# Mark scheme – Acids, Bases and Buffers

Q	ues		Answer/Indicative content	Mark s	Guidance
1	а		HCOOH + CH₃COOH ⇒ HCOO⁻ + CH₃COOH₂⁺ ✓  A1 B2 B1 A2  OR  A2 B1 B2 A1 ✓  CARE:  Both + and – charges required for products in equilibrium  DO NOT AWARD the 2nd mark from an equilibrium expression that omits either charge	2 (AO 1.2×2	IGNORE state symbols (even if wrong)  IF proton transfer is wrong way around ALLOW 2nd mark for idea of acid–base pairs, i.e.  HCOOH + CH₃COOH ⇌ HCOOH₂+ + CH₃COO−  B2 A1 A2 B1  NOTE For the 2nd marking point (acid–base pairs), this is the ONLY acceptable ECF i.e. NO ECF from impossible chemistry
	b	i	[H <sup>+</sup> ] = $10^{-2.72}$ <b>OR</b> $1.905 \times 10^{-3}$ (mol dm <sup>-3</sup> ) $\checkmark$ [CH <sub>3</sub> COOH] = $\frac{(1.905 \times 10^{-3})^2}{1.78 \times 10^{-5}}$ $\checkmark$ (= 0.204 mol dm <sup>-3</sup> )	2 (AO 2.4×2 )	ALLOW 2SF up to calculator value of 1.905460718 x 10 <sup>-3</sup> ALLOW use of [HA]  Mark is for working.
			FIRST CHECK THE ANSWER ON ANSWER LINE  If answer = $2.4 \times 10^{-2}$ (mol dm <sup>-3</sup> ) award 4 marks  Calculation of H <sup>+</sup> in buffer  [H <sup>+</sup> ] buffer = $10^{-4.00}$ OR $1 \times 10^{-4}$ (mol dm <sup>-3</sup> ) $\checkmark$ Calculation of CH <sub>3</sub> COOH in buffer $n(\text{CH}_3\text{COOH})$ OR [CH <sub>3</sub> COOH] <sub>buffer</sub> = $\frac{0.204}{1000} \times 400$ OR $8.16 \times 10^{-2} \checkmark$	4 (AO 3.3×3 )	ALLOW ECF ALLOW [HA] and [A-] in working
		ii	Calculation of [CH <sub>3</sub> COO <sup>-</sup> ] in buffer (in 1 dm <sup>3</sup> )  [CH <sub>3</sub> COO <sup>-</sup> ] <sub>buffer</sub> = $1.78 \times 10^{-5} \times \frac{8.16 \times 10^{-2}}{1 \times 10^{-4}}$ OR $1.5 \times 10^{-2}$ (mol dm <sup>-3</sup> ) $\checkmark$ Calculation of original [CH <sub>3</sub> COO <sup>-</sup> ] (in 600 cm <sup>3</sup> )  [CH <sub>3</sub> COO <sup>-</sup> ] <sub>initial</sub> = $(\frac{1.45248 \times 10^{-2} \times 1000}{600})$ = $2.4 \times 10^{-2}$ (mol dm <sup>-3</sup> ) $\checkmark$		<b>ALLOW</b> $1.5 \times 10^{-2}$ up to calculator value $1.45248 \times 10^{-2}$ (mol dm <sup>-3</sup> ) <b>ALLOW</b> $2.4 \times 10^{-2}$ up to calculator value $2.4208 \times 10^{-2}$ (mol dm <sup>-3</sup> )
			ALLOW alternative approach based on Henderson–	(AO 3.4×1 )	COMMON ERRORS BUT CHECK WORKING         [CH <sub>3</sub> COO <sup>-</sup> ] <sub>initial</sub> = $8.7 \times 10^{-3}$

	Hasselbalch equation ( <b>ALLOW</b> $-logK_a$ for $pK_a$ ) e.g.		No volumes used = 3.6 x 10 <sup>-2</sup> 2 marks
	$pH = pK_a + log \frac{[CH_3COOH]}{[CH_3COO^-]}$ <b>OR</b> $pK_a - log \frac{[CH_3COO^-]}{[CH_3COOH]}$ <b>OR</b>		
	$4 = 4.75 + \log \frac{8.16 \times 10^{-2}}{[\text{CH}_3\text{COO}^-]} \text{OR } 4.75 - \log \frac{[\text{CH}_3\text{COO}^-]}{8.16 \times 10^{-2}} \checkmark$		<b>ALLOW</b> $-\log K_a$ for $pK_a$
	$log[CH3COO-] = 4 - 4.75 - 1.09 = -1.84 \checkmark$		
	[CH <sub>3</sub> COO <sup>-</sup> ] <sub>buffer</sub> = 1.5 × 10 <sup>-2</sup> √		
	$[CH_3COO^-]_{initial} = 2.4 \times 10^{-2} \checkmark$		Examiner's Comments
			This question required the candidate to calculate the original concentration of ethanoate ions in the buffer. Higher-attaining students gained full credit. Most students calculated the concentration in the buffer solution but did not factor for the original solution. Lower-attaining candidates often scored the first two marking points but did not use the buffer equation.
	Total	8	
2	CH₃SO₂OH + H₂O ⇒ CH₃SO₂O⁻ + H₃O⁺ ✓  A1 B2 B1 A2 ✓  For an equilibrium shown using CH₃COOH instead of H₂O, mark acid–base pairs by ECF, i.e.  CH₃SO₂OH + CH₃COOH ⇒ CH₃SO₂O⁻ + CH₃COOH₂⁺ ⋈  A1 B2 B1 A2 ECF ✓  CH₃SO₂OH dissociates more (than CH₃COOH)  OR CH₃SO₂OH is a stronger acid ✓  ORA in terms of CH₃COOH being a weaker acid  Student is correct  AND  (sulfonic acid has) lower pK₃/higher K₃ OR greater [H⁺]  ORA ✓	4 (AO 2.1×2 )	ALLOW $\rightarrow$ for $\rightleftharpoons$ ALLOW acid–base pairs labelled other way round. i.e. CH <sub>3</sub> SO <sub>2</sub> OH + H <sub>2</sub> O $\rightleftharpoons$ CH <sub>3</sub> SO <sub>2</sub> O <sup>-</sup> + H <sub>3</sub> O <sup>+</sup> A2 B1 B2 A1  ALLOW small slip  If ONE charge is missing from equilibrium. ALLOW ECF for acid–base pairs mark  IGNORE 'more acidic' Response needs strength/dissociation  ALLOW maths explanation for final 2 marks, e.g.  Ka(CH <sub>3</sub> COOH) = $10^{-(4.76)}$ = $1.74 \times 10^{-5}$ [H <sup>+</sup> ] = $\sqrt{(1.74 \times 10^{-5}) \times 1}$ = $4.17 \times 10^{-3}$ pH = $-\log 4.17 \times 10^{-3}$ = $2.38 \checkmark$ $K_3$ (CH <sub>3</sub> SO <sub>2</sub> OH) = $10^{-(-1.90)}$ = $79.4$ [H <sup>+</sup> ] = $\sqrt{(79.4) \times 1}$ = $8.91$ pH = $-\log 8.91$ = $-0.95 \checkmark$ BOTH pH calcs subsumes 'Student is correct'
		(AO 3.2)	
			Examiner's Comments

					Most candidates completed a correct equilibrium equation and assigned the correct acid-base pairs. A significant number of candidates used ethanoic acid instead of water in the equation. The examiners allowed error carried forward in this case for the acid-base pairs.  Candidates found it much more difficult to explain whether the sulfonic acid had a lower pH value. The higher-attaining candidates answered concisely. They usually identifying that the sulfonic acid would have a lower pH as the pKa value was lower (or the Ka value greater), leading to more dissociation than ethanoic acid.  Lower-attaining candidates often produced unfocussed and lengthy responses, sometimes relating increased dissociation in an acid to a higher, rather than a lower, pH.  Some candidates approached their explanation mathematically, calculating pH values for ethanoic acid and sulfonic acid from their concentrations and pKa values. If correct, this approach was fully credited.
			Total	4	
3	а		FIRST CHECK THE ANSWER ON ANSWER LINE If answer = 2.98 award 2 marks	2 (AO 2.2 ×2)	ONLY ALLOW pH mark by ECF if K <sub>a</sub> AND 0.080 used and AND pH <7  Common errors (Must be to 2 DP) One mark for pH = 5.97 (No square root):  One mark for pH = 0.92 OR pH = 5.15 (Using incorrect K <sub>a</sub> values)  Examiner's Comments  Most candidates could calculate the pH of a weak acid although a significant number gave the answer as 3.0, presumably confusing the demand for two decimal points with two significant figures.
	b	İ	$n(C_2H_5COOH) = (0.0800 \times \frac{25.0}{1000}) =) 0.002 \text{ (mol)}$ AND $V(NaOH) = \frac{0.002}{0.100} \times 1000 = (= 20(.0))$	1 (AO 2.5)	ALLOW 0.02 dm³ if unit given  Mark is for WORKING which could all be shown as 1 step  ALLOW method showing 20cm³ NaOH contains the same moles as acid $n(C_2H_5COOH) = 0.08(00) \times 0.025(0) = 0.002$

	cm³)√		(mol) and n(NaOH) = 0.02(00) x 0.1 = 0.002(00) (mol) Examiner's Comments
			Showing by calculation something already known is a skill that some candidates find challenging. Many responses included rows of figures with '20 cm³' appearing at the end.
			Clarity of working is essential and in questions such as this, candidates are advised to include word descriptions of what they are calculating, even if it is abbreviations such as 'n' for number of moles.
			ALLOW ECF throughout For first mark ALLOW (Excess volume of NaOH = 25(.0) cm³)
	FIRST CHECK THE ANSWER ON ANSWER LINE If answer = 12.55 award 4 marks		$n(OH^-)_{excess} = 0.100 \times \frac{25.0}{1000} = 0.0025 \text{ (mol)}$
	Excess mol of NaOH: $n(OH^{-})_{\text{excess}} = n(OH^{-}) - n(C_2H_5COOH)$		Common errors  If initial $V(NaOH) = 45 \text{ cm}^3$ $[OH^-] = 0.0643 \text{ (mol)}$ $[H^+] = 1.56 \times 10^{-13} \text{ (mol dm}^{-3})$ pH = 12.81 award three marks (no 1st mark)
	$= (0.100 \times \frac{45.0}{1000}) - (0.0800 \times \frac{25.0}{1000})$	4	If $n(OH^-)_{excess}$ is used in [H <sup>+</sup> ] calculation $n(OH^-)_{excess} = 0.0025$ (mol)
ii	= 0.0045 – 0.002 = 0.0025 (mol) √  Concentration of OH:	(AO	$[H^{+}] = \frac{1.00 \times 10^{-14}}{0.0025} = 4.(00) \times 10^{-12} \text{ (mol dm}^{-3)}$
	[OH <sup>-</sup> ] = $(\frac{0.0025}{70.0 \times 10^{-3}})$ = 0.0357 (mol dm <sup>-3</sup> ) $\checkmark$	1.2 ×1) (AO 2.6	pH = 11.40 award three marks (no 2 <sup>nd</sup> mark) <b>ALLOW</b> pOH method for last two marks
	Concentration of H <sup>+</sup> :	×3)	pOH = - log[OH <sup>-</sup> ] =1.447 pH = 14 - 1.447 = 12.55
	$[H^{+}] = (\frac{1.00 \times 10^{-14}}{0.0357})$ = 2.8 × 10 <sup>-13</sup> (mol dm <sup>-3</sup> ) $\checkmark$		<b>ALLOW</b> ECF for conversion from [H <sup>+</sup> ] to pH provided value calculated is above 7 and from derived [H <sup>+</sup> ]
	Conversion to pH: pH = (-log 2.8 × 10 <sup>-13</sup> ) = 12.55 √		Examiner's Comments
			This calculation proved difficult with once again, many figures and sums appearing with little indication as to their relevance.

			Responses to 20bi/ii often featured rows of figures and random sums without a single word about what the figures were or sums were set to calculate. Candidates should remember to provide written indications of what it is they're working out – presenting the calculations without any annotations can make it harder for error carried forward marks to be given if there is an error in their calculation.
ii i	Shape Slight rise/flat, AND (near) vertical, AND then slight rise/flat ✓ pH Vertical section within the extremes of pH 5 to 12 and a minimum range of three pH units AND middle of vertical section (equivalence point) needs to be above pH 7 ✓ End point Vertical section at ~ 20 cm³ NaOH ✓	3 (AO 2.3 ×1) (AO 2.4 ×2)	If pH curves wrong way round (i.e. adding acid to alkali),  ONLY award mark for End point (~ 20 cm³)  Examiner's Comments  This weak acid / strong alkali titration curve required candidates to apply their knowledge. Some candidates found it difficult to draw an adequate titration curve.  The key points to titration curves are:  • A 'vertical' section at the end point • The vertical section with pH range correct to relative to the strength of acid/alkali • A correct equivalence point relative to pH 7 with respect to the strength of acid/alkali • A 'shallow curve' leading from 0 cm³ to vertical section • A 'shallow curve' leading from the vertical section to the total volume added  For this reaction:  • The vertical section was at 20 cm³ (given in 20bi) • As it was a weak acid and strong alkali reacting, the vertical section should start above pH 5 and finish around pH 11 • The equivalence point (half-way up the vertical section) for a weak acid / strong alkali titration should be above pH 7 • The starting pH should be that of the weak acid, C <sub>2</sub> H <sub>5</sub> COOH (answer to 20(a)) • The final pH should be that of the final solution (answer to 20(b)(ii))

i V	cresol purple  AND pH range matches vertical section/rapid pH change OR end point/colour change matches vertical section/rapid pH change √	1 (AO 3.3)	ALLOW pH range (of the indicator) matches equivalence point ALLOW end point/colour change matches equivalence point IGNORE colour change matches end point Colour change is the same as end point  Examiner's Comments  Some candidates realised that the most suitable indicator for a weak acid / strong alkali titration would be cresol purple. For incorrect responses, other indicators appeared to be selected at random, suggesting that candidates were unclear on the criteria for selected a suitable indicator.
V	similarity: end point / volume (20 cm³) of NaOH needed to neutralise  OR  final pH / shape of curve after end point √  difference: HCN higher starting pH  OR  HCN shorter vertical section √	2 (AO 3.2 ×2)	End point must not refer to same pH  ALLOW different equivalence point IGNORE different starting pH  Examiner's Comments  When identifying a similarity, many candidates confused the term 'equivalence point' with the term 'end point'.  For differences, many candidates realised that HCN had a different K <sub>a</sub> to C <sub>2</sub> H <sub>5</sub> COOH but often did not appreciate that this would lead to a starting point with a higher pH.
C	HIO₃ dissociation is not negligible / dissociates to a significant extent  OR  Large Ka and HIO₃ is 'stronger' (weak) acid  OR  [HIO₃]eqm is significantly lower than [HIO₃]initial/undissociated ✓	1 (AO 3.3)	ALLOW use of HA  Ignore [HIO <sub>3</sub> ] <sub>equilibrium</sub> < [HIO <sub>3</sub> ] initial/undissociated  ALLOW  [HIO <sub>3</sub> ] <sub>equilibrium</sub> ~ [HIO <sub>3</sub> ] <sub>undissociated</sub> is no longer a valid assumption  ALLOW  [HIO <sub>3</sub> ] has a larger K <sub>a</sub> so the assumption that [HIO <sub>3</sub> ] at equilibrium = [HIO <sub>3</sub> ] initially so assumption is not valid  Examiner's Comments  Very few candidates scored the mark for this question.  The most common error was to write 'HIO <sub>3</sub> dissociates'. While correct, this is true of all weak acids.  The subtlety in this question was to realise

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				that because K <sub>a</sub> was relatively high, the resultant acid strength would mean that the degree of dissociating was significant enough so initial [HIO <sub>3</sub> ] was significantly less than [HIO <sub>3</sub> ] at equilibrium. In other words, the assumption [HIO <sub>3</sub> ]initial = [HIO <sub>3</sub> ]equilibrium is not valid in this case.
		Total	14	
		Please refer to the marking instructions on page 4 of this mark scheme for guidance on how to mark this question.		Indicative scientific points may include: (State symbols not required in equations)
		Level 3 (5–6 mark)		Equilibrium and equilibrium shifts
		Detailed explanation of equilibrium, the action of the buffer and correct calculation of [HCO <sub>3</sub> -]: [H <sub>2</sub> CO <sub>3</sub> ] ratio.  There is a well-developed line of reasoning which is clear and		<ul> <li>H<sub>2</sub>CO<sub>3</sub>(aq) ≠ H<sup>+</sup>(aq) + HCO<sub>3</sub><sup>-</sup>(aq)</li> <li>Addition of H<sup>+</sup> causes ≠ to shift to left</li> </ul>
		logically structured. The information presented is relevant and substantiated.		<ul> <li>Addition of OH⁻ causes   to shift to right</li> </ul>
		110(0.41.)		Action of buffer
		Level 2 (3–4 marks)  Detailed explanation of equilibrium and the action of the buffer.  OR		Increase in H <sup>+</sup> / addition of acid leads to:
		Detailed explanation of equilibrium <b>and</b> correct calculation of [HCO <sub>3</sub> <sup>-</sup> ]: [H <sub>2</sub> CO <sub>3</sub> ] ratio.	6 (AO1.	H <sup>+</sup> (aq) + HCO₃ <sup>-</sup> (aq) → H₂CO₃(aq) <b>OR</b> HCO₃ <sup>-</sup> reacts with added acid
		OR  Detailed explanation of the action of the buffer <b>and</b> correct calculation of [HCO <sub>3</sub> -]: [H <sub>2</sub> CO <sub>3</sub> ] ratio.		<ul> <li>Increase in OH⁻ / addition of alkali leads to:</li> <li>H⁺(aq) + OH⁻(aq) → H2O(I)</li> <li>OR</li> </ul>
	4	OR Partial explanations of equilibrium, and the action of the buffer and attempt calculation of [HCO <sub>3</sub> <sup>-</sup> ] : [H <sub>2</sub> CO <sub>3</sub> ] ratio.	1 ×2) (AO1. 2 ×2)	$H_2CO_3(aq) + OH^-(aq) \rightarrow HCO_3^ (aq) + H_2O(I)$ OR
		There is a line of reasoning presented with some structure.	(AO3. 1 ×1)	H₂CO₃ reacts with added alkali
		The information presented is relevant and supported by some evidence.	(AO3. 2 ×1)	Calculation of [HCO <sub>3</sub> -] : [H <sub>2</sub> CO <sub>3</sub> ] ratio
		Level 1 (1–2 marks)		• $K_a = 10^{-6.38}$ <b>OR</b> $4.17 \times 10^{-7}$ (mol dm <sup>-3</sup> )
		Detailed explanation of equilibrium.  OR  Correct calculation of [HCO <sub>3</sub> -]: [H <sub>2</sub> CO <sub>3</sub> ] ratio.		• [H <sup>+</sup> ] = 10 <sup>-7.40</sup> <b>OR</b> 3.98 x 10 <sup>-8</sup> (mol dm <sup>-3</sup> )
		OR		[HCO <sub>3</sub> ] 4.17 x 10 <sup>-7</sup> • [H <sub>2</sub> CO <sub>3</sub> ] <b>OR</b> 3.98 x 10 <sup>-8</sup>
		Detailed explanation of the action of the buffer.  OR		• ratio = 10.47(:1) OR 10.48(:1) <b>ALLOW</b> 10.5 OR 10(:1) (after
		Partial explanations of equilibrium <b>and</b> the action of the buffer.'  OR		working shown)
		Partial explanation of equilibrium <b>and</b> attempt at calculation of [HCO <sub>3</sub> <sup>-</sup> ]: [H <sub>2</sub> CO <sub>3</sub> ] ratio.' <b>OR</b>		<b>ALLOW</b> $\frac{4.2 \times 10^{-7}}{4.0 \times 10^{-8}}$
		Partial explanation of the action of the buffer <b>and</b> attempt at calculation of [HCO <sub>3</sub> <sup>-</sup> ] : [H <sub>2</sub> CO <sub>3</sub> ] ratio.		
		There is an attempt at a logical structure with a line of reasoning. The information is in the most part relevant.		And ratio = 10.5 <b>OR</b> 11 (after working shown)

#### 0 marks

No response or no response worthy of credit.

**ALLOW** 

[H<sub>2</sub>CO<sub>3</sub>] [HCO<sub>3</sub><sup>-</sup>] **OR**  $\frac{3.98 \times 10^{-4}}{4.17 \times 10^{-7}}$ 

**And** ratio = 1 : 0.095 ..

## **Examiner's Comments**

This Level of Response question was generally well answered with many candidates achieving maximum marks by simply considering what was required in the question.

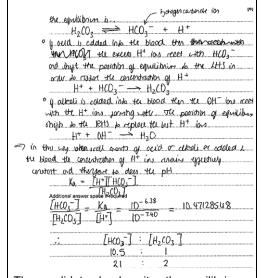
The calculation of the  $[HCO_3^-]$ :  $[H_2CO_3]$  ratio was well described although sometimes the final expression of the ratio left ambiguity as it was hard to tell whether the ratio given referred to the  $[HCO_3^-]$ :  $[H_2CO_3]$  ratio or the  $[H_2CO_3]$ :  $[HCO_3^-]$  ratio

The buffer reactions on separate addition of acid (H<sup>+</sup> ions) and alkali (OH<sup>-</sup> ions) were explained and, better still, shown in equation form.

The direction of shift on the  $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$  equilibrium was invariably correct, but many candidates did not achieve credit for responses such as 'Addition of  $H^+$  ions shifts the equilibrium to the left' because they did not give the equilibrium which was undergoing shift.

An example of a complete answer gaining L3 (6 marks) is given.

#### Exemplar 5



The candidate clearly writes the equilibrium at the top.

The first bullet point gives a chemical

		Total	6	equation for the reaction occurring when H <sup>+</sup> ions are added as well as the shift in equilibrium.  The second bullet point gives a chemical equation for the reaction occurring when OH <sup>-</sup> ions are added as well as the shift in equilibrium.  The steps in the calculation are clearly shown and the ratio is clear.
5		Initial rate = $10^{-2} \times 2.4 \times 10^{-3} \text{ s}^{-1}$ = $2.4 \times 10^{-5}$ (mol dm <sup>-3</sup> s <sup>-1</sup> ) $\checkmark$	1 AO 2.2	Examiner's Comments  This part tested an understanding of pH as a logarithmic scale and the relationship between rates and order. This part discriminated extremely well. A pH of 3 meant that the H+ concentration would be 100 times less than at a pH of 1. Being a first order reaction with respect to H+, the initial rate is simply 100 times less than at a pH of 1: 2.4 × 10 <sup>-5</sup> mol dm <sup>-3</sup> s <sup>-1</sup> .  The higher-ability candidates identified the relationships and often wrote the correct answer on the answer line with no visible working (presumably doing the calculation in their head). Others used their well-learnt equations to calculate the same correct answer.  Many candidates found the calculation difficult and 7.2 × 10 <sup>-3</sup> (3 × (2.4 × 10 <sup>-3</sup> )) was a very common incorrect answer. If candidates had fully scrutinised this answer, they may have realised that a more dilute solution cannot produce a faster rate.
		Total	1	
6	а	$CO_3^{2-} + H_2O \rightarrow OH^- + HCO_3^-$ OR $CO_3^{2-} + H_2O \rightarrow 2OH^- + CO_2 \checkmark$	1 AO 1.2	ALLOW $CO_3^{2-} + 2H_2O \rightarrow 2OH^- + H_2CO_3$ IGNORE state symbols  ALLOW inclusion of Na <sup>+</sup> as spectator ion, e.g. $2Na^+ + CO_3^{2-} + H_2O \rightarrow 2OH^- + 2Na^+ + CO_2$ IGNORE $Na_2CO_3 + H_2O \rightarrow 2NaOH + CO_2$ Ionic equation required  IGNORE equation with H <sup>+</sup> or H <sub>3</sub> O <sup>+</sup>

			e.g. CO <sub>3</sub> <sup>2-</sup> + H <sup>+</sup> → OH <sup>-</sup> + CO <sub>2</sub> <i>Question asks for reaction with H</i> <sub>2</sub> O  Examiner's Comments  This equation presented problems for many candidates, despite the question asking for an equation between carbonate ions and water. An acceptable equation had to be ionic and needed to produce OH <sup>-</sup> (for the alkaline solution) and either HCO <sub>3</sub> <sup>-</sup> or CO <sub>2</sub> .  Many candidates wrote an equation with H <sup>+</sup> instead of H <sub>2</sub> O, with lower ability candidates showing the carbonate ion with the wrong charge as CO <sub>3</sub> <sup>-</sup> .  Many candidates wrote full equations despite the question asking for an ionic equation. Candidates do need to read the instructions in the question.
b	Acid/H⁺/HCl reacts with <b>OR</b> protonates  • benzoate / C <sub>6</sub> H <sub>5</sub> COO⁻  • carboxylate / salt  (to form benzoic acid) ✓	1 AO 2.3	ALLOW suitable equation, e.g.  C <sub>6</sub> H <sub>5</sub> COO <sup>-</sup> + H <sup>+</sup> → C <sub>6</sub> H <sub>5</sub> COOH  IGNORE responses purely in terms of neutralisation of alkali, e.g. Acid/H <sup>+</sup> /HCI neutralises / reacts with/removes alkali / OH <sup>-</sup> / CO <sub>3</sub> <sup>2-</sup> / Na <sub>2</sub> CO <sub>3</sub> Examiner's Comments  Candidates found this part extremely difficult. The question was aimed to stretch and challenge.  Many candidates followed on directly from part (a), stating in simple terms that the alkaline solution needed to be neutralised to remove hydroxide ions. However, candidates were expected to recognise that the alkaline conditions would lead to benzoate ions rather than benzoic acid being present in the mixture. The mixture is acidified to protonate the benzoate. The hint in the question was about making the benzoic acid appearing when acid is added.
С	$C_6H_5CH_2OH + 2[O] \rightarrow C_6H_5COOH + H_2O \checkmark$	1 AO 2.6	ALLOW molecular, structural, displayed formulae, etc e.g. molecular: $C_7H_8O + 2[O] \rightarrow C_7H_6O_2 + H_2O$ Examiner's Comments  This part discriminated well with many

			candidates being able to write a correct equation using their knowledge of the oxidation of alcohols. Mistakes usually resulted in the balancing with either [O] instead of 2[O] or 2H <sub>2</sub> O instead of H <sub>2</sub> O.
			Written equations always need to be checked for the atoms balancing.
			ALLOW ECF for each step
			Calculator = 0.03851851852
			Calculator = 0.01303278689
	FIRST CHECK THE ANSWER ON ANSWER LINE		Alternative method using mass  1. Theoretical moles = 0.0385 mol
	If answer = 33.8 OR 33.9 (%) award 3 marks Theoretical moles		2. Mass = 0.0385 × 122.0 = 4.70 g
	$n(C_6H_5COOH)$ <b>OR</b> $n(C_6H_5CH_2OH)$	3	3. % yield = $\frac{1.59}{4.70} \times 100 = 33.8\%$
	$= \frac{4.00 \times 1.04}{108.0} \text{ OR } 0.0385 \text{ (mol) } \checkmark$		
d	Actual moles	AO2. 8×1	Common errors 35.2% → 2 marks
	$n(C_6H_5COOH)$ = $\frac{1.59}{122.0}$ <b>OR</b> 0.013(0)	AO2. 8×1	• From $\frac{4.00}{108} = 0.0370$
		101	(no use of density)
	% yield = $\frac{0.0130}{0.0385} \times 100$ = 33.8% <b>OR</b> 33.9 (3 sig fig) $\checkmark$	AO1.	36.5 <b>OR</b> 36.6% → 2 marks
			$ \bullet  \frac{4.00/1.04}{108} = \frac{3.846}{108} = 0.0356 $
	Answer depends on some intermediate roundings to 3SF		
			(÷ density instead of × density)
			Examiner's Comments  Condidates are well practiced with
			Candidates are well practised with percentage yield calculations with about half obtaining the correct percentage yield of 33.8 or 33.9% to secure all 3 marks. Many were able to secure partial credit for incorrect answers, provided that the working was laid out clearly.

			Some responses showed a simple percentage of the two masses with no consideration of moles or molar masses.  Such a response received no credit.
e	Dissolve in the <b>minimum</b> quantity of <b>hot</b> water/solvent ✓  Cool AND Filter AND (leave to) dry ✓ All three needed	2 AO 3.3 x2	DO NOT ALLOW use of drying agent (e.g. MgSO <sub>4</sub> )  IGNORE  Initial filtering hot filtration to remove insoluble impurities  Examiner's Comments  Many candidates produced thorough responses, showing that they had encountered recrystallisation as a technique in their practical work.  Most candidates were aware that the impure product is dissolved in a minimum volume of hot solvent, although 'minimum' was sometimes omitted.  The subsequent stages were sometimes incomplete or in the wrong order. Many were aware that the hot solution can be passed through fluted filter paper to remove solid impurities. (This is beyond the specification requirements for A Level but good practice).  Most candidates were aware of the need to filter (usually under reduced pressure) but the necessary cooling stage to form the crystals was sometimes omitted.  Finally, many responses omitted the need to dry the crystals. Candidates did sometimes dry the crystals by adding an anhydrous salt (e.g. CaCl <sub>2</sub> or MgSO <sub>4</sub> ), a clear confusion with drying an organic liquid. Others

				described the purification of an organic liquid for their response, including use of a separating funnel, drying and distillation.
		Total	8	
7	i	3-hydroxybutanal √	1	IGNORE lack of hyphens or addition of commas  ALLOW 4-oxobutan-2-ol OR 1-oxobutan-3-ol  DO NOT ALLOW  • 3-hydroxybutal • 3-hydroxylbutanal  Examiner's Comments  Most candidates made good attempts at the name, the difficulty being that hydroxyl group needed to be shown as a hydroxyprefix, rather than the suffix -ol.  Common errors included 2-hydroxybutanal (counting the carbon chain from the wrong end) and 2- or 3-hydroxybutanoic acid (reading the aldehyde group as a carboxylic acid).
	ii	Addition ✓	1	IGNORE nucleophilic OR electrophilic OR radical  DO NOT ALLOW addition—elimination, condensation, polymerisation  Examiner's Comments  This part was answered well with most choosing nucleophilic addition. Credit was given just for 'addition'.
	ii i	ALLOW any formula provided that number and type of atoms and charge are correct, e.g. For CH₃CHO, ALLOW CH₃COH, C₂H₄O, etc.  Step 1:  Correct equation ✓ One correct acid–base pair ✓ i.e. A1 and B1 OR A2 and B2	3	Throughout, IGNORE 'connectivity in any formula or structures shown.  Examples in Answer column and in 6a(iv) guidance below  Step 1: ALLOW H⁺ transfer from OH⁻, i.e.  CH₃CHO + OH⁻ ⇌ CH₃CH₂O⁺ + O²⁻  ✓

			CH2CHO + H20 CH3CO <sup>-</sup> + H2O			B2	<b>A</b> 1	A2	B1 B2	
	A1	B2	B1	A2 A1		OR B1 Step 2:	A2	<b>A</b> 1	52	
	CH₃CH0					CH <sub>3</sub> CHO + CH <sub>3</sub> CH <sub>2</sub> O <sup>+</sup> + O <sup>2−</sup> → CH <sub>3</sub> CHOHCH <sub>2</sub> CHO + OH <sup>−</sup> √  For CH <sub>3</sub> CH <sub>2</sub> O <sup>+</sup> : <b>ALLOW</b> CH <sub>3</sub> CHOH <sup>+</sup> ,  C <sub>2</sub> H <sub>5</sub> O <sup>+</sup> Examiner's Comments				
	For CH₃CHOH	ICH₂CHO, <b>AL</b>	<b>LOW</b> C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>			base equi Many can generate usually as equation v ability can together a responses See Exem Exemplai	libria with a didates co acid—base esigned cor was challer adidates we all the information at the acid and the information at t	a multi-ste mpleted an pairs, which rectly. The nging but there able to mation with at the corresponding to the co	he highest combine h their earlier ect equation.	
i	ОН Н   — С— С— С— СН <sub>3</sub> Н	_c, CH₃ ,			1	OR skelet OR a comunambigut For connection Connection Connection Connection Connection Control on the paper Condidate information molecules combining	ectivity,	e f above as CH <sub>3</sub> –  ing assessents  to link the pining two on the production of the production of the production on the production on the production of the production on the production of the production on the production of the	long as  C <sub>3</sub> H- OH  ced)  challenging  earlier ethanal ct for	

					candidates were able to come up with the correct structure.
			Total	6	
8	а	i	$K_{a} = \frac{[H^{+}][CH_{3}COO^{-}]}{[CH_{3}COOH]} \checkmark$	1	IGNORE state symbols  Must be square brackets  IGNORE expressions with HA or with [H <sup>+</sup> ] <sup>2</sup> Examiner's Comments  Almost universally known.  Common errors were the use of [HA], [A <sup>-</sup> ] or [H <sup>+</sup> ] <sup>2</sup> .
		ï	FIRST, CHECK ANSWER ON ANSWER LINE  IF answer = 4.76 award 3 marks  [H <sup>+</sup> ] = $10^{-pH}$ $= 10^{-2.41} = 3.89 \times 10^{-3} \text{ (mol dm}^{-3}\text{)} \checkmark$ $K_a$ $= \frac{[H^+]^2}{[CH_3COOH]} = \frac{(3.89 \times 10^{-3})^2}{0.870}$ $= 1.74 \times 10^{-5} \text{ (mol dm}^{-3}\text{)} \checkmark$ $pK_a$ $= -\log K_a = -\log 1.74 \times 10^{-5} = 4.76 \checkmark$	3	ALLOW use of HA and A <sup>-</sup> ALLOW 3 SF up to calculator value of: 3.89045145 × 10 <sup>-3</sup> correctly rounded  K <sub>a</sub> 1.739725573 × 10 <sup>-3</sup> NOTE: 1.74 × 10 <sup>-5</sup> is same from unrounded [H <sup>+</sup> ] calculator value and 3 SF [H <sup>+</sup> ] value  2 DP required  Examiner's Comments  This three-step calculation was successfully completed by almost all candidates.  The common errors were to omit giving the final answer to 2 decimal places or to use [H <sup>+</sup> ] rather than [H <sup>+</sup> ] <sup>2</sup> in the calculation, leading to a pK <sub>a</sub> of 2.35.
		<b>:=</b>	% dissociation = $\frac{[H^+]}{[CH_3COOH]} \times 100$ = $\frac{3.89 \times 10^{-3}}{0.870} \times 100 = 0.447(\%) \checkmark$	1	3 SF required  Examiner's Comments  This proved a more difficult calculation than expected, but higher ability candidates realised that [H+] (determined from the pH) divided by the given concentration of CH <sub>3</sub> COOH was required. Answers had to be expressed to three significant figures in order to receive credit.
	b		FIRST, CHECK ANSWER ON ANSWER LINE IF answer = 95.9(%) award 4 marks	2	

[H <sup>+</sup> ] = 10 <sup>-pH</sup>	

= 
$$10^{-13.48}$$
 =  $3.31 \times 10^{-14}$  (mol dm<sup>-3</sup>)  $\checkmark$ 

## [OH⁻] from K<sub>w</sub>

$$= \frac{1.00 \times 10^{-14}}{3.31 \times 10^{-14}} = 0.302 \text{ (mol dm}^{-3}\text{)} \checkmark$$

#### Mass of (NaOH)

= 
$$0.302 \times \frac{100}{1000} \times 40.0 = 1.21$$
 (g)  $\checkmark$ 

#### % of NaOH to 3 SF

$$= \frac{1.21}{1.26} \times 100 = 95.9 \,(\%) \checkmark$$

## **ALLOW ECF** throughout

**IGNORE** rounding errors beyond 3<sup>rd</sup> SF throughout

**ALLOW**  $3.3 \times 10^{-14}$  (mol dm<sup>-3</sup>)

#### **ALLOW** 0.30

**ALLOW** 0.303 if  $3.3 \times 10^{-14}$  used in the first marking point

ALLOW pOH method:,

$$pOH = 14 - 13.48 = 0.52$$

$$[OH^{-}] = 10^{-0.52} = 0.302 \text{ (mol dm}^{-3})$$

**ALLOW** 
$$[OH^{-}] \times 0.1 \times 40$$

Rounding  $[OH^{-}]$  to 0.3(0) gives 1.2/1.26 = 95.2%

Award 4 marks

Rounding [OH<sup>-</sup>] to 0.303 gives 1.212/1.26 = 96.2%

Award 4 marks

# **Examiner's Comments**

To help candidates, on this occasion early rounding was ignored and consequently most candidates scored full marks in this multi-step calculation. However, candidates should be advised not to round in the early stages of calculations such as this, as this introduces rounding errors into the final answer.

Candidates should be encouraged to indicate what they are attempting to calculate in unstructured calculations such as this.

The first step was frequently seen as  $10^{-13.48}$ =  $3.31... \times 10^{-14}$  which most examiners could take to be [H<sup>+</sup>]. However, it is clearer to write  $[H^+] = 10^{-13.48} = 3.31... \times 10^{-14} \text{ mol}$ dm<sup>-3</sup>. Even inclusion of units would help some candidates achieve partial credit as this might allow examiners to determine what a candidate is attempting to do.

		Total	9	
9	а	FIRST, CHECK THE ANSWER ON ANSWER LINE  IF answer = 0.753, award 3 marks	3	

	(mol dm	= 10 <sup>-pH</sup> = 10 <sup>-2</sup> $oldsymbol{10^{-7}} oldsymbol{10^{-7}} oldsymbol{$	<b>R</b> $\frac{(3.63 \times 10^{-7})}{1.75 \times 10^{-7}}$				ALLO 3.630  NOTE calcul  ALLO from [ end  Exam Most of seen to	780548 × E: Answel ator value OW 0.749 CH <sub>3</sub> COO candidate type of ca	up to calc 10 <sup>-3</sup> con is same and 3 S if [H <sup>+</sup> ] ha iH] for gre comments as coped	from unrouse [H+] value s been sue the accurate	ounded [H <sup>+</sup> ] ue ubtracted uracy at
		OH + FCH₂C	OOH ⇌ CH3	COOH₂ <sup>+</sup>			Take s  ALLO below  CH <sub>3</sub> C + FCH	great car  W ECF for This is to the coordinate of the coordinate o	re matching or incorrect the ONLY	<b>' ECF</b> •H ⇔CH₃0	H₂⁺ transfer as
Ь	B2 OR B1	A1 A2 els other way i	A2 A1 round	B1 B2	✓	2	Exam	B1 bels other siner's Co	omments		√ECF
							quite s candid Candi equilit negati were d decide should assign	straightfodate, theredates structure ion or	rward but re were muggled will eded a poor the produce $K_a$ vote the two expression at the protonate conjugate.	t for the wany pitfal ith the idensitive ion luct side. alues in constanting a ted. Finall	reaker Ils. a that the and a Others order to cids

	[CH <sub>3</sub> COO-] $n(\text{CH}_3\text{COONa}) = \frac{9.08}{82.0} \text{ OR } 0.111 \checkmark \text{ (Calc: } 0.1107317073)$ $[\text{CH}_3\text{COO-}] = \frac{9.08}{82.0} \times \frac{1000}{250} = 0.443 \text{ (mol dm}^{-3})$ $\text{OR } n(\text{CH}_3\text{COOH}) = 0.800 \times \frac{250}{1000} = 0.200 \text{ (mol)} \checkmark$ [H <sup>+</sup> ] $[\text{H}^+] = K_a \times \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO-}]} \text{ OR } K_a \times \frac{n(\text{CH}_3\text{COOH})}{n(\text{CH}_3\text{COO-})}$ $= 1.75 \times 10^{-5} \times \frac{0.800}{0.443} \text{ OR } 1.75 \times 10^{-5} \times \frac{0.200}{0.111} \checkmark$ $= 3.16 \times 10^{-5} \text{ (mol dm}^{-3}) \checkmark$		ALLOW 2 sig fig ALLOW use of HA and A <sup>-</sup> Mark by ECF  Alternative method (If both methods are attempted, mark the method which produces the higher mark) [H+]  [H+] = $10^{-pH} = 10^{-4.50}$ = $3.16 \times 10^{-5}$ (mol dm <sup>-3</sup> ) $\checkmark$ [CH <sub>3</sub> COO <sup>-</sup> ]  [CH <sub>3</sub> COO <sup>-</sup> ] = $K_a \times \frac{[CH_3COOH]}{[H^+]}$ OR $1.75 \times 10^{-5} \times \frac{0.800}{3.16 \times 10^{-5}} \checkmark$ = $0.443$ (mol dm <sup>-3</sup> ) $\checkmark$
c i	pH (must come from calculated [H+]) pH = −log (3.16 × 10 <sup>-5</sup> ) = 4.50 √  LAST 3 marks are NOT available using  • K <sub>a</sub> square root approach (weak acid pH) • K <sub>w</sub> /10 <sup>-14</sup> approach (strong base pH)	5	mass of CH <sub>3</sub> COONa = $0.443 \times \frac{250}{1000}$ OR $0.111 \checkmark$ $0.111 \times 82.0 = 9.08 (g) \checkmark$ Common errors
	Henderson-Hasselbalch (HH) alternative $pKa = -\log 1.75 \times 10^{-5} = 4.757 \text{ (or } 4.756961951)$ $pH = pK_a + \log \frac{[CH_3COOT]}{[CH_3COOH]} \text{ OR } = pK_a - \log \frac{[CH_3COOH]}{[CH_3COOT]}$ $OR pK_a + \log \frac{0.443}{0.800}  OR = pK_a - \log \frac{0.800}{0.443} \checkmark$ $= pK_a - 0.257 \checkmark$ $= 4.757 - 0.257 = 4.50 \checkmark$		4.64 Use of M(CH <sub>3</sub> COONa) = 60 4 marks 2.40 Use of K <sub>a</sub> of FCH <sub>2</sub> COOH 4 marks  Examiner's Comments  This question caused difficulty for all but the more able. For many weaker candidates getting beyond a concentration of CH <sub>3</sub> COONa was a problem. Once again, candidates should be advised to show every step in their calculation. This would allow method marks to be applied in the absence of a correct final answer.
ii	pH is the same/constant ✓ ratio/proportion [HA]/[A⁻] is the same ✓	2	M2 is dependent upon M1  ALLOW Change in [HA] and [A <sup>-</sup> ] is proportional  Examiner's Comments

				Only the very able were able to explain that the ratio of concentrations of acid and salt would remain constant and as $K_a$ is constant, [H <sup>+</sup> ] and therefore pH would remain constant.
		Total	12	
1 0	i	$K_{a} = \frac{[H^{+}][C_{4}H_{9}S^{-}]}{[C_{4}H_{9}SH]} \checkmark$ Square brackets required	1	ALLOW correct structural OR skeletal OR displayed formula OR mixture of the above as long as non- ambiguous  Examiner's Comment: This part was very well answered. Candidates responded with either near molecular formulae, such as C <sub>4</sub> H <sub>9</sub> SH, structural formulae or with skeletal formulae. Some candidates made careless errors such as omitting the negative charge or showing [H <sup>+</sup> ] <sup>2</sup> as numerator rather than [C <sub>4</sub> H <sub>9</sub> S <sup>-</sup> ] [H <sup>+</sup> ].
	ii	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> SH + H <sub>3</sub> C → OH    → H <sub>3</sub> C → + H <sub>2</sub> O    S-CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> Structure of thioester ✓    Complete equation ✓	2	ALLOW correct skeletal OR displayed formula OR mixture of the above as long as non-ambiguous  ALLOW C4H9SH  ALLOW CH3COOH  Thioester functional group must be fully displayed, OR as a skeletal formula but allow SC4H9 in thioester  Examiner's Comment: In this part, candidates were expected to apply their knowledge and understanding of esterification to thiols and thioesters. Over half the candidates obtained a correct structure of the thioester. Most of these candidates constructed a balanced equation although some omitted the water product. Common errors included formation of a conventional ester and H2S, and retaining the O atom from the OH in the carboxyl group to form —COOS—. As with 4(b)(i), structural and skeletal formulae were used. Candidates are less likely to omit H atoms if the skeletal formula is used.
	ii	SH V	1	IF correct skeletal formula is shown, IGNORE displayed formula in a second structure

				Examiner's Comment: Just over half the candidates drew the correct structure, displaying a good understanding of interpreting organic nomenclature when drawing a structure.  Common errors included omission of the
				CH <sub>2</sub> adjacent to the terminal –SH group and placing the branch or double bond in wrong positions. Some candidates spoilt an otherwise good response by showing a structural formula or a mixture of skeletal and structural formulae.
				ALLOW correct structural OR skeletal OR displayed formula OR mixture of the above as long as non- ambiguous
	i V	Reactants ✓  Products <b>AND</b> balanced equation ✓	2	Examiner's Comment: In this part, candidates were expected to apply their knowledge and understanding of condensation to an entirely new context. One mark was allocated for the reactants and this was usually scored. The second mark for the novel cyclic compound and water was much more difficult, aimed at stretch and challenge. A significant number of candidates interpreted the information to obtain a correct cyclic structure but this mark was the domain of the most able candidates.
		Total	6	
1 1	i	Complete dissociation would give [H <sup>+</sup> ] = 0.2 (mol dm <sup>-3</sup> ) √  pH from complete dissociation = −log 0.2 = 0.7  OR actual [H <sup>+</sup> ] = 10 <sup>-0.96</sup> = 0.11 (mol dm <sup>-3</sup> )√  Stage 1 is complete dissociation  AND  Stage 2 is partial dissociation √	3	IGNORE Stage 1 is a strong acid AND Stage 2 is a weak acid.
	ii	Observation: fizzing ✓  H⁺ reacts with carbonate  AND  (Stage 2) equilibrium shifts to the right ✓	2	ALLOW effervescence/'bubbling'

			Total	5	
			$(K_a =) \frac{[H^+][C_6H_7O_6^-]}{[C_6H_8O_6]} \checkmark$		ALLOW [H <sub>3</sub> O <sup>+</sup> ] for [H <sup>+</sup> ]
1 2	а	i	ALL species MUST have square brackets State symbols not required	1	IGNORE state symbols, even if wrong
			<b>TAKE CARE</b> that 'H' is different on top and bottom of expression		IGNORE $\frac{[H^{\uparrow}]^2}{[C_6H_8O_6]}$ OR $\frac{[H^{\uparrow}]^2[A^{\uparrow}]}{[HA]}$
		ii	$pK_a = -log K_a = -log (6.76 \times 10^{-5}) = 4.17 \checkmark$	1	Answer required to <b>two DP</b>
			FIRST, CHECK THE ANSWER ON ANSWER LINE  IF answer = 2.82 award 4 marks		
			$n(\text{vitamin C}) = \frac{3 \times 0.500}{176}$		
			= 8.52(2) × 10 <sup>-3</sup> (mol) √		<b>ALLOW ECF</b> from incorrect <i>n</i> (vitamin C)
		ii i	[vitamin C] = $8.52 \times 10^{-3} \times \frac{1000}{250}$ = $0.0341 \text{ (mol dm}^{-3}) \checkmark$ [H*] = $\sqrt{(K_a \times [C_6H_8O_6])}$ OR $\sqrt{(6.76 \times 10^{-5} \times 0.0341)}$ OR $1.52 \times 10^{-3} \text{ mol dm}^{-3} \checkmark$ pH = $-\log(1.52 \times 10^{-3}) = 2.82 \checkmark$ Answer required to <b>two DP</b>		
					ALLOW ECF from incorrect [vitamin C] must be derived from $\sqrt{(K_a \times [C_6H_8O_6])}$
					<b>ALLOW ECF</b> from incorrect [H <sup>+</sup> ] but <b>ONLY</b> if derived from $\sqrt{(K_a \times [C_6H_8O_6])}$
					<b>IF</b> there is an alternative answer, check to see if there is any <b>ECF</b> credit possible using working below
			FIRST, CHECK THE ANSWER ON ANSWER LINE  IF ratio = 0.708 award 3 marks		
			[H <sup>+</sup> ] = $10^{-pH}$ = $10^{-4.02}$ = $9.55 \times 10^{-5}$ (mol dm <sup>-3</sup> ) $\checkmark$		ANNOTATIONS MUST BE USED ALLOW ALTERNATIVE using Henderson-Hasselbalch equation
	b	i		3	<b>ALLOW</b> 9.55 × 10 <sup>-5</sup> up to calculator value of 9.54992586 × 10 <sup>-5</sup> correctly rounded
			$\frac{[C_6H_7O_6^-]}{[C_6H_8O_6]} = \frac{K_a}{[H^+]^{=}} \frac{6.76 \times 10^{-5}}{9.55 \times 10^{-5}} \checkmark$		
					ALLOW ECF from incorrect [H <sup>+</sup> ]
			$=\frac{0.708}{1}$ $\checkmark$		
					<b>ALLOW</b> 0.71 (2 SF) up to calculator value correctly rounded

			mass of C6H <sub>7</sub> O <sub>6</sub> Na = $0.708 \times \frac{300}{176} \times 198.0$		
		ii		1	ALLOW ECF from answer to (i)
			= 239 <b>OR</b> 240 (mg) √		
	O		FIRST, CHECK THE ANSWER ON ANSWER LINE IF answer = $0.0524$ (mol dm <sup>-3</sup> ) award 2 marks  [H <sup>+</sup> (aq)] = $10^{-pH}$ = $10^{-12.72}$ = $1.91/1.9 \times 10^{-13}$ (mol dm <sup>-3</sup> ) $\checkmark$ [NaOH] / [OH <sup>-</sup> (aq)] = $\frac{K_w}{[H^+(aq)]}$ = $\frac{1.0 \times 10^{-14}}{1.91 \times 10^{-13}}$	2	ALLOW alternative approach via pOH pOH = 14 − 12.72 = 1.28 √ [NaOH] / [OH⁻(aq)] = 10⁻pOH = 0.0524 (mol dm⁻³) √  ALLOW any value between 0.052 and 0.053 answer depends on degree of rounding for H⁺ but 2 SF minimum
			= 0.0524 (mol dm <sup>-3</sup> ) √		calculator: 0.052480746
			Total	12	
1 3	а		$(K_a =) \frac{[H^{+}][NO_2^{-}]}{[HNO_2]} \checkmark$ IGNORE state symbols	1	IGNORE [H <sup>+</sup> ] <sup>2</sup> OR [H <sup>+</sup> ] [A]  ALLOW H <sub>3</sub> O <sup>+</sup> for H <sup>+</sup> Square brackets required  Examiner's Comments  Almost all candidates successfully wrote the expression for K <sub>a</sub> . Responses using [H <sup>+</sup> (aq)] <sup>2</sup> were not credited. Rarely, the expression was shown inverted or square brackets were omitted from one or more of the terms. For most candidates, this was an easy mark.
	b		FIRST, CHECK THE ANSWER ON ANSWER LINE IF answer = 2.12 award 2 marks $[H^{+}] = \sqrt{K_a} \square [HNO_2] = 7.502 \times 10^{-3} \text{ (mol dm}^{-3}) \checkmark$ $pH = -\log 7.502 \times 10^{-3} = 2.12 \checkmark$ $pH to 2 DP$	2	ALLOW intermediate value from 3 SF (7.50 up to calculator value of 7.501999733 × 10 <sup>-3</sup> ALLOW 1 mark for 2.1 OR answer > 2 DP (i.e. not 2 DP)  ONLY ALLOW pH mark by ECF if K <sub>a</sub> AND 0.120 used and AND pH < 7  COMMON ERRORS (MUST be to 2 DP)  pH = 4.25 No square root:1 mark [H <sup>+</sup> ] = (4.69 × 10 <sup>-4</sup> × 0.120) = 5.628 × 10 <sup>-5</sup> (mol dm <sup>-3</sup> )

	pH = $-\log 5.628 \times 10^{-5} = 4.25 \checkmark$ pH = $0.92$ no $K_a$ used:  zero marks  pH = $-\log 0.120 = 0.92$ pH = $13.08 \ K_w \ / \ pOH \ used$ :  zero marks  pH = $-\log \frac{1.00 \times 10^{-4}}{0.120} \ OR \ 14 - \log 0.120 = 13.08$ Examiner's Comments  Most candidates calculated [H <sup>+</sup> ] as the square root of $K_a \times [HNO_2]$ , and then the correct pH value. The commonest errors were incorrect rounding of the pH value (e.g. 2.13) and missing out the square root (giving 4.25).  Answer: pH = $2.12$
FIRST, CHECK THE ANSWER ON ANSWER LINE IF answer = 3.43, AWARD 4 marks $Expression: K_a \times acid / base ratio$ Use of $K_a \times \frac{[HNO_2]}{[NO_2]}$ OR $4.69 \times 10^{-4} \times \frac{[HNO_2]}{[NO_2]} \checkmark$ $Using correct concs / mol in expression$ $[H^+] = 4.69 \times 10^{-4} \times \frac{0.0400}{0.0500} \checkmark Subsumes previous mark$ $Calculation of [H^+]$ $[H^+] = 3.752 \times 10^{-4} \text{ (mol dm}^{-3)} \checkmark$ Ph to 2 DP (From 3.42573717) $pH = -\log 3.752 \times 10^{-4} = 3.43 \checkmark$ NO marks are available using $K_a \text{ square root approach (weak acid pH)}$ $K_w/10^{-14} \text{ approach (strong base pH)}$ ALLOW alternative approach based on Henderson—Hasselbalch equation (ALLOW $-\log K_a \text{ for } pK_a$ ) $pH = pK_a + \log \frac{[NO_2]}{[HNO_2]} \text{ OR } pK_a - \log \frac{[NO_2]}{[NO_2]} \checkmark$ $pH = pK_a + \log \frac{0.0500}{0.0400} \text{ OR } pK_a - \log \frac{0.0400}{0.0500} \checkmark$ $pH = pK_a + 0.097 \checkmark$ $pH = 3.329 + 0.097 = 3.43 \checkmark$	ALLOW just $K_a \times \frac{\text{acid}}{\text{salt}}$ expression  Mark by ECF from $\frac{4.69 \times 10^{-4} \times \frac{[\text{NO}_2]}{[\text{HNO}_2]}}{\text{inverted expression}}$ Mark by ECF from incorrect [HNO <sub>2</sub> ] and [NO <sub>2</sub> -]  ONLY award marks for a pH calculation via $K_a$ AND using concentrations / mol derived from the question  DO NOT ALLOW final pH mark by ECF if pH > 7  COMMON ERRORS BUT CHECK WORKING pH = 2.82 3 marks initial concs: 0.200 and 0.0625 pH = 3.23 3 marks  0.0400 and 0.0500 acid / base ratio inverted pH = 3.83 2 marks initial concs: 0.200 and 0.0625 and ratio inverted pH = 2.73 3 marks Incorrect [NO <sub>2</sub> -] = 0.01 and correct [HNO <sub>2</sub> ] =

			pH = 4.03 3 marks correct [NO2-] = 0.05 and incorrect [HNO2] = 0.01  Examiner's Comments  This buffer calculation was easier than some on recent papers as the equilibrium moles had been provided. Some candidates tried to mimic the approach for a more complex calculation, introducing errors where there were none.  The simpler problem allowed more candidates to obtain the correct value for the pH of the buffer solution than in recent examinations. Answer: pH = 3.43
	Equilibrium: 1 mark  HNO₂ ⇌ H⁺ + NO₂⁻ ✓  (ignore state symbols)		FULL ANNOTATIONS MUST BE USED  IGNORE HA   H <sup>+</sup> + A <sup>-</sup> Equilibrium sign essential  BUT ALLOW small slips in its appearance if it is obviously an attempt to show an equilibrium sign rather than an arrow  QWC: Quality of written communication  DO NOT ALLOW HA and A <sup>-</sup> for HNO₂ and NO₂ <sup>-</sup>
ii	Control of pH: 2 marks (QWC)  Added HCI  NO₂⁻ reacts with added acid / HCI / H⁺  OR NO₂⁻ + H⁺ →  OR more HNO₂ forms ✓  Added NaOH  HNO₂ reacts with added alkali / NaOH / OH⁻  OR HNO₂ + OH⁻ →  OR more NO₂⁻ forms	4	IGNORE just acid reacts with added alkali  IGNORE just conjugate base / salt / base reacts with added acid  DO NOT ALLOW salt / base reacts with added acid
	OR H <sup>+</sup> reacts with added alkali / NaOH OR H <sup>+</sup> + OH <sup>-</sup> → ✓  Equilibrium shift:  1 mark for shifts in HNO <sub>2</sub> ⇌ H <sup>+</sup> + NO <sub>2</sub> <sup>-</sup> (See 1st mark)  Equilibrium for added acid → left  AND Equilibrium for added alkali → right ✓ (QWC)		AWARD 'shift mark' ONLY if correct equilibrium equation has been given IGNORE any other equilibria in response  Examiner's Comments  The role of buffers in controlling pH is a common question and most candidates had prepared their rehearsed answers.  Consequently these candidates could obtain the four marks easily. As always, candidates who had not learnt the work produced

		muddled responses that made little sense and could not be credited.
d i	Endothermic <b>AND</b> K <sub>w</sub> increases with temperature <b>OR</b> Endothermic <b>AND</b> dissociation increases <b>with temperature OR</b> Endothermic <b>AND</b> (dissociation) involves breaking bonds ✓	Endothermic and reason required for the mark  ALLOW Endothermic AND increasing temperature shifts equilibrium / reaction to the right / favours forward reaction  DO NOT ALLOW breaking hydrogen bond OR intermolecular bonds / forces  Examiner's Comments  Candidates were expected to predict the type of energy change using the provided information. Credit was given for response linking an endothermic change with the increase of K <sub>w</sub> with temperature or breakin bonds during dissociation.
ii	OH⁻ concentration $[OH⁻] = \frac{9.311 \times 10^{-14}}{1.00 \times 10^{-7}} = 9.311 \times 10^{-7} \text{ (mol dm}^{-3}\text{)} \checkmark$ Explanation (dependent on 1st mark) $9.311 \times 10^{-7} > 1.(00) \times 10^{-7} \text{ OR } [OH⁻] > [H⁺] \text{ OR } OH⁻ \text{ in excess}$ AND Alkaline ✓	H <sup>+</sup> OR OH <sup>-</sup> concentration (neutral pH)  [H <sup>+</sup> ] = [OH <sup>-</sup> ] = √(9.311 × 10 <sup>-14</sup> ) = 3.05 × 10  (mol dm <sup>-3</sup> ) ✓  Explanation (dependent on 1st mark)  pH = -log (3.05 × 10 <sup>-7</sup> ) = 6.5 → 6.515501837 (calc)  AND  Alkaline ✓  Examiner's Comments  Most candidates calculated a value for [H <sup>+</sup> ]  using the K <sub>w</sub> value at 60°C. Many recognised that [OH <sup>-</sup> ] > [H <sup>+</sup> ] giving an alkaline solution. An alternative and equally valid method seen was to calculate the pH of a neutral solution at 60°C as 6.52 and then to relate water at a pH of 7 as being alkaline. Many using this approach thought that water would be acidic rather than alkaline, presumable because 6.52 < 7.00.
ii	pK <sub>w</sub> = 13.03 ✓	ONLY correct answer  Examiner's Comments  Despite the novel context, almost all candidates obtained the correct pKw value 13.03.
i	FIRST, CHECK THE ANSWER ON ANSWER LINE IF answer = 10.76, award 3 marks	FULL ANNOTATIONS MUST BE USED

		Dilution 1 mark		ALLOW dilution AFTER calculation of
		$[OH^{-}(aq)] = [NaOH(aq)] = \frac{0.0270}{5} = 0.00540 \text{ (mol dm}^{-3}) \checkmark$		[H <sup>+</sup> (aq)] i.e. original [H <sup>+</sup> ] = $\frac{9.311 \times 10^{-14}}{0.0270}$ = 3.45 × 10 <sup>-12</sup> (m
		[H <sup>+</sup> ] 1 mark [H <sup>+</sup> (aq)] = $\frac{9.311 \times 10^{-14}}{0.00540}$ = 1.72 × 10 <sup>-11</sup> (mol dm <sup>-3</sup> ) $\checkmark$ Calculator: 1.724259259 × 10 <sup>-11</sup> pH 1 mark		After dilution, $[H^+] = 3.45 \times 10^{-12} \times 5 = 1.72$ $\times 10^{-11}$ (mol dm <sup>-3</sup> ) $\checkmark$ pH = -log 1.72 × 10 <sup>-11</sup> = <b>10.76</b> $\checkmark$ <b>ALLOW ECF</b> from incorrect $[H^+(aq)]$ provided that pH > 7
		pH = −log 1.72 × 10 <sup>-11</sup> = <b>10.76 √</b>		COMMON ERRORS (MUST be to 2 DP) pH = 11.73 At 25°C (1.00 × 10 <sup>-14</sup> ): 2 marks
		pOH = -log 0.00540 = 2.27 ✓ (calculator 2.26760624)		pH = $-\log 1.85 \times 10^{-12} = 11.73$
		pH = 13.03 − 2.27 = 10.76 <b>√</b>		<b>pH = 11.46</b> No dilution at 60°C (9.311 × $10^{-14}$ ) <b>2 marks</b> pH = $-\log(3.45 \times 10^{-12})$ = <b>11.46</b>
				<b>pH = 12.43</b> No dilution <b>AND</b> 25°C (1.00 × 10 <sup>-14</sup> ) <b>1 mark</b> pH = $-\log(3.70 \times 10^{-13})$ = <b>12.43</b>
				<b>pH = 12.16</b> × 5 instead of ÷ 5 at 60°C (9.311 × 10 <sup>-14</sup> ) <b>2 marks</b>
				pH = $-\log(6.879 \times 10^{-13})$ = <b>12.16</b>
				<b>pH = 13.13 ×</b> 5 instead of ÷ 5 at 25°C (1.00 × 10 <sup>-14</sup> ) <b>1 mark</b> pH = -log(7.407 × 10 <sup>-14</sup> ) = <b>13.13</b>
				<b>NOTE:</b> Attempts at dilution $\rightarrow$ 0.0270 with error in powers of 10 $\rightarrow$ 12.46 from 0.00270, etc may give 2 marks by <b>ECF</b>
				Examiner's Comments
				The majority of candidates correctly calculated the pH via $K_w$ but many had problems in initially deriving the concentration of the diluted solution of NaOH. Some candidates did not consider the dilution at all; others produced long calculations of this simple dilution, obtaining an array of concentrations. Provided that this concentration was then converted to a pH by a correct method, credit could still be given for the second part of the problem. Answer: pH = 10.76
		Total	18	
1 4	ij	$-$ H <sub>2</sub> O $\rightleftharpoons$ HCN OH $^-$ AND Base <sub>+</sub> 2 Acid 1 Acid 2 <sub>+</sub> Base 1 ✓ CN	1	State symbols <b>NOT</b> required <b>ALLOW</b> CNH and HO <sup>-</sup> (i.e. any order)
				ALLOW 1 and 2 labels the other way

					around.  ALLOW 'just acid' and 'base' labels throughout if linked by lines so that it is clear what the acid-base pairs are.  Examiner's Comments  The majority of candidates were able to complete the equation for acid-base equilibrium and to identify the acid-base pairs. Candidates are advised to use numbers to label the acid-base pairs, such as 'acid 1' and 'base 1'. Attempts at using 'acid' and 'conjugate base' are ambiguous when more than one acid-base pair is involved. Although credited, it was strange to see hydrogen cyanide often written as CNH.
		ii	H <sup>+</sup> reacts with CN <sup>-</sup> <b>OR</b> HCN forms <b>OR</b> equation: H <sup>+</sup> + CN <sup>-</sup> → HCN ( <b>ALLOW</b> ≠) <b>OR</b> CN <sup>-</sup> accepts a proton / H <sup>+</sup> <b>OR</b> equilibrium shifts right <b>AND</b> CN <sup>-</sup> is removed ✓	1	ALLOW Acid reacts with / removes OH- ions (to form HCN) ALLOW CNH (i.e. any order)  IGNORE other equilibrium comments  Examiner's Comments  The majority of candidates recognised that acid conditions would lead to protonation of CN-forming toxic HCN.
			Total	2	
1 5	а		Proton / H⁺ donor <b>AND</b> Partially dissociates / ionises <b>√</b>	1	Examiner's Comments  For most candidates, this was an easy mark, although some only responded for a weak acid (partial dissociation) or for a Brønsted–Lowry acid (proton donor).
	b		FIRST, CHECK THE ANSWER ON ANSWER LINE IF answer = 13.7(0), award 2 marks $[H^{+}] = \frac{1.00 \times 10^{-14}}{0.5(00)} \text{ OR } 2(.00) \times 10^{-14} \text{ (mol dm}^{-3}) \checkmark$		For pOH method:, <b>ALLOW</b> pOH = −log[OH⁻] = 0.3(0) ✓  (calculator 0.301029995) <b>ALLOW</b> pH = 14 − 0.3 = 13.7 ✓
			pH = $-\log 2(.00) \times 10^{-14} = 13.7(0) \checkmark$	2	ALLOW 13.7 up to calculator value of

			ALLOW ECF from incorrect [H <sup>+</sup> (aq)] provided that pH > 7  Examiner's Comments  The majority of candidates correctly calculated the pH via K <sub>w</sub> . Another less popular but successful approach was via pOH. Either approach could result in both marks. Weaker candidates sometimes calculated the pH as 0.30 (from -log 0.500). This gained no credit.  Answer: pH = 13.70
c i	$(K_a =) \frac{[H^+] [C_2 H_5 COO^-]}{[C_2 H_5 COOH]} \checkmark$	1	IGNORE $\frac{[H^+]^2}{[C_2H_5COOH]}$ OR $\frac{[H^+][A^-]}{[HA]}$ ALLOW $[H_3O^+]$ for $[H^+]$ IGNORE state symbols  Examiner's Comments  Almost all candidates successfully wrote the expression for $K_a$ . Responses using $[H^+(aq)]^2$ were not credited. Rarely, the expression was shown inverted or square brackets were omitted from one or more of the terms. Candidates are recommended to carefully check the formulae as this easy mark was sometimes not awarded for a missing C atom within a formula (even in the scripts of able candidates).
ii	FIRST, CHECK THE ANSWER ON ANSWER LINE IF answer = 2.9(0), award 3 marks $[C_2H_5COOH] = 0.12(0) \text{ mol dm}^{-3} \checkmark$ $[H^+] = \sqrt{K_a \times [C_2H_5COOH]} = \sqrt{1.35 \times 10^{-5} \times 0.12(0)}$ OR 1.27 × 10 <sup>-3</sup> (mol dm <sup>-3</sup> ) $\checkmark$		<b>ALLOW</b> HA for $C_2H_5COOH$ and $A^-$ for $C_2H_5COO^-$ <b>ALLOW ECF</b> from incorrectly calculated [ $C_2H_5COOH$ ] <b>ALLOW</b> 1.27 × 10 <sup>-3</sup> to calculator value of 1.272792206 × 10 <sup>-3</sup> correctly rounded <b>ALLOW</b> 2.9(0) × 10 <sup>-3</sup> to calculator value of 2.895242493 correctly rounded
ii	<b>NOTE</b> : The final two marks are <b>ONLY</b> available from attempted use of $K_a$ <b>AND</b> [C <sub>2</sub> H <sub>5</sub> COOH]	3	<b>ALLOW</b> use of quadratic equation which gives same answer of 2.90 from 0.120 mol dm <sup>-3</sup>

	COMMON ERRORS (MUST be to AT LEAST 2 DP unless $2^{nd}$ decimal place is 0)  pH = 2.59 2 marks $-\log\sqrt{(1.35 \times 10^{-5} \times 0.480)}$ Original conc  pH = 5.79 2 marks $-\log(1.35 \times 10^{-5} \times 0.120)$ No $$ pH = 5.19 1 mark $-\log(1.35 \times 10^{-5} \times 0.480)$ Original conc, no $$ pH = 4.87 0 marks
	Examiner's Comments  This part discriminated extremely well. The added stage of an initial dilution to a stock weak acid pH calculation created problems for many candidates. Although most were able to use the correct square root expression to obtain a value for [H <sup>+</sup> (aq)], the concentration used was often incorrect. Although just a four times dilution from 0.480 mol dm <sup>-3</sup> to 0.120 mol dm <sup>-3</sup> , many candidates obtained 0.120 using learnt equations rather than the simple ratio. Others used the original concentration of 0.480 mol dm <sup>-3</sup> or incorrectly calculated concentrations, commonly seen as 0.0480, 0.0120 or even 0.192 (from × 4). Some candidates calculated [H <sup>+</sup> (aq)] using 0.480 mol dm <sup>-3</sup> but then divided by 4 before calculating the pH. Able candidates invariably obtained the correct pH but many obtained pH values from the values above such as a pH of 2.59 (from 0.480 mol dm <sup>-3</sup> ), for which partial credit could be awarded.
d i pH = -log 1.35 × 10 <sup>-5</sup> = <b>4.87</b> ✓	ONLY correct answer DO NOT ALLOW 4.9 (Question asks for 2 DP)  Examiner's Comments  Some candidates correctly calculated the pH here as -log Ka but most used the standard buffer pH method, using a 1:1 acid-base ratio. Weak candidates often first

		took the square root of the Ka value, obtaining a pH of 2.43. Unfortunately, some candidates rounded a correct pH to 4.9, despite a two decimal place requirement being emphasised in the question.  Answer: pH = 4.87
ii	Added ammonia $C_2H_5COOH \ removes \ added \ NH_3 \ / \ alkali \ / \ base$ OR $C_2H_5COOH + NH_3 \ / \ OH^- \rightarrow$ OR $NH_3 \ / \ alkali \ reacts \ with \ / \ accepts \ H^+$ OR $H^+ + NH_3 \rightarrow$ OR $H^+ + OH^- \rightarrow \checkmark$	ALLOW use of HA / weak acid / acid for C <sub>2</sub> H <sub>5</sub> COOH;  ALLOW use of NH <sub>4</sub> OH for NH <sub>3</sub> ALLOW A <sup>-</sup> for C <sub>2</sub> H <sub>5</sub> COO <sup>-</sup> ASSUME that equilibrium applies to that
ii	Equlibrium $\rightarrow$ C <sub>2</sub> H <sub>5</sub> COO $^-$ <b>OR</b> Equilibrium $\rightarrow$ right $\checkmark$	ASSUME that equilibrium applies to that supplied in the question, i.e. IGNORE any other equilibria  Examiner's Comments  The role of buffers in controlling pH is a common recall question and most candidates had prepared their rehearsed answers. Although this question asked for the addition of ammonia as a specific base, all but the weakest candidates identified that this was a question about addition of a base. The commonest and best answers stated that NH <sub>3</sub> accepts a proton to form NH <sub>4</sub> + (with many ionic equations seen). The correct equilibrium shift was usually included.
ii	CHECK WORKING CAREFULLY AS CORRECT NUMERICAL ANSWER IS POSSIBLE FROM WRONG VALUES	FULL ANNOTATIONS MUST BE USED  For n(Mg), 1 mark ALLOW ECF for ALL marks below from incorrect n(Mg)  ECF ONLY available from concentrations that have  • subtracted 0.50 OR 0.25 from 1 for [C <sub>2</sub> H <sub>5</sub> COOH] • added 0.50 OR 0.25 to 1 for [C <sub>2</sub> H <sub>5</sub> COOT]  i.e. For moles / concentration 1 mark (1 mark lost)

NOTE: IF there is no prior working,

ALLOW 4 MARKS for [H $^{+}$ ] =1.35  $\times$  10 $^{-5}$   $\times$   $\frac{0.50}{1.50}$  AND pH = 5.35

IF the ONLY response is pH = 5.35, award 1 mark ONLY

Award a maximum of 1 mark (for n(Mg) = 0.25 mol) for: pH value from K<sub>a</sub> square root approach (weak acid pH) pH value from  $K_w / 10^{-14}$  approach (strong base pH)

.....

ALLOW alternative approach based on Henderson-Hasselbalch equation for final 1 mark

pH = pK<sub>a</sub> + log 
$$\frac{1.5}{0.5}$$
 **OR** pK<sub>a</sub> − log  $\frac{0.5}{1.5}$  pH = 4.87 + 0.48 = 5.35 ✓ **ALLOW** −log K<sub>a</sub> for pK<sub>a</sub>

- 1.  $n(C_2H_5COOH) = 0.75$  **AND**  $n(C_2H_5COO^-) = 1.25$
- 2.  $n(C_2H_5COOH) = 0.50$  **AND**  $n(C_2H_5COO^-) = 1.25$
- 3.  $n(C_2H_5COOH) = 0.75$  **AND**  $n(C_2H_5COO^-) = 1.50$

ALLOW ECF ONLY for the following giving 1 additional mark and a total of 3 marks

1. 
$$[H^{+}] = 1.35 \times 10^{-5} \times \frac{0.75}{1.25}$$
 pH =  $-\log 8.1$   
2.  $[H^{+}] = 1.35 \times 10^{-5} \times \frac{0.75}{1.25}$  pH =  $-\log 5.4$   
3.  $[H^{+}] = 1.35 \times 10^{-5} \times \frac{0.75}{1.50}$  pH =  $-\log 6.75$ 

$$_{2}$$
. [H  $^{+}$ ] = 1.35 × 10<sup>-5</sup> ×  $\frac{0.50}{1.25}$  pH =  $-\log 5.4$ 

$$_{3}$$
 [H $^{+}$ ] = 1.35 × 10<sup>-5</sup> ×  $\frac{0.75}{1.50}$  pH = -log 6.7

#### **Examiner's Comments**

This buffer calculation was aimed as stretch and challenge and the majority of candidates struggled to derive the concentrations of CH3CH2COOH and CH<sub>3</sub>CH<sub>2</sub>COO<sup>-</sup>. An easy mark for the amount of magnesium added was available for almost all candidates. The problem was then to derive the amount and concentration of CH<sub>3</sub>CH<sub>2</sub>COOH that would be obtained 0.500 mol<sup>-3</sup>. Many did not identify that Mg and CH<sub>3</sub>CH<sub>2</sub>COOH react in a 1:2 molar ratio, subtracting 0.25, instead of 0.50, from the original concentration. Rarely did candidates realise that the CH<sub>3</sub>CH<sub>2</sub>COO<sup>-</sup> concentration would increase from the initial concentration of 1 mol dm<sup>-3</sup>. Others assumed that no CH<sub>3</sub>CH<sub>2</sub>COO<sup>-</sup> was present at the start. Consequently, candidates often used a variety of acid-base ratios in their buffer calculation. Instead of the correct ratio of 0.5/1.5, it was very common to see 0.75/1.25, 0.75/0.25, and especially 0.5/1, 0.75/1 and 0.25/1.0.

The very best candidates tackled the problem with apparent ease but this was seen comparatively rarely in scripts of other candidates.

Answer: pH = 5.35

		Total	14	
1 6	а	CH <sub>3</sub> COOH + H <sub>2</sub> O $\rightleftharpoons$ H <sub>3</sub> O <sup>+</sup> + CH <sub>3</sub> COO <sup>-</sup> $\checkmark$ Acid 1 Base 2 Acid 2 Base 1 $\checkmark$	2	IGNORE state symbols (even if incorrect)

			ALLOW 1 AND 2 labels the other way around.  ALLOW 'just acid' and 'base' labels if linked by lines so that it is clear what the acid—base pairs are  ALLOW A and B for 'acid' and 'base'  IF proton transfer is wrong way around  ALLOW 2nd mark for idea of acid—base pairs, i.e.  CH₃COOH + H₂O ⇌ CH₃COOH₂⁺ + OH⁻ X  Base 2 Acid 1 Acid 2 Base 1 ✓  NOTE For the 2nd marking point (acid—base pairs), this is the ONLY acceptable ECF i.e., NO ECF from impossible chemistry  Examiner's Comments  Most candidates showed an acid-base equilibrium involving proton transfer and then identified the acid-base pairs. The acid-base pairs were usually correctly identified but the proton transfer was sometimes shown the wrong way round. Common errors included omission of a positive charge on H₃O⁺ and an equilibrium involving
b i	Water dissociates / ionises OR $H_2O \rightleftharpoons H^+ + OH^-$ OR $2H_2O \rightleftharpoons H_3O^+ + OH^- \checkmark$ FIRST, CHECK THE ANSWER ON ANSWER LINE	1	OH <sup>-</sup> ions rather than water. Neither approach could be credited. <b>ALLOW</b> $K_w = [H^+] [OH^-]$ <b>OR</b> $[H^+] [OH^-] = 10^{-14} (mol^2 dm^{-6})$ <b>IGNORE</b> breaking for dissociation <b>IGNORE</b> water contains H <sup>+</sup> and OH <sup>-</sup> <b>IGNORE</b> $H_2O \rightarrow H^+ + OH^-$ <i>i.e. no</i> equilibrium sign <b>IGNORE</b> $2H_2O \rightarrow H_3O^+ + OH^-$ <i>i.e. no</i> equilibrium sign <b>Examiner's Comments</b> The key required feature was the dissociation of water but many instead discussed dissociation of the acid. <b>IF</b> there is an alternative answer, check to
ii	IF answer = $1.15 \times 10^{-11}$ award 2 marks	2	see if there is any  ECF credit possible using working below.

		[H <sup>+</sup> ] = $10^{-3.06}$ = $8.71 \times 10^{-4}$ (mol dm <sup>-3</sup> ) $\checkmark$ [OHT] = $\frac{1.00 \times 10^{-14}}{8.71 \times 10^{-4}}$ = $1.15 \times 10^{-11}$ (mol dm <sup>-3</sup> ) $\checkmark$ <b>ALLOW</b> answer to two or more significant figures 2SF: $1.1 \times 10^{-11}$ ; 4SF: $1.148 \times 10^{-11}$ ; calculator $1.148153621 \times 10^{-11}$		ALLOW 2 SF: 8.7 × 10 <sup>-4</sup> up to calculator value of 8.7096359 × 10 <sup>-4</sup> correctly rounded  ALLOW alternative approach using pOH:  pOH = 14 − 3.06 = 10.94 ✓  [OH⁻] = 10⁻¹¹0.9⁴ = 1.15 × 10⁻¹¹¹ (mol dm⁻³) ✓  Examiner's Comments  The majority of candidates correctly calculated the hydroxide ion concentration via <i>K</i> <sub>w</sub> . Another less popular but successful approach was via pOH. Either approach could result in both marks. Weaker candidates were successful in calculating the hydrogen ion concentration but this was then often shown also as the hydroxide ion concentration in the final answer.  Answer: 1.15 × 10⁻¹¹ mol dm⁻³
С	i	2CH <sub>3</sub> COOH + CaCO <sub>3</sub> → (CH <sub>3</sub> COO) <sub>2</sub> Ca + CO <sub>2</sub> + H <sub>2</sub> O ✓	1	IGNORE state symbols  ALLOW ⇒ provided that reactants on LHS  For CO <sub>2</sub> + H <sub>2</sub> O, ALLOW H <sub>2</sub> CO <sub>3</sub> ALLOW Ca(CH <sub>3</sub> COO) <sub>2</sub> ALLOW (CH <sub>3</sub> COO <sup>-</sup> ) <sub>2</sub> Ca <sup>2+</sup> BUT DO NOT ALLOW if either charge is missing or incorrect  Examiner's Comments  The equations seen were certainly better than in previous sessions, perhaps as candidates will have practised similar questions from past papers. Ionic signs within the formula of calcium ethanoate were allowed but both were then needed. Common errors included an incorrect formula of calcium ethanoate with one ethanoate group only and an unbalanced ethanoic acid on the left-hand side of the equation.
	ii	solution contains CH₃COOH <b>AND</b> CH₃COO⁻ ✓	1	ALLOW names: ethanoic acid for CH <sub>3</sub> COOH ethanoate for CH <sub>3</sub> COO <sup>-</sup> ALLOW calcium ethanoate OR (CH <sub>3</sub> COO) <sub>2</sub> Ca for CH <sub>3</sub> COO <sup>-</sup> IGNORE 'acid, salt, conjugate base; responses must identify the acid and

			conjugate base as ethanoic acid and ethanoate
			IGNORE ethanoic acid is in excess (in question)  BUT DO ALLOW some ethanoic acid is left over / present / some ethanoic acid has reacted  IGNORE equilibrium: CH₃COOH ⇌ H⁺ + CH₃COO⁻ Dissociation of ethanoic acid only  Examiner's Comments  The mark scheme was specific in wanting the names or formulae of the components of the buffer solution and also the idea that some ethanoic acid remains. More general responses in terms of an acid and its
			conjugate base were not credited.  FULL ANNOTATIONS MUST BE USED
ii	Quality of written communication, QWC  2 marks are available for explaining how the equilibrium system allows the buffer solution to control the pH on addition of H <sup>+</sup> and OH <sup>-</sup> (see below)  CH <sub>3</sub> COOH ≈ H <sup>+</sup> + CH <sub>3</sub> COO <sup>-</sup> ✓  CH <sub>3</sub> COOH reacts with added alkali  OR CH <sub>3</sub> COOH + OH <sup>-</sup> →  OR added alkali reacts with H <sup>+</sup> OR H <sup>+</sup> + OH <sup>-</sup> → ✓	5	Note: If there is no equilibrium equation then the two subsequent equilibrium marks are not available: max 2  DO NOT ALLOW HA ⇌ H⁺ + A⁻  DO NOT ALLOW more than one equilibrium equation.  ALLOW response in terms of H⁺, A⁻ and HA  IF more than one equilibrium shown, it must be clear which one is being referred to by labeling the equilibria.  ALLOW weak acid reacts with added alkali DO NOT ALLOW acid reacts with added
	Equilibrium → right <b>OR</b> Equilibrium → CH <sub>3</sub> COO <sup>-</sup> <b>√</b> ( <b>QWC</b> )		alkali
	CH₃COO⁻ reacts with added acid ✓  Equilibrium → left <b>OR</b> Equilibrium → CH₃COOH ✓ ( <b>QWC</b> )		ALLOW conjugate base reacts with added acid  DO NOT ALLOW salt / base reacts with added acid  Examiner's Comments
			The role of buffers in controlling pH is a common recall question and most candidates had prepared their rehearsed

			answers. Well-prepared candidates were thus able to collect full or nearly full marks for this part. There was a significant minority of candidates who had obviously not learnt this part of the specification and, despite their best efforts to invent answers, there was rarely anything that the examiners could credit. This was a great pity because marks were effectively being thrown away. Candidates are recommended to construct their responses using the weak acid equilibrium equation only. Some candidates shown both the correct relevant equilibrium but also others, including for calcium ethanoate. Subsequent explanations in terms of equilibrium were then ambiguous as the examiner could not tell which equilibrium was being discussed. Some candidates thankfully did label and reference multiple equilibria so that some credit could be awarded.
	FIRST, CHECK THE ANSWER ON ANSWER LINE		FULL ANNOTATIONS MUST BE USED
	IF answer = 11.48 OR 11.5 (g), award 5 marks		Incorrect use of [H <sup>+</sup> ] = $$ ([CH <sub>3</sub> COOH] × $K_a$ ) scores zero  BUT IGNORE if an alternative successful method is present
đ	$ \frac{1.75 \times 10^{-5}}{\text{[CH}_3\text{COO}^-\text{]}} = \frac{1.75 \times 10^{-5}}{10^{-5}} \checkmark \times 0.200 = 0.350 \text{ mol dm}^{-3} \checkmark $ $ n(\text{CH}_3\text{COONa} / \text{CH}_3\text{COO}^-\text{) in 400} $ $ = 0.350 \times \frac{400}{1000} = 0.14(0) \text{ (mol)} \checkmark $	5	Incorrect use of $K_w$ , 1 max for [H <sup>+</sup> ] = 10 <sup>-5</sup> (mol dm <sup>-3</sup> )  BUT IGNORE if an alternative successful method is present
	mass CH₃COONa = 0.140 × 82.0 = 11.48 OR 11.5 (g) ✓  For ECF, n(CH₃COONa/CH₃COO⁻) must have been calculated in step before		Note: There is no mark just for  n(CH <sub>3</sub> COOH) in 400 cm <sup>3</sup> = 0.200 × 1000= 0.08 (mol)  As alternative for the 4th and 5th marks, ALLOW: mass of CH <sub>3</sub> COONa in 1 dm <sup>3</sup> = 0.350 × 82.0 = 28.7 g ✓ mass of CH <sub>3</sub> COONa in 400 cm <sup>3</sup> = 28.7 × 400

..... **COMMON ECF** 4.592 **OR** 4.6 g **AWARD** 4 marks use of 400 / 1000 twice ALLOW variants of Henderson-Hasselbalch equation.  $pK_a = -log(1.75 \times 10^{-5}) = 4.757$  Calc: 4.75696. ... . [CH<sub>3</sub>COO<sup>-</sup>]  $log \overline{[CH_3COOH]} = pH - pK_a = 5 - 4.757$ = 0.243[CH<sub>3</sub>COO<sup>-</sup>] [CH<sub>3</sub>COOH]= 10<sup>0.243</sup> = 1.75 ✓  $[CH_3COO^-] = 1.75 \times 0.200 = 0.350 \text{ mol dm}^{-3}$  $n(CH_3COONa/CH_3COO^-)$  in 400 cm<sup>3</sup>  $= 0.350 \times \overline{1000} = 0.14(0) \text{ (mol) } \checkmark$ ...... mass CH<sub>3</sub>COONa = 0.140 × 82.0 = 11.48 **OR** 11.5 (g) ✓ **Examiner's Comments** 

Able candidates answered this question with comparative ease, collecting all five marks for a carefully constructed answer. This was in contrast to weaker candidate who struggled, often resorting to the 'square root' method for calculating the pH of a weak

The calculation started off with an easy mark for calculating the hydrogen ion concentration from the pH. Unfortunately, this 'square root' method then resulted in another hydrogen ion concentration which contradicted the original. Other weak candidates resorted to use of  $K_w$ . The result was that weaker candidates would often score no marks at all for this part. Many candidates were aware of the importance of the acid/base ratio in buffer calculations and were able to gain at least some marks for this part. The commonest error in partially successful responses was with the scaling factor of 400/1000, being either omitted to give an answer of 28.7 g, or used twice to give an answer of 4.952 g

Answer: 11.48 g

			Total	17	
1 7	а	i	Using a pH probe on a data logger <b>OR</b> pH meter	1	
			FIRST CHECK THE ANSWER ON THE ANSWER LINE  IF answer = 0.11(0) (mol dm <sup>-3</sup> ), award 2 marks		IF there is an alternative answer, check to see if there is any ECF credit possible using working below.
		ii	$n(N = 0 + 1) = \frac{0.125 \times 22.0}{1000} = 2.75 \times 10^{-3} \text{ (mol)}$	2	
			concentration of CH <sub>6</sub> COOH = $\frac{2.75 \times 10^{5} \times 1000}{25.0}$		ANNOTATE WITH TICKS AND CROSSES, etc
			= 0.11(0) (mol dm <sup>-3</sup> )		<b>ALLOW ECF:</b> <i>n</i> (NaOH) × 1000/25.00
	b	i	Brilliant yellow  AND  Vertical section / rapid pH change matches the pH range / end point / colour change (of the indicator)	1	ALLOW pH range (of the indicator) matches equivalence point ALLOW end point / colour change matches equivalence point IGNORE colour change matches end point (colour change is the same as end point)
		ii	Explanation: Acid / H+ reacts with A- AND equilibrium (position) shifts towards HA (to give a red colour)  Alkali / OH- reacts with HA/H+ AND equilibrium (position) shifts towards A- (to give a yellow colour)  At end point, equal amounts of HA and A-AND orange colour	4	ALLOW direction of equilibrium shift if equilibrium shown: HA   i.e. 'towards HA' is equivalent to 'to left' i.e. 'towards A⁻' is equivalent to 'to right'
			FIRST CHECK THE ANSWER ON THE ANSWER LINE If answer = $2.33$ award 4 marks $K_a = 10^{-3.40} = 3.98 \times 10^{-4} \text{ (mol dm}^{-3}\text{)}$		ALLOW yellow-red colour
	С	İ	Concentration of aspirin $= \frac{1.00 \times 10^{-2}}{180} \times 1000$	4	
			= 0.0556 (mol dm <sup>-3</sup> )		

			$\begin{aligned} [t'] &= \sqrt{K_x} \times [tHA] \end{aligned} = \sqrt{3.58} \times 10^4 \times 0.6666) \\ &= 4.70 \times 10^5 (\text{mol dm}^3) \end{aligned}$		
			pH = $-\log 4.70 \times 10^{-3} = 2.33$		ALLOW ECF
					<b>ALLOW ECF only</b> from [H <sup>+</sup> ] calculation using [H <sup>+</sup> ] = $\sqrt{(K_a \times [HA])}$
		ii	Salts are ionic <b>AND</b> attracted to polar H <sub>2</sub> O	1	
		ii	COO⁻ reacts with H⁺ forming COOH	0	ALL CIM a mailibrium abiffa ta laff
		i	Aspirin precipitates out	2	ALLOW equilibrium shifts to left
			Total	15	
			$[H^+] = 10^{-pH} = 10^{-2.19} = 6.46 \times 10^{-3} \text{ (mol dm}^{-3}\text{)}$		
			[CH <sub>3</sub> CH(OH)COOH] = $\frac{[H^{+}]^{2}}{K_{a}} = \frac{(6.46 \times 10^{-3})^{2}}{1.38 \times 10^{-4}}$		
			$= 0.0302 (\text{mol dm}^{-3})$		
			$n(CH_3CH(OH)COOH) = \frac{0.302 \times 250}{1000} = 0.0755 \text{ mol}$		
1 8	а		Mass of CH₃CH(OH)COOH = 0.0755 × 90 = 6.80 g	8	ALLOW 5 marks for 6.80 g through any
			Dissolve 6.80 g of the solid in distilled water (less than 250 cm³) in a beaker		calculation.
			(then) transfer the solution to a 250 cm <sup>3</sup> volumetric flask <b>AND</b> ensure that all solution is washed out of beaker (washings transferred to volumetric flask)		ALLOW ECF for incorrect calculation of mass. Mass used must be linked to calculation.
			(then) make solution up to 250 cm <sup>3</sup> with distilled water <b>AND</b> ensure thorough mixing by inverting the flask several times		
	b		CH <sub>3</sub> CH(OH)COO <sup>-</sup> + CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> COOH <sub>2</sub> <sup>+</sup>	2	State symbols <b>NOT</b> required
			CH <sub>3</sub> CH(OH)COOH <b>AND</b> CH <sub>3</sub> CH(OH)COO <sup>-</sup> CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> COOH <b>AND</b> CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> COOH <sub>2</sub> <sup>+</sup> <b>Both</b> pairs identified		ALLOW labels 'acid 1', 'base 1' etc. ALLOW ECF for second mark
			$[H^{\dagger}] = 1 \times 10^{-14} = 5405 \times 10^{-14}$		<b>ALLOW</b> 5.405405405 × 10 <sup>-14</sup> and correct rounding to 5.4 × 10 <sup>-14</sup>
			$[H^+] = \frac{1 \times 10^{-14}}{0.185} = 5.405 \times 10^{-14}$	2	ALLOW alternative approach using pOH:
	С	i	(Use of $K_w$ )		pOH = -log(0.185) = 0.73 pH = 14 - 0.73 = 13.27
			pH = $-\log(5.405 \times 10^{-14}) = 13.27$		Correct answer scores <b>BOTH</b> marks
			m(A=) = 0.25 v. 40=3 (m==1)		<b>ALLOW</b> 13.267
			$n(A^{-}) = 9.25 \times 10^{-3} \text{ (mol)}$ $n(HA) = 0.0165 - 9.25 \times 10^{-3} = 7.25 \times 10^{-3} \text{ (mol)}$	4	<b>ALLOW</b> HA / acid and A <sup>-</sup> /salt throughout for butanoate and butanoic acid
		"	$[H^{+}] = K_{a} \times \underline{[HA]}$ $[A^{-}]$	7	<b>ALLOW</b> p $K_a = -\log K_a$ <b>OR</b> $-\log 1.5 \times$

		pH = $-\log(1.5 \times 10^{-5} \times \underline{0.058}) = 4.93$ 0.074		10 <sup>-3</sup> <b>OR</b> 4.82
		$OR \text{ pH} = -\log(1.5 \times 10^{-5} \times \frac{1000 \times \frac{7.25 \times 10^{-3}}{125}}{1000 \times \frac{9.25 \times 10^{-3}}{125}}) = 4.93$		<b>ALLOW ECF</b> from incorrect values of $n(A^{-})$ or $n(HA)$ <b>ALLOW</b> pH = $-\log(1.5 \times 10^{-5} \times \frac{7.25 \times 10^{-3}}{9.25 \times 10^{-3}}) =$
		Final mark also via Henderson-Hasselbalch equation: $pH = pK_a - log \frac{ HA }{[A^-]} = 4.82 - (-0.11) = 4.93$ $OR \ pH = pK_a + log \frac{ \Lambda^- }{ IIA } = 4.82 + 0.11 = 4.93$		4.93
		Total	16	
1 9		1 mark for correct reactants <b>AND</b> products <b>AND</b> correct	2	
		positioning of + and - charges on products  1 mark for two correct curly arrows  AND H <sub>2</sub> O curly arrow starting from O lone pair		
		Total	2	
2	i	$K_{a} = \frac{[[\text{Fe}(\text{H}_{2}\text{O})_{5}\text{OH}]^{2+}(\text{aq})][\text{H}^{+}(\text{aq})]}{[[\text{Fe}(\text{H}_{2}\text{O})_{6}]^{3+}(\text{aq})]}$	1	state symbols <b>not</b> required
	ii	$[H^{+}] = \sqrt{6.00 \times 10^{-3} \times 0.100}$ $\mathbf{OR} \ 0.0245 \ (\text{mol dm}^{-3})$ $pH = -\log 0.0245 = 1.61$	2	ALLOW ECF from calculated [H <sup>+</sup> ] provided that  BOTH  6.0 x 10 <sup>-3</sup> AND 0.100 only have been used  ALLOW calculation via quadratic equation  → pH 1.66
		Total	3	
2 1		$K_{\rm W}$ value from graph from 2.2 to 2.4 × 10 <sup>-14</sup> (mol <sup>2</sup> dm <sup>-6</sup> )  Using 2.4 × 10 <sup>-14</sup> , [H <sup>+</sup> ] = $\sqrt{2.4 \times 10^{-14}}$ OR 1.55 × 10 <sup>-7</sup> pH = $-\log (1.55 \times 10^{-7}) = 6.81$ (using $K_{\rm W} = 2.4 \times 10^{-14}$ )	3	Actual $K_{\rm w}$ = 2.38 × 10 <sup>-14</sup> mol <sup>2</sup> dm <sup>-6</sup> ALLOW ECF only if candidate uses a value between 2.0 and 2.6 × 10 <sup>-14</sup> (mol <sup>2</sup> dm <sup>-6</sup> ), i.e. from the approximately correct region of the graph  ALLOW 6.8 (1DP) up to calculator value ALLOW ECF only if candidate has generated a value of [H <sup>+</sup> ] by attempting to take a square root of a value between 2.0 and 3.0 × 10 <sup>-14</sup>
		Total	3	

2 2	а	i	HNO₃ is a strong acid <b>AND</b> HNO₂ is a weak acid	1	<b>ALLOW</b> HNO <sub>3</sub> completely dissociates <b>AND</b> HNO <sub>2</sub> partially dissociates <b>ALLOW</b> HNO <sub>3</sub> $\rightarrow$ H <sup>+</sup> + NO <sub>3</sub> <sup>-</sup> <b>AND</b> HNO <sub>2</sub> $\rightleftharpoons$ H <sup>+</sup> + NO <sub>2</sub> <sup>-</sup> <b>IGNORE</b> HNO <sub>3</sub> is a stronger acid <b>ORA IGNORE</b> HNO <sub>3</sub> produces more H <sup>+</sup>
		ii	pH = -log 0.0450 = 1.35 ( <b>2 DP</b> required)	1	
		ii i	FIRST CHECK THE ANSWER ON ANSWER LINE IF answer = 2.35, award all three calculation marks $K_a = 10^{-3.35}$ OR $4.47 \times 10^{-4}$ (mol dm <sup>-3</sup> )  [H <sup>+</sup> ] = $\sqrt{(K_a \times [HNO_2])}$ OR $\sqrt{(K_a \times [HA])}$ OR $\sqrt{(K_a \times 0.0450)}$ OR $4.48 \times 10^{-3}$ (mol dm <sup>-3</sup> )  pH = 2.35 (2 DP required)	3	ALLOW 2 SF to calculator value:  4.466835922 × 10 <sup>-4</sup> , correctly rounded  IGNORE HNO <sub>3</sub> in working  Always ALLOW calculator value irrespective of working as number may have been kept in calculator.  Note: pH = 2.35 is obtained from all three values above  From no square root, pH = 4.70. Worth K <sub>a</sub> mark only.
	b		FIRST CHECK THE ANSWER ON ANSWER LINE IF answer = 0.810 (g) award 4 marks $[H^+] = 10^{-12.500} = 3.16 \times 10^{-13} \text{ (mol dm}^{-3})$ $[OH^-] = \frac{K_w}{[H^+]} = \frac{1.00 \times 10^{-14}}{3.16 \times 10^{-13}} = 0.0316 \text{ (mol dm}^{-3})$ $n(RbOH) = 0.0316 \times \frac{250}{1000} = 7.91 \times 10^{-3} \text{ (mol)}$ mass RbOH = 7.91 × 10 <sup>-3</sup> × 102.5 = 0.810 (g)	4	Always <b>ALLOW</b> calculator value irrespective of working as number may have been kept in calculator. <b>ALLOW</b> alternative approach using pOH: pOH = 14.000 - 12.500 = 1.500  [OH <sup>-</sup> ] = 10 <sup>-1.500</sup> = 0.0316 <b>ALLOW ECF</b> from [H <sup>+</sup> ] derived using K <sub>w</sub> and [OH <sup>-</sup> ]  BUT <b>DO NOT ALLOW</b> an acid pH. <b>ALLOW</b> 0.81 g, up to calculator value but take care as rounding could be from any stage. <i>Last 3 SF figure is zero and is treated as a 'trailing zero' as specific number of SF has not been asked for.</i>
			Total	9	