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2002

**XVIII**

1583

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**71 Minutes**

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**Module 5: Physical chemistry and transition elements**

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## EXAM PAPERS PRACTICE

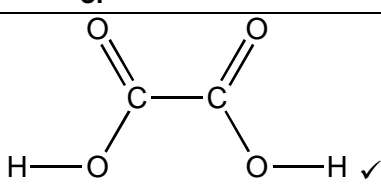
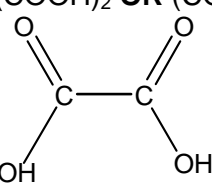
Question			er	Mark	Guidance
1	(a)	(i)	proton donor ✓	1	<b>ALLOW</b> H <sup>+</sup> donor
		(ii)	(the proportion of) dissociation ✓  Correct equation for <b>any</b> of the four acids: C <sub>6</sub> H <sub>5</sub> COOH ⇌ H <sup>+</sup> + C <sub>6</sub> H <sub>5</sub> COO <sup>-</sup> <b>OR</b> CH <sub>3</sub> COOH ⇌ H <sup>+</sup> + CH <sub>3</sub> COO <sup>-</sup> <b>OR</b> CH <sub>3</sub> COCOOH ⇌ H <sup>+</sup> + CH <sub>3</sub> COCOO <sup>-</sup> <b>OR</b> CH <sub>3</sub> CHOHCOOH ⇌ H <sup>+</sup> + CH <sub>3</sub> CHOHCOO <sup>-</sup> ✓	2	<b>ALLOW</b> a weak acid partly dissociates <b>ALLOW</b> a strong acid totally dissociates <b>ALLOW</b> ionisation for dissociation <b>ALLOW</b> the ability to donate a proton  Equilibrium sign <b>required</b> <b>ALLOW</b> equilibria involving H <sub>2</sub> O and H <sub>3</sub> O <sup>+</sup> e.g. C <sub>6</sub> H <sub>5</sub> COOH + H <sub>2</sub> O ⇌ H <sub>3</sub> O <sup>+</sup> + C <sub>6</sub> H <sub>5</sub> COO <sup>-</sup> , etc <b>DO NOT ALLOW</b> HA ⇌ H <sup>+</sup> + A <sup>-</sup>
		(iii)	weakest: CH <sub>3</sub> COOH                      acetic acid C <sub>6</sub> H <sub>5</sub> COOH                      benzoic acid CH <sub>3</sub> CHOHCOOH                  lactic acid strongest: CH <sub>3</sub> COCOOH ✓              pyruvic acid	1	<b>ALLOW</b> correct order using <b>any</b> identifier from the table, <i>ie</i> , common name, systematic name, structural formula <b>OR</b> pK <sub>a</sub> value
		(iv)	C <sub>6</sub> H <sub>5</sub> COOH <sub>2</sub> <sup>+</sup> + CH <sub>3</sub> CHOHCOO <sup>-</sup> ✓	1	<b>BOTH</b> products <b>AND</b> correct charges required for mark Mark <b>ECF</b> from incorrect order in (iii) See response from (iii) below response to (iv)

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Question		er	Mark	Guidance
(b)	(i)	$2\text{CH}_3\text{COCOOH} + \text{Ca}(\text{OH})_2 \rightarrow (\text{CH}_3\text{COCOO})_2\text{Ca} + 2\text{H}_2\text{O}$ ✓  <b>Note:</b> pyruvic acid must have been used here and formula of pyruvic acid and pyruvate <b>must</b> be correct	1	All species <b>AND</b> balancing required for the mark <b>ALLOW</b> $(\text{CH}_3\text{COCOO}^-)_2\text{Ca}^{2+}$ <b>ALLOW</b> equation showing $2\text{CH}_3\text{COCOO}^- + \text{Ca}^{2+}$ <b>IF</b> charges shown, charges <b>must</b> balance, e.g. <b>DO NOT ALLOW</b> $(\text{CH}_3\text{COCOO}^-)_2\text{Ca}$ <b>IGNORE</b> state symbols if shown <b>ALLOW</b> multiples <b>ALLOW</b> equilibrium sign
	(ii)	$\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$	1	<b>ALLOW</b> multiples but <b>not</b> same species on both sides <b>ALLOW</b> equilibrium sign <b>IGNORE</b> state symbols if shown <b>ALLOW</b> $\text{H}_3\text{O}^+ + \text{OH}^- \rightarrow 2\text{H}_2\text{O}$ <b>ALLOW</b> $\text{CH}_3\text{COCOOH} + \text{OH}^- \rightarrow \text{CH}_3\text{COCOO}^- + \text{H}_2\text{O}$
(c)		<b>FIRST, CHECK THE ANSWER ON ANSWER LINE</b> <b>IF</b> answer = 2.11, award 4 marks ----- $K_a = 10^{-\text{p}K_a}$ $= 10^{-2.39}$ <b>OR</b> 0.00407 ✓ $K_a = \frac{[\text{H}^+][\text{CH}_3\text{COCOO}^-]}{[\text{CH}_3\text{COCOOH}]}$ ( <b>ALLOW</b> use of HA, H <sup>+</sup> and A <sup>-</sup> )  <b>OR</b> $[\text{H}^+] = \sqrt{K_a \times [\text{HA}]}$ <b>OR</b> $[\text{H}^+] = \sqrt{0.00407 \times 0.0150}$ ✓ (subsumes 1st marking point) $[\text{H}^+] = 0.00782$ (mol dm <sup>-3</sup> ) ✓  pH = -log 0.00782 = <b>2.11</b> ✓	4	<b>IF</b> there is an alternative answer, check to see if there is any <b>ECF</b> credit possible using working below ----- <b>IF ECF, ANNOTATE WITH TICKS AND CROSSES, etc</b>  <b>ALLOW</b> 0.0041 to calculator value: 0.004073802  <b>IF</b> the pK <sub>a</sub> of a different weak acid has been used use <b>ECF</b> from 2nd marking point  <b>ALLOW</b> 0.0078 to calculator value (depending on previous rounding) <b>ALLOW ONLY 2.11</b> <b>(This is to take into account poor previous rounding)</b>  <b>IF</b> candidate has used 0.0150 mol dm <sup>-3</sup> (ie assumes strong acid) <b>ALLOW</b> final mark <b>ONLY</b> by <b>ECF</b> for a pH of 1.82  <b>IF</b> no square root used, pH = 4.21 3 marks



Question		er	Mark	Guidance
(d)	(i)		1	<b>ALLOW</b> correct structural <b>OR</b> displayed <b>OR</b> skeletal formula <b>OR</b> recognisable mixture of formulae  <b>DO NOT ALLOW</b> molecular formula but <b>ALLOW</b> (COOH) <sub>2</sub> <b>OR</b> (CO <sub>2</sub> H) <sub>2</sub>   <b>ALLOW</b> OH <b>BUT not</b> O-H-C
	(ii)	$C_2H_2O_4 \rightleftharpoons H^+ + C_2HO_4^- \checkmark$ $C_2HO_4^- \rightleftharpoons H^+ + C_2O_4^{2-} \checkmark$	2	<b>ALLOW</b> in <b>either</b> order <b>ALLOW</b> arrow instead of equilibrium sign <b>ALLOW</b> molecular formulae for this part <b>ALLOW</b> equilibria involving H <sub>2</sub> O and H <sub>3</sub> O <sup>+</sup> <b>ALLOW</b> equations using structures



Question	er	Mark	Guidance
(e)	<p><b>Chemicals (1 mark)</b> lactic acid / CH<sub>3</sub>CHOHCOOH <b>AND</b> (sodium) lactate / CH<sub>3</sub>CHOHCOO<sup>-</sup> (Na<sup>+</sup>) ✓</p> <p><b>Concentrations (4 marks)</b></p> <p><b>EITHER</b> [H<sup>+</sup>(aq)] = 10<sup>-3.55</sup> <b>OR</b> 2.8 x 10<sup>-4</sup> <b>OR</b> 2.82 x 10<sup>-4</sup> (mol dm<sup>-3</sup>) ✓ <i>separate marking point</i></p> <p><math>K_a = 10^{-3.86}</math> <b>OR</b> 1.4 x 10<sup>-4</sup> <b>OR</b> 1.38 x 10<sup>-4</sup> (mol dm<sup>-3</sup>) ✓ <i>separate marking point</i></p> <p><math>\frac{[HA]}{[A^-]} = \frac{[H^+]}{K_a}</math> <b>OR</b> <math>\frac{[A^-]}{[HA]} = \frac{K_a}{[H^+]}</math> ✓</p> <p><math>\frac{[HA]}{[A^-]} = \frac{2.8 \times 10^{-4}}{1.4 \times 10^{-4}}</math> <b>OR</b> <math>\frac{2}{1}</math> <b>OR</b> 2 <b>OR</b> <math>\frac{[A^-]}{[HA]} = \frac{0.5}{1}</math> <b>OR</b> 0.5 ✓</p> <p>This marking point subsumes previous marking point <b>ONLY</b></p> <p><b>Comment (1 mark)</b> Magic tang/taste could come from other chemicals/substances in the sweet <b>OR</b> The buffer would have the same taste/tang as the magic tang ✓</p>	6	<p><b>ANNOTATE WITH TICKS AND CROSSES, etc</b></p> <p><b>ALLOW</b> any lactate salt <b>ALLOW</b> lactic acid <b>AND</b> NaOH <b>OR</b> lactic acid <b>AND</b> OH<sup>-</sup></p> <p>-----</p> <p><b>FOR ALTERNATIVE</b> using Henderson–Hasselbalch equation, <b>SEE PAGE 11</b></p> <p>-----</p> <p>If another weak acid has been selected and salt has been selected, allow <b>ECF</b> for remainder of question <b>SEE PAGE 12</b></p> <p>-----</p> <p><b>ALLOW</b> 2.8 x 10<sup>-4</sup> up to calculator value of 2.81838 x 10<sup>-4</sup> <b>ALLOW</b> 0.00028, etc</p> <p><b>ALLOW</b> 1.4 x 10<sup>-4</sup> up to calculator value of 1.38038 x 10<sup>-4</sup> <b>ALLOW</b> 0.00014, etc</p> <p><b>ALLOW</b> use of CH<sub>3</sub>CHOHCOOH <b>AND</b> CH<sub>3</sub>CHOHCOO<sup>-</sup>(Na<sup>+</sup>) <b>ALLOW</b> use of acid <b>AND</b> salt</p> <p><b>ALLOW</b> value from <math>\frac{\text{calculated value of } [H^+]}{\text{calculated value of } K_a}</math></p> <p><b>ALLOW</b> 2SF up to calculator value of 2.041742129 correctly rounded but <b>ALLOW</b> 2 if 2.8 x 10<sup>-4</sup> and 1.4 x 10<sup>-4</sup> used <b>ALLOW</b> 2 mol dm<sup>-3</sup> HA <b>AND</b> 1 mol dm<sup>-3</sup> A<sup>-</sup> <b>OR</b> any concentration ratio of 2(acid) : 1(salt)</p> <p><b>ALLOW</b> 2SF up to calculator value of 0.489778819 correctly rounded but <b>ALLOW</b> 0.5 if 2.8 x 10<sup>-4</sup> and 1.4 x 10<sup>-4</sup> used</p>



Question	er	Mark	Guidance
	<p><b>ALTERNATIVE approach for concentrations</b> using Henderson–Hasselbalch equation (<b>4 marks</b>)</p> $\text{pH} = \text{p}K_{\text{a}} + \log \frac{[\text{A}^{-}]}{[\text{HA}]} \quad \text{OR} \quad -\log K_{\text{a}} + \log \frac{[\text{A}^{-}]}{[\text{HA}]} \quad \checkmark$ $\log \frac{[\text{A}^{-}]}{[\text{HA}]} = 3.55 - 3.86 \quad \checkmark \quad (\text{subsumes previous mark})$ $\log \frac{[\text{A}^{-}]}{[\text{HA}]} = -0.31 \quad \checkmark \quad (\text{subsumes previous mark})$ $\frac{[\text{A}^{-}]}{[\text{HA}]} = 10^{-0.31} = \frac{0.490}{1} \quad \text{OR} \quad 0.490 \quad \checkmark$		<p><b>ALLOW</b> use of <math>\text{CH}_3\text{CHOHCOOH}</math> <b>AND</b> <math>\text{CH}_3\text{CHOHCOO}^{-}(\text{Na}^{+})</math> <b>ALLOW</b> use of acid <b>AND</b> salt</p> <p><b>ALLOW</b> <math>\text{pH} = \text{p}K_{\text{a}} - \log \frac{[\text{HA}]}{[\text{A}^{-}]} \quad \text{OR} \quad -\log K_{\text{a}} - \log \frac{[\text{HA}]}{[\text{A}^{-}]}</math></p> <p><b>ALLOW</b> <math>\log \frac{[\text{HA}]}{[\text{A}^{-}]} = 3.86 - 3.55</math> (subsumes previous mark)</p> <p><b>ALLOW</b> <math>\log \frac{[\text{HA}]}{[\text{A}^{-}]} = 0.31</math> (subsumes previous mark)</p> <p><b>ALLOW</b> <math>\frac{[\text{HA}]}{[\text{A}^{-}]} = 10^{0.31} = \frac{2.04}{1} \quad \text{OR} \quad \frac{2}{1} \quad \text{OR} \quad 2</math></p> <p>For <math>\frac{[\text{A}^{-}]}{[\text{HA}]}</math>, <b>ALLOW</b> 2 SF up to calculator value of 0.48978819</p> <p>For <math>\frac{[\text{HA}]}{[\text{A}^{-}]}</math>, <b>ALLOW</b> 2 SF up to calculator value of 2.041737945 but <b>ALLOW</b> 2 if <math>10^{-0.31}</math> used</p>



Question	er	Mark	Guidance		
(e)	<b>SUMMARY OF 4(e) MARKING POINTS FOR EACH POSSIBLE ACID CHOSEN</b> <b>FIRST, CHECK THE ANSWER ON ANSWER LINE: IF</b> answer is correct for weak acid chosen, award MP2–MP5 <b>IF</b> there is an alternative answer, check to see if there is any <b>ECF</b> credit possible using working below				
		<b>lactic</b>	<b>yruvic</b>	<b>acetic</b>	<b>benzoic</b>
	pK <sub>a</sub>	3.86			4.19
	MP1	lactic <b>AND</b> lactate <b>OR</b> lactic acid <b>AND</b> OH <sup>-</sup>	No mark	No mark	No mark
	MP2: [H <sup>+</sup> ]	$10^{-3.55}$ <b>OR</b> $2.82 \times 10^{-4}$ ( <b>calc:</b> $2.81838 \times 10^{-4}$ )			
	MP3: K <sub>a</sub>	$10^{-3.86}$ <b>OR</b> $1.38 \times 10^{-4}$	$10^{-2.39}$ <b>OR</b> $4.07 \times 10^{-3}$	$10^{-4.76}$ <b>OR</b> $1.74 \times 10^{-5}$	$10^{-4.19}$ <b>OR</b> $6.46 \times 10^{-5}$
	<b>calc:</b>	$1.380384265 \times 10^{-4}$	$4.073802778 \times 10^{-3}$	$1.737800829 \times 10^{-5}$	$6.45654229 \times 10^{-5}$
	MP4: ratio expression	$\frac{[HA]}{[A^-]} = \frac{[H^+]}{K_a}$ <b>OR</b> $\frac{[A^-]}{[HA]} = \frac{K_a}{[H^+]}$			
	MP5: $\frac{[HA]}{[A^-]}$	$\frac{2.82 \times 10^{-4}}{1.38 \times 10^{-4}}$ <b>OR</b> 2.04	$\frac{2.82 \times 10^{-4}}{4.07 \times 10^{-3}}$ <b>OR</b> 0.0693	$\frac{2.82 \times 10^{-4}}{1.74 \times 10^{-5}}$ <b>OR</b> 16.2	$\frac{2.82 \times 10^{-4}}{6.46 \times 10^{-5}}$ <b>OR</b> 4.37
	<b>calc:</b>	2.041737945	<b>calc:</b> 0.069183097	<b>calc:</b> 16.21810097	<b>calc:</b> 4.365158322
<b>OR</b> $\frac{[A^-]}{[HA]}$	$\frac{1.38 \times 10^{-4}}{2.82 \times 10^{-4}}$ <b>OR</b> 0.489	$\frac{4.07 \times 10^{-3}}{2.82 \times 10^{-4}}$ <b>OR</b> 14.4	$\frac{1.74 \times 10^{-5}}{2.82 \times 10^{-4}}$ <b>OR</b> 0.0617	$\frac{6.46 \times 10^{-5}}{2.82 \times 10^{-4}}$ <b>OR</b> 0.229	
<b>calc:</b>	0.489778819		0.0616595	0.229086765	
<b>TAKE CARE:</b> Calc values are completely unrounded and may differ between brands of calculator Use <b>actual</b> candidate values at each stage using rounding to 2 or more SF. MP5: calculated using 3 SF from MP2 and MP3 calc values for MP5 are completely unrounded (using calculator values from MP2 and MP3) Be slightly flexible as candidates may have written down rounded values but carried on with calculator values – This appr ach is <b>ACCEPTABLE</b>					
<b>Total</b>		<b>20</b>			



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Question		Expected Answers	Marks	Additional Guidance
2	a	<p>measured pH &gt; 1 OR <math>[H^+] &lt; 0.1</math> (mol dm<sup>-3</sup>) ✓</p> <p><math>[H^+] = 10^{-pH}</math> ✓</p> <p><math>K_a = \frac{[H^+][CH_3CH_2COO^-]}{[CH_3CH_2COOH]}</math> OR <math>\frac{[H^+]^2}{[CH_3CH_2COOH]}</math> ✓</p> <p>Calculate <math>K_a</math> from <math>\frac{[H^+]^2}{0.100}</math> ✓</p>	4	<p><b>ALLOW</b> C<sub>2</sub>H<sub>5</sub> throughout question</p> <p><b>ALLOW</b> <math>[H^+] &lt; [CH_3CH_2COOH]</math> OR <math>[H^+] &lt; [HA]</math> <b>ALLOW</b> measured pH is higher than expected <b>ALLOW</b> measured pH is not as acidic as expected <b>ALLOW</b> a quoted pH value or range &gt; 1 and &lt; 7 OR between 1 and 7</p> <p><b>ALLOW</b> <math>[H^+] = \text{antilog } -pH</math> OR <math>[H^+] = \text{inverse log } -pH</math></p> <p><b>ALLOW</b> <math>\frac{[H^+][A^-]}{[HA]}</math> OR <math>\frac{[H^+]^2}{[HA]}</math></p> <p><b>IF</b> <math>K_a</math> is <b>NOT</b> given and <math>K_a = \frac{[H^+]^2}{0.100}</math> is shown, award mark for <math>K_a</math> also (i.e. <math>K_a = \frac{[H^+]^2}{0.100}</math> is automatically awarded the last 2 marks)</p>
	b	<p><b>Marks are for correctly calculated values.</b> <b>Working shows how values have been derived.</b></p> <p><math>[H^+] = 10^{-13.46} = 3.47 \times 10^{-14}</math> (mol dm<sup>-3</sup>) ✓</p> <p><math>[OH^-] = \frac{1.0 \times 10^{-14}}{3.47 \times 10^{-14}} = 0.29</math> (mol dm<sup>-3</sup>) ✓</p>	2	<p><b>ALLOW</b> <math>3.467368505 \times 10^{-14}</math> and correct rounding to <math>3.5 \times 10^{-14}</math></p> <p><b>ALLOW</b> 0.28840315 and correct rounding to 0.29, i.e. <b>ALLOW</b> 0.288</p> <p><b>ALLOW</b> alternative approach using pOH:</p> <p>pOH = 14 – 13.46 = 0.54 ✓ <math>[OH^-] = 10^{-0.54} = 0.29</math> (mol dm<sup>-3</sup>) ✓</p> <p>Correct answer gets <b>BOTH</b> marks</p>





Question	Expected Answers	Marks	Additional Guidance
c	<p>Propanoic acid reacts with sodium hydroxide forming propanoate ions/sodium propanoate <b>OR</b> <math>\text{CH}_3\text{CH}_2\text{COOH} + \text{NaOH} \rightarrow \text{CH}_3\text{CH}_2\text{COONa} + \text{H}_2\text{O}</math> ✓</p> <p>Some propanoic acid remains <b>OR</b> propanoic acid <b>AND</b> propanoate (ions) / sodium propanoate present ✓</p> <p>equilibrium: <math>\text{CH}_3\text{CH}_2\text{COOH} \rightleftharpoons \text{H}^+ + \text{CH}_3\text{CH}_2\text{COO}^-</math> ✓</p> <p><b>Added alkali</b> <math>\text{CH}_3\text{CH}_2\text{COOH}</math> reacts with added alkali <b>OR</b> <math>\text{CH}_3\text{CH}_2\text{COOH} + \text{OH}^- \rightarrow</math> <b>OR</b> added alkali reacts with <math>\text{H}^+</math> <b>OR</b> <math>\text{H}^+ + \text{OH}^- \rightarrow</math> ✓</p> <p><math>\rightarrow \text{CH}_3\text{CH}_2\text{COO}^-</math> <b>OR</b> Equilibrium <math>\rightarrow</math> right ✓</p> <p><b>Added acid</b> <math>\text{CH}_3\text{CH}_2\text{COO}^-</math> reacts with added acid <b>OR</b> <math>[\text{H}^+]</math> increases ✓</p> <p><math>\rightarrow \text{CH}_3\text{CH}_2\text{COOH}</math> <b>OR</b> Equilibrium <math>\rightarrow</math> left ✓</p>	7	<p><b>ANNOTATIONS MUST BE USED</b> <b>ALLOW</b> <math>\text{C}_2\text{H}_5</math> throughout question <b>ALLOW</b> Adding NaOH forms propanoate ions/sodium propanoate (implies that the NaOH is added to the propanoic acid)</p> <p><b>ALLOW:</b> weak acid <b>AND</b> its conjugate base/salt present</p> <p>Throughout, do not penalise comments that imply that pH is constant in presence of buffer</p> <p><b>DO NOT ALLOW</b> HA and <math>\text{A}^-</math> in this equilibrium expression</p> <p>For description of action of buffer below, <b>ALLOW</b> HA for <math>\text{CH}_3\text{CH}_2\text{COOH}</math>; <b>ALLOW</b> <math>\text{A}^-</math> for <math>\text{CH}_3\text{CH}_2\text{COO}^-</math></p> <p>Equilibrium responses must refer back to a written equilibrium. <b>IF</b> no equilibrium shown, use the equilibrium as written in expected answers (which is also written on page 6 of the paper)</p> <p><b>ALLOW</b> weak acid reacts with added alkali</p> <p><b>ALLOW</b> conjugate base reacts with added acid <b>DO NOT ALLOW</b> salt reacts with added acid</p>



Question	Expected Answers	Marks	Additional Guidance
d	$\text{HNO}_3 + \text{CH}_3\text{CH}_2\text{COOH} \rightleftharpoons \text{CH}_3\text{CH}_2\text{COOH}_2^+ + \text{NO}_3^- \checkmark$ acid 1      base 2                  acid 2                  base 1 $\checkmark$	2	State symbols <b>NOT</b> required <b>ALLOW</b> 1 <b>AND</b> 2 labels the other way around. <b>ALLOW</b> 'just acid' and 'base' labels throughout if linked by lines so that it is clear what the acid–base pairs are.  <b>IF</b> proton transfer is wrong way around then <b>ALLOW</b> 2nd mark for idea of acid–base pairs, i.e. $\text{HNO}_3 + \text{CH}_3\text{CH}_2\text{COOH} \rightleftharpoons \text{CH}_3\text{CH}_2\text{COO}^- + \text{H}_2\text{NO}_3^+ \times$ base 2      acid 1                  base 1      acid 2 $\checkmark$
e i	$2\text{CH}_3\text{CH}_2\text{COOH} + \text{Mg} \rightarrow (\text{CH}_3\text{CH}_2\text{COO})_2\text{Mg} + \text{H}_2 \checkmark$	1	<b>IGNORE</b> state symbols <b>ALLOW</b> ionic equation: $2\text{H}^+ + \text{Mg} \rightarrow \text{Mg}^{2+} + \text{H}_2$  <b>IGNORE</b> any random charges in formula of $(\text{CH}_3\text{CH}_2\text{COO})_2\text{Mg}$ as long as the charges are <b>correct (charges are treated as working)</b> i.e. $(\text{CH}_3\text{COO}^-)_2\text{Mg}$ <b>OR</b> $(\text{CH}_3\text{COO})_2^- \text{Mg}$ should <b>not</b> be penalised However, $\text{Mg}^{2+}$ instead of Mg on the left side of equation is obviously wrong
ii	$2\text{H}^+ + \text{CO}_3^{2-} \rightarrow \text{H}_2\text{O} + \text{CO}_2$ <b>OR</b> $2\text{H}^+ + \text{CO}_3^{2-} \rightarrow \text{H}_2\text{CO}_3$ <b>OR</b> $\text{H}^+ + \text{CO}_3^{2-} \rightarrow \text{HCO}_3^- \checkmark$	1	State symbols <b>NOT</b> required
<b>Total</b>		<b>17</b>	



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Question	Expected answers	Marks	Additional guidance
3 a	A strong acid completely dissociates <b>AND</b> a weak acid partially dissociates ✓	1	<b>ALLOW</b> ionises for dissociates
	ii $(K_a =) \frac{[H^+][NO_2^-]}{[HNO_2]} \checkmark$	1	<b>DO NOT ALLOW</b> $\frac{[H^+]^2}{[HNO_2]}$ Square brackets <b>are required</b>
	iii <b>FIRST, CHECK THE ANSWER ON ANSWER LINE</b> <b>IF answer = 1.89 award 2 marks</b> <b>IF answer = 1.9 award 1 mark</b> -----  pH = $-\log 0.0129 = 1.89 \checkmark\checkmark$ <b>OR</b> pH = $-\log 0.0129 = 1.9 \checkmark$ <i>not two decimal places</i>	2	<b>IF</b> there is an alternative answer to more decimal places, check calculator value ----- <b>Working to get to 0.0129 (mol dm<sup>-3</sup>)</b> <b>Not required and no credit</b> $[H^+] = \sqrt{K_a \times [HNO_2]} = \sqrt{4.43 \times 10^{-4} \times 0.375}$  <b>ALLOW 1 mark</b> for an answer with more than 2 decimal places that rounds back to 1.89
	iv $HNO_3 + HNO_2 \rightleftharpoons NO_3^- + H_2NO_2^+$ Acid 1      Base 2      Base 1      Acid 2 ✓	2	State symbols <b>NOT</b> required  <b>ALLOW 1 AND 2</b> labels the other way around. <b>ALLOW</b> 'just acid' and 'base' labels if linked by lines so that it is clear what the acid–base pairs are  <b>IF</b> proton transfer is wrong way around <b>ALLOW</b> 2nd mark for idea of acid–base pairs, <i>i.e.</i> $HNO_3 + HNO_2 \rightleftharpoons H_2NO_3^+ + NO_2^- \times$ Base 2      Acid 1      Acid 2      Base 1 ✓  <b>NOTE</b> For the 2nd marking point (acid–base pairs), this is the <b>ONLY</b> acceptable <b>ECF</b>



Question	Expected answers	Marks	Additional guidance
			<i>i.e., NO ECF from impossible chemistry</i>
<b>b</b>	Proton acceptor ✓	<b>1</b>	<b>ALLOW</b> H <sup>+</sup> acceptor
<b>ii</b>	<p><b>Marks are for correctly calculated values. Working shows how values have been derived.</b></p> <p><math>[\text{OH}^-] = 2 \times 0.04(00) = 0.08(00) \text{ (mol dm}^{-3}\text{)} \checkmark</math></p> <p><math>[\text{H}^+] = \frac{1.00 \times 10^{-14}}{0.08(00)} \text{ OR } 1.25 \times 10^{-13} \text{ (mol dm}^{-3}\text{)} \checkmark</math></p> <p><math>\text{pH} = -\log 1.25 \times 10^{-13} = \mathbf{12.90} \checkmark</math></p> <p>-----</p> <p><b>pOH variation (also worth 3 marks)</b></p> <p><math>[\text{OH}^-] = 2 \times 0.04(00) = 0.08(00) \text{ (mol dm}^{-3}\text{)} \checkmark</math></p> <p><math>\text{pOH} -\log 0.08(00) = 1.10 \checkmark</math></p> <p><math>\text{pH} = 14.00 - 1.10 = 12.90 \checkmark</math></p>	<b>3</b>	<p><b>ALLOW</b> by ECF <math>\frac{1.00 \times 10^{-14}}{\text{calculated value of } [\text{OH}^-]}</math></p> <p><b>DO NOT ALLOW</b> 12.9 <i>not two decimal places</i></p> <p>-----</p> <p><b>COMMON ERRORS</b></p> <p>12.60 ✓✓ <i>no × 2 for [OH<sup>-</sup>]</i></p> <p>12.6 ✓ <i>no × 2 for [OH<sup>-</sup>] AND 1 DP only</i></p> <p>12.30 ✓✓ <i>÷ 2 [OH<sup>-</sup>]</i></p> <p>12.3 ✓ <i>÷ 2 [OH<sup>-</sup>] AND 1 DP only</i></p> <p>1.40 <b>NO</b> marks</p>
<b>c</b>	<p><math>\text{Ca(OH)}_2 + 2\text{HNO}_2 \rightarrow \text{Ca(NO}_2)_2 + 2\text{H}_2\text{O} \checkmark</math></p> <p><math>\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} \checkmark</math></p>	<b>2</b>	<b>ALLOW:</b> $2\text{H}^+ + 2\text{OH}^- \rightarrow 2\text{H}_2\text{O}$



Question	Expected answers	Marks	Additional guidance
d	<p><b>Equilibrium</b> <math>\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \checkmark</math></p>		<p><b>ANNOTATIONS MUST BE USED</b> <b>Equilibrium sign is required</b> <b>IGNORE</b> <math>\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-</math> <b>DO NOT ALLOW</b> <math>\text{H}_2\text{CO}_3 \rightleftharpoons 2\text{H}^+ + \text{CO}_3^{2-}</math> <b>DO NOT ALLOW</b> <math>\text{NaHCO}_3 \rightleftharpoons \text{Na}^+ + \text{HCO}_3^-</math> <b>IGNORE</b> <math>\text{H}_2\text{O} + \text{CO}_2 \rightleftharpoons \text{H}_2\text{CO}_3</math></p>
	<p><b>Action of buffer</b></p> <p><b>Added alkali</b> <math>\text{H}_2\text{CO}_3</math> reacts with added alkali <b>OR</b> <math>\text{H}_2\text{CO}_3 + \text{OH}^- \rightarrow</math> <b>OR</b> added alkali reacts with <math>\text{H}^+</math> <b>OR</b> <math>\text{H}^+ + \text{OH}^- \rightarrow \checkmark</math></p> <p>Equilibrium <math>\rightarrow</math> right <b>OR</b> equilibrium shifts forming <math>\text{H}^+</math> <b>OR</b> <math>\text{HCO}_3^- \checkmark</math></p>		<p><b>IF</b> <math>\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-</math> <b>OR</b> <math>\text{H}_2\text{CO}_3 \rightleftharpoons 2\text{H}^+ + \text{CO}_3^{2-}</math> have been used above: <b>ALLOW</b> all marks that meet marking alternatives as written <b>NOTE</b> The 1st 'added acid' mark <b>cannot</b> then be accessed</p> <p>Equilibrium responses <b>must</b> refer back to a written equilibrium <b>BUT IF</b> <math>\text{H}_2\text{CO}_3 \rightarrow \text{H}^+ + \text{HCO}_3^-</math> shown above, assume that any equilibrium comments apply to the correct equilibrium</p> <p><b>IF</b> more than one equilibrium shown, it <b>must</b> be clear which equilibrium is being referred to</p> <p><b>ALLOW</b> added alkali reacts with weak acid</p> <p><b>Quality of Written Communication</b> Mark is for linking the action of the buffer in controlling added alkali and hence pH</p>



Question	Expected answers	Marks	Additional guidance
	<p><b>Added acid</b>  <math>\text{HCO}_3^-</math> reacts with added acid ✓</p> <p>Equilibrium → left  <b>OR</b> equilibrium shifts forming <math>\text{H}_2\text{CO}_3</math> ✓</p>	5	<p><math>\text{HCO}_3^-</math> is <b>required</b> for this mark <b>BUT</b> ...  <b>ALLOW</b> added acid reacts with conjugate base <b>ONLY</b> if <math>\text{HCO}_3^-</math> is present in equilibrium with <math>\text{H}_2\text{CO}_3</math>  <b>DO NOT ALLOW</b> salt reacts with added acid</p>
d ii	<p><b>FIRST, CHECK THE ANSWER ON ANSWER LINE</b>  <b>IF answer = 6.6 : 1 OR 1 : 0.15</b>  <b>CHECK</b> ratio is <math>\text{HCO}_3^- : \text{H}_2\text{CO}_3</math> and award <b>5 marks</b>.  <b>IF answer = 0.15 : 1</b> ,  <b>CHECK</b> ratio is <math>\text{H}_2\text{CO}_3 : \text{HCO}_3^-</math> and award <b>4 marks</b></p> <p>-----</p> <p>In blood at pH 7.40,  <math>[\text{H}^+] = 10^{-\text{pH}} = 10^{-7.40} = 3.98 \times 10^{-8} \text{ (mol dm}^{-3}\text{)} \checkmark</math>  <math display="block">K_a = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = \frac{3.98 \times 10^{-8} \times 10.5}{1}</math> <b>OR</b> <math>K_a = 4.18 \times 10^{-7} \text{ (mol dm}^{-3}\text{)} \checkmark</math></p> <p>In blood at pH 7.20,  <math>[\text{H}^+] = 10^{-\text{pH}} = 10^{-7.20} = 6.31 \times 10^{-8} \text{ (mol dm}^{-3}\text{)} \checkmark</math>  <math display="block">\frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = \frac{K_a}{[\text{H}^+]} \text{ OR } \frac{4.18 \times 10^{-7}}{6.31 \times 10^{-8}} \checkmark</math> <math display="block">= \frac{6.6}{1} \text{ OR } 6.6 : 1 \checkmark \text{ (up to calc. value, see below)}</math> <b>ALLOW</b> any answer with &gt; 1 decimal place that rounds back to 6.62 <b>OR</b> 6.63</p>	5	<p><b>IF</b> there is an alternative answer, check to see if there is any <b>ECF</b> credit possible using working below</p> <p>-----</p> <p><b>ANNOTATIONS MUST BE USED</b>  <b>FOR ALTERNATIVE</b> using Henderson–Hasselbalch equation below</p> <p>-----</p> <p><b>ALLOW</b> <math>3.98 \times 10^{-8}</math> up to calculator value of <math>3.981071706 \times 10^{-8}</math> correctly rounded</p> <p><b>ALLOW</b> <math>6.31 \times 10^{-8}</math> up to calculator value of <math>6.309573445 \times 10^{-8}</math> correctly rounded</p> <p>-----</p> <p><b>Common errors</b>  0.15 : 1 ✓✓✓✓ <i>Inverse ratio of <math>\text{H}_2\text{CO}_3 : \text{HCO}_3^-</math></i>  16.6 : 1 <b>OR</b> 0.06 : 1 ✓✓✓✓ <i>10.5/1 swapped over in 2nd mark giving <math>K_a</math> value of <math>3.79 \times 10^{-9}</math></i></p> <p><b>ALLOW</b> answer with &gt; 1 decimal place that rounds back to 16.64 <b>OR</b> 16.65</p>
	<p><b>ALTERNATIVE approach for concentrations</b> using Henderson–Hasselbalch equation (<b>5 marks</b>)</p> <p><math>\text{pH} = \text{p}K_a + \log \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \text{ OR } -\log K_a + \log \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \checkmark</math></p> <p><math>\text{p}K_a = \text{pH} - \log \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 7.40 - \log \frac{10.5}{1} = 6.38 \checkmark</math> (subsumes previous mark) Calculator: 6.378810701</p>		



Question	Expected answers	Marks	Additional guidance
	At pH = 7.20, $\log \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = \text{pH} - \text{p}K_a = 7.20 - 6.38 = 0.82 \checkmark$ (subsumes previous mark) $\frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 10^{0.82} \checkmark = \frac{6.6}{1}$ OR 6.6 : 1 $\checkmark$		
	<b>Total</b>	<b>22</b>	