AQA A-LEVEL CHEMISTRY · 7405

CHEMISTRY



MARK SCHEME

3.1.12 ACIDS AND BASES

SCORE	PERCENTAGE
/1449	%

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Q1.

(a) Proton donor

1

(b) Completely ionises to give H^+ ions in water

1

(c) 0.058 mol dm^{-3}

1

1.24

1

(d) Amount of NaOH = 5.25×10^{-3}

1

Since 1:1 reaction amount of OH− ions in excess

= $5.25 \times 10^{-3} - 1.45 \times 10^{-3}$ mol

= 3.80×10^{-3} moles OH^-

1

$[OH^-] = 3.80 \times 10^{-3} \times 1000/60 = 0.0633$

1

$K_w = [H^+][OH^-$ so $H^+ = \frac{10^{-14}}{0.0633} = 1.58 \times 10^{-13}$

1

pH = 12.80

1

(e) Amount of OH^- added 1.5 / 40 = 0.0375 mol

1

Use of 1:1 ratio to calculate amount of A^- formed = 0.0375 mol

1

Amount of weak acid initially = 1 × 0.15 = 0.150 mol so amount of weak acid after addition of NaOH = 0.150 − 0.0375 = 0.1125

If M3 incorrect can only score max of 3 marks

1

$[H^+] = K_a [HA]/[A^-]$ or $[H^+] = 1.79 \times 10^{-5} \times 0.1125/0.0375$

1

$= 5.37 \times 10^{-5}$

1

pH = 4.27

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1

[15]

Q2.

(a) $CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$
OR

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

Must show $\rightleftharpoons$
Allow CH_3CO_2H, $CH_3CO_2^-$
Ignore state symbols

1

(b) ($CH_3COOH + \underline{HNO_3} \longrightarrow CH_3COOH_2^+ + NO_3^-$)

IGNORE $\rightleftharpoons$
Allow CH_3CO_2H, $CH_3CO_2H_2^+$, $CH_3C^+(OH)_2$

1

(c) (i) (new $[HNO_3] = [H^+] = \frac{100}{150} \times 0.0125$)

M1 $[H^+] = 8.3(3) \times 10^{-3}$ (mol dm^{-3})
OR

new$[HNO_3]$ = $\frac{\text{mol } HNO_3}{\text{total vol}} = \frac{1.25 \times 10^{-3}}{150 \times 10^{-3}}$

1

M2 pH = − log M1 OR 2.08
Must be 2dp
Allow correct pH conseq to their $[H^+]$ *concentration*

1

(ii) M1 mol NaOH (= $50 \times 10^{-3} \times 0.0108$) = 5.40×10^{-4}

1

M2 Subtraction of M1 from moles of HNO_3 (1.25×10^{-3} or conseq from 1c(i))

Excess mol $H^+ = 7.10 \times 10^{-4}$

M2 allow ecf for subtraction of mol
If no subtraction, no further marks

1

M3 $[H^+] = \frac{M2}{150 \times 10^{-3}}$ OR $\frac{7.10 \times 10^{-4}}{150 \times 10^{-3}} = 4.73 \times 10^{-3}$

M3 <u>if no use of volume, no further marks</u> (pH=3.15)
If incorrect volume used, can score M4

1

M4 pH = -log M3 OR 2.32

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M4 Allow 2.33 Must be 2 dp

1

(d) (i) M1 $K_a = \dfrac{[H^+][CH_3COO^-]}{[CH_3COOH]}$

Penalise ( ) once here Not [H+][A-] / [HA]

If K_a expression wrong – Allow correct pH conseq to their $[H^+]$ concentration M4 only

1

M2 $K_a = \dfrac{[H^+]^2}{[CH_3COOH]}$ or with numbers or with HA

1

M3 $[H^+] = [\sqrt{(1.74 \times 10^{-5} \times 0.0125)}] = 4.66 \times 10^{-4}$

Mark for answer

1

M4 pH = 3.33

Must be 2dp

Allow correct pH conseq to their $[H^+]$ concentration

(pH = 3.83 can score M1, M2 and M4)

1

(ii) Sodium ethanoate

Ignore formula

Allow sodium acetate

1

(iii) M1 $[H^+] = 1.45 \times 10^{-5}$

Accept 1.445×10^{-5} or 1.4×10^{-5}

1

M2

$$\frac{[salt]}{[acid]} \text{ (OR } \frac{[CH_3COO^-]}{[CH_3COOH]} = \frac{Ka}{[H^+]} \text{)= } \frac{1.74 \times 10^{-5}}{1.45 \times 10^{-5}}$$

If M1 incorrect CE=0

Inclusion of 0.0125 in calculation can only score M1

1

M3 1.2(0)

Ignore units

1.4×10^{-5} gives 1.24

1

(e) M1 (Electronegative) chlorine withdraws electrons

Allow Cl has negative inductive effect

1

M2 Stabilises/reduces charge on COO-

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OR weakens O-H bond

OR makes O-H more polar

Ignore chloroethanoic acid dissociates more readily

Mark independently

1

(f) M1 Strong acids (almost) completely dissociated/ionised

OR not an equilibrium

OR equilibrium lies far to the right

Cannot have K_a value for a reaction not in equilibrium scores both marks

1

M2 K_a value for strong acids tends to infinity/is very large
OR can't divide by zero in K_a

1

[20]

Q3.

(a) Proton donor or H^+ donor

Allow donator

1

(b) (i) B B

Both need to be correct to score the mark

1

(ii) A A

Both need to be correct to score the mark

1

(iii) B A

Both need to be correct to score the mark

1

(c) **M1** $[H^+] = 10^{-1.25}$ OR 0.05623

1

M2 mol HCl = $(25 \times 10^{-3}) \times 0.0850$ $(= 2.125 \times 10^{-3})$

Mark for Working

1

M3 vol $\left(= \frac{2.125 \times 10^{-3}}{0.05623}\right)$ = 0.0378 dm^3 or 37.8 cm^3

allow 0.0375 – 0.038 dm^3 or 37.5 – 38 cm^3

Units and answer tied

Lose M3 if total given as (25 + 37.8) = 62.8 cm^3

Ignore "vol added = 12.8 cm^3 " after correct answer

1

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(d) (i) 4.52

Must be 2dp

1

(ii) $K_a = \frac{[H^+][H^-]}{[HX]}$ ignore = $\frac{[H^+]^2}{[HX]}$ but this may score M1 in (d)(iii)

Must have all brackets but allow ( ) Allow HA etc

***NO** mark for 10^{-pKa}*

1

(iii) **M1** $K_a = \frac{[H^+]^2}{[HX]}$ or with numbers

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

1

M2 $[H^+] = (\sqrt{(3.01 \times 10^{-5} \times 0.174)} = \sqrt{(5.24 \times 10^{-6})})$
$= 2.29 \times 10^{-3}$ - 2.3×10^{-3}

Mark for <u>answer</u>

1

M3 pH = 2.64 (allow more than 2dp but not fewer)

Allow 1 for correct pH from their wrong $[H^+]$

If square root forgotten, pH = 5.28 scores 2 for M1 and M3

1

(e) **M1** mol OH^- = $(10.0 \times 10^{-3}) \times 0.125 = 1.25 \times 10^{-3}$

Mark for answer

1

M2 orig mol HX = $(15.0 \times 10^{-3}) \times 0.174 = 2.61 \times 10^{\times 3}$

Mark for answer

1

M3 mol HX in buffer = orig mol HX – mol OH^-

Mark for answer

$= 2.61 \times 10^{-3} - 1.25 \times 10^{-3} = 1.36 \times 10^{-3}$

Allow conseq on their (M2 – M1)

($[HX] = 1.36 \times 10^{-3}/25 \times 10^{-3} = 0.0544$)

If no subtraction, max 3 for M1, M2 & M4 (pH = 4.20)

If $[H^+] = [X^-]$ & √used, max 3 for M1, M2 & M3 (pH = 2.89)

1

M4 mol X^- in buffer = mol OH^- = 1.25×10^{-3}

($[X^-] = 1.25 \times 10^{-3}/25 \times 10^{-3} = 0.05$)

May be scored in M5 expression

1

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M5 $[H^+]$ $\left(= \frac{Ka \times [HX]}{[X^-]}\right)$

If use $K_a = \frac{[H^+]^2}{[HX]}$ *no further marks*

$= \frac{3.01 \times 10^{-5} \times 1.36 \times 10^{-3}}{1.25 \times 10^{-3}}$ *OR* $\frac{3.01 \times 10^{-5} \times 0.0544}{0.05}$

(= 3.27 × 10⁻⁵)

If either value of HX or X^- used wrongly or expression upside down, no further marks

1

M6 pH = 4.48 or 4.49 (allow more than 2dp but not fewer)

*Do **not** allow M6 for correct calculation of pH using their $[H^+]$ - this only applies in (d)(iii) - apart from earlier AE*

1

[18]

Q4.

(a) Proton acceptor

1

(b) (i) $CH_3CH_2NH_2 + H_2O \longrightarrow CH_3CH_2NH_3^+ + OH^-$

allow eq with or without $\rightleftharpoons$

allow $C_2H_5NH_2$ and $C_2H_5NH_3^+$ (plus can be on N or H or 3)

allow RHS as $C_2H_5NH_3OH$

1

(ii) Mark independently of (b)(i)

Allow

Ethylamine is only partly/slightly dissociated

OR

Ethylamine is only partly/slightly ionized

reaction/equilibrium lies to left or low $[OH^-]$ ***OR*** little OH^- formed

OR little ethylamine has reacted

Ignore "not fully dissociated" or "not fully ionized"

Ignore reference to ionisation or dissociation of water

1

(c) **M1** Ethylamine

If wrong no marks in (c)

1

M2 alkyl group is electron releasing/donating

OR alkyl group has (positive) inductive effect

1

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M3 increases electron density <u>on N(H_2)</u>

OR increased availability of <u>lp</u>

OR increases ability of <u>lp</u> (to accept H(+))

Mark M3 is independent of M2

1

(d) $CH_3CH_2NH_3Cl$

Or any amine hydrochloride

allow name (ethylammonium chloride or ethylamine hydrochloride) or other halide for Cl

*or a strong **organic** acid*

NOT *NH_4Cl*

1

(e) Mark independently of (d)

Extra H^+ reacts with ethylamine or OH^-

Or makes reference to Equilibrium (in (b)(i)) with amine on LHS

1

OR $CH_3CH_2NH_2 + H^+ \longrightarrow CH_3CH_2NH_3^+$

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

Equilibrium shifts to RHS

OR ratio $[CH_3CH_2NH_3^+]/[CH_3CH_2NH_2]$ remains almost constant

1

[9]

Q5.

(a) $NH_4^+ \rightarrow NH_3 + H^+$

Accept multiples.

Accept $NH_4^+ + H_2O \rightarrow NH_3 + H_3O^+$

Ignore state symbols, even if incorrect.

1

(b) Test indicator / conc HCl

Do not accept 'smell'.

Do not accept precipitation reactions of aqueous ammonia.

1

Observation colour for an alkali / white fumes

If wrong test then lose second mark.

1

[3]

Q6.

C

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[1]

Q7.

D

[1]

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Q2.

Question (a) was generally well done, but a large number of students did not include a reversible sign in their equation for dissociation of the weak acid. Part (b) differentiated well as weaker students failed to show how ethanoic acid could act as a base and accept a proton.

Part (c)(i) was more straightforward but some students failed to calculate the concentration of the acid correctly and just used a number of moles. Part (c)(ii) differentiated well: many students realised a subtraction was needed in the calculation, but then failed to use the total volume to convert the amount, in moles, of H^+ ions to a concentration to calculate the pH.

Part (d)(i) was completed very well with most students gaining either 3 or 4 marks. In part (d)(iii) a significant number incorrectly used the original amount in moles of acid (0.0125) in their ratio. Even some of the strongest students struggled with the maths skills required and a frequent wrong answer was the inverse of 1.20 due to incorrect rearrangement. A significant number did not work out the hydrogen ion concentration and so lost M1 when they couldn't complete the rest of the calculation.

Part (e) differentiated well with full descriptions seen in about a third of the answers and one mark gained by another third. In part (f) the first mark proved very accessible but the second proved trickier; many students showed poor maths skills and thought that K_a would equal 1 or zero.

Q3.

Part (a) was well known, but part (b) was much less well understood. In part (c), most students scored the first two marks but then failed to use their answers correctly to calculate the total volume. Some who did not read the question fully, added 25 cm^3 to their correct answer and so lost the final mark.

In part (d)(iii), a significant number could not correctly rearrange the simplified expression for K_c. A mark was allowed, in this part only, for a correct calculation of pH using their value of $[H^+]$ even if this was not the correct concentration.

In part (e), most scored the first two marks, but many then failed to recognise that, on adding alkali, the number of moles of acid would have decreased. Others were unable to rearrange the K_a expression correctly or attempted to use the equation $K_a = [H^+]^2/[HX]$.

Moles and concentration were often confused and many responses were also badly presented with little explanation. Such omission makes it difficult for examiners to award marks in an extended calculation if the answer is wrong.

Q4.

Almost all students scored the mark in part (a), but in the rest of the parts of this question, there was less good understanding of the chemistry of weak bases and the operation of basic buffers. There were many incorrect answers in part (b)(i) where ammonia and ethanol were often given as the products of the reaction. This led to wrong answers to part (b)(ii). A number of students wrote 'inductive effect' in part (c) without any mention of what this applied to; the final mark was, however, often scored. Part (d) proved to be very difficult and although, in part (e), many students recognised that the added H^+ ions would react with OH^- ions in the solution, a large number failed to explain how the buffer would

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respond to this reaction.

Q5.

In this Question most candidates could write a correct equation but a test for ammonia was unknown to the majority of candidates. A number showed some ingenuity in suggesting one of the reactions with a transition metal ion from Task 1 but failed to appreciate that their test would be anything but simple.

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Q1.

(a) completely dissociates/ionises (to form H^+ ions)

1

(b) **M1** moles HCl = 1.035×10^{-3} and moles $Ba(OH)_2$ = 3.75×10^{-3}

If M1 incorrect, lose M1 and M6

1

M2 moles OH^- = 2 × (3.75×10^{-3} = 7.50×10^{-3})

If M2 not x2, lose M2 and M6

1

M3 XS n OH^- = 7.50×10^{-3} - 1.035×10^{-3} = 6.465×10^{-3} mol in 35.35 cm^3

If no subtraction for M3, lose M3 and M6

1

M4 [OH] = 6.465×10^{-3} / 35.35×10^{-3} = 0.182885 mol dm^{-3}

= M3/35.35 × 10^{-3}

If M4 not /35.35 × 10^{-3}, lose M4 and M6

However, if divided by 35.35 only lose M4 and allow M6 (ecf = 10.09)

1

M5 $[H^+] = K_w/[OH^-]$ = 1.47×10^{-14} /0.182885 = 8.0378 × 10–14 mol dm^{-3}

= 1.47 × 10^{-14} / M4

If incorrect rearrangement or wrong equation, lose M5 and M6

If K_w = 1.00 × 10^{-14} used only lose M5 and allow M6 (ecf = 13.26)

1

M6 pH = 13.09 to 13.10

Must be 2dp

1

Alternative MS to get M2:

Starting amounts are 1.035×10^{-3} mol HCl and 3.75×10^{-3} mol $Ba(OH)_2$ M1

So the HCl will react with 5.175×10^{-4} mol of the $Ba(OH)_2$ leaving an excess of 3.2325×10^{-3} mol of $Ba(OH)_2$ (as alternative M2)

So n OH^- = 2 × 3.2325 × 10^{-3}= 6.465×10^{-3} mol M3

Credit other methods eg limiting reagent method since HCl limiting reagent

(c) $[H^+] = [OH^-]$

1

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(d) SO_2

1

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

1

(f) **M1** moles HCl added = 0.01 mol and moles CH_3COOH = 0.035 mol

1

M2 moles CH_3COO^- = 0.025 – 0.01 (= 0.015)

M2 mol CH_3COO^- = 0.025 - M1(HCl)

1

M3 moles CH_3COOH = 0.035 + 0.01 (= 0.045)

M3 mol CH_3COOH = M1(CH_3COOH) + M1(HCl)

1

M4 $[H^+] = 1.76 \times 10^{-5} \times \frac{M3\ (/\ V)}{M2\ (/\ V)}$ (= 5.28×10^{-5})

M4 is conditional on an attempt at an addition/subtraction in M2 OR M3

1

M5 pH = 4.28

M5 must be 2dp

If used 0.07 mol for CH_3COOH can score M2, M3 and M4 (pH = 4.03)

1

[15]

Q2.

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

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

1

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

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

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

1

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

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)

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

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]

Q3.

B

[1]

Q4.

(a) Proton donor **1**

(b) Completely ionises to give H^+ ions in water **1**

(c) 0.058 mol dm^{-3} **1**

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1.24

1

(d) Amount of NaOH = 5.25×10^{-3}

1

Since 1:1 reaction amount of OH− ions in excess

= $5.25 \times 10^{-3} - 1.45 \times 10^{-3}$ mol

= 3.80×10^{-3} moles OH^-

1

$[OH^-] = 3.80 \times 10^{-3} \times 1000/60 = 0.0633$

1

$K_w = [H^+][OH^-$ so $H^+ = \frac{10^{-14}}{0.0633} = 1.58 \times 10^{-13}$

1

pH = 12.80

1

(e) Amount of OH^- added 1.5 / 40 = 0.0375 mol

1

Use of 1:1 ratio to calculate amount of A^- formed = 0.0375 mol

1

Amount of weak acid initially = 1 × 0.15 = 0.150 mol so amount of weak acid after addition of NaOH = 0.150 − 0.0375 = 0.1125

If M3 incorrect can only score max of 3 marks

1

$[H^+] = K_a [HA]/[A^-]$ or $[H^+] = 1.79 \times 10^{-5} \times 0.1125/0.0375$

1

= 5.37×10^{-5}

1

pH = 4.27

1

[15]

Q5.

(a) This question is marked using levels of response. Refer to the Mark Scheme Instructions for Examiners for guidance on how to mark this question.

All stages are covered and the explanation of each stage is generally correct and virtually complete.

Answer is communicated coherently and shows a logical progression from stage 1 and stage 2 to stage 3. Steps in stage 3 must be complete, ordered and include a comparison.

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Level 3
5 – 6 marks

All stages are covered but the explanation of each stage may be incomplete or may contain inaccuracies OR two stages are covered and the explanations are generally correct and virtually complete.

Answer is mainly coherent and shows a progression from stage 1 and stage 2 to stage 3.

Level 2
3 – 4 marks

Two stages are covered but the explanation of each stage may be incomplete or may contain inaccuracies, OR only one stage is covered but the explanation is generally correct and virtually complete.

Answer includes some isolated statements, but these are not presented in a logical order or show confused reasoning.

Level 1
1 – 2 marks

Insufficient correct Chemistry to warrant a mark.

Level 0
0 marks

Indicative Chemistry content

Stage 1: difference in structure of the two acids
- The acids are of the form RCOOH
- but in ethanoic acid R = CH_3
- whilst in ethanedioic acid R = COOH

Stage 2: the inductive effect
- The unionised COOH group contains two very electronegative oxygen atoms
- therefore has a negative inductive (electron withdrawing)effect
- The CH_3 group has a positive inductive (electron pushing) effect

Stage 3: how the polarity of OH affects acid strength
- The O–H bond in the ethanedioic acid is more polarised / H becomes more δ^+
- More dissociation into H^+ ions
- Ethanedioic acid is stronger than ethanoic acid

6

(b) Moles of NaOH = Moles of $HOOCCOO^-$ formed = 6.00×10^{-2}

Extended response

1

Moles of HOOCCOOH remaining = $1.00 \times 10^{-1} - 6.00 \times 10^{-2}$

$= 4.00 \times 10^{-2}$

1

$K_a = [H^+][A^-] / [HA]$

$[H^+] = K_a \times [HA] / [A^-]$

1

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$[H^+] = 5.89 \times 10^{-2} \times (4.00 \times 10^{-2} / V) / (6.00 \times 10^{-2} / V) = 3.927 \times 10^{-2}$

1

$pH = -\log_{10}(3.927 \times 10^{-2}) = 1.406 = 1.41$

Answer must be given to this precision

1

(c) $5H_2C_2O_4 + 6H^+ + 2MnO_4^- \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

OR $5C_2O_4^{2-} + 16H^+ + 2MnO_4^- \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

1

Moles of $KMnO_4 = 20.2 \times 2.00 \times 10^{-2} / 1000 = 4.04 \times 10^{-4}$

1

Moles of $H_2C_2O_4 = 5 / 2 \times 4.04 \times 10^{-4} = 1.01 \times 10^{-3}$

1

Concentration = moles / volume (in dm^3)

$= 1.01 \times 10^{-3} \times 1000 / 25 = 4.04 \times 10^{-2}$ (mol dm^{-3})

If 1:1 ratio or incorrect ratio used, M2 and M4 can be scored

1

[15]

Q6.

(a) $CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$
OR

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

Must show $\rightleftharpoons$
Allow CH_3CO_2H, $CH_3CO_2^-$
Ignore state symbols

1

(b) ($CH_3COOH + \underline{HNO_3} \longrightarrow CH_3COOH_2^+ + NO_3^-$)

IGNORE $\rightleftharpoons$
Allow CH_3CO_2H, $CH_3CO_2H_2^+$, $CH_3C^+(OH)_2$

1

(c) (i) (new $[HNO_3] = [H^+] = \frac{100}{150} \times 0.0125$)

M1 $[H^+] = 8.3(3) \times 10^{-3}$ (mol dm^{-3})
OR

new$[HNO_3]$ = $\frac{\text{mol } HNO_3}{\text{total vol}} = \frac{1.25 \times 10^{-3}}{150 \times 10^{-3}}$

1

M2 pH = − log M1 OR 2.08

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Must be 2dp
Allow correct pH conseq to their [H⁺] concentration

1

(ii) M1 mol NaOH (= $50 \times 10^{-3} \times 0.0108$) = 5.40×10^{-4}

1

M2 Subtraction of M1 from moles of HNO_3 (1.25×10^{-3} or conseq from 1c(i))

Excess mol $H^+ = 7.10 \times 10^{-4}$

M2 allow ecf for subtraction of mol
If no subtraction, no further marks

1

M3 $[H^+] = \frac{M2}{150 \times 10^{-3}}$ OR $\frac{7.10 \times 10^{-4}}{150 \times 10^{-3}} = 4.73 \times 10^{-3}$

M3 <u>if no use of volume, no further marks</u> (pH=3.15)
If incorrect volume used, can score M4

1

M4 pH = -log M3 OR 2.32
M4 Allow 2.33 Must be 2 dp

1

(d) (i) M1 $K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$

Penalise ( ) once here Not [H+][A-] / [HA]
If K_a expression wrong – Allow correct pH conseq to their [H⁺] concentration M4 only

1

M2 $K_a = \frac{[H^+]^2}{[CH_3COOH]}$ or with numbers or with HA

1

M3 $[H^+] = [\sqrt{(1.74 \times 10^{-5} \times 0.0125)}] = 4.66 \times 10^{-4}$

Mark for answer

1

M4 pH = 3.33
Must be 2dp
Allow correct pH conseq to their [H⁺] concentration
(pH = 3.83 can score M1, M2 and M4)

1

(ii) <u>Sodium ethanoate</u>
Ignore formula
Allow sodium acetate

1

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(iii) M1 $[H^+] = 1.45 \times 10^{-5}$

Accept 1.445×10^{-5} or 1.4×10^{-5}

1

M2

$$\frac{[salt]}{[acid]} \text{ (OR } \frac{[CH_3COO^-]}{[CH_3COOH]} = \frac{Ka}{[H^+]} \text{)= } \frac{1.74 \times 10^{-5}}{1.45 \times 10^{-5}}$$

If M1 incorrect CE=0

Inclusion of 0.0125 in calculation can only score M1

1

M3 1.2(0)

Ignore units

1.4×10^{-5} gives 1.24

1

(e) M1 (Electronegative) chlorine withdraws electrons

Allow Cl has negative inductive effect

1

M2 Stabilises/reduces charge on COO-

OR weakens O-H bond

OR makes O-H more polar

Ignore chloroethanoic acid dissociates more readily

Mark independently

1

(f) M1 Strong acids (almost) completely dissociated/ionised

OR not an equilibrium

OR equilibrium lies far to the right

Cannot have K_a value for a reaction not in equilibrium scores both marks

1

M2 K_a value for strong acids tends to infinity/is very large
OR can't divide by zero in K_a

1

[20]

Q7.

(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

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= 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

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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

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[8]

Q8.

(a) $HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$
or

$H_2O + HCO_3^- \rightleftharpoons CO_3^{2-} + H_3O^+$

Must have equilibrium sign but mark on to (b)
Ignore state symbols

1

(b) Acid: Increase in concentration of H^+ ions, equilibrium moves to the left.

Allow H^+ ions react with carbonate ions (to form HCO_3^-)

1

Alkali: OH^- reacts with H^+ ions, equilibrium moves to the right (to replace the H^+ ions)

1

Concentration of H^+ remains (almost) constant

1

[4]

Q9.

(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

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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 = 12.38 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 = 3.06

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

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

Ignore ( ) here.

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

1

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

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]

Q10.

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

Ignore (aq)

Must have [ ] not ( )

1

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

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If no square root, CE=0

1

pH = 6.73

Must be 2dp

1

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

Mark for working

1

Kw = [4.365×10^{-12} ***OR*** $4.37 \times 10^{-12} \times 0.047$] = 2.05×10^{-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) $K_a = \dfrac{[H^+][HCOO^-]}{HCOOH}$ ***OR*** $\dfrac{[H_3O^+][HCOO^-]}{HCOOH}$

Must have all brackets but allow ( )

Must be HCOOH etc.

Allow ecf in formulae from (b)(i)

1

(iii) M1

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

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*

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and M3

1

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

1

M2 Eqm <u>shifts / moves</u> 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*** $pH = 3.75 - \log \frac{2.35 \times 10^{-2}}{1.84 \times 10^{-2}}$

$(= 2.27 \times 10^{-4})$

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

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

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

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

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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]

Q11.

(a) Proton donor or H^+ donor

Allow donator

1

(b) (i) B B

Both need to be correct to score the mark

1

(ii) A A

Both need to be correct to score the mark

1

(iii) B A

Both need to be correct to score the mark

1

(c) **M1** $[H^+] = 10^{-1.25}$ OR 0.05623

1

M2 mol HCl = $(25 \times 10^{-3}) \times 0.0850$ $(= 2.125 \times 10^{-3})$

Mark for Working

1

M3 vol $\left(= \frac{2.125 \times 10^{-3}}{0.05623}\right)$ = 0.0378 dm^3 or 37.8 cm^3

allow 0.0375 – 0.038 dm^3 or 37.5 – 38 cm^3

Units and answer tied

Lose M3 if total given as (25 + 37.8) = 62.8 cm^3

Ignore "vol added = 12.8 cm^3 " after correct answer

1

(d) (i) 4.52

Must be 2dp

1

(ii) $K_a = \frac{[H^+][H^-]}{[HX]}$ ignore = $\frac{[H^+]^2}{[HX]}$ but this may score M1 in (d)(iii)

Must have all brackets but allow ( ) Allow HA etc

***NO** mark for 10^{-pKa}*

1

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(iii) **M1** $K_a = \frac{[H^+]^2}{[HX]}$ or with numbers

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

1

M2 $[H^+] = (\sqrt{(3.01 \times 10^{-5} \times 0.174)} = \sqrt{(5.24 \times 10^{-6})})$
$= 2.29 \times 10^{-3} - 2.3 \times 10^{-3}$

Mark for answer

1

M3 pH = 2.64 (allow more than 2dp but not fewer)

Allow 1 for correct pH from their wrong $[H^+]$

If square root forgotten, pH = 5.28 scores 2 for M1 and M3

1

(e) **M1** mol $OH^- = (10.0 \times 10^{-3}) \times 0.125 = 1.25 \times 10^{-3}$

Mark for answer

1

M2 orig mol HX = $(15.0 \times 10^{-3}) \times 0.174 = 2.61 \times 10^{\times 3}$

Mark for answer

1

M3 mol HX in buffer = orig mol HX – mol OH^-

Mark for answer

$= 2.61 \times 10^{-3} – 1.25 \times 10^{-3} = 1.36 \times 10^{-3}$

Allow conseq on their (M2 – M1)

($[HX] = 1.36 \times 10^{-3}/25 \times 10^{-3} = 0.0544$)

If no subtraction, max 3 for M1, M2 & M4 (pH = 4.20)

If $[H^+] = [X^-]$ & √used, max 3 for M1, M2 & M3 (pH = 2.89)

1

M4 mol X^- in buffer = mol OH^- = 1.25×10^{-3}

($[X^-] = 1.25 \times 10^{-3}/25 \times 10^{-3} = 0.05$)

May be scored in M5 expression

1

M5 $[H^+] \left(= \frac{Ka \times [HX]}{[X^-]}\right)$

If use $K_a = \frac{[H^+]^2}{[HX]}$ no further marks

$= \frac{3.01 \times 10^{-5} \times 1.36 \times 10^{-3}}{1.25 \times 10^{-3}}$ *OR* $\frac{3.01 \times 10^{-5} \times 0.0544}{0.05}$

(= 3.27 × 10⁻⁵)

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If either value of HX or X^- used wrongly or expression upside down, no further marks

1

M6 pH = 4.48 or 4.49 (allow more than 2dp but not fewer)

*Do **not** allow M6 for correct calculation of pH using their $[H^+]$ - this only applies in (d)(iii) - apart from earlier AE*

1

[18]

Q12.

(a) **Z**

Mark independently.

1

The idea that the solution contains both HA and A^-

1

(b) pH

1

$[HA] = [A^-]$

Accept solution half neutralised.

1

$pH = pK_a$

Accept $[H^+] = K_a$

1

[5]

Q13.

(a) <u>Proton acceptor</u>

1

(b) (i) $CH_3CH_2NH_2 + H_2O \longrightarrow CH_3CH_2NH_3^+ + OH^-$

allow eq with or without $\rightleftharpoons$

allow $C_2H_5NH_2$ and $C_2H_5NH_3^+$ (plus can be on N or H or 3)

allow RHS as $C_2H_5NH_3OH$

1

(ii) Mark independently of (b)(i)

Allow

Ethylamine is only partly/slightly dissociated

OR

Ethylamine is only partly/slightly ionized

reaction/equilibrium lies to left or low $[OH^-]$ ***OR*** little OH^- formed

OR little ethylamine has reacted

Ignore "not fully dissociated" or "not fully ionized"

Ignore reference to ionisation or dissociation of water

1

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(c) **M1** Ethylamine

If wrong no marks in (c)

1

M2 alkyl group is electron releasing/donating

OR alkyl group has (positive) inductive effect

1

M3 increases electron density <u>on N(H_2)</u>

OR increased availability of <u>lp</u>

OR increases ability of <u>lp</u> (to accept H(+))

Mark M3 is independent of M2

1

(d) $CH_3CH_2NH_3Cl$

Or any amine hydrochloride

allow name (ethylammonium chloride or ethylamine hydrochloride) or other halide for Cl

*or a strong **organic** acid*

NOT *NH_4Cl*

1

(e) Mark independently of (d)

Extra H^+ reacts with ethylamine or OH^-

Or makes reference to Equilibrium (in (b)(i)) with amine on LHS

1

OR $CH_3CH_2NH_2 + H^+ \longrightarrow CH_3CH_2NH_3^+$

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

Equilibrium shifts to RHS

OR ratio $[CH_3CH_2NH_3^+]/[CH_3CH_2NH_2]$ remains almost constant

1

[9]

Q14.

(a) (i) $-\log[H^+]$ or $\log 1/[H^+]$

penalise missing square brackets here only

1

(ii) 0.81

2dp required, no other answer allowed

1

(iii) **M1** mol $H^+ = 1.54 \times 10^{-3}$

if wrong no further mark

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if 1.5 × 10^{-3} allow M1 but not M2 for 2.82

1

M2 pH = 2.81

allow more than 2dp but not fewer

1

(b) **M1** $[H^+] = 3.31 \times 10^{-3}$

1

M2 $K_a = \frac{[H^+][X^-]}{[HX]}$ or $\frac{[H^+]^2}{[HX]}$ or using numbers

do not penalise ( ) or one or more missing [ ]

1

M3 $[HX] = \frac{[H^+]^2}{K_a} = \frac{(3.31 \times 10^{-3})^2}{4.83 \times 10^{-5}}$

allow conseq on their $[H^+]^2/(4.83 \times 10^{-5})$ (AE)
if upside down, no further marks after M2

1

M4 [HX] = 0.227

allow 0.225 – 0.23

1

(c) **M1** extra/added OH^- removed by reaction with H^+ or the acid

1

M2 correct discussion of equn shift i.e. $HX \rightleftharpoons H^+ + X^-$ moves to right

1

OR

ratio $\frac{[HX]}{[X^-]}$ remains almost constant

(d) (i) **M1** mol HY = $(50 \times 10^{-3}) \times 0.428 = 0.0214$

OR $[Y] = .0236 \times \frac{1000}{50} = 0.472$

mark for answer

1

M2 $[H^+] = 1.35 \times 10^{-5} \times \frac{0.0214}{0.0236}$

OR $1.35 \times 10^{-5} = [H^+] \times \frac{0.0236}{0.0214}$

OR $[H^+] = 1.35 \times 10^{-5} \times \frac{0.428}{0.472}$

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OR $1.35 \times 10^{-5} = [H^+] \times \frac{0.472}{0.428}$

must be numbers not just rearrangement of Ka expression

If either HY value or Y^- value wrong, (apart from AE -1) lose M2 and M3

1

M3 $[H^+] = 1.22 \times 10^{-5}$

mark for answer

1

M4 pH = 4.91

allow more than 2dp but not fewer

allow M4 for correct pH calculation using their $[H^+]$ (this applies in (d)(i) only)

1

If Henderson Hasselbalch equation used:

M1 mol HY = $(50 \times 10^{-3}) \times 0.428 = 0.0214$

OR $[Y] = .0236 \times \frac{1000}{50} = 0.472$

mark for answer

1

M2 p*K*a = 4.87

1

M3 $\log\left(\frac{0.0214}{0.0236}\right) = -0.043$

$\log\left(\frac{0.428}{0.472}\right) = -0.043$

If either HY value or Y^- value wrong, (apart from AE-1) lose M3 and M4

1

M4 pH = 4.87 – (– 0.043) = 4.91

allow more than 2dp but not fewer

1

(ii) Can score full marks for correct consequential use of their HY and Y^- values from d(i)

M1 Mol HY after adding NaOH = $0.0214 - 5.0 \times 10^{-4} = 0.0209$

AE in subtraction loses just M1

If wrong initial mol HY (i.e. not conseq to part d(i)) or no subtraction or subtraction of wrong amount, lose M1 and M3

1

M2 Mol Y^- after adding NaOH = $0.0236 + 5.0 \times 10^{-4} = 0.0241$

AE in addition loses just M2

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If wrong mol Y^- (i.e. not conseq to part d(i)) or no addition or addition of wrong amount lose M2 and next mark gained

1

M3 $[H^+] = 1.35 \times 10^{-5} \times \frac{0.0209}{0.0241}$ (= 1.17×10^{-5})

if convert to concentrations

$[H^+] = 1.35 \times 10^{-5} \times \frac{0.418}{0.482}$ (= 1.17×10^{-5})

1

if HY/Y^- upside down, no further marks

M4 pH = 4.93

allow more than 2dp but not fewer

NOT allow M4 for correct pH calculation using their $[H^+]$ (this allowance applies in (d)(i) only)

1

If Henderson Hasselbalch equation used:

Can score full marks for correct consequential use of their HY and Y^- values from d(i)

M1 Mol HY after adding NaOH = $0.0214 - 5.0 \times 10^{-4} = 0.0209$

AE in subtraction loses just M1
If wrong initial mol HY (i.e. not conseq to part d(i)) or no subtraction or subtraction of wrong amount lose M1 and M3

1

M2 Mol Y^- after adding NaOH = $0.0236 + 5.0 \times 10^{-4} = 0.0241$

AE in addition loses just M2
If wrong mol Y^- (i.e. not conseq to part d(i)) or no addition or addition of wrong amount lose M2 and next mark gained

1

M3 $\log \left(\frac{0.0209}{0.0241}\right) = -0.062$

if HY/Y^- upside down, no further marks

1

M4 pH = 4.87 – (– 0.062) = 4.93

allow more than 2dp but not fewer

1

[18]

Q15.

(a) (i) $-\log[H^+]$

or $\log 1/[H^+]$
penalise ( )

1

(ii) $[H^+] = 0.56$

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mark for the answer; allow 2dp or more

1

$[H_2SO_4] = ½ \times 0.56 = 0.28$

1

(b) (i) $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

OR

$CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$

Allow CH_3CO_2H etc

1

(ii) mol acid = $(25.0 \times 10^{-3}) \times 0.41 = 1.025 \times 10^{-2}$ or 1.03×10^{-2}

1

$[NaOH] = 1.025 \times 10^{-2}/22.6 \times 10^{-3} = 0.45(4)$

mark for answer
if not 0.454 look back for error

1

OR

$[NaOH] = 1.03 \times 10^{-2}/22.6 \times 10^{-3} = 0.456$ or 0.46

(iii) cresol purple

1

(iv) NaOH reacts with <u>carbon dioxide</u> (in the air)

1

(c) (i) $K_a = \dfrac{[H^+][CH_3COO^-]}{[CH_3COOH]}$

allow molecular formulae or minor slip in formulae

penalise ( )
allow H_3O^+
not allow HA etc

1

(ii) $K_a = \dfrac{[H^+]^2}{[CH_3COOH]}$ or with numbers

1

allow HA etc here
This can be scored in part (c)(i) but doesn't score there.

$[H^+] = (\sqrt{(1.74 \times 10^{-5} \times 0.410)} = \sqrt{(7.13 \times 10^{-6})}) = 2.67 \times 10^{-3}$

1

mark for 2.67×10^{-3} or 2.7×10^{-3} either gives 2.57

pH = 2.57 can give three ticks here for (c)(ii)
penalise decimal places < 2 >

1

pH mark conseq on their $[H^+]$

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so 5.15 gets 2 marks where square root not taken

(iii) **M1** mol OH^- = (10.0 × 10^{-3}) × 0.10 = 1.0 × 10^{-3}

If no subtraction or other wrong chemistry the max score is 3 for M1, M2 and M4

1

M2 orig mol HA = (25.0 × 10^{-3}) × 0.41 = 0.01025

1

or 1.025 × 10^{-2} or 1.03 × 10^{-2}

M3 mol HA in buffer = orig mol HA – mol OH^-

1

= 0.00925 or 0.0093

If A^- is wrong, max 3 for M1, M2 and M3 or use of pH = pKa – log [HA]/[A^-]

M4 mol A^- in buffer = mol OH^- = 1.0 × 10^{-3}

Mark is for insertion of correct numbers in correct expression for [H^+]

1

M5 $[H^+] = \left(\frac{K_a \times [CH_3COOH]}{[CH_3COO^-]} = \right)$

1

$$\frac{(1.74 \times 10^{-5})(0.00925)}{0.0010} \text{ or } \frac{(1.74 \times 10^{-5})(0.00930)}{0.0010}$$

(= 1.61 × 10^{-4} or 1.62 × 10^{-4})

M6 pH = 3.79 can give six ticks for 3.79

if [HA]/[A^-] upside down lose M5 & M6

If wrong method e.g. $[H^+]^2$/[HA] max 3 for M1, M2 and M3

Some may calculate concentrations
[HA] = 0.264 and [A^-] = 0.0286 and rounding this to 0.029 gives pH = 3.80 (which is OK)

NB Unlike (c)(ii), this pH mark is NOT awarded conseq to their [H^+] unless following AE

BEWARE: using 0.01025 wrongly instead of 0.00925 gives pH = 3.75
(this gets 3 for M1, M2 & M4)

1

[18]

Q16.

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

1

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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]

Q17.

(a) (i) $[H^+][OH^-]$

1

– log $[H^+]$

1

(ii) $[H^+] = [OH^-]$

1

(iii) $(2.0 \times 10^{-3}) \times 0.5 = 1.0 \times 10^{-3}$

1

(iv) $[H^+] = \frac{4.02 \times 10^{-14}}{1.0 \times 10^{-3}}$ (= 4.02×10^{-11})

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pH = 10.40 **1**

1

(b) (i) $K_a = \frac{[H^+][CH_3CH_2COO^-]}{[CH_3CH_2COOH]}$ **1**

$= \frac{[H^+]}{[CH_3CH_2COOH]}$ **1**

$[H^+] = \sqrt{(1.35 \times 10^{-5}) \times 0.125}$ $(= 1.30 \times 10^{-3})$ **1**

pH = 2.89 **1**

(c) (i) $(50.0 \times 10^{-3}) \times 0.125 = 6.25 \times 10^{-3}$ **1**

(ii) $(6.25 \times 10^{-3}) – (1.0 \times 10–3) = 5.25 \times 10^{-3}$ **1**

(iii) mol salt formed = 1.0×10^{-3} **1**

$[H^+] = K_a \times \frac{[CH_3CH_2COOH]}{[CH_3CH_2COO–)}$ **1**

$= (1.35 \times 10^{-5}) \times \frac{(5.25 \times 10^{-3})/V}{(1.0 \times 10^{-3})/V}$ $(= 7.088 \times 10^{-5})$ **1**

pH = 4.15 **1**

[16]

Q18.

(a) (i) B; **1**

C; **1**

A; **1**

(ii) cresolphthalein

OR

thymolphthalein; **1**

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(b) (i) $-\log[H^+]$;

1

(ii) $[H^+] = 1.259 \times 10^{-12}$ (or 1.26 or 1.3)

OR

OH = 14 – pH;

1

$$[OH^-] = \frac{10^{-14}}{1.258 \times 10^{-12}}$$

OR

= 2.10;

1

$= 7.9(4) \times 10^{-3}$;

(if $[H^+]$ is wrong allow 1 for $[OH] = K_w/[H^+]$ or as numbers)

1

(c) (i) $K_a = [H^+]^2/[CH_3CH_2COOH]$

OR

$[H+]^2/[HA]$

OR

$[H^+] = [A^-]$ etc;

1

$[H^+] = \sqrt{1.35 \times 10^{-5}} \times 0.117$ or expression without numbers;

1

$= 1.257 \times 10^{-3}$

pH = 2.90;

1

(iii) $K_a = [H^+]$

OR

pK_a = pH;

1

pH = 4.87;

(penalise 1dp once)

1

[13]

Q19.

(a) Concentration of acid: $m_1v_1 = m_2v_2$ hence $25 \times m_1 = 18.2 \times 0.150$

OR

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moles NaOH = 2.73 ×10^{-3}; **1**

m_1 = 18.2 × 0.150/25= 0.109; **1**

(b) (i) K_a=[H^+][A^-]/[HA] *not* K_a = [H^+]^2 / [HA]; **1**

(ii) pK_a = –logK_a; **1**

(iii) [A^-] = [HA]; **1**

hence K_a = [H^+] [A^-] / [HA] = [H^+]

and –logK_a = –log[H^+]; **1**

(c) ratio [A^-] : [HA] remains constant; **1**

hence as [H^+] = K_a [HA] / [A^-]; [H^+] remains constant; **1**

(d) (i) pH of 0.250 mol dm-^{3} HCl = 0.60
and pH of 0.150 mol dm-^{3} HCl = 0.82; **1**

pH change = 0.22; **1**

(ii) moles HCl = 30 × 0.250 × 10^{-3} = v × 0.150 × 10^{-3} = 7.50 × 10^{-3}

OR

v = 30 × 0.250 × 10^{-3}/ 0.150 × 10^{-3} =50; **1**

water added = 50 – 30 = 20 cm^3; **1**

[12]

Q20.

(a) pH = –log[H^+] **1**

$$K_a = \frac{[H^+]^2}{[CH_3COOH]} \quad \text{or } [H^+]=[A^-]$$ **1**

[H^+]= √1.74 × 10^{-5} × 0.15 (or 1.62 × 10^{-3}) **1**

pH = 2.79 (penalise 1 dp or more than 2dp once in the qu) **1**

(b) (i) Solution which resists change in pH /maintains pH

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despite the addition of (small amounts of) acid/base (or dilution) **1**

1

(ii) $CH_3COO + H^+ \rightarrow CH_3COOH$

must show an equation full or ionic in which ethanoate ions are converted to ethanoic acid **1**

(c) (i) $[H^+] = \frac{K_a[CH_3COOH]}{[CH_3COO^-]}$ if rearrangement incorrect, no further marks **1**

$= 1.74 \times 10^{-5} \times \frac{0.15}{0.10}$ **1**

(= 2.61×10^{-5})

pH = 4.58 **1**

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

M2 moles ethanoic acid after addition = 0.15 + 0.01 = 0.16 **1**

M3 moles ethanoate ions after addition = 0.10 -0.01 = 0.09 **1**

M4 $[H^+] = \frac{K_a[CH_3COOH]}{[CH_3COO^-]} = 1.74 \times 10^{-5} \times \frac{0.16/V}{0.09/V}$ **1**

(= 3.09×10^{-5})

M5 pH = 4.51

The essential part of this calculation is addition/subtraction of 0.01 moles to gain marks M2 and M3. If both of these are missing, only mark M1 is available. Thereafter treat each mark independently, except if the expression in M4 is wrong, in which case both M4 and M5 are lost. **1**

[15]

alternative scheme for part (c)(i)

$pH\ pK_a - \log \frac{[CH_3COOH]}{[CH_3COO^-]}$ **1**

$pK_a = 4.76$ **1**

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$$pH = (4.76 - \log \frac{0.15}{0.10}) = 4.58$$

1

alternative for penultimate mark of part (c)(ii)

$$pH = 4.76 - \log \frac{0.16}{0.09}$$

1

Q21.

(a) $K_a = \frac{[H^+][A^-]}{[HA]}$

(All three sets of square brackets needed, penalise missing brackets or missing charge once in the question)
(Don't penalise extra $[H^+]^2/[HA]$)

1

(b) $K_a = \frac{[H^+]^2}{[HA]}$ or $[H^+] = [A^-]$

$[H^+] = \sqrt{(1.45 \times 10^{-4}) \times 0.25}$

$= 6.02 \times 10^{-3}$ pH = 2.22

(must be to 2dp)
(allow 4th mark consequential on their $[H^+]$)

1

(c) (i) pH (almost) unchanged

(Must be correct to score explanation)

1

H^+ removed by A^- forming HA
or acid reacts with salt
or more HA formed

1

(ii) $[H^+] = 10^{-3.59} = 2.57 \times 10^{-4}$ or 2.6×10^{-4}

1

$[A^-] = \frac{K_a[HA]}{[H^+]}$

1

$= \frac{(1.45 \times 10^{-4}] \times 0.25}{2.57 \times 10^{-4}}$

1

= 0.141 (mol dm^{-3})

(Allow 0.139 to 0.141 and allow 0.14)

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(If not used 3.59, to find $[H^+]$ can only score M2 for working)

(If 3.59 used but $[H^+]$ is wrong, can score M2 for correct method and conseq M4)

If wrong method and wrong expression, can only score M1)

1

(ii) *Alternative scheme for first three marks of part (c)(ii)*

$$pH = pK_a - \log \frac{[HA]}{[A^-]}$$

1

$pK_a = 3.84$

1

$$3.59 = 3.84 - \log \frac{0.250}{[A^-]}$$

1

[11]

Q22.

(a) Hydrogen bonding **(1)**
between H_2O and NH_3 **(1)**

2

(b) (i) $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ **(1)**

(ii) Ammonia is weak base **(1)**
NOT partially ionised

Equilibrium to left or incomplete reaction **(1)**

3

(c) A proton donor **(1)**

1

(d) *Buffer solution*: A solution which resists change in pH **(1)**
when small amounts of acid or base added or on dilution **(1)**

Reagent: NH_4Cl **(1)**
Allow a correct strong acid

3

(e) (i) $K_a = [H^+][A^-] / [HA]$ **(1)**
$= [H^+][0.125 \times 4]$ **(1)** $/ 1.00$
$[H^+] = 1.70 \times 10^{-5} / 0.125 \times 4 = 3.40 \times 10^{-5}$ **(1)**

$pH = -\log_{10}[H^+] = 4.47$ **(1)**
Allow pH conseq to $[H^+]$ if 2 place decimals given

(ii) $H^+ + CH_3COO^- \rightarrow CH_3COOH$ **(1)**

5

[14]

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Q23.

(a) moles HA = $\frac{25}{10^3}$ × 0.150 = 3.75 × 10^{-3} **(1)**

∴ vol NaOH = $\frac{3.75 \times 10^{-3}}{0.20}$ = 1.875 × 10^{-2} dm^3 **(1)**

or 18.75 cm^3

2

(b) (i) pH = $-\log_{10}[H^+]$ **(1)**

(ii) Value above 7 but below 11 **(1)**

(iii) phenol red / thymol blue / phenolphthalein / thymolphthalein

i.e. indicator with $7 < pK_{in} < 11$

3

(c) (i) Only slightly dissociated/ionised **(1)**

NOT "not fully dissociated / ionised"

(ii) $K_a = \frac{[H^+][A^-]}{[HA]}$ **(1)**

NOT $\frac{[H^+]^2}{[HA]}$

(iii) For weak acid alone:

Ka = $\frac{[H^+]^2}{[HA]}$ **(1)**

∴ $[H^+] = \sqrt{(2.75 \times 10^{-5}) \times 0.15}$

= 2.03 × 10^{-3} (1)

∴ pH = 2.69 (1)

pH should be given to 2 decimal places
penalise answer to 1 d.p. once in question

5

(d) moles OH^- added = 1.875 × 10^{-3} = moles A^- = moles HA left **(1)**

or $[A^-] = [HA]$

∴ Ka = $[H^+]$ **or** pH = pK_a **(1)**

∴ pH = 4.56 (1)

3

[13]

Q24.

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(a) before any KOH added: $K_a = \frac{[H^+][A^-]}{[HA]}$ **or** $\frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$ **(1)**

$\therefore K_a = \frac{[H^+]^2}{[CH_3COOH]}$ **(1)**

$\therefore [H^+] = \sqrt{1.74 \times 10^{-5} \times 0.160} = 1.67 \times 10^{-3}$ **(1)**

$\therefore$ pH = 2.78 **(1)**

4

(b) at 8 cm^3 KOH:
Moles KOH added = $(8 \times 10^{-3}) \times 0.210 = 1.68 \times 10^{-3}$ **(1)**
$\therefore$ moles of CH_3COO^- formed = 1.68×10^{-3} **(1)**

Original moles of $CH_3COOH = (25 \times 10^{-3}) \times 0.160 = 4.0 \times 10^{-3}$ **(1)**

$\therefore$ moles of CH_3COOH left = $(4.0 \times 10^{-3}) - (1.68 \times 10^{-3})$
$= 2.32 \times 10^{-3}$ **(1)**

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

$= 1.74 \times 10^{-5} \times \frac{2.32 \times 10^{-3}/V}{1.68 \times 10^{-3}/V} = 2.40 \times 10^{-5}$ **(1)**

$\therefore$ <u>pH = 4.62</u> **(1)**

It forget subtraction : max 5
If K_a expression not used max 5
if moles of CH_3COOH wrong but substitution used max 5

7

(c) at 40 cm^3 of KOH:
Total moles of KOH = $(40 \times 10^{-3}) \times 0.21 = 8.4 \times 10^{-3}$ **(1)**
$\therefore$ **excess moles of KOH = $(8.4 \times 10^{-3}) - (4.0 \times 10^{-3})$**
$= 4.4 \times 10^{-3}$ **(1)**
in total volume = 40 + 25 = 65 cm^3 **(1)**

$\therefore [OH^-] = 4.4 \times 10^{-3} \times \frac{1000}{65} = 0.0677$ **(1)**

$\therefore [H^+] = \frac{10^{-14}}{0.0677}$

OR pOH =1.17

$= 1.477 \times 10^{-13}$ **(1)**
$\therefore$ pH = 12.8<u>3</u> **(1)**

If volume missed : max 4
If moles of acid wrong but method includes subtraction : max 5
If no subtraction : max 4

6

[Max 16]

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Q25.

(a) (i) $K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$ (or H_3O^+) **(1)**

(ii) (1) $K_a = \frac{[H^+]^2}{[CH_3COOH]}$ **(1)**

(2) $[H^+] = \sqrt{1.74 \times 10^{-5} \times 0.220}$ = 1.96×10^{-3} **(1)**

(3) $pH = -\log_{10}[H^+]$ **(1)**
can score independently

(4) pH = 2.71 **(1)**
2 d.p. essential
If forget √ can score (1) and (3) for pH = 5.42

5

(b) (i) moles acid = $\frac{25}{1000} \times 0220$ **(1)** = 5.50×10^{-3}

$= \frac{x}{10^3} \times 0.150$

$\therefore x = 25 \times \frac{0.220}{0.150}$ **or** $5.50 \times 10^{-3} \times \frac{1000}{0.150}$

= 36.7 (or 37) cm^3 (or 36.6) **(1)**

NOT 36 NOR 37.0 units must match

(ii) *Indicator*: thymol blue **(1)**
Explanation: weak acid – strong base **(1)**
equivalent at pH > 7 **(1)**
or high pH

5

(c) (1) mol NaOH added = $\frac{2.0}{40.0}$ = 0.050 **(1)**
If wrong M_r: CE ∴ lose marks (1) and (2) then mark on consequentially → max 4

(2) mol CH_3COOH left = 0.220 – 0.050 = 0.170 **(1)**

(3) mol CH_3COO^- formed = 0.050 **(1)**

(4) $[H^+] = Ka \frac{[acid]}{[salt]}$ OR $pH = pKa + \log\frac{[A^-]}{[HA]}$ etc **(1)**
If expression wrong no marks for 4 / 5 / 6

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can score (1) to (4) in (5)

(5) $[H^+] = 1.74 \times 10^{-5} \times \frac{(0.170)}{(0.05)}$ OR $pH = 4.76 + \log\left(\frac{0.05}{0.17}\right)$ **(1)**

(6) pH = 4.23 **(1)**

*Correct answer gets **(1)(1)(1)(1)(1)(1)***
Mark (5) is for use of correct values of (acid moles) and (salt moles)
if one wrong allow pH conseq
if both wrong, no further marks
e.g. if candidate forgets substitution in (2)
he loses (2) and (5) but can score (1) (3) (4) (6) = max 4

for pH = 4.12 if $\frac{[acid]}{[salt]}$ upside down; answer 5.29 scores 3 for (1) (2) (3)

6

[16]

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Q1.

(a) 86.2% of students gave the correct definition.

(b) Most students calculated the amounts, in moles, of the reactants but often did not multiply the amount of barium hydroxide by two to give the amount of hydroxide ions. Some students did not convert the amount in moles to concentration and some did not quote their pH to two decimal places. This part of the question discriminated very well, with just over 20% of students scoring full marks.

(c) 81.8% of students gave the correct reason here.

(d) 78.5% correctly identified sulphur dioxide.

(e) 91% of students could give the correct expression for K_a.

(f) Most students could calculate the amount, in moles, of hydrochloric acid and of ethanoic acid, but many were unsure of how to use these numbers. Many students failed to recognise the need to increase the amount of acid and decrease the amount of salt due to the shift in the equilibrium when H^+ ions are added. Many added and subtracted the wrong way round or managed one process but not the other. Students could generally rearrange the K_a expression correctly; just over 40% of students scored full marks for this part of the question.

Q2.

(a) This question was answered well by many students. A common incorrect answer was 0.958, where students had re-arranged the expression upside-down.

(b) Although 34.4% of students scored full marks, the question differentiated well overall. Common errors involved either failure to add/subtract the correct amount in moles of sodium hydroxide or to add/subtract the wrong way round.

Q6.

Question (a) was generally well done, but a large number of students did not include a reversible sign in their equation for dissociation of the weak acid. Part (b) differentiated well as weaker students failed to show how ethanoic acid could act as a base and accept a proton.

Part (c)(i) was more straightforward but some students failed to calculate the concentration of the acid correctly and just used a number of moles. Part (c)(ii) differentiated well: many students realised a subtraction was needed in the calculation, but then failed to use the total volume to convert the amount, in moles, of H^+ ions to a concentration to calculate the pH.

Part (d)(i) was completed very well with most students gaining either 3 or 4 marks. In part (d)(iii) a significant number incorrectly used the original amount in moles of acid (0.0125) in their ratio. Even some of the strongest students struggled with the maths skills required and a frequent wrong answer was the inverse of 1.20 due to incorrect rearrangement. A significant number did not work out the hydrogen ion concentration and so lost M1 when they couldn't complete the rest of the calculation.

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Part (e) differentiated well with full descriptions seen in about a third of the answers and one mark gained by another third. In part (f) the first mark proved very accessible but the second proved trickier; many students showed poor maths skills and thought that K_a would equal 1 or zero.

Q7.

The first part of this question was answered well and few students did not score all three marks. The most common error was in the rearrangement of the K_a expression. Some students subtracted the ethanoate concentration from the ethanoic acid concentration to give a wrong ethanoic acid concentration, although they could gain M3 for a correct pH consequential on their H^+ concentration.

Part (b) discriminated slightly better as there was scope for a variety of errors. These included using the values given in part (a), no addition or error in addition to give the new concentration of ethanoic acid, no subtraction or error in subtraction to give the new concentration of the ethanoate salt, wrong rearrangement of the K_a expression or a combination of these. Students were given credit for correct working where appropriate.

Q8.

In part (a) the missing equilibrium sign was not always penalised and part (b) often had no reference to the equilibrium shift and over-complicated answers led to contradictions in responses.

Q9.

This question was generally well attempted, with most students scoring well in the mathematical sections. In part (a), most students gave the meaning of a weak acid as ‘only partially ionised or dissociated into ions’, and this was credited. The preferred answer was ☐only slightly ionised’. ‘Not fully ionised’ did not gain the mark. The equation in part (b) was poorly answered mainly because the formula for sodium carbonate was incorrect. In some cases, the formula of sodium hydroxide or sodium hydrogen carbonate was given. A common error in part (c) was to omit the factor of 2 when calculating the concentration of hydroxide ions from the concentration of calcium hydroxide. Parts (d)(i) and (d)(ii) were answered well but in part (d)(iii) many students used an expression for K_c with $[H^+]^2$ or could not rearrange the correct expression to find the concentration of sodium benzenecarboxylate. Students should be encouraged to use words in their answers to make it clear whether the numbers they write refer to amounts in moles or to concentrations and also to which substance they refer. Answers to part (e) included many wrong substances and showed that some students think that H_2 (or H^+) is present in the atmosphere or that carbonic acid can exist in an alkaline solution.

Q10.

Students found part (a) relatively easy. The most common errors were in part (a)(iii) where some students squared the hydrogen ion concentration.

The double arrow sign for an equilibrium was frequently missed in part (b)(i) and there were several instances where the wrong proton was lost from HCOOH. Only 33% of students scored all 3 marks in part (b)(iv). Some students lost M1 for confusing higher $[H^+]$ with higher pH. Some lost M3 because they wrote an explanation in general terms, “according to Le Chatelier’s principle” rather than suggesting that the position of equilibrium shifts to oppose a specific change, ie to reduce the temperature.

Part (c) was a good discriminator and the full range of marks was seen, although there

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were more than usual who gained high marks in what has, in the past, been seen as a difficult topic. In part (c)(i), some students couldn't rearrange the K_a expression correctly and wrote the acid and salt concentrations the wrong way round. Many calculated an 'excess' of methanoic acid by subtraction.

The calculation in part (c)(ii) proved to be the most difficult calculation on the paper. Most students scored M1, but several wrote nothing further. Many also gained M2 although adding and subtracting the wrong way round caused many to lose any further marks. Incorrect rearrangement of the K_a expression was again a problem.

Q11.

Part (a) was well known, but part (b) was much less well understood. In part (c), most students scored the first two marks but then failed to use their answers correctly to calculate the total volume. Some who did not read the question fully, added 25 cm^3 to their correct answer and so lost the final mark.

In part (d)(iii), a significant number could not correctly rearrange the simplified expression for K_c. A mark was allowed, in this part only, for a correct calculation of pH using their value of $[H^+]$ even if this was not the correct concentration.

In part (e), most scored the first two marks, but many then failed to recognise that, on adding alkali, the number of moles of acid would have decreased. Others were unable to rearrange the K_a expression correctly or attempted to use the equation $K_a = [H^+]^2/[HX]$.

Moles and concentration were often confused and many responses were also badly presented with little explanation. Such omission makes it difficult for examiners to award marks in an extended calculation if the answer is wrong.

Q12.

(a) In this part many students were unable to select a correct mixture, but were awarded a mark for an explanation which was incomplete or very vague. Students needed to mention the presence of both acid and salt in the mixture to merit the mark.

(b) In this part, many students confused a half equivalence mixture with a pH graph. An explicit statement that $[HA] = [A^-]$ was often omitted, and quite frequently was not penalised. It was surprising how many students used a pH value without taking the trouble to measure this value.

Q13.

Almost all students scored the mark in part (a), but in the rest of the parts of this question, there was less good understanding of the chemistry of weak bases and the operation of basic buffers. There were many incorrect answers in part (b)(i) where ammonia and ethanol were often given as the products of the reaction. This led to wrong answers to part (b)(ii). A number of students wrote 'inductive effect' in part (c) without any mention of what this applied to; the final mark was, however, often scored. Part (d) proved to be very difficult and although, in part (e), many students recognised that the added H^+ ions would react with OH^- ions in the solution, a large number failed to explain how the buffer would respond to this reaction.

Q14.

The early parts of this question were answered well, although in part (a)(iii), about a third of the candidates did not realise that adding water had no effect on the number of moles

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of acid present. Over two thirds of the candidates scored full marks in part 2(b); a common error for the others was to rearrange the expression for K_a incorrectly. In part 2(c), many answers stated general properties of a buffer solution, without giving any explanation specific to this situation.

It was pleasing to see that over 44% of the candidates gained full marks in part (d)(i). Many of the rest thought that addition of the salt to the solution of the acid changed the amount of acid present. Part (d)(ii) discriminated well and only the better candidates were able to calculate the amounts in moles of acid and of salt present in the solution after the addition of sodium hydroxide and then use these values correctly.

Q15.

This question was generally well answered and only rarely did candidates fail to follow the instructions to give their pH values to two decimal places.

In part (a)(ii) only a fifth of the candidates realised that sulfuric acid is diprotic and in part (b)(i) only two thirds of the entry could write a correct equation for the reaction of ethanoic acid with sodium hydroxide. The following titration calculation was very straightforward but was thought more complicated by many including those who introduced K_w. It was disappointing to see that only the very best candidates understood that sodium hydroxide solution reacts with carbon dioxide in the air and many candidates showed a strange understanding of the composition of air. Part (c)(ii) was well answered; nearly four fifths of candidates answered this part completely correctly. Answers to the unstructured buffer calculation in part (c)(iii) were also quite pleasing; the question differentiated well and over twenty percent of candidates gained full marks. Other candidates were hindered by poor mathematical skills.

Q17.

The standard expressions in part (a)(i) were answered well by almost all candidates, although some quote values for Kw and pH instead of reading the question carefully.

In part (a)(ii) some missed the essential point that in pure water, the concentrations of H^+ and OH^- ions are equal at all temperatures even if the pH scale is based on a value of Kw different from 1.0^{-14}. In part (a)(iii) most were able to calculate the number of moles of OH^- present as 1.0×10^{-3}, but many failed to realise that, in part (iv), when this number of moles were added to 998 cm^3 of water, the concentration of OH^- in the solution formed would be 1.0×10^{-3} mol dm^{-3}. A few failed to use the given value of Kw but many were able to calculate the correct answer of 10.40.

Part (b) was generally very well answered and a pH of 2.89 was the most common answer. Some candidates, gave the answer 5.77 by forgetting to take the necessary square root in their working.

Part (c) was a buffer calculation, an area which candidates traditionally find difficult. Disappointingly, this again proved the case despite the lead in to the question given in parts (i) and (ii). While most were able to calculate the initial number of moles of propanoic acid and almost as many could calculate the number of moles of acid present in the buffer solution formed, few gained many more marks. Many tried to calculate the concentrations of the acid and the salt formed failing to realise that the volume involved cancels. Many were unable to rearrange the expression for Ka and many confused the number of moles of propanoic acid with the number of moles of H^+ present inn the solution.

Q18.

Only the weakest failed to recognise the titration curves in part (a) or to give either of the

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indicators which changed colour above pH 7. The definition of pH was, as expected, well known, but many candidates were unable to complete the calculation of the concentration of potassium hydroxide in part (b)(ii) by using either K_w or the expression pH + pOH =14. Part (c)(i) was well done but many failed to recognise that the solution formed in part(c) was a buffer solution of the particular type where the moles of salt and moles of acid present were equal, so that the pH of the mixture equals the pK_a of the weak acid. It was pleasing that very few ignored the stated request to quote pH values to two decimal places.

Q19.

Most candidates scored full marks for a correct calculation in part (a). Parts (b)(i) and (ii) were also well answered but (b)(iii) proved to be more difficult and many candidates failed to state that, when half the acid had been neutralised, $[A^-] = [HA]$. Only the very best candidates stated correctly that on dilution the ratio $[A^-] : [HA]$ remains constant and, as a consequence, $[H^+]$ also remains constant. The calculations in part (d) were generally well done although one mark was lost by candidates who, in (d)(ii), calculated the total final volume of acid, 50.0 cm^3, and not the volume of water which must be added as required by the question.

Q20.

Most candidates took note of the request to give all pH values to 2 decimal places in this question. Part (a) was answered very well and some who scored no further marks in the whole question were able to answer this part correctly. Most candidates were able to describe what a *buffer solution* is and although any equation which correctly showed the removal of ethanoate ions and the formation of ethanoic acid was accepted in part (b)(ii), many were unable to give a correct answer.

Part (c) involved buffer solutions. Many answers showed that some candidates have still not mastered numerical questions about buffer solutions. A good proportion of the candidates were able to use the original values of the number of moles of ethanoic acid and of sodium ethanoate in one dm^3, i.e. the concentration of these species, to calculate the correct pH of the original buffer solution. A much smaller number was able to calculate the correct answer for the final pH of the buffer solution after the addition of 0.01 mol of hydrochloric acid. Only the best realised that the number of moles of acid would have gone up by 0.01 mol and the number of moles of ethanoate ions would have fallen by the same amount. However it was pleasing to see a good number of candidates gaining full marks in this question.

Q21.

High marks were scored in this question by the more able candidates but the question discriminated well and although parts (a) and (b) were well answered by most, the weaker candidates scored poorly in part (c).
In part (a), although the expression for K_a was well known, several candidates did not give the general expression for K_a and instead wrote the more specific $[H^+]^2/[HA]$. This expression was however credited in part (b). Candidates should be reminded that square brackets are essential in these expressions.
In part (b), many correct answers were given although, in the calculation, several candidates failed to take the square root correctly. A mark was awarded for the correct calculation of a pH value from their hydrogen ion concentration.
As reported regularly before, too many candidates seem unaware that pH values should be given to two decimal places; these two figures give the value to the appropriate precision. The numbers before the decimal point only give the powers of ten involved in the hydrogen ion concentration.
In part (c)(ii), most candidates were able to state that the pH would remain unchanged,

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but fewer explained clearly that the extra hydrogen ions were removed by reaction with the A^- ions from the salt. Only the most able candidates answered the calculation in part (c)(ii) correctly. Many gained a mark for the hydrogen ion concentration at pH = 3.59, but few were able to use or, more particularly, to rearrange the expression for K_a correctly to calculate the concentration of A^-.

Q22.

Only the best candidates correctly explained the solubility of ammonia in water by reference to hydrogen bonding between water and ammonia molecules. The equation for the reaction between ammonia and water was often given correctly but few stated that, because ammonia is a weak base, it reacts reversibly with water forming a solution containing a small concentration of hydroxide ions. Most, but certainly not all, candidates knew the meaning of the term *Bronsted-Lowry* acid and answered part (c) correctly. Answers to part (d) were, by contrast, rather disappointing with many vague or incorrect statements of the term *buffer solution*. The calculation in part (e)(i) was not well done. Many candidates used the relationship Ka = $[H^+]^2/[HA]$ which can only be used for a solution of a weak acid alone. Others failed to calculate the concentration of ethanoate ions in mol dm^{-3} before calculating the hydrogen ion concentration. Part (c)(ii) proved surprisingly difficult with only the better candidates giving the correct ionic equation.

Q23.

Parts (a) and (b) were well answered. Most candidates correctly calculated the volume of sodium hydroxide needed and although some candidates attempted to answer part (b)(i) in words, most were able to define pH as $-\log_{10}[H^+]$. The indicator expected in part (b)(iii) was the familiar phenolphthalein, but thymol blue (the correct indicator to the January 2002 pH question) was a common and correct answer.

In part (c), the answer that weak acids are only *slightly dissociated* in water was required, rather than not *fully dissociated*, since even strong acids may not be fully dissociated. In part(c)(ii), the general expression for Ka was required, i.e. $[H^+][A^-]/[HA]$ rather than the more particular $[H^+]^2/[HA]$ which only applies to solutions of weak acids alone. The latter expression could however gain credit in the calculation in part (iii). This was answered well by many candidates although some used the number of moles of HA in the calculation rather than its concentration. Not all candidates seemed to be aware that **it is important that pH values are given to two decimal places**; these two figures give the value to the appropriate precision. The numbers before the decimal point only give the powers of ten involved in the hydrogen ion concentration.

Part (d) discriminated well. The better candidates realised that point b was the pH at half equivalence, i.e. when $[A^-] = [HA]$ such that pH = pK_a.

Q24.

It is important that pH values are given to two decimal places; these two figures give the value to the appropriate precision. The numbers before the decimal point only give the powers of ten involved in the hydrogen ion concentration.

Three pH values were required in this question and answers to one decimal place only were penalised, but only once on this occasion.

The question involved three calculations of pH. First the pH of a solution of ethanoic acid was required. This was usually well done even by candidates of moderate ability.

The second situation involved a buffer solution formed when some of the weak acid has been reacted with alkali. This was done less well. Many candidates correctly calculated

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the number of moles of acid used, the number of moles of hydroxide added and hence the number of moles of acid remaining. However, these values were then too often used in a calculation which assumed only a weak acid was present, as in the first part of the question rather than an acidic buffer solution. Although many candidates still seemed unfamiliar with calculations of this type, there was a definite improvement in the numbers gaining full marks compared with the January CHM4 paper.

The last part of the question involved finding the pH of the resulting solution of excess potassium hydroxide produced when all the ethanoic acid is used up. This part was usually answered more successfully than the second part.

Q25.

Many candidates scored well in parts (a) and (b) but very few seemed confident in dealing with quantitative buffer calculations in part (c). The main errors in part (a)(i) were to write the expression for K_a as

$$K_a = \frac{[H^+]^2}{[CH_3COOH]} \text{ or } \frac{[H+]^2}{[HA]} \text{ rather than } \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

The first is not a general statement while the second does not show that the acid is ethanoic. Despite the loss of this first mark many candidates were able to gain all the remaining marks in part (a). Marks were lost by those who did not take the square root to obtain the hydrogen ion concentration and also by those who gave the pH to one decimal place only. It is important that pH values are given to two decimal places; these two figures give the value to the appropriate precision.
The numbers before the decimal point only give the powers of ten involved in the hydrogen ion concentration. Part (b)(i) was the best answered part of the question and most candidates gained both marks for the calculation. In part (b)(ii) most realised that the titration involved a strong base and a weak acid but the indicator chosen was often bromothymol blue rather than thymol blue, despite the correct explanation that the equivalence point must be above pH 7 for this combination of acid and base. Part (c) was not attempted by a large number of candidates. Of those who did attempt the question, most calculated the number of moles of sodium hydroxide but then used K_w in their calculation as if there was a mixture of strong acid and strong base present. Of those who did realise that an acid buffer had been produced by the reaction of an excess of ethanoic acid with sodium hydroxide, a large proportion forgot to subtract the number of moles of acid reacted from the initial number of moles of acid before substituting in the expression for K_a and gave a pH of 4.12. This answer received four marks out of the six available for the correct answer, 4.23.

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Q1.

(a) Ans = C

1

(b) $[H^+] = \sqrt{K_w} = \sqrt{2.93 \times 10^{-15}}$ $(= 5.41 \times 10^{-8})$

1

pH = $(-\log (5.41 \times 10^{-8}) = \underline{7.27}$

Must be 2dp

7.27 scores 2 marks

1

(c) $[H^+] = [OH^-]$

allow description in words

equal moles / quantities / numbers / ratio of H^+ and OH^-

1

(d) $[OH^-] = 0.0131 \underline{\times 2} = 0.0262$

pH = 12.95 scores 3 marks

pH = 12.42 scores 2 marks ($K_w = 1 \times 10^{-14}$)

pH = 12.65 scores 1 mark (not multiplied by 2)

pH = 12.35 scores 1 mark (divided by 2)

pH = 12.12 scores 0 marks (no × 2 and wrong K_w)

1

$[H^+] = (K_w / [OH^-]) = 2.93 \times 10^{-15} / 0.0262 (= 1.118 \times 10^{-13})$

1

pH = $(-\log (1.118 \times 10^{-13}) = 12.9514 = 12.95$
Or
$[OH^-] = 0.0131 \times 2 = 0.0262$
pOH = $(-\log 0.0262) = 1.5817$
pH = $(-\log K_w - \text{pOH} = -\log 2.93 \times 10^{-15} - 1.58 = 14.53 - 1.58) = 12.95$

allow to 2dp or more

1

(e) smaller / lower pH / less alkaline / more acidic

If not smaller CE = 0/2

Allow pH number between 8 and 12

1

(magnesium hydroxide) is less soluble / sparingly soluble/ solubility of hydroxide increases down group II

M2 dependent on M1 but if blank mark on

Ignore concentration and dissociation

Ignore incorrect formula

Do not allow $Mg(OH)_2$ is insoluble

1

[9]

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Q2.

B

[1]

Q3.

(a) Burette

1

Because it can deliver variable volumes

1

(b) The change in pH is gradual / not rapid at the end point

1

An indicator would change colour over a range of volumes of sodium hydroxide

Allow indicator would not change colour rapidly / with a few drops of NaOH

1

(c) $[H^+] = 10^{-pH} = 1.58 \times 10^{-12}$

1

$K_w = [H^+]\,[OH^-]$ therefore $[OH^-] = K_w / [H^+]$

1

Therefore, $[OH^-] = 1 \times 10^{-14} / 1.58 \times 10^{-12} = 6.33 \times 10^{-3}$ (mol dm^{-3})

Allow 6.31–6.33 × 10^{-3} (mol dm^{-3})

1

(d) At this point, $[NH_3] = [H^+]$

Therefore $K_a = \dfrac{[H^+]^2}{[NH_4^+]}$

1

$[H^+] = 10^{-4.6} = 2.51 \times 10^{-5}$

1

$K_a = (2.51 \times 10^{-5})^2 / 2 = 3.15 \times 10^{-10}$ (mol dm^{-3})

Allow 3.15 – 3.16 × 10^{-10} (mol dm^{-3})

1

(e) When $[NH_3] = [NH_4^+]$, $K_a = [H^+]$ therefore $-\log K_a = -\log [H^+]$

Answer using alternative value

1

Therefore pH = $-\log_{10}(3.15 \times 10^{-10}) = 9.50$

M2 pH = $-\log_{10}(4.75 \times 10^{-9}) = 8.32$

Allow consequential marking based on answer from part (d)

1

[12]

Q4.

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(a) Proton donor

1

(b) Completely ionises to give H^+ ions in water

1

(c) 0.058 mol dm^{-3}

1

1.24

1

(d) Amount of NaOH = 5.25×10^{-3}

1

Since 1:1 reaction amount of OH^- ions in excess

= $5.25 \times 10^{-3} - 1.45 \times 10^{-3}$ mol

= 3.80×10^{-3} moles OH^-

1

$[OH^-] = 3.80 \times 10^{-3} \times 1000/60 = 0.0633$

1

$K_w = [H^+][OH^-$ so $H^+ = \frac{10^{-14}}{0.0633} = 1.58 \times 10^{-13}$

1

pH = 12.80

1

(e) Amount of OH^- added 1.5 / 40 = 0.0375 mol

1

Use of 1:1 ratio to calculate amount of A^- formed = 0.0375 mol

1

Amount of weak acid initially = 1 × 0.15 = 0.150 mol so amount of weak acid after addition of NaOH = 0.150 − 0.0375 = 0.1125

If M3 incorrect can only score max of 3 marks

1

$[H^+] = K_a [HA]/[A^-]$ or $[H^+] = 1.79 \times 10^{-5} \times 0.1125/0.0375$

1

$= 5.37 \times 10^{-5}$

1

pH = 4.27

1

[15]

Q5.

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B

[1]

Q6.

(a) $CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$
OR

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

Must show $\rightleftharpoons$
Allow CH_3CO_2H, $CH_3CO_2^-$
Ignore state symbols

1

(b) $(CH_3COOH + \underline{HNO_3} \longrightarrow CH_3COOH_2^+ + NO_3^-)$

IGNORE $\rightleftharpoons$
Allow CH_3CO_2H, $CH_3CO_2H_2^+$, $CH_3C^+(OH)_2$

1

(c) (i) (new $[HNO_3] = [H^+] = \frac{100}{150} \times 0.0125$)

M1 $[H^+] = 8.3(3) \times 10^{-3}$ (mol dm^{-3})
OR

new$[HNO_3]$ = $\frac{\text{mol } HNO_3}{\text{total vol}} = \frac{1.25 \times 10^{-3}}{150 \times 10^{-3}}$

1

M2 pH = − log M1 OR 2.08
Must be 2dp
Allow correct pH conseq to their $[H^+]$ *concentration*

1

(ii) M1 mol NaOH (= $50 \times 10^{-3} \times 0.0108$) = 5.40×10^{-4}

1

M2 Subtraction of M1 from moles of HNO_3 (1.25×10^{-3} or conseq from 1c(i))

Excess mol $H^+ = 7.10 \times 10^{-4}$

M2 allow ecf for subtraction of mol
If no subtraction, no further marks

1

M3 $[H^+] = \frac{M2}{150 \times 10^{-3}}$ OR $\frac{7.10 \times 10^{-4}}{150 \times 10^{-3}} = 4.73 \times 10^{-3}$

M3 <u>if no use of volume, no further marks</u> (pH=3.15)
If incorrect volume used, can score M4

1

M4 pH = -log M3 OR 2.32

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M4 Allow 2.33 Must be 2 dp

1

(d) (i) M1 $K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$

Penalise ( ) once here Not [H+][A-] / [HA]

If K_a expression wrong – Allow correct pH conseq to their $[H^+]$ concentration M4 only

1

M2 $K_a = \frac{[H^+]^2}{[CH_3COOH]}$ or with numbers or with HA

1

M3 $[H^+] = [\sqrt{(1.74 \times 10^{-5} \times 0.0125)}] = 4.66 \times 10^{-4}$

Mark for answer

1

M4 pH = 3.33

Must be 2dp

Allow correct pH conseq to their $[H^+]$ concentration

(pH = 3.83 can score M1, M2 and M4)

1

(ii) Sodium ethanoate

Ignore formula

Allow sodium acetate

1

(iii) M1 $[H^+] = 1.45 \times 10^{-5}$

Accept 1.445×10^{-5} or 1.4×10^{-5}

1

M2

$$\frac{[salt]}{[acid]} \text{ (OR } \frac{[CH_3COO^-]}{[CH_3COOH]} = \frac{Ka}{[H^+]} \text{)= } \frac{1.74 \times 10^{-5}}{1.45 \times 10^{-5}}$$

If M1 incorrect CE=0

Inclusion of 0.0125 in calculation can only score M1

1

M3 1.2(0)

Ignore units

1.4×10^{-5} gives 1.24

1

(e) M1 (Electronegative) chlorine withdraws electrons

Allow Cl has negative inductive effect

1

M2 Stabilises/reduces charge on COO-

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OR weakens O-H bond

OR makes O-H more polar

Ignore chloroethanoic acid dissociates more readily

Mark independently

1

(f) M1 Strong acids (almost) completely dissociated/ionised

OR not an equilibrium

OR equilibrium lies far to the right

Cannot have K_a value for a reaction not in equilibrium scores both marks

1

M2 K_a value for strong acids tends to infinity/is very large
OR can't divide by zero in K_a

1

[20]

Q7.

(a) $[H_2O]$ is very high (compared with $[H^+]$ and $[OH^-]$)
OR
Very few H^+ and OH^- ions
OR
Only / very slightly dissociates
OR
Equilibrium lies far to the left

Not partially dissociates

M1
1

$[H_2O]$ is (effectively) constant
OR is incorporated into the constant K

Allow changes by only a very small amount

M2
1

(b) (Dissociation OR breaking bonds) is endothermic

1

∴ Equilibrium moves to RHS (at higher T) to absorb heat or to lower T or oppose increase in T

Allow to oppose change only if increase T mentioned

1

(c) $[H^+]$ = $\sqrt{K_w}$ (or = $\sqrt{5.48 \times 10^{-14}}$)

Correct pH answer scores 3

1

If wrong method no marks

Using alternative K_w (1.00×10^{-14}) gives pH = 7.00 which scores 1

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= 2.34×10^{-7}

1

pH = 6.63

Final answer must have 2dp

1

(d) $[H^+]$ = K_w / $[OH^-]$ or (= 5.48×10^{-14} / 0.12)

Correct pH answer scores 3

1

If wrong method no marks

If use alternative K_w (1.00×10^{-14}) again, do not penalise repeat error so pH = 13.08 scores 3

= 4.566×10^{-13}

1

pH = 12.34

If use alternative K_w (1.00×10^{-14}) ***not*** *as a repeat error, pH = 13.08 scores 1*

If AE in K_w value made in part (c) is repeated here, do not penalise again.

Final answer must have 2dp, but if dp penalised in (c) allow more than 2dp here but not fewer.

1

[10]

Q8.

(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.

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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 = 12.38 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 = 3.06

Must be 2 decimal places ie 3.1 loses M3.

1

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

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Correct answer for mass with or without working scores 5.
Allow 1 × 10^{-4}.

1

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

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

1

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

And M5 for 7.57 × 10^{-5} g.

1

M4 = 7.572 × 10^{-3}

1

M5 Mass (C_6H_5COONa) = 7.572 × 10^{-3} × 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]

Q9.

(a) **M1** $[H^+] = 0.0170$

1

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M2 pH = 1.77

2 dp

Allow M2 for correct pH calculation from their wrong [H⁺] for this pH calculation only

1

(b) (i)

$$K_a = \frac{[H^+][X^-]}{[HX]^2}$$ Ignore $$K_a = \frac{[H^+]^2}{[HX]}$$

Penalize missing [ ] here ***and not elsewhere***

Allow HA instead of HX

1

(ii) **M1** $[H^+] = 10^{-2.79}$ OR $1.6218\ldots \times 10^{-3}$

If [H⁺] wrong, can only score M2

1

M2 $$K_a = \frac{[H^+]^2}{[HX]}$$ OR $$\frac{[1.62 \times 10^{-3}]^2}{[0.0850]}$$

Allow HA instead of HX

1

M3 $K_a = 3.09 \times 10^{-5}$ 3sfs min

(allow 3.10×10^{-5} if 1.6218 rounded to 1.622)

Ignore units

If [HX] used as $(0.0850 - 1.62 \times 10^{-3})$

this gives $K_a = 3.15 \times 10^{-5}$

$(0.0016)^2/0.085 = 3.01 \times 10^{-5}$ scores 2 for AE

1

(c) **M1** mol OH^- (= $(38.2 \times 10^{-3}) \times 0.550$)

= $2.10(1) \times 10^{-2}$ or 0.0210(1)

Mark for answer

1

M2 Mol H^+ (= $(25.0 \times 10^{-3}) \times 0.620$)

= 1.55×10^{-2} or 0.0155

Mark for answer

1

M3 excess mol OH^- = $5.5(1) \times 10^{-3}$

Allow conseq for M1 – M2

If wrong method *e.g. no subtraction or use of √*

can only score max of M1, M2, M3 and M4.

1

M4 $[OH^-] = 5.51 \times 10^{-3} \times \frac{10^3}{63.2}$ [= 0.08718 (0.0872)]

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OR $[OH^-] = 5.5 \times 10^{-3} \times \frac{10^3}{63.2} = 0.0870(2)$

(M1 – M2) / vol in dm^3 mark for dividing by volume
(take use of 63.2 without 10^{-3} as AE so 9.94 scores 5)
If no use or wrong use of vol lose M4 & M6
Can score M5 for showing (10^{-14}/ their XS alkali)

1

M5 $[H^+] = \frac{10^{-14}}{0.08718} = 1.147 \times 10^{-13}$

OR $\frac{10^{-14}}{0.0870} = 1.149 \times 10^{-13}$

OR pOH = 1.06

If no use or wrong use of K_w or pOH no further marks

1

M6 pH = 12.9(4) allow 3sf

If vol missed score max 4 for 11.7(4)
If acid– alkali reversed max 4 for pH = 1.06
Any excess acid – max 4

1

[12]

Q10.

(a) (i) $-\log[H^+]$ or $\log 1/[H^+]$

penalise missing square brackets here only

1

(ii) 0.81

2dp required, no other answer allowed

1

(iii) **M1** mol $H^+ = 1.54 \times 10^{-3}$

if wrong no further mark
if 1.5×10^{-3} allow M1 but not M2 for 2.82

1

M2 pH = 2.81

allow more than 2dp but not fewer

1

(b) **M1** $[H^+] = 3.31 \times 10^{-3}$

1

M2 $K_a = \frac{[H^+][X^-]}{[HX]}$ or $\frac{[H^+]^2}{[HX]}$ or using numbers

do not penalise ( ) or one or more missing [ ]

1

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M3 $[HX] = \frac{[H^+]^2}{K_a} = \frac{(3.31 \times 10^{-3})^2}{4.83 \times 10^{-5}}$

allow conseq on their $[H^+]^2/(4.83 \times 10^{-5})$ (AE)
if upside down, no further marks after M2

1

M4 [HX] = 0.227

allow 0.225 – 0.23

1

(c) **M1** extra/added OH^- removed by reaction with H^+ or the acid

1

M2 correct discussion of equn shift i.e. $HX \rightleftharpoons H^+ + X^-$ moves to right

1

OR

ratio $\frac{[HX]}{[X^-]}$ remains almost constant

(d) (i) **M1** mol HY = $(50 \times 10^{-3}) \times 0.428 = 0.0214$

OR $[Y] = .0236 \times \frac{1000}{50} = 0.472$

mark for answer

1

M2 $[H^+] = 1.35 \times 10^{-5} \times \frac{0.0214}{0.0236}$

OR $1.35 \times 10^{-5} = [H^+] \times \frac{0.0236}{0.0214}$

OR $[H^+] = 1.35 \times 10^{-5} \times \frac{0.428}{0.472}$

OR $1.35 \times 10^{-5} = [H^+] \times \frac{0.472}{0.428}$

must be numbers not just rearrangement of Ka expression
If either HY value or Y^- value wrong, (apart from AE -1) lose M2 and M3

1

M3 $[H^+] = 1.22 \times 10^{-5}$

mark for answer

1

M4 pH = 4.91

allow more than 2dp but not fewer

allow M4 for correct pH calculation using their $[H^+]$ (this applies in (d)(i) only)

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1

If Henderson Hasselbalch equation used:

M1 mol HY = $(50 \times 10^{-3}) \times 0.428 = 0.0214$

OR [Y] = .0236 × $\frac{1000}{50} = 0.472$

mark for answer

1

M2 p*K*a = 4.87

1

M3 $\log\left(\frac{0.0214}{0.0236}\right) = -0.043$

$\log\left(\frac{0.428}{0.472}\right) = -0.043$

If either HY value or Y^- value wrong, (apart from AE-1) lose M3 and M4

1

M4 pH = 4.87 – (– 0.043) = 4.91

allow more than 2dp but not fewer

1

(ii) Can score full marks for correct consequential use of their HY and Y^- values from d(i)

M1 Mol HY after adding NaOH = $0.0214 - 5.0 \times 10^{-4} = 0.0209$

AE in subtraction loses just M1
If wrong initial mol HY (i.e. not conseq to part d(i)) or no subtraction or subtraction of wrong amount, lose M1 and M3

1

M2 Mol Y^- after adding NaOH = $0.0236 + 5.0 \times 10^{-4} = 0.0241$

AE in addition loses just M2
If wrong mol Y^- (i.e. not conseq to part d(i)) or no addition or addition of wrong amount lose M2 and next mark gained

1

M3 $[H^+] = 1.35 \times 10^{-5} \times \frac{0.0209}{0.0241}$ $(= 1.17 \times 10^{-5})$

if convert to concentrations

$[H^+] = 1.35 \times 10^{-5} \times \frac{0.418}{0.482}$ $(= 1.17 \times 10^{-5})$

1

if HY/Y^- upside down, no further marks

M4 pH = 4.93

allow more than 2dp but not fewer

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NOT allow M4 for correct pH calculation using their $[H^+]$ (this allowance applies in (d)(i) only)

1

If Henderson Hasselbalch equation used:

Can score full marks for correct consequential use of their HY and Y^- values from d(i)

M1 Mol HY after adding NaOH = $0.0214 - 5.0 \times 10^{-4} = 0.0209$

AE in subtraction loses just M1
If wrong initial mol HY (i.e. not conseq to part d(i)) or no subtraction or subtraction of wrong amount lose M1 and M3

1

M2 Mol Y^- after adding NaOH = $0.0236 + 5.0 \times 10^{-4} = 0.0241$

AE in addition loses just M2
If wrong mol Y^- (i.e. not conseq to part d(i)) or no addition or addition of wrong amount lose M2 and next mark gained

1

M3 $\log \left(\frac{0.0209}{0.0241}\right) = -0.062$

if HY/Y^- upside down, no further marks

1

M4 pH = 4.87 – (– 0.062) = 4.93

allow more than 2dp but not fewer

1

[18]

Q11.

(a) (i) $-\log[H^+]$

*penalise missing [ ] here **and not elsewhere***

1

(ii) $[H^+][OH^-]$

Allow ( ) brackets, but must have charges

1

(iii) Mark independently from a(ii)

$[H^+] = 10^{-13.72} = 1.905 \times 10^{-14}$

If wrong no further mark

1

$K_w = 1.905 \times 10^{-14} \times 0.154 = = (2.93 - 2.94) \times 10^{-15}$

1

(b) (i) $Ka = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$

Must have charges and all brackets, allow ( )
Acid/salt shown must be CH_3COOH not HA

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and correct formulae needed

1

(ii) **In pH values penalise fewer than 3 sig figs each time but allow more than 2 dp**
For values above 10, allow 3sfs - do not insist on 2 dp

$$K_a = \frac{[H^+]^2}{[CH_3COOH]}$$

Allow HA

1

($[H^+]^2 = 1.75 \times 10^{-5} \times 0.154 = 2.695 \times 10^{-6} = 2.70 \times 10^{-6}$)
If √ shown but not done gets pH = 5.57 (scores 2)

$[H^+] = 1.64 \times 10^{-3}$

Allow mark for pH conseq to their [H+] ***here only***

1

pH = 2.78 or 2.79

1

(c) (i) **In pH values penalise fewer than 3 sig figs each time but allow more than 2 dp**

For values above 10, allow 3sfs - do not insist on 2 dp

M1 Initially

mol OH^- = $(10 \times 10^{-3}) \times 0.154$ **and**

mol HA = $(20 \times 10^{-3}) \times 0.154$

or mol OH^- = 1.54×10^{-3} **and** mol HA = 3.08×10^{-3}

1

M2 $[H^+] = K_a \frac{[CH_3COOH]}{[CH_3COOH^-]}$

or with numbers

Allow Henderson Hasselbach

$$pH = pK_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]}$$

M3 mol ethanoic acid left = (mol ethanoate ions) = 1.54×10^{-3}

$K_a = [H^+]$ **or** $pH = pK_a$ scores **M1**, **M2** and **M3**

1 If either mol acid in mixture or mol salt wrong - max 2 for M1 and M2

Any mention of $[H^+]^2$ - max 2 for M1 and M3

1

M4 pH (= - log 1.75×10^{-5}) = 4.76 or 4.757

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Not 4.75

1

If no subtraction (so mol ethanoic acid in buffer = original mol)
pH = 4.46 scores 2 for **M1** and **M2**
If $[H+]^2$ used, pH = 3.02 scores 2 for **M1** and **M3**

(ii) **In pH values penalise fewer than 3 sig figs each time but allow more than 2 dp**
For values above 10, allow 3sfs - do not insist on 2 dp

M1 XS mol KOH (= $(20 \times 10^{-3}) \times 0.154$) = 3.08×10^{-3}

If no subtraction: max 1 for correct use of volume
No subtraction and no use of volume scores zero
If wrong subtraction or wrong moles
*Can only score **M2** and **M3** for process*

1

M2 $[OH^-] = 3.08 \times 10^{-3} \times \frac{10^3}{60} = 0.0513(3)$

*Mark for dividing their answer to **M1** by correct volume (method mark)*
*If no volume or wrong volume or multiplied by volume, max 2 for **M1** and **M3** process*

1

M3 $[H^+] = \frac{10^{-14}}{0.05133}$ (= 1.948×10^{-13} to 1.95×10^{-13})

or pOH = 1.29

*Mark for K_w divided by their answer to **M2***
If pOH route, give one mark for 14 – pOH

1

M4 pH = 12.7(1)

Allow 3sf but not 12.70

1

If no subtraction and no use of volume (pH = 11.79 scores zero)
If no subtraction, max 1 for correct use of volume, ($60cm^3$)
(pH = 13.01 scores 1)
If volume not used, pH = 11.49 (gets 2)
If multiplied by vol, pH = 10.27 (gets 2)

[16]

Q12.

(a) (i) $-\log[H^+]$

*Penalise missing [ ] here **and not elsewhere***

1

(ii) $[H^+][OH^-]$

1

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(b) (i) $[H^+] = 2.34 \times 10^{-7}$

1

pH = 6.63

Penalise fewer than 3 sig figs but allow more than 2 dp

1

(ii) $[H^+] = [OH^-]$

1

(iii) **M1** $[H^+] = K_w/[OH^-]$

if upside down or CE, allow M3 only for correct use of their $[H^+]$

1

M2 $(= 5.48 \times 10^{-14}/0.140) = 3.91 \times 10^{-13}$

1

M3 pH = 12.4(1)

not 12.40 (AE from 12.407)

1

Penalise fewer than 3 sig figs but allow more than 3 sfs
For values above 10, allow 3sfs - do not insist on 2 dp.
For values below 1, allow 2dp – do not insist on 3 sig figs
Not allow pH = 14 – pOH but can award M3 only for pH = 13.1(46)
Can award all three marks if $pK_w = 13.26$ is used

(c) **M1** mol NaOH = mol OH^- = $(30 \times 10^{-3}) \times 0.20 = 6.0 \times 10^{-3}$

mark for answer

1

M2 mol H_2SO_4 = $(25 \times 10^{-3}) \times 0.15 = 3.75 \times 10^{-3}$

mark for answer

1

M3 mol H^+ = $(25 \times 10^{-3}) \times 0.15 \times 2 = 7.5 \times 10^{-3}$
OR XS mol H_2SO_4 = 0.75×10^{-3}

if factor of 2 missed or used wrongly, CE - lose M3 and next mark gained. In this case they must then use K_w to score any more.
see examples below

1

M4 XS mol H^+ = 1.5×10^{-3}

1

M5 $[H^+] = (1.5 \times 10^{-3}) \times (1000/55) = 0.0273$

if no use or wrong use of volume, lose M5 and M6 except if 1000 missed
AE –1 (pH = 4.56)

1

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M6 pH = 1.56

Penalise fewer than 3 sig figs but allow more than 3 sfs
For values above 10, allow 3sfs - do not insist on 2 dp.
For values below 1, allow 2dp – do not insist on 3 sig figs

1

[14]

Q13.

(a) –log [H^+]

ecf if [ ] wrong and already penalised

1

4.57 × 10^{-3}

allow 4.6 × 10^{-3}
ignore units

1

(b) (i) $K_a = \frac{[H^+][X^-]}{[HX]}$ allow HA etc

not $\frac{[H^+]^2}{[HX]}$ *but mark on*
If expression wrong allow conseq units in (ii)
but no other marks in (ii)

1

(ii) $\frac{[H^+]^2}{[HX]} = \frac{(4.57 \times 10^{-3})^2}{[0.150]}$

If use 4.6 × 10^{-3}

1

K_a = 1.4(1) × 10^{-4} and pKa = 3.85

= 1.39 × 10^{-4}

allow 1.39 – 1.41 × 10^{-4} mol dm^{-3}

1

(iii) pK_a = 3.86

Penalise dp of final answer < or > 2 in pH once in paper

1

(c) (i) $\frac{30}{1000}$ × 0.480 = 0.0144 or 1.4(4) ×10^{-2}

Mark is for answer (M1)

1

(ii) $\frac{18}{1000}$ × 0.350 = 0.0063 or 6.3 × 10^{-3}

Mark is for answer (M2)

1

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(iii) $0.0144 - 2(0.0063) = 1.80 \times 10^{-3}$

M3 is for (i) – 2(ii)
If x 2 missed, CE i.e. lose M3 and the next mark gained

1

(iv) $1.80 \times 10^{-3} \times \frac{1000}{48} = 0.0375$ (0.038)

M4 is for answer

If vol is not 48×10^{-3} (unless AE) lose M4 and next mark gained
If multiply by 48 - this is AE - i.e. lose only M4
If multiply by 48×10^{-3} this is AE - i.e. lose only M4

1

(v) $10^{-14} / 0.0375$ ($10^{-14} / 0.038$)

M5 for $K_w/[OH^-]$

1

($= 2.66 \times 10^{-13}$) ($= 2.63 \times 10^{-13}$)

or pOH

or pOH = 1.426 (or pOH = 1.420)

If no attempt to use K_w or pOH lose both M5 and M6

1

pH = 12.57 (12.58) M6

Allow M6 conseq on AE in M5 if method OK

1

[13]

Q14.

(a) (i) $[H^+][OH^-]$

1

$-\log [H^+]$

1

(ii) $[H^+] = [OH^-]$

1

(iii) $(2.0 \times 10^{-3}) \times 0.5 = 1.0 \times 10^{-3}$

1

(iv) $[H^+] = \frac{4.02 \times 10^{-14}}{1.0 \times 10^{-3}}$ ($= 4.02 \times 10^{-11}$)

1

pH = 10.40

1

(b) (i) $K_a = \frac{[H^+][CH_3CH_2COO^-]}{[CH_3CH_2COOH]}$

1

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$= \frac{[H^+]}{[CH_3CH_2COOH]}$

1

$[H^+] = \sqrt{(1.35 \times 10^{-5}) \times 0.125}$ $(= 1.30 \times 10^{-3})$

1

pH = 2.89

1

(c) (i) $(50.0 \times 10^{-3}) \times 0.125 = 6.25 \times 10^{-3}$

1

(ii) $(6.25 \times 10^{-3}) – (1.0 \times 10–3) = 5.25 \times 10^{-3}$

1

(iii) mol salt formed = 1.0×10^{-3}

1

$[H^+] = K_a \times \frac{[CH_3CH_2COOH]}{[CH_3CH_2COO–)}$

1

$= (1.35 \times 10^{-5}) \times \frac{(5.25 \times 10^{-3})/V}{(1.0 \times 10^{-3})/V}$ $(= 7.088 \times 10^{-5})$

1

pH = 4.15

1

[16]

Q15.

(a) k = rate/$[CH_3CH_2COOCH_3][H^+]$

1

or

$= \frac{1.15 \times 10^{-4}}{(0.150)(0.555)}$

= 1.38×10^{-3} to 1.4×10^{-3}

1

$mol^{-1}\ dm^3\ s^{-1}$

1

(b) ans = rate constant × (½ × 0.150) × (½ × 0.555)
ignore units

= rate constant × 0.0208

2.88×10^{-5} (1.38×10^{-3} gives 2.87×10^{-5})

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Allow 2.87 – 2.91 × 10^{-5} (1.4 × 10^{-3} gives 2.91 × 10^{-5})

1

(c) $[H^+]$ = rate/ $k[CH_3COOCH_2CH_3]$

1

$$= \frac{4.56 \times 10^{-5}}{(8.94 \times 10^{-4})(0.123)}$$

= 0.415 (0.4146)

1

pH = 0.38 mark independently

$[H^+]$ = 0.41 gives pH = 0.39

1

[7]

Q16.

(a) Concentration of acid: $m_1v_1 = m_2v_2$ hence $25 \times m_1 = 18.2 \times 0.150$

OR

moles NaOH = 2.73 ×10^{-3};

1

$m_1 = 18.2 \times 0.150/25 = 0.109$;

1

(b) (i) $K_a=[H^+][A^-]/[HA]$ *not* $K_a = [H^+]^2 / [HA]$;

1

(ii) $pK_a = -\log K_a$;

1

(iii) $[A^-] = [HA]$;

1

hence $K_a = [H^+] [A^-] / [HA] = [H^+]$

and $-\log K_a = -\log[H^+]$;

1

(c) ratio $[A^-]$: [HA] remains constant;

1

hence as $[H^+] = K_a [HA] / [A^-]$; $[H^+]$ remains constant;

1

(d) (i) pH of 0.250 mol dm-^{3} HCl = 0.60
and pH of 0.150 mol dm-^{3} HCl = 0.82;

1

pH change = 0.22;

1

(ii) moles HCl = $30 \times 0.250 \times 10^{-3} = v \times 0.150 \times 10^{-3} = 7.50 \times 10^{-3}$

OR

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v = 30 × 0.250 × 10^{-3}/ 0.150 × 10^{-3} =50;

1

water added = 50 – 30 = 20 cm^3;

1

[12]

Q17.

C

[1]

Q18.

B

[1]

Q19.

Penalise pH given to 1 dp <u>first</u> time it would have scored only

(a) (i) $K_w = [H^+]\,[OH^-]$ **(1)**

(ii) $pH = -\log [H^+]$ **(1)**
or in words or below unless contradiction

(iii) *Calculation*: $[H^+] = \sqrt{5.48 \times 10^{-14}}$ **(1)**

$= 2.34 \times 10^{-7}$

$\therefore$ pH = 6.63 or 6.64 **(1)**

Explanation: pure water $\therefore$ $[H^+] = [OH^-]$ **(1)**

5

(b) (i) $[OH^-] = 0.150$ $\therefore$ $[H^+] = 10^{-14}/0.15 = 6.66 \times 10^{-14}$

or pOH = 0.82

$\therefore$ pH = 13.18 **(1)**

or pH= 13.17

(ii) moles OH^- = (35 × 10^{-3}) × 0.150 = 5.25 × 10^{-3} **(1)**[a]

moles H^+ = (40 × 10^{-3}) × 0.120 = 4.8(0) × 10^{-3} **(1)**[b]

$\therefore$ excess moles of OH^- = 4.5 × 10^{-4} **(1)**[c]

$\therefore$ $[OH^-]$ = (4.5(0) × 10^{-4}) × 1000/<u>75</u>[d] **(1)**[e]
= 6.0(0) x 10^{-3}

$[H^+] = \frac{10^{-14}}{6.00 \times 10^{-3}}$ = 1.66 × 10^{-12} or pOH = 2.22

$\therefore$ pH = 11.78 **(1)**[f]

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or 11.77

8

(c) (i) $K_a = \frac{[H^+][X^-]}{[HX]}$ **(1)**

(ii) $[H^+] = 1.80 \times 10^{-2} \times 0.150 = 2.70 \times 10^{-3}$ (1)

$K_a = \frac{[H^+]^2}{[HX]}(1) = \frac{(2.70 \times 10^{-3})^2}{0.150}$ $= 4.86 \times 10^{-5}$ **(1)** mol dm^{-3} **(1)**

or $\frac{(2.70 \times 10^{-3})^2}{0.1473}$ $= 4.95 \times 10^{-5}$

5

Notes

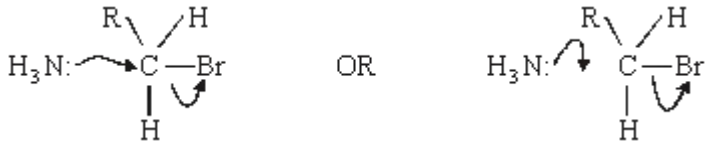
(a) If K_w includes H_2O allow 6.63 if seen otherwise no marks likely

(b) (ii) If no vol, max 4 for a, b, c, f answer = 10.65
If wrong volume max 5 for a, b, c, e, f
If no substraction max 3 for a, b, d
If missing 1000 max 5 for a, b, c, d, f answer = 8.78
If uses excess as acid, max 4 for a, b, d, f answer = 2.22
If uses excess as acid and no volume, max 2 for a, b answer = 3.35

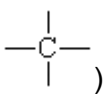
(c) If wrong K_a in (i) max 2 in part (ii) for $[H^+]$ **(1)** and conseq units **(1)**
but mark on fully from minor errors
eg no [ ] or charges missing

Organic points

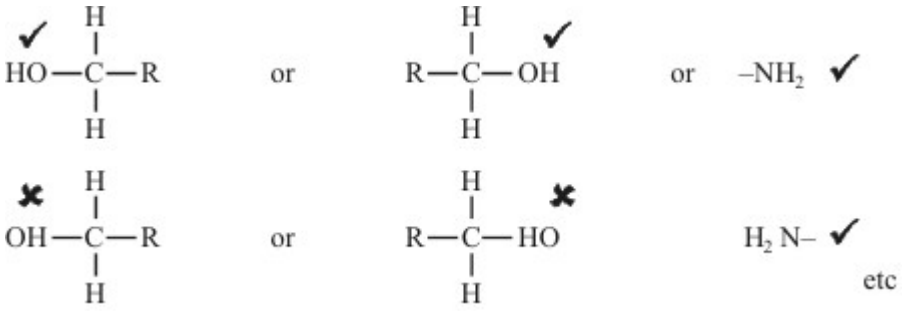
(1) Curly arrows: must show movement of a pair of electrons, i.e. from bond to atom or from lp to atom / space
e.g.



(2) Structures

penalise sticks (i.e. ) once per paper

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Penalise once per paper

allow CH_3– or –CH_3 or  or CH_3
or H_3C–

[18]

Q20.

C

[1]

Q21.

(a) *Order with respect to iodine*: 0 **(1)**
Overall order: 2 **(1)**

2

(b) *Rate constant*: $k = \frac{2 \times 10^{-5}}{(1.5) \times (3 \times 10^{-2})} = 4.4(4) \times 10^{-4}$ **(1)**

Units: $mol^{-1}\ dm^3\ s^{-1}$ **(1)**

3

(c) Appears in rate equation **(1)**
OR implied by mention of concentration or order

does not appear in (stoichiometric / overall) equation (1)

2

(d) $pH = -\log_{10}[H^+]$ **(1)**
$= 1.25$
$[H^+] = 0.056(2)$ **(1)**

$\therefore$ rate = $(4.44 \times 10^{-4}) \times (1.50) \times (0.0562)$

$= 3.75 \times 10^{-5}$ **(1)** ($mol\ dm^3\ s^{-1}$)

(3.7 — 3.8)
Can score all 3 conseq on k from part (b)

3

[10]

Q22.

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(a) before any KOH added: $K_a = \frac{[H^+][A^-]}{[HA]}$ **or** $\frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$ **(1)**

$\therefore K_a = \frac{[H^+]^2}{[CH_3COOH]}$ **(1)**

$\therefore [H^+] = \sqrt{1.74 \times 10^{-5} \times 0.160} = 1.67 \times 10^{-3}$ **(1)**

$\therefore$ pH = 2.78 **(1)**

4

(b) at 8 cm^3 KOH:
Moles KOH added = $(8 \times 10^{-3}) \times 0.210 = 1.68 \times 10^{-3}$ **(1)**
$\therefore$ moles of CH_3COO^- formed = 1.68×10^{-3} **(1)**

Original moles of $CH_3COOH = (25 \times 10^{-3}) \times 0.160 = 4.0 \times 10^{-3}$ **(1)**

$\therefore$ moles of CH_3COOH left = $(4.0 \times 10^{-3}) - (1.68 \times 10^{-3})$
$= 2.32 \times 10^{-3}$ **(1)**

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

$= 1.74 \times 10^{-5} \times \frac{2.32 \times 10^{-3}/V}{1.68 \times 10^{-3}/V} = 2.40 \times 10^{-5}$ **(1)**

$\therefore$ <u>pH = 4.62</u> **(1)**

It forget subtraction : max 5
If K_a expression not used max 5
if moles of CH_3COOH wrong but substitution used max 5

7

(c) at 40 cm^3 of KOH:
Total moles of KOH = $(40 \times 10^{-3}) \times 0.21 = 8.4 \times 10^{-3}$ **(1)**
$\therefore$ **excess moles of KOH = $(8.4 \times 10^{-3}) - (4.0 \times 10^{-3})$**
$= 4.4 \times 10^{-3}$ **(1)**
in total volume = 40 + 25 = 65 cm^3 **(1)**

$\therefore [OH^-] = 4.4 \times 10^{-3} \times \frac{1000}{65} = 0.0677$ **(1)**

$\therefore [H^+] = \frac{10^{-14}}{0.0677}$

OR pOH =1.17

$= 1.477 \times 10^{-13}$ **(1)**
$\therefore$ pH = 12.8<u>3</u> **(1)**

If volume missed : max 4
If moles of acid wrong but method includes subtraction : max 5
If no subtraction : max 4

6

[Max 16]

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Q23.

C

[1]

Q24.

D

[1]

Q25.

B

[1]

Q26.

B

[1]

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Q1.

(a) This question was answered well (89.5% correct).

(b) Many students scored both marks here, although some did not give the answer to two decimal places and thereby lost a mark; some students failed to take the square root of K_w.

(c) The answer to this question was generally well known, although some students appeared to believe that a pH of 7.27 was not sufficiently alkaline.

(d) This question differentiated well. Many students failed to appreciate that calcium hydroxide is dibasic and an answer of 12.65 was common. Some students used $K_w = 1.00 \times 10^{-14}$ and a few students failed to give the answer to two decimal places.

(e) The idea that magnesium hydroxide is less soluble than calcium hydroxide was appreciated by only a few students. Many thought the pH value should be the same. Some who gave a lower pH followed this with a discussion about the magnesium ion's greater polarising power.

Q6.

Question (a) was generally well done, but a large number of students did not include a reversible sign in their equation for dissociation of the weak acid. Part (b) differentiated well as weaker students failed to show how ethanoic acid could act as a base and accept a proton.

Part (c)(i) was more straightforward but some students failed to calculate the concentration of the acid correctly and just used a number of moles. Part (c)(ii) differentiated well: many students realised a subtraction was needed in the calculation, but then failed to use the total volume to convert the amount, in moles, of H^+ ions to a concentration to calculate the pH.

Part (d)(i) was completed very well with most students gaining either 3 or 4 marks. In part (d)(iii) a significant number incorrectly used the original amount in moles of acid (0.0125) in their ratio. Even some of the strongest students struggled with the maths skills required and a frequent wrong answer was the inverse of 1.20 due to incorrect rearrangement. A significant number did not work out the hydrogen ion concentration and so lost M1 when they couldn't complete the rest of the calculation.

Part (e) differentiated well with full descriptions seen in about a third of the answers and one mark gained by another third. In part (f) the first mark proved very accessible but the second proved trickier; many students showed poor maths skills and thought that K_a would equal 1 or zero.

Q7.

The answers to part (a) were such that few scored both marks. Not only was the reason not well known, but a lot of wrong chemistry was written. Common errors included 'H_4O is completely ionised' and 'the concentration of water is 1'.

The answers to part (b) were slightly better and most students stated that the ionisation of water is an endothermic reaction, but a high number failed either to appreciate that this ionisation produces an equilibrium mixture or to explain that the equilibrium position

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moves to the RHS to oppose the increase in temperature.

Most students answered part (c) and part (d) well. A significant number of students used the K_w value for 25°C, but this was only penalised once in the two parts. A small number failed to give their answer to the accuracy specified in the question (2 dp).

Q8.

This question was generally well attempted, with most students scoring well in the mathematical sections. In part (a), most students gave the meaning of a weak acid as 'only partially ionised or dissociated into ions', and this was credited. The preferred answer was □only slightly ionised'. 'Not fully ionised' did not gain the mark. The equation in part (b) was poorly answered mainly because the formula for sodium carbonate was incorrect. In some cases, the formula of sodium hydroxide or sodium hydrogen carbonate was given. A common error in part (c) was to omit the factor of 2 when calculating the concentration of hydroxide ions from the concentration of calcium hydroxide. Parts (d)(i) and (d)(ii) were answered well but in part (d)(iii) many students used an expression for K_c with $[H^+]^2$ or could not rearrange the correct expression to find the concentration of sodium benzenecarboxylate. Students should be encouraged to use words in their answers to make it clear whether the numbers they write refer to amounts in moles or to concentrations and also to which substance they refer. Answers to part (e) included many wrong substances and showed that some students think that H_2 (or H^+) is present in the atmosphere or that carbonic acid can exist in an alkaline solution.

Q9.

All of the pH calculations in this question were answered well. In part (a), more students than expected had difficulty calculating the $[H^+]$ after dilution but a mark was allowed for a correct calculation of pH from their $[H^+]$. In part (b)(ii), some students struggled to convert the pH into $[H^+]$ but over three quarters of the entry gained all three marks. In part (c), common mistakes included using the initial number of moles of OH^- rather than those remaining after partial neutralisation and also not using the total volume to convert the number of moles of excess hydroxide into a concentration. The degree of clarity of some students' working was also disappointing; many wrote strings of numbers with no explanation of what they were calculating. As usual, students who made errors in their calculations or gave a wrong answer with no explanation or working could gain few marks.

Q10.

The early parts of this question were answered well, although in part (a)(iii), about a third of the candidates did not realise that adding water had no effect on the number of moles of acid present. Over two thirds of the candidates scored full marks in part 2(b); a common error for the others was to rearrange the expression for K_a incorrectly. In part 2(c), many answers stated general properties of a buffer solution, without giving any explanation specific to this situation.

It was pleasing to see that over 44% of the candidates gained full marks in part (d)(i). Many of the rest thought that addition of the salt to the solution of the acid changed the amount of acid present. Part (d)(ii) discriminated well and only the better candidates were able to calculate the amounts in moles of acid and of salt present in the solution after the addition of sodium hydroxide and then use these values correctly.

Q11.

As expected, there were very few incorrect answers to parts (a)(i) and (ii). However, in part (a)(iii), some candidates assumed that $[H^+] = [OH^-]$ instead of using all the data in the

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question. Part (b) was generally well attempted, but common mistakes in part (b)(i) included incorrect formulae for ethanoic acid and the ethanoate ion, missing brackets and giving $[H^+]^2$ as the numerator.

Part (c)(i) proved to be difficult. While most candidates were able to calculate the initial numbers of moles of the acid and alkali, a large proportion could not rearrange the *K*a expression correctly or assumed that the amount of acid had not changed on addition of the alkali. Very few realised that this was a half neutralisation and their attempts to calculate the concentrations of acid and salt were often wrong and sometimes included the term $[H^+]^2$.

Part (c)(ii) was more successfully attempted, but still many candidates scored only 2 marks, either because they did not realise that some of the alkali would be neutralised by adding acid or because they failed to use the total volume to convert the number of moles of OH^- into a concentration.

Q12.

Most of this question proved to be straightforward and few candidates lost marks in part (a). Part (c) was the most discriminating section with only the better candidates scoring all six marks. Many others either forgot that sulfuric acid is diprotic and so missed that the final mixture in the questions was acidic or failed to convert the number of moles of H^+ ions present into a concentration in order to find pH.

Q13.

Part (a) was a straightforward question and was answered well. High marks were also gained in part (b), although some candidates lost the mark in part (i) for the expression for K_a because they wrote the less general expression $[H^+]^2/[HX]$ instead of $[H^+]\,[X^-]/[HX]$. The calculation in part (ii) was usually well done. The mark in part (a)(iii) was awarded for a value of pK_a correctly calculated from their $K_a$in part (ii).

-

In part (c), only the most able realised that, because the reaction was between potassium hydroxide and sulphuric acid, the mole ratio of reactants was 2:1. Hence although the answers to part (c)(i) and (ii) were usually correct, very few gained the mark in part (iii). For many, this was their only error in part (b). Others however failed to use the total volume of solution, 48 cm^3, correctly in calculating the concentration of hydroxide ions in part (iv) and/or were unable to use K_w or pOH to calculate the pH of the mixture. It was disappointing to see that a considerable number of candidates did not give the pH to two decimal places despite being asked to do so.

Q14.

The standard expressions in part (a)(i) were answered well by almost all candidates, although some quote values for Kw and pH instead of reading the question carefully.

In part (a)(ii) some missed the essential point that in pure water, the concentrations of H^+ and OH^-ions are equal at all temperatures even if the pH scale is based on a value of Kw different from 1.0^{-14}. In part (a)(iii) most were able to calculate the number of moles of OH^- present as 1.0×10^{-3}, but many failed to realise that, in part (iv), when this number of moles were added to 998 cm^3 of water, the concentration of OH^- in the solution formed would be 1.0×10^{-3} mol dm^{-3}. A few failed to use the given value of Kw but many were able to calculate the correct answer of 10.40.

Part (b) was generally very well answered and a pH of 2.89 was the most common

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answer. Some candidates, gave the answer 5.77 by forgetting to take the necessary square root in their working.

Part (c) was a buffer calculation, an area which candidates traditionally find difficult. Disappointingly, this again proved the case despite the lead in to the question given in parts (i) and (ii). While most were able to calculate the initial number of moles of propanoic acid and almost as many could calculate the number of moles of acid present in the buffer solution formed, few gained many more marks. Many tried to calculate the concentrations of the acid and the salt formed failing to realise that the volume involved cancels. Many were unable to rearrange the expression for Ka and many confused the number of moles of propanoic acid with the number of moles of H^+ present inn the solution.

Q15.

As usual with questions involving rate equations, this question was answered well, particularly parts (a) and (c). Part (b) however was poorly answered and only the very best candidates gained this mark. Many of the rest only divided the original rate by 2 instead of by 4 as the concentrations of both the ester and of If" ions were halved. Again it was disappointing to see the number of candidates who did not give the pH to two decimal places despite being asked to do so.

Q16.

Most candidates scored full marks for a correct calculation in part (a). Parts (b)(i) and (ii) were also well answered but (b)(iii) proved to be more difficult and many candidates failed to state that, when half the acid had been neutralised, $[A^-] = [HA]$. Only the very best candidates stated correctly that on dilution the ratio $[A^-] : [HA]$ remains constant and, as a consequence, $[H^+]$ also remains constant. The calculations in part (d) were generally well done although one mark was lost by candidates who, in (d)(ii), calculated the total final volume of acid, 50.0 cm^3, and not the volume of water which must be added as required by the question.

Q19.

Definitions of the terms Kw and pH in parts (a)(i) and (ii) were usually well answered except by those who failed to write mathematical definitions and attempted to describe the terms in words. Provided there were no contradictions, the marks could be earned in the later sections. The most common error in the expression for Kw was to include water. However this water term was conveniently forgotten in part (iii) and correct answers for the pH of pure water at 50°C were common. As reported regularly before, too many candidates seem not to be aware **that pH values should be given to two decimal places**; these two figures give the value to the appropriate precision. The numbers before the decimal point only give the powers of ten involved in the hydrogen ion concentration. However, failure to give pH values to the correct precision was only penalised once in the question. Part (b)(i) was answered well but (b)(ii) was more discriminating. A common error was to forget that the moles of excess sodium hydroxide were present in a total volume of solution of 75 cm^3 and needed to be converted into a molar concentration before the pH of the solution could be calculated.

A number of candidates tried to answer the question as if a buffer solution had been produced despite the use of a named strong acid. Several also gave pH values below 7 although there was an excess of alkali present. Part (c) was answered well by most candidates although some failed to give the general expression for K_a and instead wrote the more specific $[H^+]^2/[HX]$.

This expression was however credited in part (c)(ii).

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Q21.

This question on rate equations was answered well by most candidates even those who scored less well elsewhere in the paper. In part (a) most candidates deduced the overall order correctly, but to deduce that the order with respect to iodine was zero proved more difficult. Part (b) was well answered by most students, but only the better candidates were able to gain both marks in part (c). Many gave a general description of the role of a catalyst rather than the evidence that hydrogen ions appear in the rate equation but not in the overall stoichiometric equation. The use of pH to show a change of hydrogen ion concentration was understood by most candidates although some were unable to convert a pH value into a hydrogen ion concentration. Full marks were available for correct use in part (d) of an incorrect rate constant calculated in part (b).

Q22.

It is important that pH values are given to two decimal places; these two figures give the value to the appropriate precision. The numbers before the decimal point only give the powers of ten involved in the hydrogen ion concentration.

Three pH values were required in this question and answers to one decimal place only were penalised, but only once on this occasion.

The question involved three calculations of pH. First the pH of a solution of ethanoic acid was required. This was usually well done even by candidates of moderate ability.

The second situation involved a buffer solution formed when some of the weak acid has been reacted with alkali. This was done less well. Many candidates correctly calculated the number of moles of acid used, the number of moles of hydroxide added and hence the number of moles of acid remaining. However, these values were then too often used in a calculation which assumed only a weak acid was present, as in the first part of the question rather than an acidic buffer solution. Although many candidates still seemed unfamiliar with calculations of this type, there was a definite improvement in the numbers gaining full marks compared with the January CHM4 paper.

The last part of the question involved finding the pH of the resulting solution of excess potassium hydroxide produced when all the ethanoic acid is used up. This part was usually answered more successfully than the second part.

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Q1.

(a) 7–10.2

any range (i.e. 2 values) within this range

1

(b) $K_a = \frac{[H^+][X^-]}{[HX]}$

ALLOW H_3O^+ for H^+ and A for X
IGNORE $[H^+]^2/[HX]$
must be square brackets
IGNORE state symbols

1

(c) Amount NaOH = $(24.0 \times 0.100)/1000 = 2.40 \times 10^{-3}$ mol

(= amount HX)

Conc HX = $2.40 \times 10^{-3}/0.025 = 0.0960$ mol dm^{-3}

ecf for M1/0.025

(d) ($K_a = 2.62 \times 10^{-5} = [H^+]^2/0.0960$)

$[H^+] = \sqrt{(2.62 \times 10^{-5} \times 0.0960)}$ (= 1.59×10^{-3} mol dm^{-3})

ecf from part (c) $[H^+] = \sqrt{(2.62 \times 10^{-5} \times$ ans to part (c))
From alternative data
$[H^+] = \sqrt{(2.62 \times 10^{-5} \times 0.600)}$ (= 3.96×10^{-3} mol dm^{-3})

(pH = –log 1.59×10^{-3} =) 2.80 (must be 2 or more dp)

1

pH = 2.40 (must be 2 or more dp)
M2 dependent on a calculation of $[H^+]$

1

(e) (pH at half-neutralisation = pK_a)

= –log 2.62×10^{-5} = 4.58 (must be 2 or more dp)

ALLOW 1dp if already penalised in part (d)

1

(f) Both points plotted correctly and line touches both points

ecf from (d) and (e) within 1 small square

1

<u>Line steeper at start</u> then levels (to show buffering)

Mark independently

1

[9]

Q2.

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B

[1]

Q3.

(a) Formula of any strong acid (e.g. HCl)

1

Formula of a weak alkali (e.g. NH_3)

1

(b) Place a fixed volume of alkali in a flask or beaker

1

Add acid in small portions from a burette

1

Stir and use a pH meter to record the pH after each addition of acid

1

(c) Repeat the experiment with each indicator

1

Select the indicator that changes colour rapidly when the pH changes from about 7 to 4

1

[7]

Q4.

(a) Burette

1

Because it can deliver variable volumes

1

(b) The change in pH is gradual / not rapid at the end point

1

An indicator would change colour over a range of volumes of sodium hydroxide

Allow indicator would not change colour rapidly / with a few drops of NaOH

1

(c) $[H^+] = 10^{-pH} = 1.58 \times 10^{-12}$

1

$K_w = [H^+]\,[OH^-]$ therefore $[OH^-] = K_w / [H^+]$

1

Therefore, $[OH^-] = 1 \times 10^{-14} / 1.58 \times 10^{-12} = 6.33 \times 10^{-3}$ (mol dm^{-3})

Allow 6.31–6.33 × 10^{-3} (mol dm^{-3})

1

(d) At this point, $[NH_3] = [H^+]$

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Therefore $K_a = \frac{[H^+]^2}{[NH_4^+]}$

1

$[H^+] = 10^{-4.6} = 2.51 \times 10^{-5}$

1

$K_a = (2.51 \times 10^{-5})^2 / 2 = 3.15 \times 10^{-10}$ (mol dm^{-3})

Allow 3.15 – 3.16 × 10^{-10} (mol dm^{-3})

1

(e) When $[NH_3] = [NH_4^+]$, $K_a = [H^+]$ therefore $-\log K_a = -\log [H^+]$

Answer using alternative value

1

Therefore pH = $-\log_{10}(3.15 \times 10^{-10}) = 9.50$

M2 pH = $-\log_{10}(4.75 \times 10^{-9}) = 8.32$

Allow consequential marking based on answer from part (d)

1

[12]

Q5.

(a) Sensible scales

If pH not on y-axis lose M1

Both axes must have labels (does not have to have units)

1

All points plotted accurately

Plotted points must cover at least half of the grid

Allow ±1 small square

1

(b) Line is smooth

Penalise very thick or doubled lines but make some allowance for drawing a complex curve for M1

1

Avoids the anomalous point

Line must pass within ±1 small square of all points (except the anomalous)

1

(c) Reads the volume off at the equivalence point and divides by 2 to find volume at half-equivalence

Volume at equivalence should be between 19 – 20 cm^3

Consequential to their plotted points.

Half-equivalence = 9.5 – 10 cm^3

If candidate has used incorrect volume, CE loses M1 and M2 but can score M3 as a process mark.

1

Reads off pH at half-equivalence

If candidate has misread volume from their graph, lose M1

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4.40 - 4.50

1

($pH = pK_a$)
$K_a = 10^{-pKa}$

Range of values for K_a = 3.16 × 10^{-5} – 3.98 × 10^{-5}

Mark M3 independently

1

(d) Use of a buffer solution
Rinses probe (with distilled/deionised water) between measurements
Measures pH of more than one buffer solutions
Plots a graph of pH of buffer against pH on probe **OR** adjusts meter / probe **OR** draws a calibration curve

Max 3 of 4 points

Allow "solution of known pH" for "buffer"

3

(e) pH range of steep section of curve **OR** between 5 – 12 (or any values both within this range)

1

Indicator's colour change must fall within this range

Allow pK indicator approx. equal to pH of centre of range

1

(f) Adding the solution dropwise (near the end point)

1

[13]

Q6.

(a) (i) G

1

(ii) F

1

(iii) H

1

(b) (i) cresol purple

1

(ii) yellow to red

both colours needed and must be in this order

1

(iii) yellow or pale yellow

Not allow any other colour with yellow

1

[6]

Q7.

(a) Correct orientation of graph (pH on y-axis)

1

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Scale – plotted points cover at least half the grid and *y*-axis should start at pH 4

1

All points plotted correctly

+ / – one small square.

1

Curve of best fit drawn correctly

Allow some leniency here with a complex graph – it is important that the section between pH 8.5 and 9.7 is close to linear.

Lose this mark if the line is pulled towards the anomaly at 3.0 cm^3.

Lose this mark if first point at pH 5.1 is treated as an anomaly.

Do not accept doubled lines but allow some slight discontinuity where the curve changes direction.

1

(b) 11.6-11.9 (cm^3) only

Do not mark consequentially to student's graph.

1

(c) pK_a = value of pH related to part (b) **M1**

Mark consequentially on student's graph – ideally 9.0-9.1

Do not penalise precision of answer.

1

$K_a = 10^{-pKa}$ **M2**

Ideally 1.0×10^{-9} to 7.9×10^{-10}

*Ignore precision of answer but lose **M2** for 1 significant figure here.*

1

(d) pH 8.7

Ineffective stirring / swirling of the mixture

Both points needed for this mark.

Do not allow pH 5.1

Do not allow 'overshooting (at 3 cm^3 addition)'.

1

(e) Take more pH readings around the end-point / add smaller volumes of NaOH near the end-point

Do not allow 'use a more accurate / reliable pH meter / probe'.

Do not allow the use of a thermostatted mixture.

1

[9]

Q8.

(a) Proton donor or H^+ donor

1

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(b) (i) $K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$ or $\frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$

If K_a wrong, can only score M1 below.
Must be ethanoic acid not HA
Must have square brackets (penalise here only) but mark on in (b)(ii).

1

(ii) M1 $[H^+] = 10^{-2.69}$ ***OR*** 2.042×10^{-3} (mol dm^{-3})

1

M2 $CH_3COOH] = \frac{[H^+]^2}{K_a}$

Ignore ( )
Mark for correctly rearranged expression incl $[H^+]^2$

1

M3

$= \frac{(2.042 \times 10^{-3})^2}{1.75 \times 10^{-5}}$

If M2 wrong no further marks.

1

M4 = 0.238 (mol dm^{-3}) Allow 0.229 − 0.24

1

(c) (i) $ClCH_2COOH \rightleftharpoons ClCH_2COO^- + H^+$
OR $ClCH_2COOH + H_2O \rightleftharpoons ClCH_2COO^- + H_3O^+$

Allow $\longrightarrow$
Allow $ClCH_2CO_2H$ and $ClCH_2CO_2^-$

1

(ii) M1 Cl is (more electronegative so) withdraws electrons
OR negative inductive effect of Cl
Ignore electronegativity.
Ignore chloroethanoic acid has a lower K_a value.
Allow Cl reduces +ve inductive effect of methyl group.

1

M2 Weakens O–H bond
OR O–H bond is more polar
OR reduces negative charge on COO^-
OR stabilizes COO^- (more)
M1 & M2 are independent marks.
Ignore H^+ lost more easily.

1

(d) (i) **A**

1

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(ii) **C**

1

(iii) **D**

1

(e) M1 Mol NaOH = mol OH^- = $(19.6 \times 10^{-3}) \times 0.720 = 1.41(1) \times 10^{-2}$

Mark for answer.

1

M2 Mol H_2SO_4 = $(26.4 \times 10^{-3}) \times 0.550 = 1.45(2) \times 10^{-2}$

Mark for answer.

1

M3 Mol H^+ added = **2 ×** $(1.452 \times 10^{-2}) = 2.90(4) \times 10^{-2}$
OR
XS mol $H_2SO_4 = 7.46(4) \times 10^{-3}$

If factor × 2 missed completely (pH = 2.05)
or used wrongly later,
can score max 4 for M1, M2, M5 & M6

1

M4 XS mol $H^+ = 0.0149(3)$

1

M5 For dividing by volume
$[H^+] = 0.0149(3) \times (1000 / 46.0) = 0.324 - 0.325$ mol dm^{-3}

If no use or wrong use of volume lose M5 and M6
ie can score 4 for pH = 1.83 (no use of vol)
Treat missing 1000 as AE (−1) & score 5 for pH = 3.49

1

M6 pH = 0.49

2dp *(penalise more or less).*
If × 2 missed & vol not used, pH = 3.39 scores M1 & M2 only.

1

[18]

Q9.

(a) **Z**

Mark independently.

1

The idea that the solution contains both HA and A^-

1

(b) pH

1

$[HA] = [A^-]$

Accept solution half neutralised.

1

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pH = pK_a

Accept $[H^+] = K_a$

1

[5]

Q10.

(a) Over time / after storage meter does not give accurate readings

Do not allow 'to get an accurate reading' or 'reading drifts' on its own.

Allow 'temperature variations affect readings'.

1

(b) Any **five** from:

Ignore references to the use of the pipette, the filling of the burette and the calibration of the pH meter.

- Measure pH (of the acid)
- Add alkali in known small portions

  Allow 1 – 2cm^3.
- Stir mixture
- Measure pH (after each addition)
- Repeat until alkali in excess

  Allow 27 – 50cm^3.
- Add in smaller increments near endpoint

  Allow 0.1 – 0.5cm^3.

  To score full marks, the sequence must follow a logical order.

5 max

[6]

Q11.

(a) C

1

A

1

D

1

(b) (i) Bromocresol green

Allow wrong spellings

1

(ii) Purple to yellow

Must have both colours:

Purple start – yellow finish

1

[5]

Q12.

(a) $NH_4^+ \rightarrow NH_3 + H^+$

Accept multiples.

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Accept $NH_4^+ + H_2O \rightarrow NH_3 + H_3O^+$

Ignore state symbols, even if incorrect.

1

(b) Test indicator / conc HCl

Do not accept 'smell'.

Do not accept precipitation reactions of aqueous ammonia.

1

Observation colour for an alkali / white fumes

If wrong test then lose second mark.

1

[3]

Q13.

(a) pH on the y-axis, volume of alkali on the x-axis

If axes unlabelled use data to decide that pH is on y-axis.

1

Uses sensible scales

*Lose this mark if plotted paths do not cover **half** of the paper.*

Lose this mark if the graph plot goes off the squared paper.

1

Labels the axes

Allow mark for axes labelled 'pH' and 'volume'.

1

Plots all of the points correctly

1

Line through the points is smooth and has the correct profile

Ignore 0–5 cm^3 section of the graph.

Lose this mark if graph is kinked or not a single line.

1

Line ignores the point at 12 cm^3

Lose this mark if point clearly not treated as an anomaly.

1

(b) (i) 24.4 cm^3 ± 0.2

If no answer in (i) allow answer written on the graph.

*Allow this answer **only**.*

Do not penalise precision.

1

(ii) 12.2 cm^3 ± 0.1

If no answer in (ii), allow answer written on the graph.

Allow answer to (i) divided by 2.

Do not penalise precision.

1

(iii) 3.9 ± 0.2

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If no answer in (iii), allow answer written on the graph.
Consequential marking from (ii)
Lose this mark if answer not given to 1 dp.

1

(c) $pK_a = -\log K_a$ or $K_a = 10^{x}$, where $x = -$ (answer to b(iii))

1

1.26×10^{-4}

3.7 to 4.1 gives $K_a = 7.9 \times 10^{-5}$ to 2.0×10^{-4}
Consequential marking from b(i).
Correct answer without working scores 1 mark only.
Do not penalise precision.

1

(d) Methanoic acid

Consequential marking from (c).
$pK_a = 3.7$ gives methanoic acid.
$pK_a = 4.1$ gives ethanoic acid.
No lucky guesses – candidates must apply answer from (c).
Do not allow answers based on data given in (f).

1

(e) Error in using pipette is 0.2% **and**
Error in using burette is 0.15 × 100 / (answer to b(i))

Using 24.4 for burette gives 0.6%
Do not penalise precision.
Allow if errors are given without working.
Lose mark if the burette error is not calculated on b(i).
*If the error being calculated is **not** stated, allow **if** the calculations are in the same order as in the question (pipette, burette).*

1

(f) Difference is $1.6 \times 10^{-4} - 1.26 \times 10^{-4} = 0.34 \times 10^{-4}$

Allow consequential answer from (c).
Do not penalise precision.

$0.34 \times 100 / 1.6$ is a 21% error

Correct final answer without working scores 1 mark.
Using 1.9×10^{-4} gives 0.3×10^{-4} and 18.8%.

1

(g) Calibrate meter **or** thermostat the mixture **or** maintain constant temperature

Do not allow 'repeat experiment'.

1

(h) Mixture is a <u>buffer</u>

1

[16]

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Q14.

(a) (i) $-\log[H^+]$

or $\log 1/[H^+]$
penalise ( )

1

(ii) $[H^+] = 0.56$

mark for the answer; allow 2dp or more

1

$[H_2SO_4] = ½ \times 0.56 = 0.28$

1

(b) (i) $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

OR

$CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$

Allow CH_3CO_2H etc

1

(ii) mol acid = $(25.0 \times 10^{-3}) \times 0.41 = 1.025 \times 10^{-2}$ or 1.03×10^{-2}

1

$[NaOH] = 1.025 \times 10^{-2}/22.6 \times 10^{-3} = 0.45(4)$

mark for answer
if not 0.454 look back for error

1

OR

$[NaOH] = 1.03 \times 10^{-2}/22.6 \times 10^{-3} = 0.456$ or 0.46

(iii) cresol purple

1

(iv) NaOH reacts with <u>carbon dioxide</u> (in the air)

1

(c) (i) $K_a = \dfrac{[H^+][CH_3COO^-]}{[CH_3COOH]}$

allow molecular formulae or minor slip in formulae

penalise ( )
allow H_3O^+
not allow HA etc

1

(ii) $K_a = \dfrac{[H^+]^2}{[CH_3COOH]}$ or with numbers

1

allow HA etc here
This can be scored in part (c)(i) but doesn't score there.

$[H^+] = (\sqrt{(1.74 \times 10^{-5} \times 0.410)} = \sqrt{(7.13 \times 10^{-6})}) = 2.67 \times 10^{-3}$

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1

mark for 2.67×10^{-3} or 2.7×10^{-3} either gives 2.57

pH = 2.57 can give three ticks here for (c)(ii)
penalise decimal places < 2 >

1

pH mark conseq on their $[H^+]$

so 5.15 gets 2 marks where square root not taken

(iii) **M1** mol OH^- = $(10.0 \times 10^{-3}) \times 0.10 = 1.0 \times 10^{-3}$

If no subtraction or other wrong chemistry the max score is 3 for M1, M2 and M4

1

M2 orig mol HA = $(25.0 \times 10^{-3}) \times 0.41 = 0.01025$

1

or 1.025×10^{-2} or 1.03×10^{-2}

M3 mol HA in buffer = orig mol HA – mol OH^-

1

= 0.00925 or 0.0093

If A^- is wrong, max 3 for M1, M2 and M3 or use of $pH = pKa – \log [HA]/[A^-]$

M4 mol A^- in buffer = mol OH^- = 1.0×10^{-3}

Mark is for insertion of correct numbers in correct expression for $[H^+]$

1

M5 $[H^+] = \left(\frac{K_a \times [CH_3COOH]}{[CH_3COO^-]} = \right)$

1

$$\frac{(1.74 \times 10^{-5})(0.00925)}{0.0010} \text{ or } \frac{(1.74 \times 10^{-5})(0.00930)}{0.0010}$$

(= 1.61×10^{-4} or 1.62×10^{-4})

M6 pH = 3.79 can give six ticks for 3.79

if $[HA]/[A^-]$ upside down lose M5 & M6

If wrong method e.g. $[H^+]^2/[HA]$ max 3 for M1, M2 and M3

Some may calculate concentrations
[HA] = 0.264 and $[A^-]$ = 0.0286 and rounding this to 0.029 gives pH = 3.80 (which is OK)

NB Unlike (c)(ii), this pH mark is NOT awarded conseq to their $[H^+]$ unless following AE

BEWARE: using 0.01025 wrongly instead of 0.00925 gives pH = 3.75
(this gets 3 for M1, M2 & M4)

1

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[18]

Q15.

(a) (i) **B** 1

C

1

A

1

(ii) cresolphthalein or thymolphthalein

1

(b) pH = -log[H^+]

1

$K_a = \frac{[H^+]^2}{[CH_3COOH]}$ or $[H^+] = [A^-]$

1

$[H^+] = \sqrt{1.74 \times 10^{-5} \times 0.15}$ (or 1.62×10^{-3})

1

pH = 2.79 (penalise 1 dp or more than 2dp once in the qu)

1

[8]

Q16.

(a) –log [H^+]

ecf if [ ] wrong and already penalised

1

4.57×10^{-3}

allow 4.6×10^{-3}
ignore units

1

(b) (i) $K_a = \frac{[H^+][X^-]}{[HX]}$ allow HA etc

not $\frac{[H^+]^2}{[HX]}$ *but mark on*
If expression wrong allow conseq units in (ii)
but no other marks in (ii)

1

(ii) $\frac{[H^+]^2}{[HX]} = \frac{(4.57 \times 10^{-3})^2}{[0.150]}$

If use 4.6×10^{-3}

1

$K_a = 1.4(1) \times 10^{-4}$ and pKa = 3.85

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= 1.39×10^{-4}

allow 1.39 – 1.41 × 10^{-4} mol dm^{-3}

1

(iii) $pK_a = 3.86$

Penalise dp of final answer < or > 2 in pH once in paper

1

(c) (i) $\frac{30}{1000} \times 0.480 = 0.0144$ or $1.4(4) \times 10^{-2}$

Mark is for answer (M1)

1

(ii) $\frac{18}{1000} \times 0.350 = 0.0063$ or 6.3×10^{-3}

Mark is for answer (M2)

1

(iii) $0.0144 - 2(0.0063) = 1.80 \times 10^{-3}$

M3 is for (i) – 2(ii)
If x 2 missed, CE i.e. lose M3 and the next mark gained

1

(iv) $1.80 \times 10^{-3} \times \frac{1000}{48} = 0.0375$ (0.038)

M4 is for answer

If vol is not 48 × 10^{-3} (unless AE) lose M4 and next mark gained
If multiply by 48 - this is AE - i.e. lose only M4
If multiply by 48 × 10^{-3} this is AE - i.e. lose only M4

1

(v) $10^{-14} / 0.0375$ ($10^{-14} / 0.038$)

M5 for $K_w/[OH^-]$

1

(= 2.66×10^{-13}) (= 2.63×10^{-13})

or pOH

or pOH = 1.426 (or pOH = 1.420)

If no attempt to use K_w or pOH lose both M5 and M6

1

pH = 12.57 (12.58) M6

Allow M6 conseq on AE in M5 if method OK

1

[13]

Q17.

(a) (i) B;

1

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C;

1

A;

1

(ii) cresolphthalein

OR

thymolphthalein;

1

(b) (i) –log[H^+];

1

(ii) [H^+] = 1.259×10^{-12} (or 1.26 or 1.3)

OR

OH = 14 – pH;

1

$$[OH^-] = \frac{10^{-14}}{1.258 \times 10^{-12}}$$

OR

= 2.10;

1

= $7.9(4) \times 10^{-3}$;

(if [H^+] is wrong allow 1 for [OH] = K_w/[H^+] or as numbers)

1

(c) (i) $K_a = [H^+]^2/[CH_3CH_2COOH]$

OR

$[H+]^2/[HA]$

OR

[H^+] = [A^-] etc;

1

[H^+] = $\sqrt{1.35 \times 10^{-5}} \times 0.117$ or expression without numbers;

1

= 1.257×10^{-3}

pH = 2.90;

1

(iii) $K_a = [H^+]$

OR

pK_a = pH;

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1

pH = 4.8<u>7</u>;

(penalise 1dp once)

1

[13]

Q18.

(a) Concentration of acid: $m_1v_1 = m_2v_2$ hence $25 \times m_1 = 18.2 \times 0.150$

OR

moles NaOH = 2.73×10^{-3};

1

$m_1 = 18.2 \times 0.150/25 = 0.109$;

1

(b) (i) $K_a = [H^+][A^-]/[HA]$ *not* $K_a = [H^+]^2 / [HA]$;

1

(ii) $pK_a = -\log K_a$;

1

(iii) $[A^-] = [HA]$;

1

hence $K_a = [H^+] [A^-] / [HA] = [H^+]$

and $-\log K_a = -\log[H^+]$;

1

(c) ratio $[A^-]$: [HA] remains constant;

1

hence as $[H^+] = K_a [HA] / [A^-]$; $[H^+]$ remains constant;

1

(d) (i) pH of 0.250 mol dm^{-3} HCl = 0.60
and pH of 0.150 mol dm^{-3} HCl = 0.82;

1

pH change = 0.22;

1

(ii) moles HCl = $30 \times 0.250 \times 10^{-3} = v \times 0.150 \times 10^{-3} = 7.50 \times 10^{-3}$

OR

$v = 30 \times 0.250 \times 10^{-3} / 0.150 \times 10^{-3} = 50$;

1

water added = 50 – 30 = 20 cm^3;

1

[12]

Q19.

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(a) moles HA = $\frac{25}{10^3}$ × 0.150 = 3.75 × 10^{-3} **(1)**

∴ vol NaOH = $\frac{3.75 \times 10^{-3}}{0.20}$ = 1.875 × 10^{-2} dm^3 **(1)**

or 18.75 cm^3

2

(b) (i) pH = $-\log_{10}[H^+]$ **(1)**

(ii) Value above 7 but below 11 **(1)**

(iii) phenol red / thymol blue / phenolphthalein / thymolphthalein

i.e. indicator with $7 < pK_{in} < 11$

3

(c) (i) Only slightly dissociated/ionised **(1)**

NOT "not fully dissociated / ionised"

(ii) $K_a = \frac{[H^+][A^-]}{[HA]}$ **(1)**

NOT $\frac{[H^+]^2}{[HA]}$

(iii) For weak acid alone:

$Ka = \frac{[H^+]^2}{[HA]}$ **(1)**

∴ $[H^+] = \sqrt{(2.75 \times 10^{-5}) \times 0.15}$

= 2.03 × 10^{-3} (1)

∴ pH = 2.69 (1)

pH should be given to 2 decimal places
penalise answer to 1 d.p. once in question

5

(d) moles OH^- added = 1.875 × 10^{-3} = moles A^- = moles HA left **(1)**

or $[A^-] = [HA]$

∴ Ka = $[H^+]$ **or** pH = pK_a **(1)**

∴ pH = 4.56 (1)

3

[13]

Q20.

(a) before any KOH added: $K_a = \frac{[H^+][A^-]}{[HA]}$ **or** $\frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$ **(1)**

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$\therefore K_a = \frac{[H^+]^2}{[CH_3COOH]}$ **(1)**

$\therefore [H^+] = \sqrt{1.74 \times 10^{-5} \times 0.160} = 1.67 \times 10^{-3}$ **(1)**

$\therefore$ pH = 2.78 **(1)**

4

(b) at 8 cm^3 KOH:
Moles KOH added = $(8 \times 10^{-3}) \times 0.210 = 1.68 \times 10^{-3}$ **(1)**
$\therefore$ moles of CH_3COO^- formed = 1.68×10^{-3} **(1)**

Original moles of $CH_3COOH = (25 \times 10^{-3}) \times 0.160 = 4.0 \times 10^{-3}$ **(1)**

$\therefore$ moles of CH_3COOH left = $(4.0 \times 10^{-3}) - (1.68 \times 10^{-3})$
$= 2.32 \times 10^{-3}$ **(1)**

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

$= 1.74 \times 10^{-5} \times \frac{2.32 \times 10^{-3}/V}{1.68 \times 10^{-3}/V} = 2.40 \times 10^{-5}$ **(1)**

$\therefore$ <u>pH = 4.62</u> **(1)**

It forget subtraction : max 5
If K_a expression not used max 5
if moles of CH_3COOH wrong but substitution used max 5

7

(c) at 40 cm^3 of KOH:
Total moles of KOH = $(40 \times 10^{-3}) \times 0.21 = 8.4 \times 10^{-3}$ **(1)**
$\therefore$ **excess moles of KOH = $(8.4 \times 10^{-3}) - (4.0 \times 10^{-3})$**
$= 4.4 \times 10^{-3}$ **(1)**
in total volume = 40 + 25 = 65 cm^3 **(1)**

$\therefore [OH^-] = 4.4 \times 10^{-3} \times \frac{1000}{65} = 0.0677$ **(1)**

$\therefore [H^+] = \frac{10^{-14}}{0.0677}$

OR pOH =1.17

$= 1.477 \times 10^{-13}$ **(1)**
$\therefore$ pH = 12.8<u>3</u> **(1)**

If volume missed : max 4
If moles of acid wrong but method includes subtraction : max 5
If no subtraction : max 4

6

[Max 16]

Q21.

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(a) (i) $K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$ (or H_3O^+) **(1)**

(ii) (1) $K_a = \frac{[H^+]^2}{[CH_3COOH]}$ **(1)**

(2) $[H^+] = \sqrt{1.74 \times 10^{-5} \times 0.220} = 1.96 \times 10^{-3}$ **(1)**

(3) $pH = -\log_{10}[H^+]$ **(1)**
can score independently

(4) pH = 2.71 **(1)**
2 d.p. essential
If forget √ can score (1) and (3) for pH = 5.42

5

(b) (i) moles acid = $\frac{25}{1000} \times 0220$ **(1)** = 5.50×10^{-3}

$= \frac{x}{10^3} \times 0.150$

$\therefore x = 25 \times \frac{0.220}{0.150}$ **or** $5.50 \times 10^{-3} \times \frac{1000}{0.150}$

= 36.7 (or 37) cm^3 (or 36.6) **(1)**

NOT 36 NOR 37.0 units must match

(ii) *Indicator*: thymol blue **(1)**
Explanation: weak acid – strong base **(1)**
equivalent at pH > 7 **(1)**
or high pH

5

(c) (1) mol NaOH added = $\frac{2.0}{40.0}$ = 0.050 **(1)**
If wrong M_r: CE ∴ lose marks (1) and (2) then mark on consequentially → max 4

(2) mol CH_3COOH left = 0.220 – 0.050 = 0.170 **(1)**

(3) mol CH_3COO^- formed = 0.050 **(1)**

(4) $[H^+] = Ka \frac{[acid]}{[salt]}$ OR $pH = pKa + \log \frac{[A^-]}{[HA]}$ etc **(1)**
If expression wrong no marks for 4 / 5 / 6

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can score (1) to (4) in (5)

(5) $[H^+] = 1.74 \times 10^{-5} \times \frac{(0.170)}{(0.05)}$ OR $pH = 4.76 + \log\left(\frac{0.05}{0.17}\right)$ **(1)**

(6) pH = 4.23 **(1)**

*Correct answer gets **(1)(1)(1)(1)(1)(1)***
Mark (5) is for use of correct values of (acid moles) and (salt moles)
if one wrong allow pH conseq
if both wrong, no further marks
e.g. if candidate forgets substitution in (2)
he loses (2) and (5) but can score (1) (3) (4) (6) = max 4

for pH = 4.12 if $\frac{[acid]}{[salt]}$ upside down; answer 5.29 scores 3 for (1) (2) (3)

6

[16]

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Q1.

(a) Nearly 60% of students recognised that the working range should correspond to the vertical section of the titration curve.

(b) Over 80% of students recognised this expression, with the commonest error being to show it as $[H^+]^2/[HX]$.

(c) This question was another that illustrated the importance of paying attention to the information in the stem of a question. A significant number of students attempted to answer this question using the expression for K_a, instead of recognising that this is a titration and that the end-point allows the amount of NaOH to be calculated, and hence the amount and concentration of the acid. Perhaps students did not recognise that that the end point of the titration could be obtained easily from the graph.

(d) The provision of alternative data ensured that students who had difficulty with part (c) were not disadvantaged here and over 50% gained full marks. Data in the stem were again crucial here.

(e) The idea that pH = pK_a at half-equivalence was not recognised by many, so only 26% of students gained this mark.

(f) A mark was often lost as a result of students assuming that half-equivalence was at 10 or 15 cm^3 and so plotting incorrectly. Many also failed to remember the need to show an initial steep section before buffering 'levels off' the curve.

Q2.

C (followed by A) was the commonest incorrect response, suggesting that students failed to realise how low the pH is when the plot ceases to be vertical in a strong acid-weak base titration. The success rate was 41.9%.

Q5.

The graph plotting in questions **(a)** and **(b)** were generally exceptionally well done. A few students continue to try to use unusual scales on their graphs and often catch themselves out by then misplotting points. A few students tried to be answer by not plotting the anomalous point, however they then could not score the marks for plotting all of the points or for their line of best fit missing the anomalous point so it is better, on the whole, to simply follow the instructions given.

Question **(c)** was extremely well done, with the vast majority of students able to calculate a value for Ka. Question **(d)**, however, was variable with some students clearly never having calibrated a pH probe before whilst others were able to state extremely detailed methods for this process.

Most students were able to score 1 mark out of 2 for question **(e)** but, again, this was a question where students found it hard to express their ideas clearly and succinctly. Question **(f)** was, on the whole, poorly attempted. Many students stated the use of a white tile or colorimeter without realising that, if the solutions are still being added in the same increments, this would have no effect on the accuracy of the titration. Others correctly identified the need to add the alkali drop wise, but then went on to contradict themselves by listing several other, incorrect, methods as well.

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Q6.

Students showed a good understanding of this topic and part (a) was answered very well. In part (b)(ii) some answers only showed one colour rather than the two seen in a colour change. Part (b)(iii) was answered correctly by a narrow majority of students.

Q7.

(a) The graph in part was quite complex and required attention to detail. Notwithstanding this, some very good examples were seen. Unfortunately, the standard of marking was not as good with many markers failing to spot missing points, misplots and poor lines on the linear section in the middle of the graph.

(b) This last point was vital for good answers to part (b) and (c). Scale was not an issue on this graph although a few decided to ignore the instruction to start at pH 4. Quite a few students assumed that the first point was anomalous.

Part (b) and (c) proved more troublesome than expected. Some students were unable to process the information and gave the neutralisation titre (accurately) in part (b). Quite a few had a pK_a of 9.0 but then lost marks giving one significant figure answers to the second part of part (c). Often this was not penalised by the marker.

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(d) The key point in part was the recognition that swirling or full mixing of the solution had not occurred and some answers were not thought through fully as they implied that the pH should be lower and not higher than expected. However, many good answers were also seen.

(e) The marking of this part was often lenient and students were allowed to suggest that the whole experiment should be carried out with the addition of very small volumes from the start. This is neither practical nor a slight modification; it must occur near the end point. Quite a few students were incorrectly rewarded for this.

Q8.

Although parts (a) and (b) were answered well, a considerable number of students again had difficulty in rearranging the expression for Ka in part (b)(ii). Part (c)(i) was well done, although HCl was a common wrong product. Part (c)(ii) proved to be difficult and was poorly understood by many students. In part (d), the indicator for the strong acid – strong base combination was surprisingly least well answered.

Many students found part (e) difficult and the question discriminated well. Despite the instruction to assume that sulfuric acid was fully dissociated, the factor of 2 was often omitted completely or alternatively used in the wrong place. Also, the number of moles of H^+ was often used instead of the concentration of H^+ to find the pH.

Q9.

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(a) In this part many students were unable to select a correct mixture, but were awarded a mark for an explanation which was incomplete or very vague. Students needed to mention the presence of both acid and salt in the mixture to merit the mark.

(b) In this part, many students confused a half equivalence mixture with a pH graph. An explicit statement that [HA] = [A^-] was often omitted, and quite frequently was not penalised. It was surprising how many students used a pH value without taking the trouble to measure this value.

Q10.

(a) This part was unfamiliar to most students, and marking was occasionally lenient.

(b) This part was much more familiar and most students gave good answers. Some teachers awarded marks for statements such as ‘plot a pH curve’. Some centres wrongly gave credit for alkali portions outside the ranges given in mark guidelines.

Q11.

Parts (a) and (b)(i) were both answered well, but in part (b)(ii), many candidates failed to recognise that a colour *change* involves two colours; the colour of the indicator at the start and at the end were both required to score the mark.

Q12.

In this Question most candidates could write a correct equation but a test for ammonia was unknown to the majority of candidates. A number showed some ingenuity in suggesting one of the reactions with a transition metal ion from Task 1 but failed to appreciate that their test would be anything but simple.

Q13.

(a) Virtually all candidates were able to produce a suitable graph in this part. There were fewer examples of generous marking of this graph, as the nature of the graph makes it more likely that the plotted points will cover half the paper. Occasionally graphs containing incorrectly plotted points were not penalised. Some markers forgot that the line of best fit mark cannot be awarded when the line itself is poorly drawn or doubled in places. Given the shape of the graph, some minor doubling can be ignored but sometimes graphs with several doubled regions escaped the appropriate penalty.

(b) Many candidates could not determine the volume of sodium hydroxide at the end-point of the titration in part (i), quoting an amazing range of values. Most candidates could, however, obtain appropriate values for part (ii) and (iii). In part (iii), some centres did not allow a consequential mark from an incorrect answer to part (ii).

(c) Candidates either scored both marks in this part or made no useful progress.

(d) In this part, a number of candidates became confused when comparing two very small numbers and chose the wrong acid.

(e) Candidates have a good appreciation of the calculation of apparatus errors and a majority scored the mark in this part.

(f) Again the need to work with very small numbers meant that many candidates did not complete this part correctly.

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(g) Candidates either answered this part confidently, or misread the question and suggested changes to the experimental technique.

(h) Only the better candidates were able to answer this part correctly.

Q14.

This question was generally well answered and only rarely did candidates fail to follow the instructions to give their pH values to two decimal places.

In part (a)(ii) only a fifth of the candidates realised that sulfuric acid is diprotic and in part (b)(i) only two thirds of the entry could write a correct equation for the reaction of ethanoic acid with sodium hydroxide. The following titration calculation was very straightforward but was thought more complicated by many including those who introduced K_w. It was disappointing to see that only the very best candidates understood that sodium hydroxide solution reacts with carbon dioxide in the air and many candidates showed a strange understanding of the composition of air. Part (c)(ii) was well answered; nearly four fifths of candidates answered this part completely correctly. Answers to the unstructured buffer calculation in part (c)(iii) were also quite pleasing; the question differentiated well and over twenty percent of candidates gained full marks. Other candidates were hindered by poor mathematical skills.

Q16.

Part (a) was a straightforward question and was answered well. High marks were also gained in part (b), although some candidates lost the mark in part (i) for the expression for K_a because they wrote the less general expression $[H^+]^2/[HX]$ instead of $[H^+]\,[X^-]/[HX]$. The calculation in part (ii) was usually well done. The mark in part (a)(iii) was awarded for a value of pK_a correctly calculated from their K_a in part (ii).

-

In part (c), only the most able realised that, because the reaction was between potassium hydroxide and sulphuric acid, the mole ratio of reactants was 2:1. Hence although the answers to part (c)(i) and (ii) were usually correct, very few gained the mark in part (iii). For many, this was their only error in part (b). Others however failed to use the total volume of solution, 48 cm^3, correctly in calculating the concentration of hydroxide ions in part (iv) and/or were unable to use K_w or pOH to calculate the pH of the mixture. It was disappointing to see that a considerable number of candidates did not give the pH to two decimal places despite being asked to do so.

Q17.

Only the weakest failed to recognise the titration curves in part (a) or to give either of the indicators which changed colour above pH 7. The definition of pH was, as expected, well known, but many candidates were unable to complete the calculation of the concentration of potassium hydroxide in part (b)(ii) by using either K_w or the expression pH + pOH =14. Part (c)(i) was well done but many failed to recognise that the solution formed in part(c) was a buffer solution of the particular type where the moles of salt and moles of acid present were equal, so that the pH of the mixture equals the pK_a of the weak acid. It was pleasing that very few ignored the stated request to quote pH values to two decimal places.

Q18.

Most candidates scored full marks for a correct calculation in part (a). Parts (b)(i) and (ii)

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were also well answered but (b)(iii) proved to be more difficult and many candidates failed to state that, when half the acid had been neutralised, $[A^-] = [HA]$. Only the very best candidates stated correctly that on dilution the ratio $[A^-] : [HA]$ remains constant and, as a consequence, $[H^+]$ also remains constant. The calculations in part (d) were generally well done although one mark was lost by candidates who, in (d)(ii), calculated the total final volume of acid, 50.0 cm^3, and not the volume of water which must be added as required by the question.

Q19.

Parts (a) and (b) were well answered. Most candidates correctly calculated the volume of sodium hydroxide needed and although some candidates attempted to answer part (b)(i) in words, most were able to define pH as $-\log_{10}[H^+]$. The indicator expected in part (b)(iii) was the familiar phenolphthalein, but thymol blue (the correct indicator to the January 2002 pH question) was a common and correct answer.

In part (c), the answer that weak acids are only *slightly dissociated* in water was required, rather than not *fully dissociated*, since even strong acids may not be fully dissociated. In part(c)(ii), the general expression for Ka was required, i.e. $[H^+][A^-]/[HA]$ rather than the more particular $[H^+]^2/[HA]$ which only applies to solutions of weak acids alone. The latter expression could however gain credit in the calculation in part (iii). This was answered well by many candidates although some used the number of moles of HA in the calculation rather than its concentration. Not all candidates seemed to be aware that **it is important that pH values are given to two decimal places**; these two figures give the value to the appropriate precision. The numbers before the decimal point only give the powers of ten involved in the hydrogen ion concentration.

Part (d) discriminated well. The better candidates realised that point b was the pH at half equivalence, i.e. when $[A^-] = [HA]$ such that $pH = pK_a$.

Q20.

It is important that pH values are given to two decimal places; these two figures give the value to the appropriate precision. The numbers before the decimal point only give the powers of ten involved in the hydrogen ion concentration.

Three pH values were required in this question and answers to one decimal place only were penalised, but only once on this occasion.

The question involved three calculations of pH. First the pH of a solution of ethanoic acid was required. This was usually well done even by candidates of moderate ability.

The second situation involved a buffer solution formed when some of the weak acid has been reacted with alkali. This was done less well. Many candidates correctly calculated the number of moles of acid used, the number of moles of hydroxide added and hence the number of moles of acid remaining. However, these values were then too often used in a calculation which assumed only a weak acid was present, as in the first part of the question rather than an acidic buffer solution. Although many candidates still seemed unfamiliar with calculations of this type, there was a definite improvement in the numbers gaining full marks compared with the January CHM4 paper.

The last part of the question involved finding the pH of the resulting solution of excess potassium hydroxide produced when all the ethanoic acid is used up. This part was usually answered more successfully than the second part.

Q21.

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Many candidates scored well in parts (a) and (b) but very few seemed confident in dealing with quantitative buffer calculations in part (c). The main errors in part (a)(i) were to write the expression for K_a as

$$K_a = \frac{[H^+]^2}{[CH_3COOH]} \text{ or } \frac{[H+]^2}{[HA]} \text{ rather than } \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

The first is not a general statement while the second does not show that the acid is ethanoic. Despite the loss of this first mark many candidates were able to gain all the remaining marks in part (a). Marks were lost by those who did not take the square root to obtain the hydrogen ion concentration and also by those who gave the pH to one decimal place only. It is important that pH values are given to two decimal places; these two figures give the value to the appropriate precision.
The numbers before the decimal point only give the powers of ten involved in the hydrogen ion concentration. Part (b)(i) was the best answered part of the question and most candidates gained both marks for the calculation. In part (b)(ii) most realised that the titration involved a strong base and a weak acid but the indicator chosen was often bromothymol blue rather than thymol blue, despite the correct explanation that the equivalence point must be above pH 7 for this combination of acid and base. Part (c) was not attempted by a large number of candidates. Of those who did attempt the question, most calculated the number of moles of sodium hydroxide but then used K_w in their calculation as if there was a mixture of strong acid and strong base present. Of those who did realise that an acid buffer had been produced by the reaction of an excess of ethanoic acid with sodium hydroxide, a large proportion forgot to subtract the number of moles of acid reacted from the initial number of moles of acid before substituting in the expression for K_a and gave a pH of 4.12. This answer received four marks out of the six available for the correct answer, 4.23.

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Q1.

(a) completely dissociates/ionises (to form H^+ ions)

1

(b) **M1** moles HCl = 1.035×10^{-3} and moles $Ba(OH)_2$ = 3.75×10^{-3}

If M1 incorrect, lose M1 and M6

1

M2 moles OH^- = 2 × (3.75×10^{-3} = 7.50×10^{-3})

If M2 not x2, lose M2 and M6

1

M3 XS n OH^- = 7.50×10^{-3} - 1.035×10^{-3} = 6.465×10^{-3} mol in 35.35 cm^3

If no subtraction for M3, lose M3 and M6

1

M4 [OH] = 6.465×10^{-3} / 35.35×10^{-3} = 0.182885 mol dm^{-3}

= M3/35.35 × 10^{-3}

If M4 not /35.35 × 10^{-3}, lose M4 and M6

However, if divided by 35.35 only lose M4 and allow M6 (ecf = 10.09)

1

M5 $[H^+] = K_w/[OH^-]$ = 1.47×10^{-14} /0.182885 = 8.0378 × 10–14 mol dm^{-3}

= 1.47 × 10^{-14} / M4

If incorrect rearrangement or wrong equation, lose M5 and M6

If K_w = 1.00 × 10^{-14} used only lose M5 and allow M6 (ecf = 13.26)

1

M6 pH = 13.09 to 13.10

Must be 2dp

1

Alternative MS to get M2:

Starting amounts are 1.035×10^{-3} mol HCl and 3.75×10^{-3} mol $Ba(OH)_2$ M1

So the HCl will react with 5.175×10^{-4} mol of the $Ba(OH)_2$ leaving an excess of 3.2325×10^{-3} mol of $Ba(OH)_2$ (as alternative M2)

So n OH^- = $2 \times 3.2325 \times 10^{-3}$= 6.465×10^{-3} mol M3

Credit other methods eg limiting reagent method since HCl limiting reagent

(c) $[H^+] = [OH^-]$

1

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(d) SO_2

1

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

1

(f) **M1** moles HCl added = 0.01 mol and moles CH_3COOH = 0.035 mol

1

M2 moles CH_3COO^- = 0.025 – 0.01 (= 0.015)

M2 mol CH_3COO^- = 0.025 - M1(HCl)

1

M3 moles CH_3COOH = 0.035 + 0.01 (= 0.045)

M3 mol CH_3COOH = M1(CH_3COOH) + M1(HCl)

1

M4 $[H^+] = 1.76 \times 10^{-5} \times \frac{M3\ (/\ V)}{M2\ (/\ V)}$ (= 5.28×10^{-5})

M4 is conditional on an attempt at an addition/subtraction in M2 OR M3

1

M5 pH = 4.28

M5 must be 2dp

If used 0.07 mol for CH_3COOH can score M2, M3 and M4 (pH = 4.03)

1

[15]

Q2.

(a) Ans = C

1

(b) $[H^+] = \sqrt{K_w} = \sqrt{}\ 2.93 \times 10^{-15}$ (= 5.41×10^{-8})

1

pH = ($-\log (5.41 \times 10^{-8})$ = 7.27

Must be 2dp

7.27 scores 2 marks

1

(c) $[H^+]$ = [OH-]

allow description in words

equal moles / quantities / numbers / ratio of H^+ and OH^-

1

(d) $[OH^-] = 0.0131 \times 2 = 0.0262$

pH = 12.95 scores 3 marks

pH = 12.42 scores 2 marks ($K_w = 1 \times 10^{-14}$)

pH = 12.65 scores 1 mark (not multiplied by 2)

pH = 12.35 scores 1 mark (divided by 2)

pH = 12.12 scores 0 marks (no × 2 and wrong K_w)

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1

$[H^+] = (K_w / [OH^-]) = 2.93 \times 10^{-15} / 0.0262 (= 1.118 \times 10^{-13})$

1

$pH = (- \log (1.118 \times 10^{-13}) = 12.9514 = 12.95$
Or
$[OH^-] = 0.0131 \times 2 = 0.0262$
$pOH = (-\log 0.0262) = 1.5817$
$pH = (-\log K_w - pOH = -\log 2.93 \times 10^{-15} - 1.58 = 14.53 - 1.58) = 12.95$
allow to 2dp or more

1

(e) smaller / lower pH / less alkaline / more acidic
If not smaller CE = 0/2
Allow pH number between 8 and 12

1

(magnesium hydroxide) is less soluble / sparingly soluble/ solubility of hydroxide increases down group II
M2 dependent on M1 but if blank mark on
Ignore concentration and dissociation
Ignore incorrect formula
Do not allow $Mg(OH)_2$ is insoluble

1

[9]

Q3.

B

[1]

Q4.

(a) Proton donor

1

(b) Completely ionises to give H^+ ions in water

1

(c) 0.058 mol dm^{-3}

1

1.24

1

(d) Amount of NaOH = 5.25×10^{-3}

1

Since 1:1 reaction amount of OH^- ions in excess

$= 5.25 \times 10^{-3} - 1.45 \times 10^{-3}$ mol

$= 3.80 \times 10^{-3}$ moles OH^-

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1

$[OH^-] = 3.80 \times 10^{-3} \times 1000/60 = 0.0633$

1

$K_w = [H^+][OH^-$ so $H^+ = \frac{10^{-14}}{0.0633} = 1.58 \times 10^{-13}$

1

pH = 12.80

1

(e) Amount of OH^- added 1.5 / 40 = 0.0375 mol

1

Use of 1:1 ratio to calculate amount of A^- formed = 0.0375 mol

1

Amount of weak acid initially = 1 × 0.15 = 0.150 mol so amount of weak acid after addition of NaOH = 0.150 − 0.0375 = 0.1125

If M3 incorrect can only score max of 3 marks

1

$[H^+] = K_a [HA]/[A^-]$ or $[H^+] = 1.79 \times 10^{-5} \times 0.1125/0.0375$

1

$= 5.37 \times 10^{-5}$

1

pH = 4.27

1

[15]

Q5.

(a) $CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$
OR

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

Must show $\rightleftharpoons$
Allow CH_3CO_2H, $CH_3CO_2^-$
Ignore state symbols

1

(b) $(CH_3COOH + \underline{HNO_3} \longrightarrow CH_3COOH_2^+ + NO_3^-)$

IGNORE $\rightleftharpoons$
Allow CH_3CO_2H, $CH_3CO_2H_2^+$, $CH_3C^+(OH)_2$

1

(c) (i) (new $[HNO_3] = [H^+] = \frac{100}{150} \times 0.0125$)

M1 $[H^+] = 8.3(3) \times 10^{-3}$ (mol dm^{-3})
OR

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$new[HNO_3] = \frac{\text{mol } HNO_3}{\text{total vol}} = \frac{1.25 \times 10^{-3}}{150 \times 10^{-3}}$

1

M2 pH = − log M1 OR 2.08

Must be 2dp

Allow correct pH conseq to their $[H^+]$ concentration

1

(ii) M1 mol NaOH (= $50 \times 10^{-3} \times 0.0108$) = 5.40×10^{-4}

1

M2 Subtraction of M1 from moles of HNO_3 (1.25×10^{-3} or conseq from 1c(i))

Excess mol $H^+ = 7.10 \times 10^{-4}$

M2 allow ecf for subtraction of mol

If no subtraction, no further marks

1

M3 $[H^+] = \frac{M2}{150 \times 10^{-3}}$ OR $\frac{7.10 \times 10^{-4}}{150 \times 10^{-3}} = 4.73 \times 10^{-3}$

M3 <u>if no use of volume, no further marks</u> (pH=3.15)

If incorrect volume used, can score M4

1

M4 pH = -log M3 OR 2.32

M4 Allow 2.33 Must be 2 dp

1

(d) (i) M1 $K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$

Penalise ( ) once here Not [H+][A-] / [HA]

If K_a expression wrong – Allow correct pH conseq to their $[H^+]$ concentration M4 only

1

M2 $K_a = \frac{[H^+]^2}{[CH_3COOH]}$ or with numbers or with HA

1

M3 $[H^+] = [\sqrt{(1.74 \times 10^{-5} \times 0.0125)}] = 4.66 \times 10^{-4}$

Mark for answer

1

M4 pH = 3.33

Must be 2dp

Allow correct pH conseq to their $[H^+]$ concentration

(pH = 3.83 can score M1, M2 and M4)

1

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(ii) Sodium ethanoate

Ignore formula

Allow sodium acetate

1

(iii) M1 $[H^+] = 1.45 \times 10^{-5}$

Accept 1.445×10^{-5} or 1.4×10^{-5}

1

M2

$$\frac{[salt]}{[acid]} \text{ (OR } \frac{[CH_3COO^-]}{[CH_3COOH]} = \frac{Ka}{[H^+]} \text{)= } \frac{1.74 \times 10^{-5}}{1.45 \times 10^{-5}}$$

If M1 incorrect CE=0

Inclusion of 0.0125 in calculation can only score M1

1

M3 1.2(0)

Ignore units

1.4×10^{-5} gives 1.24

1

(e) M1 (Electronegative) chlorine withdraws electrons

Allow Cl has negative inductive effect

1

M2 Stabilises/reduces charge on COO-

OR weakens O-H bond

OR makes O-H more polar

Ignore chloroethanoic acid dissociates more readily

Mark independently

1

(f) M1 Strong acids (almost) completely dissociated/ionised

OR not an equilibrium

OR equilibrium lies far to the right

Cannot have K_a value for a reaction not in equilibrium scores both marks

1

M2 K_a value for strong acids tends to infinity/is very large
OR can't divide by zero in K_a

1

[20]

Q6.

(a) $[H_2O]$ is very high (compared with $[H^+]$ and $[OH^-]$)
OR
Very few H^+ and OH^- ions
OR

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Only / very slightly dissociates
OR
Equilibrium lies far to the left

Not partially dissociates

M1
1

$[H_2O]$ is (effectively) constant
OR is incorporated into the constant K

Allow changes by only a very small amount

M2
1

(b) (Dissociation OR breaking bonds) is endothermic

1

∴ Equilibrium moves to RHS (at higher T) to absorb heat or to lower T or oppose increase in T

Allow to oppose change only if increase T mentioned

1

(c) $[H^+]$ = $\sqrt{K_w}$ (or = $\sqrt{5.48 \times 10^{-14}}$)

Correct pH answer scores 3

1

If wrong method no marks

Using alternative K_w (1.00×10^{-14}) gives pH = 7.00 which scores 1

= 2.34×10^{-7}

1

pH = 6.63

Final answer must have 2dp

1

(d) $[H^+]$ = K_w / $[OH^-]$ or (= 5.48×10^{-14} / 0.12)

Correct pH answer scores 3

1

If wrong method no marks

If use alternative K_w (1.00×10^{-14}) again, do not penalise repeat error so pH = 13.08 scores 3

= 4.566×10^{-13}

1

pH = 12.34

*If use alternative K_w (1.00×10^{-14}) **not** as a repeat error, pH = 13.08 scores 1*

If AE in K_w value made in part (c) is repeated here, do not penalise again.

Final answer must have 2dp, but if dp penalised in (c) allow

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more than 2dp here but not fewer.

1

[10]

Q7.

(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 = 12.38 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) $K_a = \frac{[H^+][C_6H_5COO^-]}{[C_6H_5COOH]}$

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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 = 3.06

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

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

1

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

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*

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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 (lt) 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]

Q8.

(a) **M1** $[H^+] = 0.0170$

1

M2 pH = 1.77

2 dp

Allow M2 for correct pH calculation from their wrong $[H^+]$ for this pH calculation only

1

(b) (i)

$$K_a = \frac{[H^+][X^-]}{[HX]^2} \quad \text{Ignore} \quad K_a = \frac{[H^+]^2}{[HX]}$$

*Penalize missing [ ] here **and not elsewhere***
Allow HA instead of HX

1

(ii) **M1** $[H^+] = 10^{-2.79}$ OR $1.6218\ldots \times 10^{-3}$

If $[H^+]$ wrong, can only score M2

1

M2 $K_a = \frac{[H^+]^2}{[HX]}$ OR $\frac{[1.62 \times 10^{-3}]^2}{[0.0850]}$

Allow HA instead of HX

1

M3 $K_a = 3.09 \times 10^{-5}$ 3sfs min

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(allow 3.10 ×10^{-5} if 1.6218 rounded to 1.622)
Ignore units
If [HX] used as (0.0850 –1.62 ×10^{-3})
this gives K_a = 3.15 ×10^{-5}
(0.0016)^2/0.085 = 3.01 ×10^{-5} scores 2 for AE

1

(c) **M1** mol OH^- (= (38.2 × 10^{-3}) × 0.550)

= 2.10(1) × 10^{-2} or 0.0210(1)
Mark for answer

1

M2 Mol H^+ (= (25.0 × 10^{-3}) × 0.620)

= 1.55 × 10^{-2} or 0.0155
Mark for answer

1

M3 excess mol OH^- = 5.5(1) × 10^{-3}

Allow conseq for M1 – M2
***If wrong method** e.g. no subtraction or use of √*
can only score max of M1, M2, M3 and M4.

1

M4 $[OH^-] = 5.51 \times 10^{-3} \times \frac{10^3}{63.2}$ [= 0.08718 (0.0872)]

OR $[OH^-] = 5.5 \times 10^{-3} \times \frac{10^3}{63.2}$ = 0.0870(2)

(M1 – M2) / vol in dm^3 mark for dividing by volume
(take use of 63.2 without 10^{-3} as AE so 9.94 scores 5)
If no use or wrong use of vol lose M4 & M6
Can score M5 for showing (10^{-14}/ their XS alkali)

1

M5 $[H^+] = \frac{10^{-14}}{0.08718} = 1.147 \times 10^{-13}$

OR $\frac{10^{-14}}{0.0870} = 1.149 \times 10^{-13}$

OR pOH = 1.06
If no use or wrong use of K_w or pOH no further marks

1

M6 pH = 12.9(4) allow 3sf
If vol missed score max 4 for 11.7(4)
If acid– alkali reversed max 4 for pH = 1.06
Any excess acid – max 4

1

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[12]

Q9.

(a) (i) - log[H^+]

penalise missing [ ] here ***and not elsewhere***

1

(ii) [H^+][OH^-]

Allow ( ) brackets, but must have charges

1

(iii) Mark independently from a(ii)

[H^+] = $10^{-13.72}$ = 1.905×10^{-14}

If wrong no further mark

1

$K_w = 1.905 \times 10^{-14} \times 0.154 = = (2.93 - 2.94) \times 10^{-15}$

1

(b) (i) $Ka = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$

Must have charges and all brackets, allow ( )
Acid/salt shown must be CH_3COOH not HA
and correct formulae needed

1

(ii) **In pH values penalise fewer than 3 sig figs each time but allow more than 2 dp**
For values above 10, allow 3sfs - do not insist on 2 dp

$K_a = \frac{[H^+]^2}{[CH_3COOH]}$

Allow HA

1

($[H^+]^2 = 1.75 \times 10^{-5} \times 0.154 = 2.695 \times 10^{-6} = 2.70 \times 10^{-6}$)

If √ shown but not done gets pH = 5.57 (scores 2)

[H^+] = 1.64×10^{-3}

Allow mark for pH conseq to their [H+] ***here only***

1

pH = 2.78 or 2.79

1

(c) (i) **In pH values penalise fewer than 3 sig figs each time but allow more than 2 dp**

For values above 10, allow 3sfs - do not insist on 2 dp

M1 Initially

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mol OH^- = $(10 \times 10^{-3}) \times 0.154$ **and**

mol HA = $(20 \times 10^{-3}) \times 0.154$

or mol OH^- = 1.54×10^{-3} **and** mol HA = 3.08×10^{-3}

1

M2 $[H^+] = K_a \dfrac{[CH_3COOH]}{[CH_3COOH^-]}$

or with numbers

Allow Henderson Hasselbach

$pH = pK_a + log \dfrac{[CH_3COO^-]}{[CH_3COOH]}$

M3 mol ethanoic acid left = (mol ethanoate ions) = 1.54×10^{-3}

$K_a = [H^+]$ **or** $pH = pK_a$ scores **M1**, **M2** and **M3**

1 If either mol acid in mixture or mol salt wrong
- max 2 for M1 and M2
Any mention of $[H^+]^2$ - max 2 for M1 and M3

1

M4 pH (= - log 1.75×10^{-5}) = 4.76 or 4.757

Not 4.75

1

If no subtraction (so mol ethanoic acid in buffer = original mol)
pH = 4.46 scores 2 for **M1** and **M2**
If $[H+]^2$ used, pH = 3.02 scores 2 for **M1** and **M3**

(ii) **In pH values penalise fewer than 3 sig figs each time but allow more than 2 dp**
For values above 10, allow 3sfs - do not insist on 2 dp

M1 <u>XS mol KOH</u> (= $(20 \times 10^{-3}) \times 0.154$) = 3.08×10^{-3}

If no subtraction: max 1 for correct use of volume
No subtraction and no use of volume scores zero
If wrong subtraction or wrong moles
*Can only score **M2** and **M3** for process*

1

M2 $[OH^-] = 3.08 \times 10^{-3} \times \dfrac{10^3}{60} = 0.0513(3)$

*Mark for dividing their answer to **M1** by correct volume (method mark)*
*If no volume or wrong volume or multiplied by volume, max 2 for **M1** and **M3** process*

1

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M3 $[H^+] = \frac{10^{-14}}{0.05133}$ (= 1.948×10^{-13} to 1.95×10^{-13})

or pOH = 1.29

*Mark for K_w divided by their answer to **M2***

If pOH route, give one mark for 14 – pOH

1

M4 pH = 12.7(1)

Allow 3sf but not 12.70

1

If no subtraction and no use of volume (pH = 11.79 scores zero)
If no subtraction, max 1 for correct use of volume, ($60cm^3$)
(pH = 13.01 scores 1)
If volume not used, pH = 11.49 (gets 2)
If multiplied by vol, pH = 10.27 (gets 2)

[16]

Q10.

(a) (i) $-\log[H^+]$

*Penalise missing [ ] here **and not elsewhere***

1

(ii) $[H^+][OH^-]$

1

(b) (i) $[H^+] = 2.34 \times 10^{-7}$

1

pH = 6.63

Penalise fewer than 3 sig figs but allow more than 2 dp

1

(ii) $[H^+] = [OH^-]$

1

(iii) **M1** $[H^+] = K_w/[OH^-]$

if upside down or CE, allow M3 only for correct use of their $[H^+]$

1

M2 $(= 5.48 \times 10^{-14}/0.140) = 3.91 \times 10^{-13}$

1

M3 pH = 12.4(1)

not 12.40 (AE from 12.407)

1

Penalise fewer than 3 sig figs but allow more than 3 sfs
For values above 10, allow 3sfs - do not insist on 2 dp.
For values below 1, allow 2dp – do not insist on 3 sig figs
Not allow pH = 14 – pOH but can award M3 only for pH = 13.1(46)

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Can award all three marks if $pK_w = 13.26$ is used

(c) **M1** mol NaOH = mol OH^- = $(30 \times 10^{-3}) \times 0.20 = 6.0 \times 10^{-3}$

mark for answer

1

M2 mol H_2SO_4 = $(25 \times 10^{-3}) \times 0.15 = 3.75 \times 10^{-3}$

mark for answer

1

M3 mol H^+ = $(25 \times 10^{-3}) \times 0.15 \times 2 = 7.5 \times 10^{-3}$
OR XS mol H_2SO_4 = 0.75×10^{-3}

if factor of 2 missed or used wrongly, CE - lose M3 and next mark gained. In this case they must then use K_w to score any more.
see examples below

1

M4 XS mol H^+ = 1.5×10^{-3}

1

M5 $[H^+]$ = $(1.5 \times 10^{-3}) \times (1000/55) = 0.0273$

if no use or wrong use of volume, lose M5 and M6 except if 1000 missed
AE –1 (pH = 4.56)

1

M6 pH = 1.56

Penalise fewer than 3 sig figs but allow more than 3 sfs
For values above 10, allow 3sfs - do not insist on 2 dp.
For values below 1, allow 2dp – do not insist on 3 sig figs

1

[14]

Q11.

(a) (i) $-\log[H^+]$

or $\log 1/[H^+]$
penalise ( )

1

(ii) $[H^+] = 0.56$

mark for the answer; allow 2dp or more

1

$[H_2SO_4] = ½ \times 0.56 = 0.28$

1

(b) (i) $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

OR

$CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$

Allow CH_3CO_2H etc

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1

(ii) mol acid = $(25.0 \times 10^{-3}) \times 0.41 = 1.025 \times 10^{-2}$ or 1.03×10^{-2}

1

$[NaOH] = 1.025 \times 10^{-2}/22.6 \times 10^{-3} = 0.45(4)$

mark for answer
if not 0.454 look back for error

1

OR

$[NaOH] = 1.03 \times 10^{-2}/22.6 \times 10^{-3} = 0.456$ or 0.46

(iii) cresol purple

1

(iv) NaOH reacts with <u>carbon dioxide</u> (in the air)

1

(c) (i) $K_a = \dfrac{[H^+][CH_3COO^-]}{[CH_3COOH]}$

allow molecular formulae or minor slip in formulae

penalise ( )
allow H_3O^+
not allow HA etc

1

(ii) $K_a = \dfrac{[H^+]^2}{[CH_3COOH]}$ or with numbers

1

allow HA etc here
This can be scored in part (c)(i) but doesn't score there.

$[H^+] = (\sqrt{(1.74 \times 10^{-5} \times 0.410)} = \sqrt{(7.13 \times 10^{-6})}) = 2.67 \times 10^{-3}$

1

mark for 2.67×10^{-3} or 2.7×10^{-3} either gives 2.57

pH = 2.57 can give three ticks here for (c)(ii)
penalise decimal places < 2 >

1

pH mark conseq on their $[H^+]$
so 5.15 gets 2 marks where square root not taken

(iii) **M1** mol OH^- = $(10.0 \times 10^{-3}) \times 0.10 = 1.0 \times 10^{-3}$

If no subtraction or other wrong chemistry the max score is 3 for M1, M2 and M4

1

M2 orig mol HA = $(25.0 \times 10^{-3}) \times 0.41 = 0.01025$

1

or 1.025×10^{-2} or 1.03×10^{-2}

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M3 mol HA in buffer = orig mol HA – mol OH^-

1

= 0.00925 or 0.0093

If A^- is wrong, max 3 for M1, M2 and M3 or use of pH = pKa – log [HA]/[A^-]

M4 mol A^- in buffer = mol OH^- = 1.0×10^{-3}

Mark is for insertion of correct numbers in correct expression for [H^+]

1

M5 $[H^+] = \left(\frac{K_a \times [CH_3COOH]}{[CH_3COO^-]} = \right)$

1

$$\frac{(1.74 \times 10^{-5})(0.00925)}{0.0010} \text{ or } \frac{(1.74 \times 10^{-5})(0.00930)}{0.0010}$$

(= 1.61×10^{-4} or 1.62×10^{-4})

M6 pH = 3.79 can give six ticks for 3.79

if [HA]/[A^-] upside down lose M5 & M6

If wrong method e.g. $[H^+]^2$/[HA] max 3 for M1, M2 and M3

Some may calculate concentrations
[HA] = 0.264 and [A^-] = 0.0286 and rounding this to 0.029 gives pH = 3.80 (which is OK)

NB Unlike (c)(ii), this pH mark is NOT awarded conseq to their [H^+] unless following AE

BEWARE: using 0.01025 wrongly instead of 0.00925 gives pH = 3.75
(this gets 3 for M1, M2 & M4)

1

[18]

Q12.

(a) (i) $[H^+][OH^-]$

1

– log $[H^+]$

1

(ii) $[H^+] = [OH^-]$

1

(iii) $(2.0 \times 10^{-3}) \times 0.5 = 1.0 \times 10^{-3}$

1

(iv) $[H^+] = \frac{4.02 \times 10^{-14}}{1.0 \times 10^{-3}}$ (= 4.02×10^{-11})

1

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pH = 10.40

1

(b) (i) $K_a = \frac{[H^+][CH_3CH_2COO^-]}{[CH_3CH_2COOH]}$

1

$= \frac{[H^+]}{[CH_3CH_2COOH]}$

1

$[H^+] = \sqrt{(1.35 \times 10^{-5}) \times 0.125}$ $(= 1.30 \times 10^{-3})$

1

pH = 2.89

1

(c) (i) $(50.0 \times 10^{-3}) \times 0.125 = 6.25 \times 10^{-3}$

1

(ii) $(6.25 \times 10^{-3}) – (1.0 \times 10–3) = 5.25 \times 10^{-3}$

1

(iii) mol salt formed $= 1.0 \times 10^{-3}$

1

$[H^+] = K_a \times \frac{[CH_3CH_2COOH]}{[CH_3CH_2COO–)}$

1

$= (1.35 \times 10^{-5}) \times \frac{(5.25 \times 10^{-3})/V}{(1.0 \times 10^{-3})/V}$ $(= 7.088 \times 10^{-5})$

1

pH = 4.15

1

[16]

Q13.

(a) Hydrogen bonding **(1)**
between H_2O and NH_3 **(1)**

2

(b) (i) $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ **(1)**

(ii) Ammonia is weak base **(1)**
NOT partially ionised

Equilibrium to left or incomplete reaction **(1)**

3

(c) A proton donor **(1)**

1

(d) *Buffer solution*: A solution which resists change in pH **(1)**

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when small amounts of acid or base added or on dilution **(1)**

Reagent: NH_4Cl **(1)**

Allow a correct strong acid

3

(e) (i) $K_a = [H^+] [A^-] / [HA]$ **(1)**

$= [H^+] [0.125 \times 4]$ **(1)** / 1.00

$[H^+] = 1.70 \times 10^{-5} / 0.125 \times 4 = 3.40 \times 10^{-5}$ **(1)**

$pH = -\log_{10} [H^+] = 4.47$ **(1)**

Allow pH conseq to $[H^+]$ if 2 place decimals given

(ii) $H^+ + CH_3COO^- \rightarrow CH_3COOH$ **(1)**

5

[14]

Q14.

A

[1]

Q15.

Penalise pH given to 1 dp <u>first</u> time it would have scored only

(a) (i) $K_w = [H^+] [OH^-]$ **(1)**

(ii) $pH = -\log [H^+]$ **(1)**

or in words or below unless contradiction

(iii) *Calculation*: $[H^+] = \sqrt{5.48 \times 10^{-14}}$ **(1)**

$= 2.34 \times 10^{-7}$

$\therefore$ pH = 6.63 or 6.64 **(1)**

Explanation: pure water $\therefore$ $[H^+] = [OH^-]$ **(1)**

5

(b) (i) $[OH^-] = 0.150$ $\therefore$ $[H^+] = 10^{-14}/0.15 = 6.66 \times 10^{-14}$

or pOH = 0.82

$\therefore$ pH = 13.18 **(1)**

or pH= 13.17

(ii) moles $OH^- = (35 \times 10^{-3}) \times 0.150 = 5.25 \times 10^{-3}$ **(1)**[a]

moles $H^+ = (40 \times 10^{-3}) \times 0.120 = 4.8(0) \times 10^{-3}$ **(1)**[b]

$\therefore$ excess moles of $OH^- = 4.5 \times 10^{-4}$ **(1)**[c]

$\therefore$ $[OH^-] = (4.5(0) \times 10^{-4}) \times 1000/\underline{75}$[d] **(1)**[e]

$= 6.0(0) \times 10^{-3}$

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$[H^+] = \frac{10^{-14}}{6.00 \times 10^{-3}}$ = 1.66 × 10^{-12} or pOH = 2.22

∴ pH = 11.78 **(1)**^{f}
or 11.77

8

(c) (i) $K_a = \frac{[H^+][X^-]}{[HX]}$ **(1)**

(ii) $[H^+]$ = 1.80 × 10^{-2} × 0.150 = 2.70 × 10^{-3} (1)

$K_a = \frac{[H^+]^2}{[HX]}(1) = \frac{(2.70 \times 10^{-3})^2}{0.150}$ = 4.86 × 10^{-5} **(1)** mol dm^{-3} **(1)**

or $\frac{(2.70 \times 10^{-3})^2}{0.1473}$ = *4.95 × 10^{-5}*

5

Notes

(a) If K_w includes H_2O allow 6.63 if seen otherwise no marks likely

(b) (ii) If no vol, max 4 for a, b, c, f answer = 10.65
If wrong volume max 5 for a, b, c, e, f
If no substraction max 3 for a, b, d
If missing 1000 max 5 for a, b, c, d, f answer = 8.78
If uses excess as acid, max 4 for a, b, d, f answer = 2.22
If uses excess as acid and no volume, max 2 for a, b answer = 3.35

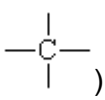
(c) If wrong K_a in (i) max 2 in part (ii) for $[H^+]$ **(1)** and conseq units **(1)**
but mark on fully from minor errors
eg no [ ] or charges missing

Organic points

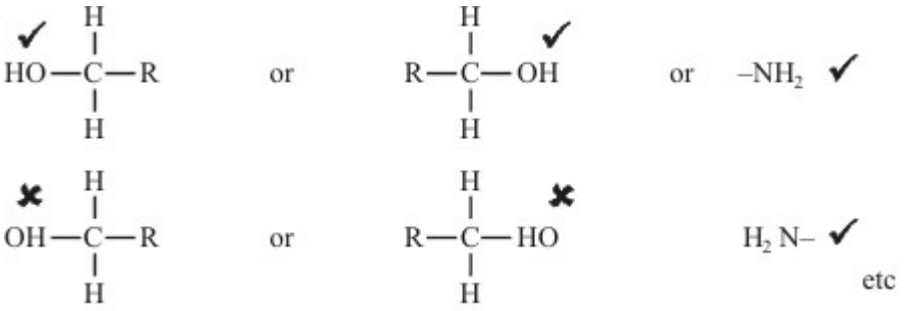
(1) Curly arrows: must show movement of a pair of electrons, i.e. from bond to atom or from lp to atom / space
e.g.



(2) Structures

penalise sticks (i.e. ) once per paper

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Penalise once per paper

allow CH_3– or –CH_3 or $\begin{matrix} & CH_3 \\ & | \end{matrix}$ or CH_3
or H_3C–

[18]

Q16.

C

[1]

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Q1.

(a) 86.2% of students gave the correct definition.

(b) Most students calculated the amounts, in moles, of the reactants but often did not multiply the amount of barium hydroxide by two to give the amount of hydroxide ions. Some students did not convert the amount in moles to concentration and some did not quote their pH to two decimal places. This part of the question discriminated very well, with just over 20% of students scoring full marks.

(c) 81.8% of students gave the correct reason here.

(d) 78.5% correctly identified sulphur dioxide.

(e) 91% of students could give the correct expression for K_a.

(f) Most students could calculate the amount, in moles, of hydrochloric acid and of ethanoic acid, but many were unsure of how to use these numbers. Many students failed to recognise the need to increase the amount of acid and decrease the amount of salt due to the shift in the equilibrium when H^+ ions are added. Many added and subtracted the wrong way round or managed one process but not the other. Students could generally rearrange the K_a expression correctly; just over 40% of students scored full marks for this part of the question.

Q2.

(a) This question was answered well (89.5% correct).

(b) Many students scored both marks here, although some did not give the answer to two decimal places and thereby lost a mark; some students failed to take the square root of K_w.

(c) The answer to this question was generally well known, although some students appeared to believe that a pH of 7.27 was not sufficiently alkaline.

(d) This question differentiated well. Many students failed to appreciate that calcium hydroxide is dibasic and an answer of 12.65 was common. Some students used $K_w = 1.00 \times 10^{-14}$ and a few students failed to give the answer to two decimal places.

(e) The idea that magnesium hydroxide is less soluble than calcium hydroxide was appreciated by only a few students. Many thought the pH value should be the same. Some who gave a lower pH followed this with a discussion about the magnesium ion's greater polarising power.

Q5.

Question (a) was generally well done, but a large number of students did not include a reversible sign in their equation for dissociation of the weak acid. Part (b) differentiated well as weaker students failed to show how ethanoic acid could act as a base and accept a proton.

Part (c)(i) was more straightforward but some students failed to calculate the concentration of the acid correctly and just used a number of moles. Part (c)(ii) differentiated well: many students realised a subtraction was needed in the calculation,

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but then failed to use the total volume to convert the amount, in moles, of H^+ ions to a concentration to calculate the pH.

Part (d)(i) was completed very well with most students gaining either 3 or 4 marks. In part (d)(iii) a significant number incorrectly used the original amount in moles of acid (0.0125) in their ratio. Even some of the strongest students struggled with the maths skills required and a frequent wrong answer was the inverse of 1.20 due to incorrect rearrangement. A significant number did not work out the hydrogen ion concentration and so lost M1 when they couldn't complete the rest of the calculation.

Part (e) differentiated well with full descriptions seen in about a third of the answers and one mark gained by another third. In part (f) the first mark proved very accessible but the second proved trickier; many students showed poor maths skills and thought that K_a would equal 1 or zero.

Q6.

The answers to part (a) were such that few scored both marks. Not only was the reason not well known, but a lot of wrong chemistry was written. Common errors included 'H_4O is completely ionised' and 'the concentration of water is 1'.

The answers to part (b) were slightly better and most students stated that the ionisation of water is an endothermic reaction, but a high number failed either to appreciate that this ionisation produces an equilibrium mixture or to explain that the equilibrium position moves to the RHS to oppose the increase in temperature.

Most students answered part (c) and part (d) well. A significant number of students used the K_w value for 25°C, but this was only penalised once in the two parts. A small number failed to give their answer to the accuracy specified in the question (2 dp).

Q7.

This question was generally well attempted, with most students scoring well in the mathematical sections. In part (a), most students gave the meaning of a weak acid as 'only partially ionised or dissociated into ions', and this was credited. The preferred answer was □only slightly ionised'. 'Not fully ionised' did not gain the mark. The equation in part (b) was poorly answered mainly because the formula for sodium carbonate was incorrect. In some cases, the formula of sodium hydroxide or sodium hydrogen carbonate was given. A common error in part (c) was to omit the factor of 2 when calculating the concentration of hydroxide ions from the concentration of calcium hydroxide. Parts (d)(i) and (d)(ii) were answered well but in part (d)(iii) many students used an expression for K_c with $[H^+]^2$ or could not rearrange the correct expression to find the concentration of sodium benzenecarboxylate. Students should be encouraged to use words in their answers to make it clear whether the numbers they write refer to amounts in moles or to concentrations and also to which substance they refer. Answers to part (e) included many wrong substances and showed that some students think that H_2 (or H^+) is present in the atmosphere or that carbonic acid can exist in an alkaline solution.

Q8.

All of the pH calculations in this question were answered well. In part (a), more students than expected had difficulty calculating the $[H^+]$ after dilution but a mark was allowed for a correct calculation of pH from their $[H^+]$. In part (b)(ii), some students struggled to convert the pH into $[H^+]$ but over three quarters of the entry gained all three marks. In part (c), common mistakes included using the initial number of moles of OH^- rather than those remaining after partial neutralisation and also not using the total volume to convert the

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number of moles of excess hydroxide into a concentration. The degree of clarity of some students' working was also disappointing; many wrote strings of numbers with no explanation of what they were calculating. As usual, students who made errors in their calculations or gave a wrong answer with no explanation or working could gain few marks.

Q9.

As expected, there were very few incorrect answers to parts (a)(i) and (ii). However, in part (a)(iii), some candidates assumed that $[H^+] = [OH^-]$ instead of using all the data in the question. Part (b) was generally well attempted, but common mistakes in part (b)(i) included incorrect formulae for ethanoic acid and the ethanoate ion, missing brackets and giving $[H^+]^2$ as the numerator.

Part (c)(i) proved to be difficult. While most candidates were able to calculate the initial numbers of moles of the acid and alkali, a large proportion could not rearrange the *K*a expression correctly or assumed that the amount of acid had not changed on addition of the alkali. Very few realised that this was a half neutralisation and their attempts to calculate the concentrations of acid and salt were often wrong and sometimes included the term $[H^+]^2$.

Part (c)(ii) was more successfully attempted, but still many candidates scored only 2 marks, either because they did not realise that some of the alkali would be neutralised by adding acid or because they failed to use the total volume to convert the number of moles of OH^- into a concentration.

Q10.

Most of this question proved to be straightforward and few candidates lost marks in part (a). Part (c) was the most discriminating section with only the better candidates scoring all six marks. Many others either forgot that sulfuric acid is diprotic and so missed that the final mixture in the questions was acidic or failed to convert the number of moles of H^+ ions present into a concentration in order to find pH.

Q11.

This question was generally well answered and only rarely did candidates fail to follow the instructions to give their pH values to two decimal places.

In part (a)(ii) only a fifth of the candidates realised that sulfuric acid is diprotic and in part (b)(i) only two thirds of the entry could write a correct equation for the reaction of ethanoic acid with sodium hydroxide. The following titration calculation was very straightforward but was thought more complicated by many including those who introduced K_w. It was disappointing to see that only the very best candidates understood that sodium hydroxide solution reacts with carbon dioxide in the air and many candidates showed a strange understanding of the composition of air. Part (c)(ii) was well answered; nearly four fifths of candidates answered this part completely correctly. Answers to the unstructured buffer calculation in part (c)(iii) were also quite pleasing; the question differentiated well and over twenty percent of candidates gained full marks. Other candidates were hindered by poor mathematical skills.

Q12.

The standard expressions in part (a)(i) were answered well by almost all candidates, although some quote values for Kw and pH instead of reading the question carefully.

In part (a)(ii) some missed the essential point that in pure water, the concentrations of H^+

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and OH^- ions are equal at all temperatures even if the pH scale is based on a value of Kw different from 1.0^{-14}. In part (a)(iii) most were able to calculate the number of moles of OH^- present as 1.0×10^{-3}, but many failed to realise that, in part (iv), when this number of moles were added to 998 cm^3 of water, the concentration of OH^- in the solution formed would be 1.0×10^{-3} mol dm^{-3}. A few failed to use the given value of Kw but many were able to calculate the correct answer of 10.40.

Part (b) was generally very well answered and a pH of 2.89 was the most common answer. Some candidates, gave the answer 5.77 by forgetting to take the necessary square root in their working.

Part (c) was a buffer calculation, an area which candidates traditionally find difficult. Disappointingly, this again proved the case despite the lead in to the question given in parts (i) and (ii). While most were able to calculate the initial number of moles of propanoic acid and almost as many could calculate the number of moles of acid present in the buffer solution formed, few gained many more marks. Many tried to calculate the concentrations of the acid and the salt formed failing to realise that the volume involved cancels. Many were unable to rearrange the expression for Ka and many confused the number of moles of propanoic acid with the number of moles of H^+ present inn the solution.

Q13.

Only the best candidates correctly explained the solubility of ammonia in water by reference to hydrogen bonding between water and ammonia molecules. The equation for the reaction between ammonia and water was often given correctly but few stated that, because ammonia is a weak base, it reacts reversibly with water forming a solution containing a small concentration of hydroxide ions. Most, but certainly not all, candidates knew the meaning of the term *Bronsted-Lowry* acid and answered part (c) correctly. Answers to part (d) were, by contrast, rather disappointing with many vague or incorrect statements of the term *buffer solution*. The calculation in part (e)(i) was not well done. Many candidates used the relationship $Ka = [H^+]^2/[HA]$ which can only be used for a solution of a weak acid alone. Others failed to calculate the concentration of ethanoate ions in mol dm^{-3} before calculating the hydrogen ion concentration. Part (c)(ii) proved surprisingly difficult with only the better candidates giving the correct ionic equation.

Q15.

Definitions of the terms Kw and pH in parts (a)(i) and (ii) were usually well answered except by those who failed to write mathematical definitions and attempted to describe the terms in words. Provided there were no contradictions, the marks could be earned in the later sections. The most common error in the expression for Kw was to include water. However this water term was conveniently forgotten in part (iii) and correct answers for the pH of pure water at 50°C were common. As reported regularly before, too many candidates seem not to be aware **that pH values should be given to two decimal places**; these two figures give the value to the appropriate precision. The numbers before the decimal point only give the powers of ten involved in the hydrogen ion concentration. However, failure to give pH values to the correct precision was only penalised once in the question. Part (b)(i) was answered well but (b)(ii) was more discriminating. A common error was to forget that the moles of excess sodium hydroxide were present in a total volume of solution of 75 cm^3 and needed to be converted into a molar concentration before the pH of the solution could be calculated.

A number of candidates tried to answer the question as if a buffer solution had been produced despite the use of a named strong acid. Several also gave pH values below 7 although there was an excess of alkali present. Part (c) was answered well by most candidates although some failed to give the general expression for K_a and instead wrote the more specific $[H^+]^2/[HX]$.

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This expression was however credited in part (c)(ii).

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Q1.

(a) completely dissociates/ionises (to form H^+ ions)

1

(b) **M1** moles HCl = 1.035×10^{-3} and moles $Ba(OH)_2$ = 3.75×10^{-3}

If M1 incorrect, lose M1 and M6

1

M2 moles OH^- = 2 × (3.75×10^{-3} = 7.50×10^{-3})

If M2 not x2, lose M2 and M6

1

M3 XS n OH^- = 7.50×10^{-3} - 1.035×10^{-3} = 6.465×10^{-3} mol in 35.35 cm^3

If no subtraction for M3, lose M3 and M6

1

M4 [OH] = 6.465×10^{-3} / 35.35×10^{-3} = 0.182885 mol dm^{-3}

= M3/35.35 × 10^{-3}

If M4 not /35.35 × 10^{-3}, lose M4 and M6

However, if divided by 35.35 only lose M4 and allow M6 (ecf = 10.09)

1

M5 $[H^+] = K_w/[OH^-]$ = 1.47×10^{-14} /0.182885 = 8.0378 × 10–14 mol dm^{-3}

= 1.47 × 10^{-14} / M4

If incorrect rearrangement or wrong equation, lose M5 and M6

If K_w = 1.00 × 10^{-14} used only lose M5 and allow M6 (ecf = 13.26)

1

M6 pH = 13.09 to 13.10

Must be 2dp

1

Alternative MS to get M2:

Starting amounts are 1.035×10^{-3} mol HCl and 3.75×10^{-3} mol $Ba(OH)_2$ M1

So the HCl will react with 5.175×10^{-4} mol of the $Ba(OH)_2$ leaving an excess of 3.2325×10^{-3} mol of $Ba(OH)_2$ (as alternative M2)

So n OH^- = $2 \times 3.2325 \times 10^{-3}$= 6.465×10^{-3} mol M3

Credit other methods eg limiting reagent method since HCl limiting reagent

(c) $[H^+] = [OH^-]$

1

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(d) SO_2

1

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

1

(f) **M1** moles HCl added = 0.01 mol and moles CH_3COOH = 0.035 mol

1

M2 moles CH_3COO^- = 0.025 – 0.01 (= 0.015)

M2 mol CH_3COO^- = 0.025 - M1(HCl)

1

M3 moles CH_3COOH = 0.035 + 0.01 (= 0.045)

M3 mol CH_3COOH = M1(CH_3COOH) + M1(HCl)

1

M4 $[H^+] = 1.76 \times 10^{-5} \times \frac{M3\ (/\ V)}{M2\ (/\ V)}$ (= 5.28×10^{-5})

M4 is conditional on an attempt at an addition/subtraction in M2 OR M3

1

M5 pH = 4.28

M5 must be 2dp

If used 0.07 mol for CH_3COOH can score M2, M3 and M4 (pH = 4.03)

1

[15]

Q2.

(a) 7–10.2

any range (i.e. 2 values) within this range

1

(b) $K_a = \frac{[H^+][X^-]}{[HX]}$

ALLOW H_3O^+ for H^+ and A for X

IGNORE $[H^+]^2/[HX]$

must be square brackets

IGNORE state symbols

1

(c) Amount NaOH = $(24.0 \times 0.100)/1000 = 2.40 \times 10^{-3}$ mol

(= amount HX)

Conc HX = $2.40 \times 10^{-3}/0.025 = 0.0960$ mol dm^{-3}

ecf for M1/0.025

(d) ($K_a = 2.62 \times 10^{-5} = [H^+]^2/0.0960$)

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$[H^+] = \sqrt{(2.62 \times 10^{-5} \times 0.0960)}$ (= 1.59×10^{-3} mol dm^{-3})

ecf from part (c) $[H^+] = \sqrt{(2.62 \times 10^{-5} \times$ ans to part (c))

From alternative data

$[H^+] = \sqrt{(2.62 \times 10^{-5} \times 0.600)}$ (= 3.96×10^{-3} mol dm^{-3})

(pH = –log 1.59×10^{-3} =) 2.80 (must be 2 or more dp)

1

pH = 2.40 (must be 2 or more dp)

M2 dependent on a calculation of $[H^+]$

1

(e) (pH at half-neutralisation = pK_a)

= –log 2.62×10^{-5} = 4.58 (must be 2 or more dp)

ALLOW 1dp if already penalised in part (d)

1

(f) Both points plotted correctly and line touches both points

ecf from (d) and (e) within 1 small square

1

Line steeper at start then levels (to show buffering)

Mark independently

1

[9]

Q3.

(a) **M1** Temperature on the y-axis and uses sensible scales (i.e. minimum 20 little squares for each °C on y-axis)

Lose mark if temperature scale starts at 0°C

*This mark scores if all points fit on the grid. Do not penalise M1 if extrapolation to 4 mins goes off the grid – this is penalised in **M3**.*

1

M2 Plots all the points correctly (± half a small square)

Lose mark if the points go off the grid Ignore a plotted point at 4 mins used to work out ΔT

1

M3 Draws two best fit lines (0-3 mins) and (6-12 mins)

Both lines must be straight and through all points except 5th minute; lose mark if the lines are kinked/doubled. Any line through 5th minute loses mark

*"S-shaped curve" through points loses **M3** and **M4***

1

M4 Extrapolates both lines to at least the 4th minute

Lose mark if the extrapolation goes off the grid.

1

M5 21.9 – 19.8 = 2.1 (°C)

Allow calculation of ΔT from S-shaped curve as: Value at 4th minute – 19.8 but not if 0 (°C)

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ΔT value ecf from incorrect lines/extrapolation
ΔT must be to at least 1dp
If value of ΔT = 2.1, then award M5

1

(b) 0.2 / 2.1 × 100 = 9.5 %
Conseq on (a)
Ignore no of sfs.

1

(c) Replace the glass beaker with a polystyrene cup / insulate the glass beaker / use a lid
Ignore use more dilute solutions
Ignore suggested materials for insulation
Do not allow copper calorimeter / bomb calorimeter

1

(d) Increase magnitude of temperature change
Ignore references to volume changes

1

by increasing the <u>concentration</u> of the acid/alkali
Mark independently

1

(e) **M1** $HOOCCOOH + 2KOH \rightarrow K_2(OOCCOO) + 2H_2O$
***M1** – equation (allow ionic KOH / $_2C_2O_4$)*
$H_2C_2O_4 + 2KOH \rightarrow K_2C_2O_4 + 2H_2O$
ignore state symbols
allow multiples
Mark independently

M2 q (= mcΔT) = 100 × 4.2 × 3.2 = 1344 J
***M2** – process*
(ignore sign here)
(allow calculations involving 4.18 which leads to 1338 J)

1

M3 n HOOCCOOH = 25 × 0.800 / 1000 = <u>0.020</u>
n KOH = 75 × 0.6 / 1000 = <u>0.045</u>
M3 – calculations of amounts, in moles, of both the ethanedioic acid and potassium hydroxide (both calculations needed)

1

M4 Moles of water = <u>0.040</u> moles
***M4** – answer (stated or used in calculation of ΔH)*

1

M5 $\Delta H = -1.344/0.04$

$= -33.6$ (kJ mol^{-1})
M5** – ecf on **M2** and **M4
Answer must be negative and to at least 2sf

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*ΔH = – **M2** (in kJ) / M4*

*–32.5 - –34 scores 4/4 (**M2**-**M5** + equation)*

*+32.5 - +34 scores 3/4 (**M2**, **M3**, **M4** + equation)*

–65 - –68 scores 3/4 (+ equation)

+65 - +68 scores 2/4 (+ equation)

–52 - –54 scores 3/4 (+ equation)

+52 - +54 scores 2/4 (+ equation)

2

(f) HOOCCOOH is a weak acid / not fully dissociated

H_2SO_4 is a strong(er)acid / fully dissociated / dissociates more

1

(more) energy needed to break bonds/complete dissociation / dissociation is endothermic

So less energy is needed for dissociation of sulfuric acid

Ignore references to heat loss

1

[16]

Q4.

B

[1]

Q5.

C

[1]

Q6.

(a) Burette

1

Because it can deliver variable volumes

1

(b) The change in pH is gradual / not rapid at the end point

1

An indicator would change colour over a range of volumes of sodium hydroxide

Allow indicator would not change colour rapidly / with a few drops of NaOH

1

(c) $[H^+] = 10^{-pH} = 1.58 \times 10^{-12}$

1

$K_w = [H^+]\,[OH^-]$ therefore $[OH^-] = K_w / [H^+]$

1

Therefore, $[OH^-] = 1 \times 10^{-14} / 1.58 \times 10^{-12} = 6.33 \times 10^{-3}$ (mol dm^{-3})

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Allow 6.31–6.33 × 10^{-3} (mol dm^{-3})

1

(d) At this point, $[NH_3] = [H^+]$

$$= \frac{[H^+]^2}{[NH_4^+]}$$

Therefore K_a

1

$[H^+] = 10^{-4.6} = 2.51 \times 10^{-5}$

1

$K_a = (2.51 \times 10^{-5})^2 / 2 = 3.15 \times 10^{-10}$ (mol dm^{-3})

Allow 3.15 – 3.16 × 10^{-10} (mol dm^{-3})

1

(e) When $[NH_3] = [NH_4^+]$, $K_a = [H^+]$ therefore – log K_a = – log $[H^+]$

Answer using alternative value

1

Therefore pH = $-\log_{10}(3.15 \times 10^{-10}) = 9.50$

M2 pH = – $\log_{10}(4.75 \times 10^{-9}) = 8.32$

Allow consequential marking based on answer from part (d)

1

[12]

Q7.

C

[1]

Q8.

(a) $CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$
OR

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

Must show $\rightleftharpoons$
Allow CH_3CO_2H, $CH_3CO_2^-$
Ignore state symbols

1

(b) ($CH_3COOH + \underline{HNO_3} \longrightarrow CH_3COOH_2^+ + NO_3^-$)

IGNORE $\rightleftharpoons$
Allow CH_3CO_2H, $CH_3CO_2H_2^+$, $CH_3C^+(OH)_2$

1

(c) (i) (new $[HNO_3] = [H^+] = \frac{100}{150} \times 0.0125$)

M1 $[H^+] = 8.3(3) \times 10^{-3}$ (mol dm^{-3})
OR

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$new[HNO_3] = \frac{\text{mol } HNO_3}{\text{total vol}} = \frac{1.25 \times 10^{-3}}{150 \times 10^{-3}}$

1

M2 pH = − log M1 OR 2.08

Must be 2dp

Allow correct pH conseq to their $[H^+]$ concentration

1

(ii) M1 mol NaOH (= $50 \times 10^{-3} \times 0.0108$) = 5.40×10^{-4}

1

M2 Subtraction of M1 from moles of HNO_3 (1.25×10^{-3} or conseq from 1c(i))

Excess mol $H^+ = 7.10 \times 10^{-4}$

M2 allow ecf for subtraction of mol

If no subtraction, no further marks

1

M3 $[H^+] = \frac{M2}{150 \times 10^{-3}}$ OR $\frac{7.10 \times 10^{-4}}{150 \times 10^{-3}} = 4.73 \times 10^{-3}$

M3 <u>if no use of volume, no further marks</u> (pH=3.15)

If incorrect volume used, can score M4

1

M4 pH = -log M3 OR 2.32

M4 Allow 2.33 Must be 2 dp

1

(d) (i) M1 $K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$

Penalise ( ) once here Not [H+][A-] / [HA]

If K_a expression wrong – Allow correct pH conseq to their $[H^+]$ concentration M4 only

1

M2 $K_a = \frac{[H^+]^2}{[CH_3COOH]}$ or with numbers or with HA

1

M3 $[H^+] = [\sqrt{(1.74 \times 10^{-5} \times 0.0125)}] = 4.66 \times 10^{-4}$

Mark for answer

1

M4 pH = 3.33

Must be 2dp

Allow correct pH conseq to their $[H^+]$ concentration

(pH = 3.83 can score M1, M2 and M4)

1

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(ii) Sodium ethanoate

Ignore formula

Allow sodium acetate

1

(iii) M1 $[H^+] = 1.45 \times 10^{-5}$

Accept 1.445×10^{-5} or 1.4×10^{-5}

1

M2

$$\frac{[salt]}{[acid]} \text{ (OR } \frac{[CH_3COO^-]}{[CH_3COOH]} = \frac{Ka}{[H^+]} \text{)= } \frac{1.74 \times 10^{-5}}{1.45 \times 10^{-5}}$$

If M1 incorrect CE=0

Inclusion of 0.0125 in calculation can only score M1

1

M3 1.2(0)

Ignore units

1.4×10^{-5} gives 1.24

1

(e) M1 (Electronegative) chlorine withdraws electrons

Allow Cl has negative inductive effect

1

M2 Stabilises/reduces charge on COO-

OR weakens O-H bond

OR makes O-H more polar

Ignore chloroethanoic acid dissociates more readily

Mark independently

1

(f) M1 Strong acids (almost) completely dissociated/ionised

OR not an equilibrium

OR equilibrium lies far to the right

Cannot have K_a value for a reaction not in equilibrium scores both marks

1

M2 K_a value for strong acids tends to infinity/is very large
OR can't divide by zero in K_a

1

[20]

Q9.

(a) $HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$
or

$H_2O + HCO_3^- \rightleftharpoons CO_3^{2-} + H_3O^+$

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Must have equilibrium sign but mark on to (b)
Ignore state symbols

1

(b) Acid: Increase in concentration of H^+ ions, equilibrium moves to the left.

Allow H^+ ions react with carbonate ions (to form HCO_3^-)

1

Alkali: OH^- reacts with H^+ ions, equilibrium moves to the right (to replace the H^+ ions)

1

Concentration of H^+ remains (almost) constant

1

[4]

Q10.

(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

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pH = 12.38 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) $K_a = \dfrac{[H^+][C_6H_5COO^-]}{[C_6H_5COOH]}$

Ignore ( ) here but brackets must be present.
Must be correct acid and salt.
If wrong, mark part (ii) independently.

1

(ii) M1 $K^a = \dfrac{[H^+]^2}{[C_6H_5COOH]}$ **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 $\sqrt{(K_a \times [C_6H_5COOH])}$
$(= \sqrt{(7.572 \times 10^{-7} = 8.70 \times 10^{-4})}$

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 $K^a = \dfrac{[H^+]}{[C_6H_5COOH]}$

used which also leads to 6.12, then zero scored.

1

M3 pH = 3.06

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 $[X^-] = \dfrac{Ka \times [HX]}{[H^+]}$

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

1

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

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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]

Q11.

(a) Proton donor or H^+ donor

1

(b) (i) $K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$ or $\frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$

If K_a wrong, can only score M1 below.
Must be ethanoic acid not HA
Must have square brackets (penalise here only) but mark on in (b)(ii).

1

(ii) M1 $[H^+] = 10^{-2.69}$ ***OR*** 2.042×10^{-3} (mol dm^{-3})

1

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M2 $CH_3COOH] = \frac{[H^+]^2}{K_a}$

Ignore ( )

Mark for correctly rearranged expression incl $[H^+]^2$

1

M3

$= \frac{(2.042 \times 10^{-3})^2}{1.75 \times 10^{-5}}$

If M2 wrong no further marks.

1

M4 = 0.238 (mol dm^{-3}) Allow 0.229 − 0.24

1

(c) (i) $ClCH_2COOH \rightleftharpoons ClCH_2COO^- + H^+$

OR $ClCH_2COOH + H_2O \rightleftharpoons ClCH_2COO^- + H_3O^+$

Allow $\longrightarrow$

Allow $ClCH_2CO_2H$ and $ClCH_2CO_2^-$

1

(ii) M1 Cl is (more electronegative so) withdraws electrons
OR negative inductive effect of Cl

Ignore electronegativity.

Ignore chloroethanoic acid has a lower K_a value.

Allow Cl reduces +ve inductive effect of methyl group.

1

M2 Weakens O–H bond
OR O–H bond is more polar
OR reduces negative charge on COO^-
OR stabilizes COO^- (more)

M1 & M2 are independent marks.

Ignore H^+ lost more easily.

1

(d) (i) **A**

1

(ii) **C**

1

(iii) **D**

1

(e) M1 Mol NaOH = mol OH^- = $(19.6 \times 10^{-3}) \times 0.720 = 1.41(1) \times 10^{-2}$

Mark for answer.

1

M2 Mol H_2SO_4 = $(26.4 \times 10^{-3}) \times 0.550 = 1.45(2) \times 10^{-2}$

Mark for answer.

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1

M3 Mol H^+ added = **2 ×** $(1.452 \times 10^{-2}) = 2.90(4) \times 10^{-2}$
OR
XS mol $H_2SO_4 = 7.46(4) \times 10^{-3}$

If factor × 2 missed completely (pH = 2.05)
or used wrongly later,
can score max 4 for M1, M2, M5 & M6

1

M4 XS mol $H^+ = 0.0149(3)$

1

M5 For dividing by volume
$[H^+] = 0.0149(3) \times (1000 / 46.0) = 0.324 - 0.325$ mol dm^{-3}

If no use or wrong use of volume lose M5 and M6
ie can score 4 for pH = 1.83 (no use of vol)
Treat missing 1000 as AE (−1) & score 5 for pH = 3.49

1

M6 pH = 0.49
2dp *(penalise more or less).*
If × 2 missed & vol not used, pH = 3.39 scores M1 & M2 only.

1

[18]

Q12.

(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 $4.37 \times 10^{-12})$
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) $HCOOH \rightleftharpoons HCOO^- + H^+$

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

Must have all brackets but allow ( )
Must be HCOOH etc.
Allow ecf in formulae from (b)(i)

1

(iii) M1

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

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 <u>shifts / moves</u> 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 $[H^+] = \dfrac{Ka \times [HX]}{[X^-]}$ ***OR*** $pH = pK_a - \log \dfrac{[HX]}{[X^-]}$

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

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1

M2 $\frac{1.78\times10^{-4} \times 2.35 \times 10^{-2}}{1.84\times10^{-2}}$ ***OR*** $\text{pH} = 3.75 - \log \frac{2.35\times10^{-2}}{1.84\times10^{-2}}$

(= 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

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

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

OR $\text{pH} = 3.75 - \log \frac{2.40\times10^{-2}}{1.79\times10^{-2}}$

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]

Q13.

(a) Proton donor or H^+ donor

Allow donator

1

(b) (i) B B

Both need to be correct to score the mark

1

(ii) A A

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Both need to be correct to score the mark

1

(iii) B A

Both need to be correct to score the mark

1

(c) **M1** $[H^+] = 10^{-1.25}$ OR 0.05623

1

M2 mol HCl = $(25 \times 10^{-3}) \times 0.0850$ $(= 2.125 \times 10^{-3})$

Mark for Working

1

M3 vol $\left(= \frac{2.125 \times 10^{-3}}{0.05623} \right)$ = 0.0378 dm^3 or 37.8 cm^3

allow 0.0375 – 0.038 dm^3 or 37.5 – 38 cm^3

Units and answer tied
Lose M3 if total given as (25 + 37.8) = 62.8 cm^3
Ignore "vol added = 12.8 cm^3 " after correct answer

1

(d) (i) 4.52

Must be 2dp

1

(ii) $K_a = \frac{[H^+][H^-]}{[HX]}$ ignore = $\frac{[H^+]^2}{[HX]}$ but this may score M1 in (d)(iii)

Must have all brackets but allow ( ) Allow HA etc
***NO** mark for 10^{-pKa}*

1

(iii) **M1** $K_a = \frac{[H^+]^2}{[HX]}$ or with numbers

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

1

M2 $[H^+] = (\sqrt{(3.01 \times 10^{-5} \times 0.174)} = \sqrt{(5.24 \times 10^{-6})})$
$= 2.29 \times 10^{-3}$ - 2.3×10^{-3}

Mark for <u>answer</u>

1

M3 pH = 2.64 (allow more than 2dp but not fewer)

Allow 1 for correct pH from their wrong $[H^+]$
If square root forgotten, pH = 5.28 scores 2 for M1 and M3

1

(e) **M1** mol OH^- = $(10.0 \times 10^{-3}) \times 0.125 = 1.25 \times 10^{-3}$

Mark for answer

1

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M2 orig mol HX = $(15.0 \times 10^{-3}) \times 0.174 = 2.61 \times 10^{\times 3}$

Mark for answer

1

M3 mol HX in buffer = orig mol HX – mol OH^-

Mark for answer

$= 2.61 \times 10^{-3} - 1.25 \times 10^{-3} = 1.36 \times 10^{-3}$

Allow conseq on their (M2 – M1)

($[HX] = 1.36 \times 10^{-3}/25 \times 10^{-3} = 0.0544$)

If no subtraction, max 3 for M1, M2 & M4 (pH = 4.20)
If $[H^+] = [X^-]$ & √used, max 3 for M1, M2 & M3 (pH = 2.89)

1

M4 mol X^- in buffer = mol OH^- = 1.25×10^{-3}

($[X^-] = 1.25 \times 10^{-3}/25 \times 10^{-3} = 0.05$)

May be scored in M5 expression

1

M5 $[H^+]$ $\left(= \frac{Ka \times [HX]}{[X^-]}\right)$

If use $K_a = \frac{[H^+]^2}{[HX]}$ *no further marks*

$= \frac{3.01 \times 10^{-5} \times 1.36 \times 10^{-3}}{1.25 \times 10^{-3}}$ *OR* $\frac{3.01 \times 10^{-5} \times 0.0544}{0.05}$

(= 3.27×10^{-5})

If either value of HX or X^- used wrongly or expression upside down, no further marks

1

M6 pH = 4.48 or 4.49 (allow more than 2dp but not fewer)

*Do **not** allow M6 for correct calculation of pH using their $[H^+]$ - this only applies in (d)(iii) - apart from earlier AE*

1

[18]

Q14.

(a) Any **two** from:

Weigh by difference or rinse weighing bottle and add to beaker

Rinse beaker and add washings to graduated flask

Invert flask several times to ensure uniform solution

Use a funnel to transfer to the flask and rinse the funnel

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Use a stirrer to prepare the solution and rinse the stirrer

If more than two answers apply the list rule.

Max 2

(b) $K_a = [H^+]^2 / [HA]$

Allow any correct expression relating K_a, $[H^+]$ and [HA]

1

$[HA] = (10^{-2.50})^2 / 1.07 \times 10^{-3}$

M2 also scores M1

1

$= 9.35 \times 10^{-3}$ (mol dm^{-3})

Do not allow 9.4 (answer is 9.346).

Correct answer only scores 1 mark.

Do not penalise precision but must be to at least two significant figures.

1

(c) (b) × 138.0 / 4

1

= 0.322

Using 8.50×10^{-3} gives 0.293

Correct answer scores M1 and M2.

Do not penalise precision but must be to at least two significant figures.

1

(d) (c) × 100 / 0.500 = 64.5%

Using 0.293 from (c) gives 58.7%

Using 0.347 gives 69.4%

Do not penalise precision.

1

[8]

Q15.

(a) **M1** $[H^+] = 0.0170$

1

M2 pH = 1.77

2 dp

Allow M2 for correct pH calculation from their wrong $[H^+]$ for this pH calculation only

1

(b) (i)

$$K_a = \frac{[H^+][X^-]}{[HX]^2} \qquad \text{Ignore} \quad K_a = \frac{[H^+]^2}{[HX]}$$

*Penalize missing [ ] here **and not elsewhere***

Allow HA instead of HX

1

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(ii) **M1** $[H^+] = 10^{-2.79}$ OR $1.6218\ldots \times 10^{-3}$

If $[H^+]$ wrong, can only score M2

1

M2 $K_a = \frac{[H^+]^2}{[HX]}$ OR $\frac{[1.62 \times 10^{-3}]^2}{[0.0850]}$

Allow HA instead of HX

1

M3 $K_a = 3.09 \times 10^{-5}$ 3sfs min
(allow 3.10×10^{-5} if 1.6218 rounded to 1.622)
Ignore units
If [HX] used as $(0.0850 - 1.62 \times 10^{-3})$
this gives $K_a = 3.15 \times 10^{-5}$
$(0.0016)^2/0.085 = 3.01 \times 10^{-5}$ scores 2 for AE

1

(c) **M1** mol OH^- (= $(38.2 \times 10^{-3}) \times 0.550$)

= $2.10(1) \times 10^{-2}$ or 0.0210(1)
Mark for answer

1

M2 Mol H^+ (= $(25.0 \times 10^{-3}) \times 0.620$)

= 1.55×10^{-2} or 0.0155
Mark for answer

1

M3 excess mol OH^- = $5.5(1) \times 10^{-3}$

Allow conseq for M1 – M2
***If wrong method** e.g. no subtraction or use of √*
can only score max of M1, M2, M3 and M4.

1

M4 $[OH^-] = 5.51 \times 10^{-3} \times \frac{10^3}{63.2}$ [= 0.08718 (0.0872)]

OR $[OH^-] = 5.5 \times 10^{-3} \times \frac{10^3}{63.2}$ = 0.0870(2)

(M1 – M2) / vol in dm^3 mark for dividing by volume
(take use of 63.2 without 10^{-3} as AE so 9.94 scores 5)
If no use or wrong use of vol lose M4 & M6
Can score M5 for showing (10^{-14}/ their XS alkali)

1

M5 $[H^+] = \frac{10^{-14}}{0.08718} = 1.147 \times 10^{-13}$

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$\frac{10^{-14}}{0.0870}$ = 1.149×10^{-13}

OR pOH = 1.06

If no use or wrong use of K_w or pOH no further marks

1

M6 pH = 12.9(4) allow 3sf

If vol missed score max 4 for 11.7(4)

If acid– alkali reversed max 4 for pH = 1.06

Any excess acid – max 4

1

[12]

Q16.

(a) (i) - log[H^+]

*penalise missing [ ] here **and not elsewhere***

1

(ii) [H^+][OH^-]

Allow ( ) brackets, but must have charges

1

(iii) Mark independently from a(ii)

[H^+] = $10^{-13.72}$ = 1.905×10^{-14}

If wrong no further mark

1

K_w = $1.905 \times 10^{-14} \times 0.154$ = = $(2.93 – 2.94) \times 10^{-15}$

1

(b) (i) Ka = $\frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$

Must have charges and all brackets, allow ( )

Acid/salt shown must be CH_3COOH not HA

and correct formulae needed

1

(ii) **In pH values penalise fewer than 3 sig figs each time but allow more than 2 dp**
For values above 10, allow 3sfs - do not insist on 2 dp

$K_a = \frac{[H^+]^2}{[CH_3COOH]}$

Allow HA

1

($[H^+]^2$ = $1.75 \times 10^{-5} \times 0.154$ = 2.695×10^{-6} = 2.70×10^{-6})

If √ shown but not done gets pH = 5.57 (scores 2)

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$[H^+] = 1.64 \times 10^{-3}$

Allow mark for pH conseq to their [H+] ***here only***

1

pH = 2.78 or 2.79

1

(c) (i) **In pH values penalise fewer than 3 sig figs each time but allow more than 2 dp**

For values above 10, allow 3sfs - do not insist on 2 dp

M1 Initially

mol OH^- = $(10 \times 10^{-3}) \times 0.154$ **and**

mol HA = $(20 \times 10^{-3}) \times 0.154$

or mol OH^- = 1.54×10^{-3} **and** mol HA = 3.08×10^{-3}

1

M2 $[H^+] = K_a \dfrac{[CH_3COOH]}{[CH_3COOH^-]}$

or with numbers

Allow Henderson Hasselbach

$pH = pK_a + log \dfrac{[CH_3COO^-]}{[CH_3COOH]}$

M3 mol ethanoic acid left = (mol ethanoate ions) = 1.54×10^{-3}

$K_a = [H^+]$ **or** $pH = pK_a$ scores **M1**, **M2** and **M3**

1 If either mol acid in mixture or mol salt wrong - max 2 for M1 and M2

Any mention of $[H^+]^2$ - max 2 for M1 and M3

1

M4 pH (= - log 1.75×10^{-5}) = 4.76 or 4.757

Not 4.75

1

If no subtraction (so mol ethanoic acid in buffer = original mol)
pH = 4.46 scores 2 for **M1** and **M2**
If $[H+]^2$ used, pH = 3.02 scores 2 for **M1** and **M3**

(ii) **In pH values penalise fewer than 3 sig figs each time but allow more than 2 dp**
For values above 10, allow 3sfs - do not insist on 2 dp

M1 XS mol KOH (= $(20 \times 10^{-3}) \times 0.154$) = 3.08×10^{-3}

If no subtraction: max 1 for correct use of volume

No subtraction and no use of volume scores zero

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If wrong subtraction or wrong moles

*Can only score **M2** and **M3** for process*

1

M2 $[OH^-] = 3.08 \times 10^{-3} \times \frac{10^3}{60} = 0.0513(3)$

*Mark for dividing their answer to **M1** by correct volume (method mark)*

*If no volume or wrong volume or multiplied by volume, max 2 for **M1** and **M3** process*

1

M3 $[H^+] = \frac{10^{-14}}{0.05133}$ (= 1.948×10^{-13} to 1.95×10^{-13})

or pOH = 1.29

*Mark for K_w divided by their answer to **M2***

If pOH route, give one mark for 14 – pOH

1

M4 pH = 12.7(1)

Allow 3sf but not 12.70

1

If no subtraction and no use of volume (pH = 11.79 scores zero)
If no subtraction, max 1 for correct use of volume, ($60cm^3$)
(pH = 13.01 scores 1)
If volume not used, pH = 11.49 (gets 2)
If multiplied by vol, pH = 10.27 (gets 2)

[16]

Q17.

(a) (i) $-\log[H^+]$ or $\log 1/[H^+]$

penalise missing square brackets here only

1

(ii) 0.81

2dp required, no other answer allowed

1

(iii) **M1** mol $H^+ = 1.54 \times 10^{-3}$

if wrong no further mark
if 1.5×10^{-3} allow M1 but not M2 for 2.82

1

M2 pH = 2.81

allow more than 2dp but not fewer

1

(b) **M1** $[H^+] = 3.31 \times 10^{-3}$

1

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M2 $K_a = \frac{[H^+][X^-]}{[HX]}$ or $\frac{[H^+]^2}{[HX]}$ or using numbers

do not penalise ( ) or one or more missing [ ]

1

M3 [HX] = $\frac{[H^+]^2}{K_a} = \frac{(3.31 \times 10^{-3})^2}{4.83 \times 10^{-5}}$

allow conseq on their $[H^+]^2/(4.83 \times 10^{-5})$ (AE)
if upside down, no further marks after M2

1

M4 [HX] = 0.227

allow 0.225 – 0.23

1

(c) **M1** extra/added OH^- removed by reaction with H^+ or the acid

1

M2 correct discussion of equn shift i.e. $HX \rightleftharpoons H^+ + X^-$ moves to right

1

OR

ratio $\frac{[HX]}{[X^-]}$ remains almost constant

(d) (i) **M1** mol HY = $(50 \times 10^{-3}) \times 0.428 = 0.0214$

OR [Y] = $.0236 \times \frac{1000}{50} = 0.472$

mark for answer

1

M2 $[H^+] = 1.35 \times 10^{-5} \times \frac{0.0214}{0.0236}$

OR $1.35 \times 10^{-5} = [H^+] \times \frac{0.0236}{0.0214}$

OR $[H^+] = 1.35 \times 10^{-5} \times \frac{0.428}{0.472}$

OR $1.35 \times 10^{-5} = [H^+] \times \frac{0.472}{0.428}$

must be numbers not just rearrangement of Ka expression
If either HY value or Y^- value wrong, (apart from AE -1) lose M2 and M3

1

M3 $[H^+] = 1.22 \times 10^{-5}$

mark for answer

1

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M4 pH = 4.91

allow more than 2dp but not fewer

allow M4 for correct pH calculation using their [H⁺] (this applies in (d)(i) only)

1

If Henderson Hasselbalch equation used:

M1 mol HY = (50 × 10^{-3}) × 0.428 = 0.0214

OR [Y] = .0236 × $\frac{1000}{50}$ = 0.472

mark for answer

1

M2 p*K*a = 4.87

1

M3 $\log\left(\frac{0.0214}{0.0236}\right)$ = –0.043

$\log\left(\frac{0.428}{0.472}\right)$ = –0.043

If either HY value or Y^- value wrong, (apart from AE-1) lose M3 and M4

1

M4 pH = 4.87 – (– 0.043) = 4.91

allow more than 2dp but not fewer

1

(ii) Can score full marks for correct consequential use of their HY and Y^- values from d(i)

M1 Mol HY after adding NaOH = 0.0214 – 5.0 × 10^{-4} = 0.0209

AE in subtraction loses just M1

If wrong initial mol HY (i.e. not conseq to part d(i)) or no subtraction or subtraction of wrong amount, lose M1 and M3

1

M2 Mol Y^- after adding NaOH = 0.0236 + 5.0 × 10^{-4} = 0.0241

AE in addition loses just M2

If wrong mol Y^- (i.e. not conseq to part d(i)) or no addition or addition of wrong amount lose M2 and next mark gained

1

M3 $[H^+]$ = 1.35 × 10^{-5} × $\frac{0.0209}{0.0241}$ (= 1.17 × 10^{-5})

if convert to concentrations

$[H^+]$ = 1.35 × 10^{-5} × $\frac{0.418}{0.482}$ (= 1.17 × 10^{-5})

1

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if HY/Y^- upside down, no further marks

M4 pH = 4.93

allow more than 2dp but not fewer

NOT allow M4 for correct pH calculation using their $[H^+]$ (this allowance applies in (d)(i) only)

1

If Henderson Hasselbalch equation used:

Can score full marks for correct consequential use of their HY and Y^- values from d(i)

M1 Mol HY after adding NaOH = $0.0214 - 5.0 \times 10^{-4} = 0.0209$

AE in subtraction loses just M1
If wrong initial mol HY (i.e. not conseq to part d(i)) or no subtraction or subtraction of wrong amount lose M1 and M3

1

M2 Mol Y^- after adding NaOH = $0.0236 + 5.0 \times 10^{-4} = 0.0241$

AE in addition loses just M2
If wrong mol Y^- (i.e. not conseq to part d(i)) or no addition or addition of wrong amount lose M2 and next mark gained

1

M3 $\log\left(\frac{0.0209}{0.0241}\right) = -0.062$

if HY/Y^- upside down, no further marks

1

M4 pH = 4.87 – (– 0.062) = 4.93

allow more than 2dp but not fewer

1

[18]

Q18.

(a) (i) $-\log[H^+]$

*Penalise missing [ ] here **and not elsewhere***

1

(ii) $[H^+][OH^-]$

1

(b) (i) $[H^+] = 2.34 \times 10^{-7}$

1

pH = 6.63

Penalise fewer than 3 sig figs but allow more than 2 dp

1

(ii) $[H^+] = [OH^-]$

1

(iii) **M1** $[H^+] = K_w/[OH^-]$

if upside down or CE, allow M3 only for correct use of their

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[H⁺]

1

M2 (= 5.48 × 10^{-14}/0.140) = 3.91 × 10^{-13}

1

M3 pH = 12.4(1)
not 12.40 (AE from 12.407)

1

Penalise fewer than 3 sig figs but allow more than 3 sfs
For values above 10, allow 3sfs - do not insist on 2 dp.
For values below 1, allow 2dp – do not insist on 3 sig figs
Not allow pH = 14 – pOH but can award M3 only for pH = 13.1(46)
Can award all three marks if pK_w = 13.26 is used

(c) **M1** mol NaOH = mol OH^- = (30 × 10^{-3}) × 0.20 = 6.0 × 10^{-3}

mark for answer

1

M2 mol H_2SO_4 = (25 × 10^{-3}) × 0.15 = 3.75 × 10^{-3}

mark for answer

1

M3 mol H^+ = (25 × 10^{-3}) × 0.15 × 2 = 7.5 ×10^{-3}
OR XS mol H_2SO_4 = 0.75 × 10^{-3}

if factor of 2 missed or used wrongly, CE - lose M3 and next mark gained. In this case they must then use K_w to score any more.
see examples below

1

M4 XS mol H^+ = 1.5 × 10^{-3}

1

M5 [H^+] = (1.5 × 10^{-3}) × (1000/55) = 0.0273
if no use or wrong use of volume, lose M5 and M6 except if 1000 missed
AE –1 (pH = 4.56)

1

M6 pH = 1.56
Penalise fewer than 3 sig figs but allow more than 3 sfs
For values above 10, allow 3sfs - do not insist on 2 dp.
For values below 1, allow 2dp – do not insist on 3 sig figs

1

[14]

Q19.

(a) pH on the y-axis, volume of alkali on the x-axis

If axes unlabelled use data to decide that pH is on y-axis.

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1

Uses sensible scales

*Lose this mark if plotted paths do not cover **half** of the paper.*
Lose this mark if the graph plot goes off the squared paper.

1

Labels the axes

Allow mark for axes labelled 'pH' and 'volume'.

1

Plots all of the points correctly

1

Line through the points is smooth and has the correct profile

Ignore 0–5 cm^3 section of the graph.
Lose this mark if graph is kinked or not a single line.

1

Line ignores the point at 12 cm^3

Lose this mark if point clearly not treated as an anomaly.

1

(b) (i) 24.4 cm^3 ± 0.2

If no answer in (i) allow answer written on the graph.
*Allow this answer **only**.*
Do not penalise precision.

1

(ii) 12.2 cm^3 ± 0.1

If no answer in (ii), allow answer written on the graph.
Allow answer to (i) divided by 2.
Do not penalise precision.

1

(iii) 3.9 ± 0.2

If no answer in (iii), allow answer written on the graph.
Consequential marking from (ii)
Lose this mark if answer not given to 1 dp.

1

(c) pK_a = – log K_a or $K_a = 10^x$, where x = – (answer to b(iii))

1

1.26×10^{-4}

3.7 to 4.1 gives $K_a = 7.9 \times 10^{-5}$ to 2.0×10^{-4}
Consequential marking from b(i).
Correct answer without working scores 1 mark only.
Do not penalise precision.

1

(d) Methanoic acid

Consequential marking from (c).

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pK_a = 3.7 gives methanoic acid.

pK_a = 4.1 gives ethanoic acid.

No lucky guesses – candidates must apply answer from (c).

Do not allow answers based on data given in (f).

1

(e) Error in using pipette is 0.2% **and**
Error in using burette is 0.15 × 100 / (answer to b(i))

Using 24.4 for burette gives 0.6%

Do not penalise precision.

Allow if errors are given without working.

Lose mark if the burette error is not calculated on b(i).

*If the error being calculated is **not** stated, allow **if** the calculations are in the same order as in the question (pipette, burette).*

1

(f) Difference is $1.6 \times 10^{-4} - 1.26 \times 10^{-4} = 0.34 \times 10^{-4}$

Allow consequential answer from (c).

Do not penalise precision.

$0.34 \times 100 / 1.6$ is a 21% error

Correct final answer without working scores 1 mark.

Using 1.9×10^{-4} gives 0.3×10^{-4} and 18.8%.

1

(g) Calibrate meter **or** thermostat the mixture **or** maintain constant temperature

Do not allow 'repeat experiment'.

1

(h) Mixture is a <u>buffer</u>

1

[16]

Q20.

(a) (i) $-\log[H^+]$

or $\log 1/[H^+]$
penalise ( )

1

(ii) $[H^+] = 0.56$

mark for the answer; allow 2dp or more

1

$[H_2SO_4] = ½ \times 0.56 = 0.28$

1

(b) (i) $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

OR

$CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$

Allow CH_3CO_2H etc

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1

(ii) mol acid = $(25.0 \times 10^{-3}) \times 0.41 = 1.025 \times 10^{-2}$ or 1.03×10^{-2}

1

$[NaOH] = 1.025 \times 10^{-2} / 22.6 \times 10^{-3} = 0.45(4)$

mark for answer
if not 0.454 look back for error

1

OR

$[NaOH] = 1.03 \times 10^{-2} / 22.6 \times 10^{-3} = 0.456$ or 0.46

(iii) cresol purple

1

(iv) NaOH reacts with <u>carbon dioxide</u> (in the air)

1

(c) (i) $K_a = \dfrac{[H^+][CH_3COO^-]}{[CH_3COOH]}$

allow molecular formulae or minor slip in formulae

penalise ( )
allow H_3O^+
not allow HA etc

1

(ii) $K_a = \dfrac{[H^+]^2}{[CH_3COOH]}$ or with numbers

1

allow HA etc here
This can be scored in part (c)(i) but doesn't score there.

$[H^+] = (\sqrt{(1.74 \times 10^{-5} \times 0.410)} = \sqrt{(7.13 \times 10^{-6})}) = 2.67 \times 10^{-3}$

1

mark for 2.67×10^{-3} or 2.7×10^{-3} either gives 2.57

pH = 2.57 can give three ticks here for (c)(ii)
penalise decimal places < 2 >

1

pH mark conseq on their $[H^+]$
so 5.15 gets 2 marks where square root not taken

(iii) **M1** mol OH^- = $(10.0 \times 10^{-3}) \times 0.10 = 1.0 \times 10^{-3}$

If no subtraction or other wrong chemistry the max score is 3 for M1, M2 and M4

1

M2 orig mol HA = $(25.0 \times 10^{-3}) \times 0.41 = 0.01025$

1

or 1.025×10^{-2} or 1.03×10^{-2}

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M3 mol HA in buffer = orig mol HA – mol OH^-

1

= 0.00925 or 0.0093

If A^- is wrong, max 3 for M1, M2 and M3 or use of pH = pKa – log [HA]/[A^-]

M4 mol A^- in buffer = mol OH^- = 1.0×10^{-3}

Mark is for insertion of correct numbers in correct expression for [H^+]

1

M5 $[H^+] = \left(\frac{K_a \times [CH_3COOH]}{[CH_3COO^-]} = \right)$

1

$$\frac{(1.74 \times 10^{-5})(0.00925)}{0.0010} \text{ or } \frac{(1.74 \times 10^{-5})(0.00930)}{0.0010}$$

(= 1.61×10^{-4} or 1.62×10^{-4})

M6 pH = 3.79 can give six ticks for 3.79

if [HA]/[A^-] upside down lose M5 & M6

If wrong method e.g. $[H^+]^2$/[HA] max 3 for M1, M2 and M3

Some may calculate concentrations
[HA] = 0.264 and [A^-] = 0.0286 and rounding this to 0.029 gives pH = 3.80 (which is OK)

NB Unlike (c)(ii), this pH mark is NOT awarded conseq to their [H^+] unless following AE

BEWARE: using 0.01025 wrongly instead of 0.00925 gives pH = 3.75
(this gets 3 for M1, M2 & M4)

1

[18]

Q21.

(a) (i) **B** 1

C

1

A

1

(ii) cresolphthalein or thymolphthalein

1

(b) pH = -log[H^+]

1

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$K_a = \frac{[H^+]^2}{[CH_3COOH]}$ or $[H^+] = [A^-]$

1

$[H^+] = \sqrt{1.74 \times 10^{-5} \times 0.15}$ (or 1.62×10^{-3})

1

pH = 2.79 (penalise 1 dp or more than 2dp once in the qu)

1

[8]

Q22.

(a) –log $[H^+]$

ecf if [ ] wrong and already penalised

1

4.57×10^{-3}

allow 4.6×10^{-3}
ignore units

1

(b) (i) $K_a = \frac{[H^+][X^-]}{[HX]}$ allow HA etc

not $\frac{[H^+]^2}{[HX]}$ *but mark on*
If expression wrong allow conseq units in (ii)
but no other marks in (ii)

1

(ii) $\frac{[H^+]^2}{[HX]} = \frac{(4.57 \times 10^{-3})^2}{[0.150]}$

If use 4.6×10^{-3}

1

$K_a = 1.4(1) \times 10^{-4}$ and pKa = 3.85

$= 1.39 \times 10^{-4}$

allow $1.39 – 1.41 \times 10^{-4}$ mol dm^{-3}

1

(iii) $pK_a = 3.86$

Penalise dp of final answer < or > 2 in pH once in paper

1

(c) (i) $\frac{30}{1000} \times 0.480 = 0.0144$ or $1.4(4) \times 10^{-2}$

Mark is for answer (M1)

1

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(ii) $\frac{18}{1000} \times 0.350 = 0.0063$ or 6.3×10^{-3}

Mark is for answer (M2)

1

(iii) $0.0144 - 2(0.0063) = 1.80 \times 10^{-3}$

M3 is for (i) – 2(ii)
If x 2 missed, CE i.e. lose M3 and the next mark gained

1

(iv) $1.80 \times 10^{-3} \times \frac{1000}{48} = 0.0375$ (0.038)

M4 is for answer

If vol is not 48×10^{-3} (unless AE) lose M4 and next mark gained
If multiply by 48 - this is AE - i.e. lose only M4
If multiply by 48×10^{-3} this is AE - i.e. lose only M4

1

(v) $10^{-14} / 0.0375$ ($10^{-14} / 0.038$)

M5 for $K_w/[OH^-]$

1

($= 2.66 \times 10^{-13}$) ($= 2.63 \times 10^{-13}$)

or pOH

or pOH = 1.426 (or pOH = 1.420)

If no attempt to use K_w or pOH lose both M5 and M6

1

pH = 12.57 (12.58) M6

Allow M6 conseq on AE in M5 if method OK

1

[13]

Q23.

C

[1]

Q24.

(a) (i) B;

1

C;

1

A;

1

(ii) cresolphthalein

OR

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thymolphthalein;

1

(b) (i) –log[H^+];

1

(ii) [H^+] = 1.259 × 10^{-12} (or 1.26 or 1.3)

OR

OH = 14 – pH;

1

$$[OH^-] = \frac{10^{-14}}{1.258 \times 10^{-12}}$$

OR

= 2.10;

1

= 7.9(4) × 10^{-3};

(if [H^+] is wrong allow 1 for [OH] = K_w/[H^+] or as numbers)

1

(c) (i) $K_a = [H^+]^2/[CH_3CH_2COOH]$

OR

$[H+]^2/[HA]$

OR

[H^+] = [A^-] etc;

1

[H^+] = $\sqrt{}$l.35×l0^{-5} × 0.117 or expression without numbers;

1

= 1.257 × l0^{-3}

pH = 2.9<u>0</u>;

1

(iii) $K_a = [H^+]$

OR

pK_a = pH;

1

pH = 4.8<u>7</u>;

(penalise 1dp once)

1

[13]

Q25.

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(a) Concentration of acid: $m_1v_1 = m_2v_2$ hence $25 \times m_1 = 18.2 \times 0.150$

OR

moles NaOH = 2.73×10^{-3};

1

$m_1 = 18.2 \times 0.150/25 = 0.109$;

1

(b) (i) $K_a=[H^+][A^-]/[HA]$ *not* $K_a = [H^+]^2 / [HA]$;

1

(ii) $pK_a = -\log K_a$;

1

(iii) $[A^-] = [HA]$;

1

hence $K_a = [H^+] [A^-] / [HA] = [H^+]$

and $-\log K_a = -\log[H^+]$;

1

(c) ratio $[A^-]$: [HA] remains constant;

1

hence as $[H^+] = K_a [HA] / [A^-]$; $[H^+]$ remains constant;

1

(d) (i) pH of 0.250 mol dm^{-3} HCl = 0.60
and pH of 0.150 mol dm^{-3} HCl = 0.82;

1

pH change = 0.22;

1

(ii) moles HCl = $30 \times 0.250 \times 10^{-3} = v \times 0.150 \times 10^{-3} = 7.50 \times 10^{-3}$

OR

$v = 30 \times 0.250 \times 10^{-3} / 0.150 \times 10^{-3} = 50$;

1

water added = 50 – 30 = 20 cm^3;

1

[12]

Q26.

(a) pH = $-\log[H^+]$

1

$$K_a = \frac{[H^+]^2}{[CH_3COOH]} \quad \text{or } [H^+]=[A^-]$$

1

$[H^+] = \sqrt{1.74 \times 10^{-5} \times 0.15}$ (or 1.62×10^{-3})

1

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pH = 2.79 (penalise 1 dp or more than 2dp once in the qu)

1

(b) (i) Solution which resists change in pH /maintains pH

1

despite the addition of (small amounts of) acid/base (or dilution)

1

(ii) $CH_3COO + H^+ \rightarrow CH_3COOH$

must show an equation full or ionic in which ethanoate ions are converted to ethanoic acid

1

(c) (i) $[H^+] = \frac{K_a[CH_3COOH]}{[CH_3COO^-]}$ if rearrangement incorrect, no further marks

1

$= 1.74 \times 10^{-5} \times \frac{0.15}{0.10}$

1

(= 2.61×10^{-5})

pH = 4.58

1

(ii) Ml moles H^+ added = $10 \times 10^{-3} \times 1.0 = 0.01$

1

M2 moles ethanoic acid after addition = 0.15 + 0.01 = 0.16

1

M3 moles ethanoate ions after addition = 0.10 -0.01 = 0.09

1

M4 $[H^+] = \frac{K_a[CH_3COOH]}{[CH_3COO^-]} = 1.74 \times 10^{-5} \times \frac{0.16/V}{0.09/V}$

1

(= 3.09×10^{-5})

M5 pH = 4.51

The essential part of this calculation is addition/subtraction of 0.01 moles to gain marks M2 and M3. If both of these are missing, only mark M1 is available. Thereafter treat each mark independently, except if the expression in M4 is wrong, in which case both M4 and M5 are lost.

1

[15]

alternative scheme for part (c)(i)

pH $pK_a - \log \frac{[CH_3COOH]}{[CH_3COO^-]}$

1

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$pK_a = 4.76$

1

$$pH = (4.76 - \log\frac{0.15}{0.10}) = 4.58$$

1

alternative for penultimate mark of part (c)(ii)

$$pH = 4.76 - \log\frac{0.16}{0.09}$$

1

Q27.

C

[1]

Q28.

(a) $K_a = \frac{[H^+][A^-]}{[HA]}$

(All three sets of square brackets needed, penalise missing brackets or missing charge once in the question)
(Don't penalise extra $[H^+]^2/[HA]$)

1

(b) $K_a = \frac{[H^+]^2}{[HA]}$ or $[H^+] = [A^-]$

$[H^+] = \sqrt{(1.45 \times 10^{-4}) \times 0.25}$

$= 6.02 \times 10^{-3}$ pH = 2.22

(must be to 2dp)
(allow 4th mark consequential on their $[H^+]$)

1

(c) (i) pH (almost) unchanged

(Must be correct to score explanation)

1

H^+ removed by A^- forming HA
or acid reacts with salt
or more HA formed

1

(ii) $[H^+] = 10^{-3.59} = 2.57 \times 10^{-4}$ or 2.6×10^{-4}

1

$[A^-] = \frac{K_a[HA]}{[H^+]}$

1

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$$= \frac{(1.45 \times 10^{-4}] \times 0.25}{2.57 \times 10^{-4}}$$

1

= 0.141 (mol dm $^{-3}$)

(Allow 0.139 to 0.141 and allow 0.14)

(If not used 3.59, to find [H$^+$] can only score M2 for working)

(If 3.59 used but [H$^+$] is wrong, can score M2 for correct method and conseq M4)

If wrong method and wrong expression, can only score M1)

1

(ii) *Alternative scheme for first three marks of part (c)(ii)*

$$pH = pK_a - \log \frac{[HA]}{[A^-]}$$

1

$pK_a = 3.84$

1

$$3.59 = 3.84 - \log \frac{0.250}{[A^-]}$$

1

[11]

Q29.

B

[1]

Q30.

A

[1]

Q31.

Penalise pH given to 1 dp <u>first</u> time it would have scored only

(a) (i) $K_w = [H^+]\,[OH^-]$ **(1)**

(ii) $pH = -\log [H^+]$ **(1)**

or in words or below unless contradiction

(iii) *Calculation*: $[H^+] = \sqrt{5.48 \times 10^{-14}}$ **(1)**

$= 2.34 \times 10^{-7}$

$\therefore$ pH = 6.63 or 6.64 **(1)**

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Explanation: pure water ∴ $[H^+] = [OH^-]$ **(1)**

5

(b) (i) $[OH^-] = 0.150$ ∴ $[H^+] = 10^{-14}/0.15 = 6.66 \times 10^{-14}$

or pOH = 0.82

∴ pH = 13.18 **(1)**

or pH= 13.17

(ii) moles $OH^- = (35 \times 10^{-3}) \times 0.150 = 5.25 \times 10^{-3}$ **(1)**[a]

moles $H^+ = (40 \times 10^{-3}) \times 0.120 = 4.8(0) \times 10^{-3}$ **(1)**[b]

∴ excess moles of $OH^- = 4.5 \times 10^{-4}$ **(1)**[c]

∴ $[OH^-] = (4.5(0) \times 10^{-4}) \times 1000/\underline{75}$[d] **(1)**[e]
$= 6.0(0) \times 10^{-3}$

$[H^+] = \frac{10^{-14}}{6.00 \times 10^{-3}} = 1.66 \times 10^{-12}$ or pOH = 2.22

∴ pH = 11.78 **(1)**[f]
or 11.77

8

(c) (i) $K_a = \frac{[H^+][X^-]}{[HX]}$ **(1)**

(ii) $[H^+] = 1.80 \times 10^{-2} \times 0.150 = 2.70 \times 10^{-3}$ (1)

$K_a = \frac{[H^+]^2}{[HX]}(1) = \frac{(2.70 \times 10^{-3})^2}{0.150} = 4.86 \times 10^{-5}$ **(1)** mol dm^{-3} **(1)**

or $\frac{(2.70 \times 10^{-3})^2}{0.1473} = 4.95 \times 10^{-5}$

5

Notes

(a) If K_w includes H_2O allow 6.63 if seen otherwise no marks likely

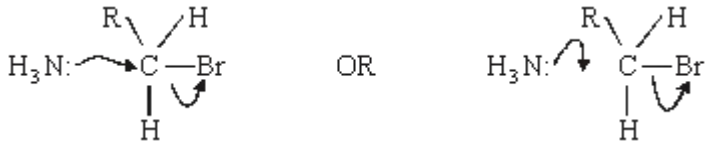
(b) (ii) If no vol, max 4 for a, b, c, f answer = 10.65
If wrong volume max 5 for a, b, c, e, f
If no substraction max 3 for a, b, d
If missing 1000 max 5 for a, b, c, d, f answer = 8.78
If uses excess as acid, max 4 for a, b, d, f answer = 2.22
If uses excess as acid and no volume, max 2 for a, b answer = 3.35

(c) If wrong K_a in (i) max 2 in part (ii) for $[H^+]$ **(1)** and conseq units **(1)**
but mark on fully from minor errors
eg no [ ] or charges missing

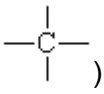
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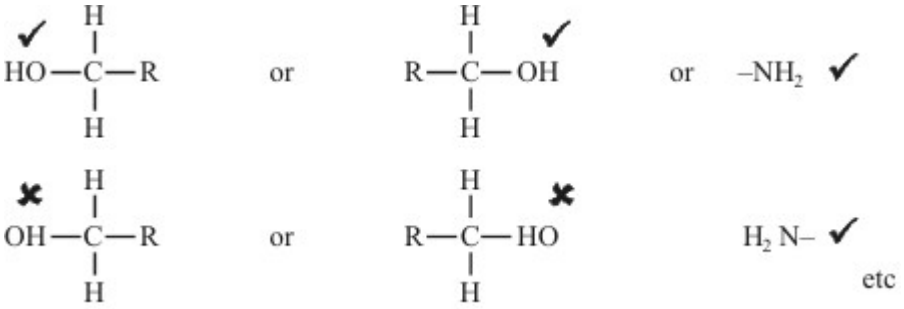
Organic points

(1) Curly arrows: must show movement of a pair of electrons,
i.e. from bond to atom or from lp to atom / space
e.g.



(2) Structures

penalise sticks (i.e. ) once per paper



Penalise once per paper

allow CH_3– or $–CH_3$ or  or CH_3
or H_3C–

[18]

Q32.

(a) moles HA = $\frac{25}{10^3}$ × 0.150 = 3.75 × 10^{-3} **(1)**

∴ vol NaOH = $\frac{3.75 \times 10^{-3}}{0.20}$ = 1.875 × 10^{-2} dm^3 **(1)**
or 18.75 cm^3

2

(b) (i) pH = $-\log_{10}[H^+]$ **(1)**

(ii) Value above 7 but below 11 **(1)**

(iii) phenol red / thymol blue / phenolphthalein / thymolphthalein
i.e. indicator with $7 < pK_{in} < 11$

3

(c) (i) Only slightly dissociated/ionised **(1)**
NOT "not fully dissociated / ionised"

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(ii) $K_a = \frac{[H^+][A^-]}{[HA]}$ **(1)**

NOT $\frac{[H^+]^2}{[HA]}$

(iii) For weak acid alone:

$Ka = \frac{[H^+]^2}{[HA]}$ **(1)**

$\therefore [H^+] = \sqrt{(2.75 \times 10^{-5}) \times 0.15}$

$= 2.03 \times 10^{-3}$ (1)

$\therefore$ pH = 2.69 (1)

pH should be given to 2 decimal places
penalise answer to 1 d.p. once in question

5

(d) moles OH^- added = 1.875×10^{-3} = moles A^- = moles HA left **(1)**

or $[A^-] = [HA]$

$\therefore$ Ka = $[H^+]$ **or** pH = pK_a **(1)**

$\therefore$ pH = 4.56 (1)

3

[13]

Q33.

(a) before any KOH added: $K_a = \frac{[H^+][A^-]}{[HA]}$ **or** $\frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$ **(1)**

$\therefore K_a = \frac{[H^+]^2}{[CH_3COOH]}$ **(1)**

$\therefore [H^+] = \sqrt{1.74 \times 10^{-5} \times 0.160} = 1.67 \times 10^{-3}$ **(1)**

$\therefore$ pH = 2.78 **(1)**

4

(b) at 8 cm^3 KOH:
Moles KOH added = $(8 \times 10^{-3}) \times 0.210 = 1.68 \times 10^{-3}$ **(1)**
$\therefore$ moles of CH_3COO^- formed = 1.68×10^{-3} **(1)**

Original moles of $CH_3COOH = (25 \times 10^{-3}) \times 0.160 = 4.0 \times 10^{-3}$ **(1)**

$\therefore$ moles of CH_3COOH left = $(4.0 \times 10^{-3}) - (1.68 \times 10^{-3})$
$= 2.32 \times 10^{-3}$ **(1)**

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

$= 1.74 \times 10^{-5} \times \frac{2.32 \times 10^{-3}/V}{1.68 \times 10^{-3}/V} = 2.40 \times 10^{-5}$ **(1)**

∴ pH = 4.62 **(1)**

It forget subtraction : max 5
If K_a expression not used max 5
if moles of CH_3COOH wrong but substitution used max 5

7

(c) at 40 cm^3 of KOH:
Total moles of KOH = $(40 \times 10^{-3}) \times 0.21 = 8.4 \times 10^{-3}$ **(1)**
∴ **excess moles of KOH = $(8.4 \times 10^{-3}) - (4.0 \times 10^{-3})$**
$= 4.4 \times 10^{-3}$ **(1)**
in total volume = 40 + 25 = 65 cm^3 **(1)**

∴ $[OH^-] = 4.4 \times 10^{-3} \times \frac{1000}{65} = 0.0677$ **(1)**

∴ $[H^+] = \frac{10^{-14}}{0.0677}$

OR pOH =1.17

$= 1.477 \times 10^{-13}$ **(1)**
∴ pH = 12.83 **(1)**

If volume missed : max 4
If moles of acid wrong but method includes subtraction : max 5
If no subtraction : max 4

6

[Max 16]

Q34.

(a) (i) $K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$ (or H_3O^+) **(1)**

(ii) (1) $K_a = \frac{[H^+]^2}{[CH_3COOH]}$ **(1)**

(2) $[H^+] = \sqrt{1.74 \times 10^{-5} \times 0.220} = 1.96 \times 10^{-3}$ **(1)**

(3) $pH = -\log_{10}[H^+]$ **(1)**
can score independently

(4) pH = 2.71 **(1)**
2 d.p. essential
If forget √ can score (1) and (3) for pH = 5.42

5

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(b) (i) moles acid = $\frac{25}{1000} \times 0220$ **(1)** = 5.50×10^{-3}

$= \frac{x}{10^3} \times 0.150$

$\therefore x = 25 \times \frac{0.220}{0.150}$ **or** $5.50 \times 10^{-3} \times \frac{1000}{0.150}$

= 36.7 (or 37) cm^3 (or 36.6) **(1)**

NOT 36 NOR 37.0 units must match

(ii) *Indicator*: thymol blue **(1)**
Explanation: weak acid – strong base **(1)**
equivalent at pH > 7 **(1)**
or high pH

5

(c) (1) mol NaOH added = $\frac{2.0}{40.0}$ = 0.050 **(1)**

If wrong M_r: CE ∴ lose marks (1) and (2) then mark on consequentially → max 4

(2) mol CH_3COOH left = 0.220 – 0.050 = 0.170 **(1)**

(3) mol CH_3COO^- formed = 0.050 **(1)**

(4) $[H^+] = Ka \frac{[acid]}{[salt]}$ OR $pH = pKa + \log\frac{[A^-]}{[HA]}$ etc **(1)**

If expression wrong no marks for 4 / 5 / 6

can score (1) to (4) in (5)

(5) $[H^+] = 1.74 \times 10^{-5} \times \frac{(0.170)}{(0.05)}$ OR $pH = 4.76 + \log\left(\frac{0.05}{0.17}\right)$ **(1)**

(6) pH = 4.23 **(1)**

*Correct answer gets **(1)(1)(1)(1)(1)(1)***
Mark (5) is for use of correct values of (acid moles) and (salt moles)
if one wrong allow pH conseq
if both wrong, no further marks
e.g. if candidate forgets substitution in (2)
he loses (2) and (5) but can score (1) (3) (4) (6) = max 4

for pH = 4.12 if $\frac{[acid]}{[salt]}$ upside down; answer 5.29 scores 3 for (1) (2) (3)

6

[16]

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Q1.

(a) 86.2% of students gave the correct definition.

(b) Most students calculated the amounts, in moles, of the reactants but often did not multiply the amount of barium hydroxide by two to give the amount of hydroxide ions. Some students did not convert the amount in moles to concentration and some did not quote their pH to two decimal places. This part of the question discriminated very well, with just over 20% of students scoring full marks.

(c) 81.8% of students gave the correct reason here.

(d) 78.5% correctly identified sulphur dioxide.

(e) 91% of students could give the correct expression for K_a.

(f) Most students could calculate the amount, in moles, of hydrochloric acid and of ethanoic acid, but many were unsure of how to use these numbers. Many students failed to recognise the need to increase the amount of acid and decrease the amount of salt due to the shift in the equilibrium when H^+ ions are added. Many added and subtracted the wrong way round or managed one process but not the other. Students could generally rearrange the K_a expression correctly; just over 40% of students scored full marks for this part of the question.

Q2.

(a) Nearly 60% of students recognised that the working range should correspond to the vertical section of the titration curve.

(b) Over 80% of students recognised this expression, with the commonest error being to show it as $[H^+]^2/[HX]$.

(c) This question was another that illustrated the importance of paying attention to the information in the stem of a question. A significant number of students attempted to answer this question using the expression for K_a, instead of recognising that this is a titration and that the end-point allows the amount of NaOH to be calculated, and hence the amount and concentration of the acid. Perhaps students did not recognise that that the end point of the titration could be obtained easily from the graph.

(d) The provision of alternative data ensured that students who had difficulty with part (c) were not disadvantaged here and over 50% gained full marks. Data in the stem were again crucial here.

(e) The idea that pH = pK_a at half-equivalence was not recognised by many, so only 26% of students gained this mark.

(f) A mark was often lost as a result of students assuming that half-equivalence was at 10 or 15 cm^3 and so plotting incorrectly. Many also failed to remember the need to show an initial steep section before buffering ‘levels off’ the curve.

Q3.

(a) The usual advice is that a scale on a graph is ‘suitable’ if the plotted points take up more than half of the available space. In this case, the decision about the suitability

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of the scale was more ‘relaxed’ due to the need for students to allow space for the extrapolation to go higher than the highest plotted point. However, a significant number of students still managed to miss the mark by choosing scales that led to the plotted points being squeezed in to only a couple of squares on the vertical axis. There still seems to be a misconception amongst some students that all scales need to start at zero. Having plotted the points, most students recognised that their lines of best fit should ignore the point at 5 minutes. Although a lot of ‘S-shaped’ curves were seen (the reminder clue in the question was that candidates should draw suitable *lines* of best fit), some students failed to draw any line between 0 and 3 minutes, and the lines were sometimes not extrapolated to the 4th minute. A surprising number of students quoted the ‘final’ temperature at the 4th minute rather than giving ΔT. Pleasingly, 34.3% of students scored all five marks.

(b) Far more students than expected failed to double the uncertainty given in the question to reflect the fact that two temperature readings are taken with the thermometer. As a result, only 19.3% of students were awarded this mark.

(c) As expected, this was the easiest question on the paper with the vast majority of candidates (90.7%) able to suggest a way to reduce heat loss.

(d) This was another example of a question where some students were let down by not reading the question, which clearly asked for a change that would reduce the percentage uncertainty *in the use of the same thermometer*. Given that percentage uncertainty is calculated as apparatus uncertainty divided by measurement made, it was hoped that more students would recognise the need to increase the size of the measurement made, i.e. the temperature change. Many students who did recognise the need to generate a bigger temperature change suggested doing so by using smaller volumes; they thus failed to appreciate that this would reduce the amounts of reactants as well as the volume, so that less heat would be given out and the change in temperature would be the same as in the larger scale experiment. 58% of students scored zero.

(e) Despite the formula and name being given in the question, many students failed to recognise that ethanedioic acid is diprotic, which affected their equation and subsequent calculation. In the calculation, most were able to calculate the initial amounts of each reactant, but many then failed to recognise the idea that one is present in excess so that the other would be the limiting reagent and so determine the amount of water formed. Calculations involving adding 0.02 to 0.045, or subtracting 0.02 from 0.045, were frequently seen, although it was not always clear what students thought they were calculating when they did so, due to poor layout of calculations. There were also a lot of variations seen in the mass used for the mcΔT calculation. In any enthalpy change or calorimetry experiment of this type, it is the solution that is increasing in temperature, so it is the mass of solution that needs to be used (100 g here as 25 cm^3 of one solution was added to 75 cm^3 of another and all have a density of 1.00 g cm^{-3}). This calculation discriminated extremely well between students of different abilities; 21.2% scored maximum marks and only 6.4% failed to score anything.

(f) This was expected to be a high-level discriminator and that certainly proved to be the case for the second mark (achieved by only 3.3% of students). Although many gained a mark for referring to the fact that sulfuric acid is a stronger acid than ethanedioic acid, the second half of their answer often then incorrectly referred to ideas such as “it therefore reacts with more KOH”, “more water is produced”, and “bonds between K$^+$ and sulfate are stronger than between K$^+$ and ethanedioate”. Only the best students recognised that the overall enthalpy change is the net result of the difference between ‘energy supplied’ and ‘energy released’. In this case, the ‘energy released’ will be the same for both acids. Therefore, the difference in the

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enthalpies of neutralisation must be due to ethanedioic acid needing more energy to be supplied, in order to break O−H bonds during the neutralisation reaction (whereas the sulfuric acid is already fully dissociated).

Q8.

Question (a) was generally well done, but a large number of students did not include a reversible sign in their equation for dissociation of the weak acid. Part (b) differentiated well as weaker students failed to show how ethanoic acid could act as a base and accept a proton.

Part (c)(i) was more straightforward but some students failed to calculate the concentration of the acid correctly and just used a number of moles. Part (c)(ii) differentiated well: many students realised a subtraction was needed in the calculation, but then failed to use the total volume to convert the amount, in moles, of H^+ ions to a concentration to calculate the pH.

Part (d)(i) was completed very well with most students gaining either 3 or 4 marks. In part (d)(iii) a significant number incorrectly used the original amount in moles of acid (0.0125) in their ratio. Even some of the strongest students struggled with the maths skills required and a frequent wrong answer was the inverse of 1.20 due to incorrect rearrangement. A significant number did not work out the hydrogen ion concentration and so lost M1 when they couldn't complete the rest of the calculation.

Part (e) differentiated well with full descriptions seen in about a third of the answers and one mark gained by another third. In part (f) the first mark proved very accessible but the second proved trickier; many students showed poor maths skills and thought that K_a would equal 1 or zero.

Q9.

In part (a) the missing equilibrium sign was not always penalised and part (b) often had no reference to the equilibrium shift and over-complicated answers led to contradictions in responses.

Q10.

This question was generally well attempted, with most students scoring well in the mathematical sections. In part (a), most students gave the meaning of a weak acid as 'only partially ionised or dissociated into ions', and this was credited. The preferred answer was □only slightly ionised'. 'Not fully ionised' did not gain the mark. The equation in part (b) was poorly answered mainly because the formula for sodium carbonate was incorrect. In some cases, the formula of sodium hydroxide or sodium hydrogen carbonate was given. A common error in part (c) was to omit the factor of 2 when calculating the concentration of hydroxide ions from the concentration of calcium hydroxide. Parts (d)(i) and (d)(ii) were answered well but in part (d)(iii) many students used an expression for K_c with $[H^+]^2$ or could not rearrange the correct expression to find the concentration of sodium benzenecarboxylate. Students should be encouraged to use words in their answers to make it clear whether the numbers they write refer to amounts in moles or to concentrations and also to which substance they refer. Answers to part (e) included many wrong substances and showed that some students think that H_2 (or H^+) is present in the atmosphere or that carbonic acid can exist in an alkaline solution.

Q11.

Although parts (a) and (b) were answered well, a considerable number of students again

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had difficulty in rearranging the expression for Ka in part (b)(ii). Part (c)(i) was well done, although HCl was a common wrong product. Part (c)(ii) proved to be difficult and was poorly understood by many students. In part (d), the indicator for the strong acid – strong base combination was surprisingly least well answered.

Many students found part (e) difficult and the question discriminated well. Despite the instruction to assume that sulfuric acid was fully dissociated, the factor of 2 was often omitted completely or alternatively used in the wrong place. Also, the number of moles of H^+ was often used instead of the concentration of H^+ to find the pH.

Q12.

Students found part (a) relatively easy. The most common errors were in part (a)(iii) where some students squared the hydrogen ion concentration.

The double arrow sign for an equilibrium was frequently missed in part (b)(i) and there were several instances where the wrong proton was lost from HCOOH. Only 33% of students scored all 3 marks in part (b)(iv). Some students lost M1 for confusing higher $[H^+]$ with higher pH. Some lost M3 because they wrote an explanation in general terms, "according to Le Chatelier's principle" rather than suggesting that the position of equilibrium shifts to oppose a specific change, ie to reduce the temperature.

Part (c) was a good discriminator and the full range of marks was seen, although there were more than usual who gained high marks in what has, in the past, been seen as a difficult topic. In part (c)(i), some students couldn't rearrange the K_a expression correctly and wrote the acid and salt concentrations the wrong way round. Many calculated an 'excess' of methanoic acid by subtraction.

The calculation in part (c)(ii) proved to be the most difficult calculation on the paper. Most students scored M1, but several wrote nothing further. Many also gained M2 although adding and subtracting the wrong way round caused many to lose any further marks. Incorrect rearrangement of the K_a expression was again a problem.

Q13.

Part (a) was well known, but part (b) was much less well understood. In part (c), most students scored the first two marks but then failed to use their answers correctly to calculate the total volume. Some who did not read the question fully, added 25 cm^3 to their correct answer and so lost the final mark.

In part (d)(iii), a significant number could not correctly rearrange the simplified expression for K_c. A mark was allowed, in this part only, for a correct calculation of pH using their value of $[H^+]$ even if this was not the correct concentration.

In part (e), most scored the first two marks, but many then failed to recognise that, on adding alkali, the number of moles of acid would have decreased. Others were unable to rearrange the K_a expression correctly or attempted to use the equation $K_a = [H^+]^2/[HX]$.

Moles and concentration were often confused and many responses were also badly presented with little explanation. Such omission makes it difficult for examiners to award marks in an extended calculation if the answer is wrong.

Q14.

(a) Many incomplete answers were given credit in this part. When the components of a two-part answer are linked by the underlined word 'and' **both** components are needed to earn the mark.

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(b) A pleasing majority of students were able to complete the calculation in this part. Occasionally, a centre was unduly harsh in penalising minor rounding in the intermediate steps.

Q15.

All of the pH calculations in this question were answered well. In part (a), more students than expected had difficulty calculating the $[H^+]$ after dilution but a mark was allowed for a correct calculation of pH from their $[H^+]$. In part (b)(ii), some students struggled to convert the pH into $[H^+]$ but over three quarters of the entry gained all three marks. In part (c), common mistakes included using the initial number of moles of OH^- rather than those remaining after partial neutralisation and also not using the total volume to convert the number of moles of excess hydroxide into a concentration. The degree of clarity of some students' working was also disappointing; many wrote strings of numbers with no explanation of what they were calculating. As usual, students who made errors in their calculations or gave a wrong answer with no explanation or working could gain few marks.

Q16.

As expected, there were very few incorrect answers to parts (a)(i) and (ii). However, in part (a)(iii), some candidates assumed that $[H^+] = [OH^-]$ instead of using all the data in the question. Part (b) was generally well attempted, but common mistakes in part (b)(i) included incorrect formulae for ethanoic acid and the ethanoate ion, missing brackets and giving $[H^+]^2$ as the numerator.

Part (c)(i) proved to be difficult. While most candidates were able to calculate the initial numbers of moles of the acid and alkali, a large proportion could not rearrange the *K*a expression correctly or assumed that the amount of acid had not changed on addition of the alkali. Very few realised that this was a half neutralisation and their attempts to calculate the concentrations of acid and salt were often wrong and sometimes included the term $[H^+]^2$.

Part (c)(ii) was more successfully attempted, but still many candidates scored only 2 marks, either because they did not realise that some of the alkali would be neutralised by adding acid or because they failed to use the total volume to convert the number of moles of OH^- into a concentration.

Q17.

The early parts of this question were answered well, although in part (a)(iii), about a third of the candidates did not realise that adding water had no effect on the number of moles of acid present. Over two thirds of the candidates scored full marks in part 2(b); a common error for the others was to rearrange the expression for K_a incorrectly. In part 2(c), many answers stated general properties of a buffer solution, without giving any explanation specific to this situation.

It was pleasing to see that over 44% of the candidates gained full marks in part (d)(i). Many of the rest thought that addition of the salt to the solution of the acid changed the amount of acid present. Part (d)(ii) discriminated well and only the better candidates were able to calculate the amounts in moles of acid and of salt present in the solution after the addition of sodium hydroxide and then use these values correctly.

Q18.

Most of this question proved to be straightforward and few candidates lost marks in part (a). Part (c) was the most discriminating section with only the better candidates scoring all

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six marks. Many others either forgot that sulfuric acid is diprotic and so missed that the final mixture in the questions was acidic or failed to convert the number of moles of H^+ ions present into a concentration in order to find pH.

Q19.

(a) Virtually all candidates were able to produce a suitable graph in this part. There were fewer examples of generous marking of this graph, as the nature of the graph makes it more likely that the plotted points will cover half the paper. Occasionally graphs containing incorrectly plotted points were not penalised. Some markers forgot that the line of best fit mark cannot be awarded when the line itself is poorly drawn or doubled in places. Given the shape of the graph, some minor doubling can be ignored but sometimes graphs with several doubled regions escaped the appropriate penalty.

(b) Many candidates could not determine the volume of sodium hydroxide at the end-point of the titration in part (i), quoting an amazing range of values. Most candidates could, however, obtain appropriate values for part (ii) and (iii). In part (iii), some centres did not allow a consequential mark from an incorrect answer to part (ii).

(c) Candidates either scored both marks in this part or made no useful progress.

(d) In this part, a number of candidates became confused when comparing two very small numbers and chose the wrong acid.

(e) Candidates have a good appreciation of the calculation of apparatus errors and a majority scored the mark in this part.

(f) Again the need to work with very small numbers meant that many candidates did not complete this part correctly.

(g) Candidates either answered this part confidently, or misread the question and suggested changes to the experimental technique.

(h) Only the better candidates were able to answer this part correctly.

Q20.

This question was generally well answered and only rarely did candidates fail to follow the instructions to give their pH values to two decimal places.

In part (a)(ii) only a fifth of the candidates realised that sulfuric acid is diprotic and in part (b)(i) only two thirds of the entry could write a correct equation for the reaction of ethanoic acid with sodium hydroxide. The following titration calculation was very straightforward but was thought more complicated by many including those who introduced K_w. It was disappointing to see that only the very best candidates understood that sodium hydroxide solution reacts with carbon dioxide in the air and many candidates showed a strange understanding of the composition of air. Part (c)(ii) was well answered; nearly four fifths of candidates answered this part completely correctly. Answers to the unstructured buffer calculation in part (c)(iii) were also quite pleasing; the question differentiated well and over twenty percent of candidates gained full marks. Other candidates were hindered by poor mathematical skills.

Q22.

Part (a) was a straightforward question and was answered well. High marks were also gained in part (b), although some candidates lost the mark in part (i) for the expression for

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K_a because they wrote the less general expression $[H^+]^2/[HX]$ instead of $[H^+]\,[X^-]/[HX]$. The calculation in part (ii) was usually well done. The mark in part (a)(iii) was awarded for a value of pK_a correctly calculated from their K_a in part (ii).

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In part (c), only the most able realised that, because the reaction was between potassium hydroxide and sulphuric acid, the mole ratio of reactants was 2:1. Hence although the answers to part (c)(i) and (ii) were usually correct, very few gained the mark in part (iii). For many, this was their only error in part (b). Others however failed to use the total volume of solution, 48 cm^3, correctly in calculating the concentration of hydroxide ions in part (iv) and/or were unable to use K_w or pOH to calculate the pH of the mixture. It was disappointing to see that a considerable number of candidates did not give the pH to two decimal places despite being asked to do so.

Q24.

Only the weakest failed to recognise the titration curves in part (a) or to give either of the indicators which changed colour above pH 7. The definition of pH was, as expected, well known, but many candidates were unable to complete the calculation of the concentration of potassium hydroxide in part (b)(ii) by using either K_w or the expression pH + pOH =14. Part (c)(i) was well done but many failed to recognise that the solution formed in part(c) was a buffer solution of the particular type where the moles of salt and moles of acid present were equal, so that the pH of the mixture equals the pK_a of the weak acid. It was pleasing that very few ignored the stated request to quote pH values to two decimal places.

Q25.

Most candidates scored full marks for a correct calculation in part (a). Parts (b)(i) and (ii) were also well answered but (b)(iii) proved to be more difficult and many candidates failed to state that, when half the acid had been neutralised, $[A^-] = [HA]$. Only the very best candidates stated correctly that on dilution the ratio $[A^-] : [HA]$ remains constant and, as a consequence, $[H^+]$ also remains constant. The calculations in part (d) were generally well done although one mark was lost by candidates who, in (d)(ii), calculated the total final volume of acid, 50.0 cm^3, and not the volume of water which must be added as required by the question.

Q26.

Most candidates took note of the request to give all pH values to 2 decimal places in this question. Part (a) was answered very well and some who scored no further marks in the whole question were able to answer this part correctly. Most candidates were able to describe what a *buffer solution* is and although any equation which correctly showed the removal of ethanoate ions and the formation of ethanoic acid was accepted in part (b)(ii), many were unable to give a correct answer.

Part (c) involved buffer solutions. Many answers showed that some candidates have still not mastered numerical questions about buffer solutions. A good proportion of the candidates were able to use the original values of the number of moles of ethanoic acid and of sodium ethanoate in one dm^3, i.e. the concentration of these species, to calculate the correct pH of the original buffer solution. A much smaller number was able to calculate the correct answer for the final pH of the buffer solution after the addition of 0.01 mol of hydrochloric acid. Only the best realised that the number of moles of acid would have gone up by 0.01 mol and the number of moles of ethanoate ions would have fallen by the same amount. However it was pleasing to see a good number of candidates gaining full marks in this question.

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Q28.

High marks were scored in this question by the more able candidates but the question discriminated well and although parts (a) and (b) were well answered by most, the weaker candidates scored poorly in part (c).

In part (a), although the expression for K_a was well known, several candidates did not give the general expression for K_a and instead wrote the more specific $[H^+]^2/[HA]$. This expression was however credited in part (b). Candidates should be reminded that square brackets are essential in these expressions.

In part (b), many correct answers were given although, in the calculation, several candidates failed to take the square root correctly. A mark was awarded for the correct calculation of a pH value from their hydrogen ion concentration.

As reported regularly before, too many candidates seem unaware that pH values should be given to two decimal places; these two figures give the value to the appropriate precision. The numbers before the decimal point only give the powers of ten involved in the hydrogen ion concentration.

In part (c)(ii), most candidates were able to state that the pH would remain unchanged, but fewer explained clearly that the extra hydrogen ions were removed by reaction with the A^- ions from the salt. Only the most able candidates answered the calculation in part (c)(ii) correctly. Many gained a mark for the hydrogen ion concentration at pH = 3.59, but few were able to use or, more particularly, to rearrange the expression for K_a correctly to calculate the concentration of A^-.

Q31.

Definitions of the terms Kw and pH in parts (a)(i) and (ii) were usually well answered except by those who failed to write mathematical definitions and attempted to describe the terms in words. Provided there were no contradictions, the marks could be earned in the later sections. The most common error in the expression for Kw was to include water. However this water term was conveniently forgotten in part (iii) and correct answers for the pH of pure water at 50°C were common. As reported regularly before, too many candidates seem not to be aware **that pH values should be given to two decimal places**; these two figures give the value to the appropriate precision. The numbers before the decimal point only give the powers of ten involved in the hydrogen ion concentration. However, failure to give pH values to the correct precision was only penalised once in the question. Part (b)(i) was answered well but (b)(ii) was more discriminating. A common error was to forget that the moles of excess sodium hydroxide were present in a total volume of solution of 75 cm^3 and needed to be converted into a molar concentration before the pH of the solution could be calculated.

A number of candidates tried to answer the question as if a buffer solution had been produced despite the use of a named strong acid. Several also gave pH values below 7 although there was an excess of alkali present. Part (c) was answered well by most candidates although some failed to give the general expression for K_a and instead wrote the more specific $[H^+]^2/[HX]$.

This expression was however credited in part (c)(ii).

Q32.

Parts (a) and (b) were well answered. Most candidates correctly calculated the volume of sodium hydroxide needed and although some candidates attempted to answer part (b)(i) in words, most were able to define pH as $-\log_{10}[H^+]$. The indicator expected in part (b)(iii) was the familiar phenolphthalein, but thymol blue (the correct indicator to the January 2002 pH question) was a common and correct answer.

In part (c), the answer that weak acids are only *slightly dissociated* in water was required,

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rather than not *fully dissociated*, since even strong acids may not be fully dissociated. In part(c)(ii), the general expression for Ka was required, i.e. $[H^+][A^-]/[HA]$ rather than the more particular $[H^+]^2/[HA]$ which only applies to solutions of weak acids alone. The latter expression could however gain credit in the calculation in part (iii). This was answered well by many candidates although some used the number of moles of HA in the calculation rather than its concentration. Not all candidates seemed to be aware that **it is important that pH values are given to two decimal places**; these two figures give the value to the appropriate precision. The numbers before the decimal point only give the powers of ten involved in the hydrogen ion concentration.

Part (d) discriminated well. The better candidates realised that point b was the pH at half equivalence, i.e. when $[A^-] = [HA]$ such that $pH = pK_a$.

Q33.

It is important that pH values are given to two decimal places; these two figures give the value to the appropriate precision. The numbers before the decimal point only give the powers of ten involved in the hydrogen ion concentration.

Three pH values were required in this question and answers to one decimal place only were penalised, but only once on this occasion.

The question involved three calculations of pH. First the pH of a solution of ethanoic acid was required. This was usually well done even by candidates of moderate ability.

The second situation involved a buffer solution formed when some of the weak acid has been reacted with alkali. This was done less well. Many candidates correctly calculated the number of moles of acid used, the number of moles of hydroxide added and hence the number of moles of acid remaining. However, these values were then too often used in a calculation which assumed only a weak acid was present, as in the first part of the question rather than an acidic buffer solution. Although many candidates still seemed unfamiliar with calculations of this type, there was a definite improvement in the numbers gaining full marks compared with the January CHM4 paper.

The last part of the question involved finding the pH of the resulting solution of excess potassium hydroxide produced when all the ethanoic acid is used up. This part was usually answered more successfully than the second part.

Q34.

Many candidates scored well in parts (a) and (b) but very few seemed confident in dealing with quantitative buffer calculations in part (c). The main errors in part (a)(i) were to write the expression for K_a as

$$K_a = \frac{[H^+]^2}{[CH_3COOH]} \text{ or } \frac{[H+]^2}{[HA]} \text{ rather than } \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

The first is not a general statement while the second does not show that the acid is ethanoic. Despite the loss of this first mark many candidates were able to gain all the remaining marks in part (a). Marks were lost by those who did not take the square root to obtain the hydrogen ion concentration and also by those who gave the pH to one decimal place only. It is important that pH values are given to two decimal places; these two figures give the value to the appropriate precision.
The numbers before the decimal point only give the powers of ten involved in the hydrogen ion concentration. Part (b)(i) was the best answered part of the question and most candidates gained both marks for the calculation. In part (b)(ii) most realised that the

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titration involved a strong base and a weak acid but the indicator chosen was often bromothymol blue rather than thymol blue, despite the correct explanation that the equivalence point must be above pH 7 for this combination of acid and base. Part (c) was not attempted by a large number of candidates. Of those who did attempt the question, most calculated the number of moles of sodium hydroxide but then used K_w in their calculation as if there was a mixture of strong acid and strong base present. Of those who did realise that an acid buffer had been produced by the reaction of an excess of ethanoic acid with sodium hydroxide, a large proportion forgot to subtract the number of moles of acid reacted from the initial number of moles of acid before substituting in the expression for K_a and gave a pH of 4.12. This answer received four marks out of the six available for the correct answer, 4.23.

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