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Mark Scheme (Results)

October 2019

Pearson Edexcel International Advanced Level In Chemistry (WCH04)
Paper 01 General Principles of Chemistry I – 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.

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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.

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Section A (multiple choice)

Question Number	Correct Answer	Mark
1(a)	**The only correct answer is C** (Graph 3) ***A*** *is not correct because this is a graph of concentration of reactant against time for a first order reaction* ***B*** *is not correct because this is a graph of rate against concentration for a zero order reaction.* ***D*** *is not correct because this is a graph of rate against temperature*	**(1)**

Question Number	Correct Answer	Mark
1(b)	**The only correct answer is C** (Graph 3) ***A*** *is not correct because the concentration of product must increase with time. This is a graph of concentration of reactant against time for a first order reaction and shows Y decreasing with time* ***B*** *is not correct because the concentration of product must increase with time. This is a graph of rate against concentration for a zero order reaction and shows Y constant.* ***D*** *is not correct because the concentration of product must increase linearly with time. This is a graph of rate against temperature and shows Y increasing exponentially*	**(1)**

Question Number	Correct Answer	Mark
1(c)	**The only correct answer is D** (Graph 4) ***A*** *is not correct because rate increases exponentially with temperature. This is a graph of concentration of reactant against time for a first order reaction so Y decreases* ***B*** *is not correct because rate increases exponentially with temperature. This is a graph of rate against concentration for a zero order reaction so Y does not change.* ***C*** *is not correct because rate increases exponentially with temperature; it is not directly proportional to temperature*	**(1)**

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Question Number	Correct Answer	Mark
2	**The only correct answer is B** (+120) ***A*** *is not correct because this is the enthalpy change of the reverse reaction* ***C*** *is not correct because this is the same as the activation energy of the forward reaction* ***D*** *is not correct because this is the sum of the activation energy and the enthalpy change for the forward reaction*	**(1)**

Question Number	Correct Answer	Mark
3	**The only correct answer is D** (positive entropy change of the system, Δ*S* system) ***A*** *is not correct because activation energy determines rate not thermodynamic feasibility* ***B*** *is not correct because a positive enthalpy change favours the reverse reaction* ***C*** *is not correct because* $\Delta S^{\ominus}_{surroundings}$ *is negative for an endothermic reaction*	**(1)**

Question Number	Correct Answer	Mark
4	**The only correct answer is D** (more ways of distributing energy quanta) ***A*** *is not correct because boiling temperature only affects molar entropy when there is a change of state.* ***B*** *is not correct because standard molar enthalpy change of formation does not affect molar entropy* ***C*** *is not correct because molar entropy increases as the number of ways of distributing energy quanta increases*	**(1)**

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Question Number	Correct Answer	Mark
5	**The only correct answer is A** (perfect crystals at absolute zero (0 K)) ***B*** *is not correct because the molar entropy of gases is never zero* ***C*** *is not correct because this refers to standard enthalpies of formation for elements* ***D*** *is not correct because this is not true*	**(1)**

Question Number	Correct Answer	Mark
6(a)	**The only correct answer is D** (unchanged and decreases) ***A*** *is not correct because activation energy does not change with temperature and the equilibrium constant of an exothermic reaction decreases with increasing temperature* ***B*** *is not correct because activation energy does not change with temperature* ***C*** *is not correct because the equilibrium constant of an exothermic reaction decreases with increasing temperature*	**(1)**

Question Number	Correct Answer	Mark
6(b)	**The only correct answer is A** (increases and increases) ***B*** *is not correct because equilibrium yield would increase because 2 mol of reactant gives 1 mol of product* ***C*** *is not correct because rate increases when pressure increases for a gas phase reaction* ***D*** *is not correct because equilibrium yield would increase because 2 mol of reactant gives 1 mol of product and rate increases when pressure increases for a gas phase reaction*	**(1)**

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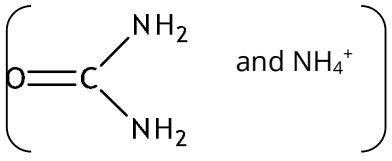
Question Number	Correct Answer	Mark
6(c)	**The only correct answer is A** $\left(K_p = \left(\frac{p(C_2H_5OH)}{p(C_2H_4) \text{ x } p(H_2O)} \right) \right)$ ***B*** *is not correct because this is K_p for the reverse reaction* ***C*** *is not correct because water is in the gas phase so it is included in the K_p expression* ***D*** *is not correct because the expression has been inverted and because water is in the gas phase so it is included in the K_p expression*	**(1)**

Question Number	Correct Answer	Mark
7	**The only correct answer is C** (produce an excess of hydrogen ions in solution) ***A*** *is not correct because this a traditional description of an acid* ***B*** *is not correct because this is just one of a number of typical reactions of acids* ***D*** *is not correct because this is the Lewis definition of acids*	**(1)**

Question Number	Correct Answer	Mark
8	**The only correct answer is D** (remains neutral and decreases) ***A*** *is not correct because water remains neutral and the pH decreases* ***B*** *is not correct because water remains neutral* ***C*** *is not correct because the pH of water decreases*	**(1)**

Question Number	Correct Answer	Mark
9	**The only correct answer is B**  and NH_4^+ ***A*** *is not correct because ammonia is a Brønsted-Lowry base* ***C*** *is not correct because both species are Brønsted-Lowry bases.*	**(1)**

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Question Number	Correct Answer	Mark
10	**The only correct answer is C** (optical isomerism only) ***A*** *is not correct because limonene does not have geometric isomers* ***B*** *is not correct because limonene does not have geometric isomers* ***D*** *is not correct because limonene does have a chiral carbon*	**(1)**

Question Number	Correct Answer	Mark
11	**The only correct answer is B** (permanent dipole-dipole forces in the liquid state and hydrogen bonds in aqueous solution) ***A*** *is not correct because ethanal does not form hydrogen bonds in the liquid state* ***C*** *is not correct because ethanal does not form hydrogen bonds in the liquid state and permanent dipole-dipole forces cannot account for the solubility of ethanal in water* ***D*** *is not correct because permanent dipole-dipole forces cannot account for the solubility of ethanal in water*	**(1)**

Question Number	Correct Answer	Mark
12	**The only correct answer is B** (warming with iodine and sodium hydroxide followed by acidifying with sulfuric acid) ***A*** *is not correct because acidified potassium dichromate(VI) does not react with butanone* ***C*** *is not correct because this would not reduce the number of carbon atoms* ***D*** *is not correct because this sequence will give 2-hydroxy-2-methylbutanoic acid*	**(1)**

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Question Number	Correct Answer	Mark
13(a)	**The only correct answer is C** (separate samples of the compound with ethanol and with ethanoic acid) ***A*** *is not correct because this reagent does not discriminate between alcohol and carboxylic acid OH groups* ***B*** *is not correct because this reagent will only show that an acid is present* ***D*** *is not correct because 2,4-dinitrophenylhydrazine does not react with the carbonyl group in carboxylic acids*	**(1)**

Question Number	Correct Answer	Mark
13(b)	**The only correct answer is A** (two singlets, two triplets and one quintet) ***B*** *is not correct because this ignores the fact that the protons on C3 are coupled to those on C2* ***and*** *C4* ***C*** *is not correct because this pattern includes the OH group on C4 in the coupling* ***D*** *is not correct because this pattern requires a proton on the carboxylic acid carbon which couples with the C2 protons*	**(1)**

Question Number	Correct Answer	Mark
14	**The only correct answer is A** (alkyl groups of alcohols replace alkyl groups of esters) ***B*** *is not correct because the alkyl groups of esters are replaced by alkyl groups of alcohols.* ***C*** *is not correct because the 'trans' does not refer to geometric isomerism* ***D*** *is not correct because transesterification involves esters reacting with alcohols*	**(1)**

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Question Number	Correct Answer	Mark
15	**The only correct answer is B** (high pressures) ***A*** *is not correct because liquid polymers are not used in HPLC* ***C*** *is not correct because lasers are not used in HPLC* ***D*** *is not correct because long columns are not a particular characteristic of HPLC*	**(1)**

(TOTAL FOR SECTION A = 20 MARKS)

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Section B

Question Number	Acceptable Answers	Reject	Mark
16(a)(i)	(ΔS^{o}_{system}) is positive **and** because a solid reactant forms gas products OR because gases have higher entropies than solids ALLOW (ΔS^{o}_{system}) is positive **and** because 1 mol goes to 3 mol OR because more moles of products (than reactants) ALLOW molecules for moles IGNORE references to disorder	Explanations with no comparison e.g. because 3 mol of gas are formed incorrect numbers of moles Just 'more products'	**(1)**

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Question Number	Acceptable Answers	Reject	Mark
16(a)(ii)	In this question and throughout the paper allow mol^{-} for mol^{-1} and 'J / K / mol' format / J mol^{-1} K^{-1} In parts (ii), (iii) and (iv) penalise omission of sign or omitted / incorrect units for 1 mark only and at the **first** occasion $NH_4NO_3(s) \rightarrow N_2O(g) + 2H_2O(g)$ $S^{\ominus}$/J K^{-1} mol^{-1} 151.1 219.7 188.7 (1) Penalise incorrect values once only ΔS^{o}_{system} = 219.7 + 2 x 188.7 – 151.1 (1) EITHER = +446(.0) J K^{-1} mol^{-1} OR = +0.446(0) kJ K^{-1} mol^{-1} (1) Ignore SF except 1 SF Correct answer with no working scores (3) TE at each stage but no TE if wrong reactants / products used		**(3)**

Question Number	Acceptable Answers	Reject	Mark
16(a)(iii)	$\Delta S^{o}_{surroundings} = -\Delta H/T$ (1) = −(−36 000/(160 + 273) (1) EITHER = +83.1409 J K^{-1} mol^{-1} OR = +0.0831409 kJ K^{-1} mol^{-1} (1) Ignore SF except 1 SF Correct answer with no working scores (3) Omission of 273 (+225.0) scores (2) Sign incorrect (−83.14 J K^{-1} mol^{-1}) scores (2)		**(3)**

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Question Number	Acceptable Answers	Reject	Mark
16(a)(iv)	$\Delta S^{\ominus}_{total} = \Delta S^{o}_{system} + \Delta S^{o}_{surroundings}$ = 446.0 + 83.1409 = 529.1409 (1) EITHER =+530 / 529 J K^{-1} mol^{-1} OR = +0.53 / 0.529 kJ K^{-1} mol^{-1} (1) Correct answer with sign and to 2 or 3 SF with no working scores (2) TE on (a)(ii) and (a)(iii) and M1	Answers not given to 2 or 3 SF	**(2)**

Question Number	Acceptable Answers	Reject	Mark
16(b)(i)	$\Delta S_{total} = R \ln K$ ALLOW $\Delta S = R \ln K$ only if ΔS = 555 is used (1) $\ln K = \Delta S_{total} / R$ = 555/8.31 = 66.787 K = 1.0121 x 10^{29} OR K = 9.80104 x 10^{28} if R = 8.314 used (1) Correct answer with no working scores (2) IGNORE units and K_c expressions Ignore SF No TE on incorrect expressions	K = 1.02 x 10^{29}	**(2)**

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Question Number	Acceptable Answers	Reject	Mark
***16(b)(ii)**	**Route 1** ΔS_{system} is (approximately) constant (with temperature) (1) (As $\Delta S_{surroundings}$ becomes less positive as T increases) ΔS_{total} becomes less positive / decreases /gets smaller (with increasing temperature) **and** so *K* decreases (1) **Route 2** ΔS_{system} becomes more positive / increases with temperature **and** because the products are gases (1) (As $\Delta S_{surroundings}$ becomes less positive as T increases) cannot tell whether ΔS_{total} increases or decreases (with increasing temperature) so cannot tell whether *K* increases or decreases (1) IGNORE Just 'entropies of substances increase with temperature' Explanations in terms of Le Chatelier's Principle	Just 'ΔS' throughout	**(2)**

(Total for Question 16 = 13 marks)

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Question Number	Acceptable Answers	Reject	Mark
17(a)(i)	**M1** Plot a graph of [C_4H_9Br] (on the y axis) against time (on the x axis) ALLOW Plot a graph of concentration (of reactant) against time OR Diagram of graph with axes labelled (1) **M2** Draw a tangent at time t = 0 / initial concentration (of 2-bromobutane) ALLOW Diagram from **M1** with tangent clearly labelled (1) **M3** Measure the gradient of the tangent OR Measure the gradient of the graph at time t = 0 / the initial concentration of 2-bromobutane ALLOW Measure the initial gradient (of the graph) (1)	[NaOH] Just 'measure the gradient of the graph'	**(3)**

Question Number	Acceptable Answers	Reject	Mark
17(a)(ii)	So that the concentration of sodium hydroxide would remain (approximately) constant OR Only the concentration of 2-bromobutane would change OR So that the rate of reaction would only vary with the (change in) concentration of 2-bromobutane OR So that the rate of reaction would not be affected by (the change in concentration of) sodium hydroxide IGNORE	So that all the 2-bromobutane reacts	**(1)**

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Question Number	Acceptable Answers	Reject	Mark
17(b)(i)	Standalone marks E1 to E2 [C_4H_9Br] x 1.5 and (initial) rate x 1.5 ([NaOH] constant) so 1st order (wrt [C_4H_9Br]) (1) E1 to E3 [C_4H_9Br] x 2 and [NaOH] x 2 and (initial) rate x 4 so 1st order wrt [NaOH] (1) (so confirms overall second order)		**(2)**

Question Number	Acceptable Answers	Reject	Mark
17(b)(ii)	k = rate /([C_4H_9Br] x [NaOH]) = 1.5 x 10^{-5} / (0.020 x 1.0) = 7.5 x 10^{-4} / 0.00075 ALLOW Use of data from any of the experiments (E2 = 7.667 x 10^{-4}; E3 = 7.375 x 10^{-4}) (1) Correct answer with no working scores (1) $dm^3\ mol^{-1}\ s^{-1}$ ALLOW Units in any order (1) No TE for either mark on incorrect rate equation		**(2)**

Question Number	Acceptable Answers	Reject	Mark
17(c)(i)	[C_4H_9Br] and [NaOH] /[OH^-] are both involved in the rate-determining step ALLOW both reactants /two reactants / two species / two substances in the slow step in the RDS IGNORE References to the rate equation	Two molecules	**(1)**

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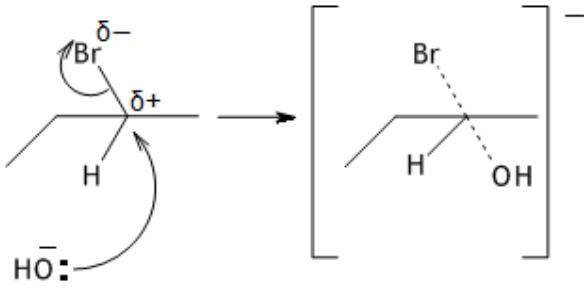
Question Number	Acceptable Answers	Reject	Mark
17(c)(ii)	Allow skeletal, displayed or semi displayed structures, use of CH_3 and C_2H_5, omission of **one** H from CH_3 and C_2H_5 in a displayed formula  IGNORE Incorrect R groups / stages after the transition state Products even if incorrect Use of 1-bromobutane **M1** Curly arrow from C—Br bond to Br or just beyond **and** dipole ALLOW This curly arrow drawn on the transition state (1) **M2** Curly arrow from **lone pair** of O on OH^- to C atom (1) COMMENT Award MP2 if arrow closer to lone pair than to oxygen / charge **M3** Transition state including partial bonds **and** charge on any part of the transition state (1) IGNORE Dipoles on the transition state S_N1 may score M1 and M2	lone pair shown on H O−H----C in intermediate	**(3)**

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Question Number	Acceptable Answers	Reject	Mark
17(d)(i)	(A chiral molecule) has a non-superimposable mirror image ALLOW (A chiral molecule has) an asymmetric carbon atom OR a carbon atom bonded to 4 different atoms / groups OR a carbon atom bonded to 4 different functional groups ALLOW for 'bonded to' Attached to / surrounded by IGNORE References to the rotation of the plane of plane polarised light / optical activity	4 molecules Just 'molecule with four different groups'	**(1)**

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Question Number	Acceptable Answers	Reject	Mark
***17(d)(ii)**	**M1** S_N1 gives a racemic mixture **and** S_N2 gives a single enantiomer / optical isomer ALLOW S_N1 gives a mixture with no optical activity / both enantiomers **and** S_N2 gives an optically active mixture / single isomer (1) **M2** In S_N1 the intermediate (carbocation) is planar (about the carbon atom carrying the positive charge) (1) **M3** So the nucleophile / OH^- attacks (equally) from either side / top and bottom (of the carbocation / intermediate) (1) **M4** In S_N2 the nucleophile attacks one side of the molecule only / on the opposite side to the Br (1) If $S_N1$and S_N2 are reversed do not award M1 but max 3 available	molecule / carbonyl is planar Alkali (for nucleophile / OH^-) attacks the carbocation	**(4)**

(Total for Question 17 = 17 marks)

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Question Number	Acceptable Answers	Reject	Mark
18(a)(i)	IGNORE use / omission of heat / reflux Reaction **1** (dry) Phosphorus(V) chloride / phosphorus pentachloride / PCl_5 OR Phosphorus(III) chloride / phosphorus trichloride / PCl_3 ALLOW Thionyl chloride $SOCl_2$ (1) Reaction **2** Methanol / CH_3OH (1) Reaction **3** Methanol / CH_3OH **and** (concentrated) sulfuric acid / H_2SO_4 (heat) ALLOW Any strong acid by name or formula Identified dilute strong acids (1) IGNORE H^+ If the same incorrect / unspecified alcohol is used in Reactions **2** and **3** award (1) for otherwise correct answers Reaction **4** Lithium tetrahydridoaluminate((III)) / lithium aluminium hydride / $LiAlH_4$ ALLOW Lithal (1) In **dry** ether /diethyl ether / ethoxyethane (1) IGNORE subsequent hydrolysis	Additional reagents Addition of acid	**(5)**

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Question Number	Acceptable Answers	Reject	Mark
18(a)(ii)	Distilling the product directly out of the reaction mixture ALLOW Just distil / distillation IGNORE Controlling temperature Using excess butan-1-ol Using limited amount of oxidising agent	Reflux Fractional distillation Steam distillation	**(1)**

Question Number	Acceptable Answers	Reject	Mark
18(a)(iii)	Advantage: (Overall) reaction goes to completion ALLOW Reaction fast(er) / does not require heat / occurs at room temperature / does not require a catalyst (1) IGNORE (For M1) Reference to purity / yield / ease of reaction / vigorous reaction / reaction not reversible / not equilibrium Disadvantage: (Toxic / corrosive) hydrogen chloride / HCl is formed (1) IGNORE Two-step process / by-products formed	References to cost reaction not reversible / equilibrium	**(2)**

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Question Number	Acceptable Answers	Reject	Mark
18(a)(iv)	Butanal is more easily reduced than butanoic acid ALLOW Butan-1-ol / butanol / alcohol is (always) formed OR difficult to stop the reduction at the aldehyde IGNORE References to the strength of the reducing agent References to speed of reaction		**(1)**

Question Number	Acceptable Answers	Reject	Mark
18(b)	Any **two** from Butanoic acid (will have stretching vibrations for) O—H at 3300-2500 (cm^{-1}) (1) OR Butanoic acid (will have stretching vibrations for) C=O at 1725-1700 (cm^{-1}) (1) OR Methyl butanoate (will have stretching vibrations for) C=O at 1750-1735 (cm^{-1}) (1) IGNORE Reference to the fingerprint region C—O at 1200-1180 / 1250-1230 / 1200-1150 (cm^{-1}) If no other mark is awarded two correct wavenumber ranges with no bonds specified scores (1) If no other mark is awarded two correct wavenumbers within the ranges with correct bonds specified scores (1)	3750-3200 (cm^{-1})	**(2)**

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Question Number	Acceptable Answers	Reject	Mark
18(c)	10 parts per billion by volume = 10 dm^3 butanoic acid (vapour) per 1 x 10^9 dm^3 of air = 1 x 10^{-8} dm^3 butanoic acid per dm^3 of air (1) IGNORE 1 x 10^{-8} without units / explanation = 1 x 10^{-8} ÷ 24.0 = 4.16667 x 10^{-10} (mol dm^{-3}) (1) Correct answer with no working scores (2) IGNORE SF		**(2)**

(Total for Question 18 = 13 marks)

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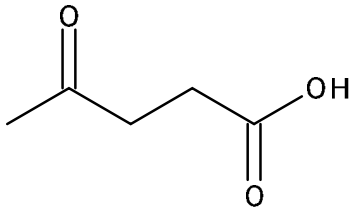
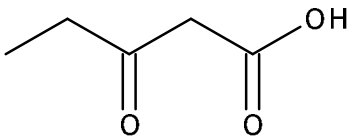
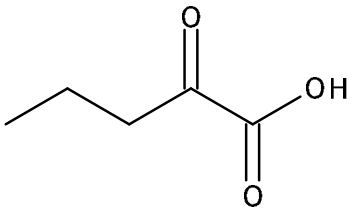
Question Number	Acceptable Answers	Reject	Mark
19	 (1)  (1)  (1) OR Structural or displayed formulae IGNORE Names even if incorrect / one missing H in displayed structures (then penalise once) **M1** (Orange) ppt with DNPH so carbonyl group (1) **M2** No reaction with Tollen's reagent so ketone / not aldehyde (1) **M3** Effervescence /reaction with $NaHCO_3$ indicates carboxylic acid (group) / carboxyl (group) ALLOW carboxylic (group) /acid (group) (1) **M4** *m / e* of molecular ion / M_r = 116 so must be $C_5H_8O_3$ ALLOW *m / e* of molecular ion = 116 so M_r of **any** structure(s)	Just 'M_r of G must be = 116'	**(7)**

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Question Number	Acceptable Answers	Reject	Mark
20(a)(i)	$HCOOH + H_2O \rightleftharpoons HCOO^- + H_3O^+$ OR $HCOOH \rightleftharpoons HCOO^- + H^+$ ALLOW $HCOOH + H_2O \rightleftharpoons HCOO^- + H^+$ → for ⇌ Ignore state symbols even if incorrect	Incorrect formulae (penalise once only in (i), (ii) and (iii)	**(1)**

Question Number	Acceptable Answers	Reject	Mark
20(a)(ii)	$K_a = \frac{[HCOO^-][H^+]}{[HCOOH]}$ OR H_3O^+ for H^+ ALLOW $K_c = \frac{[HCOO^-][H^+]}{[HCOOH]}$ OR H_3O^+ for H^+ IGNORE State symbols even if incorrect $[\ ]_{eq}$ / $[\ ]_{eqm}$ $K_a = \frac{[H^+]^2}{[HCOOH]}$	Other types of bracket Omission of K_a =	**(1)**

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Question Number	Acceptable Answers	Reject	Mark
20(a)(iii)	No TE on an incorrect expression in (a)(ii) [HCOOH] = 30/46 = 0.65217 mol dm^{-3} (1) **COMMENT** In M1 penalise multiple errors in calculation of the concentration once only $K_a = 1.70 \times 10^{-4} \approx [H^+]^2 / 0.65217$ (1) $[H^+] = \sqrt{(1.70 \times 10^{-4} \times 0.65217}$ $= 1.0529 \times 10^{-2} / 0.010529$ (1) pH = −log 0.010529 = 1.9776 / 1.98 / 2.0 (1) TE at each stage of the calculation Do not penalise premature <u>correct</u> rounding If 30 is used for the concentration (in mol dm^{-3}) pH = 1.1462 / 1.15 / 1.1 scores (3) If square root not taken pH = 3.9552 scores (3) IGNORE SF except 1 SF Allow other calculation methods	pH = 2 /1.9 / 1.97 pH = 1.2	**(4)**

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Question Number	Acceptable Answers	Reject	Mark
20(a)(iv)	IGNORE explanations ALLOW $[H_3O^+]$ for $[H^+]$ throughout Use of HA and A^- **First mark:** HCOOH / methanoic acid ionisation / dissociation negligible ALLOW Acid for HCOOH Slight / partial / incomplete / does not dissociate for negligible dissociation OR $[HCOOH]_{equilibrium} = [HCOOH]_{initial}$ / 0.65217 (mol dm^{-3}) (1) **Second mark:** ($[H^+]$ due to) ionisation of water negligible OR $[H^+]$ only due to (ionisation of) HCOOH / methanoic acid OR $[HCOO^-] = [H^+]$ (1) IGNORE references to temperature Penalise omission of [] or use of incorrect acid in discussion once only	Just 'dissociates less'	**(2)**

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Question Number	Acceptable Answers	Reject	Mark
20(b)(i)	Standalone marks A buffer resists change in pH OR Maintains a fairly / nearly constant pH ALLOW Negligible change in pH OR resists significant change in pH (1) on the addition of **small** amounts of acid / H^+ **and** of alkali / base / OH^- (1)	prevents change in pH Just constant pH	**(2)**

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Question Number	Acceptable Answers	Reject	Mark
***20(b)(ii)**	General answer in terms of HA and A^- scores max 3 (**M2**, **M3** and **M4**) ALLOW use of names for formulae **M1** HCOOH and $HCOO^-$ / HCOONa are present in high concentration / large amount / large excess / form a (large) reservoir (1) **M2** When acid is added the $HCOO^-$ / HCOONa is protonated / reacts, removing the H^+ ion from the solution / forming HCOOH OR $HCOO^- + H^+ \rightarrow HCOOH$ (1) **M3** When alkali is added the HCOOH reacts, removing the OH^- ion (from the solution) OR reacts forming $HCOO^-$ or $HCOO^{(-)}Na^{(+)}$ or water OR OH^- reacts with H^+ **and** HCOOH dissociates to replace the H^+ OR $HCOOH + OH^- \rightarrow HCOO^- + H_2O$ (1) **M4** So [HCOOH] and $[HCOO^-]$ do not change (significantly) OR the ratio [HCOOH] : $[HCOO^-]$ does not change (significantly) ALLOW Use of HCOOH and $HCOO^-$ for [HCOOH] and $[HCOO^-]$ (1) For **M2** and **M3**:		**(4)**

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Question Number	Acceptable Answers	Reject	Mark
20(c)(i)	**Route 1** $K_a = \frac{[H^+] \times [HCOO^-]}{[HCOOH]}$ $[H^+] = K_a \times \frac{[HCOOH]}{[HCOO^-]}$ (1) $= 1.70 \times 10^{-4} \times 1.25/1.50$ (1) $= 1.41667 \times 10^{-4}$ pH = 3.8487 = 3.85 / 3.8 (1) **Route 2** $pH = pK_a + \log \frac{[HCOO^-]}{[HCOOH]}$ (1) $= -\log(1.70 \times 10^{-4}) + \log(1.50/1.25)$ (1) = 3.8487 = 3.85 (1) Correct answer with no working scores (3) Inversion of concentrations pH = 3.69 scores (2) Penalise inversion once only in (i) and (ii) IGNORE SF except 1 SF	pH =3.84 / 3.9 pH =3.84 / 3.9	**(3)**

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Question Number	Acceptable Answers	Reject	Mark
20(c)(ii)	Mol NaOH = 2/40 = 0.05 / 5 x 10^{-2} (1) New [HCOOH] = 1.25 – 0.05 = 1.20 **and** New [$HCOO^-$] = 1.50 + 0.05 = 1.55 (1) [H^+] = 1.70 x 10^{-4} x 1.20/1.55 = 1.31613 x 10^{-4} pH = 3.8807 = 3.88 OR pH = −log(1.70 x 10^{-4}) + log(1.55/1.20) (1) Correct answer with no working scores (3) IGNORE SF except 1 SF		**(3)**

(Total for Question 20 = 20 marks)
TOTAL FOR SECTION C = 20 MARKS
TOTAL FOR PAPER = 90 MARKS

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