PEARSON EDEXCEL A-LEVEL CHEMISTRY · 9CH0

CHEMISTRY



MARK SCHEME

TOPIC 12: ACID-BASE EQUILIBRIA

SCORE	PERCENTAGE
/242	%

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buffer solution.

(2)

(Total for question = 2 marks)

Mark Scheme

Q1.

Question Number	Acceptable Answers	Additional Guidance	Mark
	• correct acid-base pairs identified **and** linked	Examples of acid-base pairs $CH_3COOH + HCOOH \rightarrow CH_3COOH_2^+ + HCOO^-$ base 2/B2 acid 1/A1 acid 2/ A2 base 1/B1 **or** $CH_3COOH + HCOOH \rightarrow CH_3COOH_2^+ + HCOO^-$ base acid acid base **or** $CH_3COOH + HCOOH \rightarrow CH_3COOH_2^+ + HCOO^-$ base / B acid / A conjugate acid / CA conjugate base / CB Allow any clear identification of acid and base **and** connection between the correct pairs	**(1)**

Q2.

Question Number	Correct Answer	Reject	Mark
	C		**1**

Q3.

Question Number	Acceptable Answers	Reject	Mark
(a)(i)	$HC_2O_4^-(aq) + H_2O(l) \rightleftharpoons C_2O_4^{2-}(aq) + H_3O^+(aq)$ (or →) ALLOW $H_2O(aq)$ Equation **(1)** states **(1)** ALLOW for 1 mark $HC_2O_4^-(aq) \rightleftharpoons C_2O_4^{2-}(aq) + H^+(aq)$ States mark is not stand alone but can be awarded if the equation has a minor error e.g. an incorrect charge		**2**

Question Number	Acceptable Answers	Reject	Mark
(a)(ii)	$K_a = [C_2O_4^{2-}][H_3O^+] / [HC_2O_4^-]$ OR $K_a = [C_2O_4^{2-}][H^+] / [HC_2O_4^-]$ No TE on incorrect equation in (a)(i) Penalise incorrect charges in (i) and (ii) once only	$K_a =$ $[H^+]^2 / [HC_2O_4^-]$ $[H^+][A^-]/ [HA]$	**1**

Question Number	Acceptable Answers	Reject	Mark
(a) (iii)	No TE on (a)(ii) $K_a = 10^{-4.28}$ OR 5.24807×10^{-5} (mol dm^{-3}) **(1)** $K_a = [H^+]^2 / [HC_2O_4^-]$ $K_a = [H^+]^2 / 0.050$ $[H^+] = \sqrt{(0.05 \times 10^{-4.28})} = 1.61988 \times 10^{-3}$ (mol dm^{-3}) **(1)** TE on incorrect K_a value pH = −log 1.61988×10^{-3} = 2.7905 = 2.8 **(1)** For final mark TE on algebraic / arithmetical errors providing pH ≥ 1.3 Correct answer with no working scores 3 Ignore SF except 1 SF		**3**

Question Number	Acceptable Answers	Reject	Mark
(b)(i)	IGNORE explanations **First mark:** $HC_2O_4^-$/hydrogenethanedioate ion ionization negligible ALLOW Acid for $HC_2O_4^-$ Slight / partial / incomplete / does not dissociate for negligible OR $[HC_2O_4^-]_{equilibrium} = [HC_2O_4^-]_{initial} / 0.050$ (mol dm^{-3}) **(1)** **Second mark:** $[H^+]$ due to ionization of water negligible OR auto ionization of water negligible OR $[H^+]$ only due to ionization of $HC_2O_4^-$/acid OR $[C_2O_4^{2-}] = [H^+]$ **(1)** IGNORE references to temperature and to HA and A^- Penalize omission of [] in discussion once only	Use of $NaHC_2O_4$ for $HC_2O_4^-$ OR sodium hydrogen-ethanedioate for hydrogen-ethanedioate ion throughout this item	**2**

Question Number	Acceptable Answers	Reject	Mark
(b)(ii)	Ethanedioic acid is a (much) stronger acid (than hydrogenethanedioate ion / sodium hydrogenethanedioate) OR Ethanedioic acid has a (much) smaller pK_a (than hydrogenethanedioate) OR Ionization / dissociation of ethanedioic acid is (much) greater (than hydrogenethanedioate) OR Reverse arguments **(1)** IGNORE $NaHC_2O_4$ ionization negligible Approximation of negligible ionization invalid / incorrect OR $[H_2C_2O_4]_{equilibrium}$ not equal to $[H_2C_2O_4]_{initial}$ **(1)** No TE on 18(a)(iii) IGNORE Second ionization occurs	Ethanedioic acid is a strong acid / fully dissociated Just 'approximation invalid'	**2**

Question Number	Acceptable Answers	Reject	Mark
(c)(i)	Start pH at 2.8 ALLOW 2—4 **(1)** Vertical section at 25 cm^3 within pH range 6-11 and 2.5-4 units long **(1)** end pH (approaching) value in range 12-13 (asymptotically) **(1)**	deviation from vertical maximum before final pH	**3**

Question Number	Acceptable Answers	Reject	Mark
(c)(ii)	**First mark:** Methyl yellow range = 2.9—4 and the phenolphthalein range = 8.2—10 ALLOW pK_{in} (methyl yellow) = 3.5 and pK_{in} (phenolphthalein) = 9.3 **(1)** **Second mark:** (The volumes are different) because ethanedioic acid is dibasic / diprotic / has two **replaceable/acidic** hydrogen atoms ALLOW dicarboxylic (acid) (therefore there are two stages to the neutralization) OR Methyl yellow range coincides with neutralization of first proton and phenolphthalein range coincides with neutralization of second proton **(1)**		**2**

Q4.

Question Number	Correct Answer	Reject	Mark
	A		**1**

Q5.

Question Number	Correct Answer	Reject	Mark
	D		**1**

Q6.

Question Number	Correct Answer	Reject	Mark
	A		**1**

Q7.

Question Number	Answer	Additional Guidance	Mark
	• calculation of $[H^+]$ **(1)** • use of K_a expression to calculate K_a **(1)** • calculation of pK_a **(1)**	Example of calculation $[H^+] = 10^{-2.20} = 6.3096 \times 10^{-3}$ (mol dm^{-3}) $K_a = (6.3096 \times 10^{-3})^2 / 0.240$ $= 1.6588 \times 10^{-4}$ $pK_a = -\log [1.6588 \times 10^{-4}] = 3.7802$ ignore SF except 1SF ignore units allow TE throughout correct answer with no working scores 3	**(3)**

Q8.

Question Number	Correct Answer	Reject	Mark
	A		**1**

Q9.

Question Number	Answer	Mark
	The only correct answer is A ($CH_3COOH > CH_2ClCOOH > HCl$) *B is incorrect because HCl is the only strong acid, so would have the lowest pH* *C is incorrect because $CH_2ClCOOH$ is stronger than CH_3COOH as the Cl atom stabilises the anion* *D is incorrect because the stronger the acid the lower the pH, hence these are in reverse order*	**(1)**

Q10.

Question Number	Answer	Additional Guidance	Mark
	An answer that makes reference to one of the following points • the loss of a hydrogen from the O–H group is made possible by the delocalisation of charge of/stabilisation on the carboxylate ion **or** the loss of a hydrogen from a methyl group would produce a carbanion with no stabilisation **or** similar electronegativies of carbon and hydrogen means that there is a lack of C–H bond polarity **or** the enthalpy of hydration of the ions outweighs the energy needed to break the O–H bond	Allow the C–H bond is not polar but the O–H bond is/ O–H bond is more polar Do not award the O–H bond is weaker than the C–H bond	(1)

Q11.

Question Number	Acceptable Answers	Additional Guidance	Mark
(a)	Any one from: Catalyst / speeds up reaction / increases rate / increases rate of attainment of equilibrium / lowers activation energy	Ignore any mention of protonation or mechanism for catalysis Do not award additional incorrect types of reaction	**(1)**

Question Number	Acceptable Answers	Additional Guidance	Mark
(b)(i)	• calculation of moles of H^+ in 25.0 cm^3 **(1)** • calculation of moles of H^+ in 250 cm^3 flask **(1)**	Ignore SF throughout 8(b)(i) to 8(c)(ii) except 1 SF, which should be penalised once only Example of calculation: (moles NaOH = 0.200 x $\frac{23.60}{1000}$) = 0.00472 (mol) (= mol H^+ in 25.0 cm^3) (= 10 x 0.00472) = 0.0472 (mol) (in 250 cm^3) Allow TE for M2 on moles of NaOH Correct answer with or without working scores 2 marks	**(2)**

Question Number	Acceptable Answers	Additional Guidance	Mark
(b)(ii)	• subtracts moles of H^+ in HCl from answer to (b)(i)	Example of calculation: 0.0472 – 0.00400 = 0.0432 (mol) Allow TE on answer to part (b)(i)	**(1)**

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Question Number	Acceptable Answers	Additional Guidance	Mark
(c)(i)	• calculation of moles of CH_3COOH that have reacted	Example of calculation: (0.105 — 0.0432) = 0.0618 Allow TE on part (b)(ii) unless negative value	(1)

Question Number	Acceptable Answers	Additional Guidance	Mark
(c)(ii)	• calculation of equilibrium moles of $CH_3CH_2CH_2OH$ **(1)** • calculation of equilibrium moles of $CH_3COOCH_2CH_2CH_3$ **(1)** • calculation of equilibrium moles of H_2O **(1)**	Example of calculation: 0.0800 — 0.0618 = 0.0182 0.0618 0.111 + 0.0618 = 0.1728 Allow TE on answer to part (c)(i) unless negative value	(3)

Question Number	Acceptable Answers	Additional Guidance	Mark
(d)(i)	(K_c =) $\frac{[CH_3COOCH_2CH_2CH_3][H_2O]}{[CH_3COOH][CH_3CH_2CH_2OH]}$	IGNORE state symbols even if incorrect Do not award round brackets	(1)

Question Number	Acceptable Answers	Additional Guidance	Mark
(d)(ii)	An explanation that makes reference to the following points: • Same number of moles/molecules on both sides of the equation **(1)** • (so) volume / V cancels in K_c expression **(1)**	2 marks could be scored by a correct mathematical expression showing V or dm^3 cancel Allow same number of terms on top and bottom of K_c expression Allow units cancel out Allow "**all** divided by the same volume"	(2)

Question Number	Acceptable Answers	Additional Guidance	Mark
(d)(iii)	• calculates value of K_c **(1)** • final value of K_c quoted to 2 or 3 SF **(1)**	Example of calculation $K_c = \frac{(0.0618) \times (0.1728)}{(0.0432) \times (0.0182)} = 13.58241758$ = 14 / 13.6 (no units) Correct answer with no working gains full marks Ignore units No TE on wrong K_c expression	2

Question Number	Acceptable Answers	Additional Guidance	Mark
(e)	An explanation that makes reference to the following points: • the equilibrium shifts to the left **or** the mixture absorbs carbon dioxide from the atmosphere **(1)** • so the mixture is (becoming more) acidic / the acid reforms **(1)**	Mark independently Allow no longer alkaline Do not award just "pH decreases"	**(2)**

Question Number	Acceptable Answers	Additional Guidance	Mark
(f)	An explanation that makes reference to the following points: • carry out / repeat experiment **and** leave for longer than a week **(1)** • the titre value / K_c value will remain unchanged (if equilibrium has been established) **(1)**	Ignore pH probes / checking pH Allow repeat experiment **and** check titres within first week Allow moles / concentration are unchanged Ignore just "results unchanged"	**(2)**

Question Number	Acceptable Answers	Additional Guidance	Mark
(g)	An answer that makes reference to the following points: • K_c value will be greater than that calculated in (d)(iii) **(1)** • because the (forward) reaction is endothermic **or** backward / reverse reaction is exothermic **(1)**	M2 depends on M1 Ignore References to the equilibrium position shifting to the right (with increasing temperature)	**(2)**

Q12.

Question Number	Correct Answer	Reject	Mark
(a)(i)			**2**

	$CH_2CHCHCH_2$	CO	H_2O	$HOOC(CH_2)_4COOH$
ΔH_f / kJ mol^{-1}	+109.9	**−110.5**	**−285.8**	−994.3
S / J mol^{-1} K^{-1}	278.7	**197.6**	**69.9**	250.0

4 values correct **(2)** marks

3 / 2 values correct **(1)** mark

0 / 1 values correct **(0)** marks

Question Number	Correct Answer	Reject	Mark
(a)(ii)	−994.3 − [+109.9 + (2 x −110.5) + (2 x −285.8)] **(1)** = − 311.6 (kJ mol^{-1}) **(1)** Allow TE from (a) **NOTE** If both −110.5 and −285.8 are not doubled, answer CQ = −707.9 (kJ mol^{-1}) for **1** mark Ignore SF except 1 SF		**2**

Question Number	Correct Answer	Reject	Mark
(a)(iii)	250(.0) − [278.7 + (2 x 197.6) + (2 x 69.9)] **(1)** = −563.7 (J mol^{-1} K^{-1}) **(1)** Allow TE from (a) **NOTE** If both 197.6 and 69.9 are not doubled, answer CQ = −296.2 (J mol^{-1} K^{-1}) for **1** mark Ignore SF except 1 SF		**2**

Question Number	Correct Answer	Reject	Mark
(a) (iv)	ΔS_{surr} at 298 K = $-\Delta H/T$ **(1)** = − (−311.6 x 1000) / 298 = (+) **1045.6** (J mol^{-1} K^{-1}) Allow TE from (a)(ii) e.g. ΔS_{surr} = (+)2375.5(0) (J mol^{-1} K^{-1}) scores (2) if no doubling in (a)(ii) **(1)** $\Delta S_{tot} = \Delta S_{surr} + \Delta S_{sys}$ / ΔS_{tot} = 1045.6 −563.7 / ΔS_{tot} = (+) **481.9** (J mol^{-1} K^{-1}) Allow TE from (a)(ii) and (a)(iii) **(1)** Allow correct answers given in **kJ mol^{-1} K^{-1}** e.g. 0.4819 **kJ mol^{-1} K^{-1}** Ignore SF except 1 SF If candidates forget to convert ΔH into J mol^{-1}, then ΔS_{tot} = −562.7 (J mol^{-1} K^{-1}) would score (2) if correct working is included		**3**

Question Number	Correct Answer	Reject	Mark
(a)(v)	(Decrease in T) **1st mark: consideration of ΔS_{system}** ΔS_{system} is not (significantly) changed / is unchanged / remains (approximately) constant **(1)** **2nd mark: consideration of ΔS_{surr}** ΔS_{surr} or $-\Delta H/T$ is more positive / larger / greater COMMENT ALLOW 'less negative' **(1)** **3rd mark: consideration of ΔS_{total}** (So) increases ΔS_{tot} / makes ΔS_{tot} more positive / makes ΔS_{tot} greater **(1)** **NOTE** IF no reference / an incorrect reference made to ΔS_{system}, then only the 2nd and 3rd marks can be awarded **NOTE** If candidate states that ΔS_{surr} becomes **less +ve**, no M2 But if **then** states CQ that ΔS_{tot} decreases award M3 as a TE		**3**

Question Number	Correct Answer	Reject	Mark
(b)	**DIMINISHING:** (Peak between) **1669 – 1645** (cm^{-1}) (due to C=C) **OR** (Peak between) **3095 – 3010** (cm^{-1}) (due to alkene C-H) **(1)** **INCREASING:** (Peak between) **1725 – 1700** (cm^{-1}) (due to C=O in carboxylic acid) **OR** (Peaks due to alkane C–H bonds at) EITHER **2962 – 2853** (cm^{-1}) OR **1485 – 1365** (cm^{-1}) **ALLOW** (Peak between) **3300 – 2500** (cm^{-1}) (due to O–H in carboxylic acid) **(1)**	**1740 – 1720** **3750 – 3200**	**2**

Question Number	Correct Answer	Reject	Mark
(c)	(Makes it taste) sour / sharp / tart IGNORE 'acidic' / 'bitter' NOTE Contradictory answers (e.g. 'sharp and sweeter') score **(0)**	fruity sweet(er) none	**1**

Q13.

Question Number	Answer	Additional Guidance	Mark
(i)	• named indicator **(1)** • matching colour **change** **(1)** • pH range (of indicator) / quoted range lies (completely) in the vertical region (on the titration curve) **or** indicator will change colour in the vertical / straight / steep region of the graph **or** pH range of indicator and pH range of vertical region of the graph stated, as long as they overlap **(1)**	<u>Examples of indicators and colour changes</u> phenol red – red to orange / yellow phenolphthalein ((in ethanol)) – red / pink to colourless (do not allow purple or clear) bromothymol blue – blue to yellow M2 is conditional on a correct indicator in M1 Do not allow unsuitable indicators e.g. litmus Stand alone mark Allow pK_{in} (± 1) is in the vertical jump **or** pK_{in} is nearest to the pH at the end / equivalence point **or** indicator will change colour at the end / equivalence point **or** (because it is a) titration of a weak acid with a strong base	**(3)**

Question Number	Answer	Mark
(ii)	**The only correct answer is C** ***A*** *is not correct because used the volumes the wrong way round* ***B*** *is not correct because not used the volume of glycolic acid from the graph* ***D*** *is not correct because used a 1:2 mole ratio*	**(1)**

Question Number	Answer	Mark
(iii)	**The only correct answer is C** ***A*** *is not correct because this is the pH of glycolic acid* ***B*** *is not correct because this is the pH at the end of the vertical jump in the curve* ***D*** *is not correct because this is the pH at the start of the vertical jump*	**(1)**

Q14.

Question Number	Acceptable Answer	Additional Guidance	Mark
(i)	• calculation of K_a **(1)** • calculation of $[H^+]$ **(1)** • calculation of pH **(1)**	Example of calculation $K_a = 10^{-pKa} = 10^{-9.24} = 5.7544 \times 10^{-10}$ (mol dm^{-3}) $[H^+] = \sqrt{K_a[H_3BO_3]} = \sqrt{5.7544 \times 10^{-10} \times 0.05}$ $= 5.364 \times 10^{-6}$ (mol dm^{-3}) TE on K_a $pH = -\log_{10}[H^+] = -\log_{10} 5.364 \times 10^{-6}$ $= 5.2705 / 5.271 / 5.27 / 5.3$ TE on $[H^+]$ provided pH is >2 and <7 Accept alternative methods, for example $[H^+] = \sqrt{K_a[H_3BO_3]}$ $pH = ½pK_a - ½\log[H_3BO_3]$ **(1)** $= ½9.24 - ½\log 0.05$ **(1)** $= 5.2705 / 5.271 / 5.27 / 5.3$ **(1)** Alternative method: $K_a = 10^{-pKa} = 10^{-9.24} = 5.7544 \times 10^{-10}$ (mol dm^{-3}) **(1)** $[H^+]^2 = K_a([H_3BO_3] - [H^+])$ $= 5.7544 \times 10^{-10} \times (0.05 - [H^+])$ $[H^+] = 5.135 \times 10^{-6}$ **(1)** pH = 5.29 **(1)** Ignore SF except 1SF Correct answer without working scores 3 marks	**(3)**

Question Number	Acceptable Answer	Additional Guidance	Mark
(ii)	An answer that makes reference to the following points: • $[H^+] = [H_2BO_3^-]$ **or** no H^+ from the (ionisation of) water / ionisation of water is negligible **or** H^+ is only from the acid **or** no H^+ from ionisation of $H_2BO_3^-$ **(1)** • ionisation / dissociation of the acid is negligible / very small / insignificant **or** $[H_3BO_3]_{initial} = [H_3BO_3]_{equilibrium}$ **or** $[H_3BO_3]_{equilibrium} = 0.05$ (mol dm^{-3}) **or** $[H^+]/[H_2BO_3^-] << [H_3BO_3]$ **or** $[H_3BO_3]$ / acid concentration remains constant **or** $[H_3BO_3]_{equilibrium} = [H_3BO_3]_{initial} - [H^+]$ used in calculation in (i)	Allow $[A^-]$ for $[H_2BO_3^-]$ / [HA] for $[H_3BO_3]$ Allow any of the expressions described in words Allow approximately equal to for = (in symbols or words) Ignore reference to standard conditions Do not award two marks from the same marking point Allow the effect of the third ionisation is negligible Ignore partial dissociation / not completely dissociated Do not award H_3BO_3 / [HA]is completely dissociated	**(2)**

Q15.

Question Number	Acceptable Answers	Additional Guidance	Mark
	• (a Brønsted-Lowry acid is a) proton donor	Allow donates / gives away protons / H^+ (ions) / hydrogen ions Allow releases / loses protons / H^+ / hydrogen ions Do not award 'donates H_3O^+ (ions)'	**(1)**

Q16.

Question Number	Correct Answer	Reject	Mark
	C		1

Q17.

Question Number	Correct Answer	Reject	Mark
	B		**1**

Q18.

Question Number	**Answer**	**Mark**
	The only correct answer is B ($NaOH(aq)$ and excess $CH_3COOH(aq)$) ***A*** *is incorrect because the solutions would not form a buffer* ***C*** *is incorrect because the solutions would not form a buffer* ***D*** *is incorrect because the solutions would not form a buffer*	**(1)**

Q19.

Question Number	Correct Answer	Reject	Mark
	A		1

Q20.

Question Number	Correct Answer	Reject	Mark
	D		**1**

Q21.

Question Number	Answer	Mark
	The only correct answer is D (resists changes in pH if small quantities of acid or base are added) **A** *is not correct because buffer solutions can be alkaline or acidic* **B** *is not correct because buffers do not always contain equal numbers of moles of the acid and its conjugate base* **C** *is not correct because a buffer does not prevent any change in pH*	**(1)**

Q22.

Question Number	Answer	Additional Guidance	Mark
	An answer that makes reference to the following points: • carbon dioxide dissolved in the blood forms carbonic acid (and so this concentration increases) **(1)** • the equilibrium will shift to the right and produces more H^+/acid ions **(1)** • the (high) concentration of hydrogencarbonate ions suppress the ionisation of carbonic acid (to help to control pH) **or** the (large) reservoir/excess of hydrogencarbonate ions combine with the H^+ ions (to help to control blood pH) **(1)**	Can be shown in an equation Do not award 'CO_2 reacts with H^+ to form carbonic acid' Allow Carbonic acid (partially) dissociates to produce H^+ Do not award 'CO_2 reacts with H^+ so equilibrium shifts to the right to produce more H^+' Ignore general comments about the effects of adding acid and/or alkali to a buffer which do not relate to carbon dioxide	**(3)**

Q23.

Question Number	Answer	Additional Guidance	Mark
	• calculation of the amount of NaOH / salt **(1)** • calculation of initial amount of acid **(1)** • calculation of the amount of acid left **(1)** • calculation of $[H^+]$ **(1)**	Example of calculation amount of NaOH = amount of salt formed $=0.100 \times 20.0/1000 = 0.00200$ initial amount of acid $= 0.150 \times 25.0/1000$ $= 0.00375$ amount of acid left $= 0.00375 - 0.00200$ $= 0.00175$ total volume = 20.0 + 25.0 = 45.0 (cm^3) [salt] = 0.00200 x 1000/45.0 = 0.0444 (mol dm^{-3}) [acid] = 0.00175 x 1000/45.0 = 0.0389(mol dm^{-3}) $K_a = \frac{[H^+][salt]}{[acid]}$ so $[H^+] = K_a\frac{[acid]}{[salt]}$ $[H^+] = 1.74 \times 10^{-5} \times 0.0389/0.0444$ $= 1.52446 \times 10^{-5}$ (mol dm^{-3}) Allow use of moles instead of concentrations	**(5)**

	• calculation of pH **(1)**	$pH = -\log[H^+] = -\log(1.52446 \times 10^{-5})$ $= 4.817 / 4.82 / 4.8$ Allow TE for each step Ignore SF except 1 SF Correct answer without working score (5) Allow alternative methods, for example $pH = pK_a - \log\frac{[acid]}{[salt]}$ $pH = -\log 1.74 \times 10^{-5} - \log\frac{0.0389}{0.0444}$ pH = 4.817 / 4.82 / 4.8 scores M4 and M5 **or** $pH = pK_a + \log\frac{[salt]}{[acid]}$ $pH = -\log 1.74 \times 10^{-5} + \log\frac{0.0444}{0.0389}$ pH = 4.817 / 4.82 / 4.8 scores M4 and M5	

Q24.

Question Number	Answer	Additional Guidance	Mark
(i)	• calculation of acid concentration (1) • calculation of salt concentration (1) • calculation of hydrogen ion concentration (1) • calculation of pH (1)	Example of calculation [Acid] = ((0.100 x (20 ÷ 50)) = 0.04 (mol dm^{-3}) [A^-] = ((0.305 x (30 ÷ 50)) = 0.183 (mol dm^{-3}) [H^+] = 1. 52 x 10^{-5} mol x (0.04 ÷ 0.183) = 3.322 x 10^{-6} (mol dm^{-3}) pH= -log(3.322 x 10^{-6}) = 5.48/5.5 Correct answer without working scores (4) Ignore SF except 1SF Allow M3 and M4 if just moles and no volumes are used Accept use of the Henderson-Hasselbalch equation	(4)

Question Number	Answer	Additional Guidance	Mark
(ii)	An answer which includes • suitable equation(s) (1) • The pH stays approximately constant because there is a large reservoir of undissociated acid and so the ratio of acid:salt does not change (1)	Example equation $C_3H_7COOH + NaOH \rightarrow C_3H_7COONa + H_2O$ OR $C_3H_7COOH + OH^- \rightarrow C_3H_7COO^- + H_2O$ Allow $OH^- + H^+ \rightarrow H_2O$ followed by $C_3H_7COOH \rightarrow C_3H_7COO^- + H^+$ Allow use ⇌ of in all of above equations Allow (The pH stays approximately constant) as the hydroxide ions react to form water and butanoic acid dissociates to replace the hydrogen ions used up	(2)

Q25.

Question Number	Answer	Additional Guidance	Mark
	• (M1) calculation of concentration of diluted acid (1) • (M2) calculation of pH (1)	Example of calculation c=(15 x 15.9 / 100) = 2.385 (mol dm^{-3}) pH=−log(2.385) = −0.377/−0.38 / −0.4 TE on M1 provided answer is <7 Final answer without working scores (2) Ignore SF	(2)

Q26.

Question Number	Correct Answer	Reject	Mark
	C		1

Q27.

Question Number	Answer	Additional Guidance	Mark
(i)	• expression for K_a (1) • calculation of $[H^+]$ (1) • calculation of pH to 2/3 SF (1)	Example of calculation $K_a = \frac{[H^+] \times [A^-]}{[HA]}$ $[H^+] = \sqrt{(K_a \times [HA])} = \sqrt{(1.35 \times 10^{-6})}$ $= 1.16... \times 10^{-3}$ (mol) pH= -log(1.16... x 10^{-3}) = 2.93/2.9 TE on M2 provided answer <7 Final answer without working scores (3)	(3)

Question Number	Answer	Additional Guidance	Mark
(ii)	An answer which makes reference to the following points • (assumption 1) $[C_2H_5COOH]_{initial}=[C_2H_5COOH]_{eqm}$ (1) • (assumption 2) $[H^+]=[C_2H_5COO^-]$ (1)	ACCEPT assumptions in any order Allow HA for C_2H_5COOH Allow A^- for $C_2H_5COO^-$ Dissociation of propanoic acid is negligible Ignore propanoic acid is a weak acid ALLOW for M2 "Negligible $[H^+]$ from water" Ignore reference to standard conditions	(2)

Q28.

Question number	Acceptable Answer	Additional Guidance	Marks
(i)	• pH = – log[H^+(aq)]	Allow lg / $\log_{10}$ / lg_{10} Ignore state symbol	**1**

Question number	Acceptable Answer	Additional Guidance	Marks
(ii)	HCl(aq): • calculation of pH (1) HCOOH(aq): • rearrangment of K_a equation to find [H^+(aq)] (1) • calculation of [H^+(aq)] (1) • calculation of pH (1)	HCl(aq): pH = – log 0.0540 = 1.27 HCOOH(aq): $[H^+(aq)] = \sqrt{K_a} \times [HCOOH(aq)]$ / $= \sqrt{1.60 \times 10^{-4}} \times 0.0540$ $[H^+(aq)] = 2.94 \times 10^{-3}$ (mol dm^{-3}) pH = $(- \log 2.94 \times 10^{-3})$ = 2.53 penalise lack of 2 dp in first and fourth marks once only	**4**

Q29.

Question Number	Acceptable Answers	Additional Guidance	Mark
	• calculates moles of X^- / NaOH present in the mixture **(1)** • calculates moles of HX which remain unreacted **(1)** • calculates / shows ratio of [HX] to $[X^-]$ OR ratio of moles of HX : X^- (as total V cancels) **(1)** • re-arranges K_a or pK_a expression correctly and substitutes appropriate values **(1)** • final pH to 2 or 3SF **(1)**	Example of calculation: (moles of X^- = mol NaOH = $\frac{0.8(00) \times 10.5}{1000}$) = $0.0084(0) / 8.4(0) \times 10^{-3}$ (mol) (moles of HX – mol NaOH = $\frac{0.92(0) \times 25.0}{1000} - 0.0084(0)$ = $0.023(0) - 0.0084(0)$) = $0.0146 / 1.46 \times 10^{-2}$ (mol) [HX] = $\frac{0.0146}{0.0355}$ **and** $[X^-] = \frac{0.0084(0)}{0.0355}$ = 0.411 **and** 0.237 (mol dm^{-3}) Allow use of the ratio of the moles as above (as total V cancels) $[H^+] = K_a \times \frac{[HX]}{[X^-]} = 5.25 \times 10^{-5} \times \frac{0.411}{0.237}$ $[H^+] = 9.10443038 \times 10^{-5}$ (mol dm^{-3}) pH = 4.04 Allow use of pH expression to get answer: $pH = pK_a - \log \frac{[HX]}{[X^-]}$ or $pK_a + \log \frac{[X^-]}{[HX]}$	**(5)**

		ALLOW TE M5 for calculation of pH from any $[H^+]$ Correct answer with no working scores (5)	

Q30.

Question Number	Acceptable Answers	Reject	Mark
(a)(i)	Aldehydes often contain (carboxylic) **acid** formed by oxidation (by the oxygen in air)		**1**

Question Number	Acceptable Answers	Reject	Mark
(a)(ii)	A larger volume of sodium carbonate solution is neutralized / a larger volume of carbon dioxide forms / faster reaction / more effervescence / more vigorous ALLOW reverse argument for impure aldehyde	(The old stock of) aldehyde does not react	**1**

Question Number	Acceptable Answers	Reject	Mark
(a)(iii)	$Na_2CO_3(aq) + 2C_3H_7COOH(aq) \rightarrow$ $2C_3H_7COO^{(-)}Na^{(+)}(aq) + CO_2(g) + H_2O(l)$ Correct balanced equation **(1)** Correct state symbols on correct species **(1)** ALLOW $H_2O(aq)$ $C_3H_7COO^{(-)}Na^{(+)}(s)$ $C_3H_7COOH(l)$	$NaCO_3$	**2**

Question Number	Acceptable Answers	Reject	Mark
(a)*(iv)	3300 -2500 (cm^{-1}) AND O-H (stretching) **(1)** 1725 – 1700 (cm^{-1}) AND C=O (stretching) **(1)** ALLOW single numbers or ranges within these ranges ALLOW 1300-1250 (cm^{-1}) AND C-O in COOH Very broad (O-H) due to hydrogen bonding **(1)**	COOH (group) COOH (group) Hydrogen Bonding in C=O	**3**

Question Number	Acceptable Answers	Reject	Mark
(a)(v)	**First mark** (stand alone) 4 peaks OR 4 hydrogen environments ALLOW 4 chemical shifts **(1)** **Second and Third Marks** Splitting pattern: ($CH_3CH_2CH_2COO\underline{\mathbf{H}}$) singlet /1 line ($CH_3CH_2C\underline{\mathbf{H_2}}COOH$) triplet / three lines ($CH_3C\underline{\mathbf{H_2}}CH_2COOH$) sextuplet / sextet / six lines ($C\underline{\mathbf{H_3}}CH_2CH_2COOH$) triplet / three lines All four correct **(2)** any three **(1)** ALLOW No splits, 2 splits, five splits, 2 splits scores 2 1,3,6,3 'splits' scores 1 mark	 1 split 3 splits 6 splits 3 splits	**3**

Question Number	Acceptable Answers	Reject	Mark
(b)	Start pH at 2.9 ALLOW 2—4 **(1)** Initial sharp rise to buffer region then vertical section at 25 cm^3 ALLOW Gradual rise to vertical section at 25 cm^3 **(1)** Vertical within pH range 6-11 **and** 2.5-4 units long **(1)** End pH value in range 12-13 **(1)**	 Horizontal from start deviation from vertical maximum before final pH Graph ending before 50cm^3	**4**

Question Number	Acceptable Answers	Reject	Mark
(c)(i)	White / steamy / misty fumes ALLOW 'gas' for fumes IGNORE correct indicator test on product	White smoke Effervescence Just 'fumes' Just 'gas'	**1**

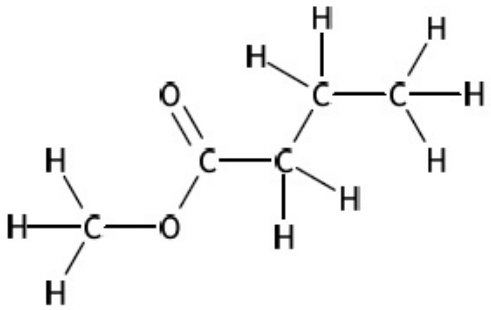
Question Number	Acceptable Answers	Reject	Mark
(c)(ii)	$CH_3CH_2CH_2COCl$ **(1)** ALLOW displayed formula butanoyl chloride **(1)** ALLOW Butanyl chloride No TE on incorrect structure	C_3H_7COCL Butyl Chloride Buthyl Chloride	**2**

Question Number	Acceptable Answers	Reject	Mark
(d)(i)	Butan-1-ol OR $CH_3CH_2CH_2CH_2OH$ If 2 answers are given both must be correct	Butanol Butanal C_4H_9OH	**1**

Question Number	Acceptable Answers	Reject	Mark
(d)(ii)	(Dry) Ethoxyethane / diethylether / Ether OR $C_2H_5OC_2H_5$ / $CH_3CH_2OCH_2CH_3$ If 2 answers are given they must both be correct		**1**

Question Number	Acceptable Answers	Reject	Mark
(d)(iii)	The responses are in pairs: a type (1) and an **associated** justification (1) Reduction (of butanoic acid) **(1)** By addition of hydrogen / loss of oxygen **(1)** **OR** Oxidation of lithium tetrahydroidaluminate / aluminium hydride / $LiAlH_4$ **(1)** By addition of oxygen **(1)** **OR** (Nucleophilic) addition **(1)** of hydride / H^- **(1)** **OR** Redox **(1)** Because butanoic acid has been reduced AND $LiAlH_4$ has been oxidised **(1)**	Any substitution Electrophilic addition	**2**

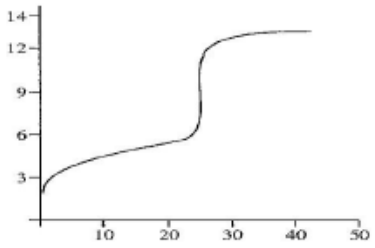
Question Number	Acceptable Answers	Reject	Mark
(e)(i)	(Concentrated / dilute) sulfuric / hydrochloric acid ALLOW any **strong** acid ALLOW 'acid (catalyst)' **(1)** (heat or boil under) reflux ALLOW Heat / warm **(1)** Elevated temp$\leq 65^0$C	Just 'catalyst' Just H^+ Just 'boil' Just 'distil' High temperature Increased concentration	**2**

Question Number	Acceptable Answers	Reject	Mark
(e)(ii)	 All bonds must be shown except ALLOW CH_3 at either end of molecule.	Omitted Hydrogen / sticks	**1**

Question Number	Acceptable Answers	Reject	Mark
(e)(iii)	Butanoyl chloride / $CH_3CH_2CH_2COCl$ ALLOW Butanyl chloride OR Butanoic anhydride / $(CH_3CH_2CH_2CO)_2O$ OR Specified alkyl butanoate (not methyl butanoate) If name and structure are both given they must both be correct	Butyl Chloride Buthyl Chloride	**1**

Question Number	Acceptable Answers	Reject	Mark
(e)(iv)	**Advantage** marks are dependent on correct reagent (or near miss e.g. propanoyl chloride) in (iii). No TE on random answer to (iii) eg H_2SO_4 Advantages – any **two** from: Higher yield / goes to completion/ not an equilibrium reaction / not reversible No heat / no refluxing / less energy needed No catalyst needed / faster By-product is a gas (so easier to separate) **(2)** Disadvantage (marked independently of (e)(iii)) any **one** of: (Acyl chloride is) more expensive / corrosive IGNORE Acyl chloride is toxic / hazardous / harmful / difficult to store OR toxic /corrosive **and** HCl /gas / fumes evolved IGNORE harmful/ hazardous/ dangerous OR has lower atom economy **(1)**	Good yield	**3**

Q31.

Question Number	Acceptable Answers	Additional Guidance	Mark
(i)	A sketch graph which shows the following: • a starting pH between 2 and 4 (inclusive) **(1)** • correct general shape and ends at pH = 12-13 **(1)** • (any) vertical at 25 cm^3 **(1)** • vertical between pH = 6 - 7 and pH = 10 – 12 **(1)**	 Vertical must be no more than 5 pH units within these ranges	**(4)**

Question Number	Acceptable Answers	Additional Guidance	Mark
(ii)	An explanation that makes reference to the following points: • (Read off) **pH** at half-neutralisation (point) / pH at 12.5 (cm^3) OR **pH** at half-equivalence (point) **(1)** • As pH = pK_a / $[H^+] = K_a$ / $K_a = 10^{-pH}$ **(1)**	May be shown on the sketch graph ALLOW read equivalence vol, add same volume of (propanoic) acid and measure pH M2 dependent on mentioning half equivalent / 12.5 cm^3	**(2)**

Q32.

Question Number	Acceptable Answers	Additional Guidance	Mark
	• calculation of $[H^+(aq)]$	<u>Example of calculation</u> $[H^+(aq)] = 10^{-pH} = 10^{-2.76}$ $= 1.7378 \times 10^{-3}$ / 1.738×10^{-3} / 1.74×10^{-3} / 1.7×10^{-3} / 0.0017378 / 0.001738 / 0.00174 / 0.0017 (mol dm^{-3}) Ignore units even if incorrect Correct answer to 2 or more SF with no working scores (1)	**(1)**

Q33.

<table>
<tr><th>Question Number</th><th>Answer</th><th>Additional Guidance</th><th>Mark</th></tr>
<tr><td>*</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><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></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, 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).</td><td></td></tr>
<tr><td></td><td>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 line of reasoning</td></tr><tr><td></td><td></td></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>In general it would be expected that 5 or 6 indicative points would get 2 reasoning marks. 3 and 4 indicative points would get 1 mark for reasoning and 0, 1 or 2 indicative points would score zero marks for reasoning.</td><td>(6)</td></tr>
</table>

	Comment: Look for the indicative marking points first, then consider the mark for the structure of answer and sustained line of reasoning. **Indicative content** **Hydrochloric acid and nitric acid** • (same value for) hydrochloric acid **and** nitric acid as they are strong / completely dissociated into ions (in solution) • reaction taking place is $H^+ + OH^- \rightarrow H_2O$ / $H_3O^+ + OH^- \rightarrow 2H_2O$	Allow correct formulae for names throughout the answer Ignore sulfuric acid as strong(est) acid Allow $HCl + NaOH \rightarrow NaCl + H_2O$ **and** $HNO_3 + NaOH \rightarrow NaNO_3 + H_2O$ Allow hydrochloric acid **and** nitric acid are both monoprotic / monobasic / provide 1 mol H^+ / produce 1 mol H_2O	

	Sulfuric acid • sulfuric acid is diprotic / dibasic **or** (1 mol of) sulfuric acid provides 2 mol H^+ / produces 2 mol H_2O • so value is (almost) twice that of hydrochloric acid / nitric acid **or** reverse argument **Ethanoic acid** • ethanoic acid is weak /partially dissociated into ions (in solution) / $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ / $CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$ • some energy is needed to break (O-H) bond(s) to release H^+ ions (so enthalpy change of neutralisation is less than for a strong acid) **or** enthalpy change of neutralisation includes the enthalpy of dissociation of ethanoic acid so it is less exothermic	Allow $H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$ Allow ethanoic acid is the weakest acid Allow some energy is needed to ionise ethanoic acid	

Q34.

Question Number	Answer	Additional Guidance	Mark
(i)	An explanation that makes reference to the following points: • the O of the (extra) OH / hydroxyl group (in the 2 / alpha position / CH_2OH) withdraws / attracts electrons **(1)** • stabilises the anion / CH_2OHCOO^- ion **or** weakens O-H bond in acid so hydrogen **ion** / H^+ lost more easily **(1)**	Allow reference to intramolecular hydrogen bonding Allow hydrogen **ion** / H^+ more easily dissociates	**(2)**

Question Number	Answer	Additional Guidance	Mark
(ii)	($CH_2OHCOOH + CH_3COOH \rightarrow$) • $CH_2OHCOO^- + CH_3COOH_2^+$	Both correct for the mark Allow formulae in either order Allow formulae in brackets with charge outside Allow displayed formulae Do not allow $CH_3C(OH)_2^+$	**(1)**

Q35.

Question Number	Correct Answer	Reject	Mark
	No, as T increases eqm moves to RHS / K_w increases / 'favours RHS' / ΔS_{total} increases **(1)** So $[H^+]$ ions increases / more H^+ ions $[H^+] > 1 \times 10^{-7}$ **(1)** Hence pH < 7 / pH decreases **(1)** **OR** reverse argument for a decrease in temperature **NOTE** If answer given is 'Yes' (i.e. candidate thinks that the pH of pure water **is** always 7.0), then max **(1)** for stating that equilibrium shifts to the right when temperature increases (since reaction is endothermic in the forward direction) **NOTE** If says K_w **decreases** as T increases, then max **(1)** for a completely logical CQ argument mentioning the effect on $[H^+]$ (decreasing) **and** pH (increasing)		**3**

Q36.

Question Number	Answer	Mark
(a)	**The only correct answer is C** ***A*** *is not correct because this is for a 100-fold increase in concentration* ***B*** *is not correct because this is for no change in concentration* ***D*** *is not correct because this is for a 10000-fold decrease in concentration*	**(1)**

Question Number	Answer	Additional Guidance	Mark
(b)	• calculation of $[H^+]$ **(1)** • expression relating K_a, $[H^+]$ and $[CH_2OHCOOH]$ **(1)** • calculation of $[CH_2OHCOOH]$ **(1)**	Example of calculation $[H^+] = 10^{-pH} = 0.01 / 1 \times 10^{-2} / 10^{-2}$ (mol dm^{-3}) $K_a = \frac{[H^+]^2}{[CH_2OHCOOH]}$ **or** $[CH_2OHCOOH] = \frac{[H^+]^2}{K_a}$ Allow [HA] in M2 and M3 $[CH_2OHCOOH] = \frac{0.01^2}{1.5 \times 10^{-4}}$ $= 0.667 / 0.67$ (mol dm^{-3}) Ignore SF except 1 SF Ignore units Correct answer with no working scores (3)	**(3)**

Q37.

Question Number	Answer	Additional Guidance	Mark
	• **(M1)** calculation of $[H^+]$ **(1)** • **(M2)** rearrangement of K_a and calculation of ethanoate concentration **(1)** • **(M3)** calculation of the number of moles of ethanoate in the buffer volume **(1)** • **(M4)** calculation of the mass of sodium ethanoate in the buffer volume **(1)** • **(M5)** answer to 2/3 SF **(1)**	Example of calculation $[H^+] = 10^{-3.9} = 1.2589..\times 10^{-4}$ (mol dm^{-3}) $[CH_3COO^-] = \frac{1.74 \times 10^{-5} \times 0.800}{1.2589.. \times 10^{-4}}$ =0.11057.. (mol dm^{-3}) n=(0.11057.. x 0.05 =) 5.5285..x 10^{-3} (mol) m=(5.5285..x 10^{-3} x 82=) 0.453339.. m=0.45/ 0.453 (g) Award this mark only if there has been some attempt at calculation using an M_r TE at each stage If Henderson-Hasselbalch equation used **(M1)** for calculation of pK_a = 4.759 **(M2)** for rearrangement and calculation of ethanoate concentration Remaining marking points as above	**(5)**

Q38.

Question Number	Answer	Mark
	The only correct answer is B ***A*** *is not correct because it is the conjugate base not acid* ***C*** *is not correct because it is not the conjugate acid* ***D*** *is not correct because it is not the conjugate acid*	**(1)**

Q39.

Question Number	Answer	Mark
	The only correct answer is C (H_2O and OH^-) **A** *is not correct because ammonia is acting as a base and not an acid* **B** *is not correct because this is the base – conjugate acid pair* **D** *is not correct because water and the ammonium ion are not an acid-conjugate base pair*	(1)

Q40.

Question Number	Correct Answer	Mark
	C	**1**

Q41.

Question Number	Answer	Mark
	The only correct answer is D (none of these three indicators) ***A*** *is incorrect because both acid and base are weak so pH range at equivalence is too narrow for bromothymol blue to change colour* ***B*** *is incorrect because both acid and base are weak so pH range at equivalence is too narrow for methyl orange to change colour* ***C*** *is incorrect because both acid and base are weak so pH range at equivalence is too narrow for phenolphthalein to change colour*	(1)

Q42.

Question Number	Correct Answer	Reject	Mark
(i)	**Q13 (a) PENALISE USE OF CH_3COOH / 'ethanoic acid' [instead of propanoic acid] once only.** **ALLOW 'NaOH' for 'KOH', however.** **1st mark: Identification of buffer** **Any** mention of **buffer** / **buffering** (region) **(1)** IGNORE references to shape / gradient of graph **2nd mark: Identification of species present responsible for buffering action** (Both) propanoic acid **and** propanoate (ions) present OR (Both) propanoic acid **and** potassium propanoate present OR (Both) a **weak** acid and its salt/conjugate base are present OR (Both) CH_3CH_2COOH **and** $CH_3CH_2COO^-$ present OR (Both) HA and A^- are present **Can be awarded from an equation** **(1)**		**3**

	3rd mark: Two routes for this mark: **1st route:** **For how these species were formed** **OR** **alternatively** **2nd route:** **For mention of how this buffer works, on small additions of OH^-** **1st ROUTE to 3rd mark** $CH_3CH_2COOH + OH^- \rightarrow H_2O + CH_3CH_2COO^-$ OR In words, **excess** CH_3CH_2COOH is left / some CH_3CH_2COOH has reacted with potassium hydroxide / KOH / OH^- (forming propanoate ions) **2nd ROUTE – buffering action** On addition of OH^- (in small quantities) H^+ ions react with (the added) OH^- **and** (the equilibrium) $CH_3CH_2COOH \rightleftharpoons CH_3CH_2COO^- + H^+$ shifts to the **right** OR (the reservoir of undissociated) CH_3CH_2COOH molecules react with (the added) OH^- **NOTE:** For the 2nd route "OR" mark here, this statement/equation must be in the context of buffering action **IGNORE** References to buffering action on addition of H^+ ions (not relevant here) **(1)**		

Question Number	Correct Answer	Reject	Mark
(a)	**1st scoring point:** Propanoate ions present (at equivalence point) OR Potassium propanoate present (at equivalence point) **(1)** **2nd scoring point:** Propanoate (ions) react with water / propanoate (ions) are hydrolysed by water / $CH_3CH_2COO^-$ ions react with water ALLOW propanoate ions react with H^+ (from water) / the salt reacts with water (molecules) **(1)** **3rd scoring point – consequential on 2nd scoring point being awarded:** Forming hydroxide ions/ leaves excess of hydroxide ions / produces OH^- / forming OH^- / forming KOH / $[OH^-] > [H^+]$ **(1)** **NOTE – the equation:** $CH_3CH_2COO^- + H_2O \rightarrow OH^- + CH_3CH_2COOH$ **OR** $CH_3CH_2COOK + H_2O \rightarrow KOH + CH_3CH_2COOH$ scores **ALL THREE MARKS** **NOTE** **Just** 'weak acid – strong base titration' scores **(1) only**		**3**

Question Number	Correct Answer	Reject	Mark
(iii)	**[FIRST, CHECK THE FINAL ANSWER IF ANSWER pH = 12(.02), award 5 marks]** Moles of acid used = 25/1000 x 0.024 OR moles of acid used = 6×10^{-4} (mol) **and** Moles of alkali added = 40/1000 x 0.032 OR Moles of alkali added = 1.28×10^{-3} (mol) **(1)** Moles of excess alkali = $1.28 \times 10^{-3} - 6 \times 10^{-4}$ OR Moles of excess alkali = 6.8×10^{-4} (mol) **(1)** $[OH^-] = 6.8 \times 10^{-4} / (65/1000)$ $= 0.01046$ (mol dm^{-3}) **(1)** Allow TE from incorrect moles of acid or alkali, **provided the alkali moles are in excess** $[H^+] = 1 \times 10^{-14} / 0.01046$ $= 9.56 \times 10^{-13}$ (mol dm^{-3}) **(1)** Allow TE from incorrect moles of excess alkali or the candidate's value of $[OH^-]$. Must use K_w value here to get $[H^+]$ pH = $-\log 9.56 \times 10^{-13}$		**5**

	= 12(.02) **(1)** Can get M4 and M5 using pH + pOH = 14 Allow TE from incorrect $[H^+]$ for M5, but their CQ pH must **>** 7 IGNORE S.F. EXCEPT 1 SF NOTE If fail to ÷ **by 0.065 dm³**, then pH = 10.8 scores 4 marks. Other answers to look for if M1 and M2 have been awarded, but division by an incorrect value for the total volume of the mixture, then each of the following would score 4 overall as shown. **If ÷ by 0.025 dm³, no M3** pH = 12(.43) scores 4 marks. **If ÷ by 0.040 dm³, no M3** pH = 12(.23) scores 4 marks. **If ÷ by 0.015 dm³, no M3** pH = 12(.66) scores 4 marks.		

Q43.

Question Number	Acceptable Answers	Additional Guidance	Mark
	• (pH =) $-\log[H^+(aq)]$ **or** (pH =) $-\log[H_3O^+(aq)]$	Allow $\log_{10}$ / lg for log Ignore missing (aq) Do not award –log conc H^+ Do not award round brackets / no brackets for concentration but allow round brackets around the square brackets e.g. $-\log([H^+(aq)])$	**(1)**

Q44.

Question Number	Acceptable Answers	Additional Guidance	Mark
	An explanation that makes reference to the following points: • $[H^+]$/ $[H_3O^+]$/ concentration of hydrogen ions from water is 1(.0) x 10^{-7} (mol dm^{-3}) **(1)** • so total $[H^+]$ is greater than 1(.0) x 10^{-7} (mol dm^{-3}) / is 1.1 x 10^{-7} (mol dm^{-3}) **or** the pH cannot be more than 7 / alkaline (for an acid) **or** concentration of hydrogen ions from water is not negligible / cannot be ignored **or** 10^{-8} is only the concentration of ions from the acid, it doesn't include those from the water **(1)**	Penalise reference to nitric acid as a weak acid in M2 only Allow $[H^+]$ from water = $\sqrt{1(.00) \times 10^{-14}}$ / $\sqrt{K_w}$ Allow this shown as part of a calculation Allow $[H_3O^+]$/ concentration of hydrogen ions for $[H^+]$ Allow$[H^+]$ is greater than 1 x 10^{-8} (mol dm^{-3}) Allow $[H^+]$ cannot be less than $[OH^-]$ / $[OH^-]$ cannot be more than $[H^+]$ Allow the addition of nitric acid to water decreases pH by increasing $[H^+]$ Allow pH is 6.96 Allow pH 8 / >7 is alkaline Allow acid must have pH below 7 Do not award $10^{-14}/10^{-8} = 10^{-6}$ so pH = 6 for M2 only Allow water also dissociates to form H^+ ions	**(2)**

Q45.

Question Number	Correct Answer	Mark
	C	**1**

Q46.

Question Number	Correct Answer	Mark
	A	**1**

Q47.

Question Number	Answer	Additional Guidance	Mark
(i)	• square root of K_w at 310K to get $[H^+]$ **(1)** • calculation of pH to 2 decimal places **(1)**	Example of calculation: $[H^+] = (\sqrt{2.40 \times 10^{-14}}) = 1.549..\times10^{-7}$ (mol dm^{-3}) pH = $(-\log 1.549..\times10^{-7})$ = (6.809894379) = 6.81 Correct answer with no working scores (2) Allow TE from incorrect $[H^+]$ as long as answer is in the pH range 6.00 – 7.00 inclusive	**(2)**

Question Number	Answer	Additional Guidance	Mark
(ii)	An answer that makes reference to the following points: • **(M1)** neutral **(1)** • **(M2)** because $[H^+(aq)] = [OH^-(aq)]$ /equal amounts of H^+ and OH^- ions **(1)**	Acidic or alkaline scores (0) Allow both $[H^+]$ and $[OH^-]$ have increased equally (from 298 K to 310 K) M2 dependent on M1	**(2)**

Question Number	Answer	Additional Guidance	Mark
(iii)	An answer that makes reference to the following point: • positive / + sign because K_w increases as the temperature increases	Allow 'positive because' bond breaking requires energy or equilibrium shifts to the right or there is greater/more ionisation/dissociation Ignore 'endothermic'	**(1)**

Q48.

Question Number	Correct Answer	Reject	Mark
(a)	C		1

Question Number	Correct Answer	Reject	Mark
(b)	B		1

Question Number	Correct Answer	Reject	Mark
(c)	C		1

Q49.

Question Number	Correct Answer	Reject	Mark
(a)	B		**1**

Question Number	Correct Answer	Reject	Mark
(b)	B		**1**

Question Number	Correct Answer	Reject	Mark
(c)	C		**1**

Q50.

Question Number	Acceptable Answers	Reject	Mark
(a)(i)	$K_w = [H^+] \times [OH^-]$ OR $K_w = [H_3O^+] \times [OH^-]$ State symbols are not required IGNORE any incorrect state symbols	Inclusion of $[H_2O]$	**1**

Question Number	Acceptable Answers	Reject	Mark
(a)(ii)	**FIRST, CHECK THE FINAL ANSWER** **IF** answer pH = 11.875 / 11.88 / 11.9 /12 award **2** marks **IGNORE** sf except 1 sf $[H^+] = \frac{K_w}{[OH^-]} = \frac{1.00 \times 10^{-14}}{0.00750}$ $= 1.3333 \times 10^{-12}$ $= 1.33 \times 10^{-12}$ (mol dm^{-3}) **(1)** **ALLOW** first mark for just $[H^+] = \frac{K_w}{[OH^-]}$ $pH = -\log_{10}[H^+] = 11.875$ $= 11.88 / 11.9$ **(1)** OR $pOH = -\log_{10}[OH^-] = 2.12$ **(1)** $pH = pK_w - pOH$ $pH = 11.88 / 11.9$ **(1)** Second mark only awarded CQ if pH between 8 and 14		**2**

Question Number	Acceptable Answers	Reject	Mark
(b)	**First mark** Moles NaOH = $\frac{0.00750 \times 20.0}{1000}$ $= 1.50 \times 10^{-4}$ (mol) **(1)** (Since HCOOH : NaOH ratio is 1:1) **Second mark** [HCOOH(aq)] = $\frac{1.50 \times 10^{-4}}{0.0250}$ **OR** $= 1.50 \times 10^{-4} \times \frac{1000}{25.0}$ **(1)** $(= 6.00 \times 10^{-3}$ mol dm$^{-3})$ **ALTERNATIVE APPROACH:** Use of an expression such as 0.00750 x 20.0 = 25 x **y** **(1)** **y** = $\frac{0.00750 \times 20.0}{25}$ **(1)**		**2**

Question Number	Acceptable Answers	Reject	Mark
(c)(i)	**(Weak)** dissociates / ionizes to a small extent **OR** dissociate / ionizes partially **OR** dissociates / ionizes incompletely **OR** does not fully dissociate / ionize **OR** forms an equilibrium when reacted with water **(1)** **(Acid)** proton donor ALLOW 'proton donator' **OR** produces / releases H^+ ions **OR** produces / releases H_3O^+ ions **(1)** Ignore reference to typical acid reactions	'not easily dissociated'	**2**

Question Number	Acceptable Answers	Reject	Mark
(c)(ii)	(K_a =) $\frac{[HCOO^-][H^+]}{[HCOOH]}$ State symbols are NOT required IGNORE any incorrect state symbols	(K_a =) $\frac{[H^+]^2}{[HCOOH]}$ Inclusion of $[H_2O]$	**1**

Question Number	Acceptable Answers	Reject	Mark
(c)(iii)	**IGNORE** sf except 1 sf THROUGHOUT **FIRST, CHECK THE FINAL ANSWER** **IF** answer $K_a = 1.59 \times 10^{-4}$ (mol dm^{-3}) award the first two **2** marks $[H^+]$ $(= 10^{-pH} = 10^{-3.01})$ $= 9.77 \times 10^{-4}$ (mol dm^{-3}) **(1)** $K_a = \frac{[H^+]^2}{[HCOOH]}$ $K_a = \frac{(9.77 \times 10^{-4})^2}{6.00 \times 10^{-3}}$ $= 1.59 \times 10^{-4}$ (mol dm^{-3}) **(1)** **Assumption 1** $[H^+] = [HCOO^-]$ **OR** no H^+ from the (ionization of) water **OR** H^+ only from the acid **(1)**	If incorrect units max 1	**4**

	Assumption 2 Ionization of the (weak) acid is negligible / very small / insignificant **OR** $[HCOOH]_{initial} - x = [HCOOH]_{eqm}$ **OR** $[HCOOH]_{eqm} = [HCOOH]_{initial}$ **OR** $[HCOOH]_{eqm} = 6.00 \times 10^{-3}$ (mol dm^{-3}) **OR** $[H^+] << [HA]$ **(1)** **Assumptions can be in either order** **OR** $[H^+]$ $(= 10^{-pH} = 10^{-3.01})$ $= 9.77 \times 10^{-4}$ (mol dm^{-3}) **(1)** $K_a = \frac{[H^+]^2}{[HCOOH]}$ $K_a = \frac{(9.77 \times 10^{-4})^2}{(6.00 \times 10^{-3} - 9.77 \times 10^{-4})}$ **(1)** $= 1.90 \times 10^{-4}$ (mol dm^{-3}) **(1)** **Assumption** $[H^+] = [HCOO^-]$ **OR** no $[H^+]$ from the (ionization of) water **OR** H^+ only from the acid **(1)** Ignore references to constant temperature	**Just** 'partial' / 'incomplete' **Or** ' no dissociation'	

Q51.

<table>
<tr><th>Question number</th><th>Acceptable Answer</th><th>Additional Guidance</th><th>Marks</th></tr>
<tr><td>* (iii)</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 of answer and sustained line 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>

Indicative content

Similarity</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, 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).</td><td></td></tr>
</table>

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	• reaction is between Mg and H^+ / $Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$	both acids produce one H^+ / are monobasic / are monoprotic	**6**
	• 100 cm^3 of HCl and 100 cm^3 HCOOH contain the same initial number of moles of the acid	the same volume <u>and</u> concentration of both acids is used	
	• therefore same total volume of gas evolved	a calculation to show the same volume	
	Difference • HCl is fully dissociated/ionised but HCOOH only partially dissociated/ionised	dissociation/ionisation of HCOOH requires energy	
	• $[H^+]$ is greater in HCl / $[H^+]$ is smaller in HCOOH		
	• therefore rate is greater with HCl / lower with HCOOH	therefore larger activation energy with HCOOH	

Q52.

Question Number	Answer	Mark
(i)	**The only correct answer is B** ***A*** *is not correct because there is no extrapolation to the largest temperature increase carried out* ***C*** *is not correct because the extrapolation is at the wrong time* ***D*** *is not correct because the extrapolation extends beyond the time of addition of alkali*	**(1)**

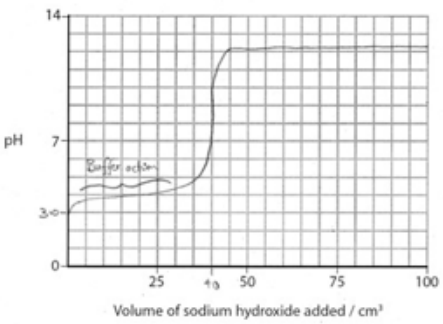
Question Number	Answer	Additional Guidance	Mark
(ii)	An explanation that makes reference to • ethanoic acid is a weak(er) acid / only partially ionised/dissociated **(1)** • (some) **energy** is used to fully/completely ionise the ethanoic acid **(1)**	Allow hydrochloric acid is a strong(er) acid/fully ionised Do not award 'more NaOH will react so more energy given off'	**(2)**

Q53.

Question Number	Answer	Additional Guidance	Mark
(i)	An assessment that includes • **(M1)** the vertical part of the graph is at ~7 - 10/ the mid-point is at 8.5-8.8 **(1)** • **(M2)** the mid-point of the colour change of methyl red is 5.1 **(1)** • **(M3)** pH range of methyl red does not lie (completely) within the vertical range of the pH curve (so it is not suitable) **(1)** • **(M4)** the colour change will be complete before the equivalence point is reached **(1)**	Allow 'equivalence point/end-point' for 'the vertical part of the graph/ the mid-point' Allow methyl red changes colour in the range/ has a pH range 4.2 - 6.3/ pK_{in} 5.1 Allow, after stating M1 and M2, 'this means that methyl red is unsuitable' Allow end-point/neutralisation point for equivalence point Do not award colour change to red Ignore references to choice of other indicators	(4)

Question Number	Answer	Additional Guidance	Mark
(ii)	An answer that includes • two ticks and two crosses as shown	<table><tr><th>Indicator</th><th>pH range</th><th>Tick or Cross</th></tr><tr><td>Bromocresol purple</td><td>5.2 - 6.8</td><td>x</td></tr><tr><td>Thymol blue</td><td>8.0 - 9.6</td><td>✓</td></tr><tr><td>Thymolphthalein</td><td>8.3 - 10.6</td><td>✓</td></tr><tr><td>Alizarin yellow R</td><td>10.1 - 13.0</td><td>x</td></tr></table>Do not award blank boxes for (x)	(1)

Q54.

Question Number	Answer	Additional Guidance	Mark
(i)	• general shape of weak acid-strong base curve **(1)** • curve starts at pH of 3.0 and ends at pH of 12-13 **(1)** • vertical part of the curve at 40 cm³ **(1)** • labelling of area indicating buffer action **(1)**	Exemplar graph  Ignore missing initial rise in pH Vertical part must cover 3-5 pH units between 6 – 11 The curve should reach pH~12-13 by 10cm³ after vertical section The curve must start at zero and continue to 100 cm³ Allow buffering area to be labelled anywhere between ~5 and 35 cm³ inclusive	**(4)**

Question Number	Answer	Additional Guidance	Mark
(ii)	An answer that makes reference to • determine the pH at the point when half of the acid is neutralised **(1)** • $K_a = 10^{-pH}$ / $K_a = 10^{-pK_a}$ **(1)**	Standalone marks Allow 'pH at half-equivalence point' Allow 'pH at half neutralisation point' Accept description in words such as inverse log of minus pH or value is pK_a and so inverse log of minus value gives K_a Allow pK_a = - log K_a Ignore any calculation	**(2)**

Q55.

Question number	Answer	Additional Guidance	Marks
(a)	**B** (the extent of dissociation into ions of the acid)		**1**

Question number	Acceptable Answer	Additional Guidance	Marks
(b)(i)	$HClO_2(aq) + HCOOH(aq) \rightleftharpoons ClO_2^-(aq) + HCOOH_2^+(aq)$ acid 1 base 2 . base 1 acid 2 **or** acid 2 base 1 . base 2 acid 1		**1**

Question number	Acceptable Answer	Additional Guidance	Marks
(b)(ii)	An explanation that makes reference to the following points: • $HCOOH + C_6H_5OH \rightleftharpoons HCOO^- + C_6H_5OH_2^+$ (1) • because methanoic acid has a larger K_a value / methanoic acid is the stronger acid (1)	Ignore state symbols second mark is conditional on correct equation	2

Q56.

Question number	Answer	Additional guidance	Marks
(a)	A		1
(b)(i)	An explanation that makes reference to the following points: • stage 2 is an equilibrium reaction / only partial ionisation occurs (1) • therefore fewer hydrogen ions are formed (1)	Accept dissociation for ionisation	2
(b)(ii)	• rearrangement of equation pH = - log $[H^+]$ and substitution to give final answer (1)	Example calculation: $[H^+] = 10^{-pH}$ $10^{-0.97} = 0.107$ (mol dm^{-3}) Allow 0.11 (mol dm^{-3}) Correct answer with no working scores 1 mark	1
(c)	• rearrangement of K_a expression (1) • calculation of $[CH_3COOH]$ and $[CH_3COO^-]$ (1) • substitution, and evaluation of $[H^+]$ in the buffer solution (1) • conversion of $[H^+]$ to pH for buffer solution (1)	Example of calculation : $[H^+] = K_a \frac{[CH_3COOH]}{[CH_3COO^-]}$ $[CH_3COOH] = 0.333$ mol dm^{-3} and $[CH_3COO^-] = 0.167$ mol dm^{-3} $[H^+] = 1.74 \times 10^{-5} \times 0.333 / 0.167 = 3.48 \times 10^{-5}$ (mol dm^{-3}) so pH = -lg $3.48 \times 10^{-5} = 4.46$ Accept answers that use forms of the Henderson-Hasselbach equation Correct answer with no working scores 4 marks	4

(Total for Question 8 = 8 marks)

Q57.

Question Number	Answer	Additional Guidance	Mark
	• $HPO_4^{2-} + H^+ \rightarrow H_2PO_4^-$ **or** $HPO_4^{2-} + H_3O^+ \rightarrow H_2PO_4^- + H_2O$ **(1)** • $H_2PO_4^- + OH^- \rightarrow HPO_4^{2-} + H_2O$ **(1)**	Penalise non-ionic equations, e.g. using NaOH or HCl once only Equations must show reaction of ions with H^+ / H_3O^+ and OH^- Allow ⇌ Ignore state symbols Allow $H_2PO_4^- \rightarrow HPO_4^{2-} + H^+$ **and** $H^+ + OH^- \rightarrow H_2O$	**(2)**