

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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October 2021

Question Paper Log Number P67130A

Publications Code WCH14_01_2110_MS

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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 <u>meaning</u> 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)	(1)
	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	

Question number	Answer	Mark
1(b)	The only correct answer is C (mol dm ⁻³ s ⁻¹)	(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	

Question number	Answer	Mark
1(c)	The only correct answer is A Rate [NH3]	(1)
	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	

Question number	Ans	wer	Mark
2	The	only correct answer is D (increased, unchanged)	(1)
	A	is incorrect because the average energy of the particles in a system increases with temperature and activation energy is not affected by temperature	
	В	is incorrect because the average energy of the particles in a system increases with temperature	
	\boldsymbol{C}	is incorrect because activation energy is not affected by temperature	

Question number	Answer	Mark
3	The only correct answer is D (the entropy change of the system, ΔS_{system} , is positive)	(1)
	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	

Question number	Answer	Mark
4	The only correct answer is B (positive, negative)	(1)
	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	

Question number	Answer	Mark
5	The only correct answer is D(changes when the temperature changes and when the substance changes state)	(1)
	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	

Question number	Answer	Mark
<i>(</i> ()	The only correct answer is $C\left(K_c = \frac{[CO][H_2]}{[H_2O]}\right)$	(1)
	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	

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

Question number	Answer	Mark
7(a)	The only correct answer is B $(y/2)$	(1)
	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	

Question number	Answer	Mark
7(b)	The only correct answer is $A(LE = u - (v + w + x + y))$	(1)
	$m{B}$ 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.	

Question number	Answer	Mark
7(c)	The only correct answer is C (the sum of the first and second ionisation energies of magnesium)	(1)
	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	

Question number	Answer	Mark
8	The only correct answer is C (CH ₂ ClCOOH and CH ₃ COOH 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	

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	

Question	Answer	Mark
number		
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	

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	
	<i>C</i> 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	

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	

Question number	Answer	Mark
13	The only correct answer is C(ethyl butanoate)	(1)
	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	

Question number	Answer	Mark
14		(1)
	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	

Question number	Answer	Mark
15	The only correct answer is B (acids only ;acids and bases)	(1)
	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	

TOTAL FOR SECTION A = 20 MARKS

Section B

Question	Answer	Additional guidance	Mark
number			
16(a)(i)			1
	• otherwise the mass of water from the combustion cannot	Allow any indication that the measurement of water is affected	
	be measured	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	

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

	Example of inductive calculation
Allow inductive calculation	$C_4H_6O_3 + 4O_2 \rightarrow 4CO_2 + 3H_2O$
balanced equation	(1) Formula mass $(4x12 + 6 + 3 \times 16) = 102 \text{ (g)}$
• Formula mass (C ₄ H ₆ O ₃)	(1) $CO_2 = 4 \times 44 = 176 \text{ (g)} \text{ and } H_2O = 3 \times 18 = 54 \text{ (g)}$
Product masses from equation	(1) $2.5 \times 176 \div 102 = 2.5 \text{ (g)}$
• Mass of CO ₂ from 2.5 g of X	(1)
• Mass of H ₂ O from 2.5 g of X	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		6
	• two structures (2)	Allow displayed or structural formulae or any combination of skeletal, displayed and structural Penalise incorrect horizontal –OH connectivity once	
	• ¹³ C spectrum shows four different (types of) carbon atom (so molecular formula same as empirical formula) (1)	Ignore names even if incorrect 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 NaHCO₃ (forming CO₂) indicates (carboxylic) acid (1) 	Accept COOH (group)	

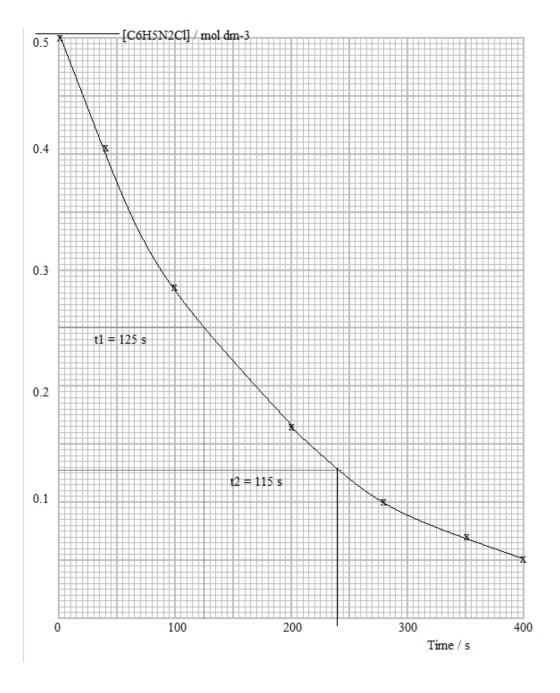
Question number	Answer		Additional guidance	Mark
16(b)(ii)	An answer that makes reference to the following			3
	reagents for iodoform test	(1)	iodine / I ₂ and sodium hydroxide /NaOH / potassium hydroxide KOH Accept NaI / KI and NaOCl	
			Allow iodine and OH ⁻ / alkali Ignore 'iodoform test'	
	result for methyl ketone	(1)	(pale) yellow precipitate Allow yellow solid / ppt /ppte /antiseptic smell	
	result for ethyl ketone	(1)	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	

Question number	Answer		Additional guidance	Mark
16(c)	An answer that makes reference to the following			5
	• structure of X	(1)	ОН	
			Answers may refer to the diagram	
	• (three) peaks indicate three proton environments	(1)	Allow number of peaks shows number of proton environments Allow if the protons in each environment are clearly labelled e.g. each set circled	
	• peak heights / areas indicate environments contain 3, 2 and 1 protons	(1)	Ignore just 'peak areas are 3:2:1'	
	all singlets / no splitting so no adjacent proton environments	(1)		
	identification of proton environments from chemical shifts	(1)	peak at δ about 11.1 is COOH	
			peak at δ about1.9 is CH ₃ CO	
			peak at δ about 2.5 is -OCCH 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 (Textal for Orestian 16 and 16	

(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)	Example of graph Allow line 0.6 0.5 0.4 [C ₆ H ₅ N ₂ Cl] / mol dm ⁻³ 0.2 0.1	3
	 any sensible (reasonably) smooth best fit curve (1) 	0 100 200 300 400 500 Time / s 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'	

Question number	Answer	Additional guidance	Mark
17(a)(ii)	• half-life / $t_{1/2} = 120$ (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 $\label{eq:condition} \mbox{Accept use of one value of $t_{1/2}$}$

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

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

Question number	Answer	Additional guidance	Mark
17(b)(ii)		Example of graph	1
	circled point correctly plotted on graph	0 0.0029 0.003 0.0031 0.0032 0.0033 0.0034 0.0035	
		-4	
		In <i>k</i>	
		-10	
		-12	
		-14 1/T / K ⁻¹	
		TE on 17(b)(i)	

Question number	Answer	Additional guidance	Mark
17(b)(iii)	An answer that makes reference to the following	Example of graph with BFL	3
	• best-fit line drawn (1)	0.0029 0.003 0.0031 0.0032 0.0033 0.0034 0.0035 -2 -4 -6 In k -10 -12 -14 1/T / K-1 Do not award BFL mark unless line goes through all the points given in the question. Mark scheme continues on next page	

• measures increase in lnk and increase in 1/T and used in correct expression (1)	$\frac{\text{Example of calculation}}{\text{Gradient}} = \frac{-10.5 - (-6.4)}{0.0034 - 0.0031}$	
• final answer with sign and units (1)	-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)			Example of calculation	3
	identification and rearrangement of relationship	(1)	Grad = $-E_a/R$ and $-E_a$ = Grad x R	
	evaluation of activation energy	(1)	$-E_a = -13667 \times R = -13667 \times 8.31$ $= 113572 $	
	• sign and units	(1)	$E_{\rm a} = (+)113570~{\rm J~mol^{-1}}/(+)114000~{\rm J~mol^{-1}}$ Or $E_{\rm a} = (+)113.570~{\rm kJ~mol^{-1}}/(+)114~{\rm kJ~mol^{-1}}$ Allow $(+)110000~{\rm J~mol^{-1}}-118000~{\rm J~mol^{-1}}$ (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	

(Total for Question 17 = 15 marks)

Question number	Answer		Additional guidance	Mark
*18	This question assesses the student's logically structured answer with lin reasoning.		Guidance on how the mark scheme should be applied.	6
	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. Number of indicative marking Number of marks awarded for points seen in answer indicative marking points 6 4 5-4 3 3-2 2 1 1 0 0		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).	
	The following table shows how the marks should be awarded for structure and lines of reasoning		In general it would be expected that 5 or 6 indicative points would get 2 reasoning marks	
		Number of marks awarded for structure of answer and sustained lines of reasoning	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 shows a coherent logical structure with linkages and fully sustained lines of reasoning demonstrated throughout	2		
	Answer is partially structured with some linkages and lines of reasoning	1		
	Answer has no linkages between points and is unstructured	0	answer and sustained line of reasoning	

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*18 cont	In	dicative content		
	•	IP1the rate equation for primary halogenoalkanes	Rate = $k[RX][OH^{-}]$ for primary	
	•	IP2 the rate equation for tertiary halogenoalkanes	Rate = k[RX] for tertiary Allow other symbols for the halogenoalkanes Rate equations are required for IP1 and IP2	
	•	IP3 primary halogenoalkanes react by S _N 2		
	•	IP4 and tertiary halogenoalkanes react by $S_{\rm N}1$		
	•	IP5 for primary halogenoalkanes the slow step / RDS is when the compound reacts with hydroxide ions via a transition state	Allow equation indicating slow step	
		compound reacts with hydroxide ions via a transition state	RX + OH [−] → [HORX] [−] and slow /rate determining step	
			(→ ROH + X ⁻)	
	•	IP6 for tertiary halogenoalkanes the slow step / RDS is when the compound forms a carbocation (in a step that only involves the	Allow equation indicating slow step	
		halogenoalkane)	$RX \longrightarrow R^+ + X^-$ and slow /rate determining step	
		Rate equations 2 IPs	Ignore curly arrows even if incorrect	
		Identifying mechanism types 2 IPs Identifying rate determining / slow steps with	Ignore detailed mechanisms even if incorrect	
		transition state and carbocation 2 IPs	If S _N 2 and S _N 1 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'	1
		Ignore correct state symbols Ignore omission of times sign	

Question number	Answer		Additional guida	Additional guidance					
19(a)(ii)			Example of calculation						
				C ₂ H ₄	H ₂ O	C ₂ H ₅ OH			
			Initial mol	1.00	1.00	0			
	• calculation of moles at equilibrium	(1)	Equil ^m mol	0.55	0.55	0.45			
	• calculation of mole fractions at equilibrium	(1)	Mole Fraction	$\frac{0.55}{1.55} = 0.3548$	$\frac{0.55}{1.55}$	$\frac{0.45}{1.55} = 0.2903$			
	1	()	Partial Pressure	50 x 0.55	50 x 0.55	50 x 0.45			
			Faitiai Flessule	1.55	1.55	1.55			
	• calculation of partial pressures at equilibrium	(1)	Partial Pressure values	17.742	17.742	14.516			
	substitution of values into equation	(1)	$K_{\rm p} = \frac{14.516}{17.742^2}$						
	• calculation of K_p and units of atm ⁻¹	(1)	(1) $ = 0.046116 / 4.6116 \times 10^{-2} \text{ atm}^{-1} $ TE on expression in (a)(i) and at each stage						
	Ignore SF except 1 SF								
			Correct answer wi	th some working	scores (5)				

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

(Total for Question 19 = 9 marks) Total for Section B = 50 marks

Section C

Question	Answer	Additional guidance	Mark
Question number 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 $HSO_4^- \rightleftharpoons H_3O^+ + SO_4^{2^-}$	Mark 1
		Accept → for ⇌ Ignore state symbols even if incorrect.	

Question number	Answer		Additional guidance	Mark
20(a)(ii)			Example of calculation:	5
	• expression for K_a (1	1)	$K_{a} = \frac{[H^{+}][SO_{4}^{2-}]}{[HSO_{4}^{-}]} \text{ or } K_{a} = \frac{[H^{+}]^{2}}{[HSO_{4}^{-}]}$	
			M1 is scored if implied in the calculation but if given must be correct	
			Comment: Do not penalise SO_4^- for $SO_4^{\ 2^-}$	
	• calculation of K_a from pK_a and $[H^+]$ from pH	1)	$K_{\rm a} = 10^{-1.92} \ (= 0.012023) \ {\rm and} \ [{\rm H}^+] = 10^{-1.13} \ (= 0.074131)$	
	• rearrangement of expression for K_a and substitution of values calculation of [NaHSO ₄] in mol dm ⁻³ (1)	and	[HSO ₄ ⁻] = $\frac{0.074131^2}{0.012023}$ = 0.45709 (mol dm ⁻³)*	
	• calculation of M_r (NaHSO ₄) (1	1)	$M_{\rm r}({ m NaHSO_4}) = 120.1$ Allow 120	
	• calculation of [NaHSO ₄] in g dm ⁻³ (1	1)	$[NaHSO_4] = 120.1 \times 0.45709$	
			$= 54.896(g dm^{-3})* (54.851 if 120 used)$	
			* These are obtained using unrounded intermediate values	
			If $M_r(HSO_4^-) = 97.1$ is used 44.383 (g dm ⁻³) scores M5	
			Accept $[HSO_4^-] - [H^+] = 0.45709$	
			$[HSO_4^-] = 0.45709 + 0.074131$	
			= $0.53122 \text{ (mol dm}^{-3}\text{)}$ = $63.799 \text{ (g dm}^{-3}\text{)}$	
			TE at each stage	
			Ignore SF except 1 SF	
			COMMENT Correct answer with some working scores (5)	

Question number	Answer		Additional guidance	Mark
20(a)(iii)	An answer that makes reference to the following: • hydrogensulfate (ion) dissociation / ionisation negligible	(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)	2
	• [H ⁺] only due to (dissociation / ionisation of) HSO ₄ ⁻ / hydrogensulfate (ion)	(1)	Allow $[H^+]$ due to) dissociation / ionisation of water negligible Or dissociation / ionisation of water negligible Or $[SO_4^{2-}] = [H^+]$	
			Allow [H ₃ O ⁺] 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	

Question number	Answer		Additional guidance	Mark
20(b)(i)	An answer that makes reference to the following:			2
	a buffer resists change in pH	(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	
	• on the addition of small amounts of acid and / or of alkali	(1)	Allow H ⁺ for acid base / OH ⁻ for alkali	

Question number	Answer		Additional guidance	Mark
20(b)(ii)			Example of calculation:	3
			$K_{\rm a} = {[{ m H}^+][{ m SO}_4^{2^-}] \over [{ m HSO}_4^{2^-}]}$	
	• substitution of values into K_a expression	(1)	$K_{\rm a} = 10^{-1.92} \ (=0.012023) = \frac{\rm [H^+] \ x \ 0.500}{0.750}$	
	• rearrangement of K_a expression	(1)	$[H^+] = \frac{K_a \times 0.750}{0.500} \text{ (mol dm}^{-3})$	
	• calculation of pH to at least 1 dp	(1)	pH = $-\log(1.5 \times 0.012023)$ (= $-\log 0.018034$) = 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^{-}]} \text{ or } \log \frac{[salt]}{[acid]} $ (1)	
			$= 1.92 + \log \frac{0.500}{0.750} \tag{1}$	
			= 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))	

Answer		Additional guidance	Mark
calculation of pH and change in pH for water	(1)	Example of calculation: $pH (0.00500 \text{ mol dm}^{-3} \text{ HCl}) = -\log(0.00500) = 2.30$ $\Delta(pH) = 7 - 2.30 = 4.70$ Accept changes from 7 to 2.3 If no other mark is scored in (b)(iii) pH = 2.3 scores 1	4
• calculation of new [HSO ₄ ⁻] and calculation of new [SO ₄ ²⁻]	(1)	$0.750 + 0.00500 = 0.755 \text{ (mol dm}^{-3}\text{)}$ $0.500 - 0.00500 = 0.495 \text{ (mol dm}^{-3}\text{)}$	
• calculation of [H ⁺]	(1)	$[H^{+}] = \frac{K_a \times 0.755}{0.495} = \frac{0.012023 \times 0.755}{0.495}$ $= 0.018338 \text{ (mol dm}^{-3}\text{)}$ TE only on arithmetical errors and if at least one change in concentration calculated	
• calculation of pH and change in pH for buffer	(1)	$pH = -\log(0.018338) = 1.737$ $\Delta(pH) = 1.744 - 1.737 = 0.007$ OR $\Delta(pH) = 1.74 - 1.737 = 0.003$ if rounded value given in	
Use of H-H for M3 and M4 $pH = 1.92 + \log \frac{0.495}{0.755} \tag{1}$		(b)(ii) Accept changes from 1.744 / 1.74 to 1.737 Allow 1.74 to 1.74 (3 SF) / no change	
= 1.92 + (-0.18334) = 1.7367 from 1.7439 (1)		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 $\Delta(pH) \leq 0.2$	
	 calculation of pH and change in pH for water calculation of new [HSO₄⁻] and calculation of new [SO₄²⁻] calculation of [H⁺] calculation of pH and change in pH for buffer Use of H-H for M3 and M4 pH = 1.92 + log 0.495 / 0.755 (1) 	 calculation of pH and change in pH for water (1) calculation of new [HSO₄⁻] and calculation of new [SO₄²-] (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 0.495 / 0.755 (1) 	• calculation of pH and change in pH for water • calculation of new [HSO ₄] and calculation of new [SO ₄] (1) $A(pH) = 7 - 2.30 = 4.70$ Accept changes from 7 to 2.3 If no other mark is scored in (b)(iii) pH = 2.3 scores 1 • calculation of new [SO ₄] (1) $0.500 - 0.00500 = 0.495$ (mol dm ⁻³) • calculation of [H'] (1) $B(a) = \frac{K_a \times 0.755}{0.495} = \frac{0.012023 \times 0.755}{0.495} = 0.018338$ (mol dm ⁻³) TE only on arithmetical errors and if at least one change in concentration calculated • calculation of pH and change in pH for buffer (1) $A(b) = 1.744 - 1.737 = 0.007$ (1) $A(b) = 1.744 - 1.737 = 0.003$ if rounded value given in (b)(iii) $A(b) = 1.92 + (-0.18334) = 1.7367$ from 1.7439 (1) $A(b) = 1.744 - 1.74$ (3 SF) / no change

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)	Ignore just 'red to yellow'	3
	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)	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	
	• the end-point (shown by the methyl orange) will occur (well) below the equivalence point (1)	Ignore just 'colour change of methyl orange occurs at 3.2-4.4'	

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

