**Q15.**

In order to obtain a pH curve, you are provided with a conical flask containing 25.0 $cm^3$ of a 0.100 mol $dm^{-3}$ carboxylic acid solution and a burette filled with 0.100 mol $dm^{-3}$ sodium hydroxide solution. You are also provided with a calibrated pH meter.

(a) State why calibrating a pH meter just before it is used improves the accuracy of the pH measurement.

___

___

**(1)**

(b) Describe how you would obtain the pH curve for the titration.

___

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**(5)**

**(Total 6 marks)**

**Q16.**

When 1.00 mol $dm^{-3}$ solutions of salicylic acid and sodium hydroxide are mixed a buffer solution can be formed. Salicylic acid is a monoprotic acid that can be represented by the formula HA.

(a) Select a mixture from the table below that would produce a buffer solution. Give a reason for your choice.

| **Mixture** | **Volume of 1.00 mol $dm^{-3}$ salicylic acid solution / $cm^3$** | **Volume of 1.00 mol $dm^{-3}$ sodium hydroxide solution / $cm^3$** |
|---|---|---|
| **X** | 25 | 75 |
| **Y** | 50 | 50 |

| | | |
|---|---|---|
| **Z** | 75 | 25 |

Mixture ____________________________________________

Reason ____________________________________________

____________________________________________

____________________________________________

**(2)**

(b) Another mixture, formed by adding 50 $cm^3$ of 1.00 mol $dm^{-3}$ salicylic acid solution to 25 $cm^3$ of 1.00 mol $dm^{-3}$ sodium hydroxide solution, can be used to determine the $pK_a$ of salicylic acid. State **one** measurement that must be made for this mixture and explain how this measurement can be used to determine the $pK_a$ of salicylic acid.

Measurement ____________________________________________

Explanation ____________________________________________

____________________________________________

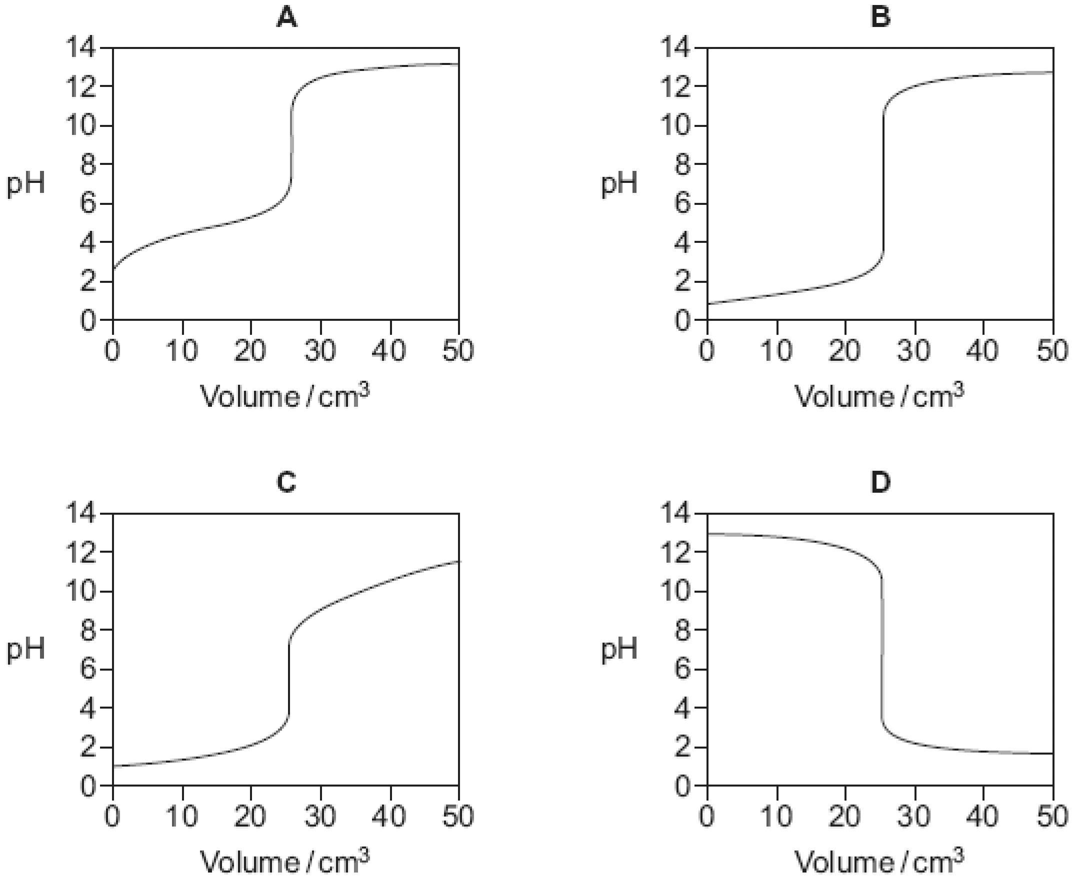
____________________________________________

**(3)**

**(Total 5 marks)**

## Q17.

Titration curves labelled **A**, **B**, **C** and **D** for combinations of different aqueous solutions of acids and bases are shown below.
All solutions have a concentration of 0.1 mol $dm^{-3}$.




(a) In this part of the question write the appropriate letter in each box.

From the curves **A**, **B**, **C** and **D**, choose the curve produced by the addition of

ammonia to 25 cm$^3$ of hydrochloric acid ☐

sodium hydroxide to 25 cm$^3$ of ethanoic acid ☐

nitric acid to 25 cm$^3$ of potassium hydroxide ☐

**(3)**

(b) A table of acid.base indicators is shown below.
The pH ranges over which the indicators change colour and their colours in acid and alkali are also shown.

| Indicator | pH range | Colour in acid | Colour in alkali |
|---|---|---|---|
| Trapaeolin | 1.3 – 3.0 | red | yellow |
| Bromocresol green | 3.8 – 5.4 | yellow | blue |
| Cresol purple | 7.6 – 9.2 | yellow | purple |
| Alizarin yellow | 10.1 – 12.0 | yellow | orange |

(i) Select from the table an indicator that could be used in the titration that produces curve **B** but **not** in the titration that produces curve **A**.

___________________________________________________________________________

**(1)**

(ii) Give the colour change at the end point of the titration that produces curve **D** when cresol purple is used as the indicator.

___________________________________________________________________________

**(1)**
**(Total 5 marks)**

## Q18.

When iron(II) sulfate is used for killing weeds in lawns, it is often mixed with the fertiliser ammonium sulfate. Ammonium sulfate also makes the soil acidic.

(a) Write an equation to show how the ammonium ion behaves as a Brønsted–Lowry acid in water.

___________________________________________________________________________

**(1)**

(b) Compounds such as ammonium sulfate react on warming with sodium hydroxide solution as shown in the equation below.

$$(NH_4)_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2NH_3 + 2H_2O$$

Use this information to describe a simple test, other than smell, to show that ammonia is evolved. State what you would observe.

Test ______________________________________________________________________

___________________________________________________________________________

Observation _______________________________________________________________

**(2)**
**(Total 3 marks)**

## Q19.

Ethanoic acid is manufactured in industry from methanol and carbon monoxide in a multi-step process involving hydrogen iodide. Ethanoic acid is obtained from the reaction mixture by fractional distillation. Methanoic acid is a useful by-product of this process.

The $K_a$ value of an organic acid can be determined by using the pH curve obtained when the acid is titrated against sodium hydroxide. The pH of the solution formed when exactly half of the acid has been neutralised is equal to the p$K_a$ value of the acid. The $K_a$ value of the acid can be used to confirm its identity.

A chemist used a pH curve to determine the p$K_a$ value of acid **Y**, formed during the manufacture of ethanoic acid. The chemist transferred 25.0 $cm^3$ of a solution of acid **Y** into a beaker using a pipette, and measured the pH of the acid solution using a pH meter which could be read to one decimal place. A solution of sodium hydroxide of concentration 0.100 mol $dm^{-3}$ was added from a burette in small portions. The pH of the mixture was recorded after each addition of the sodium hydroxide solution. The chemist's results are given in the table below.

| Volume of sodium hydroxide solution added / $cm^3$ | pH |
|---|---|
| 0.0 | 3.0 |
| 2.0 | 3.4 |
| 4.0 | 3.5 |
| 8.0 | 3.7 |
| 12.0 | 4.3 |
| 16.0 | 4.1 |
| 20.0 | 4.3 |
| 22.0 | 4.7 |

| Volume of sodium hydroxide solution added / $cm^3$ | pH |
|---|---|
| 23.5 | 5.1 |
| 24.0 | 5.5 |
| 24.5 | 11.8 |
| 25.0 | 12.1 |
| 26.0 | 12.3 |
| 27.0 | 12.4 |
| 28.0 | 12.5 |
| 30.0 | 12.5 |

(a) Use the results given in the table above to plot a graph of pH (*y*-axis) against volume of sodium hydroxide solution added. Use the points to draw the pH curve, ignoring any anomalous results.

**(6)**

(b) Use your graph from part (a) to determine the

(i) volume of sodium hydroxide solution at the end-point of the titration

___________ $cm^3$

(ii) volume of sodium hydroxide solution needed to neutralise half the acid

___________ $cm^3$

(iii) pH of the half-neutralised mixture. Give your answer to one decimal place.

____________________

**(3)**

(c) Use the pH of the half-neutralised mixture from part (b) (iii) to calculate the value of the acid dissociation constant, $K_a$, of the acid **Y**. Show your working.

____________________________________________________________________

____________________________________________________________________

____________________________________________________________________

____________________________________________________________________

**(2)**

(d) The table below shows the $K_a$ values for some organic acids.

| Acid | $K_a$ / mol dm$^{-3}$ |
|---|---|
| Methanoic acid | $1.6 \times 10^{-4}$ |
| Ethanoic acid | $1.7 \times 10^{-5}$ |
| Iodoethanoic acid | $6.8 \times 10^{-4}$ |
| Propanoic acid | $1.3 \times 10^{-5}$ |

Use your answer from part (c) to identify acid **Y** from this table.

____________________________________________________________________

**(1)**

(e) For the pipette and the burette, the maximum total errors are shown below. These errors take into account multiple measurements.

| | |
|---|---|
| pipette | ± 0.05 cm$^3$ |
| burette | ± 0.15 cm$^3$ |

Estimate the percentage error in using each of these pieces of apparatus. You should use your answer to part (b) (i) to estimate the percentage error in using the burette.

____________________________________________________________________

____________________________________________________________________

____________________________________________________________________

**(1)**

(f) Calculate the difference between the $K_a$ value from part (c) and the $K_a$ value of the acid you identified as the acid **Y** in the table in part (d).

Express this difference as a percentage of the value given in the table in part (d). (If you could not complete the calculation in part (c), you should assume that the $K_a$ value determined from the graph is $1.9 \times 10^{-4}$ mol dm$^{-3}$. This is not the correct value.)

___________________________________________________________________

___________________________________________________________________

**(1)**

(g) Other than by using a different pH meter, state **one** way in which the accuracy of the pH readings could be improved.

___________________________________________________________________

___________________________________________________________________

**(1)**

(h) State why there was little change in the pH value of the mixture when between 8 cm$^3$ and 20 cm$^3$ of alkali were added.

___________________________________________________________________

**(1)**
**(Total 16 marks)**

## Q20.

In this question, give all values of pH to 2 decimal places.

(a) (i) Write an expression for the term pH.

___________________________________________________________________

**(1)**

(ii) Calculate the concentration, in mol dm$^{-3}$, of an aqueous solution of sulfuric acid that has a pH of 0.25

___________________________________________________________________

___________________________________________________________________

___________________________________________________________________

___________________________________________________________________

**(2)**

(b) A student carried out a titration by adding an aqueous solution of sodium hydroxide from a burette to an aqueous solution of ethanoic acid. The end-point was reached when 22.60 cm$^3$ of the sodium hydroxide solution had been added to 25.00 cm$^3$ of 0.410 mol dm$^{-3}$ ethanoic acid.

(i) Write an equation for the reaction between sodium hydroxide and ethanoic acid.

___________________________________________________________________

**(1)**

(ii) Calculate the concentration, in mol $dm^{-3}$, of the sodium hydroxide solution used.

**(2)**

(iii) A list of indicators is shown below.

| Indicator | pH range |
|---|---|
| thymol blue | 1.2–2.8 |
| bromophenol blue | 3.0–4.6 |
| litmus | 5.0–8.0 |
| cresol purple | 7.6–9.2 |

Select from the list the most suitable indicator for the end-point of this titration.

**(1)**

(iv) Suggest why the concentration of sodium hydroxide in a solution slowly decreases when left open to air.

**(1)**

(c) At 298 K, the value of the acid dissociation constant, $K_a$, for ethanoic acid in aqueous solution is $1.74 \times 10^{-5}$ mol $dm^{-3}$

(i) Write an expression for the acid dissociation constant, $K_a$, for ethanoic acid.

**(1)**

(ii) Calculate the pH of 0.410 mol $dm^{-3}$ ethanoic acid at this temperature.

**(3)**

(iii) Calculate the pH of the buffer solution formed when 10.00 $cm^3$ of 0.100 mol $dm^{-3}$ potassium hydroxide are added to 25.00 $cm^3$ of 0.410 mol $dm^{-3}$ ethanoic acid.

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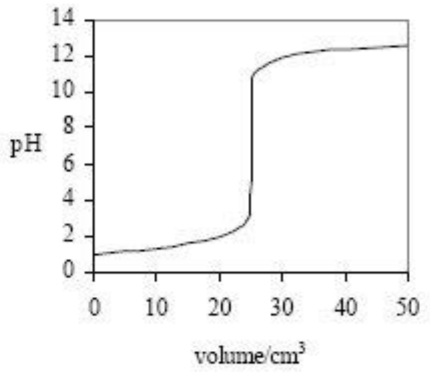
**(6)**

**(Total 18 marks)**

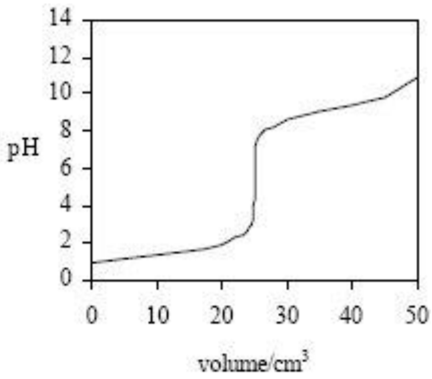
**Q21.**

Indicators and pH curves can be used to determine the end point in a titration.

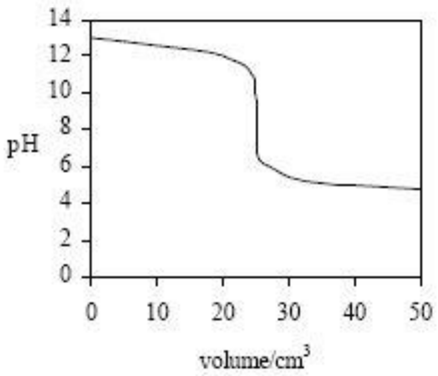
(a) The pH curves labelled **J, K, L** and **M** for combinations of different acids and bases are shown below. All solutions have a concentration of 0.1 mol $dm^{-3}$.



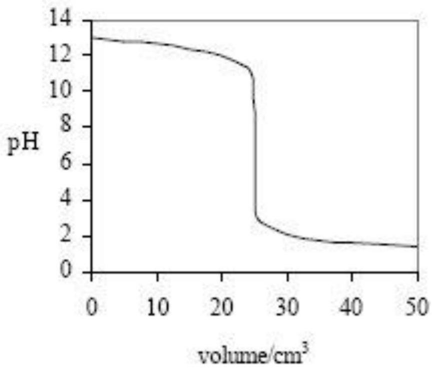

**J**




**K**




**L**




**M**

(i) Select from **J**, **K**, **L** and **M** the curve produced by the addition of

ammonia to 25 cm³ of hydrochloric acid ________________________________

ethanoic acid to 25 cm³ of sodium hydroxide ____________________________

sodium hydroxide to 25 cm³ of hydrochloric acid _________________________

(ii) A table of acid–base indicators and the pH ranges over which they change colour is shown below.

| Indicator | pH range |
|---|---|
| Thymol blue | 1.2 – 2.8 |
| Bromophenol blue | 3.0 – 4.6 |
| Methyl red | 4.2 – 6.3 |
| Cresolphthalein | 8.2 – 9.8 |
| Thymolphthalein | 9.3 – 10.5 |

Select from the list above an indicator which could be used in the titration which produces curve **J** but not in the titration which produces curve **K**.

_______________________________________________________________

**(4)**

(b) The acid dissociation constant, $K_a$, for the weak acid, ethanoic acid, has a value of $1.74 \times 10^{-5}$ mol dm$^{-3}$ at 25 °C.

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

(i) Write an expression for the term pH.

___

(ii) Calculate the pH of a 0.15 mol dm$^{-3}$ solution of ethanoic acid. Give your answer to 2 decimal places.

___

___

___

___

**(4)**

**(Total 8 marks)**

**Mark Scheme**

## Q15.

(a) <u>Over time</u> / <u>after storage</u> 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]**

## Q16.

(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 = p$K_a$

*Accept $[H^+] = K_a$*

**1**

**[5]**

## Q17.

(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]**

**Q18.**

(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]**

**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.*

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**

$1.26 \times 10^{-4}$
*3.7 to 4.1 gives $K_a = 7.9 \times 10^{-5}$ to $2.0 \times 10^{-4}$*
*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 $1.9 \times 10^{-4}$ gives $0.3 \times 10^{-4}$ 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 buffer

**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*

**1**

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

**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 carbon dioxide (in the air)

**1**

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

allow molecular formulae or minor slip in formulae

*penalise ( )*
*allow $H_3O^+$*
*not allow HA etc*

**1**

(ii) $K_a = \frac{[H^+]^2}{[CH_3COOH]}$ 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 $2.67 \times 10^{-3}$ or $2.7 \times 10^{-3}$ 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 $1.025 \times 10^{-2}$ or $1.03 \times 10^{-2}$

**M3** mol <u>HA</u> 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 $OH^-$ = $1.0 \times 10^{-3}$

*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**

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

(= $1.61 \times 10^{-4}$ or $1.62 \times 10^{-4}$)

**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

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

$[H^+] = \sqrt{1.74 \times 10^{-5} \times 0.15}$ (or $1.62 \times 10^{-3}$) 1

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

**[8]**