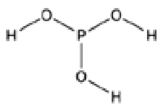
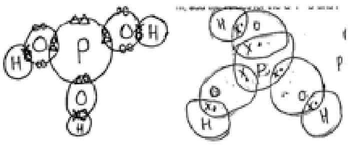
Mark scheme

Question			Answer/Indicative content	Marks	Guidance
1		i	In (Equilibrium) **1**, $H_2PO_4^-$/It acts as a base **AND** accepts/gains H^+/a proton **OR** $H_2PO_4^-$ forms H_3PO_4 ✓ In (Equilibrium) **2**, $H_2PO_4^-$/It acts as an acid, **AND** donates/loses H^+/a proton **OR** $H_2PO_4^-$ forms HPO_4^{2-} ✓	2	**ALLOW** description for 1 or 2 as long as unambiguous, e.g. Equation 1, etc **IGNORE** missing charge on $H_2PO_4^-$ throughout **IGNORE** reference to $H_2PO_4^{2-}$ acting as an acid/base **OR** Equilibrium **3** *Question is about $H_2PO_4^-$* **ALLOW** 'dissociates into H^+ and $H_2PO_4^{2-}$' **IGNORE** 'partially' **<u>Examiner's Comments</u>** Candidates were expected to link proton-transfer behaviour in acids and bases to the provided equilibria. The question differentiated between candidates well. Some candidates just stated that an acid is a proton donor and a base a proton acceptor without referring to the provided equilibria. This was the answer to a much simpler question and could not be given marks. The best responses demonstrated excellent understanding within the context of the equilibria. Such candidates clearly explained how $H_2PO_4^-$ behaves as an acid in the forward reaction of Equilibrium 2 and as a base in the reverse reaction of Equilibrium 1.
		ii	Diagram showing **all** bonds correctly ✓ 	3	**IGNORE** geometry **ALLOW** dot and cross diagram showing 2 shared electrons for each bond .... and **IGNORE** any lone pairs e.g.

			• 3 bonds only around each P • 2 bonds only around each O • Each O bonded to an H **Bond angles** O-P-O = 107° ✓ P-O-H = 104.5° ✓		 Unambiguous bond angles may be shown on dot and cross diagram **ALLOW** 106-108° **ALLOW** 104-105° **<u>Examiner's Comments</u>** Most candidates used the information in the question to draw a correct displayed formula of H_3PO_3. Another acceptable approach was to show a 'dot-and-cross' diagram. Candidates usually chose 104.5° for the P-O-H bond angles although a significant number suggested 180°. The O-P-O bond angle proved to be more difficult. Many suggested 120° by ignoring the lone pair of electrons on the P atom. The shape was analogous with NH_3 giving a bond angle of 107°. Overall, candidates answered this question well. Candidates are advised to assess the number of bonded pairs and lone pairs around each atom when suggesting bond angles. This would have reduced the number of incorrect bond angles such as 180° for P-O-H and 120° for O-P-O.
		iii	phosphoric(III) **acid** ✓ *Oxidation number **MUST** be in correct place*	1	**DO NOT ALLOW** phosphoric acid (III) **DO NOT ALLOW** phosphorous acid **<u>Examiner's Comments</u>** Most candidates wrote the correct systematic name of phosphorus(III) acid and the clue given in the question for the name of H_3PO_4 should have helped.

					Common errors included phosphorus(IV) acid, the same as for H_3PO_4, and the (III) oxidation number being placed after 'acid' in the name. The commonest error though, was hydrogen phosphate. Candidates are advised to use any information provided in the question, which often contains clues. This certainly would have prevented hydrogen phosphate as a response.
			Total	**6**	
2	a		**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF pH = 13.6(0), award 2 marks** --- K_w = [H^+] × 0.400 **OR** 1.00 × 10^{-14} = [H^+] × 0.400 **OR** $[H^+] = \frac{K_w}{0.400}$ **OR** $[H^+] = \frac{1.00 \times 10^{-14}}{0.400}$ **OR** $[H^+] = 2.5 \times 10^{-14}$ ✓ pH = −log 2.5 × 10^{-14} = 13.6(0) ✓ **ALLOW** 13.6..... up to calculator value of 13.60205999 correctly rounded	2	**ALLOW ECF** from incorrect [H^+] calculated from [OH−] **AND** K_w ....for pH > 7 **ONLY** **ALLOW** method based on pOH: **pOH** = −log 0.400 = 0.40 ✓ *Calculator: 0.39794...* pH = 14 − 0.40 = 13.6(0) ✓ **Examiner's Comments** Questions 1 (a), 1 (b) and 1 (c) required candidates to calculate the pH of a base, a diluted strong acid and a buffer solution. These different types of pH calculation form the basis of acid-base chemistry, all requiring the relationship pH = −log[H^+] at some stage. Most candidates showed competency in their pH calculations. A number of candidates often did not appreciate the type of pH calculation required. Question 1(a) was a standard pH calculation of a strong base and this was an easy start to the paper. Most candidates used K_w and the concentration of NaOH to determine the H^+ concentration of 2.5 ✓ $10{-}^{14}$ mol dm^{-3}, from which the pH of 13.60 can be calculated using pH =

					−log[H^+]. Some candidates first determined pOH as 0.40, and the pH using 14.00 − 0.40. This approach is based on sound chemistry and is acceptable. Several candidates often calculated the pH as −log 0.4 = 0.4 and gave this as their answer. NaOH is a common alkali and cannot have a pH <7 and this should have triggered that the candidate had made an error.
	b		**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF pH = 1.12, award 1 mark** -- -------------------- pH = −log 0.075 = **1.12** ✓ ***2 DP required***	1	<u>**Examiner's Comments**</u> This question was answered well although nearly a half of candidates made errors. The initial solution had been diluted by 10 times and its concentration had been reduced from 0.750 to 0.0750 mol dm^{-3}. From here pH = −log[H^+] gives the correct answer of 1.12 to 2 decimal places, required by the question. Candidates found Question 1 (b) more difficult than 1 (a) or 1 (c). There seemed to be little pattern in candidate errors, the dilution being the difficult part of the question. Some did not dilute the initial concentration of 0.750 mol dm^{-3}, giving 2.12. Others divided 0.750 by 2 instead of 10 or introduced 90 into the calculation as 90 cm3 of water would have been added. The most disappointing error was for a correct calculation to be displayed using the wrong number of decimal places. Two decimal places should be the norm for pH, reflecting the accuracy of most pH meters.
	c		**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF pH = 4.28, award 2 marks** -- -------------------- $1.75 \times 10^{-5} = \frac{[H^+] \times 0.100}{0.300}$ **OR** $[H^+] = \frac{1.75 \times 10^{-5} \times 0.300}{0.100}$ **OR** $[H^+] = 5.25 \times 10^{-5}$ (mol dm^{-3}) ✓	2	COMMON ERRORS **1 mark for 5.23** inverted [HA] and [A^-] $[H^+] = \frac{1.75 \times 10^{-5} \times 0.100}{0.300}$ **OR** 5.83.... × 10^{-6} ✗ pH = -log 5.83.... × 10^{-6} = **5.23** ✓ **ECF** **1 mark for 4.46** [HA] = 0.2 instead of 0.3

			pH = -log 5.25×10^{-5} = 4.28 ✓ ***2 DP required***		$[H^+] = \frac{1.75 \times 10^{-5} \times 0.200}{0.100}$ **OR** 3.5×10^{-5} ✗ pH = -log 3.5×10^{-5} = **4.46 ✓ ECF** Other **ECF** available from **ONE** transcription error **ONLY, e.g.** 1.57×10^{-5} for $K_a = 1.75 \times 10^{-5}$ **Zero marks for square root approach e.g. via** $K_a = \frac{[H^+]^2}{0.300}$ **Zero marks for [A$^-$] : [HA] = 0.1 : 0.1** **i.e.** $[H^+] = \frac{1.75 \times 10^{-5} \times 0.100}{0.100} = 1.75 \times 10^{-5}$ ✗ pH = 4.76 ✗ **ALLOW Henderson-Hasselbalch for both marks:** e.g. $pH = 4.76 + \log \frac{0.100}{0.300}$ **OR** $pH = -\log(1.75 \times 10^{-5}) + \log \frac{0.100}{0.300}$ ✓ **OR** $pH = -\log(1.75 \times 10^{-5}) - \log \frac{0.300}{0.100}$ pH = **4.28** ✓ **<u>Examiner's Comments</u>** This question was a standard calculation for the pH of a buffer solution and most candidates correctly identified the mixture as being a buffer. Most candidates used the expression for K_a and the concentrations of the weak acid and its salt to determine the H^+ concentration of 5.25×10^{-5} mol dm^{-3}. From here, the pH of 4.28 can easily be calculated. A common error was for the concentrations of the weak acid and its salt to be substituted into the K_a expression the wrong way round, producing an answer of 5.23. As there was only one error, this answer was given 1 mark with error carried forward (ECF). A few candidates first

<table>
<tr><td></td><td></td><td></td><td></td><td></td><td>subtracted 0.1 from 0.3, using concentration values of 0.2 and 0.1 instead of 0.3 and 0.1. This gave an answer of 4.46 which was also given 1 mark.

The substantial number of less successful responses fell into the trap of using the pH method for calculating the pH of a weak acid rather than a buffer, squaring the H^+ concentration. This was the wrong method to apply for a pH buffer calculation and was not given any marks.</td></tr>
<tr><td></td><td></td><td></td><td>Total</td><td>5</td><td></td></tr>
<tr><td>3</td><td></td><td></td><td>Oxygen (O lone pair) forms a coordinate/dative bond to Fe(II)/Fe/Iron/Fe^{2+} ✓

replaced by H_2O or CO_2
OR
O_2 bonds reversibly (with metal ion) ✓

FIRST CHECK ANSWER ON ANSWER LINE
If 7.3(0) AND not healthy / below 7.35 award three calculation marks
----

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

$[H^+] = 5.02 \times 10^{-8}$ ✓

pH = $-\log(5.02 \times 10^{-8}) = 7.3(0)$
AND not healthy / below 7.35 ✓

Alternative method 1:

pH of healthy blood is between 7.35 and 7.45

<table>
<tr><td>pH 7.35</td><td></td><td>pH 7.45</td><td></td></tr>
<tr><td>$[H^+] = 4.47 \times 10^{-8}$</td><td>OR</td><td>$[H^+] = 3.55 \times 10^{-8}$</td><td>✓</td></tr>
<tr><td>$\frac{[HCO_3^-]}{[H_2CO_3]} = \frac{K_a}{[H^+]}$</td><td></td><td>$\frac{[HCO_3^-]}{[H_2CO_3]} = \frac{K_a}{[H^+]}$</td><td>✓</td></tr>
</table>
</td><td>5</td><td>ALLOW word equations using → and ⇌

IGNORE number of coordinate bonds

ALLOW ORA

Check for alternative methods on mark scheme.
ALLOW ECF throughout

ALLOW $[A^-]$ for $[HCO_3^-]$ AND/OR [HA] for $[H_2CO_3]$ (asked for in 19 a) ii))

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

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

$[H^+]$ value subsumes MP3

ALLOW $[H^+] = 5.02 \times 10^{-8}$ up to the calculator value ($5.023529412 \times 10^{-8}$)

DO NOT ALLOW a weak acid approach for marking points 3 and 5. i.e. $[H^+]$ can be awarded.

ALLOW 7.3 up to calculator value (pH =7.298991951)

ALLOW $[H^+] = 3.98 \times 10^{-8}$ from average pH 7.40 used.
3

Examiner's Comments

The key chemistry that candidates</td></tr>
</table>

<table>
<tr><th></th><th></th><th></th><th></th><th></th><th></th></tr>
<tr>
<td></td><td></td><td></td>
<td>
<table>
<tr><td>$\frac{[HCO_3^-]}{[H_2CO_3]}$ =
$\frac{4.27 \times 10^{-7}}{4.47 \times 10^{-8}}$</td><td></td><td>$\frac{[HCO_3^-]}{[H_2CO_3]}$ =
$\frac{4.27 \times 10^{-7}}{3.55 \times 10^{-8}}$</td><td></td></tr>
<tr><td>$\frac{[HCO_3^-]}{[H_2CO_3]}$ = 9.55:1</td><td></td><td>$\frac{[HCO_3^-]}{[H_2CO_3]}$ = 12:03:1</td><td></td></tr>
</table>

8.5:1 does not lie in the range of 9.55:1 to 12.03:1 AND unhealthy ✓

<u>Alternative method 2:</u>

$\text{pH} = \text{p}K_a + \log \frac{[HCO_3^-]}{[H_2CO_3]}$ ✓

pKa = 6.37 ✓

$6.37 + \log \frac{(8.5)}{(1)}$

7.3(0) AND not healthy / below 7.35 ✓
</td>
<td></td>
<td>needed to discuss in their response was as follows:

• O_2 molecules forming coordinate bonds with and Fe^{2+} ions in haemoglobin. Often candidates omitted the Fe^{2+} and just stated it was to haemoglobin
• O_2 molecules being replaced by another ligand (e.g. H_2O or CO_2)

The calculation using the $[HCO_3^-]$: $[H_2CO_3]$ ratio of 8.5 : 1 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. ECF was given for the $[H^+]$ and then the pH linked to whether the blood was healthy.

A smaller number of candidates approached the question by calculating the ratio of $[HCO_3^-]$: $[H_2CO^3]$ for both pH 7.35 <u>and</u> pH 7.45 and then compared <u>both</u> ratios to the ratio of 8.5 : 1 for healthy blood. A few candidates attempted the calculation by the weak acid approach using $[H^+]^2$. In this case only the $[H^+]$ was given.</td>
</tr>
<tr><td></td><td></td><td></td><td>Total</td><td>5</td><td></td></tr>
<tr>
<td>4</td><td>a</td><td>i</td>
<td>$(K_a) = \frac{[H^+]\,[ClCH_2COO^-]}{[ClCH_2COOH]}$</td>
<td>1</td>
<td>DO NOT ALLOW without square brackets

DO NOT ALLOW $\frac{[H^+]^2}{[ClCH_2COOH]}$

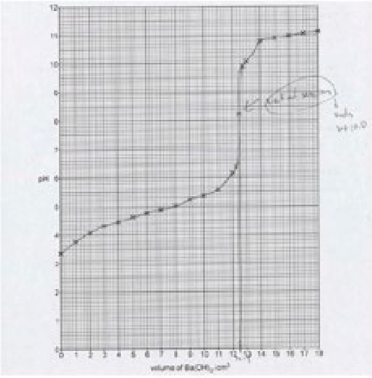
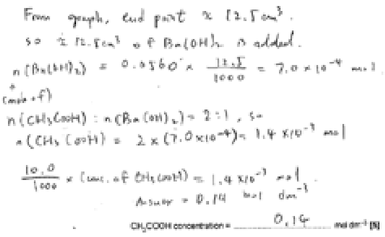
DO NOT ALLOW $\frac{[H^+][A^-]}{[HA]}$

<u>Examiner’s Comments</u>

Most candidates scored the marking point. They realised that the full formulae were needed although some candidates left off the square brackets or used HA or $[H]^2$. Care should be taken in checking the correct amount</td>
</tr>
</table>

					and location of H in the formula. As an acid dissociates to form a H^+, it is important to acknowledge only one H^+ is dissociated from the correct part of the molecule.
		ii	$[H^+] = [A^-]$ **OR** $[H^+]$ from water is negligible **OR** dissociation of water is negligible ✓	1	Answer must be in terms of concentration **ALLOW** $[H^+] \approx [A^-]$ **IGNORE** $HA \rightleftharpoons H^+ + A^-$ is a 1:1 mole ratio. **<u>Examiner's Comments</u>** This question required the candidate to understand that the dissociation of water to produce H^+ ions had no effect on the overall $[H^+]$ of the solution, leading to $[H^+] = [A^-]$. This was mostly answered well but some candidates used the idea of $[H^+] = [OH^-]$.
		iii	**FIRST CHECK ANSWER ON ANSWER LINE** **If answer = 2.85 OR 2.86 OR 2.87 award 3 marks** --- ($[H^+]$ =) $10^{-1.95}$ **OR** = $1.1(22\ldots) \times 10^{-2}$ ✓ $(K_a) = \left(\frac{[H^+]^2}{[ClCH_2COOH]}\right)$ $= \frac{(1.122\ldots \times 10^{-2})^2}{(0.090)}$ **OR** $\frac{(1.12 \times 10^{-2})^2}{(0.090)}$ **OR** $\frac{(1.1 \times 10^{-2})^2}{(0.090)}$ = $1.4(0) \times 10^{-3}$ **OR** = 1.39×10^{-3} **OR** = 1.34×10^{-3} ✓ ($pK_a = -\log_{10}(K_a)$ =) 2.85, 2.86 OR 2.87 (**2DP**) ✓	3	**ALLOW ECF** throughout **ALLOW** $[H^+] = 1.1 \times 10^{-2}$ up to calculator value **ALLOW** 2 sig figs up to calculator value. **ALLOW** calculations based on finding the $[HA]_{equ}$ $\frac{(1.122\ldots \times 10^{-2})^2}{(0.079)}$ **OR** $\frac{(1.12 \times 10^{-2})^2}{(0.079)}$ **OR** $\frac{(1.1 \times 10^{-2})^2}{(0.079)}$ = 1.59×10^{-3} **OR** = 1.59×10^{-3} **OR** = 1.53×10^{-3} ✓ ($pK_a = -\log_{10}(K_a)$ =) 2.80 **OR** 2.80 **OR** 2.81 (**2DP**) ✓ **Must be 2DP** **Common error:** **2 marks** 0.90 (not using $[H^+]^2$) **<u>Examiner's Comments</u>** Candidates made good progress with this calculation, many gaining 2 or 3 marks, including error carried forward. Common errors included, in various

					combinations: using -log[-1.95]; using an incorrect value for the concentration of C/CH_2COOH; and using 10^{-K_a}.
	b	i	Smooth s-shaped curve using a best fit line that goes through the majority of points. ✓ Reading off x-axis at 12.5 cm^3 ✓ $n(Ba(OH)_2)$ =) $0.0560 \times \frac{12.5}{1000}$ = 7.00×10^{-4} ✓ $n(CH_3COOH$ =) 2 × (moles $Ba(OH)_2$) = 1.40×10^{-3} ✓ (concentration =) $\frac{1.4 \times 10^{-3}}{(10/1000)}$ = 0.14(0) (mol dm^{-3}) ✓ <u>Alternative method based on calculating pK_a from the half neutralisation point.</u> pH and [H$^+$] reading will come from the candidates graph and the data points provided. e.g. pH at half neutralisation 6.25 cm^3 = pH 4.7 = pK_a ✓ $K_a = 10^{-4.7}$ = 1.995×10^{-5} ✓ [H$^+$] at pH 3.3 (obtained from data on the graph provided) $10^{-3.3} = 5.012 \times 10^{-4}$ (mol dm^{-3}) ✓ $[HA] = \frac{[H^+]^2}{[K_a]}$ $= \frac{(5.012 \times 10^{-4})^2}{(1.995 \times 10^{-5})}$ = 0.0126 (mol dm^{-3}) ✓	5	**DO NOT ALLOW** point to point **DO NOT ALLOW** tram/feather lines. **ALLOW** Reading off x-axis from 12.4 − 12.6 cm^3 **ALLOW** ECF throughout **ALLOW** 3SF or more unless there is a trailing zero <u>Alternative answers:</u> 0.139 (mol dm^{-3}) (from reading off x-axis at 12.4 cm^3) 0.141 (mol dm^{-3}) (from reading off x-axis at 12.6 cm^3) **Common errors:** 3 Marks 0.134 (Use of 12 cm^3) 0.202 (use of 18 cm^3) **ALLOW** MP2 for K_a = 1.7 x 10^{-5} to 1.8 x 10^{-5} (knowledge of actual K_a value) **ALLOW** ECF from any quoted K_a **<u>Examiner's Comments</u>** Nearly all candidates were able to draw the line of best fit and linked the sharp vertical section of the graph with the volume of $Ba(OH)_2$ needed to neutralise the ethanoic acid. Candidates should aim to produce a smooth line of best fit and avoid 'tram' lines when the pencil is taken off the paper and the curve started again. The line should go through most points. Some candidates misinterpreted the graph and used values of 8, 12, 12.2, 12.25 and 18. However, the

					remainder of the calculation was accessible, and most candidates scored well with ECF marks from this point. There was occasional division of 2 for the moles of ethanoic acid and dividing by the original volume of Ba(OH)$_2$ rather than the 10cm^3 of ethanoic acid. Exemplar 3   From graph, end point ≈ 12.5cm^3. so ≈ 12.5cm^3 of Ba(OH)$_2$ is added. n(Ba(OH)$_2$) = 0.0560 × $\frac{12.5}{1000}$ = 7.0 × 10^{-4} mol n(CH$_3$COOH) : n(Ba(OH)$_2$) = 2 : 1, so n(CH$_3$COOH) = 2 × (7.0×10^{-4}) = 1.4 × 10^{-3} mol $\frac{10.0}{1000}$ × (conc. of CH$_3$COOH) = 1.4 × 10^{-3} mol. Answer = 0.14 mol dm^{-3} CH$_3$COOH concentration = 0.14 mol dm^{-3} [5] This candidate scored all available marks. This is a very good example of a candidate displaying their working. The response was well communicated indicating the end point, links were made to what was being calculated and how the next number was obtained.
		ii	Phenol red **OR** Phenolphthalein ✓	1	Both indicators can change colour on the sharp vertical section of the candidates curve. **Examiner's Comments** Nearly all candidates scored this marking point. Phenol red and Phenolphthalein were good choices of indicator as their colour changed on the sharp vertical section of the graph, depending on how the top end of the line of best fit was drawn. Occasionally malachite green and bromophenol blue were seen.

			Total	**11**	
5			**A**	1	**Examiner's Comments** The correct answer was A. Formation of a buffer solution can either be from either: • a weak acid and a salt of the weak acid, e.g. CH3COOH/CH3COONa • an excess of a weak acid and a strong alkali, e.g. excess CH3COOH/NaOH A few candidates suggested the other alternatives in equal measure.
			Total	**1**	
6			**FIRST CHECK THE ANSWER ON ANSWER LINE** **If range = 4.4 × 10^{-5} – 4.5 × 10^{-5} (kJ mol^{-1}) award 3 marks** -- [H+] = $10^{-1.50}$ **OR** 0.0316 … **OR** 0.032 mol dm^{-3} ✓ **1 mark** ***THEN 2 APPROACHES:*** ***EITHER:*** **Factor that concentration changes by** **1 mark** Factor = $\frac{0.0316.....}{0.680}$ = 0.0465… times **OR** $\frac{0.680}{0.0316.....}$ = 21.5..... times ✓ **Initial rate with diluted acid** **1 mark**	3 (AO 3.1 ×3)	Calculator: 0.0316227766 **ALLOW** $10^{-1.5}$ **ECF** possible from incorrect [H^+] From unrounded [H+], Calculator: 0.04650408324 **From [H^+] = 0.032**, Factor = 21.25 From unrounded [H^+], Calculator = 4.427188724 × 10^{-5} **From [H^+] = 0.032**, rate = 4.48 × 10^{-5} -- **ECF** possible from incorrect [H^+] **DO NOT ALLOW ECF** unless derived from concentration and rate **SUMMARY** **M1 [H^+] 0.0316…. OR 0.032** **1 mark** **M2 Working 0.0465 OR 21.5**

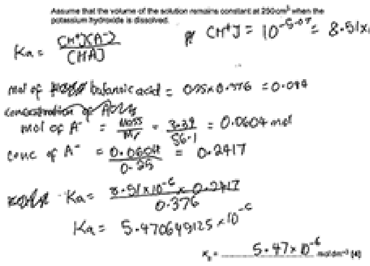
			$= 0.0465\ldots \times 9.52 \times 10^{-4}$ **OR** $\frac{9.52 \times 10^{-4}}{21.5\ldots\ldots}$ $= 4.43 \times 10–5$ (mol dm^{-3} s^{-1}) ✓ *OR:* **Rate α concentration (1st order) 1 mark** $k = \frac{rate}{[HCl]} = \frac{9.52 \times 10^{-4}}{0.680} = 1.4(0) \times 10^{-3}$ **OR** Constant = $\frac{0.680}{9.52 \times 10^{-4}} =$ 714.2857… ✓ **Initial rate with diluted acid** $= 1.4(0) \times 10^{-3} \times 0.0316\ldots$ **OR** $\frac{0.0316\ldots}{714.2857\ldots}$ $= 4.43 \times 10^{-5}$ (mol dm^{-3} s^{-1}) ✓		**OR 1.4 × 10^{-3} OR 714 1 mark** **M3 Initial rate Range: 4.4 × 10^{-5} – 4.5 × 10^{-5} 2 SF or more** *depends on intermediate rounding* ***CHECK*** **1 mark** **Examiner's Comments** The marks for this calculation were much more polarised than the calculation in Question 2 (a). Many candidates worked through the problem methodically to get an answer for the initial rate between 4.4 × 10^{-5} and 4.5 × 10^{-5} mol dm^{-3} s^{-1}. A substantial number of candidates worked out $[H^+]$ using 10^{-pH} for 1 mark but were then unable to progress any further. This was a novel calculation, requiring candidates to develop their own strategy for its solution. Candidates who found this question difficult often attempted a solution based on stock weak acid calculation, using $[H^+]^2/[HA]$.
			Total	**3**	
7	a	i	**FIRST CHECK THE ANSWER ON ANSWER LINE** **if answer = 6.77 award 2 marks** --- $K_w = [H^+][OH^-]$ **OR** $K_w = [H^+]^2$ **OR** $[H^+] = \sqrt{K_w}$ ✓ $([H^+] = \sqrt{(2.92 \times 10^{-14})})$ pH = $-\log(1.71 \times 10^{-7}) = 6.77$ ✓	2 (AO 1.1 × 1) (AO 2.2 × 1)	**DO NOT ALLOW** use of A^- or X^- **Examiner's Comments** Most candidates were given the first mark from a correct or rearranged equation. Many candidates then answered this question correctly and were given both marks. Those who didn't, either used 1.00×10^{-7} as $[OH^-]$ when calculating $[H^+]=Kw/[OH^-]$ or calculated pH as $-\log(2.92 \times 10^{-14})$.
		ii	(In pure water), $[H^+]$ (always) equals $[OH^-]$	1 (AO 3.2 × 1)	**ALLOW** moles/number of H^+ is (always) equal to moles/number of OH^-. **DO NOT ALLOW** ratio $[H^+]$: $[OH^-]$ doesn't change **Examiner's Comments** This question proved difficult with only a few candidates able to state that in neutral water, $[H^+] = [OH^-]$. Many candidates said that as the pH is close to 7, water is therefore neutral.

	b		• **Equation** $Sr + 2H_2O \rightarrow Sr(OH)_2 + H_2$ ✓ **CHECK THE ANSWER ON ANSWER LINE** **if answer = 11.51 award 4 calculation marks** --- • **n(Sr(OH)$_2$)** $= \frac{0.145}{121.6} = 1.1924\ldots \times 10^{-3}$ ✓ • **[OH$^-$]** $= 2 \times (1.1924 \times 10^{-3} \div 0.25) = 9.539\ldots \times 10^{-3}$ ✓ • **[H+]** = $K_w \div [OH^-]$ $= \frac{0.145}{121.6} = 3.061\ldots \times 10^{-12}$ ✓ • **pH** = $-\log(3.061\ldots \times 10^{-12}) = 11.51$ ✓ **2 DP** required	5 (AO 2.6) (AO 2.4 × 3) (AO 1.2 × 1)	**IGNORE** state symbols (even if wrong) **ALLOW** multiples **ALLOW** $Sr^{2+} + 2OH^-$ for $Sr(OH)_2$ **ALLOW** 3 SF up to the calculated value. Ignore RE after 3SF. **ALLOW** ECF throughout but final answer must be pH>7 **Final answer must be from calculated values.** **Common errors for 3 calculation marks** 11.98 *(Use of $K_w = 1 \times 10^{-14}$)* 11.21 *(no × 2)* 10.91 *(÷ by 2)* **Common error for 2 calculation marks** pH = 11.67 *(no × 2 and wrong K_w)* --- **Alternative method for:-** **pH = pKw – pOH** ○ ***n*(Sr(OH)$_2$)** $= \frac{0.145}{121.6} = 1.1924\ldots \times 10^{-3}$ ○ **[OH$^-$]** $= 2 \times (1.1924 \times 10^{-3} \div 0.25) = 9.539\ldots \times 10^{-3}$

					○ ***pH*** *= pKw - pOH* *= (-log 2.92 x* 10^{-14}*) - (-log 9.539..x* 10^{-3}*)* - ***pH*** *= 13.53(46) - 2.02(05)* **= 11.51** **<u>Examiner's Comments</u>** Most candidates wrote the correct equation. Common errors were using Sr^{2+} as reactant, not balancing the H_2O and not having the H_2 as second product. Most candidates calculated the moles of $Sr(OH)_2$ correctly but fewer recognised that $[OH^-]$ = twice the $[Sr(OH)_2]$. As a result, most candidates scored 3 calculation marks. A few candidates chose the incorrect K_w value.
	c	i	$Mg + 2H^+ \rightarrow Mg^{2+} + H_2$ ✓	1 (AO 2.6)	**ALLOW** multiples **ALLOW** Mg^{+2} **IGNORE** state symbols **<u>Examiner's Comments</u>** Ionic equations still present candidates with a challenge. A few candidates scored the mark but many candidates gave a full equation or one that contained a mismatch of spectator ions as well as the correct ions.
		ii	HC*l* is a strong acid/completely dissociates **AND** CH_3COOH is a weak acid/partially dissociates ✓ Greater H^+ concentration in HC*l* **AND** More frequent collisions / faster rate of reaction ✓	3 (AO 1.1 × 1) (AO 3.1 × 2)	**IGNORE** HCl is a strong**<u>er</u>** acid than ethanoic acid. **ALLOW** ORA **DO NOT ALLOW** dibasic/tribasic

			More CH_3COOH dissociates until same number of moles of H^+ released **OR** same total moles H^+ produced (by the end) **OR** (Both acids are monobasic) and have the same number of moles of acid ✓		**Examiner's Comments** This question proved challenging for the candidates to identify the three ideas: Those of comparing acids, comparing moles and comparing rates. Very few candidates were able to score the 3 marks. Most candidates recognised the different strength of the two acids, but some only used comparative language. Some linked the moles of acid used to the volume of gas produced but many simply restated the same volume and concentration which is given within the question. Only a few candidates linked the higher initial $[H^+]$ in HCl to the increased rate through more frequent collisions. A common issue was describing the rate of dissociation rather than the $[H^+]$ present in determining the rate of the reactions or mentioning that it dissociates more but not linking this to the H+ concentration.
	d	i	One **mole** of (butanoic) acid donates/dissociates to form one **mole** of protons/H^+ ✓	1 (AO 1.1)	**ALLOW** One **molecule** of (butanoic) acid donates/dissociates to form one proton/H^+ **ALLOW** only one hydrogen ion in the acid can be replaced per molecule (in an acid-base reaction) **Examiner's Comments** Very few candidates wrote the complete definition of a monobasic acid. Most wrote "donates one proton" only, omitting mole or molecule. Some candidates described donating electrons or OH^-.
		ii	**FIRST CHECK THE ANSWER ON ANSWER LINE** **IF ANSWER = 1.5(3) x 10^{-5} award 4 marks** --- • $[H^+] = 10^{-pH}$ **OR** $10^{-5.07}$ **OR** 8.51×10^{-6} ✓	4 (AO 1.2 × 1) (AO 2.6 × 3)	**FULL ANNOTATIONS MUST BE USED** --- **ALLOW ECF** throughout **ALLOW 2 SF** for $[H^+]$ (use of pH)

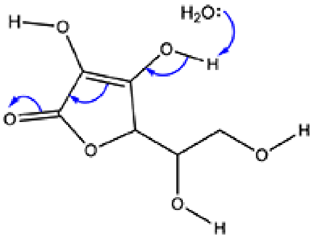
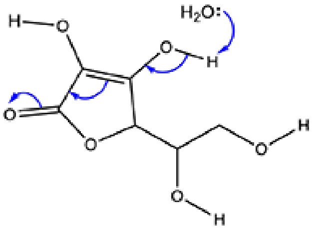
			- $(\frac{3.39}{56.1})$ **OR** 0.0604 (0.06042781) (*n*A⁻ in buffer) = (n(KOH)) **OR** 0.0604 x 4 **OR** 0.242 ✓ ([A⁻] in buffer) - *n*HA in buffer = (0.376 x 0.25) – 0.0604 = (0.094) – 0.0604 **OR** 0.0336 (0.03357219...) **OR** [HA] in buffer = (0.376 – 0.242) **OR** 0.0336 x 4 **OR** 0.134 (0.13428877) ✓ - $K_a = [H^+][A^-] \div [HA]$ $= \frac{8.51 \times 10^{-6} \times 0.242}{0.134}$ = 1.5..... × 10^{-5} (1.5319942 × 10^{-5})✓		**ALLOW** 3 SF up to the calculated value. Ignore RE after 3SF for moles and concentration values Mark use of 2SF in working as incorrect **once** and then allow ECF **ALLOW** full marks for use of moles (volumes cancel) $K_a = \frac{8.51 \times 10^{-6} \times 0.0604}{0.0336}$ =1.53 x 10^{-5} **ALLOW** final answer to 2SF **Common errors for 3 marks** 5.47(1731026) x 10^{-6} (not subtracting moles of KOH from HA) **<u>Examiner's Comments</u>** This calculation proved difficult with many figures and sums appearing with little indication as to their relevance. 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. Few candidates scored all 4 marks. Most found the concentration of H^+ from the pH and the moles of KOH correctly but did not recognise they had to take away the moles of KOH from those of HA to find the remaining concentration of HA. Some candidates then used the [H+] as the [HA]. A few candidates tried a $[H^+]$ squared expression of a weak acid.

					Exemplar 2  Assume that the volume of the solution remains constant at 250cm^3 when the potassium hydroxide is dissolved. $K_a = \frac{[H^+][A^-]}{[HA]}$ $[H^+] = 10^{-5.07} = 8.51 \times 10^{-6}$ mol of butanoic acid = $0.25 \times 0.376 = 0.094$ ~~concentration of~~ mol of A^- = $\frac{mass}{Mr} = \frac{3.39}{56.1} = 0.0604$ mol conc of A^- = $\frac{0.0604}{0.25} = 0.2417$ $K_a = \frac{8.51 \times 10^{-6} \times 0.2417}{0.376}$ $K_a = 5.470649125 \times 10^{-6}$ K_a = 5.47 × 10^{-6} mol dm^{-3} [4] The candidate has clearly set out the calculation so each numerical value can be linked and the steps understood. The only error is not calculating the excess acid (i.e. not subtracting moles OH- from initial moles acid) so 3 marks were given.
	e		ratio/proportion [HA]/[A-] is the same	1 (AO 3.1)	**ALLOW** Change in [HA] and [A-] is proportional **ALLOW** the concentrations of the weak acid and conjugate base change by same amount **Examiner's Comments** ? **Misconception** Only the most successful candidates linked the pH not changing to the ratio of [HA] and [A-] not changing on addition of water. The majority of candidates described the buffer being able to minimise pH change on addition of small amounts of acid or base or that water being neutral would not affect the pH.
			Total	**18**	
8			**D**	1 (AO 2.6)	**Examiner's Comments** The most successful candidates showed their workings for the correct answer of D.
			Total	**1**	

9		i	(Glycolic) acid is in **excess/partially neutralised** **AND** glycolate/potassium glycolate (ions) are present/produced ✓	1 (AO1.1)	**ALLOW** some acid remains **ALLOW** conjugate base for glycolate ions/salt of weak acid **ALLOW** $HOCH_2COO^-$ **<u>Examiner's Comments</u>** Many candidates did not answer the question and instead described what a buffer was. Very few candidates correctly explained that a weak acid was being added to a base, sometimes mentioning the formation of the salt or conjugate base. The majority also did not include the importance of there being excess acid, or some acid remaining, after the partial neutralisation.
		ii	**FIRST CHECK THE ANSWER ON ANSWER LINE** **If answer = 3.93 award 4 marks** **---** **Initial amounts** $n(HOCH_2COOH) = 0.750 \times \frac{60.0}{1000}$ **OR** 0.045(0) (mol) **AND** $n(KOH) = 0.625 \times \frac{40.0}{1000}$ **OR** 0.025(0) ✓ **Amounts in the buffer solution** $n(HOCH_2COOH) = 0.0450 - 0.0250$ **OR** 0.02(00) (mol) **AND** $n(HOCH_2COO^-)$ 0.025(0) (mol) ✓ **pH** $K_a = 10^{-3.83}$ **OR** 1.479 & $\times 10^{-4}$ ✓ $[H^+] = \frac{1.479 \ldots \times 10^{-4} \times 0.200}{0.250}$ **OR** 1.183×10^{-4} (mol dm^{-3}) pH = 3.93 (**2 DP**) ✓	4 (AO1.2×1) (AO2.8×3)	**ALLOW ECF** throughout **ALLOW use of moles for concentration** $[H^+] = \frac{1.479 \ldots \times 10^{-4} \times 0.0200}{0.0250}$ **Common errors** **3 marks** pH = 3.57 not using n(HA) remaining **2 marks** pH = 3.75 using HA and KOH concentrations within question **<u>Examiner's Comments</u>** Most candidates were able to derive a value for K_a from pK_a and calculate the number of moles of glyolic acid and potassium hydroxide reacting.

					Less were successful in determining the moles or concentrations present in the buffer solution causing many to get the common error of 3.57. Many candidates tried to calculate pH for the weak acid, without considering changes to concentrations or the buffering effect. 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.
		iii	NH_3 / OH^- reacts with H^+ / $HOCH_2COOH$ / (Glycolic) acid ✓ $HOCH_2COOH \rightleftharpoons H^+ + HOCH_2COO^-$ **AND** Equilibrium shifts to the right ✓	2 (AO1.2×2)	**ALLOW** NH_3 will act as a base (and form NH_4^+) **ALLOW** NH_3 decreases $[H^+]$ **ALLOW** $HA \rightleftharpoons H^+ + A^-$ Equilibrium equation needs to be shown. **<u>Examiner’s Comments</u>** Most candidates correctly described the ammonia reacting with the glycolic acid or with hydrogen ions, although some thought that ammonia was acidic. Many of them then went on to say that “the equilibrium will move to the right” without realising that the equilibrium had not itself appeared within the question, and so they needed to write it out to gain marks. A few candidates thought that ammonia was an acid, due to the 3 × Hs in the molecule.
			Total	**7**	
10		i	**FIRST CHECK THE ANSWER ON ANSWER LINE** **If answer = 2.53(g) award 5 marks** **---** **$[H^+]$** = $10^{-13.12}$ **OR** 7.58..... × 10^{-14} (mol dm^{-3}) ✓ $[OH^-] = \frac{1 \times 10^{-14}}{7.58........ \times 10^{-14}}$ **OR** 0.1318 .... (mol dm^{-3}) ✓	5 (AO2.4×5)	**ALLOW ECF and 3SF throughout.** **ALLOW** calculation process in any order. **IGNORE** rounding errors past **3SF** **--** Calculator: 7.58577575 × 10^{-14} Calculator: 0.1318256739 **ALLOW** alternative approach using

			$n(OH^-)$ in 250 cm^3 = $\frac{0.1318.....}{4}$ **OR** 0.0329...... (mol) ✓ $n(Ba(OH)_2)$ or $n(BaO)$ = $\frac{0.0329.......}{2}$ **OR** 0.0164….. (mol) ✓ **Mass of BaO** = 0.0164..... × 153.3 = 2.53 (g) **3SF** ✓		pOH for first 2 marks. p[OH^-] = 14 − 13.12 = 0.88 [OH^-] = $10^{-0.88}$ = 0.1318….. Calculator: 0.03295641846 0.033(0) comes from [OH^-] = 0.132 Calculator: 0.01647820923 Calculator: 2.526109475 **Common errors 4 marks** 5.05g Not dividing by 2 2.82g Use of M_r for $Ba(OH)_2$ 5.06g rounds to 0.132 in M2 then not dividing by 2 **3 marks** 5.65g not dividing by 2 and using Mr for $Ba(OH)_2$ **Examiner's Comments** Although few candidates got the correct final answer, however almost all achieved some marks from this calculation through error carried forward, with marks spread across the available range. Almost all candidates were able to find the concentrations of hydrogen and hence hydroxide ions. A few candidates successfully used p[OH^-] method. Most were able to calculate the moles of hydroxide ions in 250cm^3. Many then did not realise the need to half this number to find the moles of barium, and/or used the Mr for barium hydroxide instead of barium oxide.
		ii	Ba^{2+}(aq) +2H^+(aq) + SO_4^{2-}(aq) +2OH^-(aq) → $BaSO_4$(s) +2H_2O(l)✓	1 (AO3.2)	**ALLOW** multiples **ALLOW** H^+(aq)+ OH^-(aq) → H2O(l) **OR** Ba^{2+}(aq) + SO_4^{2-}(aq) → $BaSO_4$(s) **Examiner's Comments** This question was answered well, with

					many candidates giving one of the equations in the 'ALLOW' part of the mark scheme. Those candidates who did not gain this mark gave full equations or missed out state symbols.
			Total	**6**	
11			**D**	1(AO2.3)	**Examiner's Comments** This was well answered, with many candidates understanding that the addition of an alkali will react with the H^+ ions and will keep the position of equilibrium on the right hand side.
			Total	**1**	
12			**C**	1(AO1.2)	**Examiner's Comments** This was generally well answered. The key to candidates arriving at the correct answer ,C, was to write out the equation for ammonia reacting with water. The correct identification of the acids can then be made. Option B was chosen as the candidate identified the B-L bases and option D was chosen by candidates who linked up a B-L acid – base pair.
			Total	**1**	
13		i	 3 **OR** 4 curly arrows correct → 2 marks ✓ ✓ 1 curly arrow correct → 1 mark ✓	2 (2 ×AO3.2)	**IGNORE incorrect curly arrows** **IGNORE** 'double' curly arrows such as:  **H_2O Curly arrow** must • start from, **OR** be traced back to **any point across width** of lone pair on H_2O**:** **Examiner's Comments** This novel mechanism assessed a

					candidate's understanding of curly arrows, and four curly arrows were needed. One mark was available for one correct curly arrow, usually from the H_2O: or from the C=O. 2 marks were given for three or four correct curly arrows. The two curly arrows within the ring structure proved to be the most difficult. The question discriminated extremely well: many candidates were able to secure one mark with the most able being given both marks. A candidate showing all four curly arrows correctly demonstrated an excellent understanding of curly arrows.
		ii	**FIRST CHECK ANSWER ON THE ANSWER LINE** **If answer = 2.16 award 3 marks** --- [Vitamin C] = 0.150 × 4 = 0.600 (mol dm^{-3}) ✓ *0.6 seen anywhere* [H$^+$] = √ (K_a × [Vitamin C]) = √ (7.94 × 10^{-5} × 0.600) = 6.90 × 10^{-3} (mol dm^{-3}) ✓ pH = -log [H$^+$] = -log 6.90 × 10^{-3} = 2.16 ✓ **2 DP required**	3 (2 ×AO2.4) (1 ×AO1.2)	**For [H$^+$]** **ALLOW ECF** from incorrect [vitamin C] for pH **ALLOW ECF ONLY** if [H$^+$] has been derived from K_a **AND** [vitamin C] --- **COMMON ERRORS** pH = 4.32 2/3 calculation marks *No square root of* (7.94 × 10^{-5} × 0.600) pH = 2.46 2/3 calculation marks *No ×2 4* (7.94 × 10^{-5} × 0.150) pH = 2.76 2/3 calculation marks *÷ 4* (7.94 × 10^{-5} × 0.0375) pH = 4.92 1/3 calculation mark *No square root AND 0.150* pH = 5.53 1/3 calculation mark *No square root AND 0.0375* **Examiner's Comments** Most candidates had learnt a standard method for calculating the pH of a weak acid. with the correct answer of 2.16 being seen on very many scripts. Success required conversion of 0.150 moles of vitamin C in 250 cm^3 to its concentration as 0.600 mol^{-3}, calculation of [H$^+$] using [H$^+$] = √ (K_a × [HA]) and determination of pH using -log[H$^+$]. Common errors usually resulted from one mistake and could still be

					rewarded with 2 of the available 3 marks. Examples are shown below. • pH = 4.32 *No square root of* (7.94 × 10^{-5} × 0.600) • pH = 2.46 *No conversion of 0.150 mol to 0.600 mol* dm^{-3} → (7.94 × 10^{-5} × 0.150) • pH = 2.76 ÷ 4 instead of × 4 for concentration → (7.94 × 10^{-5} × 0.0375) **AfL** pH calculations are common in A Level Chemistry There are four different types, and it is essential that the standard methods for determination of [H^+] in the calculations are **learnt**: • pH of strong acids • pH of weak acids, using K_a and [HA] • pH of strong bases, using Kw and [OH^-] • pH of buffers, using K_a and [HA]/[A^-] It is extremely likely that at least one of these types of pH calculation will feature in at least one of the A Level units.
			Total	**5**	