Pearson Edexcel

Mark Scheme (Results)

June 2024

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

Edexcel and BTEC Qualifications

Edexcel and BTEC qualifications are awarded by Pearson, the UK's largest awarding body. We provide a wide range of qualifications including academic, vocational, occupational and specific programmes for employers. For further information visit our qualifications websites at www.edexcel.com or www.btec.co.uk. Alternatively, you can get in touch with us using the details on our contact us page at www.edexcel.com/contactus.

Pearson: helping people progress, everywhere

Pearson aspires to be the world's leading learning company. Our aim is to help everyone progress in their lives through education. We believe in every kind of learning, for all kinds of people, wherever they are in the world. We've been involved in education for over 150 years, and by working across 70 countries, in 100 languages, we have built an international reputation for our commitment to high standards and raising achievement through innovation in education. Find out more about how we can help you and your students at: www.pearson.com/uk

June 2024
Question paper log number P75781A
Publications Code WCH14_01_2406_MS

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

Question Number	Answer	Mark
1(a)	**The only correct answer is A** (colorimetry) ***B*** *is not correct because there is no change in mass* ***C*** *is not correct because titration is not a continuous monitoring method* ***D*** *is not correct because no gas is produced*	**1**

Question Number	Answer	Mark
1(b)	**The only correct answer is D** ($dm^9\ mol^{-3}\ s^{-1}$) ***A*** *is not correct because these are the units of rate* ***B*** *is not correct because these are the units of the rate constant for a second order reaction* ***C*** *is not correct because these are the units of the rate constant for a third order reaction*	**1**

Question Number	Answer	Mark
1(c)	**The only correct answer is D** (1/16) ***A*** *is not correct because the rate would change by this factor for an overall first order reaction* ***B*** *is not correct because the rate would change by this factor for an overall second order reaction* ***C*** *is not correct because the rate would change by this factor for an overall third order reaction*	**1**

Question Number	Answer	Mark
1(d)	**The only correct answer is C** (Step **3**) ***A*** *is not correct because 1 mol of* Br^- *and 2 mol of* H^+ *are also involved up to and including the rate-determining step* ***B*** *is not correct because 1 mol of* Br^- *is also involved up to and including the rate-determining step* ***D*** *is not correct because 1 mol of* Br_2O_2 *is not involved in the rate-determining step*	**1**

Question Number	Answer	Mark
2	**The only correct answer is B** (AgBr) ***A*** *is not correct because the difference between the lattice energies is not as great as for AgBr* ***C*** *is not correct because the difference between the lattice energies is not as great as for AgBr* ***D*** *is not correct because the difference between the lattice energies is not as great as for AgBr*	**1**

Question Number	Answer	Mark
3(a)	**The only correct answer is C** (the enthalpy change of hydration of a lead(II) ion is more exothermic than that of a nitrate ion) ***A*** *is not correct because this is the lattice energy of lead(II) nitrate* ***B*** *is not correct because the enthalpy change of solution of lead(II) nitrate is endothermic* ***D*** *is not correct because the entropy change of the surroundings is negative (as the enthalpy change is positive)*	**1**

Question Number	Answer	Mark
3(b)	**The only correct answer is D** (–314) ***A*** *is not correct because the wrong sign has been used for the enthalpy change of hydration of lead(II) ions and this is for 2 mol of nitrate ions* ***B*** *is not correct because the wrong sign has been used for the enthalpy change of hydration of lead(II) ions* ***C*** *is not correct because this is the enthalpy change for hydrating 2 mol of nitrate ions*	**1**

Question Number	Answer	Mark
4a)	**The only correct answer is C** (32) ***A*** *is not correct because 6 mol of unreacted N_2 and 18 mol of unreacted H_2 are also present* ***B*** *is not correct because the reaction is an equilibrium and does not go to completion* ***D*** *is not correct because 4 mol of N_2 and 12 mol of H_2 have reacted*	**1**

Question Number	Answer	Mark
4(b)	**The only correct answer is C** ($\frac{p(NH_3)^2}{p(N_2) \times p(H_2)^3}$) ***A*** *is not correct because the reactant partial pressures should be multiplied, and the expression should be inverted* ***B*** *is not correct because the reactant partial pressures should be multiplied* ***D*** *is not correct because the expression should be inverted*	**1**

Question Number	Answer	Mark
4(c)	**The only correct answer is A** (decreasing the temperature) ***B*** *is not correct because only temperature affects the value of* K_p ***C*** *is not correct because only temperature affects the value of* K_p ***D*** *is not correct because only temperature affects the value of* K_p	**1**

Question Number	Answer	Mark
5	**The only correct answer is A** (the value of *K* is less than 1) ***B*** *is not correct because this would give a positive total entropy change* ***C*** *is not correct because the value of K cannot be negative* ***D*** *is not correct because the position of equilibrium would lie to the left*	**1**

Question Number	Answer	Mark
6	**The only correct answer is D** (5.4) ***A*** *is not correct because this is the pH of 1 mol* dm^{-3} CH_3COOH ***B*** *is not correct because this is the pH when the ratio is inverted* ***C*** *is not correct because this is the pH when the concentrations of* CH_3COOH *and* CH_3COONa *are equal*	**1**

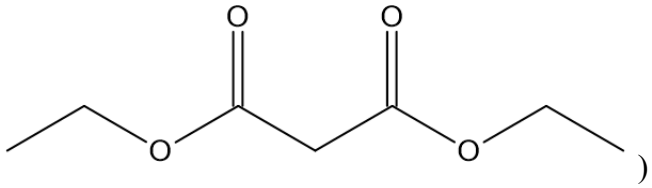
Question Number	Answer	Mark
7	**The only correct answer is B** (HCO_3^- + H^+ → H_2CO_3) ***A*** *is not correct because this reaction provides buffer action when the pH is raised* ***C*** *is not correct because* HCO_3^- *does not dissociate when the pH is reduced* ***D*** *is not correct because* CO_3^{2-} *is not present at significant concentrations in blood and in cells*	**1**

Question Number	Answer	Mark
8	**The only correct answer is C** (6) ***A*** *is not correct because there are 6 chiral centres* ***B*** *is not correct because there are 6 chiral centres* ***D*** *is not correct because there are 6 chiral centres*	**1**

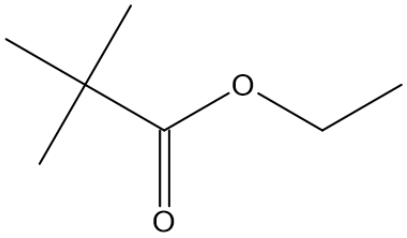
Question Number	Answer	Mark
9	**The only correct answer is A** (the mechanism involves a carbocation intermediate) ***B*** *is not correct because the mechanism is* S_N1 ***C*** *is not correct because primary halogenoalkanes do not react by* S_N1 ***D*** *is not correct because the main nucleophile is* OH^-	**1**

Question Number	Answer	Mark
10	**The only correct answer is B** (a racemic mixture is formed) ***A*** *is not correct because* CN^- *acts as a nucleophile* ***C*** *is not correct because the product is not optically active* ***D*** *is not correct because the product is 2-hydroxy-2-methylpropanenitrile*	**1**

Question Number	Answer	Mark
11	**The only correct answer is B** (Only 1 and 2) ***A*** *is not correct because acyl chlorides do not react with tertiary amines* ***C*** *is not correct because acyl chlorides also form amides with primary amines and do not react with tertiary amines* ***D*** *is not correct because acyl chlorides also form amides with secondary amines*	**1**

Question Number	Answer	Mark
12	**The only correct answer is A (**  **)** ***B*** *is not correct because the acid hydrolysis of this ester forms ethanoic acid and propan-1-ol* ***C*** *is not correct because the acid hydrolysis of this ester forms propanoic acid and ethanol* ***D*** *is not correct because the acid hydrolysis of this ester forms propanoic acid and ethane-1,2-diol*	**1**

Question Number	Answer	Mark
13	**The only correct answer is B** ($CH_3COCH_2CH_3$) ***A*** *is not correct because* CH_3COCH_3 *has only two peaks in its* ^{13}C *NMR spectrum* ***C*** *is not correct because* $CH_3CH_2COCH_2CH_3$ *has only three peaks in its* ^{13}C *NMR spectrum* ***D*** *is not correct because* $CH_3COCH_2CH_2COCH_3$ *has only three peaks in its* ^{13}C *NMR spectrum*	**1**

Question Number	Answer	Mark
14	 **The only correct answer is D** ( ) ***A*** *is not correct because the singlet would have a relative peak area of 3H and a chemical shift in the range for H–C–C=O* ***B*** *is not correct because the chemical shifts of the quartet and singlet would be in the ranges for H–C–C=O and for H–C–O– respectively, and the singlet would have a relative peak area of 3H* ***C*** *is not correct because the quartet would have a chemical shift in the range for H–C–C=O*	**1**

Total for Section A = 20 marks

Section B

Question Number	Answer	Additional Guidance	Mark
15(a)(i)	An answer that makes reference to the following points: • any one or two types of bonding **(1)** • third type of bonding **(1)**	Ignore giant throughout • covalent (in SiO_2) Ignore macromolecular Do not award simple/molecular Do not award dative/coordinate • metallic (in Mg) Allow metal • ionic (in MgO) Allow ion	**2**

Question Number	Answer	Additional Guidance	Mark
15(a)(ii)	An answer that makes reference to the following points: • (as) moles (decreases) from 5 to 3 **(1)** • decreases in disorder **(1)**	Accept reverse arguments Allow particles or molecules for moles Ignore any reference to standard entropies of reactants and products Allow just number of moles decreases Do not award incorrect numbers of moles Do not award incorrect explanation relating to states Accept fewer ways of distributing energy (in products) Accept fewer ways of arranging moles (in products) Ignore just less arranged for less disordered Ignore randomness for disorder Ignore just decreases in entropy	**2**

Question Number	Answer	Additional Guidance	Mark
15(a)(iii)	• expression for $\Delta S_{surroundings}$ **(1)** • value of $\Delta S_{surroundings}$ **(1)**	Example of calculation: $\Delta S_{surroundings} = \frac{-\Delta H}{T} = \frac{-(-370 \times 10^3)}{(23.0 + 273)}$ Allow just –(–370)/–(–370000)/370/370000 divided by any temperature in K or °C (+)1250 ($J\,K^{-1}\,mol^{-1}$) Allow (+)1.25 $kJ\,K^{-1}\,mol^{-1}$ Ignore SF except 1 SF Do not award any other answer Correct answer with some working scores (2) If neither mark awarded, –1250 ($J\,K^{-1}\,mol^{-1}$) / –1.25 $kJ\,K^{-1}\,mol^{-1}$ scores (1)	**2**

Question Number	Answer	Additional Guidance	Mark
15(a)(iv)	• expression for ΔS_{total} **(1)** • calculation of ΔS_{total} to 2, 3 or 4 SF **(1)**	Example of calculation: $\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$ = –43.8 + answer to (a)(iii) where answer to (a)(iii) is 1250 ($J\,K^{-1}\,mol^{-1}$) ΔS_{total} = (+)1206 / 1210 / 1200 ($J\,K^{-1}\,mol^{-1}$) Allow (+)1.206 / 1.21 / 1.2 $kJ\,K^{-1}\,mol^{-1}$ where answer to (a)(iii) is –1250 ($J\,K^{-1}\,mol^{-1}$) ΔS_{total} = –1294 / –1290 / –1300 ($J\,K^{-1}\,mol^{-1}$) Allow –1.294 / –1.29 / –1.3 $kJ\,K^{-1}\,mol^{-1}$ TE on transcription error of –48.3 for –43.8 No TE on incorrect expression from M1	**2**

Question Number	Answer	Additional Guidance	Mark
15(a)(v)	An answer that makes reference to the following point: • bonding / electrostatic attraction (in SiO_2) is strong **or** a large amount of energy is needed to break bond(s) (in SiO_2)	Ignore SiO_2/reaction/reactants is/are kinetically stable Ignore reactions between solids are slow Allow Mg/reactants for SiO_2 Allow a large amount of energy is needed to break covalent / metallic bond(s) Do not award any reference to the breaking of ionic bonds / intermolecular forces	**1**

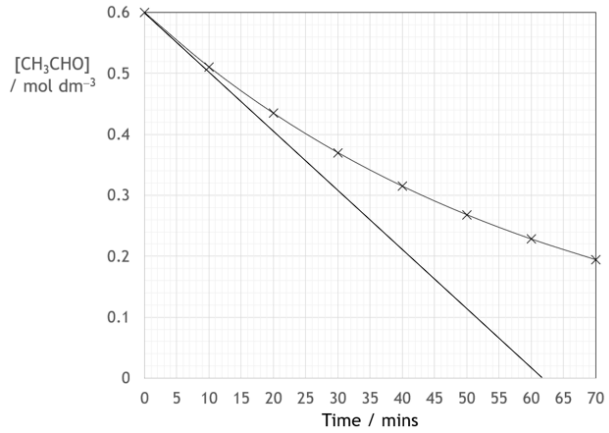
Question Number	Answer	Additional Guidance	Mark
15(b)(i)	An answer that makes reference to the following point: • correct equation	<u>Examples of equation:</u> $Mg_2Si + 4HCl \rightarrow SiH_4 + 2MgCl_2$ Allow ionic equations: $Mg_2Si + 4H^+ \rightarrow SiH_4 + 2Mg^{2+}$ $Mg_2Si + 4H^+ + 4Cl^- \rightarrow SiH_4 + 2Mg^{2+} + 4Cl^-$ Allow multiples Allow reversible arrow Ignore state symbols even if incorrect	**1**

Question Number	Answer	Additional Guidance	Mark
15(b)(ii)	An answer that makes reference to the following points: • name of shape **(1)** • bond angle **(1)**	 tetrahedral Allow tetrahedron $109.5^{(\circ)}$ Allow $109^{(\circ)}$ No TE on incorrect shape	**2**

Question Number	Answer	Additional Guidance	Mark
15(c)(i)	• use of $\Delta S_{system} = \Sigma S^{\ominus}_{products} - \Sigma S^{\ominus}_{reactants}$ **(1)** • calculation of ΔS_{system} **(1)**	<u>Example of calculation:</u> $\Delta S_{system} = (41.8 + 2 \times 69.9) - (204.5 + 2 \times 205.0)$ Allow just $\Delta S_{system} = \Sigma S^{\ominus}_{products} - \Sigma S^{\ominus}_{reactants}$ –432.9 TE on $\Delta S_{system} = \Sigma S^{\ominus}_{reactants} - \Sigma S^{\ominus}_{products}$ TE on incorrect numbers of moles and transcription errors Ignore units, even if incorrect Ignore SF except 1SF Correct answer with some working scores (2) +432.9 / –297.8 / +297.8 scores (1)	**2**

Question Number	Answer	Additional Guidance	Mark
15(c)(ii)	An answer that makes reference to the following point: • O–H bonds are strong(er than Si–H bonds)	Accept reverse arguments Ignore $\Delta S_{surroundings}$ is (very) positive Ignore reaction is (highly) exothermic / ΔH is (very) negative Allow Si–O bonds are strong(er than Si–H bonds) Allow (covalent) bonding in H_2O / SiO_2 / products is strong Allow formation of product bonds releases more energy (than is required to break reactant bonds) Allow more energy required to break product bonds (than reactant bonds) Ignore any reference to O=O bond strength (which is greater than O–H / Si–O) Do not award intermolecular forces for bonds Do not award $\Delta S_{surroundings}$ is negative Do not award reaction is endothermic / ΔH is positive	**1**

(Total for Question 15 = 15 marks)

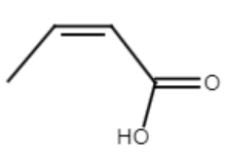
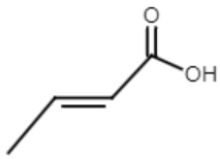
Question Number	Answer	Additional Guidance	Mark
16(a)(i)	• tangent drawn at $t = 0$ **(1)** • calculation of gradient **of tangent** **(1)** • calculation of rate in mol dm^{-3} s^{-1} **(1)**	Example of calculation:  gradient = (-)0.6 ÷ 62 = (-)0.0096774 / (-)9.6774 × 10^{-3} Allow value in range of 0.0086 to 0.011 TE on any **tangent** Ignore sign and units Ignore SF except 1SF rate = (-)0.0096774 ÷ 60 = (-)0.00016129 / (-)1.6129 × 10^{-4} (mol dm^{-3} s^{-1}) Allow value in range of 0.00014 to 0.00019 / 1.4 × 10^{-4} to 1.9 × 10^{-4} TE on any concentration ÷ time value from M2 Ignore sign Ignore SF except 1SF Correct answer with tangent drawn at $t = 0$ scores (3) Correct answer with no tangent at $t = 0$ scores (2)	**3**

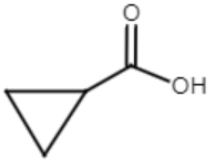
Question Number	Answer	Additional Guidance	Mark
16(a)(ii)	An answer that makes reference to the following points: • working to show determination of two (or more) half-life values **(1)** • (constant half-life so first order and rate =) $k[CH_3CHO]$ **(1)**	eg, time for $[CH_3CHO]$ to fall from 0.6 to 0.3 = 43 – 0 = 43 eg, time for $[CH_3CHO]$ to fall from 0.4 to 0.2 = 68 – 25 = 43 Allow half-lives in range of 42 to 44 (mins) Allow half-lives in range of 2520 to 2640 (s) Accept working from either a statement in words or from working on the graph. Ignore 86 – 43 = 43 (mins) Ignore any attempt to find half-lives by extrapolation of the graph beyond 70 mins **Standalone mark** Do not award any other rate equation Do not award omission of k	**2**

Question Number	Answer		Additional Guidance	Mark
16(b)	• calculation of gradient	**(1)**	Example of calculation: gradient = $\frac{(-8.2 - 9.4)}{(0.0010 - 0.000588)}$ = –42718 (K) Allow value in range of –40500 to –44500 Ignore units Ignore SF except 1SF Do not award omission of negative sign	**4**
	• use of E_a = –gradient × R	**(1)**		
	• calculation of E_a	**(1)**	E_a = –(–42718) × 8.31 = (+)354 990 TE on M1 TE on M2 for omission of negative sign only Accept use of 8.314 for 8.31 Ignore SF except 1SF Ignore units in M3	
	• calculated answer to 3SF **and** units	**(1)**	(+)355 000 J mol^{-1} OR (+)355 kJ mol^{-1} TE on M3 Calculated final answer to 3SF with correct units in allowed range scores (4) gradient of –40500 gives 337 000 J mol^{-1} / 337 kJ mol^{-1} gradient of –44500 gives 370 000 J mol^{-1} / 370 kJ mol^{-1}	

(Total for Question 16 = 9 marks)

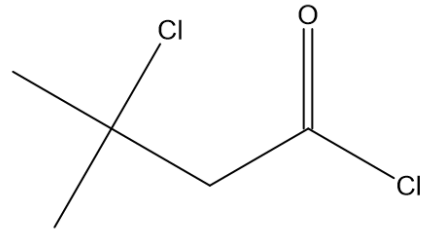
Question Number	Answer	Additional Guidance	Mark
17(a)(i)	An answer that makes reference to the following points: • but-3-enoic acid (for first isomer) **(1)** • 2-methylpropenoic acid (for second isomer) **(1)**	Ignore missing or incorrect hyphens, spaces or commas and use of capitals Accept 3-butenoic acid Allow buten-3-oic acid Allow but-3-en-1-oic acid / 3-buten-1-oic acid Allow "ene" for "en" Do not award "butan" or "butyl" for "but" Accept 2-methylprop-2-enoic acid Accept 2-methyl-2-propenoic acid Allow 2-methylpropen-2-oic acid Allow "ene" for "en" Do not award "propan" or "propyl" for "prop"	**2**

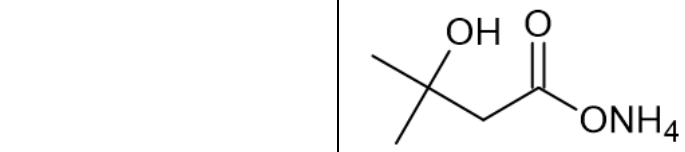
Question Number	Answer	Additional Guidance	Mark
17(a)(ii)	An answer that makes reference to the following points: • correct structure of *Z*-but-2-enoic acid **(1)** • correct structure of *E*-but-2-enoic acid **(1)**	<u>Example of structures:</u>   Allow displayed formula, or any correct combination of formulae Ignore bond lengths and bond angles	**2**

Question Number	Answer	Additional Guidance	Mark
17(a)(iii)	An answer that makes reference to the following point: • correct structure of cyclopropanecarboxylic acid	<u>Example of structure:</u>  Allow displayed or structural formula, or any correct combination of formulae Ignore bond lengths and bond angles	**1**

Question Number	Answer	Additional Guidance	Mark
17(b)(i)	An answer that makes reference to the following points: • $K_2Cr_2O_7$ / potassium dichromate((VI)) **and** H_2SO_4 / sulfuric acid **and** (heat under) **reflux**	If name and formula given both must be correct Accept sodium salts Allow dichromate((VI) ions) / $Cr_2O_7^{2-}$ for $K_2Cr_2O_7$ Allow acidified / H^+ Ignore concentration of acid Do not award use of HCl Do not award mention of acid as catalyst Do not award incorrect oxidation states Ignore distillation	**1**

Question Number	Answer	Additional Guidance	Mark
17(b)(ii)	An answer that makes reference to the following points: • H_2O and HCl reactants **(1)** • NH_4Cl product **and** organic species **and** balanced **(1)**	<u>Example of equation:</u> $(CH_3)_2C(OH)CH_2CN + 2H_2O + HCl \rightarrow (CH_3)_2C(OH)CH_2COOH + NH_4Cl$ Allow H^+ for HCl Allow H_3O^+ for H_2O and HCl Allow H_2O in equation and HCl shown above arrow Ignore just HCl(aq) **M2 dependent on M1** Allow NH_4^+ for NH_4Cl where H^+ used for HCl Allow multiples Allow structural, displayed, skeletal or molecular formulae for organic species Ignore connectivity in organic species Ignore state symbols, even if incorrect $(CH_3)_2C(OH)CH_2CN + 2H_2O + H^+ \rightarrow (CH_3)_2C(OH)CH_2COOH + NH_4^+$ scores (2)	**2**

Question Number	Answer	Additional Guidance	Mark
17(b)(iii)	An answer that makes reference to the following points: • RCOOH group converted to RCOCl group **(1)** • $(CH_3)_2C(OH)CH_2R$ group converted to $(CH_3)_2C(Cl)CH_2R$ **(1)**	Allow displayed or structural formula, or any correct combination of formulae If more than one type of formula given all must be correct <u>Examples of structure:</u> $(CH_3)_2CClCH_2COCl$ scores (2)  scores (2)	**2**

Question Number	Answer	Additional Guidance	Mark
17(b)(iv)	An answer that makes reference to the following point: • correct structure of ammonium salt	Allow displayed or structural formula, or any correct combination of formulae If more than one type of formula given all must be correct <u>Examples of structure:</u> $(CH_3)_2C(OH)CH_2COO^{(-)}NH_4^{(+)}$  Allow $(CH_3)_2C(OH)CH_2COO^-$ (+ NH_4^+) Do not award covalent O–NH_4 Do not award sodium/potassium salt	**1**

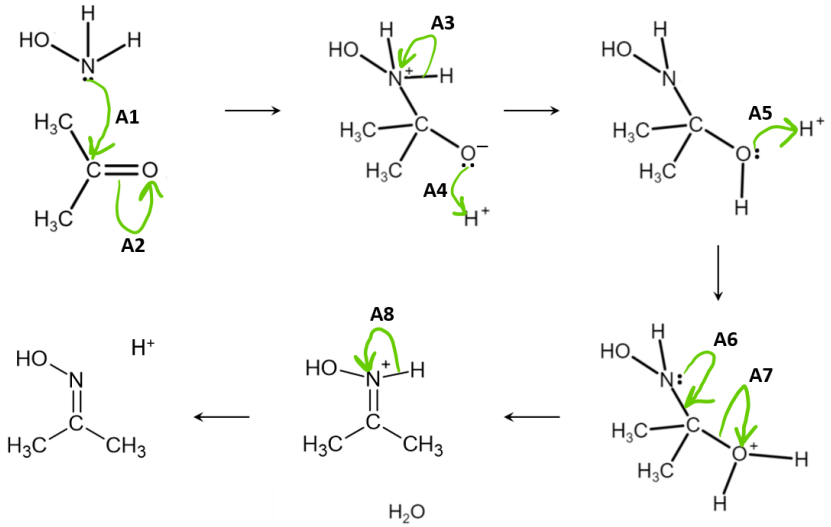
(Total for Question 17 = 11 marks)

Question Number	Answer	Additional Guidance	Mark
18(a)	An answer that makes reference to the following points: Formula of lithium tetrahydridoaluminate(III): • $LiAlH_4$ **and** Essential reaction conditions: • (dry) ether **(1)** Type of reaction: • reduction **(1)** Name of organic product with propanal: • propan-1-ol **(1)** Name of organic product with propanone: • propan-2-ol **(1)**	Do not award any other answer Allow anhydrous / no water Ignore any reference to heat / temperature Do not award any reference to aqueous / acid Ignore redox Ignore (nucleophilic) addition Allow 1-propanol Allow 1-hydroxypropane Ignore propanol / *n*-propanol / *n*-propyl alcohol Ignore primary alcohol Allow 2-propanol Allow 2-hydroxypropane Ignore isopropanol / isopropyl alcohol / sec-propyl alcohol Ignore secondary alcohol Penalise structures for names in M3 and M4 once only	**4**

Question Number	Answer	Additional Guidance	Mark
18(b)	An answer that makes reference to the following points: • silver mirror with propanal **(1)** • no change with propanone **(1)**	 Allow aldehyde for propanal Allow precipitate/coating for mirror Allow black/grey solid for silver mirror Allow ketone for propanone Allow any of the following for no change: no reaction / no observation / nothing / solution remains colourless / no silver mirror	**2**

Question Number	Answer	Additional Guidance	Mark
18(c)	An answer that makes reference to the following points: • CHI_3 product **(1)** • CH_3COONa product **(1)** • remaining species **and** balanced **and** state symbols **(1)**	<u>Examples of equation:</u> $CH_3COCH_3(aq) + 3I_2(aq) + 4NaOH(aq) \rightarrow CH_3COO^{(-)}Na^{(+)}(aq) + CHI_3(s) + 3Na^{(+)}I^{(-)}(aq) + 3H_2O(l)$ $CH_3COCH_3(aq) + 3I_2(aq) + (4Na^+(aq)) + 4OH^-(aq) \rightarrow CH_3COO^-(aq) + (Na^+(aq)) + CHI_3(s) + (3Na^+(aq)) + 3I^-(aq) + 3H_2O(l)$ Accept CH_3COO^- Do not award CH_3COOH Do not award any other organic species Allow multiples Allow $CH_3COCH_3(l)$ Allow $H_2O(aq)$	**3**

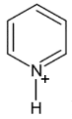
Question Number	Answer	Additional Guidance	Mark
18(d)	An answer that makes reference to the following points: • filter (to collect precipitate) **(1)** • recrystallise **(1)** • (measure) melting temperature (of derivatives) **and** compare to database / data book **(1)**	 Allow collect (precipitate) using Buchner funnel Ignore any reference to colour of precipitate Allow purify **and** crystallise Allow melting point for melting temperature Do not award boiling temperature Allow known set of values for database / data book Ignore (record) IR / NMR / mass spectrum	**3**

Question Number	Answer	Additional Guidance	Mark
18(e)	An answer that makes reference to the following points: • 8 curly arrows **(4)** • 6 or 7 curly arrows **(3)** • 4 or 5 curly arrows **(2)** • 2 or 3 curly arrows **(1)**	Example of mechanism:  A1 and A6 curly arrows must start from N lone pairs Do not award A1 curly arrow if incorrect C=O dipole Ignore incorrect C=O dipole for A2 curly arrow Ignore N–H dipole for A3/A8 curly arrows Do not award A3/A8 curly arrows from N–H bond to H Allow curly arrow A4 from negative charge on O^- Do not award A4/A5 curly arrows starting at H^+ If more than 8 curly arrows shown, each incorrect arrow negates one correct arrow	**4**

(Total for Question 18 = 16 marks)

Total for Section B = 51 marks

Question Number	Answer	Additional Guidance	Mark
19(a)(i)	$C_5H_5NH^+$ K_a: • calculation of inverse log(−5.25) to 2SF **(1)** $CHCl_2COOH$ pK_a: • calculation of $-\log(4.5 \times 10^{-2})$ to 3SF **(1)**	<u>Example of calculation:</u> $(5.6234 \times 10^{-6} =) 5.6 \times 10^{-6}$ Do not award 6×10^{-6} (1.3468 =) 1.35 Do not award 1.4 or 1.34 Penalise inconsistent SF once only Penalise incorrect rounding once only	**2**

Question Number	Answer	Additional Guidance	Mark
19(a)(ii)	An answer that makes reference to the following point: • (Ka =) $\frac{[H^+]\,[C_5H_5N]}{[C_5H_5NH^+]}$	Do not award C_6 for C_5 Do not award non-square brackets Allow $[H_3O^+]$ for $[H^+]$ Allow use of  for C_5H_5N Do not award C_5H_4NH for C_5H_5N Do not award charged C_5H_5N, eg $C_5H_5N^-$ Allow use of  for $C_5H_5NH^+$ Allow $C_5H_6N^+$ for $C_5H_5NH^+$ Do not award omission of charge from $C_5H_5NH^+$	**1**

Question Number	Answer	Additional Guidance	Mark
19(a)(iii)	An answer that makes reference to the following points: • $CH_3CH_2COOH_2^+$ **and** $HCOO^-$ **(1)** • HCOOH A1 **and** $HCOO^{(-)}$ B1 **and** CH_3CH_2COOH B2 **and** $CH_3CH_2COOH_2^{(+)}$ A2 **(1)**	Allow $COOH^-$ Allow A2 and B2 for A1 and B1 Allow B1 and A1 for B2 and A2 TE on M1 for $HCOOH_2^{(+)}$ and $CH_3CH_2COO^{(-)}$ only	**2**

<table>
<tr><th>Question Number</th><th>Answer</th><th>Additional Guidance</th><th>Mark</th></tr>
<tr>
<td>19(a)(iv)</td>
<td>
This question assesses a student’s ability to show a coherent and logically structured answer with linkages and fully-sustained reasoning.

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

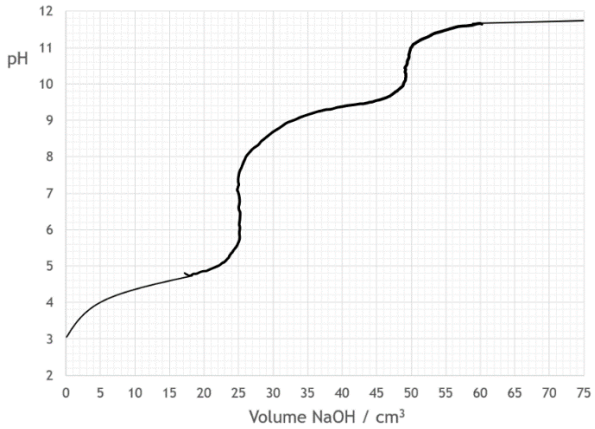
The following table shows how the marks should be awarded for indicative content.
<table>
<tr><th>Number of indicative marking points seen in answer</th><th>Number of marks awarded for indicative marking points</th></tr>
<tr><td>6</td><td>4</td></tr>
<tr><td>5-4</td><td>3</td></tr>
<tr><td>3-2</td><td>2</td></tr>
<tr><td>1</td><td>1</td></tr>
<tr><td>0</td><td>0</td></tr>
</table>
The following table shows how the marks should be awarded for structure and lines of reasoning.
<table>
<tr><th></th><th>Number of marks awarded for structure and sustained lines of reasoning</th></tr>
<tr><td>Answer shows a coherent and 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>
The mark for indicative content should be added to the mark for lines of reasoning. For example, an answer 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 are no linkages between points, the same five indicative marking points would yield an overall score of 3 marks (3 marks for indicative content and no marks for linkages).

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 points: • **IP1:** use of $[H^+] = \sqrt{(K_a \times [HA])}$ • **IP2:** use of $pH = -\log[H^+]$ • **IP3:** indication that $[HA]_{equilibrium}$ is lower than $[HA]_{initial}$ • **IP4:** (because) dissociation (of both acids) is significant • **IP5:** (calculated pH values lower than measured pH values because) [HA] is overestimated in the **calculations** • **IP6:** (difference greatest for) $CHCl_2COOH$ (as is) stronger acid **or** two Cl atoms in $CHCl_2COOH$ are more electron withdrawing than one / stabilise anion more / weaken O–H bond more	If calculations shown, pH values are 2.0775 and 1.3239 Ignore $[H^+] = [A^-]$ assumption is not valid Ignore $[H^+] > [A^-]$ Do not award $[A^-] > [H^+]$ Allow dissociation is not negligible Allow dissociation occurs Do not award dissociation is negligible Do not award dissociation is complete Do not award $[H^+]$ overestimated in calculation due to dissociation of water Allow more dissociated for stronger Ignore strong acid for stronger acid Ignore $CHCl_2COOH$ has larger K_a / smaller p*K*a	

Question Number	Answer	Additional Guidance	Mark
19(b)	An answer that makes reference to the following points:	<u>Example of completed titration curve:</u> 	**3**
	• vertical section at 25 cm^3 **and** with height in the range of 1 to 4 pH units **(1)**	Allow slight slope in range of 24 cm^3 to 26 cm^3	
	• vertical section at 50 cm^3 **and** with height greater than 0.4 pH units **(1)**		
	• (buffered section with) pH 9.3 at 37.5 cm^3 **(1)**	Allow any pH between 9.0 and 9.6 Allow reading of pH from midpoint volume between two vertical sections as TE on M1/M2	

Question Number	Answer	Additional Guidance	Mark
19(c)	**M1 and M2:** • calculation of $[H^+]$ at both pH values **or** calculation of pOH at both pH values **(1)** • calculation of $[OH^-]$ at both pH values **(1)** **M3, M4 and M5 (Method 1):** • calculation of moles of NaOH in 50.0 cm^3 at pH 12.43 **(1)** • calculation of volume of NaOH required at pH 12.00 **(1)** • volume of water required in cm^3 **(1)** **M3, M4 and M5 (Method 2):** • expression for dilution **(1)** • calculation of volume of NaOH required at pH 12.00 **(1)** • volume of water required in cm^3 **(1)**	Example of calculation: $[H^+] = 10^{-12.43} = 3.7154 \times 10^{-13}$; $[H^+] = 10^{-12.00} = 1 \times 10^{-12}$ **or** pOH = 14 – 12.43 = 1.57; pOH = 14 – 12.00 = 2.00 $[OH^-] = 1 \times 10^{-14} \div 3.7154 \times 10^{-13} = 10^{-1.57} = 0.026915$ $[OH^-] = 1 \times 10^{-14} \div 1 \times 10^{-12} = 10^{-2.00} = 0.01$ $0.026915 \times \frac{50.0}{1000} = 1.3458 \times 10^{-3}$ $1.3458 \times 10^{-3} \div 0.01 = 0.13458\ dm^3 = 134.58\ cm^3$ 134.58 – 50.0 = 84.58 / 84.6 / 85 (cm^3) TE on M4 $c_1v_1 = c_2v_2$ $v_2 = \frac{c_1v_1}{c_2} = \frac{0.026915}{0.01} \times 50.0 = 134.58\ cm^3$ 134.58 – 50.0 = 84.58 / 84.6 / 85 (cm^3)	**5**

	M3, M4 and M5 (Method 3): • calculation of moles of NaOH in 50.0 cm^3 at pH 12.43	**(1)**	$0.026915 \times \frac{50.0}{1000} = 1.3458 \times 10^{-3}$	
	• calculation of moles of NaOH in 50.0 cm^3 at pH 12.00 **and** difference in moles of NaOH	**(1)**	$0.01 \times \frac{50.0}{1000} = 5 \times 10^{-4}$ **and** $1.3458 \times 10^{-3} - 5 \times 10^{-4} = 8.458 \times 10^{-4}$	
	• calculation of volume of NaOH required	**(1)**	$8.458 \times 10^{-4} \div 0.01 = 84.58\ (cm^3)$	
	M3, M4 and M5 (Method 4): • difference in concentrations of NaOH	**(1)**	$0.026915 - 0.01 = 0.016915$	
	• difference in moles of NaOH	**(1)**	$0.016915 \times \frac{50.0}{1000} = 8.458 \times 10^{-4}$	
	• calculation of volume of NaOH required	**(1)**	$8.458 \times 10^{-4} \div 0.01 = 84.58\ (cm^3)$	
	OHER METHODS MAY BE POSSIBLE		If no other marks awarded, calculation of $[H^+]$/pOH **and** calculation of $[OH^-]$ at either pH scores (1)	

(Total for Question 19 = 19 marks)

Total for Section C = 19 marks

Total for Paper = 90 marks

Pearson Education Limited. Registered company number 872828
with its registered office at 80 Strand, London, WC2R 0RL, United Kingdom