Mark Scheme (Results)

October 2023

Pearson Edexcel International Advanced Level
In Chemistry (WCH14)
Paper 01 Unit 4: Rates, Equillibria and Further Organic Chemistry

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General Marking Guidance

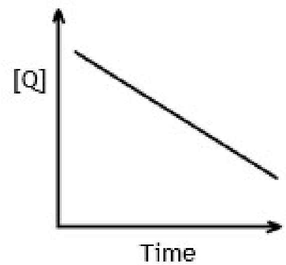
- All candidates must receive the same treatment. Examiners must mark the first candidate in exactly the same way as they mark the last.
- Mark schemes should be applied positively. Candidates must be rewarded for what they have shown they can do rather than penalised for omissions.
- Examiners should 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.

Section A (multiple choice)

Question Number	Answer	Mark
1(a)	**The only correct answer is B** (measurement of change in volume) ***A*** *is incorrect because none of the gases is coloured* ***C*** *is incorrect because there is no loss or gain of mass* ***D*** *is incorrect because there are no bases in the mixture*	(1)

Question Number	Answer	Mark
1(b)	**The only correct answer is D** (quenching followed by titrating with acid) ***A*** *is incorrect because nothing in the mixture is coloured* ***B*** *is incorrect because there is no change in volume* ***C*** *is incorrect because there is no loss or gain of mass*	(1)

Question Number	Answer	Mark
2	**The only correct answer is D** (16) ***A*** *is incorrect because doubling* $[BrO_3^-]$ *and* $[Br^-]$ *will both double the rate, doubling* $[H^+]$ *increases the rate by* 2^2 ***B*** *is incorrect because doubling* $[BrO_3^-]$ *and* $[Br^-]$ *will both double the rate, doubling* $[H^+]$ *increases the rate by* 2^2 ***C*** *is incorrect because doubling* $[BrO_3^-]$ *and* $[Br^-]$ *will both double the rate, doubling* $[H^+]$ *increases the rate by* 2^2	(1)

Question Number	Answer	Mark
3(a)	**The only correct answer is A** () ***B*** *is incorrect because the graph shows a reaction where the rate decreases as concentration of Q increases* ***C*** *is incorrect because the graph shown is correct when rate is plotted against concentration of Q* *D is incorrect because the graph shows a reaction where the rate increases as concentration of Q increases*	(1)

Question Number	Answer	Mark
3(b)	**The only correct answer is B** (20s) ***A*** *is incorrect because the half-life for a first order reaction is constant* ***C*** *is incorrect because the half-life for a first order reaction is constant* *D is incorrect because the half-life for a first order reaction is constant*	(1)

Question Number	Answer	Mark
4	**The only correct answer is C** ((–gradient) × *R*) ***A*** *is incorrect because the gradient* = –E_a / R ***B*** *is incorrect because the gradient* = –E_a / R ***D*** *is incorrect because the gradient* = –E_a / R	(1)

Question Number	Answer	Mark
5 (a)	**The only correct answer is B** (–364) ***A*** *is incorrect because the value must be divided by 2 as there are 2* Cl^- ***C*** *is incorrect because the signs are the wrong way round giving an endothermic value* ***D*** *is incorrect because the signs are the wrong way round giving an endothermic value and the value must be divided by 2 as there are 2* Cl^-	(1)

Question Number	Answer	Mark
5(b)	**The only correct answer is C** (magnesium ions have a higher charge density) ***A*** *is incorrect because the radius of magnesium ions are smaller* ***B*** *is incorrect because this is true but it does not explain the hydration enthalpy* ***D*** *is incorrect because this is true but it does not explain the hydration enthalpy*	(1)

Question Number	Answer	Mark
6	**The only correct answer is D** ($K_p = (pNO_2)^4 \times (pO_2)$) ***A*** *is incorrect because solids are not included in the K_p expression and the value should be raised to the power not multiplied by the number from the equation* ***B*** *is incorrect because solids are not included in the K_p expression* ***C*** *is incorrect because the value should be raised to the power not multiplied by the number from the equation*	(1)

<table>
<tr><th>Question Number</th><th>Answer</th><th>Mark</th></tr>
<tr><td>7</td><td>The only correct answer is D (<table><tr><th>Acid 1</th><th>Conjugate base of Acid 1</th><th>Acid 2</th><th>Conjugate base of Acid 2</th></tr><tr><td>HCl</td><td>Cl^-</td><td>$HCOOH_2^+$</td><td>HCOOH</td></tr></table>)

A is incorrect because the conjugate bases are the wrong way round

B is incorrect because $HCOOH_2^+$ is an acid not a base and HCOOH is a base and not an acid in this reaction

C is incorrect because $HCOOH_2^+$ is an acid not a base and so should be exchanged with HCOOH</td><td>(1)</td></tr>
</table>

Question Number	Answer	Mark
8	**The only correct answer is C** (the dissociation of water is endothermic, so the concentration of hydrogen ions is higher at 100ºC than at 25ºC) ***A*** *is incorrect because at lower pH the concentration of hydrogen ions is higher* ***B*** *is incorrect because at lower pH the concentration of hydrogen ions is higher and the reaction is endothermic* ***D*** *is incorrect because the forward reaction is endothermic*	(1)

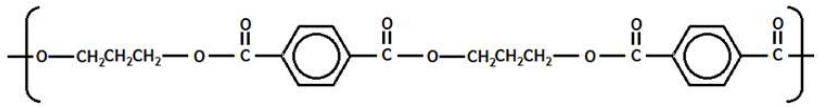
Question Number	Answer	Mark
9	**The only correct answer is D** (4, 3, 1, 2) ***A*** *is not correct because Beaker 4 has the highest pH* ***B*** *is not correct because Beaker 4 has the highest pH* ***C*** *is not correct because Beaker 4 has the highest pH*	(1)

Question Number	**Answer**	**Mark**
10(a)	**The only correct answer is D** (lithium tetrahydridoaluminate(III)) ***A*** *is incorrect because these are the reagents for the reverse reaction* ***B*** *is incorrect because this will not reduce a carboxylic acid* ***C*** *is incorrect because this will not reduce the carboxylic acid to the primary alcohol*	(1)

Question Number	Answer	Mark
10(b)	**The only correct answer is D** (8.80 g) ***A*** *is incorrect because this answer comes from swapping the* M_r *values* ***B*** *is incorrect because this assumes that 90% of methylpropanoic acid is required to give this yield* ***C*** *is incorrect because this assumes the yield is 100%*	(1)

Question Number	Answer	Mark
10(c)	**The only correct answer is B** (anhydrous) ***A*** *is incorrect because the reaction requires no catalyst* ***C*** *is incorrect because the reaction works at room temperature.* ***D*** *is incorrect because ether solvent is required for use with* $LiAlH_4$	(1)

Question Number	Answer	Mark
10(d)	**The only correct answer is A** (it can be carried out at room temperature) ***B*** *is incorrect because a catalyst is not required* ***C*** *is incorrect because the atom economy is lower as HCl is formed rather than* H_2O ***D*** *is incorrect because the formation of toxic HCl is a disadvantage*	(1)

Question Number	Answer	Mark
11	**The only correct answer is D** () ***A*** *is incorrect because it is a single repeat unit* ***B*** *is incorrect because it is missing a dicarboxylic acid group* ***C*** *is incorrect because the groups are reversed*	(1)

Question Number	Answer	Mark
12	**The only correct answer is D** (44.0632 43.9898) ***A*** *is not correct because 27.9949 is the mass of CO and 29.0395 is the mass of* C_2H_5 ***B*** *is not correct because 27.9949 is the mass of CO and 29.0395 is the mass of* C_2H_5 ***D*** *is not correct because 43.9898 is the mass of propane and 44.0632 is the mass of carbon dioxide*	(1)

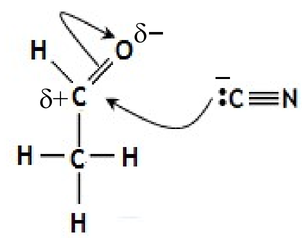
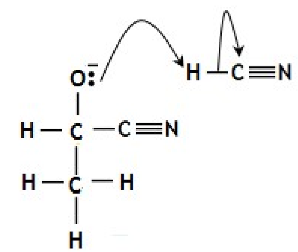
Question Number	Answer	Mark
13(a)	**The only correct answer is B** (0.38) ***A** is incorrect because this is the ratio of the spot to the top of the chromatogram slide* ***C** is incorrect because this is the ratio of the distanced travelled by X compared to Y* ***D** is incorrect because this is (1 – the correct answer)*	(1)

Question Number	Answer	Mark
13(b)	**The only correct answer is C** (is weaker than the attraction between X and the stationary phase | is stronger than the attraction between X and the mobile phase) ***A** is incorrect because a stronger attraction to the stationary phase means it will move more slowly* ***B** is incorrect because a stronger attraction to the stationary phase means it will move more slowly* ***D** is incorrect because a weaker attraction to the mobile phase means it will move more slowly*	(1)

(Total for Section A = 20 marks)

Section B

Question Number	Answer	Additional Guidance	Mark
14(a)(i)	An answer that makes reference to the following point: • 2-hydroxypropanenitrile	Allow 2-hydroxypropannitrile Allow 2-hydroxypropanitrile Do not award 2-hydroxo versions of allowable answers Do not award 2-hydroxyl versions of allowable answers Do not award Hydroxy-2-propanenitrile Do not award nitride versions of allowable answers Do not award additional numbers e.g. 2-hydroxypropane-2-nitrile Ignore additional spaces, omission of hyphen, use of comma instead of hyphen e.g. 2 hydroxy propanenitrile	**(1)**

Question Number	Answer	Additional Guidance	Mark
14(a)(ii)	An answer that makes reference to the following points: • structure of the intermediate carbanion including negative charge anywhere on the ion or outside a bracket around the ion **(1)** Step 1 mechanism • lone pair of electrons on C of C≡N⁻ • arrow from lone pair on C of C≡N⁻ to C(δ+) in ethanal • arrow from C=O bond to, or just beyond, O • dipole on C=O Step 2 mechanism • lone pair on O • arrow from lone pair on O of intermediate to H of H–C≡N / HCN • arrow from H–C bond to C, or just beyond C, of H–C≡N / HCN **(3)**	Intermediate is stand alone and scores (1) Allow $-CH_3$ Allow –CN Ignore absence of lone pair Triple bond does not need to be shown Do not award C≡N–C   Ignore dipole on HCN even if incorrect Do not award Step 2 point 2 for +ve charge on H For the mechanism all 7 points scores 3 marks 4, 5 or 6 points scores 2 marks 2 or 3 points scores 1 mark Only 1 step mark scores 0 step marks	**(4)**

Question Number	Answer	Additional Guidance	Mark
14(a)(iii)	An answer that makes reference to the following points: This mark is for the description of nucleophilic attack • in the first step of the reaction the (negative) cyanide ion / $^{-}C{\equiv}N$ attacks a δ+ centre / seeks out regions of low electron density **(1)** This mark is for the description of addition • two substances join together to make one **(1)**	Mark independently Allow donates a pair of electrons Allow seeks out positive charge / centre Allow carbon (of the C=O) is positive Ignore acts as a nucleophile Ignore general descriptions of nucleophile which are not specific to CN^{-} Do not award just CN (with no charge) Allow CN^{-} is added onto the ethanal with nothing substituted / eliminated / with no other product formed. Allow there is only one product / no other molecule is formed Allow there are fewer products than reactants Allow hydrogen cyanide and ethanal join together Allow unsaturated compound becomes more saturated Allow a π (pi) bond is broken and (two) single bonds are made Allow HCN is joined/bonded onto ethanal Ignore just HCN / CN^{-} is added onto the ethanal Ignore added NOTE; Allow a description of the cyanide ion and hydrogen ion joining the ethanal in the steps of the mechanism, but ignore comments about adding instead of joining	**(2)**

Question Number	Answer	Additional Guidance	Mark
14(b)	An answer that makes reference to the following points: • because the product is a racemic mixture / equal concentrations of both enantiomers are formed **(1)** • as the cyanide / nitrile ion attacks / approach from above and below the **plane** of the C=O bond equally **(1)**	Marks are standalone Allow two mirror images are formed in equal amounts / concentrations Accept can attack / approach equally from either side / both sides / opposite sides / top and bottom of the **plane** of the C=O bond Ignore 'both directions' or 'two directions' without 'opposite' Do not award from any sides COMMENT Allow plane of the molecule in this case because a carbon chain and functional group are all in the same plane COMMENT Do not penalise errors in the nucleophilic attack, e.g., CN^- attacking C^+ as this has been penalised in (a)(iii). There is no mark for there being no net rotation of the plane polarised light in this question	**(2)**

(Total for Question 14 = 9 marks)

Question Number	Answer	Additional Guidance	Mark
15(a)(i)	• calculation of moles of oxygen at equilibrium **(1)** • calculation of moles of NO at equilibrium **(1)** • calculation of moles of NO_2 at equilibrium **(1)**	<u>Example of calculation</u> = 7.000 ÷ 32 = 0.21875 / 0.219 (mol) Allow 7/32 = moles of oxygen x 2 = 0.4375 / 0.438 (mol) Allow 7/16 = total moles – moles of O_2 – moles of NO = 0.69625 – 0.21875 – 0.4375 = 0.0400 (mol) COMMENT: (a)(ii) may help with confusion about which number of moles goes with which molecule. If you cannot work out which goes with which award 1 mark for all 3, but as soon as 1 can be identified ignore other values which cannot Allow TE throughout Ignore SF	**(3)**

Question Number	Answer	Additional Guidance	Mark
15(a)(ii)	• divides the moles of the three substances by 15 to find the concentrations **(1)** • gives the formula for K_c **(1)** • substitution of concentrations in the expression given in M2 **(1)** • calculation of final value including units **(1)**	<u>Example of calculation</u> $[NO_2]$ = 0.0400 ÷ 15 = 0.0026667 / 2.6667×10^{-3} (mol dm^{-3}) [NO] = 0.4375 ÷ 15 = 0.029167 / 2.9167×10^{-2} (mol dm^{-3}) $[O_2]$ = 0.21875 ÷ 15 = 0.014583 / 1.4583×10^{-2} (mol dm^{-3}) Allow TE on incorrect values in (a)(i) = $[NO_2]^2 \div [NO]^2[O_2]$ Allow an expression showing moles ÷ V for each substance Do not award round brackets Do not award K_p expressions K_c = $0.0026667^2 \div (0.029167^2 \times 0.014583)$ K_c = $7.1113 \times 10^{-6} \div (8.5071 \times 10^{-4} \times 1.4583 \times 10^{-2})$ Award M2 for the correct expression if no formula has been given Allow TE on incorrect formula in M2 Allow TE on incorrect values calculated in M1 Allow TE on moles in (a)(i) used without converting to concentration = 0.57320 / 5.7320×10^{-1} dm^3 mol^{-1} / mol^{-1} dm^3 Allow TE on incorrect formula in M2 0.038213 dm^3 mol^{-1} (not ÷ 15) scores (3) 68.57 add Correct answer with some working scores (4) Ignore SF except 1 SF in final answer	**(4)**

Question Number	Answer	Additional Guidance	Mark
15(b)	• rearrangement of $pV = nRT$ **(1)** • conversion of volume in dm^3 to m^3 **and** moles of gas = 0.69625 **(1)** • calculation of final value **(1)**	<u>Example of calculation</u> $T = pV \div nR$ Allow with values substituted in 15 dm^3 = 0.015 / 1.5×10^{-2} m^3 / 15×10^{-3} m^3 = (200,000 × 0.015) ÷ (0.69625 × 8.31) = 518.51 / 519 (K) Allow use of 8.314 rather than 8.31 Allow conversion of pressure to kPa and use of dm^3 giving = (200 × 15) ÷ (0.69625 × 8.31) = 518.51 / 519 (K) Allow 245.5(1) ºC / 246 ºC 518510 / 519000 (no conversion) scores (2) If given in ºC units must be given Allow TE on incorrect moles of gas and volume Do not award 518(K) or 519ºC Correct answer with some working scores (3) Ignore SF except 1 SF	**(3)**

Question Number	Answer	Additional Guidance	Mark
15(c)(i)	An answer that makes reference to the following point: • the reactants / NO and O_2 are colourless but the product / NO_2 is reddish brown / coloured	Allow just NO / O_2 is colourless and NO_2 is brown Allow just nitrogen dioxide / product is reddish brown / coloured / dark colour Allow any combination of yellow, red, orange and brown for the colour of NO_2 Allow measure the time for the brown gas to form Ignore just 'there will be a colour change' / mixture will darken Ignore NO_2 is a different colour form NO and O_2 Do not award NO is coloured so there is a colour change Do not award NO is yellow / red / orange / brown	**(1)**

Question Number	Answer	Additional Guidance	Mark
15(c)(ii)	• rearrangement of rate equation expression and inserting values **(1)** • calculation of *k* **and** units **(1)**	<u>Example of calculation</u> $= 6.87 \times 10^{-4} \div ((6.50 \times 10^{-2})^2 \times 1.25 \times 10^{-2})$ $= 13.008$ / 13.0 $dm^6\ mol^{-2}\ s^{-1}$ Correct answer with no working scores (2) Correct numerical answer with incorrect units scores (1) Allow units in any order Allow dm^6/mol^2s 0.84554 / 0.846 $dm^3\ mol^{-1}\ s^{-1}$ (not squaring 6.50×10^{-2}) scores (1) for final value and units for M2 Ignore SF except 1SF	**(2)**

Question Number	Answer	Additional Guidance	Mark
15(c)(iii)	An answer that makes reference to the following point • a three particle collision is unlikely	Accept it is unlikely that more than two molecules will collide / Allow hard / difficult / impossible instead of unlikely Allow there are three molecules involved in the reaction Ignore it is a third order reaction Do not award just three moles colliding / just three reactants colliding	**(1)**

Question Number	Answer	Additional Guidance	Mark
15(c)(iv)	An answer that makes reference to the following points: • adding the two steps together gives the overall equation **(1)** • the steps do not match the rate equation because the slow step should be the second step **(1)**	Allow the two steps match the overall equation as the reactants and products are the same Allow N_2O_2 is formed then reacts / cancels out / is an intermediate Ignore just the overall equation is $2NO + O_2 \rightarrow 2NO_2$ Allow it does not match because there is no oxygen in the slow step / rate determining step / rds Allow because in this mechanism oxygen is zero order / is not first order Allow because with these steps the rate equation would be $rate = k[NO]^2$	**(2)**

(Total for Question 15 = 16 marks)

Question Number	Answer	Additional Guidance	Mark
16(a)(i)	• calculation of the standard entropy of the reactants (1) • calculation of the standard entropy of the products (1) • calculation of the entropy change (products – reactants) (1)	Example of calculation COMMENT If enthalpy and entropy calculations are swapped allow max (2) scoring enthalpy calculation in enthalpy answer space and vice versa Penalise units once only $= 87.4 + (3 \times 197.6) = (680.2)\ (J\ K^{-1}\ mol^{-1})$ $= (2 \times 27.3) + (3 \times 213.6) = (695.4)\ (J\ K^{-1}\ mol^{-1})$ $= (695.4 - 680.2) = (+)15.2\ (J\ K^{-1}\ mol^{-1})$ Ignore SF in final answer except 1 SF Correct answer with no working scores (3) Allow TE	**(3)**

Question Number	Answer		Additional Guidance	Mark
16(a)(ii)			<u>Example of calculation</u> COMMENT If enthalpy and entropy calculations are swapped allow max (2) scoring enthalpy calculation in enthalpy answer space and vice versa	**(3)**
	• calculation of the standard enthalpy of formation of the reactants	**(1)**	$= –824 + (3 \times –111) = (–1157\ (\text{kJ mol}^{–1}))$	
	• calculation of the standard enthalpy of formation of the products	**(1)**	$= 3 \times –394 = (–1182)\ (\text{kJ mol}^{–1})$	
	• calculation of the enthalpy change (products – reactants)	**(1)**	$= (–1182) – (–1157) = –25\ (\text{kJ mol}^{–1})$ –2339 (kJ mol$^{–1}$) scores M1 and M2 +25 (kJ mol$^{–1}$) scores M1 and M2 Ignore calculates the enthalpy change and then goes on to calculate $\Delta S_{surroundings}$ BUT allow the equations in (a)(iii) Ignore SF except 1 SF Correct answer with no working scores (3)	

Question Number	Answer	Additional Guidance	Mark
16(a)(iii)	An answer that makes reference to the following points: Either (using entropy arguments) • $\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$ **and** $\Delta S_{surroundings} = -\Delta H \div T$ **(1)** • (ΔH is negative so) $\Delta S_{surroundings}$ **or** $-\Delta H \div T$ is (always) positive **and** ΔS_{system} is positive **(1)** • ΔS_{total} is positive (at all temperatures) **and** so the reaction is feasible (at all temperatures) **(1)**	Candidates may use their values instead of symbols Penalise omission of Δ once only $\Delta S_{total} = \Delta S_{system} - \frac{\Delta H}{T}$ scores M1 Allow either equation described in words COMMENT These may be scored in (a)(ii) COMMENT If they have a +ve ΔH in (a)(ii), they must have -ve $\Delta S_{surroundings}$ (and ΔS_{system} is +ve) to score M2, but then cannot score M3 Allow spontaneous	**(3)**

	OR (using Gibbs free energy arguments) • $\Delta G = \Delta H - T\Delta S$ **(1)** • (ΔS is positive so) $T\Delta S$ **or** ΔS is (always) positive **and** ΔH is negative **(1)** • ΔG is (always) negative **and** so the reaction is (always) feasible **(1)**	Allow spontaneous Allow TE on values in (a)(i) and (a)(ii) Allow > 0 for positive and < 0 for negative throughout	

Question Number	Answer		Additional Guidance	Mark
16(b)(i)	An answer that makes reference to the following points: • calculation of ΔS_{system}	(1)	$= ((2 \times 28.3) + (3 \times 213.6)) - (50.9 + (3 \times 197.6))$ $= 697.4 - 643.7$ $= 53.7$ (J K^{-1} mol)	(4)
	• calculation of ΔH	(1)	$= (3 \times -394) - (-1676 + (3 \times -111)$ $= -1182 + 2009$ $= 827$ (kJ mol^{-1})	
	• conversion of ΔS_{system} or ΔH so units match	(1)	$\Delta S = 0.0537$ (kJ K^{-1} mol) or $\Delta H = 827000$ (J mol^{-1})	
	• rearrange $\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$ when $\Delta S_{total} = 0$ and calculation of T	(1)	$T = \Delta H \div \Delta S_{system}$ $= \frac{827000}{53.7} = 15400$ / 1.5400×10^4 (K) Correct answer scores (4) 15.4 (no M3) scores (3) Ignore incorrect units throughout except in final answer Allow TE thoughout except for M4 for a negative temperature	

Question Number	Answer	Additional Guidance	Mark
16(b)(ii)	An answer that makes reference to the following points: • because this temperature cannot be achieved in a Blast Furnace	COMMENT Unfortunately we cannot see (b)(i). Award only answers which suggest that the temperature is too high for the blast furnace to reach Allow the temperature in the Blast Furnace is too low Allow the temperature required is too high Ignore temperature required is very high Ignore the energy needed is too high Ignore activation energy is too high Ignore cost	**(1)**

(Total for Question 16 = 14 marks)

<table>
<tr><th>Question number</th><th>Answer</th><th>Additional guidance</th><th>Mark</th></tr>
<tr>
<td>*17a</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><td>Number of indicative marking points seen in answer</td><td>Number of marks awarded for indicative marking points</td></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><td></td><td>Number of marks awarded for structure of answer and sustained lines of reasoning</td></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 0 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>

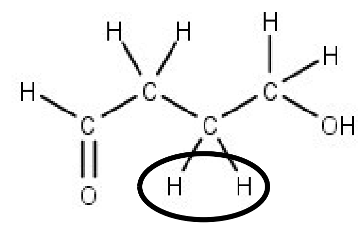
	Indicative content • **IP1** sodium carbonate solution / sodium hydrogencarbonate solution gives fizzing (due to the formation of carbon dioxide) • **IP2** identifies butanoic acid is the only (carboxylic) acid / compound with an acidic proton / only compound with –COOH • **IP3** Tollens' reagent / ammoniacal silver nitrate gives a silver mirror • **IP4** identifies 4-hydroxybutanal, which is the only aldehyde / only compound containing –CHO • **IP5** iodine and sodium hydroxide (solution) gives a yellow precipitate / antiseptic smell • **IP6** identifies 3-hydroxybutanone, which is the only compound with a CH_3CO– group / only compound with a methyl ketone group	1 IP for each test **and** positive result, 1 IP for the compound and the functional group. Compound IP dependent on correct test or very near miss Allow reactive metal such as magnesium giving fizzing but do not award sodium / potassium Allow produces gas Ignore produces CO_2 / bubbling through limewater Allow butanoic acid is a carboxylic acid Accept Fehling's / Benedict's test gives a red precipitate Allow has a carbonyl group which can be oxidised Allow 4-hydroxybutanal is an aldehyde Allow 'use of the triiodomethane / iodoform test / iodoform reaction' / alkaline iodine Accept is the only compound with a secondary OH group attached to a methyl group If IP3 (and IP4) OR IP5 (and IP6) have been scored, Allow 2,4 DNP and red/orange ppt as an alternative to the other pair of IPs (IP3 & IP4 or IP5 & IP6) BUT deduct 1 reasoning mark Ignore Brady's reagent / 2,4 DNP other than as above Ignore indicator / PCl5 / hydrolysis of ethyl ethanoate / acidified potassium dichromate(VI) / ethyl ethanoate has a fruity / gluey smell	

Question Number	Answer	Additional Guidance	Mark
17(b)(i)	An answer that makes reference to the following point: • they / all (four isomers) have four carbon environment / produce four peaks	Allow they have the same number of peaks Allow they all have four carbons in different environments Allow they / all (four) have the same number of carbon environments / peaks Ignore just they all have four carbons Ignore they have the same molecular formula Ignore they have the same proton environments Ignore they all have five different proton environments Do not award they have the same peaks Do not award the wrong number of carbon atoms Do not award all have four different proton environments	**(1)**

Question Number	Answer	Additional Guidance	Mark
17(b)(ii)	• Two correct numbers of peaks **(1)** • Third correct number of peaks **(1)** • Fourth correct number of peaks **(1)**	see table below	**(3)**

Name	Skeletal structure	Number of peaks
butanoic acid		4
4-hydroxybutanal		5
ethyl ethanoate		3
3-hydroxybutanone		4

Question Number	Answer	Additional Guidance	Mark
17(b)(iii)	An answer that makes reference to the following point: • butanoic acid / $CH_3CH_2CH_2COOH$ **and** the hydrogen / proton in COOH	If both are given, both must be correct May be shown on a labelled diagram Allow any formula showing structure including skeletal formula to identify the acid Allow COOH to indicate the proton If name and formula are given both must be correct Do not award positive ions such as $[COOH]^+$	**(1)**

Question Number	Answer	Additional Guidance	Mark
17(b)(iv)	An answer that makes reference to the following points: • the quintet results from a hydrogen with four hydrogens on adjacent carbons / the hydrogen is split by four other hydrogens **(1)** • because 4-hydroxybutanal has (a carbon with) a hydrogen / two hydrogens with four hydrogens on adjacent carbons **(1)**	This marking point is to justify the quintet. This may be scored within M2 Ignore next to a carbon with 4 hydrogens attached? This marking point justifies 4-hydroxybutanal as the isomer. May be shown by a diagram indicating the either the hydrogens giving the signal or the hydrogens causing the quintet in some way for example  Do not award 4-hydroxybutanal and arguments related to having 5 hydrogen environments	**(2)**

(Total for Question 17 = 13 marks)

(Total for Section B = 52 marks)

Question Number	Answer	Additional Guidance	Mark
18(a)(i)	**Route 1** – Solving the expression to find $[H^+]$ • M1 expression for K_a **(1)** • M2 uses expression to calculate $[H^+]$ **(1)** Then Either • M3 calculates pH **(1)** Or • M3 calculates $[H^+]$ from given pH **(1)** Or • M3 calculates $[C_4H_9COOH]$ **(1)** Or	Allow any alternative methods Ignore throughout $-\log_{10}0.00120 = 2.9$ $K_a = \frac{[C_4H_9COO^-][H^+]}{[C_4H_9COOH]}$ Allow use of $[H^+]^2$ [HA] and / or $[A^-]$ Allow correct rearranged expression $= \sqrt{1.38 \times 10^{-5} \times 0.12}$ This also scores M1 $= 0.0012869$ / 1.2869×10^{-3} (mol dm^{-3}) $= -\log_{10}0.0012869$ $= 2.8905$ / 2.9 $= 0.0012589$ / 1.2589×10^{-3} $= \frac{0.0012869^2}{1.38 \times 10^{-5}} = 0.12001$	**(3)**

	• M3 uses Henderson-Hasselbalch equation to find pH **(1)**	pH = pKa + $\log_{10}([CH_3COO^-] / [CH_3COOH])$ or pH = $-\log_{10}Ka + \log_{10} [CH_3COO^-] - \log_{10} [CH_3COOH]$ or pH = $-\log_{10}(0.0000138) + \log_{10}0.0012869 - \log_{10}0.12$ and pH = 4.8601 + –2.8905 + 0.92082 = 2.8904	
	Route 2 – Equating expression for $[H^+]$ to expression for pH		
	• expression for K_a **(1)**	$K_a = \frac{[C_4H_9COO^-][H^+]}{[C_4H_9COOH]}$	
	• gives a mathematical expression relating pH and $[H^+]$ **(1)**	pH = $-\log_{10}[H^+]$ or $[H^+] = 10^{-pH}$	
	• equates expression to calculate $[H^+]$ to 10^{-pH} **or** equates expression to calculate $[H^+]$ to pH **(1)**	$10^{-2.9} = \sqrt{1.38 \times 10^{-5} \times 0.12}$ or $2.9 = -\log_{10}\sqrt{1.38 \times 10^{-5} \times 0.12}$ Do not award a statement that $-\log_{10}0.00120 = 2.9$	

Question Number	Answer		Additional Guidance	Mark
18(a)(ii)	An answer that makes reference to the following points: **EITHER** **Route 1** • estimates concentration of H^+ • calculates pH **and** so pH must be less than 13 as concentration diluted (by pentanoic acid solution / by reaction with pentanoic acid) **OR** **Route 2** • estimates pOH • calculates pH **and** so pH must be less than 13 as concentration diluted (by pentanoic acid solution / by reaction with pentanoic acid) **OR**	 **(1)** **(1)** **(1)** **(1)**	Allow alternative methods Allow TE throughout as long as the final pH is less than 13 and greater than 9 $K_w = [H^+][OH^-]$ $[H^+] = 1.0 \times 10^{-14} \div 0.1 = 1.0 \times 10^{-13}$ (mol dm^{-3}) pH = 13 Ignore incomplete dissociation of alkali $= -\log_{10}[OH^-] = 1$ pH = 14 – pOH = 13 Ignore incomplete dissociation of alkali	**(2)**

	Route 3 • calculates the concentration of OH^- in 75 cm^3 assuming none has reacted **(1)** • calculates pH of this concentration **(1)** **OR** **Route 4** • calculates concentration of OH^- after addition of 50 cm^3 to the pentanoic acid • calculates pH	mol OH^- = 0.1 × 50 × 10^{-3} = 5 × 10^{-3} (mol) $[OH^-]$ = 5 × 10^{-3} ÷ 75 × 10^{-3} = 0.066667 (mol dm^{-3}) $-\log_{10}[OH^-]$ = 1.1761 pH = 14 - 1.1761 = 12.824 (which is less than 13) Or $[H^+]$ = 1.0 × 10^{-14} ÷ 0.066667 = 1.5 × 10^{-13} pH = $-\log_{10}[H^+]$ = 12.824 $[OH^-] = \frac{\text{moles of OH}^- \text{ added} - \text{moles of pentanoic acid}}{\text{Volume of water}}$ $[OH^-] = \frac{0.00500 - 0.00300}{75 \div 1000}$ = 0.026667 (mol dm^{-3}) pOH = $-\log_{10}[OH^-]$ = 1.574 pH = 14 – pOH = 14 – 1.574 = 12.426 Or $[H^+]$ = 1.0 × 10^{-14} ÷ 0.026667 = 1.5 × 10^{-13} pH = $-\log_{10}[H^+]$ = 12.426 (which is less than 13)	

Question Number	Answer	Additional Guidance	Mark
18(a)(iii)	(Neutralisation should occur at 30 cm^3 because) • calculation of number of moles of pentanoic acid **(1)** EITHER • calculation of volume of potassium hydroxide OR calculation of moles of potassium hydroxide assuming volume is 30 cm^3 **(1)**	<u>Example of calculation</u> $= 0.12 \times \frac{25}{1000} = 0.003 / 3.0 \times 10^{-3}$ (mol) $= \frac{0.003}{0.1} \times 1000 = 30$ (cm^3) $= 0.100 \times \frac{30}{1000} = 0.003 / 3.0 \times 10^{-3}$ (mol)	**(2)**

Question Number	Answer	Additional Guidance	Mark
18(a)(iv)	An answer that makes reference to the following point: • the titration between a weak acid and a strong base (results in pH greater than 7 / alkaline pH at the equivalence point)	Accept the product of the neutralisation / the potassium pentanoate / the pentanoate ion / the salt of weak acid forms an alkaline solution when dissolved in water Allow $C_4H_9COO^- + H_2O \rightleftharpoons C_4H_9COOH + OH^-$ Allow some H^+ (from water) will combine with $C_4H_9COO^-$	**(1)**

Question Number	Answer	Additional Guidance	Mark
18(a)(v)	An answer that makes reference to the following points: • at 15.0 cm^3 the concentration of pentanoic acid and pentanoate ion are equal / the pentanoic acid has been half-neutralised / this is the half-neutralisation point **(1)** • (at the half-neutralisation point) pH = pK_a **and** calculation of pH **(1)**	COMMENT If a full buffer calculation is attempted, then score (2) for correct answer Accept this is the half-equivalence point Allow numbers of moles of **both** = 0.0015 (mol) Allow concentration of **both** = 0.0375 (mol dm^{-3}) This can be scored from a full buffer calculation $= -\log_{10} 1.38 \times 10^{-5} = 4.8601$ / 4.9 The value of 4.9 from a full buffer calculation scores M2 Ignore $pH = -\log_{10} 1.2589 \times 10^{-5} = 4.9$ Ignore SF except 1SF COMMENT Calculations of a pH giving 4.9 must be of the correct concentration of H^+ (from a buffer calculation) or K_a. Accept use of Henderson-Hasselbalch. All of the following would score M1 and the first half of M2 $pH = pK_a + \log_{10}\frac{0.0375}{0.0375}$ $pH = pK_a + \log_{10}1$ $pH = pK_a + 0$ Common incorrect calculations give values of 2.82, 3.14 and 4.35. These will generally score (0) BUT look for both moles or both concentrations calculated to score M1	**(2)**

Question Number	Answer	Additional Guidance	Mark
18(b)	An answer that makes reference to the following points: • because this region is a buffer / is the buffering region **(1)** • because there is a large reservoir of undissociated pentanoic acid (and pentanoate ions) in solution **(1)** **EITHER** • added OH^- reacts with H^+ and pentanoic acid dissociates and keeping the concentration of H^+ (almost) constant **OR** pentanoic acid reacts with the small quantity of hydroxide ions added and keeping the concentration of H^+ (almost) constant **(1)**	Do not award the addition of buffer Allow the concentration of pentanoic acid is high Ignore C_4H_9COOH and $C_4H_9COO^-$ are both present in solution Allow equations $H^+ + OH^- \rightarrow H_2O$ $C_4H_9COOH \rightleftharpoons C_4H_9COO^- + H^+$ Allow descriptions using formulae Allow ratio of $[C_4H_9COO^-]$ to $[C_4H_9COOH]$ hardly changes Allow balanced equation $C_4H_9COOH + OH^- \rightleftharpoons C_4H_9COO^- + H_2O$ Allow descriptions using formulae Allow ratio of $[C_4H_9COO^-]$ to $[C_4H_9COOH]$ hardly changes Ignore just quoting the Henderson-Hasselbalch equation without explanation	**(3)**

Question Number	Answer	Additional Guidance	Mark
18(c)(i)	An answer that makes reference to the following points: • at the start of the titration the solution will be red **(1)** • it will change to orange before key point 2 / in the buffering region / at pH 3.2 **and** remains orange in the buffering region / until about 25 cm^3 of KOH is added / until the pH reaches 4.4 **(1)** • it will be yellow before the neutralisation point / before the vertical portion of the graph / before key point 3 / when pH is (about) 4.4 **and** is still yellow at key point 4 **(1)**	Allow answers describing colour at the pH values OR volumes of KOH(aq) added Allow it will be red at key point 1 Allow it will be red between key points 1 and 2 Allow at / before pH 3.2 Allow it changes to orange after adding a small volume / a few cm^3 of KOH **and** remains orange until just before key point 2 / until about 20cm^3 are added Allow it gradually changes (from red) to orange around key point 2 / between and key points 1 and 2 / 3 Allow any volume of KOH up to 5cm^3 for the change to orange and from 15-25 cm^3 for change to yellow Allow it changes to yellow before key point 3 / at key point 3 **and** stays yellow Allow it will be yellow at key point 3 **and** stays yellow COMMENT: M1 is for initial red M2 is for orange from about pH 3.2 to about pH 4.4 (from the data booklet M3 is for yellow from about / after pH 4.4 to the end NOTE: The colour will change from red to orange to yellow scores (1) for M1	**(3)**

		The colour change from red to orange to yellow before the neutralisation point / end-point then does not change scores M1	

Question Number	Answer	Additional Guidance	Mark
18(c)(ii)	An answer that makes reference to the following points: • bromothymol blue **(1)** • (at the neutralisation point) there is a mixture of yellow and blue forms (of the indicator) so the solution appears green **(1)**	M2 dependent on M1 OR the selection of bromocresol green or bromocresol blue or bromophenol blue (which will not score M1) Allow indicator is yellow in acid and blue in alkali so green (at the neutralisation point) is observed Allow indicator is yellow below pH 6.0 and blue above pH 7.6 and grren at the neutralisation point Allow green is between yellow in acid and blue in alkali	**(2)**

(Total for Question 18 = 18 marks)

(Total for Section C = 18 marks)

Total for Paper = 90 marks

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