A-Level Chemistry

Buffers

Mark Scheme

Time available: 68 minutes
Marks available: 65 marks

Mark schemes

1. (a) $[H^+] = (10^{-3.87} =)\ 1.3489 \times 10^{-4}$

Allow 1.35×10^{-4}. If M1 wrong can only score M2. **1**

$$[CH_3COOH] = \frac{[H^+][CH_3COO^-]}{[Ka]} = \left(\frac{[1.3489 \times 10^{-4}][0.136]}{[1.74 \times 10^{-5}]} = 1.05436\right)$$

Mark is for correctly rearranged equation. **1**

1.05 – 1.06 (mol dm^{-3})

3 sf or more **1**

(b) **If 0.007 moles in 500 cm^3 seen follow Mark Scheme 1**

Mark Scheme 1

moles ethanoic acid = 0.130 **1**

moles sodium ethanoate = 0.0605 **1**

mol CH_3COOH after addition = (0.130 - 0.007) = 0.123 **1**

mol CH_3COO^- after addition = (0.0605+0.007) = 0.0675 **1**

$$[H^+] = \left(\frac{[Ka][CH_3COOH]}{[CH_3COO^-]}\right) = \frac{[1.74 \times 10^{-5}][0.123]}{[0.0675]} \left(= 3.171 \times 10^{-5}\right)$$ **1**

pH = <u>4.50</u> (must be 2dp) **1**

Method 1
For M3 allow M1 – 0.007
For M4 allow M2 + 0.007

If 0.014 moles in 1 dm^3 follow Mark Scheme 2

Mark Scheme 2

moles CH_3COOH after addition = (0.260 - 0.014) = 0.246 (This scores 2 marks)
moles CH_3COO^- after addition = (0.121 + 0.014) = 0.135 (This scores 2 marks)

$$[H^+] = \left(\frac{[Ka][CH_3COOH]}{[CH_3COO^-]}\right) = \frac{[1.74 \times 10^{-5}][0.246]}{[0.135]}$$

pH = <u>4.50</u> (must be 2dp)

Method 1 and 2
M5 = expression with their numbers
M6 = answer to 2 dp

pH = 4.50 scores 6 marks

If √ used in K_a expression, stop at M4
If divide by 2 after M5, lose M6

Allow solutions which use Henderson-Hasselbach Equation

[9]

2.

(a) $[H^+] = \frac{K_a \times [CH_3COOH]}{CH_3COO^-}$ or = $1.74 \times 10^{-5} \times \frac{0.186}{0.105}$

Allow ( )

M1 **1**

= 3.08×10^{-5}

If [HX] / [X^-] or $\frac{0.186}{0.105}$ upside down, or any addition or subtraction lose M1 & M2.

M2 **1**

pH = 4.51 (correct answer scores 3)

Can score M3 for correct pH conseq to their [H^+], so pH = 5.01 scores one
Must be to 2 dp

M3 **1**

Alternative using Henderson−Hasselbach Equation

pH = pKa − log[HX] / X⁻] = −log(1.74 × 10^{-5}) − log($\frac{0.186}{0.105}$)

Allow ( )

M1

pKa = 4.76 − 0.248

If [HX] / [X⁻] or $\frac{0.186}{0.105}$ upside down, can only score 1

M2

pH = = 4.51

so pH = 5.01

Must be to 2 dp

M3

(b) mol HX after addition (= 0.251 + 0.015) = 0.266

For HX, if no addition or error in addition (other than AE) (or subsequent extra add or sub) MAX 3

M1

1

mol X^- after subtraction (= 0.140 − 0.015) = 0.125

For X^- if no subtraction or error in subtraction (other than AE) (or subsequent extra add or sub) MAX 3

M2

1

$[H^+] = \left(\frac{K_a \times [CH_3COOH]}{CH_3COO^-} \right) = \frac{1.74 \times 10^{-5} \times 0.266}{0.125}$

If errors above in both addition AND subtraction can only score M3 for insertion of their numbers in rearranged expression. One exception, if addition and subtraction reversed then pH =4.58 scores 2

M3

1

$[H^+] = 3.703 \times 10^{-5}$ (mol dm^{-3})

If [HX] / [X^-] upside down, lose M3 & M4 (or next two marks) but can score M5 for correct pH conseq to their [H^+], so if M1 & M2 correct, pH = 5.09 scores 3.

M4

1

pH = 4.43

Correct use of HX and X^- values from (d) gives
pH= 4.41 and scores 4

If wrong method, e.g. √ or no use of rearranged K_a expression, may score M1 & M2 but no more.

Allow more but not fewer than 2dp here.

M5

1

Alternative using Henderson−Hasselbach Equation

mol acid after addition = 0.251 + 0.015 = 0.266

For HX, if no addition or error in addition (other than AE) (or subsequent extra add or sub) MAX 3

M1

mol salt after addition = 0.140 − 0.015 = 0.125

For X^- if no subtraction or error in subtraction (other than AE) (or subsequent extra add or sub) MAX 3

M2

pH = (pKa − log[HX] / [X^-]) = −log(1.74 × 10^{-5}) − log(0.266 / 0.125)

If errors above in both addition AND subtraction can only score M3 for insertion of their numbers − except if addition and subtraction reversed then pH = 4.58 scores 2

M3

pH = 4.76 − 0.328

M4

pH = = 4.43

If [HX] / [X^-] upside down, lose M3 & M4 (or next two marks) but can score M5 for correct pH conseq to their working, so if M1 & M2 correct, pH = 5.09 scores 3.

Allow more but not fewer than 2dp here.

M5

[8]

3. (a) (only) slightly or partially dissociated / ionised

Ignore 'not fully dissociated'.

Allow low tendency to dissociate or to lose / donate a proton.

Allow shown equilibrium well to the left.

Otherwise ignore equations.

1

(b) $2CH_3CH_2COOH + Na_2CO_3 \longrightarrow 2CH_3CH_2COONa + H_2O + CO_2$

OR

$2CH_3CH_2COOH + CO_3^{2-} \longrightarrow 2CH_3CH_2COO^- + H_2O + CO_2$

OR

$CH_3CH_2COOH + Na_2CO_3 \longrightarrow CH_3CH_2COONa + NaHCO_3$

OR

$CH_3CH_2COOH + CO_3^{2-} \longrightarrow CH_3CH_2COO^- + HCO_3^-$

Must be propanoic acid, allow C_2H_5COOH.

Not molecular formulae.

Allow multiples.

Ignore reversible sign.

Not H_2CO_3.

1

(c) $[OH^-] = 2 \times 0.0120 = 0.0240$ M1

Correct answer for pH with or without working scores 3.

1

$[H^+] = \frac{1 \times 10^{-14}}{0.0240} = 4.166 \times 10^{-13}$ ***OR*** pOH = 1.62 M2

If × 2 missed or used wrongly can only score M3 for correct calculation of pH from their $[H^+]$.

1

pH = 12.<u>38</u> M3

Lose M3 if not 2 decimal places: 12.4 scores 2.

12.08 scores 1 (missing × 2) ; 12.1 scores 0.

11.78 scores 1 (dividing by 2) 11.8 scores 0.

1

(d) (i) $K_a = \frac{[H^+][C_6H_5COO^-]}{[C_6H_5COOH]}$

Ignore ( ) here but brackets must be present.

Must be correct acid and salt.

If wrong, mark part (ii) independently.

1

(ii) M1 $K^a = \frac{[H^+]^2}{[C_6H_5COOH]}$ **OR** with numbers

Correct answer for pH with or without working scores 3.

Allow HX, HA and ignore ( ) here.

May score M1 in part (i).

1

M2 $[H^+] = \sqrt{(6.31 \times 10^{-5} \times 0.0120)}$ or $\sqrt{(K_a \times [C_6H_5COOH])}$

$(= \sqrt{(7.572 \times 10^{-7}} = 8.70 \times 10^{\times 4})$

pH = 6.12 may score 2 if correct working shown and they show the square root but fail to take it.

But if no working shown or wrong $K^a = \frac{[H^+]}{[C_6H_5COOH]}$

used which also leads to 6.12, then zero scored.

1

M3 pH = 3.<u>06</u>

Must be 2 decimal places ie 3.1 loses M3.

1

(iii) M1 $[H^+] = 10^{-4.00} = 1.00 \times 10^{-4}$

Correct answer for mass with or without working scores 5.

Allow 1×10^{-4}.

1

M2 $[X^-] = \frac{Ka \ x \ [HX]}{[H^+]}$

Ignore ( ) here.

If [HX] / [X⁻] upside down, can score M1 plus M4 for 5.26×10^{-7}.

1

M3 $= \frac{6.31 \times 10^{-5} \ x \ 0.0120}{1.00 \times 10^{-4}}$

And M5 for 7.57×10^{-5} *g.*

1

M4 $= 7.572 \times 10^{-3}$

1

M5 Mass (C_6H_5COONa) = $7.572 \times 10^{-3} \times 144$ =1.09 g
or 1.1 g

Wrong method, eg using $[H^+]^2$ may only score M1 and M5 for correct multiplication of their M4 by 144

(provided not of obviously wrong substance).

1

(e) M1 CO_2

Allow NO_x and SO_2.

1

M2 pH (It) falls / decreases

If M1 wrong, no further marks.

1

M3 mark M2 & M3 independently

acidic (gas)

OR reacts with alkali(ne solution) / OH^-

OR $CO_2 + 2OH^- \longrightarrow CO_3^{2-} + H_2O$

OR $CO_2 + OH^- \longrightarrow HCO_3^-$

Not forms H_2CO_3 H_2SO_3 H_2SO_4 etc OR H^+ ions.

1

[17]

4. (a) (i) $[H^+][OH^-]$ ***OR*** $[H_3O^+][OH^-]$

Ignore (aq)

Must have [ ] not ( )

1

(ii) $\sqrt{3.46 \times 10^{-14}}$ ($= 1.86 \times 10^{-7}$)

If no square root, CE=0

1

pH = 6.73

Must be 2dp

1

(iii) $[H^+] = 10^{-11.36}$ ($= 4.365 \times 10^{-12}$ OR 4.37×10^{-12})

Mark for working

1

$Kw = [4.365 \times 10^{-12}$ ***OR*** $4.37 \times 10^{-12} \times 0.047] = 2.05 \times 10^{-13}$

Allow $2.05 \times 10^{-13} - 2.1 \times 10^{-13}$

Mark for answer

Ignore units

1

(b) (i) $HCOOH \rightleftharpoons HCOO^- + H^+$

Must have $\rightleftharpoons$ but ignore brackets.

OR $HCOOH + H_2O \rightleftharpoons HCOO^- + H_3O^+$

Allow HCO_2^- or $CHOO^-$ ie minus must be on oxygen, so penalise $COOH^-$

1

(ii) $K_a = \frac{[H^+][HCOO^-]}{HCOOH}$ ***OR*** $\frac{[H_3O^+][HCOO^-]}{HCOOH}$

Must have all brackets but allow ( )

Must be HCOOH etc.

Allow ecf in formulae from (b)(i)

1

(iii) M1

$K_a = \frac{[H^+]^2}{[HCOOH]}$ $\left([H^+]^2 = 1.78 \times 10^{-4} \times 0.056 = 9.97 \times 10^{-6}\right)$

Allow HA or HX etc.

Allow $[H^+] = \sqrt{(Ka \times [HA])}$ for M1

1

M2 $[H^+] = 3.16 \times 10^{-3}$

Mark for answer

1

M3 pH = 2.50 allow more than 2 dp but not fewer

Allow correct pH from their wrong *$[H^+]$* ***here only*** *If square root shown but not taken, pH = 5.00 can score max 2 for M1 and M3*

1

(iv) M1 Decrease **Mark M1 independently**

1

M2 Eqm shifts / moves to RHS ***OR*** more H^+ ***OR*** K_a increases ***OR*** more dissociation

1

M3 To reduce temperature or oppose increase / change in temperature

Only award M3 following correct M2

1

(c) (i) M1 $[H^+] = \frac{Ka \times [HX]}{[X^-]}$ ***OR*** $pH = pK_a - \log \frac{[HX]}{[X^-]}$

If $[HX]/[X^-]$ upside down, no marks

1

M2 $\frac{1.78 \times 10^{-4} \times 2.35 \times 10^{-2}}{1.84 \times 10^{-2}}$ ***OR*** $pH = 3.75 - \log \frac{2.35 \times 10^{-2}}{1.84 \times 10^{-2}}$

(= 2.27×10^{-4})

1

M3 pH = 3.64 allow more than 2 dp but not fewer

pH calc NOT allowed from their wrong $[H^+]$ here

1

(ii) M1 Mol H^+ added = 5.00×10^{-4}

Mark on from AE in moles of HCl (eg 5×10^{-3} gives pH = 3.42 scores 3)

1

M2 Mol HCOOH = 2.40×10^{-2} **and** Mol $HCOO^-$ = 1.79×10^{-2}

If either wrong no further marks except AE (−1) OR if ECF in mol acid and / or mol salt from (c)(i), can score all 4

1

M3 $[H^+] \left(= \frac{Ka \times [XH]}{[X^-]}\right) = \frac{1.78 \times 10^{-4} \times 2.40 \times 10^{-2}}{1.79 \times 10^{-2}}$ (= 2.39×10^{-4})

If $[HX]/[X^-]$ upside down here after correct expression in (c)(i), no further marks

OR $pH = 3.75 - \log \frac{2.40 \times 10^{-2}}{1.79 \times 10^{-2}}$

If $[HX]/[X^-]$ upside down here and is repeat error from (c)(i), max 3 (pH = 3.88 after 3.86 in (c)(i))

1

M4 pH = 3.62 allow more than 2 dp but not fewer

pH calc NOT allowed from their wrong $[H^+]$ here

1

[20]

5. (a) (i) addition of small amounts of acid send eqm to left or extra H^+ removed by reaction with HCO_3^- **1**

ratio $[H_2CO_3]/[HCO_3^-]$ remains constant hence $[H^+]$ and pH remain const **1**

(ii) pH = 7.41 ∴ $[H^+] = 3.89 \times 10^{-8}$ mol dm^{-3} **1**

$$K_a = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$$ **1**

$$= \frac{(3.89 \times 10^{-8})(2.5 \times 10^{-2})}{1.25 \times 10^{-2}} = 7.78 \times 10^{-8} \text{ mol dm}^{-3}$$

allow error carried forward mark. Do not penalise twice. **1**

(b) (i) moles H^+ added = $10 \times 10^{-3} \times 1.0 = 0.01$ **1**

(ii) moles ethanoic acid after addition = 0.15 + 0.01 = 0.16 **1**

moles ethanoate ions after addition = 0.10 – 0.01 = 0.09 **1**

(iii) $$[H^+] = \frac{K_a[CH_3COOH]}{[CH_3COO^-]}$$ **1**

$$= 1.74 \times 10^{-5} \times \frac{0.16/V}{0.09/V}$$ **1**

pH = 4.51 **1**

[11]