Mark scheme – Acids, Bases and Buffers

Question			Answer/Indicative content	Marks	Guidance
1	a		$HCOOH + CH_3COOH \rightleftharpoons HCOO^- + CH_3COOH^{2+}$ ✓ **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***. $HCOOH + CH_3COOH \rightleftharpoons HCOOH_2^+ + CH_3COO^-$ **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	$[H^+] = 10^{-2.72}$ **OR** 1.905×10^{-3} (mol dm^{-3}) ✓ $[CH_3COOH] = \frac{(1.905 \times 10^{-3})^2}{1.78 \times 10^{-5}}$ ✓ (= 0.204 mol dm^{-3})	2 (AO 2.4×2)	**ALLOW** 2SF up to calculator value of $1.905460718 \times 10^{-3}$ **ALLOW** use of [HA] Mark is for working.
		ii	**FIRST CHECK THE ANSWER ON ANSWER LINE** **If answer =** 2.4×10^{-2} (mol dm^{-3}) **award 4 marks** --- **Calculation of H^+ in buffer** $[H^+]$ buffer = $10^{-4.00}$ **OR** 1×10^{-4} (mol dm^{-3}) ✓ **Calculation of CH_3COOH in buffer** *n*(CH_3COOH) **OR** $[CH_3COOH]_{buffer}$ $= \frac{0.204}{1000} \times 400$ **OR** 8.16×10^{-2} ✓ **Calculation of $[CH_3COO^-]$ in buffer (in 1 dm^3)** $[CH_3COO^-]_{buffer} = 1.78 \times 10^{-5} \times \frac{8.16 \times 10^{-2}}{1 \times 10^{-4}}$ **OR** 1.5×10^{-2} (mol dm^{-3}) ✓ **Calculation of original $[CH_3COO^-]$ (in 600 cm^3)** $[CH_3COO^-]_{initial} = (\frac{1.45248 \times 10^{-2} \times 1000}{600})$ $= 2.4 \times 10^{-2}$ (mol dm^{-3}) ✓ --- **ALLOW** alternative approach based on Henderson–	4 (AO 3.3×3) (AO 3.4×1)	**ALLOW ECF** **ALLOW** [HA] and [A$^-$] in working **ALLOW** 1.5×10^{-2} up to calculator value 1.45248×10^{-2} (mol dm^{-3}) **ALLOW** 2.4×10^{-2} up to calculator value 2.4208×10^{-2} (mol dm^{-3}) **COMMON ERRORS BUT CHECK WORKING** $[CH_3COO^-]_{initial} = 8.7 \times 10^{-3}$ *600 and 1000 inverted* 3 marks $[CH_3COO^-]_{initial} = 3.6 \times 10^{-6}$ *$[CH_3COOH] : [H^+]$ inverted* 3 marks $[CH_3COO^-]_{initial} = 1.3 \times 10^{-6}$ *$[CH_3COOH] : [H^+]$ inverted AND 600 and 1000 inverted* 2 marks

			Hasselbalch equation (**ALLOW** –logK_a for pK_a) e.g. $\mathrm{pH} = \mathrm{p}K_a + \log\frac{[CH_3COOH]}{[CH_3COO^-]}$ **OR** $\mathrm{p}K_a - \log\frac{[CH_3COO^-]}{[CH_3COOH]}$ **OR** $4 = 4.75 + \log\frac{8.16 \times 10^{-2}}{[CH_3COO^-]}$ **OR** $4.75 - \log\frac{[CH_3COO^-]}{8.16 \times 10^{-2}}$ ✓ $\log[CH_3COO^-] = 4 - 4.75 - 1.09 = -1.84$ ✓ $[CH_3COO^-]_{buffer} = 1.5 \times 10^{-2}$ ✓ $[CH_3COO^-]_{initial} = 2.4 \times 10^{-2}$ ✓		No volumes used = 3.6×10^{-2} 2 marks **ALLOW** –logK_a for pK_a -- **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			$CH_3SO_2OH + H_2O \rightleftharpoons CH_3SO_2O^- + H_3O^+$ ✓ **A1 B2 B1 A2** ✓ For an equilibrium shown using CH_3COOH instead of H_2O, mark acid–base pairs by **ECF**, i.e. $CH_3SO_2OH + CH_3COOH \rightleftharpoons CH_3SO_2O^- + CH_3COOH_2^+$ ☒ **A1 B2 B1 A2 ECF** ✓ CH_3SO_2OH dissociates more (than CH_3COOH) **OR** CH_3SO_2OH is a stronger acid ✓ ***ORA*** *in terms of CH_3COOH being a weaker acid* Student is correct **AND** (sulfonic acid has) lower pK_a/higher K_a **OR** greater $[H^+]$ **ORA** ✓	4 (AO 2.1×2) (AO 3.1) (AO 3.2)	**ALLOW** → for ⇌ **ALLOW** acid–base pairs labelled other way round. i.e. $CH_3SO_2OH + H_2O \rightleftharpoons CH_3SO_2O^- + H_3O^+$ **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. $K_a(CH_3COOH) = 10^{-(4.76)} = 1.74 \times 10^{-5}$ $[H^+] = \sqrt{(1.74 \times 10^{-5}) \times 1} = 4.17 \times 10^{-3}$ $\mathrm{pH} = -\log 4.17 \times 10^{-3} = 2.38$ ✓ $K_a(CH_3SO_2OH) = 10^{-(-1.90)} = 79.4$ $[H^+] = \sqrt{(79.4) \times 1} = 8.91$ $\mathrm{pH} = -\log 8.91 = -0.95$ ✓ **BOTH** pH calcs subsumes 'Student is correct' **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 pK_a value was lower (or the K_a 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	a		**FIRST CHECK THE ANSWER ON ANSWER LINE** **If answer = 2.98 award 2 marks** --------------------------------------- $[H^+] = \sqrt{(Ka \times [C_2H_5COOH])} = 1.039 \times 10^{-3}$ (mol dm^{-3}) ✓ pH = –log 1.039×10^{-3} = 2.98 (**Must be to 2 DP**) ✓	2 (AO 2.2 ×2)	**ALLOW ECF** throughout **ONLY ALLOW** pH mark by **ECF** if K_a **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_a values*) **<u>Examiner's Comments</u>** 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	i	$n(C_2H_5COOH) = (0.0800 \times \frac{25.0}{1000}) =) 0.002$ (mol) **AND** $V(NaOH) = \frac{0.002}{0.100} \times 1000 = (= 20(.0)$	1 (AO 2.5)	**ALLOW** 0.02 dm^3 if unit given Mark is for **WORKING** which could all be shown as 1 step **ALLOW** method showing 20cm^3 NaOH contains the same moles as acid $n(C_2H_5COOH) = 0.08(00) \times 0.025(0) = 0.002$

			cm^3) ✓		(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 cm^3' 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.
		ii	**FIRST CHECK THE ANSWER ON ANSWER LINE** **If answer = 12.55 award 4 marks** --- ***Excess mol of NaOH:*** n(OH$^-$)$_{excess}$ = n(OH$^-$) – n(C$_2$H$_5$COOH) $= (0.100 \times \frac{45.0}{1000}) - (0.0800 \times \frac{25.0}{1000})$ = 0.0045 – 0.002 = 0.0025 (mol) ✓ ***Concentration of OH$^-$:*** $[OH^-] = (\frac{0.0025}{70.0 \times 10^{-3}})$ = 0.0357 (mol dm^{-3}) ✓ ***Concentration of H$^+$:*** $[H^+] = (\frac{1.00 \times 10^{-14}}{0.0357})$ = 2.8 × 10^{-13} (mol dm^{-3}) ✓ ***Conversion to pH:*** pH = (–log 2.8 × 10^{-13}) = 12.55 ✓	4 (AO 1.2 ×1) (AO 2.6 ×3)	**ALLOW ECF** throughout For first mark **ALLOW** (Excess volume of NaOH = 25(.0) cm^3) $n(OH^-)_{excess} = 0.100 \times \frac{25.0}{1000} = 0.0025$ (mol) Common errors If initial V(NaOH) = 45 cm^3 [OH$^-$] = 0.0643 (mol) [H$^+$] = 1.56 × 10^{-13} (mol dm^{-3}) pH = 12.81 award three marks (no 1st mark) If n(OH$^-$)$_{excess}$ is used in [H$^+$] calculation n(OH$^-$)$_{excess}$ = 0.0025 (mol) $[H^+] = \frac{1.00 \times 10^{-14}}{0.0025}$ =4.(00) × 10^{-12} (mol dm^{-3}) pH = 11.40 award three marks (no 2nd mark) **ALLOW** pOH method for last two marks pOH = – log[OH$^-$] =1.447 pH = 14 – 1.447 = 12.55 **ALLOW** ECF for conversion from [H$^+$] to pH provided value calculated is above 7 and from derived [H$^+$] **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.
		iii	**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 cm^3 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 cm^3) **<u>Examiner's Comments</u>** 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 cm^3 (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_2H_5COOH (answer to 20(a)) • The final pH should be that of the final solution (answer to 20(b)(ii))

		iv	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 cm^3) 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_a to C_2H_5COOH but often did not appreciate that this would lead to a starting point with a higher pH.
	c		HIO_3 dissociation is not negligible / dissociates to a significant extent **OR** Large K_a **and** HIO_3 is 'stronger' (weak) acid **OR** $[HIO_3]_{eqm}$ is significantly lower than $[HIO_3]_{initial/undissociated}$ ✓	1 (AO 3.3)	**ALLOW** use of HA **Ignore** $[HIO_3]_{equilibrium} < [HIO_3]_{initial/undissociated}$ **ALLOW** $[HIO_3]_{equilibrium} \sim [HIO_3]_{undissociated}$ is no longer a valid assumption **ALLOW** $[HIO_3]$ has a larger K_a so the assumption that $[HIO_3]$ at equilibrium = $[HIO_3]$ 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_3 dissociates'. While correct, this is true of all weak acids. The subtlety in this question was to realise

					that because K_a was relatively high, the resultant acid strength would mean that the degree of dissociating was significant enough so initial [HIO_3] was significantly less than [HIO_3] at equilibrium. In other words, the assumption [HIO_3]initial = [HIO_3]equilibrium is not valid in this case.
			Total	**14**	
4			***Please refer to the marking instructions on page 4 of this mark scheme for guidance on how to mark this question.*** **Level 3 (5–6 mark)** Detailed explanation of equilibrium, the action of the buffer and correct calculation of [HCO_3^-] : [H_2CO_3] ratio. *There is a well-developed line of reasoning which is clear and logically structured. The information presented is relevant and substantiated.* **Level 2 (3–4 marks)** Detailed explanation of equilibrium **and** the action of the buffer. **OR** Detailed explanation of equilibrium **and** correct calculation of [HCO_3^-] : [H_2CO_3] ratio. **OR** Detailed explanation of the action of the buffer **and** correct calculation of [HCO_3^-] : [H_2CO_3] ratio. **OR** Partial explanations of equilibrium, **and** the action of the buffer **and** attempt calculation of [HCO_3^-] : [H_2CO_3] ratio. *There is a line of reasoning presented with some structure. The information presented is relevant and supported by some evidence.* **Level 1 (1–2 marks)** Detailed explanation of equilibrium. **OR** Correct calculation of [HCO_3^-] : [H_2CO_3] ratio. **OR** Detailed explanation of the action of the buffer. **OR** Partial explanations of equilibrium **and** the action of the buffer.' **OR** Partial explanation of equilibrium **and** attempt at calculation of [HCO_3^-] : [H_2CO_3] ratio.' **OR** Partial explanation of the action of the buffer **and** attempt at calculation of [HCO_3^-] : [H_2CO_3] ratio. *There is an attempt at a logical structure with a line of reasoning. The information is in the most part relevant.*	6 (AO1.1 ×2) (AO1.2 ×2) (AO3.1 ×1) (AO3.2 ×1)	**Indicative scientific points may include:** *(State symbols not required in equations)* **Equilibrium and equilibrium shifts** • $H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$ • Addition of H^+ causes $\rightleftharpoons$ to shift to left • Addition of OH^- causes $\rightleftharpoons$ to shift to right **Action of buffer** • Increase in H^+ / addition of acid leads to: $H^+(aq) + HCO_3^-(aq) \rightarrow H_2CO_3(aq)$ **OR** HCO_3^- reacts with added acid • Increase in OH^- / addition of alkali leads to: $H^+(aq) + OH^-(aq) \rightarrow H2O(l)$ **OR** $H_2CO_3(aq) + OH^-(aq) \rightarrow HCO_3^-(aq) + H_2O(l)$ **OR** H_2CO_3 reacts with added alkali **Calculation of [HCO_3^-] : [H_2CO_3] ratio** • $K_a = 10^{-6.38}$ **OR** 4.17×10^{-7} (mol dm^{-3}) • $[H^+] = 10^{-7.40}$ **OR** 3.98×10^{-8} (mol dm^{-3}) • $\frac{[HCO_3^-]}{[H_2CO_3]}$ **OR** $\frac{4.17 \times 10^{-7}}{3.98 \times 10^{-8}}$ • ratio = 10.47(:1) OR 10.48(:1) **ALLOW** 10.5 OR 10(:1) (after working shown) **ALLOW** $\frac{4.2 \times 10^{-7}}{4.0 \times 10^{-8}}$ **And** ratio = 10.5 **OR** 11 (after working shown)

0 marks
No response or no response worthy of credit.

ALLOW $\frac{[H_2CO_3]}{[HCO_3^-]}$ **OR** $\frac{3.98 \times 10^{-}}{4.17 \times 10^{-7}}$

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.

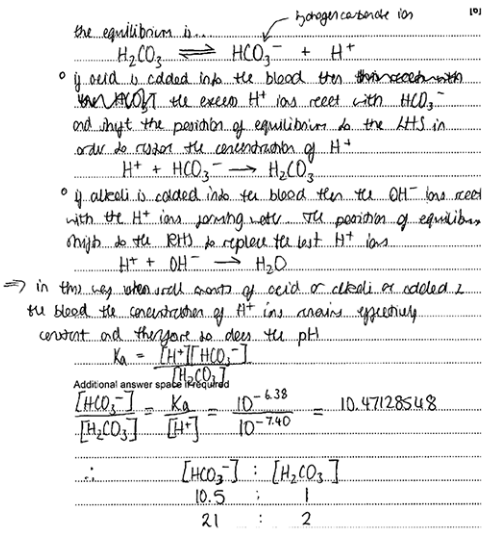
The calculation of the $[HCO_3^-]$: $[H_2CO_3]$ ratio was well described although sometimes the final expression of the ratio left ambiguity as it was hard to tell whether the ratio given referred to the $[HCO_3^-]$: $[H_2CO_3]$ ratio or the $[H_2CO_3]$: $[HCO_3^-]$ ratio

The buffer reactions on separate addition of acid (H^+ ions) and alkali (OH^- 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



hydrogencarbonate ion [6]

the equilibrium is...

$H_2CO_3 \rightleftharpoons HCO_3^- + H^+$

° if acid is added into the blood then ~~this reacts with the HCO_3^-~~ the excess H^+ ions react with HCO_3^- and shift the position of equilibrium to the LHS in order to restore the concentration of H^+

$H^+ + HCO_3^- \longrightarrow H_2CO_3$

° if alkali is added into the blood then the OH^- ions react with the H^+ ions forming water. The position of equilibrium shifts to the RHS to replace the lost H^+ ions

$H^+ + OH^- \longrightarrow H_2O$

⇒ in this way when small amounts of acid or alkali are added to the blood the concentration of H^+ ions remains effectively constant and therefore so does the pH

$K_a = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$

Additional answer space if required

$\frac{[HCO_3^-]}{[H_2CO_3]} = \frac{K_a}{[H^+]} = \frac{10^{-6.38}}{10^{-7.40}} = 10.47128548$

∴ $[HCO_3^-] : [H_2CO_3]$

10.5 : 1

21 : 2

The candidate clearly writes the equilibrium at the top.

The first bullet point gives a chemical

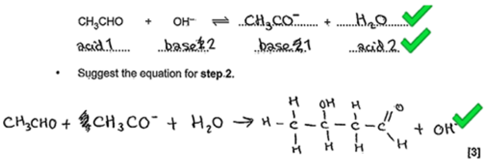
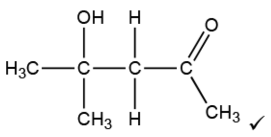
					equation for the reaction occurring when H^+ ions are added as well as the shift in equilibrium. The second bullet point gives a chemical equation for the reaction occurring when OH^- ions are added as well as the shift in equilibrium. The steps in the calculation are clearly shown and the ratio is clear.
			Total	**6**	
5			Initial rate = $10^{-2} \times 2.4 \times 10^{-3}$ s^{-1} **= 2.4×10^{-5} (mol dm^{-3} s^{-1}) ✓**	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^{-5} mol dm^{-3} s^{-1}. 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^{-3} ($3 \times (2.4 \times 10^{-3})$) 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	a		$CO_3^{2-} + H_2O \rightarrow OH^- + HCO_3^-$ **OR** $CO_3^{2-} + H_2O \rightarrow 2OH^- + CO_2$ ✓	1 AO 1.2	**ALLOW** $CO_3^{2-} + 2H_2O \rightarrow 2OH^- + H_2CO_3$ **IGNORE** state symbols **ALLOW** inclusion of Na^+ 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^+ or H_3O^+

					e.g. $CO_3^{2-} + H^+ \rightarrow OH^- + CO_2$ *Question asks for reaction with H_2O* **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^- (for the alkaline solution) and either HCO_3^- or CO_2. Many candidates wrote an equation with H^+ instead of H_2O, with lower ability candidates showing the carbonate ion with the wrong charge as CO_3^-. 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 **OR** protonates • benzoate / $C_6H_5COO^-$ • carboxylate / salt (to form benzoic acid) ✓	1 AO 2.3	**ALLOW** suitable equation, e.g. $C_6H_5COO^- + H^+ \rightarrow C_6H_5COOH$ **IGNORE** responses purely in terms of neutralisation of alkali, e.g. Acid/H^+/HCl **neutralises** / reacts with/removes alkali / OH^- / CO_3^{2-} / Na_2CO_3 **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.
	c		$C_6H_5CH_2OH + 2[O] \rightarrow C_6H_5COOH + H_2O$ ✓	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 $2H_2O$ instead of H_2O. Written equations always need to be checked for the atoms balancing.
	d		**FIRST CHECK THE ANSWER ON ANSWER LINE** **If answer = 33.8 OR 33.9 (%) award 3 marks** --- **Theoretical moles** *n*(C_6H_5COOH) **OR** *n*($C_6H_5CH_2OH$) $= \frac{4.00 \times 1.04}{108.0}$ **OR** 0.0385….. (mol) ✓ **Actual moles** n(C_6H_5COOH) $= \frac{1.59}{122.0}$ **OR** 0.013(0)…. (mol) ✓ % yield $= \frac{0.0130\ldots}{0.0385\ldots} \times 100$ = 33.8% **OR** 33.9 (3 sig fig) ✓ *Answer depends on some intermediate roundings to 3SF*	3 AO2.8×1 AO2.8×1 AO1.2	**ALLOW ECF** for each step Calculator = 0.03851851852 Calculator = 0.01303278689 --- **Alternative method using mass** 1. Theoretical moles = 0.0385 mol 2. Mass = 0.0385 × 122.0 = 4.70 g 3. % yield $= \frac{1.59}{4.70} \times 100$ = 33.8% --- **Common errors** 35.2% → 2 marks • From $\frac{4.00}{108}$ = 0.0370 *(no use of density)* 36.5 **OR** 36.6% → 2 marks • $\frac{4.00/1.04}{108} = \frac{3.846}{108}$ = 0.0356 *(÷ density instead of × density)* **<u>Examiner's Comments</u>** 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 **minimum** quantity of **hot** water/solvent ✓ Cool **AND** Filter **AND** (leave to) dry ✓ *All three needed*	2 AO 3.3 x2	**ALLOW** any solvent **DO NOT ALLOW** use of drying agent (e.g. $MgSO_4$) **IGNORE** • Initial filtering • hot filtration to remove insoluble impurities **<u>Examiner's Comments</u>** 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. $CaCl_2$ or $MgSO_4$), 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	**ALLOW** 3-hydroxybutan-1-al **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 hydroxy- prefix, 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 CH_3CHO, **ALLOW** CH_3COH, C_2H_4O, 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. $CH_3CHO + OH^- \rightleftharpoons CH_3CH_2O^+ + O^{2-}$ ✓

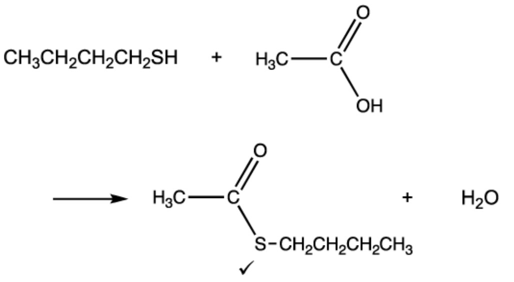
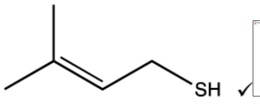
			$CH_3CHO + OH^- \rightleftharpoons {}^-CH_2CHO + H_2O$ **OR** $CH_3CHO + OH^- \rightleftharpoons CH_3CO^- + H_2O$ ✓ **A1** **B2** **B1** **A2** **OR A2** **B1** **B2** **A1** **Step 2**: $CH_3CHO + {}^-CH_2CHO + H_2O \rightarrow CH_3CHOHCH_2CHO + OH^-$ ✓ For $^-CH_2CHO$: **ALLOW** CH_2CHO^-; CH_3CO^-; $C_2H_3O^-$ For $CH_3CHOHCH_2CHO$, **ALLOW** $C_4H_8O_2$		**B2** **A1** **A2** **B1** **OR B1** **A2** **A1** **B2** **Step 2:** $CH_3CHO + CH_3CH_2O^+ + O^{2-} \rightarrow CH_3CHOHCH_2CHO + OH^-$ ✓ For $CH_3CH_2O^+$: **ALLOW** CH_3CHOH^+, $C_2H_5O^+$ **Examiner's Comments** This novel question linked together acid–base equilibria with a multi-step process. Many candidates completed an equation to generate acid–base pairs, which were then usually assigned correctly. The final equation was challenging but the highest ability candidates were able to combine together all the information with their earlier responses to arrive at the correct equation. See Exemplar 15. **Exemplar 15**  CH_3CHO + OH^- ⇌ CH_3CO^- + H_2O ✓ acid 1 base ~~1~~2 base ~~2~~1 acid 2 ✓ • Suggest the equation for step.2. CH_3CHO + ~~2~~ CH_3CO^- + H_2O → + OH^- ✓ [3]
		iv	 ✓	1	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** a combination of above as long as unambiguous For connectivity, **ALLOW** $\underset{\text{OH}}{\vert}$ $\underset{CH_3}{\vert}$ $CH_3–$ $C_3H–$ OH *(Connectivity not being assessed)* **Examiner's Comments** This part was one of the most challenging on the paper. Candidates needed to link the earlier information for combining two ethanal molecules to derive the product for combining two propanone molecules. Despite the challenge, the highest ability

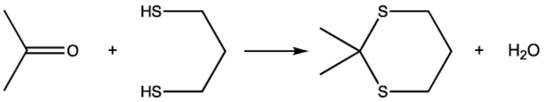
					candidates were able to come up with the correct structure.
			Total	**6**	
8	a	i	$K_a = \frac{[H^+]\,[CH_3COO^-]}{[CH_3COOH]}$ ✓	**1**	**IGNORE** state symbols Must be square brackets **IGNORE** expressions with HA or with $[H^+]^2$ **Examiner's Comments** Almost universally known. Common errors were the use of [HA], $[A^-]$ or $[H^+]^2$.
		ii	**FIRST, CHECK ANSWER ON ANSWER LINE** **IF answer = 4.76 award 3 marks** **--** **$[H^+] = 10^{-pH}$** $= 10^{-2.41} = 3.89 \times 10^{-3}$ (mol dm^{-3}) ✓ **K_a** $= \frac{[H^+]^2}{[CH_3COOH]} = \frac{(3.89 \times 10^{-3})^2}{0.870}$ $= 1.74 \times 10^{-5}$ (mol dm^{-3}) ✓ **pK_a** $= -\log K_a = -\log 1.74 \times 10^{-5} = 4.76$ ✓	**3**	**ALLOW** use of **HA** and **A^-** **ALLOW 3 SF** up to calculator value of: $3.89045145 \times 10^{-3}$ correctly rounded K_a $1.739725573 \times 10^{-3}$ **NOTE:** 1.74×10^{-5} is same from unrounded $[H^+]$ calculator value and 3 SF $[H^+]$ 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 $[H^+]$ rather than $[H^+]^2$ in the calculation, leading to a pK_a of 2.35.
		iii	% dissociation = $\frac{[H^+]}{[CH_3COOH]} \times 100$ $= \frac{3.89 \times 10^{-3}}{0.870} \times 100 = 0.447$(%) ✓	**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_3COOH 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**	

			-- **$[H^+] = 10^{-pH}$** $= 10^{-13.48} = 3.31 \times 10^{-14}$ (mol dm^{-3}) ✓ **$[OH^-]$ from K_w** $= \frac{1.00 \times 10^{-14}}{3.31 \times 10^{-14}} = 0.302$ (mol dm^{-3}) ✓ ***Mass of* (NaOH)** $= 0.302 \times \frac{100}{1000} \times 40.0 = 1.21$ (g) ✓ **% of NaOH to 3 SF** $= \frac{1.21}{1.26} \times 100 = 95.9$ (%) ✓		**ALLOW ECF** throughout **IGNORE** rounding errors beyond 3rd SF throughout **ALLOW** 3.3×10^{-14} (mol dm^{-3}) **ALLOW** 0.30 **ALLOW** 0.303 if 3.3×10^{-14} used in the first marking point **ALLOW** pOH method:, pOH = 14 − 13.48 = 0.52 $[OH^-] = 10^{-0.52} = 0.302$ (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 $[OH^-]$ to 0.303 gives 1.212/1.26 = 96.2% Award 4 marks **<u>Examiner's Comments</u>** 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 $10^{-13.48} = 3.31\ldots \times 10^{-14}$ which most examiners could take to be $[H^+]$. However, it is clearer to write $[H^+] = 10^{-13.48} = 3.31\ldots \times 10^{-14}$ mol dm^{-3}. 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	a		**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = **0.753,** award **3 marks**	3	

			…………………………………………………………… [H+] m= $10^{-pH} = 10^{-2.440} = 3.63 \times 10^{-3}$ (mol dm^{-3}) ✓ $[CH_3COOH] = \frac{[H^+]^2}{K_a}$ **OR** $\frac{(3.63 \times 10^{-3})^2}{1.75 \times 10^{-5}}$ ✓ = 0.753 (mol dm^{-3}) ✓		**ALLOW** use of **HA** and **A$^-$** **ALLOW 3 SF** up to calculator value of $3.630780548 \times 10^{-3}$ correctly rounded **NOTE:** Answer is same from unrounded [H$^+$] calculator value and 3 SF [H$^+$] value **ALLOW** 0.749 if [H$^+$] has been subtracted from [CH_3COOH] for greater accuracy at end **Examiner's Comments** Most candidates coped with this commonly seen type of calculation and were able to correctly calculate the concentration of the weak acid
	b		$CH_3COOH + FCH_2COOH \rightleftharpoons CH_3COOH_2^+ + FCH_2COO^-$ ✓ **B2** **A1** **A2** **B1** **OR** **B1** **A2** **A1** **B2** ✓ *i.e. labels other way round*	2	Watch for opposite order on RHS, i.e.: $FCH_2COO^- + CH_3COOH_2^+$ Take **great care** matching labels **ALLOW ECF** for incorrect proton transfer as below. This is the **ONLY ECF** $CH_3COOH + FCH_2COOH \rightleftharpoons CH_3COO^- + FCH_2COOH_2^+$ × **A1** **B2** **B1** **A2** **OR** **A2** **B1** **B2** **A1** **✓ECF** *i.e. labels other way round* **Examiner's Comments** For the able candidate, this question was quite straightforward but for the weaker candidate, there were many pitfalls. Candidates struggled with the idea that the equilibrium needed a positive ion and a negative ion on the product side. Others were unable to use K_a values in order to decide which of the two starting acids should become protonated. Finally, the assigning of the conjugate acid-base pairs was also challenging.

	c	i	**[CH_3COO^-]** $n(CH_3COONa) = \frac{9.08}{82.0}$ **OR** 0.111 ✓ (Calc: 0.1107317073) $[CH_3COO^-] = \frac{9.08}{82.0} \times \frac{1000}{250} = 0.443$ (mol dm^{-3}) **OR** $n(CH_3COOH) = 0.800 \times \frac{250}{1000} = 0.200$ (mol) ✓ **[H^+]** $[H^+] = K_a \times \frac{[CH_3COOH]}{[CH_3COO^-]}$ **OR** $K_a \times \frac{n(CH_3COOH)}{n(CH_3COO^-)}$ $= 1.75 \times 10^{-5} \times \frac{0.800}{0.443}$ **OR** $1.75 \times 10^{-5} \times \frac{0.200}{0.111}$ ✓ $= 3.16 \times 10^{-5}$ (mol dm^{-3}) ✓ **pH** **(must come from *calculated* [H+])** pH = −log (3.16×10^{-5}) = 4.50 ✓ …………………………………………………………… **LAST 3 marks** are **NOT** available using • K_a square root approach (weak acid pH) • $K_w/10^{-14}$ approach (strong base pH) …………………………………………………………… **Henderson-Hasselbalch (HH) alternative** pKa = −log 1.75×10^{-5} = 4.757 (or 4.756961951..) pH = pK_a + log $\frac{[CH_3COO^-]}{[CH_3COOH]}$ **OR** = pK_a – log $\frac{[CH_3COOH]}{[CH_3COO^-]}$ **OR** pK_a + log $\frac{0.443}{0.800}$ **OR** = pK_a – log $\frac{0.800}{0.443}$ ✓ = pK_a – 0.257 ✓ = 4.757 – 0.257 = 4.50 ✓	5	**ALLOW** 2 sig fig **ALLOW** use of **HA** and **A⁻** 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^{-3}) ✓ **[CH_3COO^-]** $[CH_3COO^-] = K_a \times \frac{[CH_3COOH]}{[H^+]}$ **OR** $1.75 \times 10^{-5} \times \frac{0.800}{3.16 \times 10^{-5}}$ ✓ = 0.443 (mol dm^{-3}) ✓ **mass of CH_3COONa** mass $CH_3COONa = 0.443 \times \frac{250}{1000}$ **OR** 0.111 ✓ 0.111 × 82.0 = **9.08** (g) ✓ ………………………………………………………… **Common errors** **4.64** Use of $M(CH_3COONa)$ = 60 4 marks **2.40** Use of K_a of FCH_2COOH 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_3COONa 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⁻] 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, $[H^+]$ and therefore pH would remain constant.
			Total	**12**	
10		i	$K_a = \frac{[H^+]\,[C_4H_9S^-]}{[C_4H_9SH]}$ ✓ *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_4H_9SH, structural formulae or with skeletal formulae. Some candidates made careless errors such as omitting the negative charge or showing $[H^+]^2$ as numerator rather than $[C_4H_9S^-]\,[H^+]$.
		ii	 Structure of thioester ✓ Complete equation ✓	**2**	**ALLOW** correct skeletal **OR** displayed formula **OR** mixture of the above as long as non-ambiguous **ALLOW** C_4H_9SH **ALLOW** CH_3COOH Thioester functional group **must** be fully displayed, **OR** as a skeletal formula but allow SC_4H_9 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 H_2S, 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.
		iii		**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_2 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.
		iv	 Reactants ✓ Products **AND** balanced equation ✓	**2**	**ALLOW** correct structural **OR** skeletal **OR** displayed formula **OR** mixture of the above as long as non- ambiguous **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**	
11		i	Complete dissociation would give [H⁺] = 0.2 (mol dm $^{-3}$) ✓ pH from complete dissociation = −log 0.2 = 0.7 **OR** actual [H⁺] = $10^{-0.96}$ = 0.11 (mol dm^{-3})✓ **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**	
12	a	i	$(K_a =) \frac{[H^+][C_6H_7O_6^-]}{[C_6H_8O_6]}$ ✓ **ALL** species **MUST** have square brackets State symbols **not** required **TAKE CARE** that 'H' is different on top and bottom of expression	1	**ALLOW** $[H_3O^+]$ for $[H^+]$ **IGNORE** state symbols, even if wrong **IGNORE** $\frac{[H^+]^2}{[C_6H_8O_6]}$ **OR** $\frac{[H^+]^2[A^-]}{[HA]}$
		ii	$pK_a = -\log K_a = -\log (6.76 \times 10^{-5}) = 4.17$ ✓	1	Answer required to **two DP**
		iii	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF answer** = 2.82 award 4 marks ……………………………………………………… **n(vitamin C)** $= \frac{3 \times 0.500}{176}$ $= 8.52(2) \times 10^{-3}$ (mol) ✓ **[vitamin C]** $= 8.52 \times 10^{-3} \times \frac{1000}{250}$ $= 0.0341$ (mol dm^{-3}) ✓ **$[H^+]$** $= \sqrt{(K_a \times [C_6H_8O_6])}$ **OR** $\sqrt{(6.76 \times 10^{-5} \times 0.0341)}$ **OR** 1.52×10^{-3} mol dm^{-3} ✓ **pH** $= -\log(1.52 \times 10^{-3}) = 2.82$ ✓ Answer required to **two DP**	4	**ALLOW ECF** from incorrect n(vitamin C) **ALLOW ECF** from incorrect [vitamin C] **must** be derived from $\sqrt{(K_a \times [C_6H_8O_6])}$ **ALLOW ECF** from incorrect $[H^+]$ but **ONLY** if derived from $\sqrt{(K_a \times [C_6H_8O_6])}$
	b	i	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF ratio** = 0.708 award 3 marks ……………………………………………………… $[H^+] = 10^{-pH} = 10^{-4.02} = 9.55 \times 10^{-5}$ (mol dm^{-3}) ✓ $\frac{[C_6H_7O_6^-]}{[C_6H_8O_6]} = \frac{K_a}{[H^+]} = \frac{6.76 \times 10^{-5}}{9.55 \times 10^{-5}}$ ✓ $= \frac{0.708}{1}$ ✓	3	**IF** there is an alternative answer, check to see if there is any **ECF** credit possible using working below ……………………………………………………… ***ANNOTATIONS MUST BE USED*** **ALLOW ALTERNATIVE** using Henderson−Hasselbalch equation ……………………………………………………… **ALLOW** 9.55×10^{-5} up to calculator value of $9.54992586 \times 10^{-5}$ correctly rounded **ALLOW** ECF from incorrect $[H^+]$ **ALLOW** 0.71 (2 SF) up to calculator value correctly rounded

		ii	mass of $C_6H_7O_6Na = 0.708 \times \frac{300}{176} \times 198.0$ = 239 **OR** 240 (mg) ✓	1	**ALLOW ECF** from answer to **(i)**
	c		**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF answer** = 0.0524 (mol dm^{-3}) award 2 marks …………………………………………………… $[H^+(aq)] = 10^{-pH} = 10^{-12.72}$ $= 1.91/1.9 \times 10^{-13}$ (mol dm^{-3}) ✓ $[NaOH] / [OH^-(aq)] = \frac{K_w}{[H^+(aq)]} = \frac{1.0 \times 10^{-14}}{1.91 \times 10^{-13}}$ = 0.0524 (mol dm^{-3}) ✓	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* calculator: 0.052480746
			Total	**12**	
13	a		$(K_a =) \frac{[H^+]\,[NO_2^-]}{[HNO_2]}$ ✓ **IGNORE** state symbols	1	**IGNORE** $\frac{[H^+]^2}{[HNO_2]}$ **OR** $\frac{[H^+]\,[A^-]}{[A]}$ **ALLOW** H_3O^+ for H^+ Square brackets **required** **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. For most candidates, this was an easy mark.
	b		**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = 2.12 award **2 marks** ………………………………………… $[H^+] = \sqrt{K_a \times [HNO_2]} = 7.502 \times 10^{-3}$ (mol dm^{-3}) ✓ pH = −log 7.502×10^{-3} = 2.12 ✓ **pH to 2 DP**	2	………………………………………… **ALLOW** intermediate value from 3 SF (7.50 up to calculator value of $7.501999733 \times 10^{-3}$ **ALLOW** 1 mark for 2.1 **OR** answer > 2 DP (i.e. not 2 DP) **ONLY ALLOW** pH mark by **ECF** if K_a **AND** 0.120 used and **AND** pH < 7 ………………………………………… **COMMON ERRORS (MUST be to 2 DP)** **pH = 4.25 No square root:1 mark** $[H^+] = (4.69 \times 10^{-4} \times 0.120) = 5.628 \times 10^{-5}$ (mol dm^{-3})

					pH = −log 5.628 × 10^{-5} = 4.25 ✓ **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 $[H^+]$ as the square root of K_a × $[HNO_2]$, 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
c	i	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = **3.43**, **AWARD 4 marks** …………………………………………… *Expression: K_a × acid / base ratio* Use of $K_a \times \frac{[HNO_2]}{[NO_2^-]}$ **OR** $4.69 \times 10^{-4} \times \frac{[HNO_2]}{[NO_2^-]}$ ✓ *Using correct concs / mol in expression* $[H^+] = 4.69 \times 10^{-4} \times \frac{0.0400}{0.0500}$ ✓ *Subsumes previous mark* *Calculation of* $[H^+]$ $[H^+] = 3.752 \times 10^{-4}$ (mol dm^{-3}) ✓ *pH to 2 DP (From 3.42573717)* pH = −log 3.752 × 10^{-4} = 3.43 ✓ **NO marks** are available using K_a square root approach (weak acid pH) $K_w/10^{-14}$ approach (strong base pH) …………………………………………… **ALLOW** alternative approach based on Henderson–Hasselbalch equation (**ALLOW** −logK_a for pK_a) pH = pK_a + log $\frac{[NO_2^-]}{[HNO_2]}$ **OR** pK_a – log $\frac{[HNO_2]}{[NO_2^-]}$ ✓ pH = pK_a + log $\frac{0.0500}{0.0400}$ **OR** pK_a – log $\frac{0.0400}{0.0500}$ ✓ pH = pK_a + 0.097 ✓ pH = 3.329 + 0.097 = 3.43 ✓		4	***FULL ANNOTATIONS MUST BE USED*** …………………………………………… **ALLOW** just $K_a \times \frac{acid}{salt}$ *expression* **Mark** by **ECF** from $4.69 \times 10^{-4} \times \frac{[NO_2^-]}{[HNO_2]}$ *inverted expression* **Mark** by **ECF** from incorrect $[HNO_2]$ and $[NO_2^-]$ **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 $[NO_2^-]$ = 0.01 and correct $[HNO_2]$ =

					0.04 **pH = 4.03 3 marks** correct $[NO_2^-]$ = 0.05 and incorrect $[HNO_2]$ = 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
		ii	**Equilibrium: 1 mark** $HNO_2 \rightleftharpoons H^+ + NO_2^-$ ✓ (ignore state symbols) **Control of pH: 2 marks (QWC)** ***Added HCl*** NO_2^- reacts with added acid / HCl / H^+ **OR** $NO_2^- + H^+ \rightarrow$ **OR** more HNO_2 forms ✓ ***Added NaOH*** HNO_2 reacts with added alkali / NaOH / OH^- **OR** $HNO_2 + OH^- \rightarrow$ **OR** more NO_2^- forms **OR** H^+ reacts with added alkali / NaOH **OR** $H^+ + OH^- \rightarrow$ ✓ **Equilibrium shift:** **1 mark for shifts in $HNO_2 \rightleftharpoons H^+ + NO_2^-$ (See 1st mark)** Equilibrium for added **acid → left** **AND** Equilibrium for added **alkali → right** ✓ (**QWC**)	4	***FULL ANNOTATIONS MUST BE USED*** ………………………………………… **IGNORE** $HA \rightleftharpoons H^+ + A^-$ 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^- for HNO_2 and NO_2^- **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 **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 **AND** K_w increases with temperature **OR** Endothermic **AND** dissociation increases **with temperature** **OR** Endothermic **AND** (dissociation) involves breaking bonds ✓	1	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 bonds **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 responses linking an endothermic change with the increase of K_w with temperature or breaking bonds during dissociation.
		ii	***OH^- concentration*** $[OH^-] = \frac{9.311 \times 10^{-14}}{1.00 \times 10^{-7}} = 9.311 \times 10^{-7}$ (mol dm^{-3}) ✓ ***Explanation (dependent on 1st mark)*** $9.311 \times 10^{-7} > 1.(00) \times 10^{-7}$ **OR** $[OH^-] > [H^+]$ **OR** OH^- in excess **AND** Alkaline ✓	2	***H^+ OR OH^- concentration (neutral pH)*** $[H^+] = [OH^-] = \sqrt{(9.311 \times 10^{-14})} = 3.05 \times 10^{-7}$ (mol dm^{-3}) ✓ ***Explanation (dependent on 1st mark)*** pH = $-\log(3.05 \times 10^{-7}) = 6.5 \rightarrow 6.515501837$ (calc) **AND** Alkaline ✓ **Examiner's Comments** Most candidates calculated a value for $[H^+]$ using the K_w value at 60°C. Many recognised that $[OH^-] > [H^+]$ 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.
		iii	pK_w = 13.03 ✓	1	**ONLY** correct answer **Examiner's Comments** Despite the novel context, almost all candidates obtained the correct pK_w value of 13.03.
		iv	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = **10.76**, award **3 marks** …………………………………………	3	***FULL ANNOTATIONS MUST BE USED*** …………………………………………

			Dilution 1 mark $[OH^-(aq)] = [NaOH(aq)] = \frac{0.0270}{5} = 0.00540$ (mol dm^{-3}) ✓ ***[H⁺] 1 mark*** $[H^+(aq)] = \frac{9.311 \times 10^{-14}}{0.00540} = 1.72 \times 10^{-11}$ (mol dm^{-3}) ✓ Calculator: $1.724259259 \times 10^{-11}$ ***pH 1 mark*** pH = $-\log 1.72 \times 10^{-11}$ = **10.76 ✓** ………………………………………… **ALLOW** pOH method for 2nd and 3rd mark: pOH = −log 0.00540 = 2.27 ✓ (calculator 2.26760624) pH = 13.03 − 2.27 = 10.76 ✓		**ALLOW** dilution **AFTER** calculation of $[H^+(aq)]$ i.e. original $[H^+] = \frac{9.311 \times 10^{-14}}{0.0270} = 3.45 \times 10^{-12}$ (m After dilution, $[H^+] = 3.45 \times 10^{-12} \times 5 = 1.72 \times 10^{-11}$ (mol dm^{-3}) ✓ pH = $-\log 1.72 \times 10^{-11}$ = **10.76 ✓** **ALLOW ECF** from incorrect $[H^+(aq)]$ provided that pH > 7 ………………………………………… **COMMON ERRORS (MUST be to 2 DP)** **pH = 11.73** At 25°C (1.00×10^{-14}): **2 marks** pH = $-\log 1.85 \times 10^{-12}$ = **11.73** **pH = 11.46** No dilution at 60°C (9.311×10^{-14}) **2 marks** pH = $-\log(3.45 \times 10^{-12})$ = **11.46** **pH = 12.43** No dilution **AND** 25°C (1.00×10^{-14}) **1 mark** pH = $-\log(3.70 \times 10^{-13})$ = **12.43** **pH = 12.16** × 5 instead of ÷ 5 at 60°C (9.311×10^{-14}) **2 marks** pH = $-\log(6.879 \times 10^{-13})$ = **12.16** **pH = 13.13 ×** 5 instead of ÷ 5 at 25°C (1.00×10^{-14}) **1 mark** pH = $-\log(7.407 \times 10^{-14})$ = **13.13** **NOTE:** Attempts at dilution → 0.0270 with error in powers of 10 → 12.46 from 0.00270, etc may give 2 marks by **ECF** **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**	
14		i	CN^- H_2O ⇌ **HCN** **OH^-** **AND** Base 2 + Acid 1 Acid 2 + Base 1 ✓	1	State symbols **NOT** required **ALLOW** CNH and HO^- (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^+ reacts with CN^- **OR** HCN forms **OR** equation: $H^+ + CN^- \rightarrow HCN$ (**ALLOW** ⇌) **OR** CN^- accepts a proton / H^+ **OR** equilibrium shifts right **AND** CN^- 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**	
15	a		Proton / H^+ donor **AND** Partially dissociates / ionises ✓	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** …………………………………………………… $[H^+] = \frac{1.00 \times 10^{-14}}{0.5(00)}$ **OR** $2(.00) \times 10^{-14}$ (mol dm^{-3}) ✓		For pOH method:, **ALLOW** pOH = −log[OH^-] = 0.3(0) ✓ (calculator 0.301029995)
			pH = −log $2(.00) \times 10^{-14}$ = **13.7(0)** ✓	2	**ALLOW** pH = 14 − 0.3 = 13.7 ✓ **ALLOW** 13.7 up to calculator value of 13.69897 correctly rounded.

					ALLOW ECF from incorrect $[H^+(aq)]$ provided that pH > 7 **Examiner's Comments** The majority of candidates correctly calculated the pH via K_w. 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	$(K_a =) \dfrac{[H^+]\,[C_2H_5COO^-]}{[C_2H_5COOH]}$ ✓	1	**IGNORE** $\dfrac{[H^+]^2}{[C_2H_5COOH]}$ **OR** $\dfrac{[H^+]\,[A^-]}{[HA]}$ **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** ………………………………………………………… $[C_2H_5COOH] = 0.12(0)$ mol dm^{-3} ✓ $[H^+] = \sqrt{K_a \times [C_2H_5COOH]} = \sqrt{1.35 \times 10^{-5} \times 0.12(0)}$ **OR** 1.27×10^{-3} (mol dm^{-3}) ✓		**ALLOW** HA for C_2H_5COOH and A^- for $C_2H_5COO^-$ **ALLOW ECF** from incorrectly calculated $[C_2H_5COOH]$ **ALLOW** 1.27×10^{-3} to calculator value of $1.272792206 \times 10^{-3}$ correctly rounded
		ii	pH = $-\log 1.27 \times 10^{-3}$ = **2.9(0)** ✓ **NOTE**: The final two marks are **ONLY** available from attempted use of K_a **AND** $[C_2H_5COOH]$	3	**ALLOW** $2.9(0) \times 10^{-3}$ to calculator value of 2.895242493 correctly rounded **ALLOW** use of quadratic equation which gives same answer of 2.90 from 0.120 mol dm^{-3}

					…………………………………………………… **COMMON ERRORS (MUST be to AT LEAST 2 DP unless 2^{nd} decimal place is 0)** **pH = 2.59 2 marks** −log√($1.35 \times 10^{-5} \times 0.480$) *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** −log(1.35×10^{-5}) = 4.87 *−log K_a* **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^+(aq)], the concentration used was often incorrect. Although just a four times dilution from 0.480 mol dm^{-3} to 0.120 mol dm^{-3}, many candidates obtained 0.120 using learnt equations rather than the simple ratio. Others used the original concentration of 0.480 mol dm^{-3} or incorrectly calculated concentrations, commonly seen as 0.0480, 0.0120 or even 0.192 (from × 4). Some candidates calculated [H^+(aq)] using 0.480 mol dm^{-3} 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^{-3}), for which partial credit could be awarded. Answer: pH = 2.90
	d	i	pH = −log 1.35×10^{-5} = **4.87** ✓	1	**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** $H^+ + OH^- \rightarrow$ ✓		**ALLOW** use of HA / weak acid / acid for C_2H_5COOH; **ALLOW** use of NH_4OH for NH_3
		ii	Equlibrium → $C_2H_5COO^-$ **OR** Equilibrium → right ✓	2	**ALLOW** A^- for $C_2H_5COO^-$ **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_3 accepts a proton to form NH_4^+ (with many ionic equations seen). The correct equilibrium shift was usually included.
		iii	***CHECK WORKING CAREFULLY AS CORRECT NUMERICAL ANSWER IS POSSIBLE FROM WRONG VALUES*** …… **ALLOW** HA and A^- throughout **Amount of Mg (1 mark)** $n(\text{Mg}) = \frac{6.075}{24.3} = 0.25(0)$ mol ✓ …… **Moles / concentrations (2 marks)** $n(C_2H_5COOH) = 1.00 - (2 \times 0.25) = 0.50$ (mol) ✓ $n(C_2H_5COO^-) = 1.00 + (2 \times 0.25) = 1.50$ (mol) ✓ …… **[H⁺] and pH (1 mark)** $[H^+] = 1.35 \times 10^{-5} \times \frac{0.50}{1.50}$ **OR** 4.5×10^{-6} (mol dm^{-3}) pH = −log 4.5×10^{-6} = **5.35 2 dp required** ✓	4	***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 $[C_2H_5COOH]$ • added 0.50 **OR** 0.25 to 1 for $[C_2H_5COO^-]$ ***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_a 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 $\text{pH} = \text{p}K_a + \log\frac{1.5}{0.5}$ **OR** $\text{p}K_a - \log\frac{0.5}{1.5}$ pH = 4.87 + 0.48 = 5.35 ✓ **ALLOW** $-\log K_a$ for $\text{p}K_a$		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. $[H^+] = 1.35 \times 10^{-5} \times \frac{0.50}{1.25}$ pH = –log 5.4 3. $[H^+] = 1.35 \times 10^{-5} \times \frac{0.75}{1.50}$ pH = –log 6.75 **Examiner's Comments** This buffer calculation was aimed as stretch and challenge and the majority of candidates struggled to derive the concentrations of CH_3CH_2COOH and $CH_3CH_2COO^-$. 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_3CH_2COOH that would be obtained 0.500 mol^{-3}. Many did not identify that Mg and CH_3CH_2COOH react in a 1:2 molar ratio, subtracting 0.25, instead of 0.50, from the original concentration. Rarely did candidates realise that the $CH_3CH_2COO^-$ concentration would increase from the initial concentration of 1 mol dm^{-3}. Others assumed that no $CH_3CH_2COO^-$ 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**	
16	a		$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$ ✓ Acid 1 Base 2 Acid 2 Base 1 ✓	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.* CH_3COOH + H_2O ⇌ $CH_3COOH_2^+$ + OH^- ✗ 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 H_3O^+ and an equilibrium involving OH^- ions rather than water. Neither approach could be credited.
	b	i	Water dissociates / ionises **OR** $H_2O \rightleftharpoons H^+ + OH^-$ **OR** $2H_2O \rightleftharpoons H_3O^+ + OH^-$ ✓	1	**ALLOW** $K_w = [H^+][OH^-]$ **OR** $[H^+][OH^-] = 10^{-14}$ ($mol^2\ dm^{-6}$) **IGNORE** breaking for dissociation **IGNORE** water contains H^+ and OH^- **IGNORE** $H_2O \rightarrow H^+ + OH^-$ *i.e. no equilibrium sign* **IGNORE** $2H_2O \rightarrow H_3O^+ + OH^-$ *i.e. no equilibrium sign* **Examiner's Comments** The key required feature was the dissociation of water but many instead discussed dissociation of the acid.
		ii	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF answer = 1.15×10^{-11}, award 2 marks** ……………………………………	2	**IF** there is an alternative answer, check to see if there is any **ECF** credit possible using working below. ……………………………………

			$[H^+] = 10^{-3.06} = 8.71 \times 10^{-4}$ (mol dm^{-3}) ✓ $[OH^-] = \frac{1.00 \times 10^{-14}}{8.71 \times 10^{-4}} = 1.15 \times 10^{-11}$ (mol dm^{-3}) ✓ **ALLOW** answer to two or more significant figures 2SF: 1.1×10^{-11}; 4SF: 1.148×10^{-11}; calculator $1.148153621 \times 10^{-11}$		**ALLOW 2 SF:** 8.7×10^{-4} up to calculator value of 8.7096359×10^{-4} correctly rounded **ALLOW** alternative approach using pOH: pOH = 14 − 3.06 = 10.94 ✓ $[OH^-] = 10^{-10.94} = 1.15 \times 10^{-11}$ (mol dm^{-3}) ✓ **Examiner's Comments** The majority of candidates correctly calculated the hydroxide ion concentration via K_w. 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}
	c	i	$2CH_3COOH + CaCO_3 \rightarrow (CH_3COO)_2Ca + CO_2 + H_2O$ ✓	1	**IGNORE** state symbols **ALLOW** ⇌ provided that reactants on LHS For $CO_2 + H_2O$, **ALLOW** H_2CO_3 **ALLOW** $Ca(CH_3COO)_2$ **ALLOW** $(CH_3COO^-)_2Ca^{2+}$ **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 CH_3COOH **AND** CH_3COO^- ✓	1	**ALLOW** names: ethanoic acid for CH_3COOH ethanoate for CH_3COO^- **ALLOW** calcium ethanoate **OR** $(CH_3COO)_2Ca$ for CH_3COO^- **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: $CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$ *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.
		iii	**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^+ and OH^- (see below) .... $CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$ ✓ .... CH_3COOH reacts with added alkali **OR** $CH_3COOH + OH^- \rightarrow$ **OR** added alkali reacts with H^+ **OR** $H^+ + OH^- \rightarrow$ ✓ Equilibrium → right **OR** Equilibrium → CH_3COO^- ✓ (**QWC**) CH_3COO^- reacts with added acid ✓ Equilibrium → left **OR** Equilibrium → CH_3COOH ✓ (**QWC**)	5	***FULL ANNOTATIONS MUST BE USED*** .... **Note: If there is no equilibrium equation then the two subsequent equilibrium marks are not available: max 2** **DO NOT ALLOW** $HA \rightleftharpoons H^+ + A^-$ **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 alkali **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.
	d		**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF answer = 11.48 OR 11.5 (g), award 5 marks** …………………………………… $[H^+] = 10^{-5}$ (mol dm^{-3}) ✓ …………………………………… **$[CH_3COO^-]$** = $\frac{1.75\times10^{-5}}{10^{-5}}$ ✓ × 0.200 = 0.350 mol dm^{-3} ✓ *n*(**CH_3COONa / CH_3COO^-**) in 400 cm^3 = $0.350 \times \frac{400}{1000}$ = 0.14(0) (mol) ✓ …………………………………… mass **CH_3COONa** = 0.140 × 82.0 = 11.48 **OR** 11.5 (g) ✓ For **ECF**, ***n*(CH_3COONa/CH_3COO^-) must** have been calculated in step before	5	***FULL ANNOTATIONS MUST BE USED*** …………………………………… **IF** there is an alternative answer, check to see if there is any **ECF** credit possible. **Incorrect use of $[H^+] = \sqrt{([CH_3COOH] \times K_a)}$ scores zero** **BUT IGNORE** if an alternative successful method is present **Incorrect use of K_w, 1 max for $[H^+] = 10^{-5}$ (mol dm^{-3})** **BUT IGNORE** if an alternative successful method is present …………………………………… **ALLOW** *n*(**CH_3COONa / CH_3COO^-**) = $\frac{1.75\times10^{-5}}{10^{-5}}$ ✓ × 0.08 = 0.14(0) (mol) ✓✓ **Note: There is no mark just for** *n*(**CH_3COOH**) in 400 cm^3 = 0.200 × $\frac{400}{1000}$= 0.08 (mol) …………………………………… As alternative for the 4th and 5th marks, **ALLOW**: mass of CH_3COONa in 1 dm^3 = 0.350 × 82.0 = 28.7 g ✓ mass of CH_3COONa in 400 cm^3 = 28.7 × $\frac{400}{1000}$= 11.48 g ✓

……………………………………

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 × 10^{-5}) = 4.757 ✓ *Calc: 4.75696. … .*

$\log \frac{[CH_3COO^-]}{[CH_3COOH]}$ = pH − pK_a = 5 − 4.757

= 0.243

$\frac{[CH_3COO^-]}{[CH_3COOH]} = 10^{0.243} = 1.75$ ✓

$[CH_3COO^-] = 1.75 \times 0.200 = 0.350$ mol dm^{-3} ✓

n(**CH_3COONa/CH_3COO^-**) in 400 cm^3

$= 0.350 \times \frac{400}{1000} = 0.14(0)$ (mol) ✓

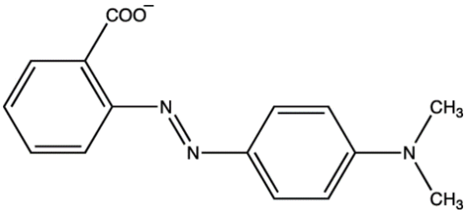
……………………………………

mass **CH_3COONa** = 0.140 × 82.0 = 11.48 **OR** 11.5 (g) ✓

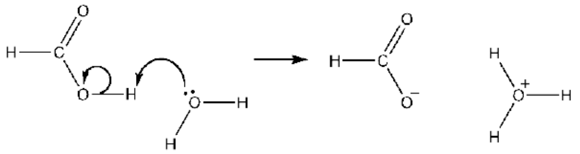
Examiner's Comments

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 acid.
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**	
17	a	i	Using a pH probe on a data logger **OR** pH meter	1	
		ii	**FIRST CHECK THE ANSWER ON THE ANSWER LINE** **IF** answer = **0.11(0)** (mol dm^{-3}), award **2 marks** …………………………………………………. $n(\text{NaOH}) = \frac{0.125 \times 22.0}{1000} = 2.75 \times 10^{-3}$ (mol) $\text{concentration of } CH_3COOH = \frac{2.75 \times 10^{-3} \times 1000}{25.0}$ = 0.11(0) (mol dm^{-3})	2	**IF** there is an alternative answer, check to see if there is any **ECF** credit possible using working below. ……………………………………………………… **ANNOTATE WITH TICKS AND CROSSES, etc** **ALLOW ECF:** *n*(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 ⇌ H$^+$ + A$^-$ i.e. 'towards HA' is equivalent to 'to left' i.e. 'towards A^{-}' is equivalent to 'to right' **ALLOW** yellow−red colour
	c	i	**FIRST CHECK THE ANSWER ON THE ANSWER LINE** **If** answer = 2.33 **award 4 marks** $K_a = 10^{-3.40} = 3.98 \times 10^{-4}$ (mol dm^{-3}) $\text{Concentration of aspirin} = \frac{1.00 \times 10^{-2}}{180} \times 1000$ = 0.0556 (mol dm^{-3})	4	

			$[H^+] = \sqrt{(K_a \times [HA])}$ $= \sqrt{(3.98 \times 10^{-4} \times 0.0556)}$ $= 4.70 \times 10^{-3}$ (mol dm^{-3}) pH = $-\log 4.70 \times 10^{-3} = 2.33$		**ALLOW ECF** **ALLOW ECF only** from $[H^+]$ calculation using $[H^+] = \sqrt{(K_a \times [HA])}$
		ii	Salts are ionic **AND** attracted to polar H_2O	1	
		iii	COO^- reacts with H^+ forming COOH Aspirin precipitates out	2	**ALLOW** equilibrium shifts to left
			Total	**15**	
18	a		$[H^+] = 10^{-pH} = 10^{-2.19} = 6.46 \times 10^{-3}$ (mol dm^{-3}) $[CH_3CH(OH)COOH] = \frac{[H^+]^2}{K_a} = \frac{(6.46 \times 10^{-3})^2}{1.38 \times 10^{-4}}$ = 0.0302(mol dm^{-3}) $n(CH_3CH(OH)COOH) = \frac{0.302 \times 250}{1000} = 0.0755$ mol Mass of $CH_3CH(OH)COOH$ = 0.0755 × 90 = 6.80 g Dissolve 6.80 g of the solid in distilled water (less than 250 cm^3) in a beaker (then) transfer the solution to a 250 cm^3 volumetric flask **AND** ensure that all solution is washed out of beaker (washings transferred to volumetric flask) (then) make solution up to 250 cm^3 with distilled water **AND** ensure thorough mixing by inverting the flask several times	8	**ALLOW** 5 marks for 6.80 g through any calculation. **ALLOW ECF** for incorrect calculation of mass. Mass used must be linked to calculation.
	b		$CH_3CH(OH)COO^- + CH_3CH_2CH_2COOH_2^+$ $CH_3CH(OH)COOH$ **AND** $CH_3CH(OH)COO^-$ $CH_3CH_2CH_2COOH$ **AND** $CH_3CH_2CH_2COOH_2^+$ **Both** pairs identified	2	State symbols **NOT** required **ALLOW** labels 'acid 1', 'base 1' etc. **ALLOW ECF** for second mark
	c	i	$[H^+] = \frac{1 \times 10^{-14}}{0.185} = 5.405 \times 10^{-14}$ (Use of K_w) pH = $-\log(5.405 \times 10^{-14}) = 13.27$	2	**ALLOW** $5.405405405 \times 10^{-14}$ and correct rounding to 5.4×10^{-14} **ALLOW** alternative approach using pOH: pOH = –log(0.185) = 0.73 pH = 14 – 0.73 = 13.27 Correct answer scores **BOTH** marks **ALLOW** 13.267
		ii	$n(A^-) = 9.25 \times 10^{-3}$ (mol) $n(HA) = 0.0165 - 9.25 \times 10^{-3} = 7.25 \times 10^{-3}$ (mol) $[H^+] = K_a \times \frac{[HA]}{[A^-]}$	4	**ALLOW** HA / acid and A^-/salt throughout for butanoate and butanoic acid **ALLOW** $pK_a = -\log K_a$ **OR** −log 1.5 ×

			pH = $-\log(1.5 \times 10^{-5} \times \frac{0.058}{0.074}) = 4.93$ **OR** pH = $-\log(1.5 \times 10^{-5} \times \frac{1000 \times \frac{7.25 \times 10^{-3}}{125}}{1000 \times \frac{9.25 \times 10^{-3}}{125}}) = 4.93$ **Final mark** also via Henderson-Hasselbalch equation: pH = p$K_a - \log\frac{[HA]}{[A^-]}$ = 4.82 – (–0.11) = 4.93 **OR** pH = p$K_a + \log\frac{[A^-]}{[HA]}$ = 4.82 + 0.11 = 4.93		10^{-3} **OR** 4.82 **ALLOW ECF** from incorrect values of $n(A^-)$ or n(HA) **ALLOW** pH = $-\log(1.5 \times 10^{-5} \times \frac{7.25 \times 10^{-3}}{9.25 \times 10^{-3}})$ = 4.93
			Total	**16**	
19			 1 mark for correct reactants **AND** products **AND** correct positioning of + and − charges on products 1 mark for two correct curly arrows **AND** H_2O curly arrow starting from O lone pair	2	
			Total	**2**	
20	i		$K_a = \frac{[[Fe(H_2O)_5OH]^{2+}(aq)][H^+(aq)]}{[[Fe(H_2O)_6]^{3+}(aq)]}$	1	state symbols **not** required
	ii		$[H^+] = \sqrt{6.00 \times 10^{-3} \times 0.100}$ **OR** 0.0245 (mol dm^{-3}) pH = −log 0.0245 = 1.61	2	**ALLOW ECF** from calculated $[H^+]$ provided that **BOTH** 6.0 x 10^{-3} **AND** 0.100 only have been used **ALLOW** calculation via quadratic equation → pH 1.66
			Total	**3**	
21			K_w value from graph from 2.2 to 2.4 × 10^{-14} (mol^2 dm^{-6}) Using 2.4 × 10^{-14}, $[H^+] = \sqrt{2.4 \times 10^{-14}}$ **OR** 1.55 × 10^{-7} pH = −log (1.55 × 10^{-7}) = 6.81 (using K_w = 2.4 × 10^{-14})	3	Actual K_w = 2.38 × 10^{-14} mol^2 dm^{-6} **ALLOW ECF** only if candidate uses a value between 2.0 and 2.6 × 10^{-14} (mol^2 dm^{-6}), 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 $[H^+]$ by attempting to take a square root of a value between 2.0 and 3.0 × 10^{-14}
			Total	**3**	

22	a	i	HNO_3 is a strong acid **AND** HNO_2 is a weak acid	1	**ALLOW** HNO_3 completely dissociates **AND** HNO_2 partially dissociates **ALLOW** $HNO_3 \rightarrow H^+ + NO_3^-$ **AND** $HNO_2 \rightleftharpoons H^+ + NO_2^-$ **IGNORE** HNO_3 is a stronger acid **ORA** **IGNORE** HNO_3 produces more H^+
		ii	pH = −log 0.0450 = 1.35 (**2 DP** required)	1	
		iii	**FIRST CHECK THE ANSWER ON ANSWER LINE** **IF** answer = 2.35, award all **three** calculation marks $K_a = 10^{-3.35}$ **OR** 4.47×10^{-4} (mol dm^{-3}) $[H^+] = \sqrt{(K_a \times [HNO_2])}$ **OR** $\sqrt{(K_a \times [HA])}$ **OR** $\sqrt{(K_a \times 0.0450)}$ **OR** 4.48×10^{-3} (mol dm^{-3}) pH = 2.35 (**2 DP** required)	3	**ALLOW** 2 SF to calculator value: $4.466835922 \times 10^{-4}$, correctly rounded **IGNORE** HNO_3 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_a mark only.*
	b		**FIRST CHECK THE ANSWER ON ANSWER LINE** **IF** answer = 0.810 (g) award 4 marks $[H^+] = 10^{-12.500} = 3.16 \times 10^{-13}$ (mol dm^{-3}) $[OH^-] = \frac{K_w}{[H^+]} = \frac{1.00 \times 10^{-14}}{3.16 \times 10^{-13}} = 0.0316$ (mol dm^{-3}) n(RbOH) $= 0.0316 \times \frac{250}{1000} = 7.91 \times 10^{-3}$ (mol) mass RbOH = $7.91 \times 10^{-3} \times 102.5 = 0.810$ (g)	4	Always **ALLOW** calculator value irrespective of working as number may have been kept in calculator. **ALLOW** alternative approach using pOH: pOH = 14.000 − 12.500 = 1.500 $[OH^-] = 10^{-1.500} = 0.0316$ **ALLOW ECF** from $[H^+]$ derived using K_w and $[OH^-]$ BUT **DO NOT ALLOW** an acid pH. **ALLOW** 0.81 g, up to calculator value but take care as rounding could be from any stage. *Last 3 SF figure is zero and is treated as a 'trailing zero' as specific number of SF has not been asked for.*
			Total	**9**	