AQA A-LEVEL CHEMISTRY · 7405

CHEMISTRY



EXAM QUESTION PACK

3.1.12 ACIDS AND BASES

SCORE	PERCENTAGE
/1449	%

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Q1.

This question is about Brønsted–Lowry acids.

(a) Give the meaning of the term Brønsted–Lowry acid.

_____

_____

(1)

(b) What is meant by the term strong when describing an acid?

_____

_____

(1)

(c) At 298 K, 25.0 cm^3 of a solution of a strong monoprotic acid contained 1.45×10^{-3} mol of hydrogen ions.

Calculate a value for the pH of this solution.
Give your answer to 2 decimal places.

pH _____

(2)

(d) Calculate the pH of the solution formed after the addition of 35.0 cm^3 of 0.150 mol dm^{-3} NaOH to the original 25.0 cm^3 of monoprotic acid.

The ionic product of water K_w = 1.00×10^{-14} mol^2 dm^{-6} at 298 K.
Give your answer to two decimal places.

pH _____

(5)

(e) A buffer solution is made when 1.50 g of sodium hydroxide are added to 1.00 dm^3 of a 0.150 mol dm^{-3} solution of a weak acid HA.

For HA, the acid dissociation constant, K_a = 1.79×10^{-5} mol dm^{-3}.

Calculate the pH of this buffer solution.

pH _____

(6)

(Total 15 marks)

Q2.

Nitric acid (HNO_{-3}) is a strong acid. Ethanoic acid (CH_3COOH) is a weak acid.

(a) Write an equation to show how ethanoic acid behaves as a weak acid in its reaction with water.

_____

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(1)

(b) When pure ethanoic acid reacts with pure nitric acid, ethanoic acid acts as a base.

Write an equation for this reaction.

_____

(1)

(c) Two beakers, **A** and **B**, each contain 100.0 cm^{-3} of 0.0125 mol dm^{-3} nitric acid.

(i) Calculate the pH of the solution formed after 50.0 cm^{-3} of distilled water are added to beaker **A**.
Give your answer to 2 decimal places.

_____

_____

_____

(2)

(ii) Calculate the pH of the solution formed after 50.0 cm^3 of 0.0108 mol dm^{-3} aqueous sodium hydroxide are added to beaker **B**.
Give your answer to 2 decimal places.

_____

_____

_____

_____

_____

_____

_____

(4)

(d) A third beaker, **C**, contains 100.0 cm^3 of 0.0125 mol dm^{-3} ethanoic acid.
The acid dissociation constant K_a for ethanoic acid has the value 1.74×10^{-5} mol dm^{-3} at 25 °C.

(i) Write an expression for K_a for ethanoic acid and use it to calculate the pH of the ethanoic acid solution in beaker **C**.
Show your working. Give your answer to 2 decimal places.

K_a _____

_____

Calculation _____

_____

_____

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_____

(4)

(ii) Aqueous sodium hydroxide is added to beaker **C** until the pH of the solution becomes 4.84.

Name the salt formed in the reaction of ethanoic acid with sodium hydroxide.

_____

(1)

(iii) Calculate the value of $\frac{[\text{salt}]}{[\text{ethanoic acid}]}$ in the solution with the pH of 4.84.

_____

_____

_____

_____

_____

_____

(3)

(e) Explain why chloroethanoic acid is a stronger acid than ethanoic acid.

_____

_____

_____

_____

(2)

(f) Explain why data books do not usually contain values of K_a for strong acids.

_____

_____

_____

_____

(2)

(Total 20 marks)

Q3.

This question is about several Brønsted–Lowry acids and bases.

(a) Define the term *Brønsted–Lowry* acid.

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_____

_____

(1)

(b) Three equilibria are shown below. For each reaction, indicate whether the substance immediately **above** the box is acting as a Brønsted–Lowry acid (**A**) or a Brønsted–Lowry base (**B**) by writing **A** or **B** in each of the six boxes.

(i) CH_3COOH + H_2O ⇌ CH_3COO^- + H_3O^+

(1)

(ii) CH_3NH_2 + H_2O ⇌ $CH_3NH_3^+$ + OH^-

(1)

(iii) HNO_3 + H_2SO_4 ⇌ $H_2NO_3^+$ + HSO_4^-

(1)

(c) A 25.0 cm^3 sample of 0.0850 mol dm^{-3} hydrochloric acid was placed in a beaker. Distilled water was added until the pH of the solution was 1.25.

Calculate the total volume of the solution formed. State the units.

_____

_____

_____

_____

_____

(3)

(d) At 298 K, the value of the acid dissociation constant (K_a) for the weak acid HX in aqueous solution is 3.01×10^{-5} mol dm^{-3}.

(i) Calculate the value of pK_a for HX at this temperature.
Give your answer to 2 decimal places.

_____

_____

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(1)

(ii) Write an expression for the acid dissociation constant (K_a) for the weak acid HX.

(1)

(iii) Calculate the pH of a 0.174 mol dm^{-3} solution of HX at this temperature.
Give your answer to 2 decimal places.

(3)

(e) An acidic buffer solution is formed when 10.0 cm^3 of 0.125 mol dm^{-3} aqueous sodium hydroxide are added to 15.0 cm^3 of 0.174 mol dm^{-3} aqueous HX.
The value of K_a for the weak acid HX is 3.01×10^{-5} mol dm^{-3}.

Calculate the pH of this buffer solution at 298 K.
Give your answer to 2 decimal places.

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_____

(6)

(Total 18 marks)

Q4.

Ammonia and ethylamine are examples of weak Brønsted–Lowry bases.

(a) State the meaning of the term *Brønsted–Lowry base*.

_____

_____

(1)

(b) (i) Write an equation for the reaction of ethylamine ($CH_3CH_2NH_2$) with water to form a weakly alkaline solution.

_____

_____

(1)

(ii) In terms of this reaction, state why the solution formed is **weakly** alkaline.

_____

_____

(1)

(c) State which is the stronger base, ammonia or ethylamine. Explain your answer.

Stronger base _____

Explanation _____

_____

_____

_____

(3)

(d) Give the formula of an organic compound that forms an alkaline buffer solution when added to a solution of ethylamine.

_____

(1)

(e) Explain qualitatively how the buffer solution in part (d) maintains an almost constant pH when a small amount of hydrochloric acid is added to it.

_____

_____

_____

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_____

(2)

(Total 9 marks)

Q5.

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)

Q6.

Summarised directions for recording responses to multiple completion questions			
A (i), (ii) and (iii) correct only	**B** (i) and (iii) correct only	**C** (ii) and (iv) correct only	**D** (iv) alone correct

Brønsted-Lowry acid-base reactions include

(i) $OH^- + CH_3Cl \rightarrow CH_3OH + Cl^-$

(ii) $NH_3 + HCl \rightarrow NH_4^+ + Cl^-$

(iii) $KF + PF_5 \rightarrow K^+ + PF_6^-$

(iv) $H_2O + H_2O \rightarrow H_3O^+ + OH^-$

(Total 1 mark)

Q7.

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In which one of the following reactions is the role of the reagent stated correctly?

	Reaction	**Role of reagent**
A	$TiO_2 + 2C + 2Cl_2 \rightarrow TiCl_4 + 2CO$	TiO_2 is an oxidising agent
B	$HNO_3 + H_2SO_4 \rightarrow H_2NO_3^+ + HSO_4^-$	HNO_3 is a Brønsted-Lowry acid
C	$CH_3COCl + AlCl_3 \rightarrow CH_3CO^+ + AlCl_4^-$	$AlCl_3$ is a Lewis base
D	$2CO + 2NO \rightarrow 2CO_2 + N_2$	CO is a reducing agent

(Total 1 mark)

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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.

Hydrochloric acid is a strong acid and ethanoic acid is a weak acid.

(a) State the meaning of the term strong acid.

_____

_____

(1)

(b) In an experiment, 10.35 cm^3 of 0.100 mol dm^{-3} hydrochloric acid are added to 25.0 cm^3 of 0.150 mol dm^{-3} barium hydroxide solution.

Calculate the pH of the solution that forms at 30 °C

$K_w = 1.47 \times 10^{-14}$ mol^2 dm^{-6} at 30 °C

Give your answer to 2 decimal places.

pH _____

(6)

(c) The pH of water at 30 °C is 6.92

Give the reason why water is neutral at this temperature.

_____

_____

(1)

(d) Identify the oxide that could react with water to form a solution with pH = 2

Tick (✔) **one** box.

Al_2O_3 ☐

Na_2O ☐

SiO_2 ☐

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SO_2 ☐

(1)

(e) Give the expression for the acid dissociation constant (K_a) for ethanoic acid (CH_3COOH).

K_a

(1)

(f) A buffer solution contains 0.025 mol of sodium ethanoate dissolved in 500 cm^3 of 0.0700 mol dm^{-3} ethanoic acid at 25 °C

A sample of 5.00 cm^3 of 2.00 mol dm^{-3} hydrochloric acid is added to this buffer solution.

Calculate the pH of the solution formed.

For ethanoic acid, $K_a = 1.76 \times 10^{-5}$ mol dm^{-3} at 25 °C

pH _____

(5)

(Total 15 marks)

Q2.

This question is about acidic solutions.

(a) The acid dissociation constant, K_a, for ethanoic acid is given by the expression

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

The value of K_a for ethanoic acid is 1.74×10^{-5} mol dm^{-3} at 25 °C

A buffer solution with a pH of 3.87 was prepared using ethanoic acid and sodium ethanoate. In the buffer solution, the concentration of ethanoate ions was 0.136 mol dm^{-3}

Calculate the concentration of the ethanoic acid in the buffer solution.

Give your answer to three significant figures.

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Concentration of acid = _____ mol dm^{-3}

(3)

(b) In a different buffer solution, the concentration of ethanoic acid was 0.260 mol dm^{-3} and the concentration of ethanoate ions was 0.121 mol dm^{-3}

A 7.00 × 10^{-3} mol sample of sodium hydroxide was added to 500 cm^3 of this buffer solution.

Calculate the pH of the buffer solution after the sodium hydroxide was added.

Give your answer to two decimal places.

pH of buffer solution _____

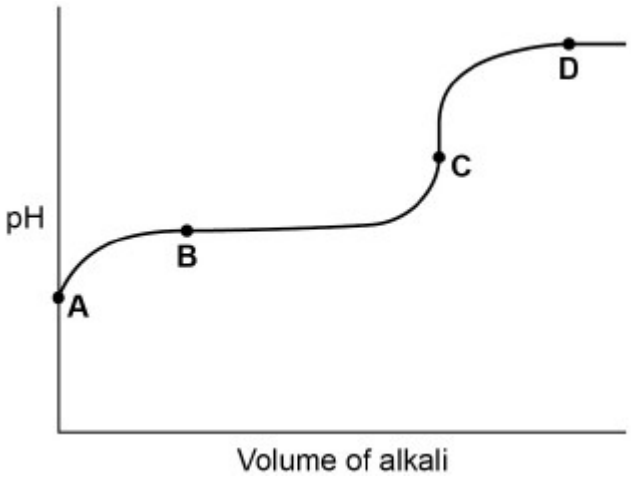
(6)

(Total 9 marks)

Q3.

The diagram shows a pH curve produced by adding a strong alkali to a weak acid.

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Which point on the curve represents a solution that can act as a buffer?

A ⬭

B ⬭

C ⬭

D ⬭

(Total 1 mark)

Q4.

This question is about Brønsted–Lowry acids.

(a) Give the meaning of the term Brønsted–Lowry acid.

_____

_____

(1)

(b) What is meant by the term strong when describing an acid?

_____

_____

(1)

(c) At 298 K, 25.0 cm^3 of a solution of a strong monoprotic acid contained 1.45×10^{-3} mol of hydrogen ions.

Calculate a value for the pH of this solution.
Give your answer to 2 decimal places.

pH _____

(2)

(d) Calculate the pH of the solution formed after the addition of 35.0 cm^3 of 0.150 mol dm^{-3} NaOH to the original 25.0 cm^3 of monoprotic acid.

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The ionic product of water K_w = 1.00 × 10^{-14} mol^2 dm^{-6} at 298 K.
Give your answer to two decimal places.

pH _____

(5)

(e) A buffer solution is made when 1.50 g of sodium hydroxide are added to 1.00 dm^3 of a 0.150 mol dm^{-3} solution of a weak acid HA.

For HA, the acid dissociation constant, K_a = 1.79 × 10^{-5} mol dm^{-3}.

Calculate the pH of this buffer solution.

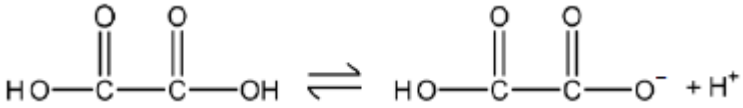
pH _____

(6)

(Total 15 marks)

Q5.

Ethanedioic acid is a weak acid.
Ethanedioic acid acts, initially, as a monoprotic acid.



(a) Use the concept of electronegativity to justify why the acid strengths of ethanedioic acid and ethanoic acid are different.

_____

_____

_____

_____

_____

_____

_____

_____

(6)

(b) A buffer solution is made by adding 6.00 × 10^{-2} mol of sodium hydroxide to a solution containing 1.00 × 10^{-1} mol of ethanedioic acid ($H_2C_2O_4$).
Assume that the sodium hydroxide reacts as shown in the following equation and that in this buffer solution, the ethanedioic acid behaves as a monoprotic acid.

$$H_2C_2O_4(aq) + OH^-(aq) \longrightarrow HC_2O_4^-(aq) + H_2O(l)$$

The dissociation constant K_a for ethanedioic acid is 5.89 × 10^{-2} mol dm^{-3}.

Calculate a value for the pH of the buffer solution.
Give your answer to the appropriate number of significant figures.

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pH = _____

(5)

(c) In a titration, the end point was reached when 25.0 cm^3 of an acidified solution containing ethanedioic acid reacted with 20.20 cm^3 of 2.00 $\times 10^{-2}$ mol dm^{-3} potassium manganate(VII) solution.

Deduce an equation for the reaction that occurs and use it to calculate the original concentration of the ethanedioic acid solution.

Equation _____

Calculation

Original concentration = _____ mol dm^{-3}

(4)

(Total 15 marks)

Q6.

Nitric acid (HNO_{-3}) is a strong acid. Ethanoic acid (CH_3COOH) is a weak acid.

(a) Write an equation to show how ethanoic acid behaves as a weak acid in its reaction with water.

_____

(1)

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(b) When pure ethanoic acid reacts with pure nitric acid, ethanoic acid acts as a base.

Write an equation for this reaction.

_____

(1)

(c) Two beakers, **A** and **B**, each contain 100.0 cm^{-3} of 0.0125 mol dm^{-3} nitric acid.

(i) Calculate the pH of the solution formed after 50.0 cm^{-3} of distilled water are added to beaker **A**.
Give your answer to 2 decimal places.

_____

_____

_____

(2)

(ii) Calculate the pH of the solution formed after 50.0 cm^3 of 0.0108 mol dm^{-3} aqueous sodium hydroxide are added to beaker **B**.
Give your answer to 2 decimal places.

_____

_____

_____

_____

_____

_____

_____

(4)

(d) A third beaker, **C**, contains 100.0 cm^3 of 0.0125 mol dm^{-3} ethanoic acid.
The acid dissociation constant K_a for ethanoic acid has the value 1.74×10^{-5} mol dm^{-3} at 25 °C.

(i) Write an expression for K_a for ethanoic acid and use it to calculate the pH of the ethanoic acid solution in beaker **C**.
Show your working. Give your answer to 2 decimal places.

K_a _____

_____

Calculation _____

_____

_____

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_____

(4)

(ii) Aqueous sodium hydroxide is added to beaker **C** until the pH of the solution becomes 4.84.

Name the salt formed in the reaction of ethanoic acid with sodium hydroxide.

_____

(1)

(iii) Calculate the value of $\frac{[\text{salt}]}{[\text{ethanoic acid}]}$ in the solution with the pH of 4.84.

_____

_____

_____

_____

_____

_____

(3)

(e) Explain why chloroethanoic acid is a stronger acid than ethanoic acid.

_____

_____

_____

_____

(2)

(f) Explain why data books do not usually contain values of K_a for strong acids.

_____

_____

_____

_____

(2)

(Total 20 marks)

Q7.

The acid dissociation constant, K_a, for ethanoic acid is given by the expression

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

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The value of K_a for ethanoic acid is 1.74×10^{-5} mol dm^{-3} at 25 °C.

(a) A buffer solution is prepared using ethanoic acid and sodium ethanoate. In the buffer solution, the concentration of ethanoic acid is 0.186 mol dm^{-3} and the concentration of sodium ethanoate is 0.105 mol dm^{-3}.

Calculate the pH of this buffer solution.
Give your answer to 2 decimal places.

(3)

(b) In a different buffer solution, the concentration of ethanoic acid is 0.251 mol dm^{-3} and the concentration of sodium ethanoate is 0.140 mol dm^{-3}.

A sample of hydrochloric acid containing 0.015 mol of HCl is added to 1000 cm^3 of this buffer solution.

Calculate the pH of the buffer solution after the hydrochloric acid has been added.
You should ignore any change in total volume.
Give your answer to 2 decimal places.

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_____

(5)

(Total 8 marks)

Q8.

A solution of chlorine in water is acidic. Swimming pool managers maintain pool water at a constant pH by using a buffer. They do so by adding sodium hydrogencarbonate and sodium carbonate.

(a) Hydrogen carbonate ions (HCO_3^-) act as a weak acid in aqueous solution. Write an equation for this equilibrium.

_____

_____

_____

(1)

(b) Use the equation in part (a) to explain how a solution containing sodium hydrogencarbonate and sodium carbonate can act as a buffer when small amounts of acid or small amounts of alkali are added.

_____

_____

_____

_____

_____

_____

_____

_____

(3)

(Total 4 marks)

Q9.

This question is about alkalis and carboxylic acids.

In this question, all data are quoted at 25 °C.

(a) Carboxylic acids are weak acids.

State the meaning of the term **weak** as applied to carboxylic acids.

_____

_____

(1)

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(b) Write an equation for the reaction of propanoic acid with sodium carbonate.

_____

(1)

(c) Calculate the pH of a 0.0120 mol dm^{-3} solution of calcium hydroxide.
The ionic product of water $K_w = 1.00 \times 10^{-14}$ mol^2 dm^{-6}.
Give your answer to 2 decimal places.

_____

_____

_____

_____

_____

_____

(3)

(d) The value of the acid dissociation constant K_a for benzenecarboxylic acid (C_6H_5COOH) is 6.31×10^{-5} mol dm^{-3}.

(i) Write an expression for the acid dissociation constant K_a for benzenecarboxylic acid.

_____

_____

(1)

(ii) Calculate the pH of a 0.0120 mol dm^{-3} solution of benzenecarboxylic acid.
Give your answer to 2 decimal places.

_____

_____

_____

_____

_____

_____

_____

_____

(3)

(iii) A buffer solution with a pH of 4.00 is made using benzenecarboxylic acid and sodium benzenecarboxylate.

Calculate the mass of sodium benzenecarboxylate (M_r = 144.0) that should be dissolved in 1.00 dm^3 of a 0.0120 mol dm^{-3} solution of benzenecarboxylic acid

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to produce a buffer solution with a pH of 4.00

The value of the acid dissociation constant K_a for benzenecarboxylic acid (C_6H_5COOH) is 6.31×10^{-5} mol dm^{-3}.

(5)

(e) Two solutions, one with a pH of 4.00 and the other with a pH of 9.00, were left open to the air.

The pH of the pH 9.00 solution changed more than that of the other solution.

Suggest what substance might be present in the air to cause the pH to change. Explain how and why the pH of the pH 9.00 solution changes.

Substance present in air _____

Explanation _____

(3)

(Total 17 marks)

Q10.

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

(a) The ionic product of water has the symbol K_w

(i) Write an expression for the ionic product of water.

(1)

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(ii) At 42°C, the value of K_w is 3.46×10^{-14} mol^2 dm^{-6}.

Calculate the pH of pure water at this temperature.

(2)

(iii) At 75 °C, a 0.0470 mol dm^{-3} solution of sodium hydroxide has a pH of 11.36.
Calculate a value for K_w at this temperature.

(2)

(b) Methanoic acid (HCOOH) dissociates slightly in aqueous solution.

(i) Write an equation for this dissociation.

(1)

(ii) Write an expression for the acid dissociation constant K_a for methanoic acid.

(1)

(iii) The value of K_a for methanoic acid is 1.78×10^{-4} mol dm^{-3} at 25 °C.
Calculate the pH of a 0.0560 mol dm^{-3} solution of methanoic acid.

(3)

(iv) The dissociation of methanoic acid in aqueous solution is endothermic.

Deduce whether the pH of a solution of methanoic acid will increase, decrease or stay the same if the solution is heated. Explain your answer.

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Effect on pH _____

Explanation _____

_____

_____

_____

(3)

(c) The value of K_a for methanoic acid is 1.78×10^{-4} mol dm^{-3} at 25°C.
A buffer solution is prepared containing 2.35×10^{-2} mol of methanoic acid and 1.84×10^{-2} mol of sodium methanoate in 1.00 dm^3 of solution.

(i) Calculate the pH of this buffer solution at 25°C.

_____

_____

_____

_____

_____

(3)

(ii) A 5.00 cm^3 sample of 0.100 mol dm^{-3} hydrochloric acid is added to the buffer solution in part (c)(i).

Calculate the pH of the buffer solution after this addition.

_____

_____

_____

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_____

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_____

(4)

(Total 20 marks)

Q11.

This question is about several Brønsted–Lowry acids and bases.

(a) Define the term *Brønsted–Lowry* acid.

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_____

_____

(1)

(b) Three equilibria are shown below. For each reaction, indicate whether the substance immediately **above** the box is acting as a Brønsted–Lowry acid (**A**) or a Brønsted–Lowry base (**B**) by writing **A** or **B** in each of the six boxes.

(i) CH_3COOH + H_2O ⇌ CH_3COO^- + H_3O^+

(1)

(ii) CH_3NH_2 + H_2O ⇌ $CH_3NH_3^+$ + OH^-

(1)

(iii) HNO_3 + H_2SO_4 ⇌ $H_2NO_3^+$ + HSO_4^-

(1)

(c) A 25.0 cm^3 sample of 0.0850 mol dm^{-3} hydrochloric acid was placed in a beaker. Distilled water was added until the pH of the solution was 1.25.

Calculate the total volume of the solution formed. State the units.

_____

_____

_____

_____

_____

(3)

(d) At 298 K, the value of the acid dissociation constant (K_a) for the weak acid HX in aqueous solution is 3.01×10^{-5} mol dm^{-3}.

(i) Calculate the value of pK_a for HX at this temperature.
Give your answer to 2 decimal places.

_____

_____

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(1)

(ii) Write an expression for the acid dissociation constant (K_a) for the weak acid HX.

_____

_____

_____

(1)

(iii) Calculate the pH of a 0.174 mol dm^{-3} solution of HX at this temperature.
Give your answer to 2 decimal places.

_____

_____

_____

_____

_____

(3)

(e) An acidic buffer solution is formed when 10.0 cm^3 of 0.125 mol dm^{-3} aqueous sodium hydroxide are added to 15.0 cm^3 of 0.174 mol dm^{-3} aqueous HX.
The value of K_a for the weak acid HX is 3.01×10^{-5} mol dm^{-3}.

Calculate the pH of this buffer solution at 298 K.
Give your answer to 2 decimal places.

_____

_____

_____

_____

_____

_____

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_____

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_____

(6)

(Total 18 marks)

Q12.

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)

Q13.

Ammonia and ethylamine are examples of weak Brønsted–Lowry bases.

(a) State the meaning of the term *Brønsted–Lowry base*.

_____

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_____

(1)

(b) (i) Write an equation for the reaction of ethylamine ($CH_3CH_2NH_2$) with water to form a weakly alkaline solution.

_____

_____

(1)

(ii) In terms of this reaction, state why the solution formed is **weakly** alkaline.

_____

_____

(1)

(c) State which is the stronger base, ammonia or ethylamine. Explain your answer.

Stronger base _____

Explanation _____

_____

_____

_____

(3)

(d) Give the formula of an organic compound that forms an alkaline buffer solution when added to a solution of ethylamine.

_____

(1)

(e) Explain qualitatively how the buffer solution in part (d) maintains an almost constant pH when a small amount of hydrochloric acid is added to it.

_____

_____

_____

_____

(2)

(Total 9 marks)

Q14.

This question is about the pH of several solutions.

Give all values of pH to 2 decimal places.

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

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_____

(1)

(ii) Calculate the pH of 0.154 mol dm^{-3} hydrochloric acid.

_____

_____

(1)

(iii) Calculate the pH of the solution formed when 10.0 cm^3 of 0.154 mol dm^{-3} hydrochloric acid are added to 990 cm^3 of water.

_____

_____

_____

_____

(2)

(b) The acid dissociation constant, K_a, for the weak acid HX has the value 4.83×10^{-5} mol dm^{-3} at 25 °C.
A solution of HX has a pH of 2.48

Calculate the concentration of HX in the solution.

_____

_____

_____

_____

_____

_____

(4)

(c) Explain why the pH of an acidic buffer solution remains almost constant despite the addition of a small amount of sodium hydroxide.

_____

_____

_____

_____

_____

_____

(2)

(d) The acid dissociation constant, K_a, for the weak acid HY has the value

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1.35×10^{-5} mol dm^{-3} at 25 °C.

A buffer solution was prepared by dissolving 0.0236 mol of the salt NaY in 50.0 cm^3 of a 0.428 mol dm^{-3} solution of the weak acid HY

(i) Calculate the pH of this buffer solution.

(4)

(ii) A 5.00×10^{-4} mol sample of sodium hydroxide was added to this buffer solution.

Calculate the pH of the buffer solution after the sodium hydroxide was added.

(4)

(Total 18 marks)

Q15.

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

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(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)

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(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 1.74×10^{-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)

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Q16.

Buffer solutions are important in biological systems and in industry to maintain almost constant pH values.

(a) In the human body, one important buffer system in blood involves the hydrogencarbonate ion, HCO_3^-, and carbonic acid, H_2CO_3, which is formed when carbon dioxide dissolves in water.

(i) Use the following equation to explain how this buffer maintains a constant pH of 7.41 even if a small amount of acid enters the bloodstream.

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

_____

_____

_____

(ii) In a sample of blood with a pH of 7.41, the concentration of $HCO_3^-(aq)$ ions is 2.50×10^{-2} mol dm^{-3} and the concentration of $H_2CO_3(aq)$ is 1.25×10^{-3} mol dm^{-3}.

Calculate a value for the acid dissociation constant, K_a, for carbonic acid at this temperature.

_____

_____

_____

_____

(5)

(b) In industry, the pH of a solution used to dye cloth must be controlled or else the colour varies.

A solution of dye in a beaker is buffered by the presence of ethanoic acid and sodium ethanoate. In the solution, the concentration of ethanoic acid is 0.15 mol dm^{-3} and the concentration of sodium ethanoate is 0.10 mol dm^{-3}. The value of K_a for ethanoic acid is 1.74×10^{-5} mol dm^{-3} at 298 K.

(i) A 10.0 cm^3 portion of 1.00 mol dm^{-3} hydrochloric acid is added to 1000 cm^3 of this buffered solution.

Calculate the number of moles of hydrochloric acid added.

_____

(ii) Calculate the number of moles of ethanoic acid and the number of moles of sodium ethanoate in the solution after addition of the hydrochloric acid.

Mol of ethanoic acid after addition _____

_____

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Mol of sodium ethanoate after addition _____

_____

(iii) Hence calculate the pH of this new solution. Give your answer to 2 decimal places.

_____

_____

_____

(6)

(Total 11 marks)

Q17.

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

(a) (i) Write expressions for the ionic product of water, K_w, and for pH.

K_W = _____

pH = _____

(ii) At 318 K, the value of K_w is 4.02×10^{-14} mol^2 dm^{-6} and hence the pH of pure water is 6.70
State why pure water is not acidic at 318 K.

_____

_____

(iii) Calculate the number of moles of sodium hydroxide in 2.00 cm^3 of 0.500 mol dm^{-3} aqueous sodium hydroxide.

_____

_____

(iv) Use the value of K_w given above and your answer to part (a)(iii) to calculate the pH of the solution formed when 2.00 cm^3 of 0.500 mol dm^{-3} aqueous sodium hydroxide are added to 998 cm^3 of pure water at 318 K.

_____

_____

_____

_____

_____

(6)

(b) At 298 K, the acid dissociation constant, K_a, for propanoic acid, CH_3CH_2COOH, has the value 1.35×10^{-5}mol dm^{-3}.

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(i) Write an expression for K_a for propanoic acid.

(ii) Calculate the pH of 0.125 mol dm^{-3} aqueous propanoic acid at 298 K.

(4)

(c) Sodium hydroxide reacts with propanoic acid as shown in the following equation.

$$NaOH + CH_3CH_2COOH \rightarrow CH_3CH_2COONa + H_2O$$

A buffer solution is formed when sodium hydroxide is added to an excess of aqueous propanoic acid.

(i) Calculate the number of moles of propanoic acid in 50.0 cm^3 of 0.125 mol dm^{-3} aqueous propanoic acid.

(ii) Use your answers to part (a)(iii) and part (c)(i) to calculate the number of moles of propanoic acid in the buffer solution formed when 2.00 cm^3 of 0.500 mol dm^{-3} aqueous sodium hydroxide are added to 50.0 cm^3 of 0.125 mol dm^{-3} aqueous propanoic acid.

(iii) Hence calculate the pH of this buffer solution at 298 K.

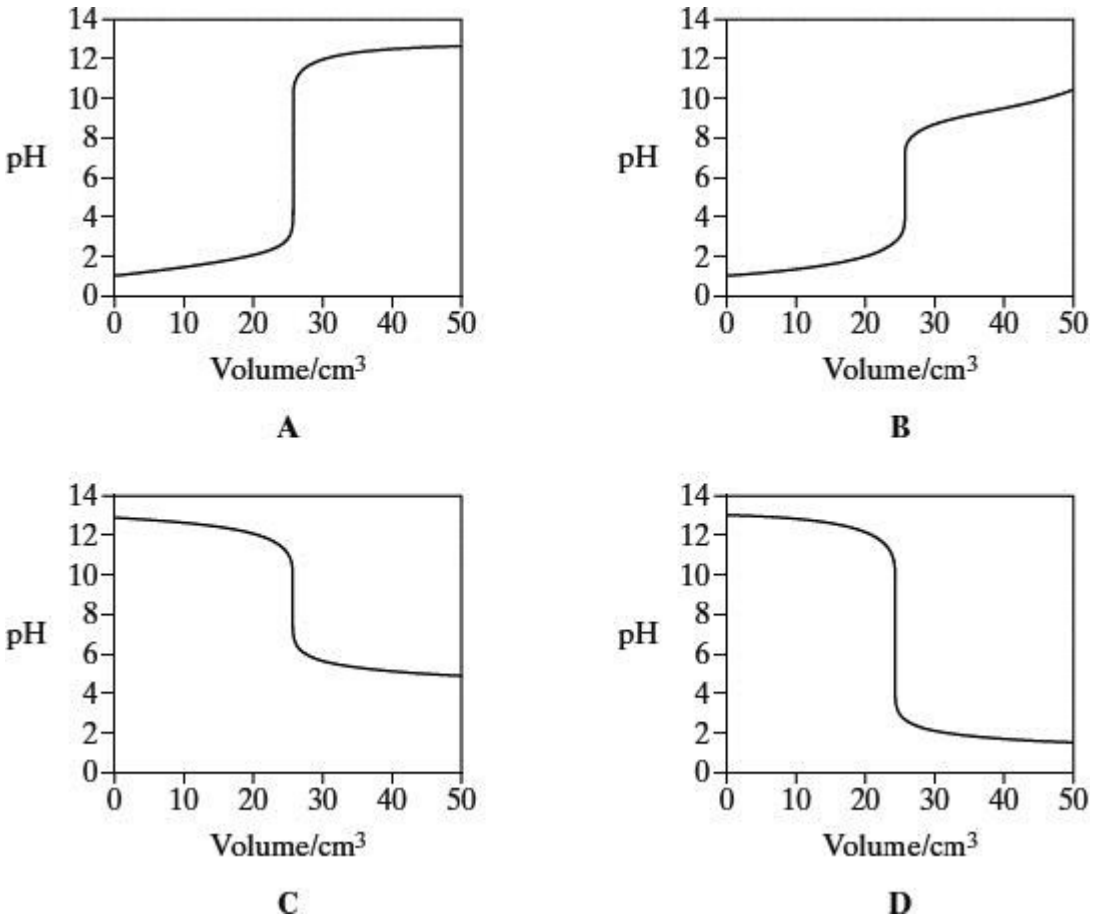
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(6)

(Total 16 marks)

Q18.

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



(i) Select from **A**, **B**, **C** and **D** the curve produced by the addition of

ammonia to 25 cm^3 of hydrochloric acid _____

ethanoic acid to 25 cm^3 of sodium hydroxide _____

sodium hydroxide to 25 cm^3 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

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Cresolphthalein	8.2 – 9.8
Thymolphthalein	9.3 – 10.5

Select from the table an indicator which could be used in the titration which produces curve **A** but not in the titration which produces curve **B**.

_____

(4)

(b) (i) Write an expression for the term *pH*.

_____

(ii) A solution of potassium hydroxide has a pH of 11.90 at 25°C. Calculate the concentration of potassium hydroxide in the solution.

_____

_____

_____

_____

(4)

(c) The acid dissociation constant, K_a, for propanoic acid has the value of 1.35×10^{-5} mol dm^{-3} at 25 °C.

$$K_a = \frac{[H^+][CH_3CH_2COO^-]}{[CH_3CH_2COOH]}$$

In each of the calculations below, give your answer to 2 decimal places.

(i) Calculate the pH of a 0.117 mol dm^{-3} aqueous solution of propanoic acid.

_____

_____

_____

_____

(ii) Calculate the pH of a mixture formed by adding 25 cm^3 of a 0.117 mol dm^{-3} aqueous solution of sodium propanoate to 25 cm^3 of a 0.117 mol dm^{-3} aqueous solution of propanoic acid.

_____

_____

_____

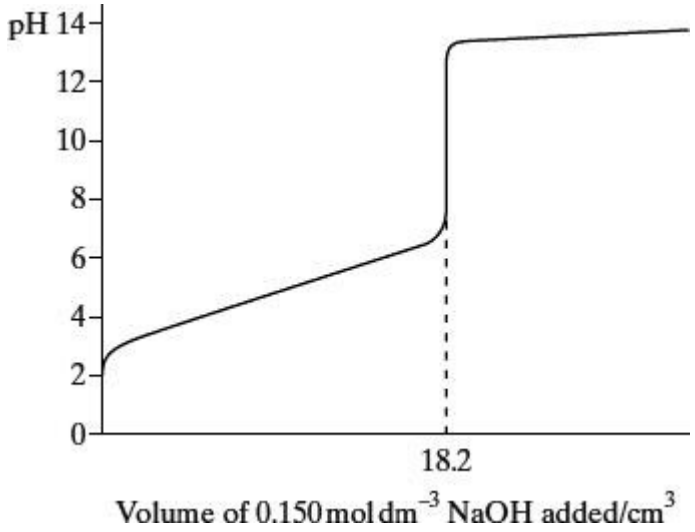
(5)

(Total 13 marks)

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Q19.

The pH curve shown below was obtained when a 0.150 mol dm^{-3} solution of sodium hydroxide was added to 25.0 cm^3 of an aqueous solution of a weak monoprotic acid, HA.



(a) Use the information given to calculate the concentration of the acid.

_____

_____

_____

(2)

(b) (i) Write an expression for the acid dissociation constant, K_a, for HA.

_____

(ii) Write an expression for pK_a

_____

(iii) Using your answers to parts (b)(i) and (b)(ii), show that when sufficient sodium hydroxide has been added to neutralise half of the acid,

pH of the solution = pK_a for the acid HA

_____

_____

_____

(4)

(c) Explain why dilution with a small volume of water does not affect the pH of a buffer solution.

_____

_____

(2)

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(d) (i) Calculate the change in pH when 0.250 mol dm^{-3} hydrochloric acid is diluted with water to produce 0.150 mol dm^{-3} hydrochloric acid.

_____

_____

_____

(ii) Calculate the volume of water which must be added to 30.0 cm^3 of 0.250 mol dm^{-3} hydrochloric acid in order to reduce its concentration to 0.150 mol dm^{-3}.

_____

_____

_____

(4)

(Total 12 marks)

Q20.

This question concerns the weak acid, ethanoic acid, for which the acid dissociation constant, K_a, has a value of 1.74×10^{-5} mol dm^{-3} at 25 °C.

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

In each of the calculations below, give your answer to 2 decimal places.

(a) Write an expression for the term *pH*. Calculate the pH of a 0.150 mol dm^{-3} solution of ethanoic acid.

_____

_____

_____

_____

_____

_____

_____

_____

(4)

(b) A buffer solution is prepared by mixing a solution of ethanoic acid with a solution of sodium ethanoate.

(i) Explain what is meant by the term *buffer solution*.

_____

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(2)

(ii) Write an equation for the reaction which occurs when a small amount of hydrochloric acid is added to this buffer solution.

(1)

(c) In a buffer solution, the concentration of ethanoic acid is 0.150 mol dm^{-3} and the concentration of sodium ethanoate is 0.100 mol dm^{-3}.

(i) Calculate the pH of this buffer solution.

(3)

(ii) A 10.0 cm^3 portion of 1.00 mol dm^{-3} hydrochloric acid is added to 1000 cm^3 of this buffer solution.
Calculate the number of moles of ethanoic acid and the number of moles of sodium ethanoate in the solution after addition of the hydrochloric acid. Hence, find the pH of this new solution.

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(5)
(Total 15 marks)

Q21.

The value of the acid dissociation constant, K_a, for the weak acid HA, at 298 K, is 1.45×10^{-4} mol dm^{-3}.

(a) Write an expression for the term K_a for the weak acid HA.

_____

_____

(1)

(b) Calculate the pH of a 0.250 mol dm^{-3} solution of HA at 298 K.

_____

_____

_____

_____

_____

(4)

(c) A mixture of the acid HA and the sodium salt of this acid, NaA, can be used to prepare a buffer solution.

(i) State and explain the effect on the pH of this buffer solution when a small amount of hydrochloric acid is added.

_____

_____

_____

(ii) The concentration of HA in a buffer solution is 0.250 mol dm^{-3}. Calculate the concentration of A^- in this buffer solution when the pH is 3.59

_____

_____

_____

_____

_____

_____

(6)
(Total 11 marks)

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Q22.

(a) By reference to the forces between molecules, explain why ammonia is very soluble in water.

_____

_____

(2)

(b) Aqueous solutions of ammonia have a pH greater than 7.

(i) Write an equation for the reaction of ammonia with water.

_____

(ii) Explain why the pH of a solution containing 1.0 mol dm^{-3} of ammonia is less than
14 at 298 K.

_____

_____

(3)

(c) An ammonium ion in aqueous solution can behave as a Brønsted–Lowry acid. State what is meant by the term *Brønsted–Lowry acid*.

_____

(1)

(d) State what is meant by the term *buffer solution*. Identify a reagent which could be added to a solution of ammonia in order to form a buffer solution.

Buffer solution _____

_____

Reagent _____

(3)

(e) An acidic buffer solution is obtained when sodium ethanoate is dissolved in aqueous ethanoic acid.

(i) Calculate the pH of the buffer solution formed at 298 K when 0.125 mol of sodium ethanoate is dissolved in 250 cm^3 of a 1.00 mol dm^{-3} solution of ethanoic acid.
The acid dissociation constant, K_a, for ethanoic acid is 1.70×10^{-5} mol dm^{-3} at 298 K.

_____

_____

_____

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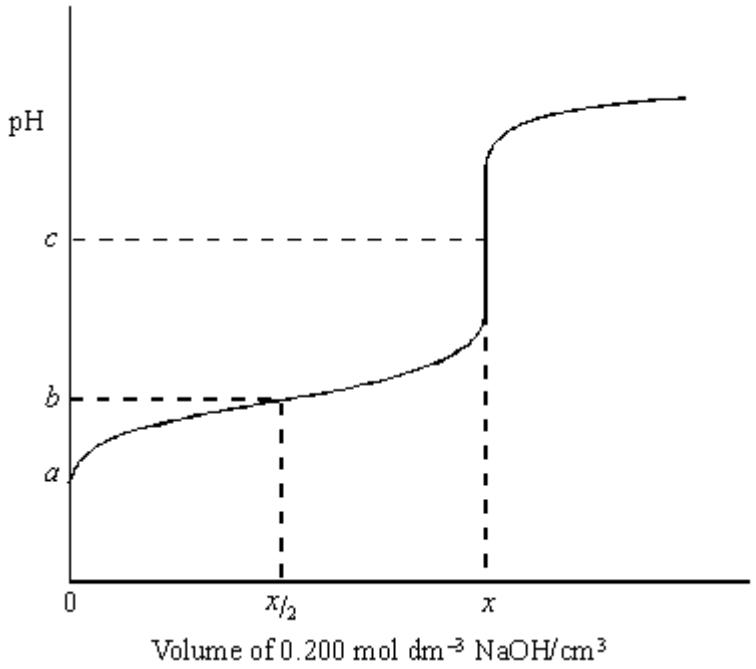
(ii) Write an ionic equation for the reaction which occurs when a small volume of dilute hydrochloric acid is added to this buffer solution.

(5)

(Total 14 marks)

Q23.

The sketch below shows the change in pH when a 0.200 mol dm^{-3} solution of sodium hydroxide is added from a burette to 25.0 cm^3 of a 0.150 mol dm^{-3} solution of the weak acid HA at 25 °C.



(a) The volume of sodium hydroxide solution added at the equivalence point is x cm^3. Calculate the value of x.

(2)

(b) (i) Define the term pH.

(ii) The pH at the equivalence point is *c*. Suggest a value for *c*.

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(iii) Identify a suitable indicator for detecting the equivalence point of the titration.

_____

(3)

(c) The value of K_c for the weak acid HA at 25 °C is 2.75×10^{-5} mol dm^{-3}.

(i) Explain the term *weak* as applied to the acid HA.

_____

(ii) Write an expression for K_a for the acid HA.

_____

(iii) Calculate the pH of the 0.150 mol dm^{-3} solution of acid HA before any sodium hydroxide is added, i.e. the pH at point *a*.

_____

_____

_____

_____

_____

(5)

(d) Calculate the pH of the solution formed when $^{x}/_{2}$ cm^3 of the 0.200 mol dm^{-3} solution of sodium hydroxide are added to 25.0 cm^3 of the 0.150 mol dm^{-3} solution of HA, i.e. the pH at point *b*.

_____

_____

_____

(3)

(Total 13 marks)

Q24.

A 0.210 mol dm^{-3} solution of potassium hydroxide was added from a burette to 25.0 cm^3 of a 0.160 mol dm^{-3} solution of ethanoic acid in a conical flask.
Given that the value of the acid dissociation constant, K_a, for ethanoic acid is 1.74×10^{-5} mol dm^{-3}, calculate the pH at 25 °C of the solution in the conical flask at the following three points:

before any potassium hydroxide had been added;

after 8.0 cm^3 of potassium hydroxide solution had been added;

after 40.0 cm^3 of potassium hydroxide solution had been added.

_____

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_____

_____

_____

_____

_____

_____

_____

_____

_____

_____

_____

(Total 16 marks)

Q25.

The value of the acid dissociation constant, K_a, for ethanoic acid is 1.74×10^{-5} mol dm^{-3} at 298 K.

(a) (i) Write an expression for K_a for ethanoic acid.

_____

(ii) Calculate the pH at 298 K of a 0.220 mol dm^{-3} solution of ethanoic acid.

_____

_____

_____

_____

_____

_____

(5)

(b) A sample of the 0.220 mol dm^{-3} solution of ethanoic acid was titrated against sodium hydroxide solution.

(i) Calculate the volume of a 0.150 mol dm^{-3} solution of sodium hydroxide required to neutralise 25.0 cm^3 of the ethanoic acid solution.

_____

_____

_____

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_____

(ii) From the list below, select the best indicator for this titration and explain your choice.

Name of indicator	**pH range**
bromophenol blue	3.0 – 4.6
methyl red	4.2 – 6.3
bromothymol blue	6.0 – 7.6
thymol blue	8.0 – 9.6

Indicator _____

Explanation _____

_____

_____

(5)

(c) A buffer solution is formed when 2.00 g of sodium hydroxide are added to 1.00 dm^3 of a 0.220 mol dm^{-3} solution of ethanoic acid.

Calculate the pH at 298 K of this buffer solution.

_____

_____

_____

_____

_____

_____

_____

(6)

(Total 16 marks)

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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.

The ionic product of water, $K_w = 2.93 \times 10^{-15}\ mol^2\ dm^{-6}$ at 10 °C

(a) Which is the correct expression for K_w?

Tick (✔) **one** box.

A $K_w = \frac{[H_2O]}{[H^+][OH^-]}$ ☐

B $K_w = [H^+][H_2O]$ ☐

C $K_w = [H^+][OH^-]$ ☐

D $K_w = \frac{[H^+][OH^-]}{[H_2O]}$ ☐

(1)

(b) Calculate the pH of pure water at 10 °C

Give your answer to two decimal places.

pH of water _____

(2)

(c) Suggest why this pure water at 10 °C is **not** alkaline.

_____

_____

_____

(1)

(d) Calculate the pH of a 0.0131 mol dm^{-3} solution of calcium hydroxide at 10 °C

Give your answer to two decimal places.

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pH of solution _____

(3)

(e) The 0.0131 mol dm^{-3} calcium hydroxide solution at 10 °C was a saturated solution.

A student added 0.0131 mol of magnesium hydroxide to 1.00 dm^3 of water at 10 °C and stirred the mixture until no more solid dissolved.

Predict whether the pH of the magnesium hydroxide solution formed at 10 °C is larger than, smaller than or the same as the pH of the calcium hydroxide solution at 10 °C

Explain your answer.

pH of magnesium hydroxide compared to calcium hydroxide

_____

Explanation _____

_____

_____

(2)

(Total 9 marks)

Q2.

The rate equation for the acid-catalysed reaction between iodine and propanone is:

$$\text{rate} = k\,[H^+]\,[C_3H_6O]$$

The rate of reaction was measured for a mixture of iodine, propanone and sulfuric acid at pH = 0.70

In a second mixture the concentration of the sulfuric acid was different but the concentrations of iodine and propanone were unchanged. The new rate of reaction was a quarter of the original rate.

What was the pH of the second mixture?

A 1.00 ⬭

B 1.30 ⬭

C 1.40 ⬭

D 2.80 ⬭

(Total 1 mark)

Q3.

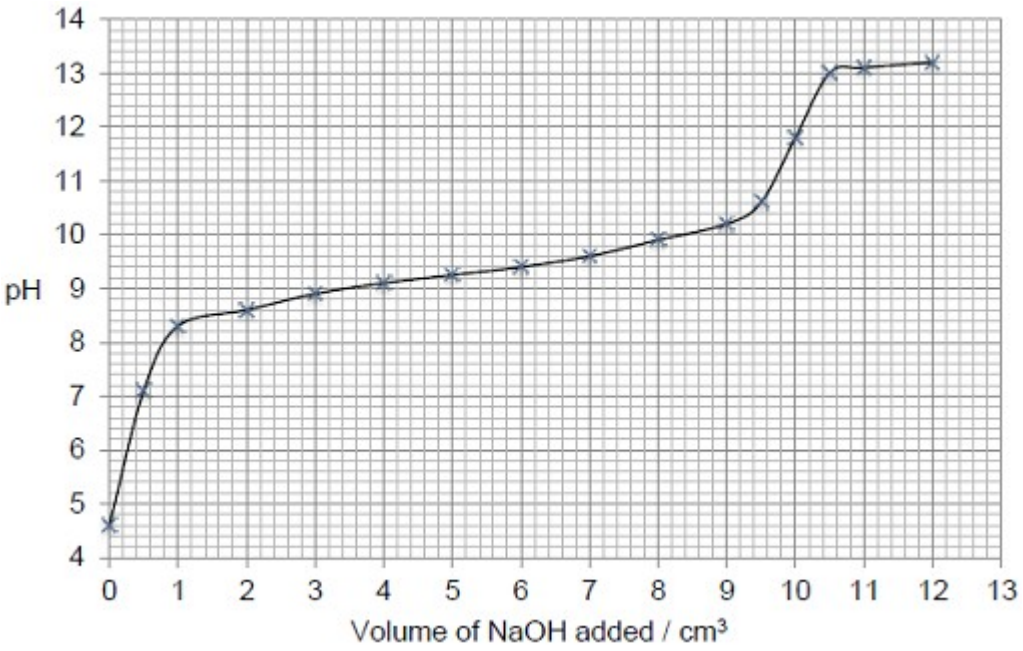
Ammonium chloride, when dissolved in water, can act as a weak acid as shown by the

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following equation.

$$NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq)$$

The following figure shows a graph of data obtained by a student when a solution of sodium hydroxide was added to a solution of ammonium chloride. The pH of the reaction mixture was measured initially and after each addition of the sodium hydroxide solution.



(a) Suggest a suitable piece of apparatus that could be used to measure out the sodium hydroxide solution.
Explain why this apparatus is more suitable than a pipette for this purpose.

Apparatus_____

Explanation _____

_____

_____

(2)

(b) Use information from the curve in the figure above to explain why the end point of this reaction would be difficult to judge accurately using an indicator.

_____

_____

_____

_____

_____

(2)

(c) The pH at the end point of this reaction is 11.8.

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Use this pH value and the ionic product of water, $K_w = 1.0 \times 10^{-14}$ mol^2 dm^{-6}, to calculate the concentration of hydroxide ions at the end point of the reaction.

Concentration = _____ mol dm^{-3}

(3)

(d) The expression for the acid dissociation constant for aqueous ammonium ions is

$$k_a = \frac{[NH_3][H^+]}{[NH_4^+]}$$

The initial concentration of the ammonium chloride solution was 2.00 mol dm^{-3}.

Use the pH of this solution, before any sodium hydroxide had been added, to calculate a value for K_a

K_a = _____ mol dm^{-3}

(3)

(e) A solution contains equal concentrations of ammonia and ammonium ions.

Use your value of K_a from part **(d)** to calculate the pH of this solution. Explain your working.

(If you were unable to calculate a value for K_a you may assume that it has the value 4.75×10^{-9} mol dm^{-3}. This is **not** the correct value.)

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pH = _____

(2)

(Total 12 marks)

Q4.

This question is about Brønsted–Lowry acids.

(a) Give the meaning of the term Brønsted–Lowry acid.

_____

_____

(1)

(b) What is meant by the term strong when describing an acid?

_____

_____

(1)

(c) At 298 K, 25.0 cm^3 of a solution of a strong monoprotic acid contained 1.45×10^{-3} mol of hydrogen ions.

Calculate a value for the pH of this solution.
Give your answer to 2 decimal places.

pH _____

(2)

(d) Calculate the pH of the solution formed after the addition of 35.0 cm^3 of 0.150 mol dm^{-3} NaOH to the original 25.0 cm^3 of monoprotic acid.

The ionic product of water $K_w = 1.00 \times 10^{-14}$ mol^2 dm^{-6} at 298 K.
Give your answer to two decimal places.

pH _____

(5)

(e) A buffer solution is made when 1.50 g of sodium hydroxide are added to 1.00 dm^3 of a 0.150 mol dm^{-3} solution of a weak acid HA.

For HA, the acid dissociation constant, $K_a = 1.79 \times 10^{-5}$ mol dm^{-3}.

Calculate the pH of this buffer solution.

pH _____

(6)

(Total 15 marks)

Q5.

What is the pH of a 0.020 mol dm^{-3} solution of a diprotic acid which is completely dissociated?

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A 1.00 ⬭

B 1.40 ⬭

C 1.70 ⬭

D 4.00 ⬭

(Total 1 mark)

Q6.

Nitric acid (HNO_{-3}) is a strong acid. Ethanoic acid (CH_3COOH) is a weak acid.

(a) Write an equation to show how ethanoic acid behaves as a weak acid in its reaction with water.

_____

(1)

(b) When pure ethanoic acid reacts with pure nitric acid, ethanoic acid acts as a base.

Write an equation for this reaction.

_____

(1)

(c) Two beakers, **A** and **B**, each contain 100.0 cm^{-3} of 0.0125 mol dm^{-3} nitric acid.

(i) Calculate the pH of the solution formed after 50.0 cm^{-3} of distilled water are added to beaker **A**.
Give your answer to 2 decimal places.

_____

_____

_____

(2)

(ii) Calculate the pH of the solution formed after 50.0 cm^3 of 0.0108 mol dm^{-3} aqueous sodium hydroxide are added to beaker **B**.
Give your answer to 2 decimal places.

_____

_____

_____

_____

_____

_____

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_____

(4)

(d) A third beaker, **C**, contains 100.0 cm^3 of 0.0125 mol dm^{-3} ethanoic acid.
The acid dissociation constant K_a for ethanoic acid has the value 1.74×10^{-5} mol dm^{-3} at 25 °C.

(i) Write an expression for K_a for ethanoic acid and use it to calculate the pH of the ethanoic acid solution in beaker **C**.
Show your working. Give your answer to 2 decimal places.

K_a _____

_____

Calculation _____

_____

_____

_____

(4)

(ii) Aqueous sodium hydroxide is added to beaker **C** until the pH of the solution becomes 4.84.

Name the salt formed in the reaction of ethanoic acid with sodium hydroxide.

_____

(1)

(iii) Calculate the value of $\frac{[\text{salt}]}{[\text{ethanoic acid}]}$ in the solution with the pH of 4.84.

_____

_____

_____

_____

_____

_____

(3)

(e) Explain why chloroethanoic acid is a stronger acid than ethanoic acid.

_____

_____

_____

_____

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(2)

(f) Explain why data books do not usually contain values of K_a for strong acids.

_____

_____

_____

_____

(2)

(Total 20 marks)

Q7.

Water dissociates slightly according to the equation:

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

The ionic product of water, K_w, is given by the expression

$$K_w = [H^+][OH^-]$$

K_w varies with temperature as shown in the table.

Temperature / °C	**K_w / mol² dm⁻⁶**
25	1.00×10^{-14}
50	5.48×10^{-14}

(a) Explain why the expression for K_w does **not** include the concentration of water.

_____

_____

_____

_____

_____

(2)

(b) Explain why the value of K_w increases as the temperature increases.

_____

_____

_____

_____

_____

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(2)

(c) Calculate the pH of pure water at 50 °C.
Give your answer to 2 decimal places.

(3)

(d) Calculate the pH of 0.12 mol dm^{-3} aqueous NaOH at 50 °C.
Give your answer to 2 decimal places.

(3)
(Total 10 marks)

Q8.

This question is about alkalis and carboxylic acids.

In this question, all data are quoted at 25 °C.

(a) Carboxylic acids are weak acids.

State the meaning of the term **weak** as applied to carboxylic acids.

(1)

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(b) Write an equation for the reaction of propanoic acid with sodium carbonate.

_____

(1)

(c) Calculate the pH of a 0.0120 mol dm^{-3} solution of calcium hydroxide.
The ionic product of water $K_w = 1.00 \times 10^{-14}$ mol^2 dm^{-6}.
Give your answer to 2 decimal places.

_____

_____

_____

_____

_____

_____

(3)

(d) The value of the acid dissociation constant K_a for benzenecarboxylic acid (C_6H_5COOH) is 6.31×10^{-5} mol dm^{-3}.

(i) Write an expression for the acid dissociation constant K_a for benzenecarboxylic acid.

_____

_____

(1)

(ii) Calculate the pH of a 0.0120 mol dm^{-3} solution of benzenecarboxylic acid.
Give your answer to 2 decimal places.

_____

_____

_____

_____

_____

_____

_____

_____

(3)

(iii) A buffer solution with a pH of 4.00 is made using benzenecarboxylic acid and sodium benzenecarboxylate.

Calculate the mass of sodium benzenecarboxylate (M_r = 144.0) that should be dissolved in 1.00 dm^3 of a 0.0120 mol dm^{-3} solution of benzenecarboxylic acid

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to produce a buffer solution with a pH of 4.00

The value of the acid dissociation constant K_a for benzenecarboxylic acid (C_6H_5COOH) is 6.31×10^{-5} mol dm^{-3}.

(5)

(e) Two solutions, one with a pH of 4.00 and the other with a pH of 9.00, were left open to the air.

The pH of the pH 9.00 solution changed more than that of the other solution.

Suggest what substance might be present in the air to cause the pH to change.
Explain how and why the pH of the pH 9.00 solution changes.

Substance present in air _____

Explanation _____

(3)

(Total 17 marks)

Q9.

This question involves calculations about two strong acids and one weak acid.
All measurements were carried out at 25 °C.

(a) A 25.0 cm^3 sample of 0.0850 mol dm^{-3} hydrochloric acid was placed in a beaker and 100 cm^3 of distilled water were added.
Calculate the pH of the new solution formed.
Give your answer to 2 decimal places.

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(2)

(b) HX is a weak monobasic acid.

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

(1)

(ii) The pH of a 0.0850 mol dm^{-3} solution of HX is 2.79
Calculate a value for the acid dissociation constant, K_a, of this acid.
Give your answer to 3 significant figures.

(3)

(c) A 25.0 cm^3 sample of 0.620 mol dm^{-3} nitric acid was placed in a beaker and 38.2 cm^3 of 0.550 mol dm^{-3} aqueous sodium hydroxide were added.
Calculate the pH of the solution formed.
Give your answer to 2 decimal places.

The ionic product of water $K_w = 1.00 \times 10^{-14}$ mol^2 dm^{-6} at 25 °C.

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_____

(6)

(Total 12 marks)

Q10.

This question is about the pH of several solutions.

Give all values of pH to 2 decimal places.

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

_____

(1)

(ii) Calculate the pH of 0.154 mol dm^{-3} hydrochloric acid.

_____

_____

(1)

(iii) Calculate the pH of the solution formed when 10.0 cm^3 of 0.154 mol dm^{-3} hydrochloric acid are added to 990 cm^3 of water.

_____

_____

_____

_____

(2)

(b) The acid dissociation constant, K_a, for the weak acid HX has the value 4.83×10^{-5} mol dm^{-3} at 25 °C.
A solution of HX has a pH of 2.48

Calculate the concentration of HX in the solution.

_____

_____

_____

_____

_____

_____

(4)

(c) Explain why the pH of an acidic buffer solution remains almost constant despite the addition of a small amount of sodium hydroxide.

_____

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(2)

(d) The acid dissociation constant, K_a, for the weak acid HY has the value 1.35×10^{-5} mol dm^{-3} at 25 °C.

A buffer solution was prepared by dissolving 0.0236 mol of the salt NaY in 50.0 cm^3 of a 0.428 mol dm^{-3} solution of the weak acid HY

(i) Calculate the pH of this buffer solution.

(4)

(ii) A 5.00×10^{-4} mol sample of sodium hydroxide was added to this buffer solution.

Calculate the pH of the buffer solution after the sodium hydroxide was added.

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_____

_____

_____

(4)

(Total 18 marks)

Q11.

This question is about the pH of some solutions containing potassium hydroxide and ethanoic acid.

Give all values of pH to 2 decimal places.

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

_____

(1)

(ii) Write an expression for the ionic product of water, K_w

_____

(1)

(iii) At 10 °C, a 0.154 mol dm^{-3} solution of potassium hydroxide has a pH of 13.72. Calculate the value of K_w at 10 °C.

_____

_____

_____

_____

(2)

(b) At 25 °C, the acid dissociation constant K_a for ethanoic acid has the value 1.75×10^{-5} mol dm^{-3}.

(i) Write an expression for K_a for ethanoic acid.

_____

_____

(1)

(ii) Calculate the pH of a 0.154 mol dm^{-3} solution of ethanoic acid at 25 °C.

_____

_____

_____

_____

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(3)

(c) At 25 °C, the acid dissociation constant K_a for ethanoic acid has the value 1.75×10^{-5} mol dm^{-3}.

(i) Calculate the pH of the solution formed when 10.0 cm^3 of 0.154 mol dm^{-3} potassium hydroxide are added to 20.0 cm^3 of 0.154 mol dm^{-3} ethanoic acid at 25 °C.

(4)

(ii) Calculate the pH of the solution formed when 40.0 cm^3 of 0.154 mol dm^{-3} potassium hydroxide are added to 20.0 cm^3 of 0.154 mol dm^{-3} ethanoic acid at 25 °C.

At 25 °C, K_w has the value 1.00×10^{-14} mol^2 dm^{-6}.

(4)

(Total 16 marks)

Q12.

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

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Calculating the pH of aqueous solutions can involve the use of equilibrium constants such as K_w and K_a

K_w is the ionic product of water. The value of K_w is 5.48×10^{-14} mol^2 dm^{-6} at 50 °C.

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

_____

(1)

(ii) Write an expression for K_w

_____

(1)

(b) (i) Calculate the pH of pure water at 50 °C.

_____

_____

_____

(2)

(ii) Suggest why this pure water is **not** acidic.

_____

_____

(1)

(iii) Calculate the pH of 0.140 mol dm^{-3} aqueous sodium hydroxide at 50 °C.

_____

_____

_____

_____

_____

(3)

(c) Calculate the pH of the solution formed when 25.0 cm^3 of 0.150 mol dm^{-3} aqueous sulfuric acid are added to 30.0 cm^3 of 0.200 mol dm^{-3} aqueous potassium hydroxide at 25 °C. Assume that the sulfuric acid is fully dissociated.

_____

_____

_____

_____

_____

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_____

_____

_____

_____

_____

(6)

(Total 14 marks)

Q13.

(a) A sample of hydrochloric acid has a pH of 2.34
Write an expression for pH and calculate the concentration of this acid.

pH _____

Concentration _____

_____

(2)

(b) A 0.150 mol dm^{-3} solution of a weak acid, HX, also has a pH of 2.34

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

_____

_____

(ii) Calculate the value of K_a for this acid and state its units.

Calculation _____

_____

_____

Units

_____

(iii) Calculate the value of pK_a for the acid HX. Give your answer to two decimal places.

_____

(5)

(c) A 30.0 cm^3 sample of a 0.480 mol dm^{-3} solution of potassium hydroxide was partially neutralised by the addition of 18.0 cm^3 of a 0.350 mol dm^{-3} solution of sulphuric acid.

(i) Calculate the initial number of moles of potassium hydroxide.

_____

_____

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(ii) Calculate the number of moles of sulphuric acid added.

_____

_____

(iii) Calculate the number of moles of potassium hydroxide remaining in excess in the solution formed.

_____

_____

(iv) Calculate the concentration of hydroxide ions in the solution formed.

_____

_____

_____

(v) Hence calculate the pH of the solution formed. Give your answer to two decimal places.

_____

_____

_____

(6)

(Total 13 marks)

Q14.

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

(a) (i) Write expressions for the ionic product of water, K_w, and for pH.

K_W = _____

pH = _____

(ii) At 318 K, the value of K_w is 4.02×10^{-14} mol^2 dm^{-6} and hence the pH of pure water is 6.70
State why pure water is not acidic at 318 K.

_____

_____

(iii) Calculate the number of moles of sodium hydroxide in 2.00 cm^3 of 0.500 mol dm^{-3} aqueous sodium hydroxide.

_____

_____

(iv) Use the value of K_w given above and your answer to part (a)(iii) to calculate the

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pH of the solution formed when 2.00 cm^3 of 0.500 mol dm^{-3} aqueous sodium hydroxide are added to 998 cm^3 of pure water at 318 K.

(6)

(b) At 298 K, the acid dissociation constant, K_a, for propanoic acid, CH_3CH_2COOH, has the value 1.35×10^{-5}mol dm^{-3}.

(i) Write an expression for K_a for propanoic acid.

(ii) Calculate the pH of 0.125 mol dm^{-3} aqueous propanoic acid at 298 K.

(4)

(c) Sodium hydroxide reacts with propanoic acid as shown in the following equation.

$$NaOH + CH_3CH_2COOH \rightarrow CH_3CH_2COONa + H_2O$$

A buffer solution is formed when sodium hydroxide is added to an excess of aqueous propanoic acid.

(i) Calculate the number of moles of propanoic acid in 50.0 cm^3 of 0.125 mol dm^{-3} aqueous propanoic acid.

(ii) Use your answers to part (a)(iii) and part (c)(i) to calculate the number of moles of propanoic acid in the buffer solution formed when 2.00 cm^3 of 0.500 mol dm^{-3} aqueous sodium hydroxide are added to 50.0 cm^3 of 0.125 mol dm^{-3} aqueous propanoic acid.

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(iii) Hence calculate the pH of this buffer solution at 298 K.

(6)

(Total 16 marks)

Q15.

The hydrolysis of methyl propanoate was studied in acidic conditions at 25°C and the rate equation was found to be

$$\text{rate} = k[CH_3CH_2COOCH_3][H^+]$$

(a) Use the data below to calculate the value of the rate constant, *k*, at this temperature. Deduce its units.

Initial rate of reaction / mol dm^{-3} s^{-1}	Initial concentration of methyl propanoate / mol dm^{-3}	Initial concentration of hydrochloric acid / mol dm^{-3}
1.15×10^{-4}	0.150	0.555

Rate constant

Units

(3)

(b) The reaction in part (a) was repeated at the same temperature, but water was added so that the volume of the reaction mixture was doubled. Calculate the initial rate of reaction under these conditions.

(1)

(c) A third experiment was carried out at a different temperature. Some data from this

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experiment are shown in the table below.

Initial rate of reaction / mol dm^{-3} s^{-1}	Value of rate constant at this different temperature	Initial methyl propanoate / mol dm^{-3}
4.56×10^{-5}	8.94×10^{-4}	0.123

Calculate the initial pH of the reaction mixture. Give your answer to two decimal places.

_____

_____

_____

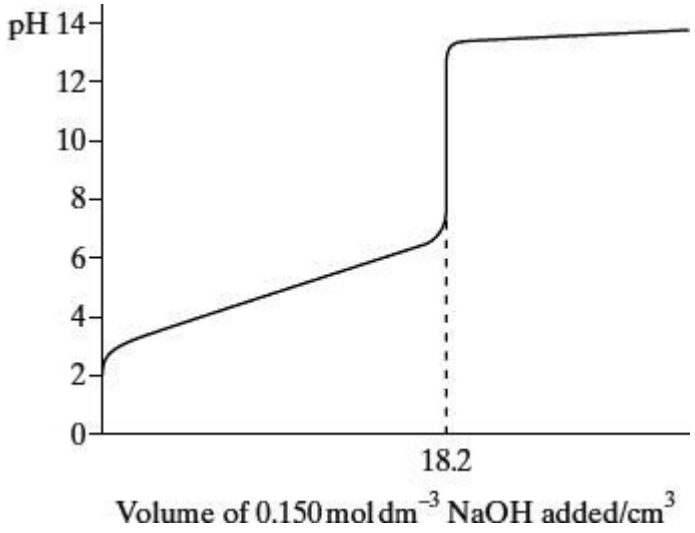
_____

(3)

(Total 7 marks)

Q16.

The pH curve shown below was obtained when a 0.150 mol dm^{-3} solution of sodium hydroxide was added to 25.0 cm^3 of an aqueous solution of a weak monoprotic acid, HA.



(a) Use the information given to calculate the concentration of the acid.

_____

_____

_____

(2)

(b) (i) Write an expression for the acid dissociation constant, K_a, for HA.

_____

(ii) Write an expression for pK_a

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(iii) Using your answers to parts (b)(i) and (b)(ii), show that when sufficient sodium hydroxide has been added to neutralise half of the acid,

pH of the solution = pK_a for the acid HA

(4)

(c) Explain why dilution with a small volume of water does not affect the pH of a buffer solution.

(2)

(d) (i) Calculate the change in pH when 0.250 mol dm^{-3} hydrochloric acid is diluted with water to produce 0.150 mol dm^{-3} hydrochloric acid.

(ii) Calculate the volume of water which must be added to 30.0 cm^3 of 0.250 mol dm^{-3} hydrochloric acid in order to reduce its concentration to 0.150 mol dm^{-3}.

(4)

(Total 12 marks)

Q17.

Use the information about the following solutions to answer the question below.

Solution F: This is a mixture of 1 mol of propanoic acid, 1 mol of methanol and 2 mol of water.

Solution G: This was originally the same mixture as solution **F** but it has been left to reach equilibrium.

Compared to the pH of solution **F**, the pH of solution **G** will be

A considerably lower.

B slightly lower.

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C slightly higher.

D exactly the same.

(Total 1 mark)

Q18.

For this question **one or more** of the options given may be correct. Select your answer by means of the following code

A if **1**, **2** and **3** only are correct

B if **1** and **3** only are correct

C if **2** and **4** only are correct

D if **4** alone is correct

Directions summarised			
A	**B**	**C**	**D**
1, **2** and **3** only correct	**1** and **3** only correct	**2** and **4** only correct	**4** only correct

Solutions with a pH of 1.0 include

1 0.1 mol dm^{-3} hydrochloric acid

2 0.1 mol dm^{-3} ethanoic acid

3 0.05 mol dm^{-3} sulphuric acid

4 0.2 mol dm^{-3} nitric acid

(Total 1 mark)

Q19.

(a) At 50°C, the ionic product of water, K_w, has the value 5.48×10^{-14} mol^2 dm^{-6}.

(i) Define the term K_w

_____

(ii) Define the term *pH*

_____

(iii) Calculate the pH of pure water at 50 °C. Explain why pure water at 50 °C is still neutral even though its pH is not 7.

Calculation _____

_____

_____

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Explanation _____

_____

(5)

(b) At 25°C, K_w has the value 1.00×10^{-14} mol^2 dm^{-6}. Calculate the pH at 25 °C of

(i) a 0.150 mol dm^{-3} solution of sodium hydroxide,

_____

_____

_____

(ii) the solution formed when 35.0 cm^3 of this solution of sodium hydroxide is mixed with 40.0 cm^3 of a 0.120 mol dm^{-3} solution of hydrochloric acid.

_____

_____

_____

_____

_____

_____

_____

(8)

(c) In a 0.150 mol dm^{-3} solution of a weak acid HX at 25 °C, 1.80% of the acid molecules are dissociated into ions.

(i) Write an expression for K_a for the acid HX.

_____

_____

(ii) Calculate the value of K_a for the acid HX at this temperature and state its units.

_____

_____

_____

_____

_____

_____

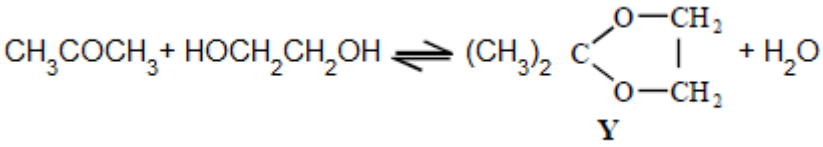
(5)

(Total 18 marks)

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Q20.

This question is about the reaction between propanone and an excess of ethane-1,2-diol, the equation for which is given below.



Y

In a typical procedure, a mixture of 1.00 g of propanone, 5.00 g of ethane-1,2-diol and 0.100 g of benzenesulphonic acid, $C_6H_5SO_3H$, is heated under reflux in an inert solvent. Benzenesulphonic acid is a strong acid.

If 0.100 g of the strong monoprotic acid, benzenesulphonic acid, was dissolved in 100 cm^3 of water, the pH of the solution would be

A 0.20

B 1.20

C 2.20

D 3.20

(Total 1 mark)

Q21.

Iodine and propanone react in acid solution according to the equation

$$I_2 + CH_3COCH_3 \rightarrow CH_3COCH_2I + HI$$

The rate equation for the reaction is found to be

$$\text{rate} = k\,[CH_3COCH_3][H^+]$$

(a) Deduce the order of reaction with respect to iodine and the overall order of reaction.

Order with respect to iodine _____

Overall order _____

(2)

(b) At the start of the experiment, the rate of reaction was found to be 2.00×10^{-5} mol dm^{-3} s^{-1} when the concentrations of the reactants were as shown below.

Reactant	Concentration / mol dm^{-3}
CH_3COCH_3	1.50
I_2	2.00×10^{-2}
H^+	3.00×10^{-2}

Use these data to calculate a value for the rate constant and deduce its units.

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Rate constant _____

_____

_____

Units _____

(3)

(c) How can you tell that H^+ acts as a catalyst in this reaction?

_____

_____

_____

(2)

(d) Calculate the initial rate of reaction if the experiment were to be repeated at the same temperature and with the same concentrations of iodine and propanone as in part (b) but at a pH of 1.25

_____

_____

_____

_____

_____

_____

(3)

(Total 10 marks)

Q22.

A 0.210 mol dm^{-3} solution of potassium hydroxide was added from a burette to 25.0 cm^3 of a 0.160 mol dm^{-3} solution of ethanoic acid in a conical flask.
Given that the value of the acid dissociation constant, K_a, for ethanoic acid is 1.74×10^{-5} mol dm^{-3}, calculate the pH at 25 °C of the solution in the conical flask at the following three points:

before any potassium hydroxide had been added;

after 8.0 cm^3 of potassium hydroxide solution had been added;

after 40.0 cm^3 of potassium hydroxide solution had been added.

_____

_____

_____

_____

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_____

_____

_____

_____

_____

_____

_____

_____

(Total 16 marks)

Q23.

The equation and rate law for the reaction of substance P with substance Q are given below.

$$2P + Q \rightarrow R + S$$
$$rate = k[P]^2[H^+]$$

Under which one of the following conditions, all at the same temperature, would the rate of reaction be slowest?

	[P] / mol dm^{-3}	pH
A	0.1	0
B	1	2
C	3	3
D	10	4

(Total 1 mark)

Q24.

Addition of which one of the following to 10 cm^3 of 1.0 M NaOH would result in the pH being halved?

A 10 cm^3 of water

B 100 cm^3 of water

C 5 cm^3 of 1.0 M HCl

D 10 cm^3 of 1.0 M HCl

(Total 1 mark)

Q25.

The pH of 0.001 M NaOH at 25°C is

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A 13

B 11

C 9

D 3

(Total 1 mark)

Q26.

Which one of the following is the change in units of pH which occurs when 10.0 cm^3 of a 1.0 M solution of a strong monoprotic acid are made up to 1.0 dm^3 with water?

A 1

B 2

C 3

D 5

(Total 1 mark)

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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

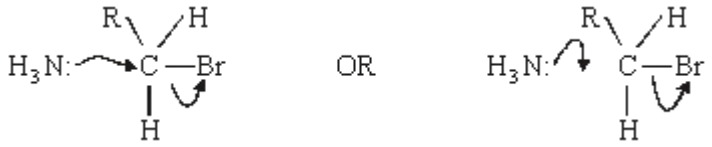
(a) If K_w includes H_2O allow 6.63 if seen otherwise no marks likely

(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

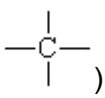
(c) If wrong K_a in (i) max 2 in part (ii) for $[H^+]$ **(1)** and conseq units **(1)**
but mark on fully from minor errors
eg no [ ] or charges missing

Organic points

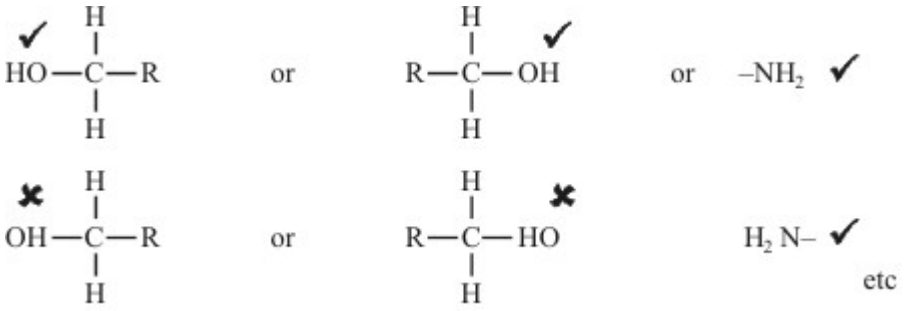
(1) Curly arrows: must show movement of a pair of electrons, i.e. from bond to atom or from lp to atom / space
e.g.



(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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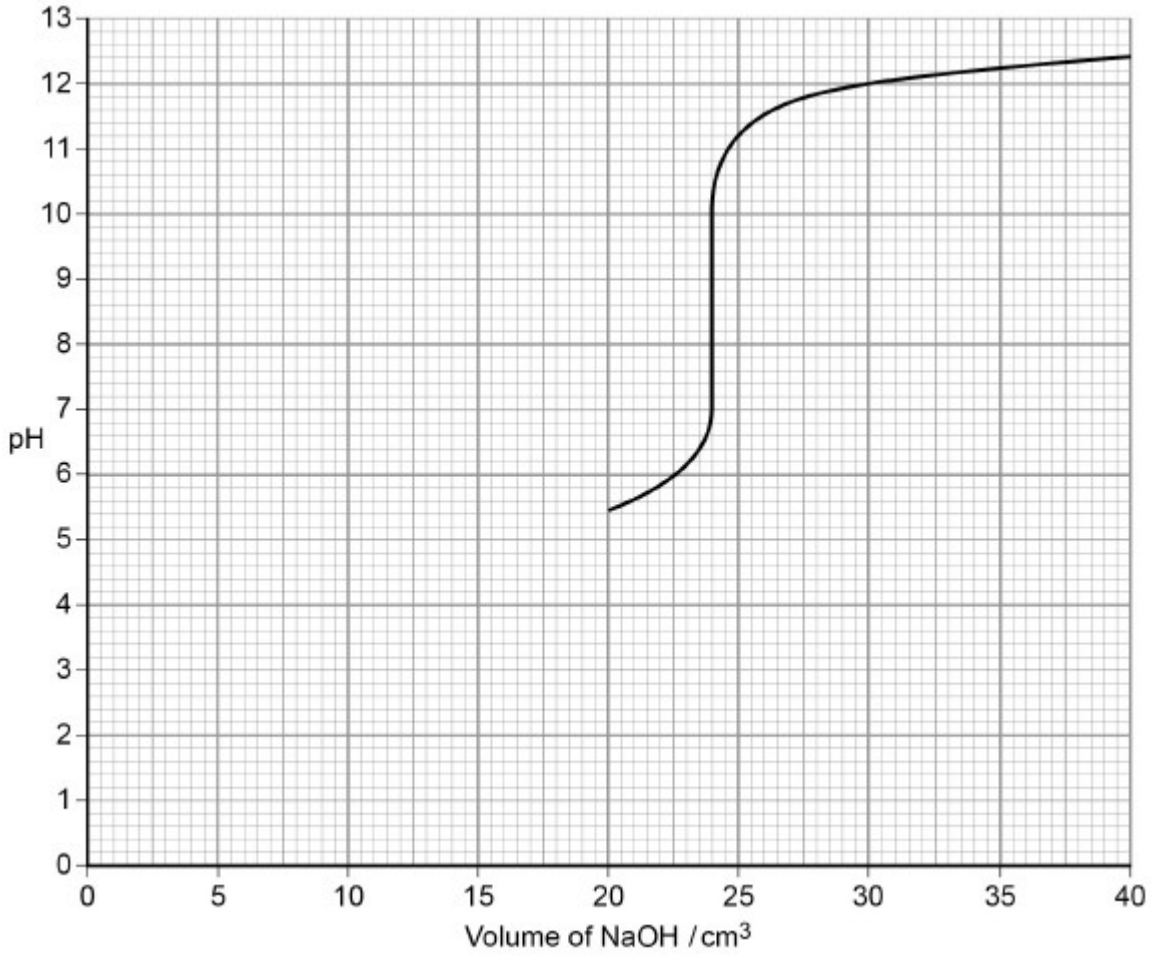
Q1.

A 0.100 mol dm^{-3} solution of sodium hydroxide was gradually added to 25.0 cm^3 of a solution of a weak acid, HX, in the presence of a suitable indicator.

A graph was plotted of pH against the volume of sodium hydroxide solution, as shown in the figure below.

The first pH reading was taken after 20.0 cm^3 of sodium hydroxide solution had been added.

The acid dissociation constant of HX, K_a, = 2.62 × 10^{-5} mol dm^{-3}



(a) The pH range of an indicator is the range over which it changes colour.

Suggest the pH range of a suitable indicator for this titration.

_____

(1)

(b) Give the expression for the acid dissociation constant of HX.

K_a =

(1)

(c) Calculate the concentration of HX in the original solution.

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Concentration _____ mol dm^{-3}

(2)

(d) Calculate the pH of the solution of HX before the addition of any sodium hydroxide.

(If you were unable to calculate a value for the concentration of HX in part (c) you should use a value of 0.600 mol dm^{-3} in this calculation. This is not the correct value.)

pH of HX _____

(2)

(e) Calculate the pH of the solution when half of the acid has reacted.

pH of solution _____

(1)

(f) Plot your answers to part (d) and part (e) on the grid in the figure above.

Use these points to sketch the missing part of the curve between 0 and 20 cm^3 of NaOH solution added.

(2)

(Total 9 marks)

Q2.

Which indicator should be used in a titration to find the concentration of a solution of methylamine using 0.010 mol dm^{-3} hydrochloric acid?

A Thymol blue (pH range 1.2–2.8) ⬭

B Bromophenol blue (pH range 3.0–4.6) ⬭

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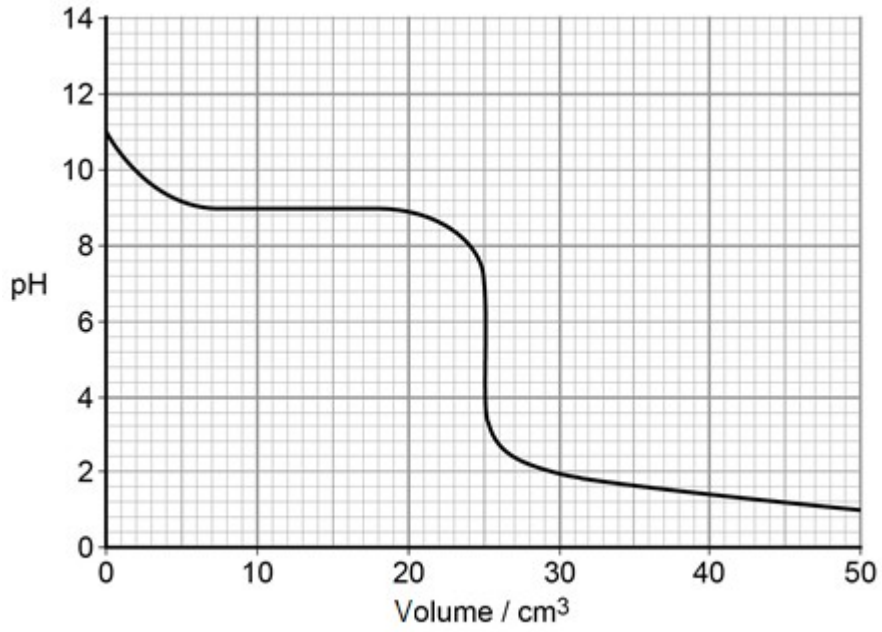
C Phenol red. (pH range 6.8–8.4) ⬭

D Phenolphthalein (pH range 8.3–10.0) ⬭

(Total 1 mark)

Q3.

The graph was obtained from an experiment in which an acid was reacted with an alkali.



(a) Suggest possible formulae for an acid and an alkali that could be used to produce the curve shown in the graph.

Acid _____

Alkali _____

(2)

(b) Suggest briefly a practical procedure that a student could use to obtain data from which the curve in the graph could be plotted.

_____

_____

_____

_____

_____

_____

_____

(3)

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(c) The student was provided with samples of three different indicators.

Suggest how the practical procedure in part **(b)** could be refined by the student to identify the most suitable indicator.

_____

_____

_____

_____

_____

(2)

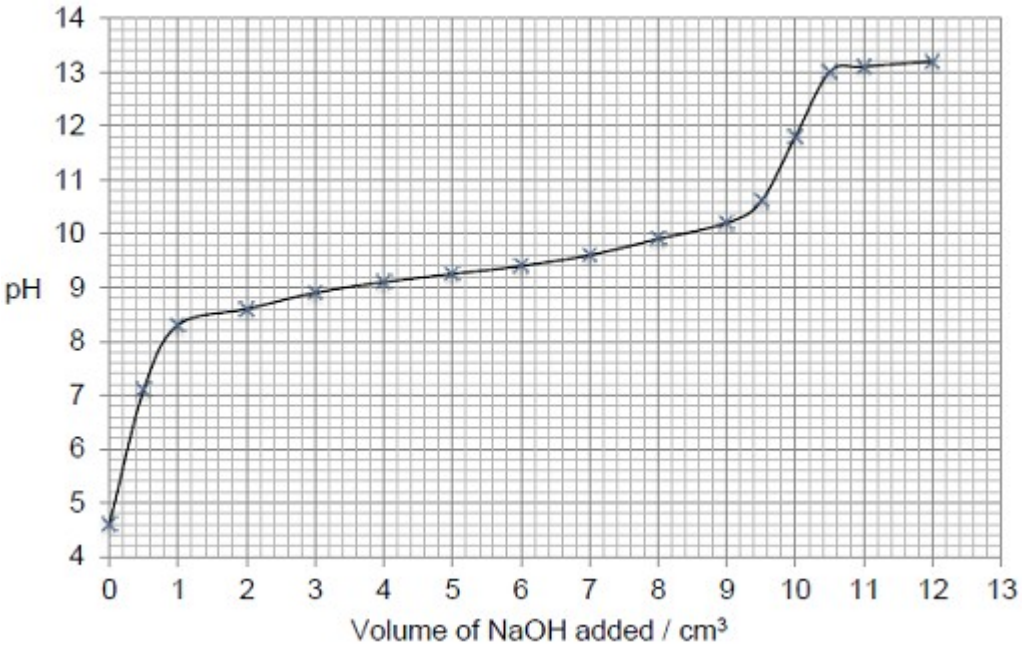
(Total 7 marks)

Q4.

Ammonium chloride, when dissolved in water, can act as a weak acid as shown by the following equation.

$$NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq)$$

The following figure shows a graph of data obtained by a student when a solution of sodium hydroxide was added to a solution of ammonium chloride. The pH of the reaction mixture was measured initially and after each addition of the sodium hydroxide solution.



(a) Suggest a suitable piece of apparatus that could be used to measure out the sodium hydroxide solution.
Explain why this apparatus is more suitable than a pipette for this purpose.

Apparatus_____

Explanation _____

_____

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_____

(2)

(b) Use information from the curve in the figure above to explain why the end point of this reaction would be difficult to judge accurately using an indicator.

_____

_____

_____

_____

_____

(2)

(c) The pH at the end point of this reaction is 11.8.

Use this pH value and the ionic product of water, $K_w = 1.0 \times 10^{-14}$ mol^2 dm^{-6}, to calculate the concentration of hydroxide ions at the end point of the reaction.

Concentration = _____ mol dm^{-3}

(3)

(d) The expression for the acid dissociation constant for aqueous ammonium ions is

$$K_a = \frac{[NH_3][H^+]}{[NH_4^+]}$$

The initial concentration of the ammonium chloride solution was 2.00 mol dm^{-3}.

Use the pH of this solution, before any sodium hydroxide had been added, to calculate a value for K_a

K_a = _____ mol dm^{-3}

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(3)

(e) A solution contains equal concentrations of ammonia and ammonium ions.

Use your value of K_a from part **(d)** to calculate the pH of this solution. Explain your working.

(If you were unable to calculate a value for K_a you may assume that it has the value 4.75×10^{-9} mol dm^{-3}. This is **not** the correct value.)

pH = _____

(2)

(Total 12 marks)

Q5.

A solution of 4-chlorobutanoic acid was titrated with sodium hydroxide solution. The pH was measured after each addition. Small volumes of sodium hydroxide solution were added. The titration data is shown in the table.

Volume of NaOH / cm^3	0.0	5.0	10.0	15.0	18.0	19.0	20.0	21.0	22.0	25.0	30.0
pH	3.81	4.28	4.50	4.52	4.70	4.96	12.05	12.54	13.32	13.02	13.00

(a) Plot the values of the pH of the solution (*y*-axis) against the volume of NaOH.

(2)

(b) Draw a curve of best fit for these points.

(2)

(c) The pK_a of a weak acid is equal to the pH of the solution in which half of the weak acid has been neutralised.

Use your graph to calculate a value of K_a for 4-chlorobutanoic acid.

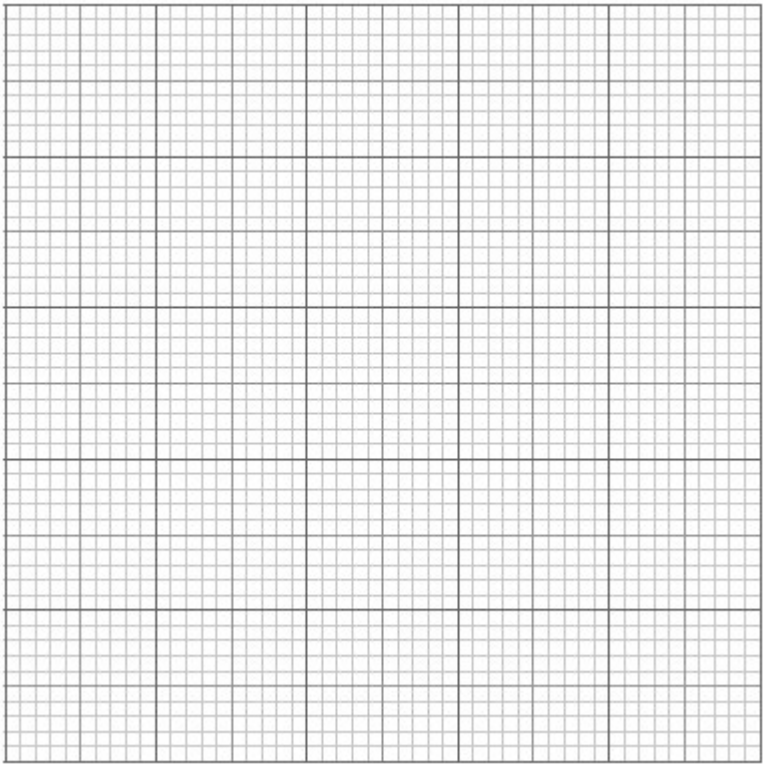
_____

_____

_____

_____

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(3)

(d) Before this titration can take place, the pH probe needs to be calibrated.

Outline a simple method for calibrating a pH probe, including any measurements made and how they should be used.

(3)

(e) Explain how you would use the curve you have plotted in part **(a)** to choose a suitable indicator for this titration.

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(2)

(f) Suggest an improvement a student could make to increase the accuracy of the end point when using an indicator in this experiment instead of a pH probe.

_____

_____

_____

_____

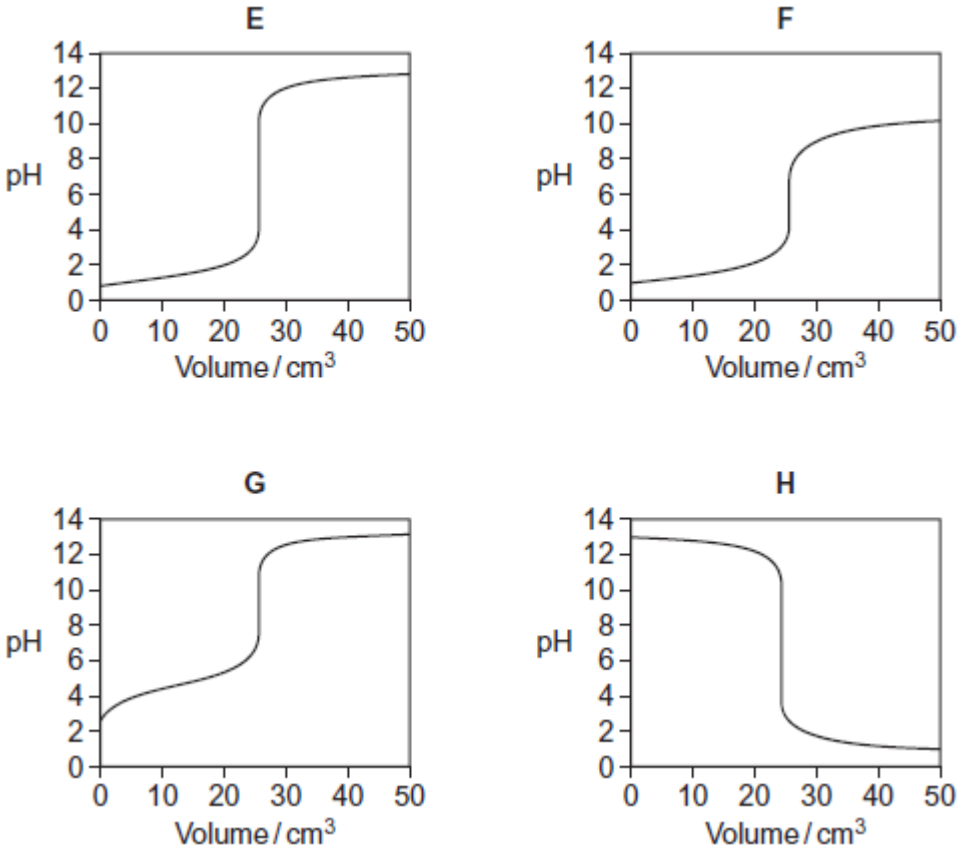
(1)

(Total 13 marks)

Q6.

Titration curves, labelled **E**, **F**, **G** and **H**, for combinations of different aqueous solutions of acids and bases are shown below.

All solutions have concentrations of 0.1 mol dm^{-3}.



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

From the curves **E**, **F**, **G** and **H**, choose the curve produced by the addition of

(i) sodium hydroxide to 25 cm^3 of ethanoic acid ☐

(1)

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(ii) ammonia to 25 cm^3 hydrobromic acid ☐

(1)

(iii) hydrochloric acid to 25 cm^3 of potassium hydroxide ☐

(1)

(b) The table shows information about some acid-base indicators.

Indicator	**pH range**	**Lower pH colour**	**Higher pH colour**
pentamethoxy red	1.2−3.2	violet	colourless
naphthyl red	3.7−5.0	red	yellow
4−nitrophenol	5.6−7.0	colourless	yellow
cresol purple	7.6−9.2	yellow	purple

(i) Which indicator in the table could be used for the titration that produces curve **E** but **not** for the titration that produces curve **F**?

Tick (✓) **one** box.

pentamethoxy red ☐

naphthyl red ☐

4−nitrophenol ☐

cresol purple ☐

(1)

(ii) Give the colour change at the end point of the titration that produces curve **H** when naphthyl red is used as the indicator.

_____

(1)

(iii) A beaker contains 25 cm^3 of a buffer solution at pH = 6.0

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Two drops of each of the four indicators in the table are added to this solution.

State the colour of the mixture of indicators in this buffer solution.
You should assume that the indicators do **not** react with each other.

_____

(1)

(Total 6 marks)

Q7.

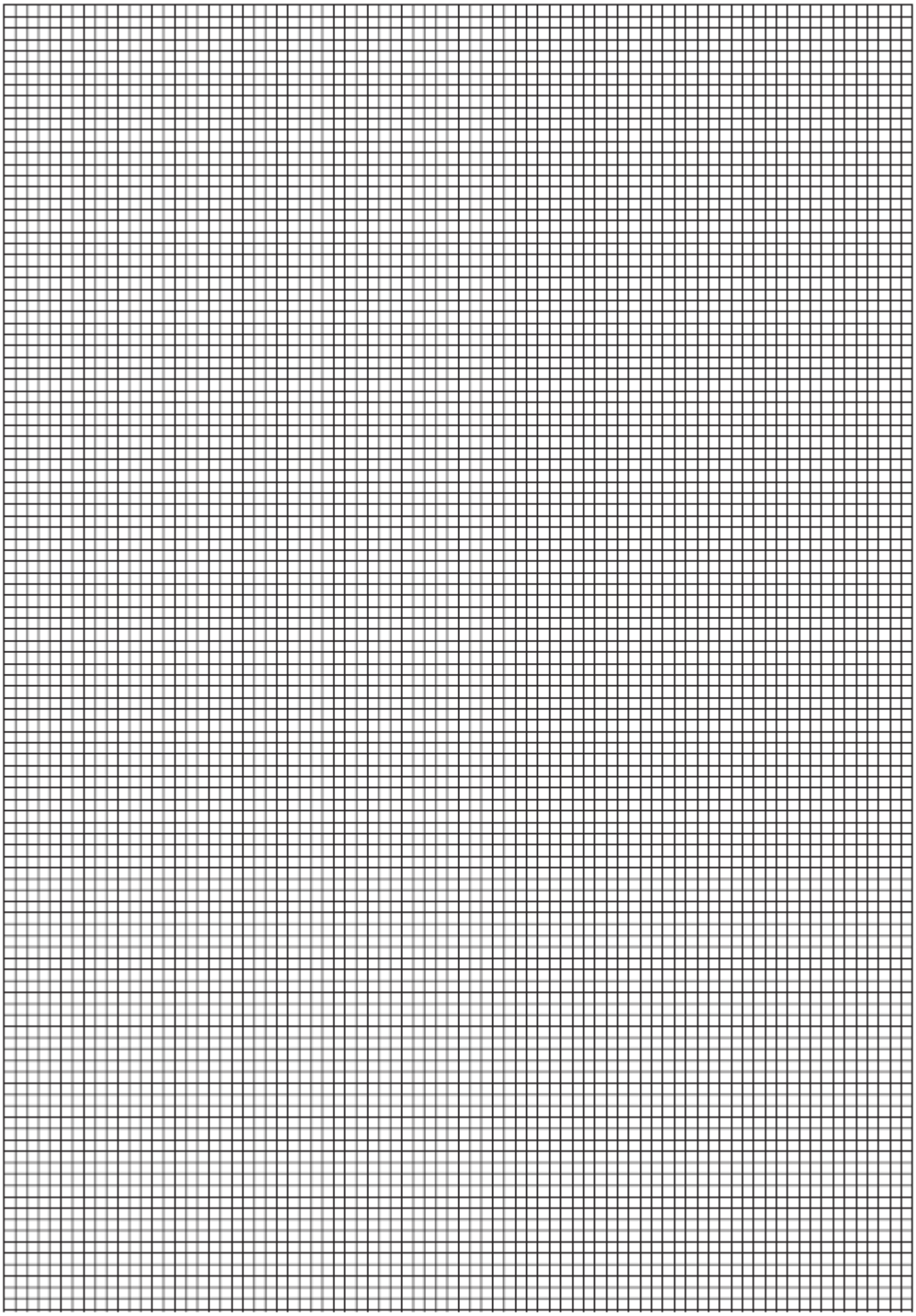
In an experiment to determine the acid dissociation constant (K_a) of a weak acid, 25.0 cm^3 of an approximately 0.1 mol dm^{-3} solution of this acid were titrated with a 0.10 mol dm^{-3} solution of sodium hydroxide.
The pH was measured at intervals and recorded. The table below shows the results.

Volume of NaOH / cm^3	0.0	1.0	2.0	3.0	4.0	5.0	10.0	15.0
pH	5.1	7.8	8.1	8.7	8.4	8.5	8.9	9.3

Volume of NaOH / cm^3	20.0	22.0	23.0	24.0	25.0	26.0	27.0	28.0
pH	9.7	10.0	10.2	11.0	11.3	11.4	11.5	11.6

(a) On the grid below, plot the values from the table above on a graph of pH (y-axis) against volume of NaOH.
You should start your y-axis at pH 4.0.
Draw a curve that represents the curve of best fit through these points. Ignore any anomalous points.

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(4)

(b) Deduce the volume of the sodium hydroxide solution that would have been added at the half-neutralisation point of this experiment. This is the point where half the amount of the weak acid has been neutralised.

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_____

(1)

(c) When half of the weak acid has been neutralised, the pH of the mixture at this point is equal to the pK_a of the weak acid.

Use your answer to part (b) and your graph to determine the pK_a of the weak acid and, hence, its K_a value.

pK_a _____

K_a _____

(2)

(d) State the pH value for the anomalous point on your graph.
Suggest **one** reason for this anomaly. Assume that the reading on the pH meter is correct.

pH _____

Reason for anomaly _____

_____

_____

(1)

(e) Suggest how the experimental procedure could be slightly modified in order to give a more reliable value for the end-point.

_____

_____

_____

(1)

(Total 9 marks)

Q8.

This question is about Brønsted-Lowry acids of different strengths.

(a) State the meaning of the term *Brønsted–Lowry acid*.

_____

(1)

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

_____

_____

(1)

(ii) The value of K_a for ethanoic acid is 1.75×10^{-5} mol dm^{-3} at 25 °C.

Calculate the concentration of ethanoic acid in a solution of the acid that has a

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pH of 2.69

(4)

(c) The value of K_a for chloroethanoic acid ($ClCH_2COOH$) is 1.38×10^{-3} mol dm^{-3} at 25 °C.

(i) Write an equation for the dissociation of chloroethanoic acid in aqueous solution.

(1)

(ii) Suggest why chloroethanoic acid is a stronger acid than ethanoic acid.

(2)

(d) **P** and **Q** are acids. **X** and **Y** are bases. The table shows the strength of each acid and base.

Acids		**Bases**	
strong	weak	strong	weak
P	**Q**	**X**	**Y**

The two acids were titrated separately with the two bases using methyl orange as indicator.
The titrations were then repeated using phenolphthalein as indicator.
The pH range for methyl orange is 3.1 − 4.4
The pH range for phenolphthalein is 8.3 − 10.0

For each of the following titrations, select the letter, **A, B, C,** or **D**, for the correct statement about the indicator(s) that would give a precise end-point.
Write your answer in the box provided.

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A Both indicators give a precise end-point.

B Only methyl orange gives a precise end-point.

C Only phenolphthalein gives a precise end-point.

D Neither indicator gives a precise end-point.

(i) Acid **P** with base **X** ☐

(1)

(ii) Acid **Q** with base **X** ☐

(1)

(iii) Acid **Q** with base **Y** ☐

(1)

(e) Using a burette, 26.40 cm^3 of 0.550 mol dm^{-3} sulfuric acid were added to a conical flask containing 19.60 cm^3 of 0.720 mol dm^{-3} aqueous sodium hydroxide. Assume that the sulfuric acid is fully dissociated.

Calculate the pH of the solution formed.

Give your answer to 2 decimal places.

_____

_____

_____

_____

_____

_____

_____

_____

(6)

(Total 18 marks)

Q9.

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.

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(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)

Q10.

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.

_____

_____

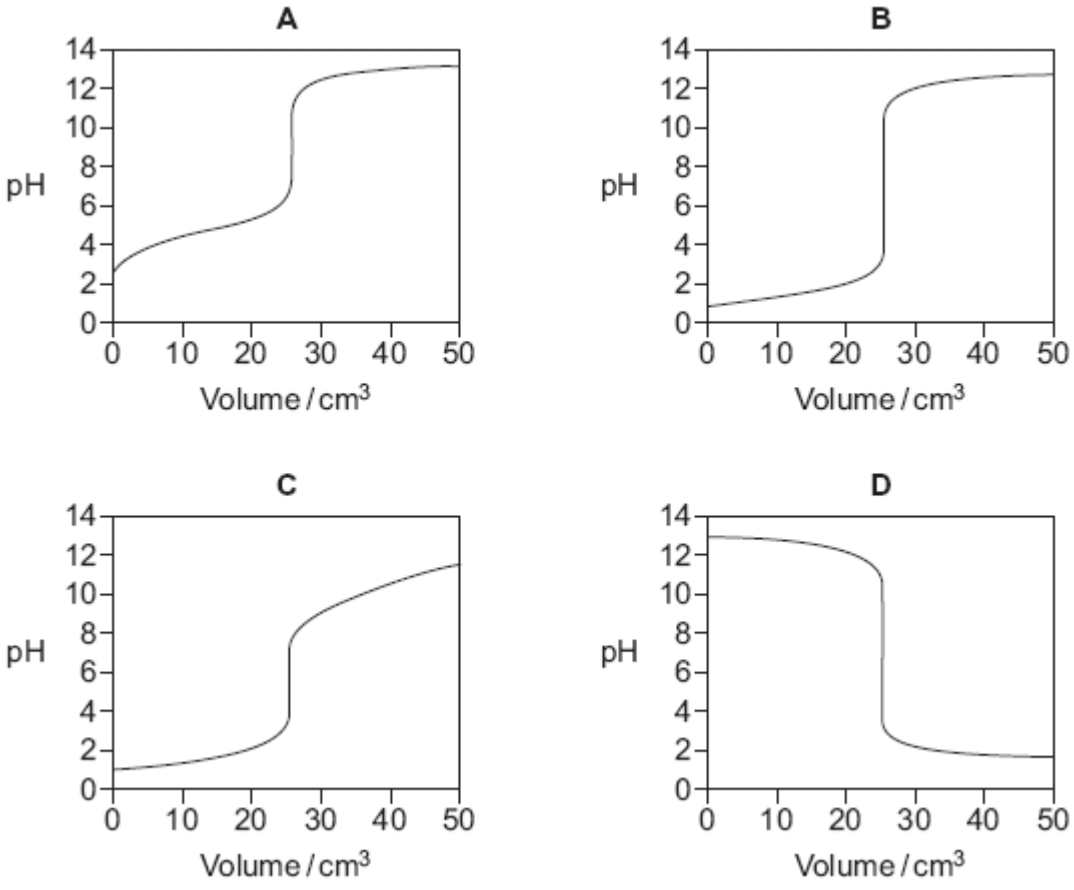
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(5)

(Total 6 marks)

Q11.

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

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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)

Q12.

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.

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Test _____

_____

Observation _____

(2)

(Total 3 marks)

Q13.

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 pK_a value of the acid. The K_a value of the acid can be used to confirm its identity.

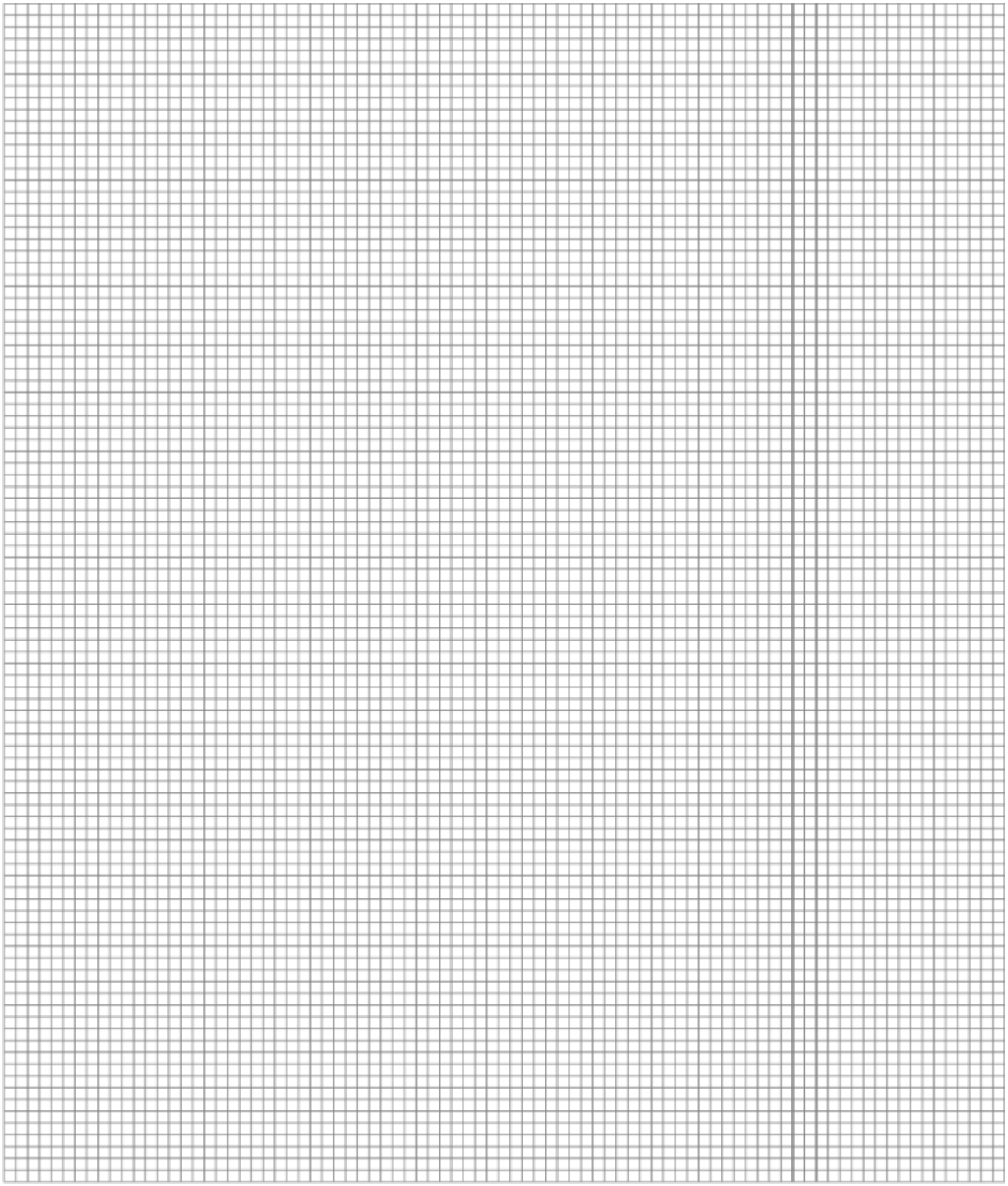
A chemist used a pH curve to determine the pK_a value of acid **Y**, formed during the manufacture of ethanoic acid. The chemist transferred 25.0 cm^3 of a solution of acid **Y** into a beaker using a pipette, and measured the pH of the acid solution using a pH meter which could be read to one decimal 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.

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(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

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(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	1.6×10^{-4}
Ethanoic acid	1.7×10^{-5}
Iodoethanoic acid	6.8×10^{-4}
Propanoic acid	1.3×10^{-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).

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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 1.9×10^{-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)

Q14.

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

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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 1.74×10^{-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)

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(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.

(6)

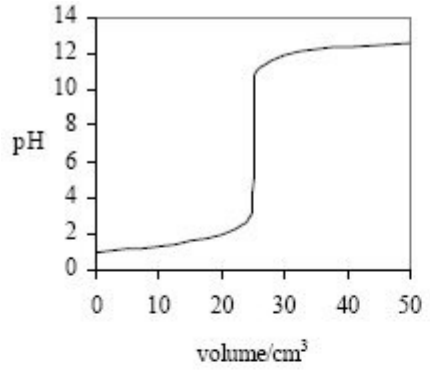
(Total 18 marks)

Q15.

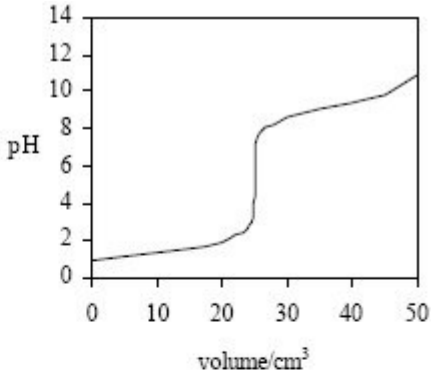
Indicators and pH curves can be used to determine the end point in a titration.

(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}.

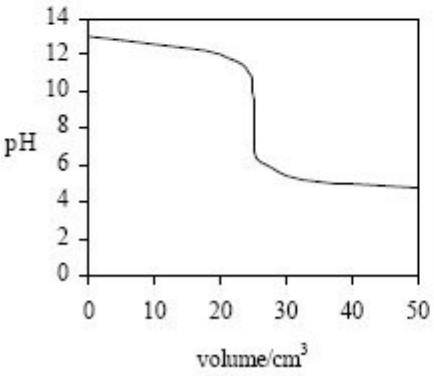
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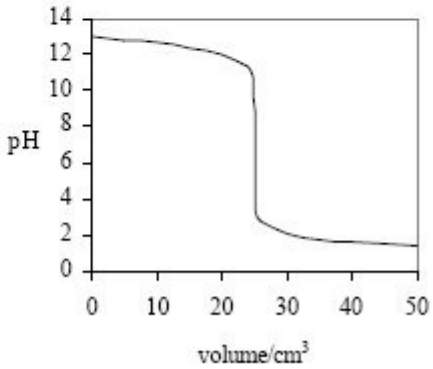
J



K



L



M

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

ammonia to 25 cm^3 of hydrochloric acid _____

ethanoic acid to 25 cm^3 of sodium hydroxide _____

sodium hydroxide to 25 cm^3 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**.

_____

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(4)

(b) The acid dissociation constant, K_a, for the weak acid, ethanoic acid, has a value of 1.74×10^{-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)

Q16.

(a) A sample of hydrochloric acid has a pH of 2.34
Write an expression for pH and calculate the concentration of this acid.

pH _____

Concentration _____

_____

(2)

(b) A 0.150 mol dm^{-3} solution of a weak acid, HX, also has a pH of 2.34

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

_____

_____

(ii) Calculate the value of K_a for this acid and state its units.

Calculation _____

_____

_____

Units

_____

(iii) Calculate the value of pK_a for the acid HX. Give your answer to two decimal

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places.

_____

(5)

(c) A 30.0 cm^3 sample of a 0.480 mol dm^{-3} solution of potassium hydroxide was partially neutralised by the addition of 18.0 cm^3 of a 0.350 mol dm^{-3} solution of sulphuric acid.

(i) Calculate the initial number of moles of potassium hydroxide.

_____

_____

(ii) Calculate the number of moles of sulphuric acid added.

_____

_____

(iii) Calculate the number of moles of potassium hydroxide remaining in excess in the solution formed.

_____

_____

(iv) Calculate the concentration of hydroxide ions in the solution formed.

_____

_____

_____

(v) Hence calculate the pH of the solution formed. Give your answer to two decimal places.

_____

_____

_____

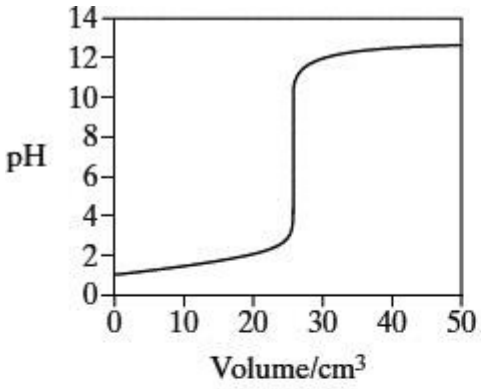
(6)

(Total 13 marks)

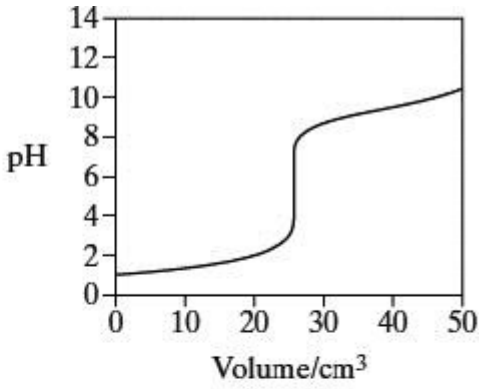
Q17.

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

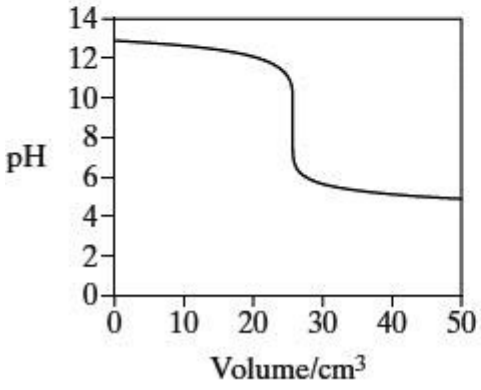
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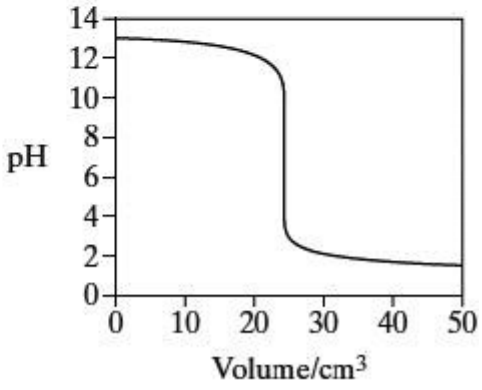
A



B



C



D

(i) Select from **A**, **B**, **C** and **D** the curve produced by the addition of

ammonia to 25 cm^3 of hydrochloric acid _____

ethanoic acid to 25 cm^3 of sodium hydroxide _____

sodium hydroxide to 25 cm^3 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 table an indicator which could be used in the titration which produces curve **A** but not in the titration which produces curve **B**.

_____

(4)

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(b) (i) Write an expression for the term *pH*.

_____

(ii) A solution of potassium hydroxide has a pH of 11.90 at 25°C. Calculate the concentration of potassium hydroxide in the solution.

_____

_____

_____

_____

(4)

(c) The acid dissociation constant, K_a, for propanoic acid has the value of 1.35×10^{-5} mol dm^{-3} at 25 °C.

$$K_a = \frac{[H^+][CH_3CH_2COO^-]}{[CH_3CH_2COOH]}$$

In each of the calculations below, give your answer to 2 decimal places.

(i) Calculate the pH of a 0.117 mol dm^{-3} aqueous solution of propanoic acid.

_____

_____

_____

_____

(ii) Calculate the pH of a mixture formed by adding 25 cm^3 of a 0.117 mol dm^{-3} aqueous solution of sodium propanoate to 25 cm^3 of a 0.117 mol dm^{-3} aqueous solution of propanoic acid.

_____

_____

_____

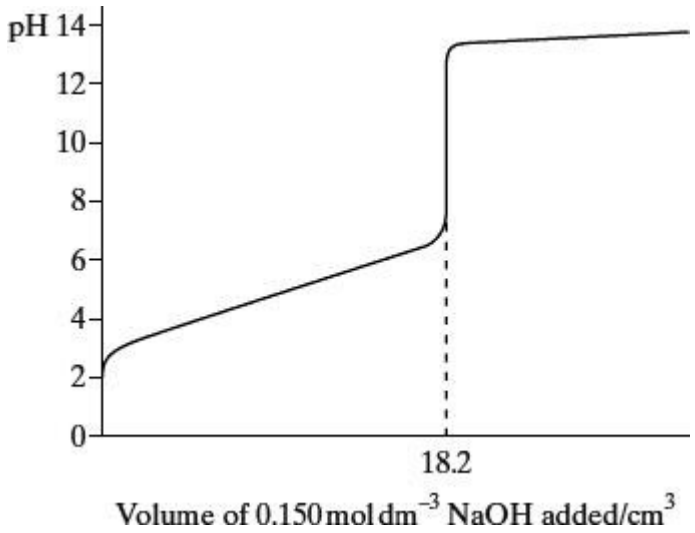
(5)

(Total 13 marks)

Q18.

The pH curve shown below was obtained when a 0.150 mol dm^{-3} solution of sodium hydroxide was added to 25.0 cm^3 of an aqueous solution of a weak monoprotic acid, HA.

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(a) Use the information given to calculate the concentration of the acid.

_____

_____

_____

(2)

(b) (i) Write an expression for the acid dissociation constant, K_a, for HA.

_____

(ii) Write an expression for pK_a

_____

(iii) Using your answers to parts (b)(i) and (b)(ii), show that when sufficient sodium hydroxide has been added to neutralise half of the acid,

pH of the solution = pK_a for the acid HA

_____

_____

_____

(4)

(c) Explain why dilution with a small volume of water does not affect the pH of a buffer solution.

_____

_____

(2)

(d) (i) Calculate the change in pH when 0.250 mol dm^{-3} hydrochloric acid is diluted with water to produce 0.150 mol dm^{-3} hydrochloric acid.

_____

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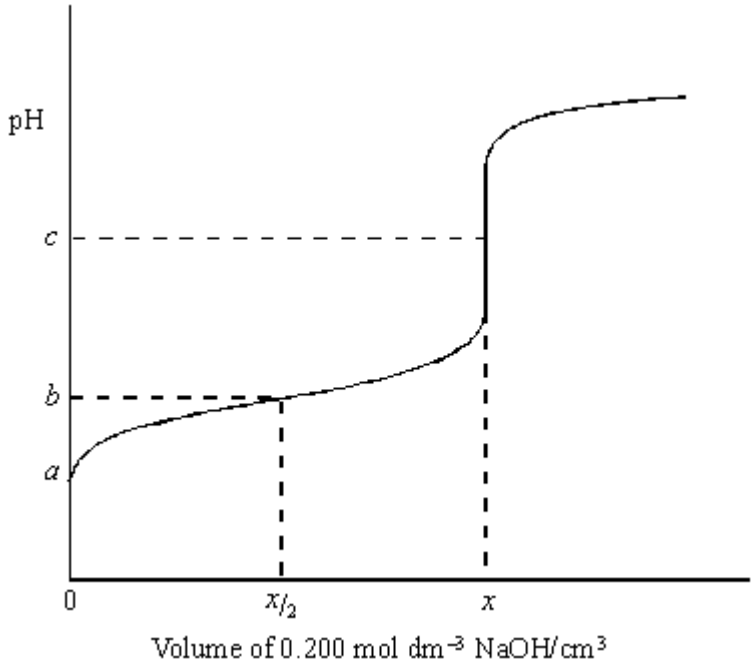
(ii) Calculate the volume of water which must be added to 30.0 cm^3 of 0.250 mol dm^{-3} hydrochloric acid in order to reduce its concentration to 0.150 mol dm^{-3}.

(4)

(Total 12 marks)

Q19.

The sketch below shows the change in pH when a 0.200 mol dm^{-3} solution of sodium hydroxide is added from a burette to 25.0 cm^3 of a 0.150 mol dm^{-3} solution of the weak acid HA at 25 °C.



(a) The volume of sodium hydroxide solution added at the equivalence point is x cm^3. Calculate the value of x.

(2)

(b) (i) Define the term pH.

(ii) The pH at the equivalence point is *c*. Suggest a value for *c*.

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_____

(iii) Identify a suitable indicator for detecting the equivalence point of the titration.

_____

(3)

(c) The value of K_c for the weak acid HA at 25 °C is 2.75×10^{-5} mol dm^{-3}.

(i) Explain the term *weak* as applied to the acid HA.

_____

(ii) Write an expression for K_a for the acid HA.

_____

(iii) Calculate the pH of the 0.150 mol dm^{-3} solution of acid HA before any sodium hydroxide is added, i.e. the pH at point *a*.

_____

_____

_____

_____

_____

(5)

(d) Calculate the pH of the solution formed when $x/2$ cm^3 of the 0.200 mol dm^{-3} solution of sodium hydroxide are added to 25.0 cm^3 of the 0.150 mol dm^{-3} solution of HA, i.e. the pH at point *b*.

_____

_____

_____

(3)

(Total 13 marks)

Q20.

A 0.210 mol dm^{-3} solution of potassium hydroxide was added from a burette to 25.0 cm^3 of a 0.160 mol dm^{-3} solution of ethanoic acid in a conical flask.
Given that the value of the acid dissociation constant, K_a, for ethanoic acid is 1.74×10^{-5} mol dm^{-3}, calculate the pH at 25 °C of the solution in the conical flask at the following three points:

before any potassium hydroxide had been added;

after 8.0 cm^3 of potassium hydroxide solution had been added;

after 40.0 cm^3 of potassium hydroxide solution had been added.

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_____

_____

_____

_____

_____

_____

_____

_____

_____

_____

_____

_____

(Total 16 marks)

Q21.

The value of the acid dissociation constant, K_a, for ethanoic acid is 1.74×10^{-5} mol dm^{-3} at 298 K.

(a) (i) Write an expression for K_a for ethanoic acid.

_____

(ii) Calculate the pH at 298 K of a 0.220 mol dm^{-3} solution of ethanoic acid.

_____

_____

_____

_____

_____

_____

(5)

(b) A sample of the 0.220 mol dm^{-3} solution of ethanoic acid was titrated against sodium hydroxide solution.

(i) Calculate the volume of a 0.150 mol dm^{-3} solution of sodium hydroxide required to neutralise 25.0 cm^3 of the ethanoic acid solution.

_____

_____

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_____

_____

(ii) From the list below, select the best indicator for this titration and explain your choice.

Name of indicator	**pH range**
bromophenol blue	3.0 – 4.6
methyl red	4.2 – 6.3
bromothymol blue	6.0 – 7.6
thymol blue	8.0 – 9.6

Indicator _____

Explanation _____

_____

_____

(5)

(c) A buffer solution is formed when 2.00 g of sodium hydroxide are added to 1.00 dm^3 of a 0.220 mol dm^{-3} solution of ethanoic acid.

Calculate the pH at 298 K of this buffer solution.

_____

_____

_____

_____

_____

_____

_____

(6)

(Total 16 marks)

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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.

(c) 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.

(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.

Hydrochloric acid is a strong acid and ethanoic acid is a weak acid.

(a) State the meaning of the term strong acid.

_____

_____

(1)

(b) In an experiment, 10.35 cm^3 of 0.100 mol dm^{-3} hydrochloric acid are added to 25.0 cm^3 of 0.150 mol dm^{-3} barium hydroxide solution.

Calculate the pH of the solution that forms at 30 °C

$K_w = 1.47 \times 10^{-14}$ mol^2 dm^{-6} at 30 °C

Give your answer to 2 decimal places.

pH _____

(6)

(c) The pH of water at 30 °C is 6.92

Give the reason why water is neutral at this temperature.

_____

_____

(1)

(d) Identify the oxide that could react with water to form a solution with pH = 2

Tick (✔) **one** box.

Al_2O_3 ☐

Na_2O ☐

SiO_2 ☐

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SO_2 ☐

(1)

(e) Give the expression for the acid dissociation constant (K_a) for ethanoic acid (CH_3COOH).

K_a

(1)

(f) A buffer solution contains 0.025 mol of sodium ethanoate dissolved in 500 cm^3 of 0.0700 mol dm^{-3} ethanoic acid at 25 °C

A sample of 5.00 cm^3 of 2.00 mol dm^{-3} hydrochloric acid is added to this buffer solution.

Calculate the pH of the solution formed.

For ethanoic acid, $K_a = 1.76 \times 10^{-5}$ mol dm^{-3} at 25 °C

pH _____

(5)

(Total 15 marks)

Q2.

The ionic product of water, $K_w = 2.93 \times 10^{-15}$ $mol^2\,dm^{-6}$ at 10 °C

(a) Which is the correct expression for K_w?

Tick (✔) **one** box.

A $K_w = \frac{[H_2O]}{[H^+][OH^-]}$ ☐

B $K_w = [H^+][H_2O]$ ☐

C $K_w = [H^+][OH^-]$ ☐

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D $K_w = \frac{[H^+][OH^-]}{[H_2O]}$ ☐

(1)

(b) Calculate the pH of pure water at 10 °C

Give your answer to two decimal places.

pH of water _____

(2)

(c) Suggest why this pure water at 10 °C is **not** alkaline.

_____

_____

_____

(1)

(d) Calculate the pH of a 0.0131 mol dm^{-3} solution of calcium hydroxide at 10 °C

Give your answer to two decimal places.

pH of solution _____

(3)

(e) The 0.0131 mol dm^{-3} calcium hydroxide solution at 10 °C was a saturated solution.

A student added 0.0131 mol of magnesium hydroxide to 1.00 dm^3 of water at 10 °C and stirred the mixture until no more solid dissolved.

Predict whether the pH of the magnesium hydroxide solution formed at 10 °C is larger than, smaller than or the same as the pH of the calcium hydroxide solution at 10 °C

Explain your answer.

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pH of magnesium hydroxide compared to calcium hydroxide

_____

Explanation _____

_____

_____

(2)

(Total 9 marks)

Q3.

What is the pH of a 0.46 mol dm^{-3} solution of potassium hydroxide at 298 K?

(K_w = 1.0 × 10^{-14} mol^2 dm^{-6} at 298 K)

A 0.34 ○

B 13.66 ○

C 13.96 ○

D 14.34 ○

(Total 1 mark)

Q4.

This question is about Brønsted–Lowry acids.

(a) Give the meaning of the term Brønsted–Lowry acid.

_____

_____

(1)

(b) What is meant by the term strong when describing an acid?

_____

_____

(1)

(c) At 298 K, 25.0 cm^3 of a solution of a strong monoprotic acid contained 1.45 × 10^{-3} mol of hydrogen ions.

Calculate a value for the pH of this solution.
Give your answer to 2 decimal places.

pH _____

(2)

(d) Calculate the pH of the solution formed after the addition of 35.0 cm^3 of 0.150 mol

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dm^{-3} NaOH to the original 25.0 cm^3 of monoprotic acid.

The ionic product of water K_w = 1.00 × 10^{-14} mol^2 dm^{-6} at 298 K.
Give your answer to two decimal places.

pH _____

(5)

(e) A buffer solution is made when 1.50 g of sodium hydroxide are added to 1.00 dm^3 of a 0.150 mol dm^{-3} solution of a weak acid HA.

For HA, the acid dissociation constant, K_a = 1.79 × 10^{-5} mol dm^{-3}.

Calculate the pH of this buffer solution.

pH _____

(6)

(Total 15 marks)

Q5.

Nitric acid (HNO_{-3}) is a strong acid. Ethanoic acid (CH_3COOH) is a weak acid.

(a) Write an equation to show how ethanoic acid behaves as a weak acid in its reaction with water.

_____

(1)

(b) When pure ethanoic acid reacts with pure nitric acid, ethanoic acid acts as a base.

Write an equation for this reaction.

_____

(1)

(c) Two beakers, **A** and **B**, each contain 100.0 cm^{-3} of 0.0125 mol dm^{-3} nitric acid.

(i) Calculate the pH of the solution formed after 50.0 cm^{-3} of distilled water are added to beaker **A**.
Give your answer to 2 decimal places.

_____

_____

_____

(2)

(ii) Calculate the pH of the solution formed after 50.0 cm^3 of 0.0108 mol dm^{-3} aqueous sodium hydroxide are added to beaker **B**.
Give your answer to 2 decimal places.

_____

_____

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_____

_____

_____

_____

_____

(4)

(d) A third beaker, **C**, contains 100.0 cm^3 of 0.0125 mol dm^{-3} ethanoic acid.
The acid dissociation constant K_a for ethanoic acid has the value 1.74×10^{-5} mol dm^{-3} at 25 °C.

(i) Write an expression for K_a for ethanoic acid and use it to calculate the pH of the ethanoic acid solution in beaker **C**.
Show your working. Give your answer to 2 decimal places.

K_a _____

_____

Calculation _____

_____

_____

_____

(4)

(ii) Aqueous sodium hydroxide is added to beaker **C** until the pH of the solution becomes 4.84.

Name the salt formed in the reaction of ethanoic acid with sodium hydroxide.

_____

(1)

(iii) Calculate the value of $\frac{[\text{salt}]}{[\text{ethanoic acid}]}$ in the solution with the pH of 4.84.

_____

_____

_____

_____

_____

_____

(3)

(e) Explain why chloroethanoic acid is a stronger acid than ethanoic acid.

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_____

_____

_____

_____

(2)

(f) Explain why data books do not usually contain values of K_a for strong acids.

_____

_____

_____

_____

(2)

(Total 20 marks)

Q6.

Water dissociates slightly according to the equation:

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

The ionic product of water, K_w, is given by the expression

$$K_w = [H^+][OH^-]$$

K_w varies with temperature as shown in the table.

Temperature / °C	**K_w / mol² dm⁻⁶**
25	1.00×10^{-14}
50	5.48×10^{-14}

(a) Explain why the expression for K_w does **not** include the concentration of water.

_____

_____

_____

_____

_____

(2)

(b) Explain why the value of K_w increases as the temperature increases.

_____

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(2)

(c) Calculate the pH of pure water at 50 °C.
Give your answer to 2 decimal places.

(3)

(d) Calculate the pH of 0.12 mol dm^{-3} aqueous NaOH at 50 °C.
Give your answer to 2 decimal places.

(3)

(Total 10 marks)

Q7.

This question is about alkalis and carboxylic acids.

In this question, all data are quoted at 25 °C.

(a) Carboxylic acids are weak acids.

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State the meaning of the term **weak** as applied to carboxylic acids.

_____

_____

(1)

(b) Write an equation for the reaction of propanoic acid with sodium carbonate.

_____

(1)

(c) Calculate the pH of a 0.0120 mol dm^{-3} solution of calcium hydroxide.
The ionic product of water $K_w = 1.00 \times 10^{-14}$ mol^2 dm^{-6}.
Give your answer to 2 decimal places.

_____

_____

_____

_____

_____

_____

(3)

(d) The value of the acid dissociation constant K_a for benzenecarboxylic acid (C_6H_5COOH) is 6.31×10^{-5} mol dm^{-3}.

(i) Write an expression for the acid dissociation constant K_a for benzenecarboxylic acid.

_____

_____

(1)

(ii) Calculate the pH of a 0.0120 mol dm^{-3} solution of benzenecarboxylic acid.
Give your answer to 2 decimal places.

_____

_____

_____

_____

_____

_____

_____

_____

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(3)

(iii) A buffer solution with a pH of 4.00 is made using benzenecarboxylic acid and sodium benzenecarboxylate.

Calculate the mass of sodium benzenecarboxylate (M_r = 144.0) that should be dissolved in 1.00 dm^3 of a 0.0120 mol dm^{-3} solution of benzenecarboxylic acid to produce a buffer solution with a pH of 4.00

The value of the acid dissociation constant K_a for benzenecarboxylic acid (C_6H_5COOH) is 6.31 × 10^{-5} mol dm^{-3}.

_____

_____

_____

_____

_____

_____

_____

_____

_____

(5)

(e) Two solutions, one with a pH of 4.00 and the other with a pH of 9.00, were left open to the air.

The pH of the pH 9.00 solution changed more than that of the other solution.

Suggest what substance might be present in the air to cause the pH to change. Explain how and why the pH of the pH 9.00 solution changes.

Substance present in air _____

Explanation _____

_____

_____

_____

_____

(3)

(Total 17 marks)

Q8.

This question involves calculations about two strong acids and one weak acid.
All measurements were carried out at 25 °C.

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(a) A 25.0 cm^3 sample of 0.0850 mol dm^{-3} hydrochloric acid was placed in a beaker and 100 cm^3 of distilled water were added.
Calculate the pH of the new solution formed.
Give your answer to 2 decimal places.

(2)

(b) HX is a weak monobasic acid.

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

(1)

(ii) The pH of a 0.0850 mol dm^{-3} solution of HX is 2.79
Calculate a value for the acid dissociation constant, K_a, of this acid.
Give your answer to 3 significant figures.

(3)

(c) A 25.0 cm^3 sample of 0.620 mol dm^{-3} nitric acid was placed in a beaker and 38.2 cm^3 of 0.550 mol dm^{-3} aqueous sodium hydroxide were added.
Calculate the pH of the solution formed.
Give your answer to 2 decimal places.

The ionic product of water $K_w = 1.00 \times 10^{-14}$ mol^2 dm^{-6} at 25 °C.

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_____

_____

_____

_____

(6)

(Total 12 marks)

Q9.

This question is about the pH of some solutions containing potassium hydroxide and ethanoic acid.

Give all values of pH to 2 decimal places.

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

_____

(1)

(ii) Write an expression for the ionic product of water, K_w

_____

(1)

(iii) At 10 °C, a 0.154 mol dm^{-3} solution of potassium hydroxide has a pH of 13.72. Calculate the value of K_w at 10 °C.

_____

_____

_____

_____

(2)

(b) At 25 °C, the acid dissociation constant K_a for ethanoic acid has the value 1.75×10^{-5} mol dm^{-3}.

(i) Write an expression for K_a for ethanoic acid.

_____

_____

(1)

(ii) Calculate the pH of a 0.154 mol dm^{-3} solution of ethanoic acid at 25 °C.

_____

_____

_____

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(3)

(c) At 25 °C, the acid dissociation constant K_a for ethanoic acid has the value 1.75×10^{-5} mol dm^{-3}.

(i) Calculate the pH of the solution formed when 10.0 cm^3 of 0.154 mol dm^{-3} potassium hydroxide are added to 20.0 cm^3 of 0.154 mol dm^{-3} ethanoic acid at 25 °C.

(4)

(ii) Calculate the pH of the solution formed when 40.0 cm^3 of 0.154 mol dm^{-3} potassium hydroxide are added to 20.0 cm^3 of 0.154 mol dm^{-3} ethanoic acid at 25 °C.

At 25 °C, K_w has the value 1.00×10^{-14} mol^2 dm^{-6}.

(4)

(Total 16 marks)

Q10.

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

Calculating the pH of aqueous solutions can involve the use of equilibrium constants such as K_w and K_a

K_w is the ionic product of water. The value of K_w is 5.48×10^{-14} mol^2 dm^{-6} at 50 °C.

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

_____

(1)

(ii) Write an expression for K_w

_____

(1)

(b) (i) Calculate the pH of pure water at 50 °C.

_____

_____

_____

(2)

(ii) Suggest why this pure water is **not** acidic.

_____

_____

(1)

(iii) Calculate the pH of 0.140 mol dm^{-3} aqueous sodium hydroxide at 50 °C.

_____

_____

_____

_____

_____

(3)

(c) Calculate the pH of the solution formed when 25.0 cm^3 of 0.150 mol dm^{-3} aqueous sulfuric acid are added to 30.0 cm^3 of 0.200 mol dm^{-3} aqueous potassium hydroxide at 25 °C. Assume that the sulfuric acid is fully dissociated.

_____

_____

_____

_____

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_____

_____

_____

_____

_____

_____

(6)

(Total 14 marks)

Q11.

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)

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(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 1.74×10^{-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)

Q12.

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

(a) (i) Write expressions for the ionic product of water, K_w, and for pH.

K_w = _____

pH = _____

(ii) At 318 K, the value of K_w is 4.02×10^{-14} mol^2 dm^{-6} and hence the pH of pure water is 6.70
State why pure water is not acidic at 318 K.

_____

_____

(iii) Calculate the number of moles of sodium hydroxide in 2.00 cm^3 of 0.500 mol dm^{-3} aqueous sodium hydroxide.

_____

_____

(iv) Use the value of K_w given above and your answer to part (a)(iii) to calculate the pH of the solution formed when 2.00 cm^3 of 0.500 mol dm^{-3} aqueous sodium hydroxide are added to 998 cm^3 of pure water at 318 K.

_____

_____

_____

_____

_____

(6)

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(b) At 298 K, the acid dissociation constant, K_a, for propanoic acid, CH_3CH_2COOH, has the value 1.35×10^{-5} mol dm^{-3}.

(i) Write an expression for K_a for propanoic acid.

_____

_____

(ii) Calculate the pH of 0.125 mol dm^{-3} aqueous propanoic acid at 298 K.

_____

_____

_____

_____

_____

_____

(4)

(c) Sodium hydroxide reacts with propanoic acid as shown in the following equation.

$$NaOH + CH_3CH_2COOH \rightarrow CH_3CH_2COONa + H_2O$$

A buffer solution is formed when sodium hydroxide is added to an excess of aqueous propanoic acid.

(i) Calculate the number of moles of propanoic acid in 50.0 cm^3 of 0.125 mol dm^{-3} aqueous propanoic acid.

_____

_____

(ii) Use your answers to part (a)(iii) and part (c)(i) to calculate the number of moles of propanoic acid in the buffer solution formed when 2.00 cm^3 of 0.500 mol dm^{-3} aqueous sodium hydroxide are added to 50.0 cm^3 of 0.125 mol dm^{-3} aqueous propanoic acid.

_____

_____

_____

(iii) Hence calculate the pH of this buffer solution at 298 K.

_____

_____

_____

_____

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_____

_____

(6)

(Total 16 marks)

Q13.

(a) By reference to the forces between molecules, explain why ammonia is very soluble in water.

_____

_____

(2)

(b) Aqueous solutions of ammonia have a pH greater than 7.

(i) Write an equation for the reaction of ammonia with water.

_____

(ii) Explain why the pH of a solution containing 1.0 mol dm^{-3} of ammonia is less than
14 at 298 K.

_____

_____

(3)

(c) An ammonium ion in aqueous solution can behave as a Brønsted–Lowry acid. State what is meant by the term *Brønsted–Lowry acid*.

_____

(1)

(d) State what is meant by the term *buffer solution*. Identify a reagent which could be added to a solution of ammonia in order to form a buffer solution.

Buffer solution _____

_____

Reagent _____

(3)

(e) An acidic buffer solution is obtained when sodium ethanoate is dissolved in aqueous ethanoic acid.

(i) Calculate the pH of the buffer solution formed at 298 K when 0.125 mol of sodium ethanoate is dissolved in 250 cm^3 of a 1.00 mol dm^{-3} solution of ethanoic acid.
The acid dissociation constant, K_a, for ethanoic acid is 1.70×10^{-5} mol dm^{-3} at 298 K.

_____

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_____

_____

_____

_____

_____

(ii) Write an ionic equation for the reaction which occurs when a small volume of dilute hydrochloric acid is added to this buffer solution.

_____

(5)

(Total 14 marks)

Q14.

Use the information below to answer this question.

A saturated solution of magnesium hydroxide, $Mg(OH)_2$, contains 0.1166 g of $Mg(OH)_2$ in 10.00 dm^3 of solution. In this solution the magnesium hydroxide is fully dissociated into ions.

Which one of the following is the pH of a solution of magnesium hydroxide containing 4.0×10^{-5} mol dm^{-3} of hydroxide ions at 298 K?
($K_w = 1.0 \times 10^{-14}$ mol^2 dm^{-6} at 298 K)

A 9.6

B 9.5

C 8.6

D 8.3

(Total 1 mark)

Q15.

(a) At 50°C, the ionic product of water, K_w, has the value 5.48×10^{-14} mol^2 dm^{-6}.

(i) Define the term K_w

_____

(ii) Define the term *pH*

_____

(iii) Calculate the pH of pure water at 50 °C. Explain why pure water at 50 °C is still neutral even though its pH is not 7.

Calculation _____

_____

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_____

Explanation _____

_____

(5)

(b) At 25°C, K_w has the value 1.00×10^{-14} mol^2 dm^{-6}. Calculate the pH at 25 °C of

(i) a 0.150 mol dm^{-3} solution of sodium hydroxide,

_____

_____

_____

(ii) the solution formed when 35.0 cm^3 of this solution of sodium hydroxide is mixed with 40.0 cm^3 of a 0.120 mol dm^{-3} solution of hydrochloric acid.

_____

_____

_____

_____

_____

_____

_____

(8)

(c) In a 0.150 mol dm^{-3} solution of a weak acid HX at 25 °C, 1.80% of the acid molecules are dissociated into ions.

(i) Write an expression for K_a for the acid HX.

_____

_____

(ii) Calculate the value of K_a for the acid HX at this temperature and state its units.

_____

_____

_____

_____

_____

_____

(5)

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(Total 18 marks)

Q16.

An aqueous solution contains 4.0 g of sodium hydroxide in 250 cm^3 of solution.
(K_w = 1.00 × 10^{-14} mol^2 dm^{-6})

The pH of the solution is

A 13.0

B 13.3

C 13.6

D 13.9

(Total 1 mark)

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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

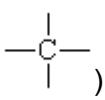
(c) If wrong K_a in (i) max 2 in part (ii) for $[H^+]$ **(1)** and conseq units **(1)**
but mark on fully from minor errors
eg no [ ] or charges missing

Organic points

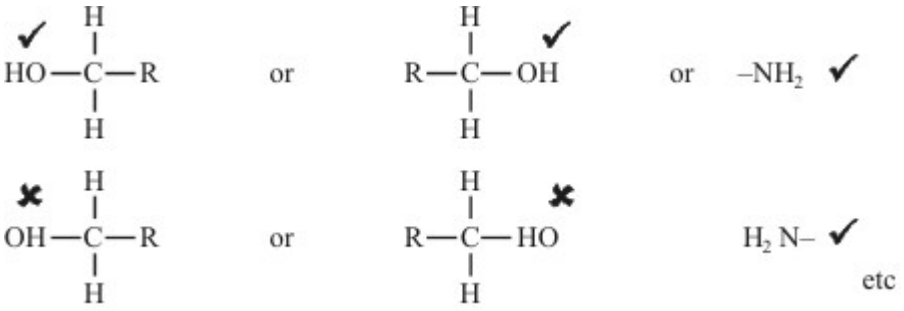
(1) Curly arrows: must show movement of a pair of electrons, i.e. from bond to atom or from lp to atom / space
e.g.



(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.

Hydrochloric acid is a strong acid and ethanoic acid is a weak acid.

(a) State the meaning of the term strong acid.

_____

_____

(1)

(b) In an experiment, 10.35 cm^3 of 0.100 mol dm^{-3} hydrochloric acid are added to 25.0 cm^3 of 0.150 mol dm^{-3} barium hydroxide solution.

Calculate the pH of the solution that forms at 30 °C

$K_w = 1.47 \times 10^{-14}$ mol^2 dm^{-6} at 30 °C

Give your answer to 2 decimal places.

pH _____

(6)

(c) The pH of water at 30 °C is 6.92

Give the reason why water is neutral at this temperature.

_____

_____

(1)

(d) Identify the oxide that could react with water to form a solution with pH = 2

Tick (✔) **one** box.

Al_2O_3 ☐

Na_2O ☐

SiO_2 ☐

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SO_2 ☐

(1)

(e) Give the expression for the acid dissociation constant (K_a) for ethanoic acid (CH_3COOH).

K_a

(1)

(f) A buffer solution contains 0.025 mol of sodium ethanoate dissolved in 500 cm^3 of 0.0700 mol dm^{-3} ethanoic acid at 25 °C

A sample of 5.00 cm^3 of 2.00 mol dm^{-3} hydrochloric acid is added to this buffer solution.

Calculate the pH of the solution formed.

For ethanoic acid, $K_a = 1.76 \times 10^{-5}$ mol dm^{-3} at 25 °C

pH _____

(5)

(Total 15 marks)

Q2.

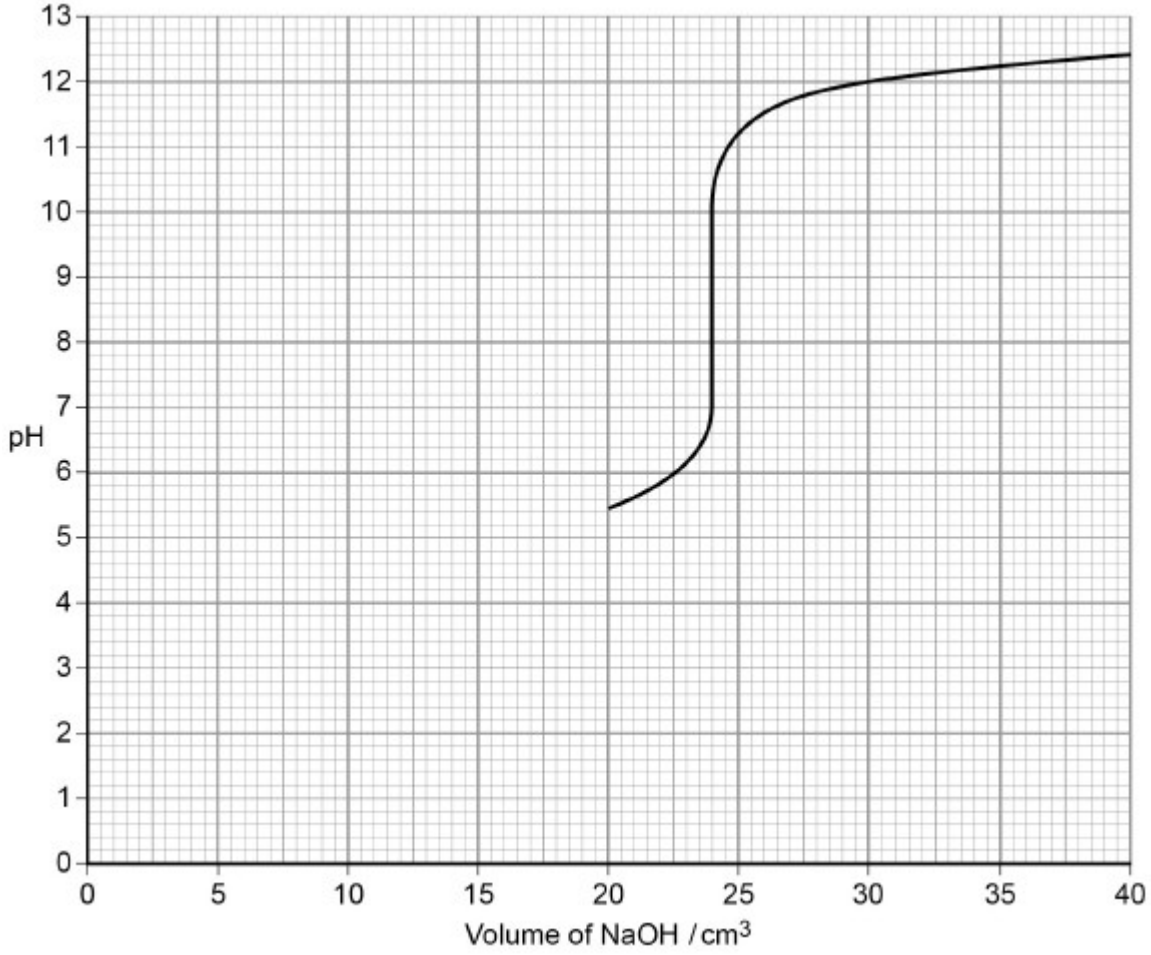
A 0.100 mol dm^{-3} solution of sodium hydroxide was gradually added to 25.0 cm^3 of a solution of a weak acid, HX, in the presence of a suitable indicator.

A graph was plotted of pH against the volume of sodium hydroxide solution, as shown in the figure below.

The first pH reading was taken after 20.0 cm^3 of sodium hydroxide solution had been added.

The acid dissociation constant of HX, K_a, = 2.62×10^{-5} mol dm^{-3}

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(a) The pH range of an indicator is the range over which it changes colour.

Suggest the pH range of a suitable indicator for this titration.

_____

(1)

(b) Give the expression for the acid dissociation constant of HX.

K_a =

(1)

(c) Calculate the concentration of HX in the original solution.

Concentration _____ mol dm^{-3}

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(2)

(d) Calculate the pH of the solution of HX before the addition of any sodium hydroxide.

(If you were unable to calculate a value for the concentration of HX in part (c) you should use a value of 0.600 mol dm^{-3} in this calculation. This is not the correct value.)

pH of HX _____

(2)

(e) Calculate the pH of the solution when half of the acid has reacted.

pH of solution _____

(1)

(f) Plot your answers to part (d) and part (e) on the grid in the figure above.

Use these points to sketch the missing part of the curve between 0 and 20 cm^3 of NaOH solution added.

(2)

(Total 9 marks)

Q3.

A student carried out an experiment to find the temperature rise for a reaction between hydrochloric acid and sodium hydroxide solution.

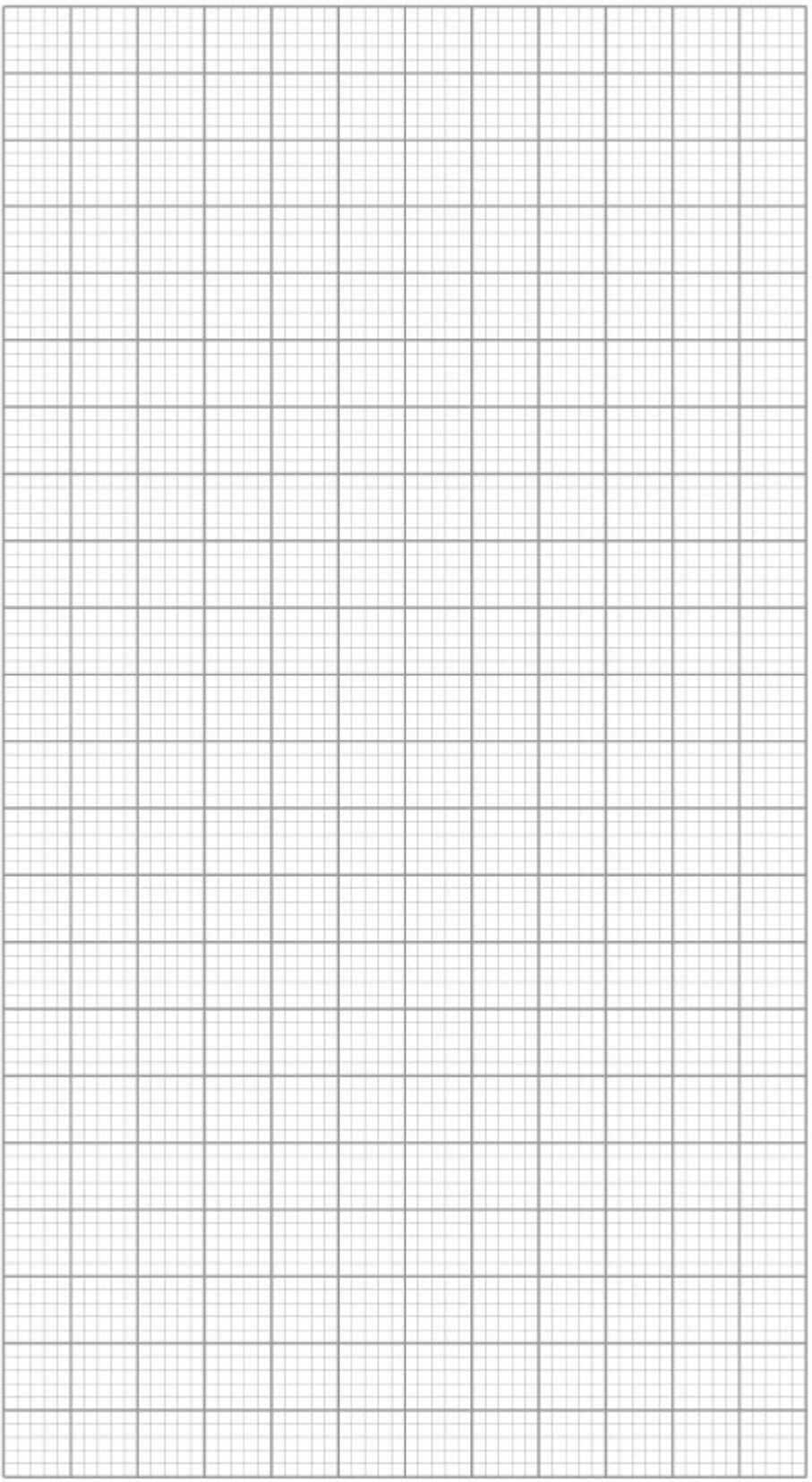
- The student used a measuring cylinder to place 50 cm^3 of 0.400 mol dm^{-3} hydrochloric acid into a glass beaker.
- The student recorded the temperature at one-minute intervals for three minutes.
- At the fourth minute the student added 50 cm^3 of 0.400 mol dm^{-3} sodium hydroxide solution and stirred to mix the solutions, but did not record the temperature.
- The student recorded the temperature at one-minute intervals for a further eight minutes.

The results are shown in the table.

Time / min	0	1	2	3	4	5	6	7	8	9	10	11	12
Temperature / °C	19.8	19.8	19.8	19.8		21.4	21.7	21.6	21.5	21.4	21.3	21.2	21.1

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(a) Plot a graph of temperature against time on the grid below.



Use your graph to find the temperature rise, ΔT, at the fourth minute.
Show your working on the graph by drawing suitable lines of best fit.

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ΔT _____ °C

(5)

(b) The uncertainty in each of the temperature readings from the thermometer used in this experiment was ±0.1° C

Calculate the percentage uncertainty in the value for the temperature rise.

Percentage uncertainty _____

(1)

(c) Suggest a change to the experiment that would minimise heat loss.

_____

_____

(1)

(d) Suggest and explain another change to the experiment that would decrease the percentage uncertainty in the use of the same thermometer.

_____

_____

_____

_____

(2)

(e) A second student completed an experiment to determine the enthalpy of neutralisation for the reaction between ethanedioic acid solution (HOOCCOOH) and potassium hydroxide solution.

The student added 25 cm^3 of 0.80 mol dm^{-3} ethanedioic acid solution to 75 cm^3 of 0.60 mol dm^{-3} potassium hydroxide solution.
The temperature increased by 3.2 °C

Give an equation for the reaction between ethanedioic acid solution and potassium hydroxide solution.
Calculate the enthalpy change (ΔH) per mole of water formed in this reaction.
Assume that the specific heat capacity of the reaction mixture is 4.2 J K^{-1} g^{-1}
Assume that the density of the reaction mixture is 1.00 g cm^{-3}
Equation _____

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ΔH _____ kJ mol^{-1}

(5)

(f) In a similar experiment to that in **part (e)**, the enthalpy of neutralisation for the reaction between sulfuric acid and potassium hydroxide solution was found to be –57.0 kJ mol^{-1} per mole of water formed.

Suggest an explanation for the difference between this value and your answer to **part (e)**.

(If you were unable to obtain an answer to **part (e)** you should assume a value of –28.5 kJ mol^{-1}. This is **not** the correct answer.)

_____

_____

_____

_____

_____

_____

(2)

(Total 16 marks)

Q4.

2,4,6-Trichlorophenol is a weak monoprotic acid, with $K_a = 2.51 \times 10^{-8}$ mol dm^{-3} at 298 K.

What is the concentration, in mol dm^{-3}, of hydrogen ions in a 2.00×10^{-3} mol dm^{-3} solution of 2,4,6-trichlorophenol at 298 K?

A 5.02×10^{-11} ⬭

B 7.09×10^{-6} ⬭

C 1.26×10^{-5} ⬭

D 3.54×10^{-3} ⬭

(Total 1 mark)

Q5.

The table shows the pK_a values for two acids.

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Name of acid	pK_a
Propanoic acid	4.87
Butanoic acid	4.82

Which statement is correct?

A Propanoic acid is a stronger acid than butanoic acid. ⬭

B The value of K_a for propanoic acid is greater than that for butanoic acid. ⬭

C The value of K_a for propanoic acid is 1.35×10^{-5} mol dm^{-3} ⬭

D The value of K_a for butanoic acid is 6.61 × 104 mol dm–$^{-3}$ ⬭

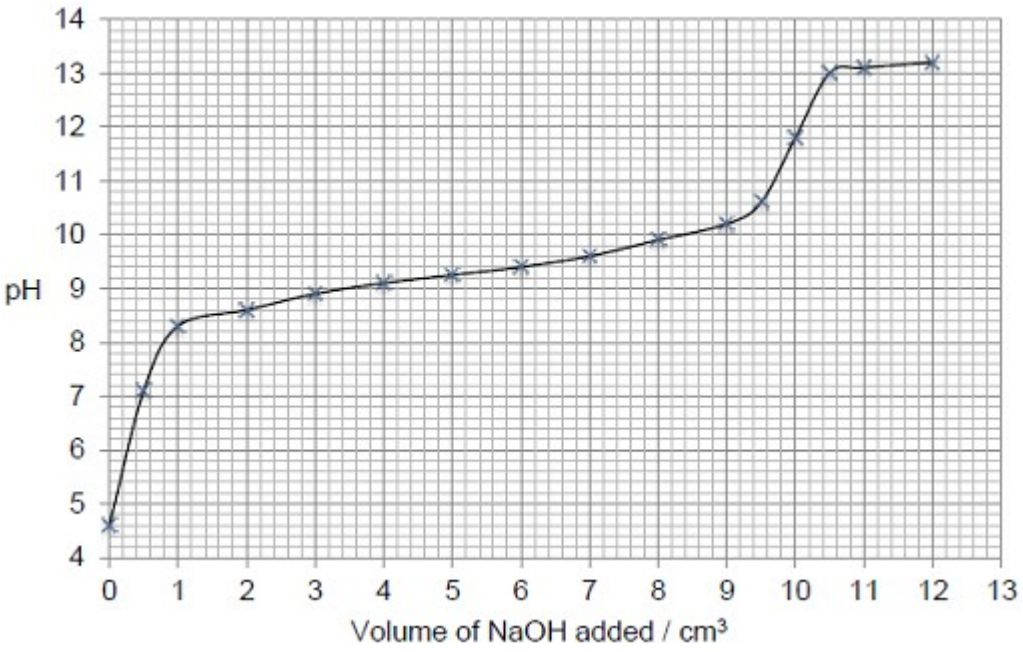
(Total 1 mark)

Q6.

Ammonium chloride, when dissolved in water, can act as a weak acid as shown by the following equation.

$$NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq)$$

The following figure shows a graph of data obtained by a student when a solution of sodium hydroxide was added to a solution of ammonium chloride. The pH of the reaction mixture was measured initially and after each addition of the sodium hydroxide solution.



(a) Suggest a suitable piece of apparatus that could be used to measure out the sodium hydroxide solution.
Explain why this apparatus is more suitable than a pipette for this purpose.

Apparatus_____

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Explanation _____

_____

_____

(2)

(b) Use information from the curve in the figure above to explain why the end point of this reaction would be difficult to judge accurately using an indicator.

_____

_____

_____

_____

_____

(2)

(c) The pH at the end point of this reaction is 11.8.

Use this pH value and the ionic product of water, $K_w = 1.0 \times 10^{-14}$ mol^2 dm^{-6}, to calculate the concentration of hydroxide ions at the end point of the reaction.

Concentration = _____ mol dm^{-3}

(3)

(d) The expression for the acid dissociation constant for aqueous ammonium ions is

$$K_a = \frac{[NH_3][H^+]}{[NH_4^+]}$$

The initial concentration of the ammonium chloride solution was 2.00 mol dm^{-3}.

Use the pH of this solution, before any sodium hydroxide had been added, to calculate a value for K_a

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K_a = _____ mol dm^{-3}

(3)

(e) A solution contains equal concentrations of ammonia and ammonium ions.

Use your value of K_a from part **(d)** to calculate the pH of this solution. Explain your working.

(If you were unable to calculate a value for K_a you may assume that it has the value 4.75×10^{-9} mol dm^{-3}. This is **not** the correct value.)

pH = _____

(2)

(Total 12 marks)

Q7.

The acid dissociation constant, K_a, of a weak acid HA has the value 2.56×10^{-4} mol dm^{-3}.

What is the pH of a 4.25×10^{-3} mol dm^{-3} solution of HA?

A 5.96 ⬭

B 3.59 ⬭

C 2.98 ⬭

D 2.37 ⬭

(Total 1 mark)

Q8.

Nitric acid (HNO_3) is a strong acid. Ethanoic acid (CH_3COOH) is a weak acid.

(a) Write an equation to show how ethanoic acid behaves as a weak acid in its reaction with water.

_____

(1)

(b) When pure ethanoic acid reacts with pure nitric acid, ethanoic acid acts as a base.

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Write an equation for this reaction.

_____

(1)

(c) Two beakers, **A** and **B**, each contain 100.0 cm^{-3} of 0.0125 mol dm^{-3} nitric acid.

(i) Calculate the pH of the solution formed after 50.0 cm^{-3} of distilled water are added to beaker **A**.
Give your answer to 2 decimal places.

_____

_____

_____

(2)

(ii) Calculate the pH of the solution formed after 50.0 cm^3 of 0.0108 mol dm^{-3} aqueous sodium hydroxide are added to beaker **B**.
Give your answer to 2 decimal places.

_____

_____

_____

_____

_____

_____

_____

(4)

(d) A third beaker, **C**, contains 100.0 cm^3 of 0.0125 mol dm^{-3} ethanoic acid.
The acid dissociation constant K_a for ethanoic acid has the value 1.74×10^{-5} mol dm^{-3} at 25 °C.

(i) Write an expression for K_a for ethanoic acid and use it to calculate the pH of the ethanoic acid solution in beaker **C**.
Show your working. Give your answer to 2 decimal places.

K_a _____

_____

Calculation _____

_____

_____

_____

(4)

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(ii) Aqueous sodium hydroxide is added to beaker **C** until the pH of the solution becomes 4.84.

Name the salt formed in the reaction of ethanoic acid with sodium hydroxide.

_____

(1)

(iii) Calculate the value of $\frac{[\text{salt}]}{[\text{ethanoic acid}]}$ in the solution with the pH of 4.84.

_____

_____

_____

_____

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_____

(3)

(e) Explain why chloroethanoic acid is a stronger acid than ethanoic acid.

_____

_____

_____

_____

(2)

(f) Explain why data books do not usually contain values of K_a for strong acids.

_____

_____

_____

_____

(2)

(Total 20 marks)

Q9.

A solution of chlorine in water is acidic. Swimming pool managers maintain pool water at a constant pH by using a buffer. They do so by adding sodium hydrogencarbonate and sodium carbonate.

(a) Hydrogen carbonate ions (HCO_3^-) act as a weak acid in aqueous solution. Write an equation for this equilibrium.

_____

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_____

_____

(1)

(b) Use the equation in part (a) to explain how a solution containing sodium hydrogencarbonate and sodium carbonate can act as a buffer when small amounts of acid or small amounts of alkali are added.

_____

_____

_____

_____

_____

_____

_____

_____

(3)

(Total 4 marks)

Q10.

This question is about alkalis and carboxylic acids.

In this question, all data are quoted at 25 °C.

(a) Carboxylic acids are weak acids.

State the meaning of the term **weak** as applied to carboxylic acids.

_____

_____

(1)

(b) Write an equation for the reaction of propanoic acid with sodium carbonate.

_____

(1)

(c) Calculate the pH of a 0.0120 mol dm^{-3} solution of calcium hydroxide.
The ionic product of water $K_w = 1.00 \times 10^{-14}$ mol^2 dm^{-6}.
Give your answer to 2 decimal places.

_____

_____

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_____

_____

_____

(3)

(d) The value of the acid dissociation constant K_a for benzenecarboxylic acid (C_6H_5COOH) is 6.31×10^{-5} mol dm^{-3}.

(i) Write an expression for the acid dissociation constant K_a for benzenecarboxylic acid.

_____

_____

(1)

(ii) Calculate the pH of a 0.0120 mol dm^{-3} solution of benzenecarboxylic acid. Give your answer to 2 decimal places.

_____

_____

_____

_____

_____

_____

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_____

(3)

(iii) A buffer solution with a pH of 4.00 is made using benzenecarboxylic acid and sodium benzenecarboxylate.

Calculate the mass of sodium benzenecarboxylate (M_r = 144.0) that should be dissolved in 1.00 dm^3 of a 0.0120 mol dm^{-3} solution of benzenecarboxylic acid to produce a buffer solution with a pH of 4.00

The value of the acid dissociation constant K_a for benzenecarboxylic acid (C_6H_5COOH) is 6.31×10^{-5} mol dm^{-3}.

_____

_____

_____

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_____

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_____

_____

(5)

(e) Two solutions, one with a pH of 4.00 and the other with a pH of 9.00, were left open to the air.

The pH of the pH 9.00 solution changed more than that of the other solution.

Suggest what substance might be present in the air to cause the pH to change. Explain how and why the pH of the pH 9.00 solution changes.

Substance present in air _____

Explanation _____

_____

_____

_____

_____

(3)

(Total 17 marks)

Q11.

This question is about Brønsted-Lowry acids of different strengths.

(a) State the meaning of the term *Brønsted–Lowry acid*.

_____

(1)

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

_____

_____

(1)

(ii) The value of K_a for ethanoic acid is 1.75×10^{-5} mol dm^{-3} at 25 °C.

Calculate the concentration of ethanoic acid in a solution of the acid that has a pH of 2.69

_____

_____

_____

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_____

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_____

(4)

(c) The value of K_a for chloroethanoic acid ($ClCH_2COOH$) is 1.38×10^{-3} mol dm^{-3} at 25 °C.

(i) Write an equation for the dissociation of chloroethanoic acid in aqueous solution.

_____

(1)

(ii) Suggest why chloroethanoic acid is a stronger acid than ethanoic acid.

_____

_____

_____

_____

_____

(2)

(d) **P** and **Q** are acids. **X** and **Y** are bases. The table shows the strength of each acid and base.

Acids		**Bases**	
strong	weak	strong	weak
P	**Q**	**X**	**Y**

The two acids were titrated separately with the two bases using methyl orange as indicator.
The titrations were then repeated using phenolphthalein as indicator.
The pH range for methyl orange is 3.1 − 4.4
The pH range for phenolphthalein is 8.3 − 10.0

For each of the following titrations, select the letter, **A, B, C,** or **D**, for the correct statement about the indicator(s) that would give a precise end-point.
Write your answer in the box provided.

A Both indicators give a precise end-point.

B Only methyl orange gives a precise end-point.

C Only phenolphthalein gives a precise end-point.

D Neither indicator gives a precise end-point.

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(i) Acid **P** with base **X** ☐

(1)

(ii) Acid **Q** with base **X** ☐

(1)

(iii) Acid **Q** with base **Y** ☐

(1)

(e) Using a burette, 26.40 cm^3 of 0.550 mol dm^{-3} sulfuric acid were added to a conical flask containing 19.60 cm^3 of 0.720 mol dm^{-3} aqueous sodium hydroxide. Assume that the sulfuric acid is fully dissociated.

Calculate the pH of the solution formed.

Give your answer to 2 decimal places.

_____

_____

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_____

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_____

(6)

(Total 18 marks)

Q12.

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

(a) The ionic product of water has the symbol K_w

(i) Write an expression for the ionic product of water.

_____

(1)

(ii) At 42°C, the value of K_w is 3.46×10^{-14} mol^2 dm^{-6}.

Calculate the pH of pure water at this temperature.

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_____

_____

_____

_____

(2)

(iii) At 75 °C, a 0.0470 mol dm^{-3} solution of sodium hydroxide has a pH of 11.36. Calculate a value for K_w at this temperature.

_____

_____

_____

_____

(2)

(b) Methanoic acid (HCOOH) dissociates slightly in aqueous solution.

(i) Write an equation for this dissociation.

_____

(1)

(ii) Write an expression for the acid dissociation constant K_a for methanoic acid.

_____

_____

(1)

(iii) The value of K_a for methanoic acid is 1.78×10^{-4} mol dm^{-3} at 25 °C. Calculate the pH of a 0.0560 mol dm^{-3} solution of methanoic acid.

_____

_____

_____

_____

_____

(3)

(iv) The dissociation of methanoic acid in aqueous solution is endothermic.

Deduce whether the pH of a solution of methanoic acid will increase, decrease or stay the same if the solution is heated. Explain your answer.

Effect on pH _____

Explanation _____

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_____

_____

_____

(3)

(c) The value of K_a for methanoic acid is 1.78×10^{-4} mol dm^{-3} at 25°C.
A buffer solution is prepared containing 2.35×10^{-2} mol of methanoic acid and 1.84×10^{-2} mol of sodium methanoate in 1.00 dm^3 of solution.

(i) Calculate the pH of this buffer solution at 25°C.

_____

_____

_____

_____

_____

(3)

(ii) A 5.00 cm^3 sample of 0.100 mol dm^{-3} hydrochloric acid is added to the buffer solution in part (c)(i).

Calculate the pH of the buffer solution after this addition.

_____

_____

_____

_____

_____

_____

_____

_____

(4)

(Total 20 marks)

Q13.

This question is about several Brønsted–Lowry acids and bases.

(a) Define the term *Brønsted–Lowry* acid.

_____

_____

(1)

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(b) Three equilibria are shown below. For each reaction, indicate whether the substance immediately **above** the box is acting as a Brønsted–Lowry acid (**A**) or a Brønsted–Lowry base (**B**) by writing **A** or **B** in each of the six boxes.

(i) CH_3COOH + H_2O ⇌ CH_3COO^- + H_3O^+

(1)

(ii) CH_3NH_2 + H_2O ⇌ $CH_3NH_3^+$ + OH^-

(1)

(iii) HNO_3 + H_2SO_4 ⇌ $H_2NO_3^+$ + HSO_4^-

(1)

(c) A 25.0 cm^3 sample of 0.0850 mol dm^{-3} hydrochloric acid was placed in a beaker. Distilled water was added until the pH of the solution was 1.25.

Calculate the total volume of the solution formed. State the units.

(3)

(d) At 298 K, the value of the acid dissociation constant (K_a) for the weak acid HX in aqueous solution is 3.01×10^{-5} mol dm^{-3}.

(i) Calculate the value of pK_a for HX at this temperature.
Give your answer to 2 decimal places.

(1)

(ii) Write an expression for the acid dissociation constant (K_a) for the weak acid HX.

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(1)

(iii) Calculate the pH of a 0.174 mol dm^{-3} solution of HX at this temperature.
Give your answer to 2 decimal places.

(3)

(e) An acidic buffer solution is formed when 10.0 cm^3 of 0.125 mol dm^{-3} aqueous sodium hydroxide are added to 15.0 cm^3 of 0.174 mol dm^{-3} aqueous HX.
The value of K_a for the weak acid HX is 3.01×10^{-5} mol dm^{-3}.

Calculate the pH of this buffer solution at 298 K.
Give your answer to 2 decimal places.

(6)

(Total 18 marks)

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Q14.

A student was given a task to determine the percentage purity of a sample of salicylic acid. The method used by the student to prepare a solution of salicylic acid is described below.

- 0.500 g of an impure sample of salicylic acid was placed in a weighing bottle.
- The contents were tipped into a beaker and 100 cm^3 of distilled water were added.
- Salicylic acid does not dissolve well in cold water so the beaker and its contents were heated gently until all the solid had dissolved.
- The solution was poured into a 250 cm^3 graduated flask and made up to the mark with distilled water.

(a) Give **two** additional instructions that would improve this method for making up the salicylic acid solution.

_____

_____

_____

_____

_____

(2)

(b) The pH of this solution was measured and a value of 2.50 was obtained.
Calculate the concentration of salicylic acid in this solution.
Assume that salicylic acid is the only acid in this solution. The K_a for salicylic acid is 1.07×10^{-3} mol dm^{-3}. You may represent salicylic acid as HA.
Show your working.

_____

_____

_____

_____

_____

(3)

(c) Use your answer to part (b) to calculate the mass of salicylic acid (M_r = 138.0) present in the original sample.
(If you were unable to complete the calculation in part (b), assume that the concentration of salicylic acid is 8.50×10^{-3} mol dm^{-3}. This is **not** the correct answer.)

_____

_____

_____

(2)

(d) Use your answer to part (c) to calculate the percentage purity of the salicylic acid

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used to make the solution.
(If you were unable to complete the calculation in part (c), assume that the mass of salicylic acid is 0.347 g. This is **not** the correct answer.)

_____

_____

(1)

(Total 8 marks)

Q15.

This question involves calculations about two strong acids and one weak acid.
All measurements were carried out at 25 °C.

(a) A 25.0 cm^3 sample of 0.0850 mol dm^{-3} hydrochloric acid was placed in a beaker and 100 cm^3 of distilled water were added.
Calculate the pH of the new solution formed.
Give your answer to 2 decimal places.

_____

_____

_____

_____

(2)

(b) HX is a weak monobasic acid.

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

_____

_____

(1)

(ii) The pH of a 0.0850 mol dm^{-3} solution of HX is 2.79
Calculate a value for the acid dissociation constant, K_a, of this acid.
Give your answer to 3 significant figures.

_____

_____

_____

_____

_____

_____

(3)

(c) A 25.0 cm^3 sample of 0.620 mol dm^{-3} nitric acid was placed in a beaker and 38.2 cm^3 of 0.550 mol dm^{-3} aqueous sodium hydroxide were added.

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Calculate the pH of the solution formed.
Give your answer to 2 decimal places.

The ionic product of water $K_w = 1.00 \times 10^{-14}$ mol^2 dm^{-6} at 25 °C.

(6)

(Total 12 marks)

Q16.

This question is about the pH of some solutions containing potassium hydroxide and ethanoic acid.

Give all values of pH to 2 decimal places.

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

(1)

(ii) Write an expression for the ionic product of water, K_w

(1)

(iii) At 10 °C, a 0.154 mol dm^{-3} solution of potassium hydroxide has a pH of 13.72. Calculate the value of K_w at 10 °C.

(2)

(b) At 25 °C, the acid dissociation constant K_a for ethanoic acid has the value

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1.75×10^{-5} mol dm^{-3}.

(i) Write an expression for K_a for ethanoic acid.

_____

_____

(1)

(ii) Calculate the pH of a 0.154 mol dm^{-3} solution of ethanoic acid at 25 °C.

_____

_____

_____

_____

_____

_____

(3)

(c) At 25 °C, the acid dissociation constant K_a for ethanoic acid has the value 1.75×10^{-5} mol dm^{-3}.

(i) Calculate the pH of the solution formed when 10.0 cm^3 of 0.154 mol dm^{-3} potassium hydroxide are added to 20.0 cm^3 of 0.154 mol dm^{-3} ethanoic acid at 25 °C.

_____

_____

_____

_____

_____

_____

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(4)

(ii) Calculate the pH of the solution formed when 40.0 cm^3 of 0.154 mol dm^{-3} potassium hydroxide are added to 20.0 cm^3 of 0.154 mol dm^{-3} ethanoic acid at 25 °C.

At 25 °C, K_w has the value 1.00×10^{-14} mol^2 dm^{-6}.

_____

_____

_____

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_____

_____

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_____

_____

(4)

(Total 16 marks)

Q17.

This question is about the pH of several solutions.

Give all values of pH to 2 decimal places.

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

_____

(1)

(ii) Calculate the pH of 0.154 mol dm^{-3} hydrochloric acid.

_____

_____

(1)

(iii) Calculate the pH of the solution formed when 10.0 cm^3 of 0.154 mol dm^{-3} hydrochloric acid are added to 990 cm^3 of water.

_____

_____

_____

_____

(2)

(b) The acid dissociation constant, K_a, for the weak acid HX has the value 4.83×10^{-5} mol dm^{-3} at 25 °C.
A solution of HX has a pH of 2.48

Calculate the concentration of HX in the solution.

_____

_____

_____

_____

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(4)

(c) Explain why the pH of an acidic buffer solution remains almost constant despite the addition of a small amount of sodium hydroxide.

(2)

(d) The acid dissociation constant, K_a, for the weak acid HY has the value 1.35×10^{-5} mol dm^{-3} at 25 °C.

A buffer solution was prepared by dissolving 0.0236 mol of the salt NaY in 50.0 cm^3 of a 0.428 mol dm^{-3} solution of the weak acid HY

(i) Calculate the pH of this buffer solution.

(4)

(ii) A 5.00×10^{-4} mol sample of sodium hydroxide was added to this buffer solution.

Calculate the pH of the buffer solution after the sodium hydroxide was added.

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_____

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_____

_____

_____

(4)

(Total 18 marks)

Q18.

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

Calculating the pH of aqueous solutions can involve the use of equilibrium constants such as K_w and K_a

K_w is the ionic product of water. The value of K_w is 5.48×10^{-14} mol^2 dm^{-6} at 50 °C.

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

_____

(1)

(ii) Write an expression for K_w

_____

(1)

(b) (i) Calculate the pH of pure water at 50 °C.

_____

_____

_____

(2)

(ii) Suggest why this pure water is **not** acidic.

_____

_____

(1)

(iii) Calculate the pH of 0.140 mol dm^{-3} aqueous sodium hydroxide at 50 °C.

_____

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(3)

(c) Calculate the pH of the solution formed when 25.0 cm^3 of 0.150 mol dm^{-3} aqueous sulfuric acid are added to 30.0 cm^3 of 0.200 mol dm^{-3} aqueous potassium hydroxide at 25 °C. Assume that the sulfuric acid is fully dissociated.

(6)

(Total 14 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 pK_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 pK_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	pH

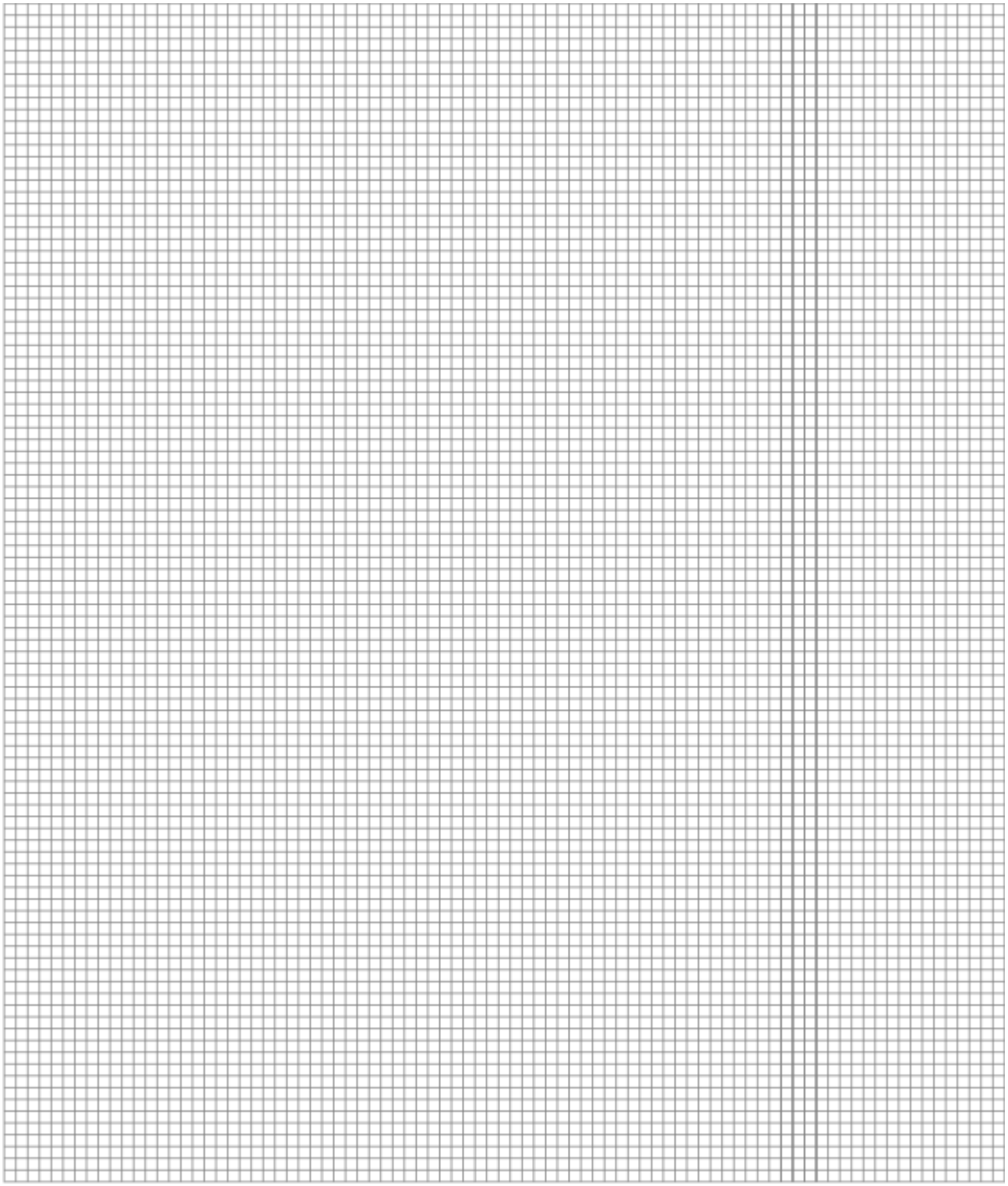
Volume of sodium	pH

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hydroxide solution added / cm^3		hydroxide solution added / cm^3	
0.0	3.0	23.5	5.1
2.0	3.4	24.0	5.5
4.0	3.5	24.5	11.8
8.0	3.7	25.0	12.1
12.0	4.3	26.0	12.3
16.0	4.1	27.0	12.4
20.0	4.3	28.0	12.5
22.0	4.7	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.

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(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

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(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	1.6×10^{-4}
Ethanoic acid	1.7×10^{-5}
Iodoethanoic acid	6.8×10^{-4}
Propanoic acid	1.3×10^{-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).

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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 1.9×10^{-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

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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 1.74×10^{-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)

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(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.

(6)

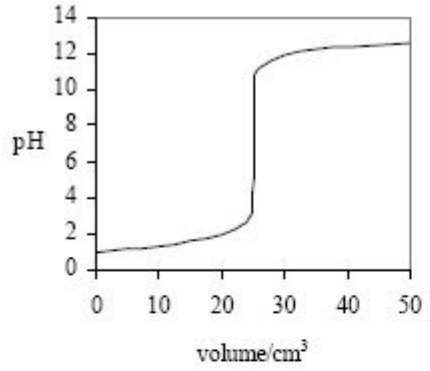
(Total 18 marks)

Q21.

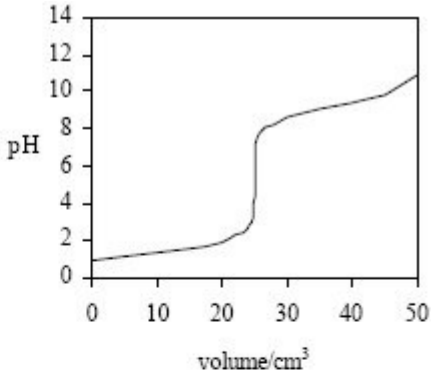
Indicators and pH curves can be used to determine the end point in a titration.

(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}.

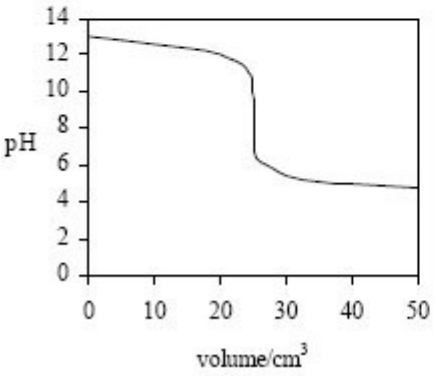
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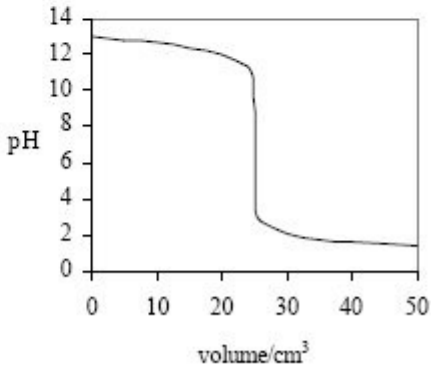
J



K



L



M

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

ammonia to 25 cm^3 of hydrochloric acid _____

ethanoic acid to 25 cm^3 of sodium hydroxide _____

sodium hydroxide to 25 cm^3 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**.

_____

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(4)

(b) The acid dissociation constant, K_a, for the weak acid, ethanoic acid, has a value of 1.74×10^{-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)

Q22.

(a) A sample of hydrochloric acid has a pH of 2.34
Write an expression for pH and calculate the concentration of this acid.

pH _____

Concentration _____

_____

(2)

(b) A 0.150 mol dm^{-3} solution of a weak acid, HX, also has a pH of 2.34

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

_____

_____

(ii) Calculate the value of K_a for this acid and state its units.

Calculation _____

_____

_____

Units

_____

(iii) Calculate the value of pK_a for the acid HX. Give your answer to two decimal

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places.

_____

(5)

(c) A 30.0 cm^3 sample of a 0.480 mol dm^{-3} solution of potassium hydroxide was partially neutralised by the addition of 18.0 cm^3 of a 0.350 mol dm^{-3} solution of sulphuric acid.

(i) Calculate the initial number of moles of potassium hydroxide.

_____

_____

(ii) Calculate the number of moles of sulphuric acid added.

_____

_____

(iii) Calculate the number of moles of potassium hydroxide remaining in excess in the solution formed.

_____

_____

(iv) Calculate the concentration of hydroxide ions in the solution formed.

_____

_____

_____

(v) Hence calculate the pH of the solution formed. Give your answer to two decimal places.

_____

_____

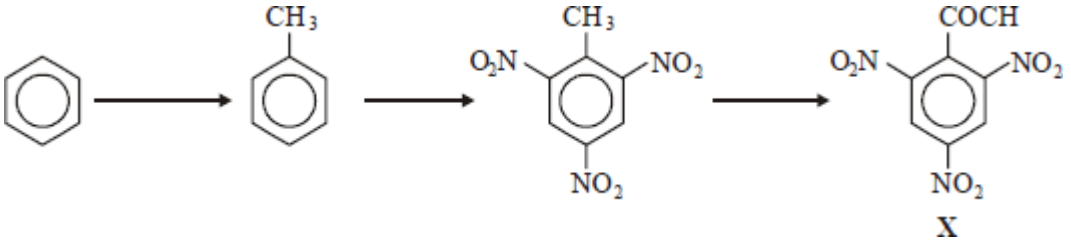
_____

(6)

(Total 13 marks)

Q23.

This question is based on the reactions and compounds shown in the scheme below.



X

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A 0.100 mol dm^{-3} solution of **X** is found to have a pH of 2.50. The value of K_a in mol dm^{-3} is

A 3.16×10^{-2}

B 3.16×10^{-3}

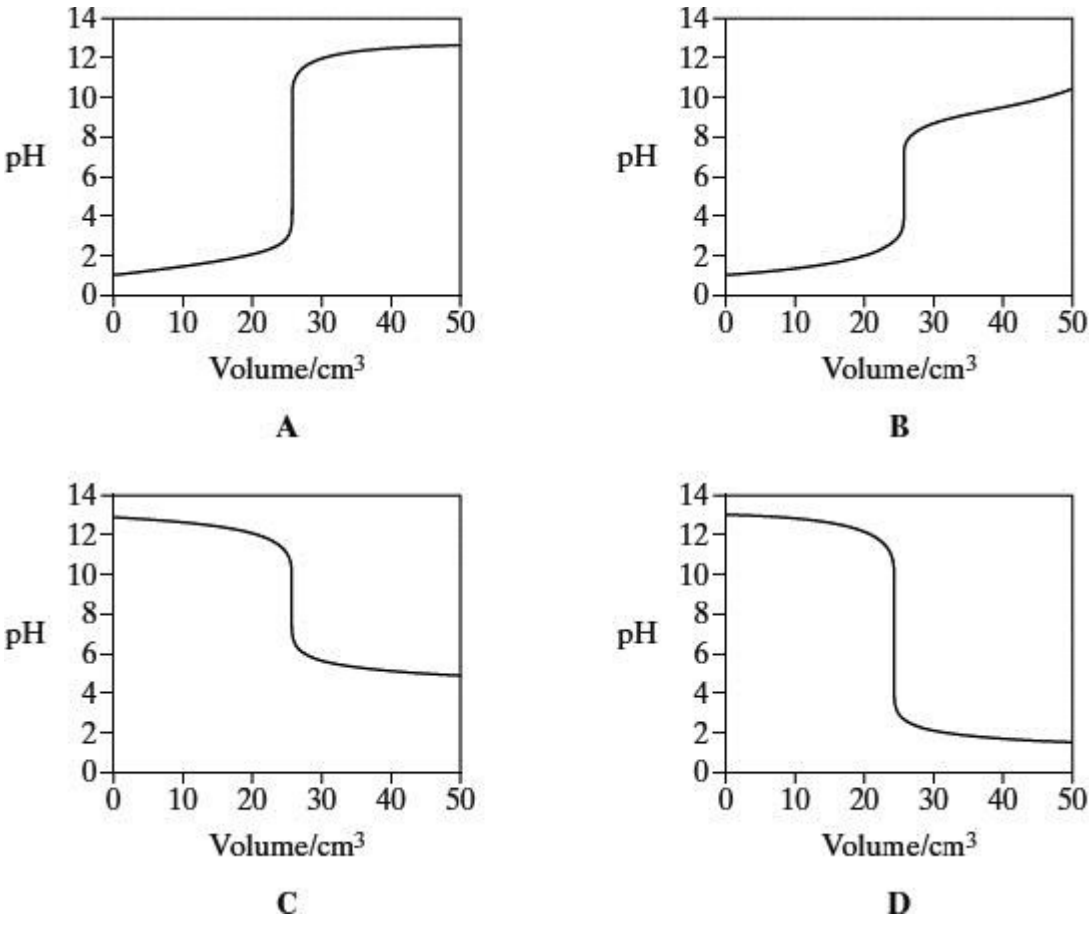
C 1.00×10^{-4}

D 1.00×10^{-5}

(Total 1 mark)

Q24.

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



(i) Select from **A**, **B**, **C** and **D** the curve produced by the addition of

ammonia to 25 cm^3 of hydrochloric acid _____

ethanoic acid to 25 cm^3 of sodium hydroxide _____

sodium hydroxide to 25 cm^3 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

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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 table an indicator which could be used in the titration which produces curve **A** but not in the titration which produces curve **B**.

(4)

(b) (i) Write an expression for the term *pH*.

(ii) A solution of potassium hydroxide has a pH of 11.90 at 25°C. Calculate the concentration of potassium hydroxide in the solution.

(4)

(c) The acid dissociation constant, K_a, for propanoic acid has the value of 1.35×10^{-5} mol dm^{-3} at 25 °C.

$$K_a = \frac{[H^+][CH_3CH_2COO^-]}{[CH_3CH_2COOH]}$$

In each of the calculations below, give your answer to 2 decimal places.

(i) Calculate the pH of a 0.117 mol dm^{-3} aqueous solution of propanoic acid.

(ii) Calculate the pH of a mixture formed by adding 25 cm^3 of a 0.117 mol dm^{-3} aqueous solution of sodium propanoate to 25 cm^3 of a 0.117 mol dm^{-3} aqueous solution of propanoic acid.

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_____

_____

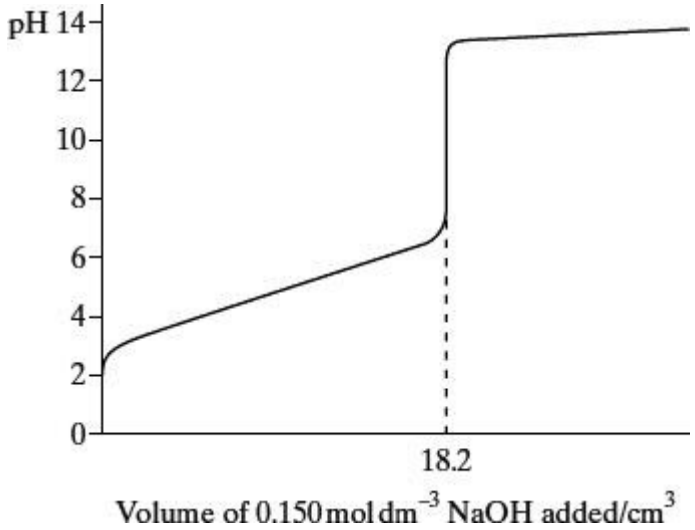
_____

(5)

(Total 13 marks)

Q25.

The pH curve shown below was obtained when a 0.150 mol dm^{-3} solution of sodium hydroxide was added to 25.0 cm^3 of an aqueous solution of a weak monoprotic acid, HA.



(a) Use the information given to calculate the concentration of the acid.

_____

_____

_____

(2)

(b) (i) Write an expression for the acid dissociation constant, K_a, for HA.

_____

(ii) Write an expression for pK_a

_____

(iii) Using your answers to parts (b)(i) and (b)(ii), show that when sufficient sodium hydroxide has been added to neutralise half of the acid,

pH of the solution = pK_a for the acid HA

_____

_____

_____

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(4)

(c) Explain why dilution with a small volume of water does not affect the pH of a buffer solution.

_____

_____

(2)

(d) (i) Calculate the change in pH when 0.250 mol dm^{-3} hydrochloric acid is diluted with water to produce 0.150 mol dm^{-3} hydrochloric acid.

_____

_____

_____

(ii) Calculate the volume of water which must be added to 30.0 cm^3 of 0.250 mol dm^{-3} hydrochloric acid in order to reduce its concentration to 0.150 mol dm^{-3}.

_____

_____

_____

(4)

(Total 12 marks)

Q26.

This question concerns the weak acid, ethanoic acid, for which the acid dissociation constant, K_a, has a value of 1.74×10^{-5} mol dm^{-3} at 25 °C.

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

In each of the calculations below, give your answer to 2 decimal places.

(a) Write an expression for the term *pH*. Calculate the pH of a 0.150 mol dm^{-3} solution of ethanoic acid.

_____

_____

_____

_____

_____

_____

_____

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_____

(4)

(b) A buffer solution is prepared by mixing a solution of ethanoic acid with a solution of sodium ethanoate.

(i) Explain what is meant by the term *buffer solution*.

_____

_____

_____

_____

(2)

(ii) Write an equation for the reaction which occurs when a small amount of hydrochloric acid is added to this buffer solution.

_____

_____

(1)

(c) In a buffer solution, the concentration of ethanoic acid is 0.150 mol dm^{-3} and the concentration of sodium ethanoate is 0.100 mol dm^{-3}.

(i) Calculate the pH of this buffer solution.

_____

_____

_____

_____

_____

_____

(3)

(ii) A 10.0 cm^3 portion of 1.00 mol dm^{-3} hydrochloric acid is added to 1000 cm^3 of this buffer solution.
Calculate the number of moles of ethanoic acid and the number of moles of sodium ethanoate in the solution after addition of the hydrochloric acid. Hence, find the pH of this new solution.

_____

_____

_____

_____

_____

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_____

_____

_____

_____

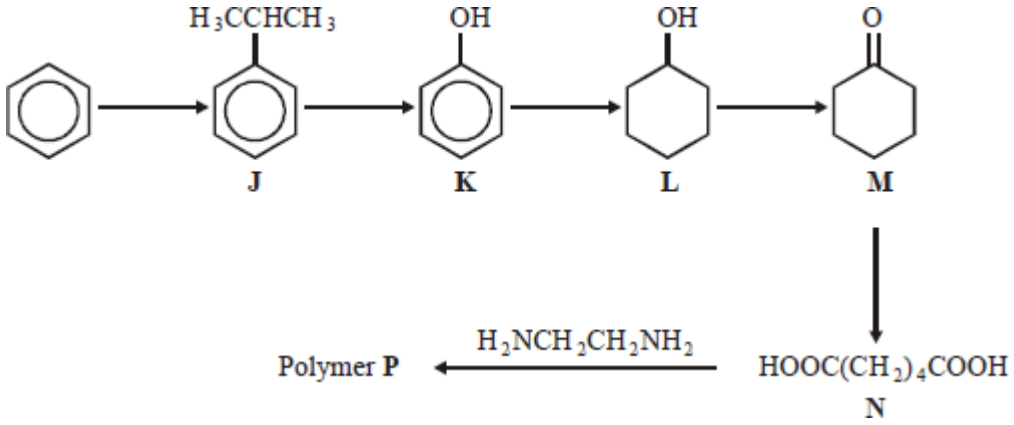
_____

(5)

(Total 15 marks)

Q27.

This question is about the following reaction scheme which shows the preparation of polymer **P**.



K is a weak acid with a pK_a of 9.95. The pH of a 0.10 mol dm^{-3} solution of **K** is

A 4.48

B 4.98

C 5.48

D 5.98

(Total 1 mark)

Q28.

The value of the acid dissociation constant, K_a, for the weak acid HA, at 298 K, is 1.45×10^{-4} mol dm^{-3}.

(a) Write an expression for the term K_a for the weak acid HA.

_____

_____

(1)

(b) Calculate the pH of a 0.250 mol dm^{-3} solution of HA at 298 K.

_____

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_____

_____

_____

_____

(4)

(c) A mixture of the acid HA and the sodium salt of this acid, NaA, can be used to prepare a buffer solution.

(i) State and explain the effect on the pH of this buffer solution when a small amount of hydrochloric acid is added.

_____

_____

_____

(ii) The concentration of HA in a buffer solution is 0.250 mol dm^{-3}. Calculate the concentration of A^- in this buffer solution when the pH is 3.59

_____

_____

_____

_____

_____

_____

(6)

(Total 11 marks)

Q29.

For this question **one or more** of the options given may be correct. Select your answer by means of the following code

A if **1**, **2** and **3** only are correct

B if **1** and **3** only are correct

C if **2** and **4** only are correct

D if **4** alone is correct

Directions summarised			
A	**B**	**C**	**D**

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1, **2** and **3** only correct	**1** and **3** only correct	**2** and **4** only correct	**4** only correct

Solutions with a pH of 1.0 include

1 0.1 mol dm^{-3} hydrochloric acid

2 0.1 mol dm^{-3} ethanoic acid

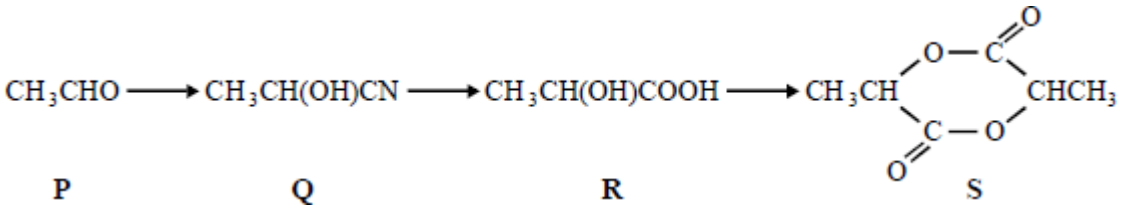
3 0.05 mol dm^{-3} sulphuric acid

4 0.2 mol dm^{-3} nitric acid

(Total 1 mark)

Q30.

This question refers to the reaction sequence below.



P **Q** **R** **S**

HCN is a weak acid with a pK_a value of 9.40. If a 0.010 mol dm^{-3} solution of HCN was used in the first step, the concentration of cyanide ions, in mol dm^{-3}, would be

A 2.0×10^{-6}

B 6.4×10^{-5}

C 2.0×10^{-5}

D 3.1×10^{-1}

(Total 1 mark)

Q31.

(a) At 50°C, the ionic product of water, K_w, has the value 5.48×10^{-14} mol^2 dm^{-6}.

(i) Define the term K_w

_____

(ii) Define the term *pH*

_____

(iii) Calculate the pH of pure water at 50 °C. Explain why pure water at 50 °C is still neutral even though its pH is not 7.

Calculation _____

_____

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_____

Explanation _____

_____

(5)

(b) At 25°C, K_w has the value 1.00×10^{-14} mol^2 dm^{-6}. Calculate the pH at 25 °C of

(i) a 0.150 mol dm^{-3} solution of sodium hydroxide,

_____

_____

_____

(ii) the solution formed when 35.0 cm^3 of this solution of sodium hydroxide is mixed with 40.0 cm^3 of a 0.120 mol dm^{-3} solution of hydrochloric acid.

_____

_____

_____

_____

_____

_____

_____

(8)

(c) In a 0.150 mol dm^{-3} solution of a weak acid HX at 25 °C, 1.80% of the acid molecules are dissociated into ions.

(i) Write an expression for K_a for the acid HX.

_____

_____

(ii) Calculate the value of K_a for the acid HX at this temperature and state its units.

_____

_____

_____

_____

_____

_____

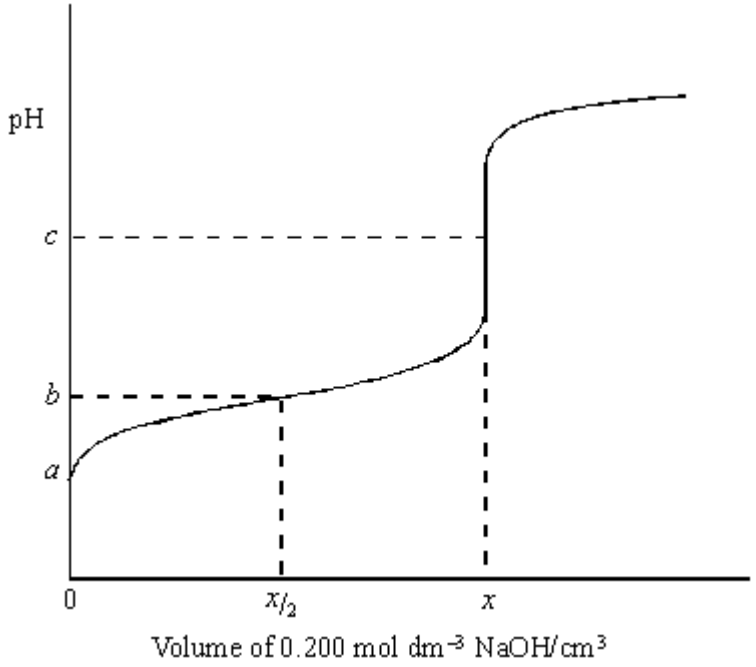
(5)

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(Total 18 marks)

Q32.

The sketch below shows the change in pH when a 0.200 mol dm^{-3} solution of sodium hydroxide is added from a burette to 25.0 cm^3 of a 0.150 mol dm^{-3} solution of the weak acid HA at 25 °C.



(a) The volume of sodium hydroxide solution added at the equivalence point is x cm^3. Calculate the value of x.

_____

_____

_____

(2)

(b) (i) Define the term pH.

_____

(ii) The pH at the equivalence point is *c*. Suggest a value for *c*.

_____

(iii) Identify a suitable indicator for detecting the equivalence point of the titration.

_____

(3)

(c) The value of K_c for the weak acid HA at 25 °C is 2.75×10^{-5} mol dm^{-3}.

(i) Explain the term *weak* as applied to the acid HA.

_____

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(ii) Write an expression for K_a for the acid HA.

_____

(iii) Calculate the pH of the 0.150 mol dm^{-3} solution of acid HA before any sodium hydroxide is added, i.e. the pH at point *a*.

_____

_____

_____

_____

_____

(5)

(d) Calculate the pH of the solution formed when $x/2$ cm^3 of the 0.200 mol dm^{-3} solution of sodium hydroxide are added to 25.0 cm^3 of the 0.150 mol dm^{-3} solution of HA, i.e. the pH at point *b*.

_____

_____

_____

(3)

(Total 13 marks)

Q33.

A 0.210 mol dm^{-3} solution of potassium hydroxide was added from a burette to 25.0 cm^3 of a 0.160 mol dm^{-3} solution of ethanoic acid in a conical flask.
Given that the value of the acid dissociation constant, K_a, for ethanoic acid is 1.74×10^{-5} mol dm^{-3}, calculate the pH at 25 °C of the solution in the conical flask at the following three points:

before any potassium hydroxide had been added;

after 8.0 cm^3 of potassium hydroxide solution had been added;

after 40.0 cm^3 of potassium hydroxide solution had been added.

_____

_____

_____

_____

_____

_____

_____

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_____

_____

_____

_____

_____

(Total 16 marks)

Q34.

The value of the acid dissociation constant, K_a, for ethanoic acid is 1.74×10^{-5} mol dm^{-3} at 298 K.

(a) (i) Write an expression for K_a for ethanoic acid.

_____

(ii) Calculate the pH at 298 K of a 0.220 mol dm^{-3} solution of ethanoic acid.

_____

_____

_____

_____

_____

_____

(5)

(b) A sample of the 0.220 mol dm^{-3} solution of ethanoic acid was titrated against sodium hydroxide solution.

(i) Calculate the volume of a 0.150 mol dm^{-3} solution of sodium hydroxide required to neutralise 25.0 cm^3 of the ethanoic acid solution.

_____

_____

_____

_____

(ii) From the list below, select the best indicator for this titration and explain your choice.

Name of indicator	**pH range**
bromophenol blue	3.0 – 4.6
methyl red	4.2 – 6.3
bromothymol blue	6.0 – 7.6
thymol blue	8.0 – 9.6

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Indicator _____

Explanation _____

_____

_____

(5)

(c) A buffer solution is formed when 2.00 g of sodium hydroxide are added to 1.00 dm^3 of a 0.220 mol dm^{-3} solution of ethanoic acid.

Calculate the pH at 298 K of this buffer solution.

_____

_____

_____

_____

_____

_____

_____

(6)

(Total 16 marks)

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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 <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^- = 1.0×10^{-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

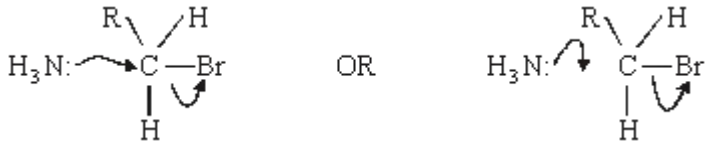
(b) (ii) If no vol, max 4 for a, b, c, f answer = 10.65
If wrong volume max 5 for a, b, c, e, f
If no substraction max 3 for a, b, d
If missing 1000 max 5 for a, b, c, d, f answer = 8.78
If uses excess as acid, max 4 for a, b, d, f answer = 2.22
If uses excess as acid and no volume, max 2 for a, b answer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

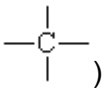
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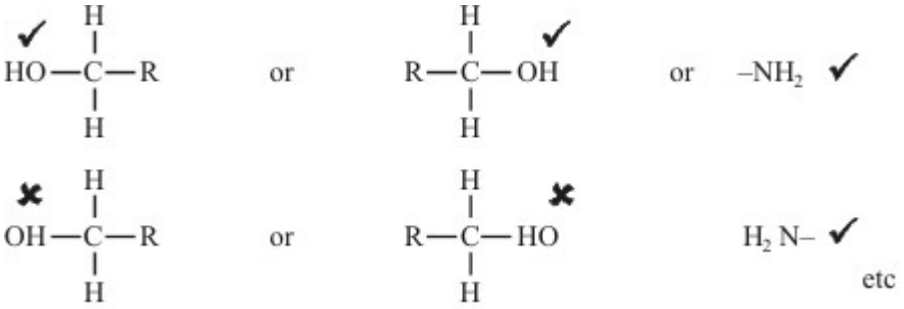
Organic points

(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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