COMMENT Correct answer with some working scores (5)	**5**

Question number	Answer	Additional guidance	Mark
20(a)(iii)	An answer that makes reference to the following: • hydrogensulfate (ion) dissociation / ionisation negligible **(1)** • $[H^+]$ only due to (dissociation / ionisation of) HSO_4^- / hydrogensulfate (ion) **(1)**	Comment: Do not penalise SO_4^- for SO_4^{2-} Allow $[HSO_4^-]_{equilibrium} = [HSO_4^-]_{initial}$ $[NaHSO_4]_{equilibrium} = [NaHSO_4]_{initial}$ Allow Slight / partial / incomplete / does not dissociate for 'negligible' (dissociation) Allow $[H^+]$ due to) dissociation / ionisation of water negligible Or dissociation / ionisation of water negligible Or $[SO_4^{2-}] = [H^+]$ Allow $[H_3O^+]$ for $[H^+]$ throughout Penalise omission of [] in discussion once only Penalise use of HA or 'weak acid' or A^- once only Ignore references to temperature	**2**

Question number	Answer	Additional guidance	Mark
20(b)(i)	An answer that makes reference to the following: • a buffer resists change in pH **(1)** • on the addition of **small** amounts of acid and / or of alkali **(1)**	Accept Maintains a **fairly / nearly** constant pH Allow withstands change in pH Allow large change or small change for change Do not award maintains constant pH Ignore references to the acid-salt ratio Allow H^+ for acid base / OH^- for alkali	**2**

Question number	Answer	Additional guidance	Mark
20(b)(ii)	• substitution of values into K_a expression **(1)** • rearrangement of K_a expression **(1)** • calculation of pH to at least 1 dp **(1)**	Example of calculation: $K_a = \frac{[H^+][SO_4^{2-}]}{[HSO_4^{2-}]}$ $K_a = 10^{-1.92}$ (=0.012023) $= \frac{[H^+] \times 0.500}{0.750}$ $[H^+] = \frac{K_a \times 0.750}{0.500}$ (mol dm^{-3}) pH = −log(1.5 x 0.012023) (= −log 0 .018034) = 1.744 Ignore SF except 1 SF Correct answer with some working scores (3) TE at each stage but M3 dependent on some use of K_a **and** calculation of $[H^+]$ **and** value of pH < 7 Accept use of Henderson-Hasselbalch equation: pH = pK_a + log $\frac{[SO_4^{2-}]}{[HSO_4^-]}$ or log $\frac{[salt]}{[acid]}$ (1) = 1.92 + log $\frac{0.500}{0.750}$ (1) = 1.7439 (1) TE on arithmetical errors If salt and acid reversed in H-H equation max 1 (M3 only for 2.0961) No TE on any other error in H-H equation (scores (0))	**3**

Question number	Answer	Additional guidance	Mark
20(b)(iii)	• calculation of pH **and** change in pH for water **(1)** • calculation of new $[HSO_4^-]$ **and** calculation of new $[SO_4^{2-}]$ **(1)** • calculation of $[H^+]$ **(1)** • calculation of pH **and** change in pH for buffer **(1)** Use of H-H for M3 and M4 pH = 1.92 + log $\frac{0.495}{0.755}$ (1) = 1.92 + (− 0.18334) = 1.7367 from 1.7439 (1)	Example of calculation: pH (0.00500 mol dm^{-3} HCl) = −log(0.00500) = 2.30 Δ(pH) = 7− 2.30 = 4.70 Accept changes from 7 to 2.3 If no other mark is scored in (b)(iii) pH = 2.3 scores 1 0.750 + 0.00500 = 0.755 (mol dm^{-3}) 0.500 − 0.00500 = 0.495 (mol dm^{-3}) $[H^+] = \frac{K_a \times 0.755}{0.495} = \frac{0.012023 \times 0.755}{0.495}$ = 0.018338 (mol dm^{-3}) TE only on arithmetical errors and if at least one change in concentration calculated pH = −log(0.018338) = 1.737 Δ(pH) = 1.744− 1.737 = 0.007 OR Δ(pH) = 1.74− 1.737 = 0.003 if rounded value given in (b)(ii) Accept changes from 1.744 / 1.74 to 1.737 Allow 1.74 to 1.74 (3 SF) / no change TE on M4 for arithmetical errors on correct method Allow TE if there has been some attempt at calculating a new $[H^+]$. In both cases final pH must be lower than the start pH of the buffer **and** Δ(pH) ≤ 0.2 Ignore SF	**4**

Question number	Answer	Additional guidance	Mark
20(c)	An explanation that makes reference to the following: • the colour of the methyl orange indicator will change from red to orange to yellow **(1)** • The volume of alkali added between the start of the indicator colour change and the formation of the end-point colour is large (compared with the volume used if the indicator change colour in the vertical section of the titration curve) **(1)** • the end-point (shown by the methyl orange) will occur (well) below the equivalence point **(1)**	Ignore just 'red to yellow' Allow There is only a gradual change in colour or the (indicator) colour changes slowly or there is no sharp change in colour or colour change will not occur on the addition of just a few drops of alkali Ignore just 'colour change of methyl orange occurs at 3.2-4.4'	**3**

(Total for Question 20 = 20 marks)
Total for Section C = 20 marks
Total for paper = 90 marks

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