PEARSON EDEXCEL IAL CHEMISTRY · YCH11

CHEMISTRY



EXAM QUESTION PACK

UNIT 4: ACID-BASE EQUILIBRIA

SCORE	PERCENTAGE
/214	%

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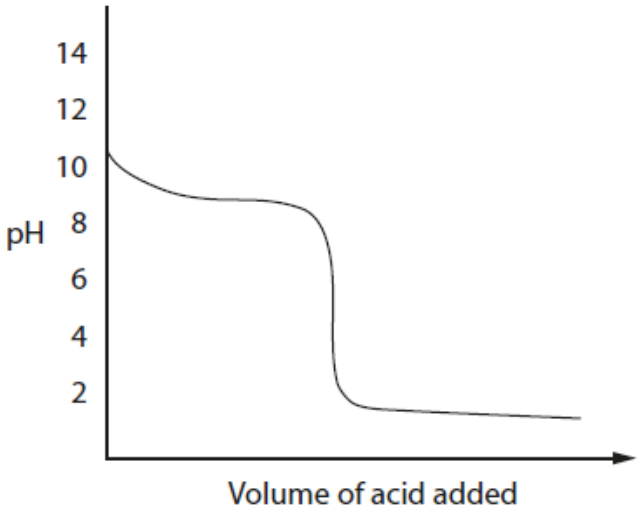
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Q1.

Answer the question with a cross in the box you think is correct ☒ . If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒ .

A graph of pH against volume of acid added for an acid-base titration is shown.



(a) Which acidic solution was used in the titration?

(1)

☒ **A** 0.1 mol dm^{-3} CH_3COOH

☒ **B** 1.0 mol dm^{-3} CH_3COOH

☒ **C** 0.1 mol dm^{-3} HCl

☒ **D** 1.0 mol dm^{-3} HCl

(b) Which basic solution was used in the titration?

(1)

☒ **A** NH_3

☒ **B** LiOH

☒ **C** $Ba(OH)_2$

☒ **D** NaOH

(c) A student suggested five indicators that might be used in this titration:

thymol blue
methyl orange
bromophenol blue
bromocresol green
phenolphthalein

How many of these indicators would be suitable? Use your Data Booklet.

(1)

☒ **A** 5

☒ **B** 4

☒ **C** 3

☒ **D** 2

(Total for question = 3 marks)

Q2.

This question concerns acidic solutions.

(a) (i) A solution of hydrochloric acid has a pH of 1.125.

Calculate the concentration of hydrogen ions and of hydroxide ions, in mol dm^{-3}, in this solution.

[$K_w = 1.00 \times 10^{-14}$ mol^2 dm^{-6}]

(2)

(ii) Calculate the volume of water which must be added to 25.0 cm^3 of this solution to increase the pH from 1.125 to 1.500, giving your answer to an appropriate number of significant figures.

(4)

(b) Phosphoric(V) acid, H_3PO_4, is a weak acid, which dissolves in water, giving the equilibrium

Equation 1 $H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + H_3O^+(aq)$

The $H_2PO_4^-$ ion formed when phosphoric(V) acid is added to water can dissociate further into HPO_4^{2-}.

Equation 2 $H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + H_3O^+(aq)$

....

(i) Identify the acids and bases in the spaces below Equation 2, linking the acid-base conjugate pairs.

(2)

(ii) Explain why very little dissociation of the $H_2PO_4^-$ ion occurs in solutions of phosphoric(V) acid.

(2)

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(c) (i) Using Equation 1, write an expression for the acid dissociation constant, K_{a1}, for phosphoric(V) acid, H_3PO_4 .

(1)

(ii) A 0.500 mol dm^{-3} solution of phosphoric(V) acid has a pH of 1.20.

Calculate the value of K_{a1} , stating its units.

Assume that there is no further dissociation of the $H_2PO_4^-$ ion.

(4)

(d) Phosphate buffer solutions containing hydrogenphosphate ions, HPO_4^{2-} , and dihydrogenphosphate ions, $H_2PO_4^-$, are commonly used in biological research.

Explain, using a relevant ionic equation, how a solution containing these ions can act as a buffer when a small amount of **alkali** is added.

(3)

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(Total for question = 18 marks)

Q3.

This question is about acids.

(a) Calculate the pH of the following acidic solutions. Give your answers to **two** decimal places.

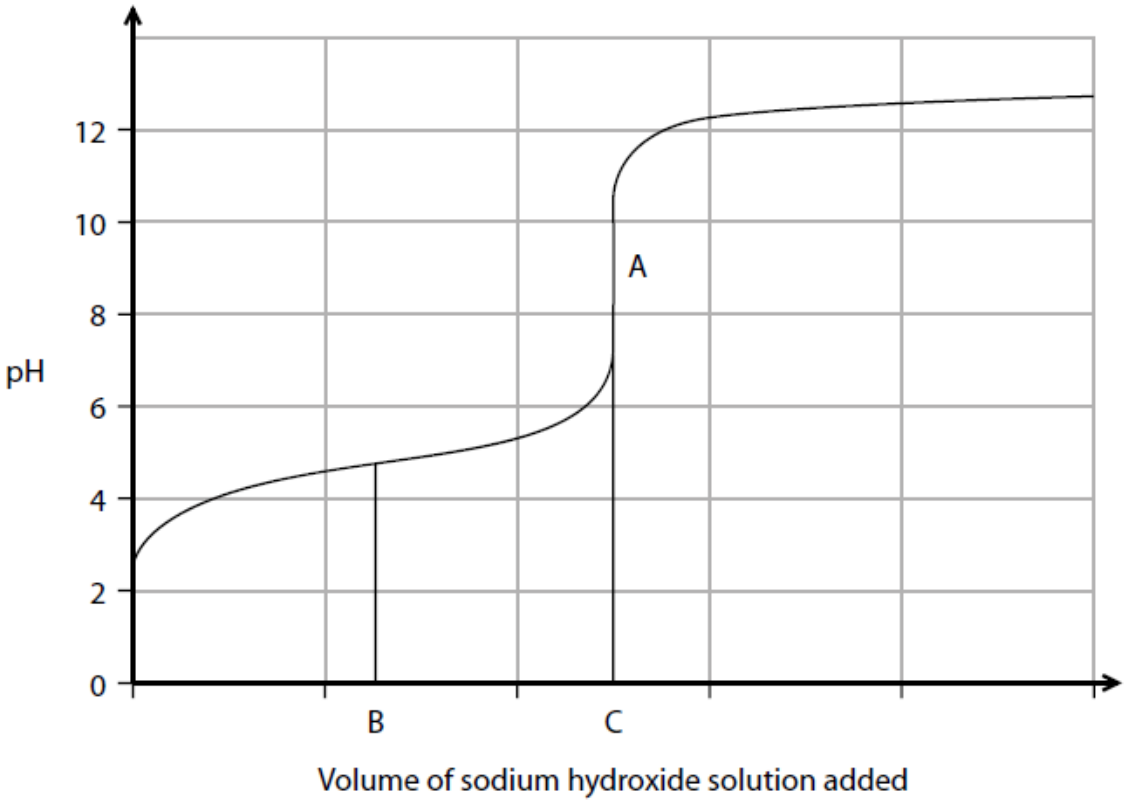
(i) 0.14 mol dm^{-3} solution of hydrochloric acid

(1)

(ii) 0.14 mol dm^{-3} solution of ethanoic acid ($K_a = 1.76 \times 10^{-5}$ mol dm^{-3})

(3)

(b) The graph shows the titration curve for a weak acid with a strong base. The equivalence point is A and the volume of alkali added at the equivalence point is C. Volume B is half of volume C.



(i) Use the graph to determine the dissociation constant, K_a, of the weak acid.

(3)

(ii) Explain the rapid rise in pH from 2.8 to 4 at the start of the titration.

(2)

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(c) In another experiment, 10 cm^3 of 1.0 mol dm^{-3} sodium hydroxide was added to 30 cm^3 1.0 mol dm^{-3} propanoic acid (K_a = 1.3 × 10^{-5} mol dm^{-3}).

(i) Calculate the pH of the resulting solution.

(3)

(ii) State one assumption you have made in this calculation.

(1)

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(Total for question = 13 marks)

Q4.

This question is about ammonia and ammonium chloride.

(a) Ammonia is produced by reacting nitrogen and hydrogen as shown.

$$N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g)$$

(i) Write the expression for the equilibrium constant, K_p.

(1)

(ii) An equilibrium was established by mixing nitrogen and hydrogen in a 1 : 3 ratio by volume, at a temperature of 450 °C and pressure of 200 atm.
The equilibrium mixture contained 28 % of ammonia by volume.

Complete the table.

(3)

Substance	Mole fraction	Partial pressure / atm
N_2		
H_2		
NH_3	0.28	56

(iii) Calculate the equilibrium constant.

Give your answer to an appropriate number of significant figures and include units, if required.

(3)

(iv) When the temperature was reduced to 400 °C at the same pressure, the equilibrium mixture contained 36 % of ammonia.

Explain what can be deduced about this reaction from this information.

(2)

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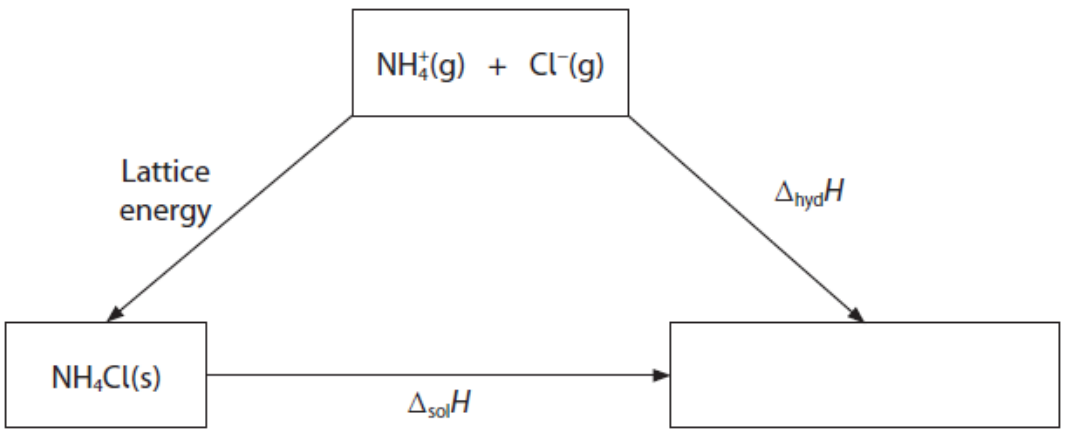
(b) Ammonium chloride can be produced by reacting ammonia with hydrogen chloride.

Ammonium chloride is a white solid that is very soluble in water.

Hess's Law can be used to calculate the enthalpy of solution of ammonium chloride, using hydration enthalpies and lattice energy.

(i) Complete the Hess cycle by filling in the empty box.

(1)



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(ii) Complete the expression for the enthalpy change of solution using the hydration enthalpies and lattice energy.

(1)

$\Delta_{sol}H =$

(iii) Calculate the enthalpy change of solution, using your expression in (b)(ii) and these data.

Enthalpy change of hydration of NH_4^+ = −307 kJ mol^{-1}

Enthalpy change of hydration of Cl^- = −378 kJ mol^{-1}

Lattice energy of NH_4Cl = −705 kJ mol^{-1}

(2)

(iv) A student suggested that the enthalpy change of solution of ammonium bromide would be of a similar magnitude to the enthalpy change of solution of ammonium chloride.

Comment on this suggestion in terms of the hydration enthalpies and lattice energies of these two compounds.

(3)

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(c) Write an **ionic** equation to show why aqueous solutions of ammonium chloride are acidic. State symbols are not required.

(1)

(Total for question = 17 marks)

Q5.

Answer the question with a cross in the box you think is correct ☒. If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒.

When ethanoic acid and chloroethanoic acid are mixed, an equilibrium is set up.

$$CH_3COOH + CH_2ClCOOH \rightleftharpoons CH_3COOH_2^+ + CH_2ClCOO^-$$

The Brønsted-Lowry acids in this equilibrium are

☒ **A** CH_3COOH and $CH_2ClCOOH$

☒ **B** CH_3COOH and $CH_3COOH_2^+$

☒ **C** $CH_2ClCOOH$ and $CH_3COOH_2^+$

☒ **D** $CH_3COOH_2^+$ and CH_2ClCOO^-

(Total for question = 1 mark)

Q6.

Answer the question with a cross in the box you think is correct ☒. If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒.

A buffer solution contains ethanoic acid, with a concentration of 0.10 mol dm^{-3}, and sodium ethanoate, with a concentration of 0.050 mol dm^{-3}.

K_a for ethanoic acid = 1.7×10^{-5} mol dm^{-3}

The pH of this buffer solution is

☒ **A** 2.88

☒ **B** 4.47

☒ **C** 4.77

☒ **D** 5.07

Use this space for any rough working. Anything you write in this space will gain no credit.

(Total for question = 1 mark)

Q7.

A solution of sodium hydroxide of concentration 0.0080 mol dm^{-3} has a pH

- ☒ **A** between 7 and 9
- ☒ **B** between 9 and 11
- ☒ **C** between 11 and 13
- ☒ **D** above 13

(Total for question = 1 mark)

Q8.

How are 20 cm^3 of 0.05 mol dm^{-3} $H_2SO_4(aq)$ and 20 cm^3 of 0.10 mol dm^{-3} $CH_3COOH(aq)$ alike?

Both solutions

- ☒ **A** have the same pH
- ☒ **B** have the same total concentration of ions
- ☒ **C** have the same total concentration of **negative** ions
- ☒ **D** require 20 cm^3 of 0.10 mol dm^{-3} NaOH(aq) for complete reaction

(Total for question = 1 mark)

Q9.

Which indicator should be used to determine the end point in a titration of a strong acid with a weak base?

(1)

☒ **A** universal indicator

☒ **B** methyl orange

☒ **C** phenolphthalein

☒ **D** litmus

(Total for question = 1 mark)

Q10.

Answer the question with a cross in the box you think is correct ☒ . If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒ .

A diprotic acid, H_2A, was titrated with sodium hydroxide solution.

$$H_2A(aq) + 2NaOH(aq) \rightarrow Na_2A(aq) + 2H_2O(l)$$

A 25.0 cm^3 portion of 0.100 mol dm^{-3} sodium hydroxide solution required 12.80 cm^3 of the solution of the diprotic acid for complete neutralisation.

What is the concentration of H_2A in mol dm^{-3}?

☒ **A** 2.56×10^{-2}

☒ **B** 9.77×10^{-2}

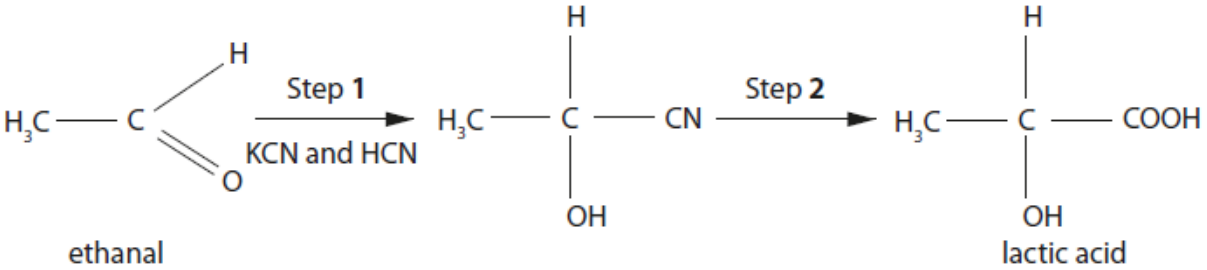
☒ **C** 1.95×10^{-1}

☒ **D** 3.91×10^{-1}

(Total for question = 1 mark)

Q11.

The compound lactic acid can be synthesised from ethanal in two steps.



(a) (i) Give the mechanism for Step **1**. Include curly arrows, and any relevant lone pairs and dipoles.

(4)

(ii) A student predicted that the product of Step **1** would rotate the plane of plane-polarised light.

Comment on this prediction.

(3)

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(iii) Complete the table that summarises information about Step **2**.
State symbols are not required for the equation.

(4)

Conversion of $CH_3CH(OH)CN$ to lactic acid	
Reaction type	
Reagent	
Conditions	
Equation	

(b) Sodium hydrogencarbonate, $NaHCO_3$, has been used by some athletes to help prevent lactic acid causing muscle pain during exercise.

Write an equation for the reaction between sodium hydrogencarbonate and lactic acid.

(1)

(c) Sodium hydrogencarbonate is part of a buffer in the body that controls the pH of blood. Two of the equilibria involved in this process are shown.

Equilibrium 1 $HCO_3^- + H_3O^+ \rightleftharpoons H_2CO_3 + H_2O$

Equilibrium 2 $H_2CO_3 \rightleftharpoons CO_2 + H_2O$

(i) Use the equilibria to explain how the buffer keeps the pH of blood nearly constant when a small increase in the concentration of hydrogen ions occurs.

(3)

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(ii) The pH of a blood sample was found to be 7.41.
Calculate the ratio of the concentration of HCO_3^- to H_2CO_3 in the blood sample.

$$H_2CO_3 + H_2O \rightleftharpoons HCO_3^- + H_3O^+$$

$$K_a = 4.50 \times 10^{-7} \text{ mol dm}^{-3}$$

(3)

(Total for question = 18 marks)

Q12.

This question is about ethanoic acid and some of its compounds.

(a) Three students, A, B and C, carried out an investigation to determine the amount of isoamyl acetate, an ester of ethanoic acid, in a banana food flavouring.

They hydrolysed the ester with excess sodium hydroxide solution.

$$CH_3COOCH_2CH_2CH(CH_3)_2 + NaOH \rightarrow CH_3COONa + (CH_3)_2CHCH_2CH_2OH$$

The amount of sodium hydroxide remaining was determined by titrating the reaction mixture with hydrochloric acid.

(i) Give the systematic name for isoamyl acetate.

(1)

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(ii) 6.06×10^{-3} mol of sodium hydroxide reacted with the ester present in 1.07 g of the flavouring.

Calculate the percentage by mass of the ester in the food flavouring.

(3)

(iii) The students used 25.0 cm^3 of sodium hydroxide solution with concentration 0.980 mol dm^{-3} for the hydrolysis.

Calculate the pH of the reaction mixture when the hydrolysis is complete. Assume the total volume is 25.0 cm^3.

[Ionic product of water, $K_w = 1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$]

(3)

(iv) Two indicators, methyl orange and phenolphthalein, were available for this titration.

Student A thought only methyl orange could be used.
Student B thought only phenolphthalein could be used.
Student C suggested either indicator could be used.

Explain which student is correct.

(2)

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(v) Describe how the sodium ethanoate in the final reaction mixture could be converted into ethanoic acid.

(1)

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(b) Ethanoic acid can be used to form buffer solutions.

(i) Calculate the pH of the buffer solution formed when 50.0 cm^3 of ethanoic acid with concentration of 0.150 mol dm^{-3} is mixed with 30.0 cm^3 of sodium hydroxide solution with concentration of 0.142 mol dm^{-3}.

[K_a for ethanoic acid = 1.70×10^{-5} mol dm^{-3}]

(5)

(ii) Small amounts of sodium hydroxide and hydrochloric acid are added to separate samples of the buffer solution in (b)(i).

Explain why these samples resist change in pH.

Illustrate your answer with at least two equations.

(5)

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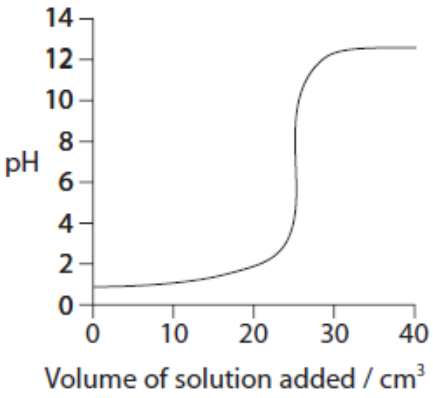
(Total for question = 20 marks)

Q13.

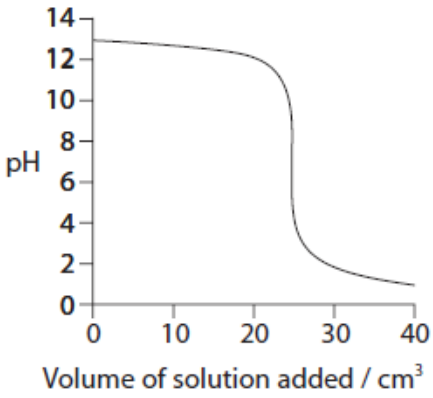
Answer the questions with a cross in the boxes you think are correct ☒. If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒.

The graphs show the changes in pH during a series of titrations.
Each titration involves two solutions, each of concentration 0.1 mol dm^{-3}.

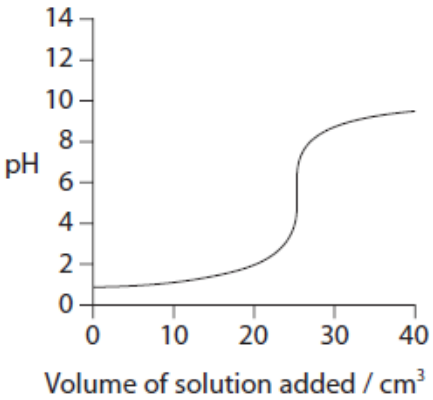
Graph **1**



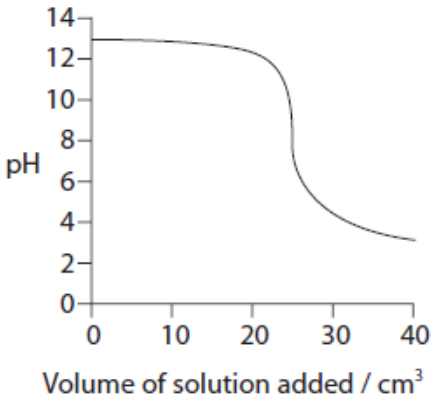
Graph **2**



Graph **3**



Graph **4**



(a) Which graph has ethanoic acid as one of the reactants?

(1)

☒ **A** Graph **1**

☒ **B** Graph **2**

☒ **C** Graph **3**

☒ **D** Graph **4**

(b) Which graph shows a solution that has an acidic pH at the end-point?

(1)

☒ **A** Graph **1**

☒ **B** Graph **2**

☒ **C** Graph **3**

☒ **D** Graph **4**

(c) Which indicator is suitable for the titration shown in Graph **3**?

Use your Data Booklet.

(1)

☒ **A** bromocresol green

☒ **B** bromothymol blue

☒ **C** phenol red

☒ **D** thymol blue (acid)

Use this space for any rough working. Anything you write in this space will gain no credit.

(Total for question = 3 marks)

Q14.

This question is about compounds with the molecular formula $C_6H_{12}O_2$.

(a) Hexanoic acid, $C_5H_{11}COOH$, is a weak acid.

(i) Write the equation for the acid dissociation constant, K_a, of hexanoic acid.

(1)

(ii) Calculate the pH of a 0.100 mol dm^{-3} solution of hexanoic acid.

[pK_a of hexanoic acid = 4.88]

(4)

(iii) The solubility of hexanoic acid in water is 1.08 g per 100 g of water.

The isomer of hexanoic acid, butyl ethanoate, $CH_3CO_2C_4H_9$, has a solubility of 0.68 g per 100 g of water.

Explain the differences in these data in terms of the hydrogen bonding between hexanoic acid and water, and between butyl ethanoate and water.

(3)

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(b)(i) Compound **A** is thought to be another isomer of hexanoic acid.

10 g of compound **A** is found to contain 6.21 g of carbon and 1.03 g of hydrogen, with the remainder being oxygen.

Use the data to calculate the empirical formula of compound **A**.

You must show **all** your working.

(3)

(ii) State how you might use your answer to (b)(i) and a mass spectrum of compound **A** to prove that compound **A** is an isomer of hexanoic acid.

(1)

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*(iii) A series of tests was performed on compound **A**.

	Test	Observation
1	addition of phosphorus(V) chloride	misty fumes
2	addition of 2,4-dinitrophenylhydrazine	orange precipitate
3	addition of Benedict's or Fehling's reagent	solution remains blue with no precipitate
4	addition of acidified potassium dichromate(VI)	solution remains orange
5	test using polarimetry	plane of plane polarised light is rotated

Deduce the structure for compound **A**.
Justify your answer by using all the test results.

(6)

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(c) Compound **B**, another isomer with the molecular formula $C_6H_{12}O_2$, contains a ring of six carbon atoms.

The carbon-13 NMR spectrum has only two peaks, one of which is at 69 ppm.

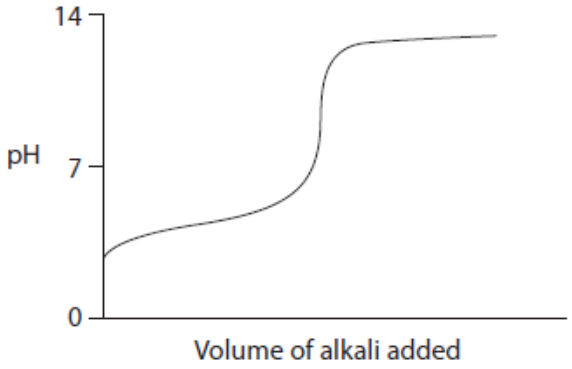
Draw the structure of compound **B**.

(2)

(Total for question = 20 marks)

Q15.

Which two solutions, both of concentration 0.10 mol dm^{-3}, have been used to produce this titration curve?



☒ **A** HCl(aq) and KOH(aq)

☒ **B** HCOOH(aq) and KOH(aq)

☒ **C** HCl(aq) and NH_3(aq)

☒ **D** HCOOH(aq) and NH_3(aq)

(Total for question = 1 mark)

Mark Scheme

Q1.

Q	Correct Answer	Mark
(a)	**The only correct answer is C** (0.1 mol dm^{-3} HCl) *A is incorrect as final pH would be greater than 2 (weak acid)* *B is incorrect as final pH would be greater than 2 (weak acid)* *D is incorrect as final pH would be less than 1 (strong acid)*	1

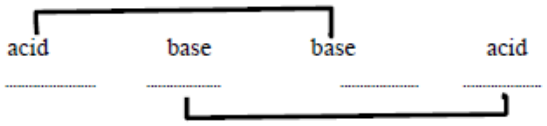
Q	Correct Answer	Mark
(b)	**The only correct answer is A** (NH_3) ***B*** *is incorrect as strong base so vertical section would begin at a higher pH / curve has a buffer region* ***C*** *is incorrect as strong base so vertical section would begin at a higher pH / curve has a buffer region* ***D*** *is incorrect as strong base so vertical section would begin at a higher pH / curve has a buffer region*	1

Q	Correct Answer	Mark
(c)	**The only correct answer is C** (3) ***A*** *is incorrect as only methyl orange, bromophenol blue and bromocresol green would change colour in the vertical section of the 'curve'* ***B*** *is incorrect as only methyl orange, bromophenol blue and bromocresol green would change colour in the vertical section of the 'curve'* ***D*** *is incorrect as methyl orange, bromophenol blue and bromocresol green would change colour in the vertical section of the 'curve'*	1

Q2.

Question Number	Answer	Additional guidance	Mark
(a)(i)	• Calculation of hydrogen ion concentration **(1)** • Calculation of hydroxide ion concentration **(1)**	Example of calculation ($[H^+] = 10^{-pH}$) $[H^+] = 0.074989 / 0.075 / 7.4989 \times 10^{-2}$ (mol dm^{-3}) Do not award just $[H^+] = 10^{-1.125}$ ($[OH^-] = 1.0 \times 10^{-14} \div 0.074989$) $[OH^-] = 1.3335 \times 10^{-13}$ (mol dm^{-3}) Allow = $1 \times 10^{-12.875}$ Allow 1 mark for correct unidentified concentrations whatever order they are given Ignore SF except 1 SF	**(2)**

Question Number	Answer	Additional guidance	Mark
(a)(ii)	• Calculation of moles of H^+ in original solution **(1)** • Calculation of concentration of H^+ in new solution **(1)** • Calculation of volume of new solution **(1)** • Calculation of volume of water needed to add giving answer to 2 or 3 SF **(1)** OR • Calculation of change in pH **(1)** • Concentration of change of concentration of H^+ **(1)** • Calculation of volume of new solution **(1)** • Calculation of volume of water needed to add giving answer to 2 or 3 SF **(1)**	Example of calculation $= 0.074989 \times 25 \div 1000 = 0.0018747 / 1.8747 \times 10^{-3}$ (mol) $[H^+] = 10^{-1.5} / 0.031623 / 3.1623 \times 10^{-2}$ (mol dm^{-3}) $0.0018747 \div 0.031623 = 0.059284$ (dm^3) $59.284 - 25.000 = 34.29284$ (cm^3) $= 34.3 / 34$ (cm^3) $= 1.5 - 1.125 = 0.375$ $[H^+] = 10^{-0.375} / 0.42170 / 4.2170 \times 10^{-1}$ (mol dm^{-3}) $= 25 \div 0.42170 = 59.284$ (cm^3) $59.284 - 25.000 = 34.29284$ (cm^3) $= 34.3 / 34$ (cm^3) Allow 0.034 / 0.0343 dm^3 Allow TE throughout including from (a)(i) Correct answer with no working scores (4) Ignore SF except 1 SF until final answer	**(4)**

Question Number	Answer	Additional guidance	Mark
(b)(i)	• Any two correct acid or base **(1)** • All four correct acid and base plus indication of pairings **(1)**	e.g. $H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + H_3O^+(aq)$ Acid Base Conjugate Base Conjugate Acid OR  linked in some way to show pairs (eg as shown) scores (2) Just acid base base acid scores (1)	**(2)**

Question Number	Answer	Additional guidance	Mark
(b)(ii)	An explanation that makes reference to the following points: • oxonium / H_3O^+ ion produced in first dissociation **(1)** • (prevents further dissociation by) pushing second equilibrium to the left. **(1)**	Allow hydronium / hydroxonium ion / H^+	**(2)**

Question Number	Answer	Additional guidance	Mark
(c)(i)	• Correct expression for K_{a1}	$K_{a1} = \frac{[H_2PO_4^-((aq))][H_3O^+((aq))]}{[H_3PO_4((aq))]}$ Allow use of H^+ instead of H_3O^+ Do not award the charge outside of the square bracket	**(1)**

Question Number	Answer	Additional guidance	Mark
(c)(ii)	• Calculate hydrogen ion concentration **(1)** • States $[H_2PO_4^-((aq))] = [H_3O^+((aq))]$ or shown in the expression for K_{a1} **(1)** • Calculates K_{a1} **(1)** • Units **(1)**	Example of calculation: $= 10^{-pH}$ / $10^{-1.2}$ / 0.063096 / 6.3096×10^{-2} / 0.0631 / 6.31×10^{-2} Do not award 0.0630 but TE can be awarded for the remaining marks Allow TE for an incorrect expression for K_{a1} $K_{a1} = \frac{[H_3O^+((aq))]^2}{[H_3PO_4((aq))]}$ $K_{a1} = \frac{(0.063096)^2}{0.500 - 0.063096} = \frac{0.0039811}{0.43690}$ $= 0.0091121$ / 9.1121×10^{-3} / 0.00911 / 9.11×10^{-3} ALLOW Use of assumption $[H_3PO_4(aq)] = 0.500$ $= 0.0079621$ / 7.9621×10^{-3} / 0.00796 / 7.96×10^{-3} Correct value with no working scores (3) mol dm^{-3} Correct answer with no working and correct units scores (4) Ignore SF except 1 SF but allow 0.5 for concentration	**(4)**

Question Number	Answer	Additional guidance	Mark
(d)	An explanation that makes reference to the following points: • The mixture contains a (large) reservoir / high concentration of **both** phosphate ions / of hydrogen phosphate and dihydrogen phosphate ions / of $H_2PO_4^-$ and HPO_4^{2-} **(1)** **Either** • Added OH^- combines with H^+ to form water / $H^+ + OH^- \rightarrow H_2O$ **AND** Dihydrogen phosphate ion / $H_2PO_4^-$ dissociates to form more H^+ / $H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+$ **Or** Added OH^- reacts with dihydrogen phosphate ion (to form water) / $OH^- + H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H_2O$ **(1)** • (pH changes very little because added OH^- is removed) and change in concentration of $H_2PO_4^-$ **and** HPO_4^{2-} is small / ratio [salt]/[acid] hardly changes **(1)**	Allow large amount / abundance For this mark to be scored at least one ionic equation is required If the equilibrium is given allow 'added OH^- causes the equilibrium to move to the right' Allow pH is unchanged Allow ratio changes a little / changes slightly Ignore there is no change in concentrations / the ratio is unchanged	**(3)**

Q3.

Question number	Answer	Additional guidance	Mark
(a)(i)	• pH = (0.85387) = 0.85		1

Question number	Answer		Additional guidance	Mark
(a)(ii)	• re-arrangement of K_a expression	(1)	Example of calculation: $[H^+]^2 = K_a\,[HA]$	3
	• calculation of $[H^+]$	(1)	$[H^+]^2 = 1.76 \times 10^{-5} \times 0.14$ $= 2.464 \times 10^{-6}$ $[H^+] = \sqrt{(1.76 \times 10^{-5} \times 0.14)}$ $= 1.5697 \times 10^{-3}$	
	• calculation of pH	(1)	pH = (2.8042) = 2.8(0) Penalise not to 2DP once only in (a)(i) and (ii) Correct answer with no working scores 3	

Question number	Answer		Additional guidance	Mark
(b)(i)	• at half equivalence point, pH = pK_a	(1)	Example of calculation:	3
	• reads off pH from graph	(1)	= 4.8 Allow 4.5 to 5.2	
	• calculates K_a	(1)	$K_a = 10^{-pH} = 10^{-4.8} =$ 1.6×10^{-5} (mol dm^{-3}) Allow answers in the range 6.3×10^{-6} to 3.2×10^{-5}	

Question number	Answer		Additional guidance	Mark
(b)(ii)	• [HA] >>[A-]	(1)	Allow for 1 mark 'not buffered'	2
	• ratio [A-]:[HA] changes (significantly) in this region	(1)		

Question number	Answer	Additional guidance	Mark
(c)(i)	• calculation of [HA]/[A-] = 2/1 (1) • correct calculation of $[H^+] = 2.6 \times 10^{-5}$ (mol dm^{-3}) (1) • correct calculation of pH (1)	Example of calculation: [HA] = 1.0 × 20 ÷ 40 = 0.50 $[A^-]$ = 1.0 × 10 ÷ 40 = 0.25 or any recognition that [HA]/$[A^-]$ = 2/1 $[H^+] = 2.6 \times 10^{-5}$ (mol dm^{-3}) pH = 4.6/4.59/4.58 Correct answer with no working scores 3 marks	3

Question number	Answer	Additional guidance	Mark
(c)(ii)	• no H^+ ions come from (ionisation of) water or $[acid]_{initial} = [acid]_{eqm}$		1

Q4.

Question Number	Answer	Additional Guidance	Mark
(a)(i)	$K_p = \frac{p_2NH_3}{pN_2\ p^3H_2}$	Allow round or no brackets Allow upper case Allow pp/PP Allow $p(NH_3)_2$ pNH_{32} etc Ignore units even if incorrect Do not award square brackets	(1)

Question Number	Answer	Additional Guidance	Mark
(a)(ii)	• mole fraction of N_2 (1) • mole fraction of H_2 (1) • both partial pressures (1)	Example of completed table Substance / Mole fraction / Partial pressure/atm N_2 / 0.18 / 36 H_2 / 0.54 / 108 NH_3 / 0.28 / 56 TE for M3 on calculated mole fractions multiplied by 200	(3)

Question Number	Answer	Additional Guidance	Mark
(a)(iii)	An answer that makes reference to the following points: • correct use of K_p expression **(1)** • correct answer **and** 1 or 2 SF **(1)** • correct units **(1)**	Example of calculation $56^2 \div (108^3 \times 36)$ 7 or 6.9×10^{-5} / 0.00007 or 0.000069 Allow 3SF 6.92×10^{-5} /0.0000692 Do not award 7.0×10^{-5} / 0.000070 atm^{-2} Allow TE from (a)(i) and (a)(ii) If mole fractions are used for the calculation max score 1 for the correct answer **and** 1-3 SF Correct answer with or without working scores 3	**(3)**

Question Number	Answer	Additional Guidance	Mark
(a)(iv)	An answer that makes reference to the following points: • the (forward) reaction is/ must be exothermic **(1)** • (more ammonia shows that) the equilibrium has moved/shifted to the right **OR** (more ammonia shows that) a new K_p is established which is larger **(1)**	Allow reverse argument Allow favours forward reaction/shifts to the product side Allow K_p increases/eqm constant increases Ignore just 'more ammonia produced' or 'yield increases'	**(2)**

Question Number	Answer	Additional Guidance	Mark
(b)(i)	• $NH_4^+(aq) + Cl^-(aq)$	Do not award $NH_4^+Cl^-(aq)$ Do not award $NH_4Cl(aq)$ Do not award any other state symbols	**(1)**

Question Number	Answer	Additional Guidance	Mark
(b)(ii)	• $\Delta_{sol}H = \Delta_{hyd}H$ – Lattice Energy or $\Delta_{sol}H = -$ Lattice Energy + $\Delta_{hyd}H$	Allow LE for Lattice Energy Allow $\Delta_{sol}H = -$ Lattice Energy + hydration enthalpies Allow $\Delta_{sol}H = -$ Lattice Energy + hydration enthalpies Allow ΔH_{hyd} etc Ignore standard signs	(1)

Question Number	Answer	Additional Guidance	Mark
(b)(iii)	• enthalpy change of hydration of ammonium chloride (1) • enthalpy change of solution (1)	Example of calculation $-307 + (-378) = -685$ (kJ mol^{-1}) Allow (kJ mol^{-}) $705 + (-685) = (+)20$ (kJ mol^{-1}) Allow TE on arithmetical errors Do not award use of incorrect expression Correct answer with or without working scores 2 Units are not required but if wrong penalise only once.	(2)

Question Number	Answer	Additional Guidance	Mark
(b)(iv)	An explanation that makes reference to three of the following points • M1 the bromide (ion) is larger than the chloride (ion) **(1)** And any 2 of the following • M2 hydration enthalpy of the bromide ion less exothermic/less negative (than the chloride) **(1)** • M3 lattice energy of ammonium bromide would be less exothermic/less negative (than ammonium chloride) **(1)** • M4 the enthalpy of solutions depends on the values of both hydration and lattice energies (so the enthalpies of solution should be similar) **(1)**	Allow bromine ion larger than the chlorine ion Do not award larger atomic radius Allow smaller/lower Allow hydration enthalpy of bromine would be less exothermic/less negative (than the chlorine) Allow hydration enthalpy of ammonium bromide would be less exothermic/less negative (than ammonium chloride) Allow smaller/lower Accept because we don't know the magnitude of the reduction in hydration and lattice energies it is not possible to assess the overall effect Allow reverse arguments for MP1, MP2 and MP3 Ignore any reference to reactivity, polarisation and charge density	**(3)**

Question Number	Answer	Additional Guidance	Mark
(c)	• $NH_4^+ + H_2O \longrightarrow NH_3 + H_3O^+$	Accept $NH_4^+ \longrightarrow NH_3 + H^+$ Allow eqm sign Ignore $NH_4Cl \longrightarrow NH_4^+ + Cl^-$ Ignore $NH_4Cl + aq \longrightarrow NH_4^+ + Cl^-$ Ignore state symbols even if incorrect Do not award $NH_4Cl + aq \longrightarrow NH_3 + HCl$ Do not award $NH_4Cl \longrightarrow NH_3 + HCl$ Do not award $NH_4Cl \longrightarrow NH_3 + H^+ + Cl^-$ Do not award $NH_4^+ + OH^- \longrightarrow NH_3 + H_2O$	**(1)**

Q5.

Question number	Answer	Mark
	The only correct answer is C ($CH_2ClCOOH$ and $CH_3COOH_2^+$) ***A*** *is incorrect because ethanoic acid accepts a proton in this system so is a base* ***B*** *is incorrect because ethanoic acid accepts a proton in this system so is a base* ***D*** *is incorrect because CH_2ClCOO^- is a base*	**(1)**

Q6.

Question Number	Answer	Mark
	The only correct answer is B (4.47) ***A*** *is incorrect because this answer assumes the concentration of ethanoate ion = concentration of hydrogen ion (as it would be in a weak acid calculation)* *C is incorrect because this answer is $-\log K_a$ so does not consider the concentrations* ***D*** *is incorrect because this answer is $-\log(2xK_a)$ which has the concentrations upside down*	(1)

Q7.

Question Number	Answer	Mark
	The only correct answer is **C** (between 11 and 13) *A is incorrect the solution is a strong base whose concentration is > $1x10^{-5}$ mol dm^{-3}* *B is incorrect the solution is a strong base whose concentration is > $1x10^{-3}$ mol dm^{-3}* *D is incorrect the solution is a strong base whose concentration is < $1x10^{-1}$ mol dm^{-3}*	**1**

Q8.

Question Number	Answer	Mark
	The only correct answer is **D** (require 20 cm^3 of 0.10 mol dm^{-3} NaOH (aq) to react completely) *A is incorrect as one acid is strong, the other is weak* *B is incorrect as the solutions have different concentrations and ethanoic acid is a weak acid* *C is incorrect as the solutions have different concentrations and ethanoic acid is a weak acid*	1

Q9.

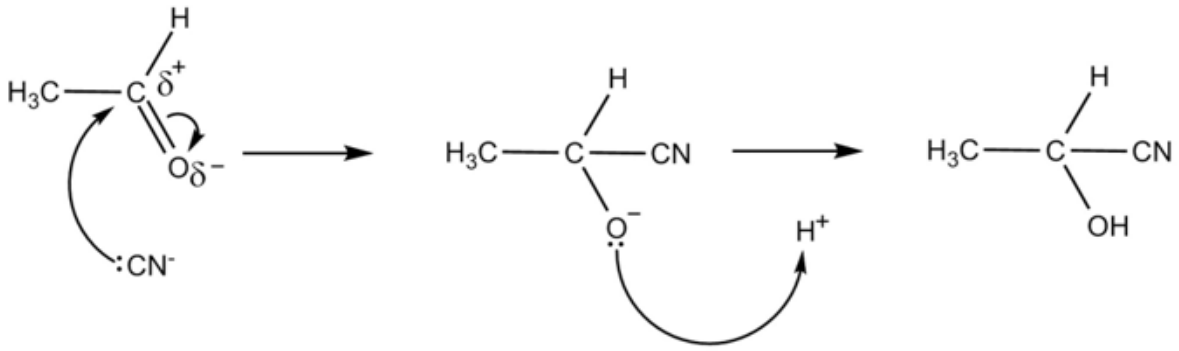
Question number	Answer	Mark
	B methyl orange	1

Q10.

Question Number	Answer	Mark
	The only correct answer is B (9.77×10^{-2} (mol dm^{-3})) *A is not correct because the two volumes have been reversed* *C is not correct because a mole ratio of 1:1 has been used instead of 1 mol of acid : 2 mol NaOH* *D is not correct because a mole ratio of 2 mol of acid : 1 mol NaOH has been used*	(1)

Q11.

Q	Acceptable Answers	Additional Guidance	Mark
(a)(i)	• arrow from lone pair on carbon of cyanide ion to carbonyl carbon **(1)** • dipoles on carbon and oxygen in carbonyl bond **and** arrow from carbonyl bond to oxygen or just beyond **(1)** • structure of intermediate, including charge **(1)** • arrow from lone pair of oxygen in intermediate to hydrogen ion / H in HCN **(1)**	Penalise absence of lone pair only once in M1, M3 and M4 If HCN used to protonate in step 2, dipole on HCN and curly arrow to break HCN bond are **not** required Ignore product	4



Q	Acceptable Answers	Additional Guidance	Mark
(a)(ii)	The prediction is incorrect because • ethanal is planar around the carbonyl carbon atom / planar around the CHO **(1)** • (so in Step 1) the (carbonyl) carbon can be attacked from above or below **(1)** • hence both stereoisomers (of intermediate / product) will form in equal amounts **or** so product mixture is racemic / rotates the plane of plane-polarised light equally in both directions **(1)**	Accept planar at the site of the nucleophilic attack / planar about C=O Do not award planar molecule / cation / intermediate Allow attack from any direction / either side Ignore 'has no effect on the plane of plane-polarised light' Ignore comments related to SN1 or SN2 If no other mark scored allow 1 mark for idea that product will rotate plane of plane polarised light as it has a chiral centre / carbon	**3**

Q	Acceptable Answers	Additional Guidance	Mark
(a)(iii)	• hydrolysis **(1)** • (dilute) hydrochloric acid / HCl((aq)) **(1)** • heat (under reflux) / reflux **(1)** • $CH_3CH(OH)CN + 2H_2O + H^+ \rightarrow CH_3CH(OH)COOH + NH_4^+$ **(1)** OR $CH_3CH(OH)CN + 2H_2O \rightarrow CH_3CH(OH)COOH + NH_3$ OR $CH_3CH(OH)CN + 2H_2O + HCl \rightarrow CH_3CH(OH)COOH + NH_4Cl$ OR $CH_3CH(OH)CN + H_2O + OH^- \rightarrow CH_3CH(OH)COO^- + NH_3$ **and** $CH_3CH(OH)COO^- + H^+ \rightarrow CH_3CH(OH)COOH$	Allow any strong acid by name or formula Allow sodium hydroxide **followed by** any (strong) acid Ignore conc / concentrated Allow 'boil' for heat Allow NaOH for OH^- Allow HCl for H^+ Ignore state symbols even if incorrect	**4**

Q	Acceptable Answers	Additional Guidance	Mark
(b)	• $CH_3CH(OH)COOH + NaHCO_3 \rightarrow CH_3CH(OH)COO^-Na^+ + H_2O + CO_2$ OR $H^+ + HCO_3^- \rightarrow H_2O + CO_2$	Allow $CH_3CH(OH)COONa$ Allow H_2CO_3 Ignore state symbols even if incorrect Do not award if covalent bond shown between O and Na	**1**

Q	Acceptable Answers	Additional Guidance	Mark
(c)(i)	• (large concentration of) HCO_3^- react with (extra) H^+ ions **(1)** • equilibrium 1 moves to the RHS to keep concentration of H^+ ions constant / H_2CO_3 forms to keep concentration of H^+ ions constant **(1)** • equilibrium 2 moves to RHS to form CO_2 (which can be excreted from the body) / H_2CO_3 then forms CO_2 (and water) **(1)**	Allow ratio of $[HCO_3^-]$ to $[H_2CO_3]$ remains constant / ratio of [salt] to [acid] remains constant Allow H_3O^+ for H^+ Allow equilibrium 1 moves to the RHS to remove excess H^+ ions / H_2CO_3 forms to remove excess H^+ ions If no reference to H^+ and CO_2 in M2 and M3 but direction of movement of equilibria are correct in both cases, allow 1 mark	3

Q	Acceptable Answers	Additional Guidance	Mark
(c)(ii)	• calculation of $[H^+]$ / $[H_3O^+]$ **(1)** • K_a expression **(1)** • rearrangement of K_a expression and calculation of $[HCO_3^-] : [H_2CO_3]$ **(1)** OR • calculation of pK_a **(1)** • Henderson Hasselbach expression **(1)** • rearrangement of K_a expression and calculation of $[HCO_3^-] : [H_2CO_3]$ **(1)**	$[H^+] = 10^{-7.41}$ / = 3.8905×10^{-8} $K_a = \frac{[HCO_3^-][H^+]}{[H_2CO_3]}$ Allow $[H_3O^+]$ in K_a Do not award $[H_2O]$ in K_a expression $[HCO_3^-] : [H_2CO_3]$ $= 4.5 \times 10^{-7} \div 3.8905 \times 10^{-8} = 11.567 : 1 = 11.6 (: 1)$ Ignore SF except 1 Allow correct rounding of $[H^+]$ to 3.9×10^{-8} Allow 1 : 0.086444 if it's clear that 1 relates to $[HCO_3^-]$ p$K_a = -\log 4.5 \times 10^{-7} = 6.3468$ pH = pK_a + log($[HCO_3^-] \circ [H_2CO_3]$) 7.41 - 6.3468 = log($[HCO_3^-] \circ [H_2CO_3]$) $[HCO_3^-] : [H_2CO_3] = 11.567 (: 1)$ Correct answer with no working scores (3) If final answer close, check for and allow correct rounding	3
		(Total for Question = 18 marks)	

Q12.

Question Number	Acceptable Answers	Additional Guidance	Mark
(a)(i)	3- methylbutyl ethanoate or 3-methyl-1-butyl ethanoate	Allow butanyl for butyl Do not award butanoyl Allow methly formethyl	1

Question Number	Acceptable Answers	Additional Guidance	Mark
(a)(ii)	• Calculation of M_r of ester (1) • Calculation of mass of ester (1) • Calculation of percentage of ester (1)	Example of calculation M_r of ester = 130 Mass of ester = $6.06 \times 10^{-3} \times 130$ = 0.7878 (g) TE on incorrect M_r of ester % of ester = (0.7878/1.07) x 100 =73.6 % Allow 73.8% as M2 rounded to 0.79 Correct answer with no working scores 3 marks. Allow TE from M2 Ignore SF except 1SF	3

Question Number	Acceptable Answers	Additional Guidance	Mark
(a)(iii)	• Calculation of mol of excess sodium hydroxide (1) • Calculation of concentration of excess sodium hydroxide (1) • Calculation of pH to at least 1 dp (1)	Example of calculation Excess amount of sodium hydroxide = $(0.025 \times 0.980) - 6.06 \times 10^{-3} = 0.01844$ (mol) Concentration of excess sodium hydroxide = 0.01844/0.025 = 0.7376 (mol dm^{-3}) allow TE from M1 if some attempt at subtraction pH = 14–(–log(0.7376)) = 13.8678 = 13.9 allow TE from M2 if pH is greater than7 and less than or equal to 14 Allow 1 mark for pH =13.99 (based on 0.98 mol dm^{-3} NaOH)	3

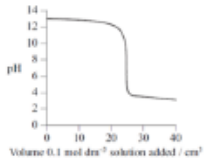
Question Number	Acceptable Answers	Additional Guidance	Mark
(a)(iv)	• student C is correct as the titration is between a strong acid and a strong base (1) • Both methyl orange and phenolphthalein change colour at equivalence / vertical section of the graph (1)	Allow A and B are incorrect Allow both pK_{IN} values / range of indicators are within vertical section (of the graph) If values are quoted they must be correct PP = 9.3 ; MO = 3.7	2

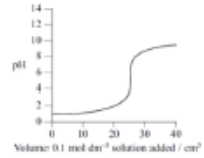
Question Number	Acceptable Answers	Additional Guidance	Mark
(a)(v)	Add (excess) HCl(aq) (1)	Allow 'add a strong acid' Allow name or formula of any strong acid but if both are given, both must be correct Ignore references to dilute / conc / heat / reflux	1

Question Number	Acceptable Answers	Additional Guidance	Mark
(b)(i)	**M1** Calculates moles of CH_3COONa/ NaOH (1) **M2** Calculates moles ofexcess CH_3COOH (1) **M3** Calculates / shows ratio of $[CH_3COOH]$ to $[CH_3COONa]$ OR ratio of moles CH_3COOH to CH_3COONa (1) **M4** re-arranges K_a or pK_a expression correctly and substitutes appropriate values to find $[H^+]$ (1) **M5** Calculation of pH (1)	Example of calculation Moles of NaOH = moles of CH_3COONa = (30/1000) x 0.142 = 4.26×10^{-3} (mol) Moles of excess CH_3COOH = [(50/1000) x 0.15] - 4.26×10^{-3} = 3.24×10^{-3} (mol) $[CH_3COOH] = 3.24 \times 10^{-3} / (80/1000)$ = 0.0405 (mol dm^{-3}) $[CH_3COONa] = 4.26 \times 10^{-3} / (80/1000)$ = 0.05325 (mol dm^{-3}) ▫ 0.0405 / 05325 Allow ratio using moles as V cancels NOTE can be subsumed in M4 $[H^+] = 1.70 \times 10^{-5} \times (0.0405/0.05325) = 1.29 \times 10^{-5}$ (mol dm^{-3}) Or pH=pKa – log([acid]/[base]) / pH= 4.77-log (0.0405/0.05325) pH = 4.89 Correct answer with no working scores 5 marks Ignore SF except 1SF Allow TE throughout Comment 4.52 will score 4 (omission of subtraction)	5

Question Number	Acceptable Answers	Additional Guidance	Mark
(b) (ii)	**M1** (Large) 'reservoir' of CH_3COOH and CH_3COO^- (1) **M2** The OH^- ions react with CH_3COOH / H^+ ions (1) **M3** $H^+ + OH^- \rightarrow H_2O$ or $CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$ (1) **M4** The H^+ ions react with CH_3COO^- or $H^+ + CH_3COO^- \rightleftharpoons CH_3COOH$ (1) **M5** The ratio of acid to base remains (almost) constant (1)	If both equations given both must be correct If equation given must be correct Allow base/salt remains (almost) constant Allow $[H^+]$ remains(almost) constant	5

Q13.

Question Number	Answer	Mark
(a)	**The only correct answer is D**  *A is incorrect because, if the graph starts or finishes at a pH of about 1, a strong acid is present* *B is incorrect because, if the graph starts or finishes at a pH of about 1, a strong acid is present* *C is incorrect because, if the graph starts or finishes at a pH of about 1, a strong acid is present*	(1)

Question Number	Answer	Mark
(b)	**The only correct answer is C**  *A is incorrect because the mid-point of the vertical portion of the graph is at pH = 7* *B is incorrect because the mid-point of the vertical portion of the graph is at pH = 7* *D is incorrect because the mid-point of the vertical portion of the graph is at pH > 7*	(1)

Question Number	Answer	Mark
(c)	**The only correct answer is A** *B is incorrect because the range of colour change for bromothymol blue (6.0 – 7.6) is not within the vertical portion of the graph* *C is incorrect because the range of colour change for phenol red (6.8 – 8.4) is not within the vertical portion of the graph* *D is incorrect because the range of colour change for thymol blue (acid) (1.2 – 2.8) is not within the vertical portion of the graph*	(1)

Q14.

Question Number	Answer	Additional Guidance	Mark
(a)(i)	An answer that makes reference to the following points: • $K_a = \frac{[C_5H_{11}COO^-][H^+]}{[C_5H_{11}COOH]}$	Accept $[CH_3CH_2CH_2CH_2CH_2CO_2^-]$ and $[CH_3CH_2CH_2CH_2CH_2CO_2H]$ Accept $[H_3O^+]$ instead of $[H^+]$ Accept other representations of the chain of hexanoic acid / hexanoate ion, such as $[CH_3(CH_2)_4COO^-]$ Ignore equation for dissociation Do not award $[H^+]^2/[C_5H_{11}COOH]$ Do not award brackets that are not square brackets Do not award molecular formulae	**(1)**

Question Number	Answer	Additional Guidance	Mark
(a)(ii)	• uses expression for pK_a **(1)** • use of K_a expression **(1)** • rearrange and solve for H^+ **(1)** • find pH	Example calculation $K_a = 10^{-pK_a}$ / $K_a = 10^{-4.88}$ / $pK_a = -\log_{10}K_a$ / $4.88 = -\log_{10}K_a$ / $K_a = 0.000013183$ / 1.3183×10^{-5} $10^{-4.88} / 1.3183 \times 10^{-5}$ / $0.000013183 = \frac{[H^+]^2}{0.1}$ $[H^+] = \sqrt{0.000013183 \times 0.1}$ = 0.0011482 / 0.00115 / 1.1482×10^{-3} / 1.15×10^{-3} (mol dm^{-3}) $pH = -\log_{10}[H^+] = 2.94$ / 2.9400 Do not award M4 with units Final correct answer with no working scores (4) Final correct answer scores (4) Allow TE at each stage Omitting the square root gives 5.88 scores (3) Use of 4.88 for K_a gives 0.1558 scores (3) Ignore SF except 1 SF	**(4)**

Question Number	Answer	Additional Guidance	Mark
(a)(iii)	An answer that makes reference to the following points: • hexanoic acid forms more hydrogen bonds (per molecule) with water than butyl ethanoate does **(1)** **(1)** • hexanoic acid has an -OH group which forms hydrogen bonds (with water) **(1)** • butyl ethanoate / hexanoic acid has a C=O group which forms hydrogen bonds (with water)	All marks may be scored with a diagram or diagrams Allow hexanoic forms two hydrogen bonds per molecule but butyl ethanoate forms only one Ignore references to the strength of the hydrogen bonds Ignore all references to other intermolecular forces	**(3)**

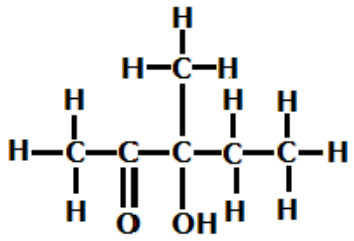
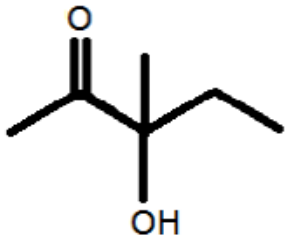
Question Number	Answer	Additional Guidance	Mark
(b)(i)	• calculate mass of oxygen **(1)** **(1)** • divides masses by atomic mass • divides by smallest to find the simplest ratio **(1)** **and** correct empirical formula	Example calculation Mass of O = 10 - 6.21 - 1.03 = 2.76(g) Element / Mass / Mass / Atomic Mass / Ratio C: 6.21 / 6.21 / 12 = 0.5175 / 3 H: 1.03 / 1.03 / 1 = 1.03 / 6 O: 2.76 / 2.76 / 16 = 0.1725 / 1 C_3H_6O Correct answer with mass/atomic mass ratios calculated scores (3) Do not award $C_6H_{12}O_2$ stated as empirical formula Ignore SF Ignore reference to $C_6H_{12}O_2$ after finding empirical formula Allow 1 mark for CH_2 deduced without finding the mass of oxygen Allow max 1 mark for incorrect masses of oxygen divided correctly by atomic mass Correct answer with no working scores (1)	**(3)**

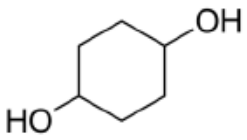
Question Number	Answer	Additional Guidance	Mark
(b)(ii)	An answer that makes reference to the following points: • molecular ion peak / peak at highest mass will be at twice the mass of the empirical formula / will be at 116	Ignore references to n.m.r or i.r.	**(1)**

Question Number	Answer	Additional guidance	Mark
(b)(iii)	This question assesses a student's ability to show a coherent and logically structured answer with linkages and fully-sustained reasoning. Marks are awarded for indicative content and for how the answer is structured and shows lines of reasoning. The following table shows how the marks should be awarded for indicative content. Number of indicative marking points seen in answer / Number of marks awarded for indicative marking points 6 / 4 5–4 / 3 3–2 / 2 1 / 1 0 / 0 The following table shows how the marks should be awarded for structure and lines of reasoning.	Guidance on how the mark scheme should be applied: The mark for indicative content should be added to the mark for lines of reasoning. For example, an answer with five indicative marking points that is partially structured with some linkages and lines of reasoning scores 4 marks (3 marks for indicative content and 1 mark for partial structure and some linkages and lines of reasoning). If there are no linkages between points, the same five indicative marking points would yield an overall score of 3 marks (3 marks for indicative content and no marks for linkages). In general, an answer with 5 or 6 IPs would score 2 reasoning marks, 3 or 4 IPs would score 1 reasoning mark, 0, 1 or 2 IPs would score 0 reasoning marks.	**(6)**

	<table><tr><td></td><td>Number of marks awarded for structure of answer and sustained line of reasoning</td></tr><tr><td>Answer shows a coherent and logical structure with linkages and fully sustained lines of reasoning demonstrated throughout.</td><td>2</td></tr><tr><td>Answer is partially structured with some linkages and lines of reasoning.</td><td>1</td></tr><tr><td>Answer has no linkages between points and is unstructured.</td><td>0</td></tr></table>	If there is any incorrect chemistry, deduct mark(s) from the reasoning. If no reasoning mark(s) awarded, do not deduct mark(s). Candidates may treat each test separately or may build on each test. Accept statements in any order.

	Indicative content • **IP1** Misty fumes suggest OH group present • **IP2** Orange precipitate suggests a carbonyl group is present (so no carboxylic acid, must be alcohol) • **IP3** (Negative) Benedict's / Fehling's reagent suggests no aldehyde group present / a ketone is present	Accept alcohol or carboxylic acid group present (must state both) Accept ketone or aldehyde present (must state both Ignore C=O is present Accept just 'no oxidisable groups present / cannot be oxidised' in either IP3 or IP4 but not both Allow tertiary alcohol is present	

	• **IP4** Acidified potassium dichromate(VI) suggests not a primary, a secondary alcohol or an aldehyde present	Accept just no primary or secondary alcohol present Ignore references to ketone and carboxylic acid giving no result	
	• **IP5** Polarimetry indicates a chiral centre is present / it is a chiral molecule	Ignore S_N2 Allow 4 different groups on a carbon Allow optically active Allow contains a single enantiomer	
	• **IP6** Structure of 3-hydroxy-3-methylpentan-2-one  	Allow the correct name Allow displayed or structural formula or combinations Allow contractions such as CH_3- C_2H_5-	

Question Number	Answer	Additional Guidance	Mark
(c)	An answer that makes reference to the following points: • a structure containing **two** –OH groups **(1)** • correct structure **(1)**	Do not award an –OH group and a -COOH group Award this mark even if the structure does not contain a ring of six atoms.  Structure may be skeletal or displayed or a mixture, as long as it is clear. Allow, for example, a displayed formula with condensed CH_2. Ignore connectivity of -OH	**(2)**

Q15.

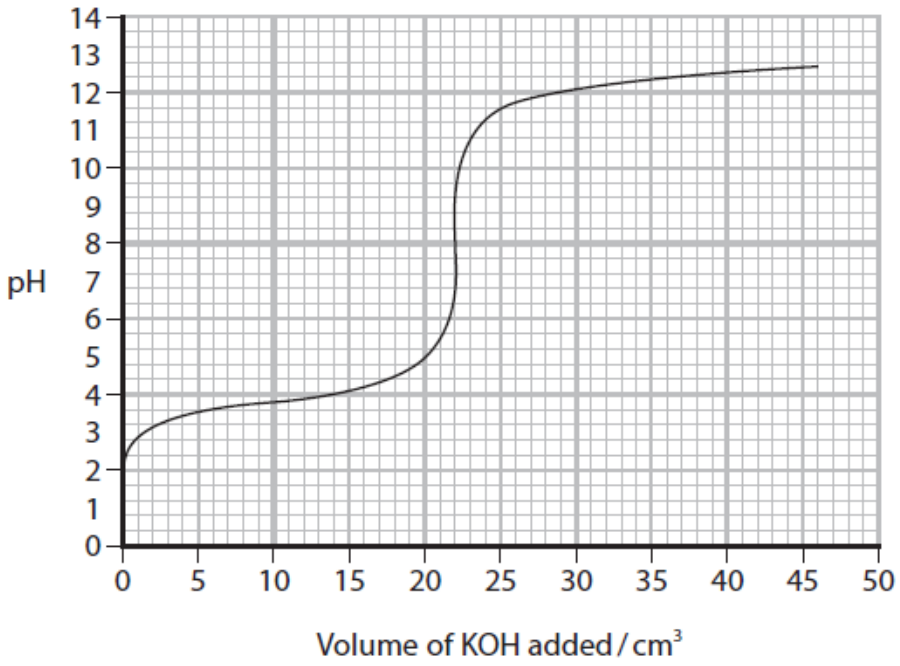
Question Number	Answer	Mark
	The only correct answer is **B** (*HCOOH(aq) and KOH(aq)*) *A is incorrect as both the acid and base are strong* *C is incorrect as the acid is strong and the base is weak* *D is incorrect as both the acid and base are weak*	1

Q1.

This question is about methanoic acid and propanoic acid.

(a) A student carried out a titration to find the concentration of an aqueous solution of potassium hydroxide.

25.00 cm^3 of 0.150 mol dm^{-3} aqueous methanoic acid was pipetted into a conical flask. Potassium hydroxide was added from a burette while measuring the pH. The titration curve is shown.



(i) Complete the equation for the reaction taking place in this titration. State symbols are not required.

(1)

HCOOH +

(ii) Calculate the concentration of the potassium hydroxide solution, using your equation in (i) and the titration curve.

(2)

(iii) Use the titration curve to determine a value for the acid dissociation constant, K_a, of methanoic acid.

(3)

(b) A student prepared a buffer by mixing together equimolar aqueous solutions of propanoic acid, CH_3CH_2COOH, and sodium propanoate, CH_3CH_2COONa.

The acid dissociation constant, K_a, for propanoic acid is 1.3×10^{-5} mol dm^{-3}.

Calculate the volume ratio of propanoic acid to sodium propanoate needed to produce a buffer solution
with a pH of 4.6

(2)

(Total for question = 8 marks)

Q2.

Answer the question with a cross in the box you think is correct ☒. If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒.

What is the pH of a 0.010 mol dm^{-3} aqueous solution of carbonic acid?

[K_a of carbonic acid = 4.5 × 10^{-7} mol dm^{-3} at 298 K]

☐ **A** 2.00

☐ **B** 4.17

☐ **C** 6.35

☐ **D** 8.35

(Total for question = 1 mark)

Q3.

Answer the question with a cross in the box you think is correct ☒. If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒.

What is the pH of a 0.27 mol dm^{-3} aqueous solution of sodium hydroxide?

[K_w = 1.0 × 10^{-14} mol2 dm^{-6} at 298 K]

☐ **A** 0.57

☐ **B** 13.43

☐ **C** 13.73

☐ **D** 14.57

Use this space for any rough working. Anything you write in this space will gain no credit.

(Total for question = 1 mark)

Q4.

Answer the question with a cross in the box you think is correct ☒. If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒.

What is the pH of 0.010 mol dm^{-3} aqueous calcium hydroxide, $Ca(OH)_2(aq)$?

[pK_w = 14]

☐ **A** 11.7

☐ **B** 12.0

☐ **C** 12.3

☐ **D** 13.3

(Total for question = 1 mark)

Q5.

The equation for the dissociation of water is:

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

The ionic product of water, K_w, varies with temperature.

Temperature/°C	K_w / mol²dm⁻⁶
25	1.01×10^{-14}
30	1.47×10^{-14}
50	5.48×10^{-14}
100	7.16×10^{-14}

What is the pH of pure water at 60 °C?

(1)

☒ **A** approximately 6.5

☒ **B** exactly 7

☒ **C** approximately 7.4

☒ **D** greater than 7.4

(Total for question = 1 mark)

Q6.

For each question, select one answer from A to D and put a cross in the box ☒. If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒.

At 25 °C, the pH of pure water is 7.00 and at 100 °C, the pH of pure water is 6.14. What can be deduced from this information?

	Enthalpy change of dissociation of water	Concentration of hydrogen ions
☒ **A**	endothermic	higher at 100 °C than at 25 °C
☒ **B**	endothermic	lower at 100 °C than at 25 °C
☒ **C**	exothermic	higher at 100 °C than at 25 °C
☒ **D**	exothermic	lower at 100 °C than at 25 °C

(Total for question = 1 mark)

Q7.

For each question, select one answer from A to D and put a cross in the box ☒. If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒.

Propanone reacts with iodine in both acidic and alkaline conditions.

(a) The products of the reactions under the stated conditions include

(1)

	Acidic conditions	Alkaline conditions
☒ **A**	CH_3I	CH_3COO^-
☒ **B**	CH_3COCI_3	CH_3COO^-
☒ **C**	CH_3COCH_2I	CH_3I
☒ **D**	CH_3COCH_2I	CHI_3

(b) The rate equation for the reaction between propanone and iodine in acidic conditions is

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

The reaction was carried out at two different pH values, all other conditions remaining unchanged.

In the first reaction pH = 2.0

In the second reaction the rate was found to be $\frac{1}{3}$ of the original value.

What was the pH of the second reaction, to 1 decimal place?

(1)

☒ **A** 0.7

☒ **B** 1.5

☒ **C** 2.5

☒ **D** 2.7

(Total for question = 2 marks)

Q8.

Answer the questions with a cross in the boxes you think are correct ☒. If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒.

Propanone reacts with iodine in the presence of a sulfuric acid catalyst.

$$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + HI(aq)$$

(a) Which method would be most suitable for following this reaction?

(1)

☒ **A** colorimetry

☒ **B** timing how long the solution takes to go cloudy

☒ **C** quenching and titrating with an acid

☒ **D** quenching and titrating with starch solution

(b) The rate equation for this reaction is:

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

Two experiments were carried out. In both experiments the concentration of propanone and iodine remained the same but the concentration of the sulfuric acid was changed.

The initial rate in the first experiment was three times faster than the initial rate in the second experiment.

In the first experiment the initial pH was 1.50

What is the initial pH in the second experiment?

(1)

☒ **A** 1.02

☒ **B** 1.98

☒ **C** 2.28

☒ **D** 4.50

Use this space for any rough working. Anything you write in this space will gain no credit.

(Total for question = 2 marks)

Q9.

Propanal reacts very slowly with HCN at 298 K. To increase the rate of reaction potassium cyanide, KCN, is added.

(a)(i) Complete the mechanism for this reaction by adding curly arrows, and relevant lone pairs and dipoles to Step **1** and Step **2**.

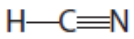
(4)

Step **1**

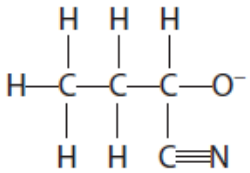


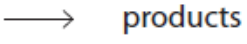
intermediate





Step **2**





products

intermediate

(ii) Explain why the reaction between propanal and HCN in the absence of KCN is very slow, referring to the value of K_a. No calculation is required.

[For HCN, $K_a = 4.9 \times 10^{-10}$ mol dm^{-3}]

(2)

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(iii) KCN is a **homogeneous catalyst** in this reaction.

Justify this description by referring to the mechanism.

(2)

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(b) The organic products of this reaction are enantiomers.

Draw the three-dimensional structures of these enantiomers.

(2)

(Total for question = 10 marks)

Q10.

This question is about sulfuric acid and its salts.

(a) The manufacture of sulfuric acid involves the equilibrium

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad \Delta_r H = -197 \text{ kJ mol}^{-1}$$

(i) A catalyst of vanadium(V) oxide is used in this reaction.

State the effect, if any, of the catalyst on the value of the equilibrium constant, K_p .

(1)

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(ii) The temperature used for this reaction in industry is 700 K.

Explain, in terms of the equilibrium constant and the equilibrium position, the effect of an increase in temperature on the equilibrium yield of sulfur trioxide.

(2)

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(iii) Write the expression for the equilibrium constant, K_p , for this equilibrium. State symbols are not required.

(1)

(iv) A mixture of 2.00 mol of sulfur dioxide and 1.00 mol of oxygen is allowed to reach equilibrium at 5.00 atm pressure.
1.60 mol of sulfur trioxide is formed.

Calculate the value of K_p.
Include units and give your answer to an appropriate number of significant figures.

(4)

(b) Sulfur trioxide is used to produce sulfuric acid.

(i) Commercial concentrated sulfuric acid contains 98.5 % H_2SO_4 and 1.5 % water by mass.
The density of concentrated sulfuric acid is 1800 g dm^{-3}.

Calculate the concentration of this sulfuric acid in mol dm^{-3}.

(2)

(ii) The pH of a 0.10 mol dm^{-3} solution of sulfuric acid at 25 °C is 0.97.

Calculate the concentration of hydrogen ions, in mol dm^{-3}, in this solution.

(1)

(iii) In an aqueous solution of sulfuric acid, the following equilibria exist.

$H_2SO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HSO_4^-(aq)$ $\quad K_a$ very large

$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq)$ $\quad K_a = 0.012\,mol\,dm^{-3}$

Explain, in terms of these equilibria, why the concentration of hydrogen ions in a 0.10 mol dm^{-3} solution of sulfuric acid is **not** 0.20 mol dm^{-3}. No calculation is required.

(2)

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(c) A buffer solution is made from HSO_4^- and SO_4^{2-} ions.

(i) Write two ionic equations involving HSO_4^- and SO_4^{2-} ions to show how this solution acts as a buffer.
State symbols are not required.

(2)

(ii) A buffer solution is formed by mixing

25.0 cm^3 of a solution that is 0.150 mol dm^{-3} with respect to SO_4^{2-} ions with
75.0 cm^3 of a solution that is 0.100 mol dm^{-3} with respect to HSO_4^- ions.

Calculate the pH of this buffer solution.

[K_a for HSO_4^- ions = 0.012 mol dm^{-3}]

(5)

(Total for question = 20 marks)

Q11.

The equation for the formation of ammonia in the Haber Process is shown

$$\tfrac{1}{2}N_2(g) + 1\tfrac{1}{2}H_2(g) \rightleftharpoons NH_3(g)$$

(a) At 298 K the standard entropy change of the system, $\Delta S^{\ominus}_{system} = -98\,JK^{-1}mol^{-1}$.

Calculate the standard entropy of one mole of ammonia.

Use the value of $\Delta S^{\ominus}_{system}$ and the data in the table.

Substance	Standard molar entropy, $S^{\ominus}$ / $JK^{-1}mol^{-1}$
N_2	192
H_2	131

(2)

(b) The value of the total entropy change, ΔS_{total}, varies with temperature.

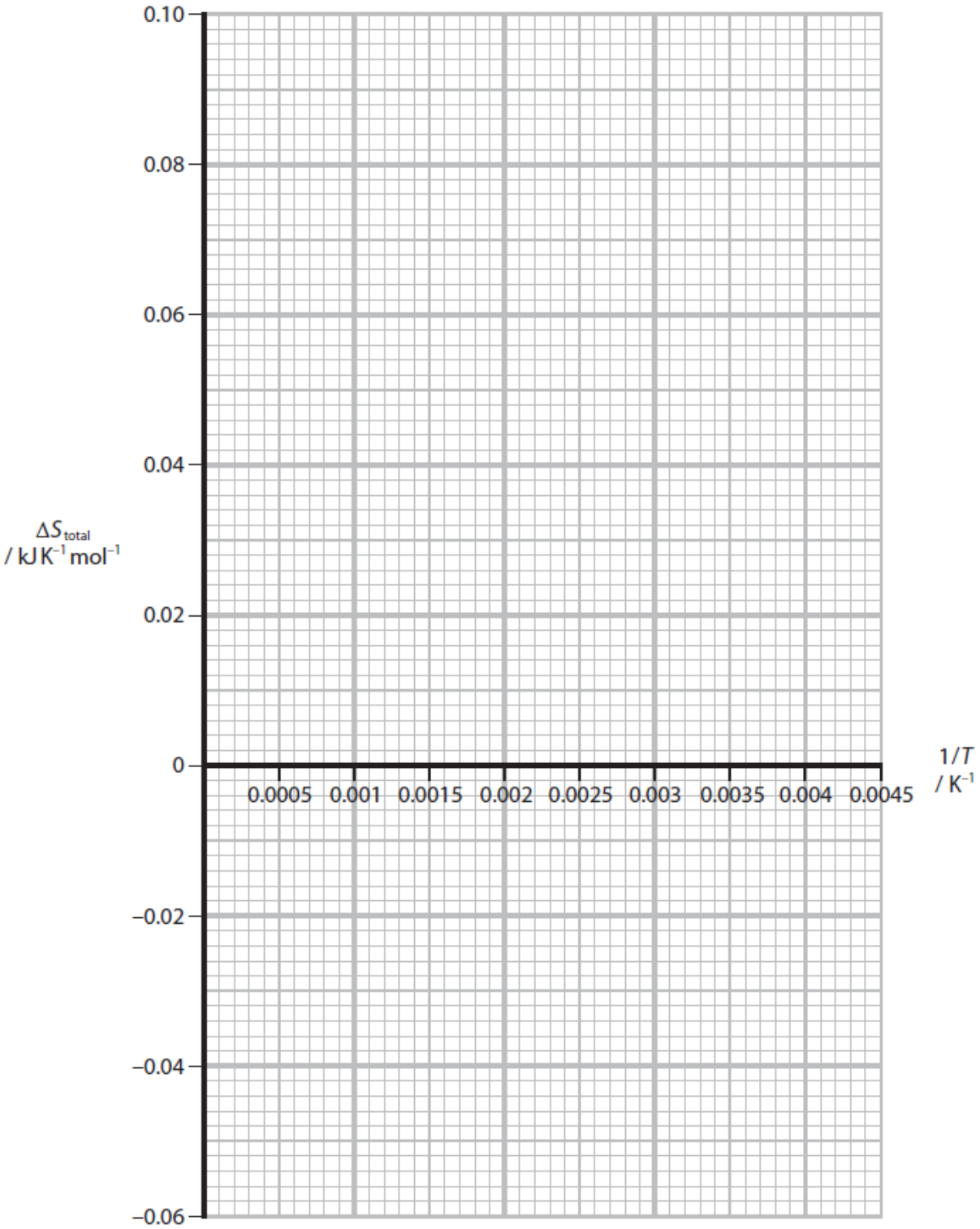
Data for the value of ΔS_{total} at different temperatures but at standard pressure of 100 kPa are given for this reaction.

Temperature / K	$1/T$ / K^{-1}	ΔS_{total} / kJ K^{-1} mol^{-1}
250	4.00×10^{-3}	8.27×10^{-2}
375	2.67×10^{-3}	2.25×10^{-2}
500	2.00×10^{-3}	-0.764×10^{-2}
625	1.60×10^{-3}	-2.57×10^{-2}
750	1.33×10^{-3}	-3.77×10^{-2}

Plot a graph of ΔS_{total} against $1/T$ on the grid.

Include a line of best fit.

(2)



(c) The relationship between ΔS_{total} and $1/T$ can be found by combining the two equations:

$\Delta S_{total} = \Delta S_{surroundings} + \Delta S_{system}$

and $\Delta S_{surroundings} = -\Delta H/T$

to give

$\Delta S_{total} = -\Delta H/T + \Delta S_{system}$

(i) Determine the gradient of the line plotted in (b), including units in your answer.

(1)

(ii) Identify the thermodynamic quantity that can be obtained from this gradient.

(1)

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(iii) Determine the temperature at which the reaction ceases to be thermodynamically feasible at a pressure of 100 kPa.

(1)

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(d) The industrial synthesis of ammonia

$$\tfrac{1}{2}N_2(g) + 1\tfrac{1}{2}H_2(g) \rightleftharpoons NH_3(g)$$

is carried out at pressures of about 20 000 kPa and temperatures between 700K and 750K. These temperatures are higher than the answer to (c)(iii).

(i) State the relationship between the total entropy, ΔS_{total}, and the equilibrium constant, K.

(1)

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(ii) Calculate the value of the equilibrium constant K at 750K.

[ΔS_{total} at 750K = –37.7 J K^{-1} mol^{-1}]

(2)

(iii) Explain why ΔS_{total} decreases with an increase in temperature.

(3)

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(iv) State how the Haber Process is made economically feasible at 750 K even though the total entropy change is negative.

(1)

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(e) Ammonia from the Haber Process reacts with acids.

With phosphoric acid, H_3PO_4, a number of products are formed in solution.
One of these is the fertiliser diammonium hydrogenphosphate.

(i) Write an equation for the production of this fertiliser.

State symbols are not required.

(2)

(ii) Write an **ionic** equation to show that ammonium ions are acidic in aqueous solution.

State symbols are not required.

(1)

(iii) A solution containing both ammonia and ammonium ions acts as a buffer.

Explain, using a relevant ionic equation, the effect of adding a small amount of acid to this buffer.

(3)

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(Total for question = 20 marks)

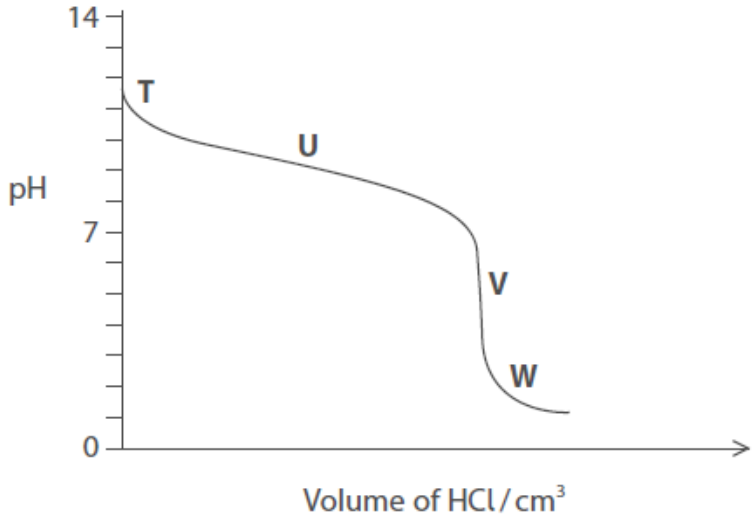
Q12.

Answer the question with a cross in the box you think is correct ☒ . If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒ .

A titration was carried out by adding 0.1 mol dm^{-3} hydrochloric acid to 0.1 mol dm^{-3} aqueous ammonia.

$$HCl(aq) + NH_3(aq) \rightarrow NH_4Cl(aq)$$

The titration curve is shown.



(a) Which region of the graph represents the most effective buffer solution?

(1)

☒ **A** region **T**

☒ **B** region **U**

☒ **C** region **V**

☒ **D** region **W**

(b) Which of these is the best indicator to use in this titration?

[Refer to the Data Booklet]

(1)

☒ **A** methyl red

☒ **B** phenol red

☒ **C** phenolphthalein

☒ **D** thymol blue

(c) What is the approximate pH of an ammonium chloride solution?

☒ **A** 2.0

☒ **B** 5.8

☒ **C** 9.7

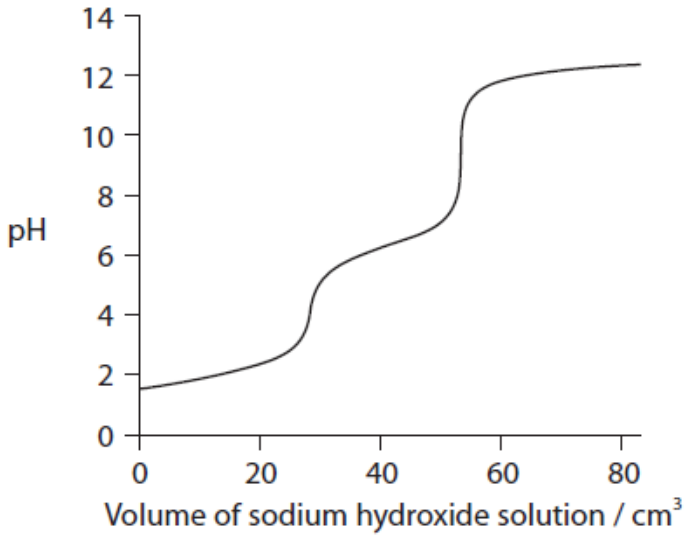
☒ **D** 11.3

(Total for question = 3 marks)

Q13.

For each question, select one answer from A to D and put a cross in the box ☒. If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒.

An example of a diprotic acid is *cis*-butenedioic acid. Titration of this acid using sodium hydroxide solution gave the titration curve shown.



Which indicator would be most suitable for measuring the end-point of the neutralisation of the proton in *cis*-butenedioic acid which has a pK_a = 6.33?

Use your Data Booklet.

☒ **A** bromocresol green

☒ **B** bromothymol blue

☒ **C** litmus

☒ **D** phenolphthalein

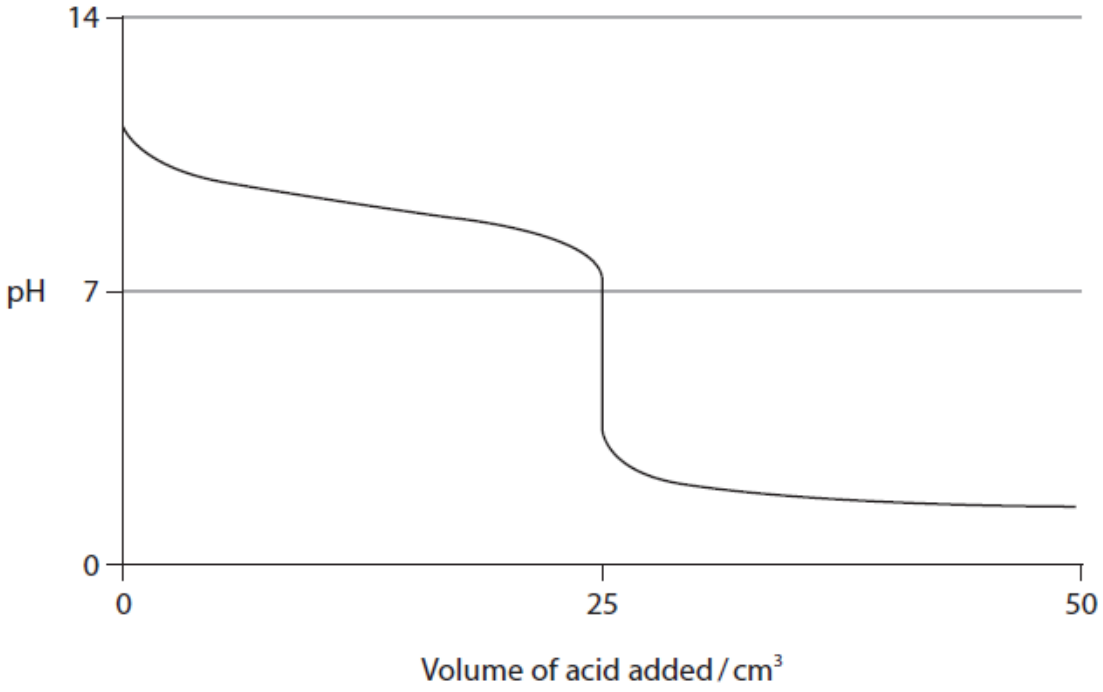
(Total for question = 1 mark)

Q14.

Answer the questions with a cross in the box you think is correct ☒. If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒.

A 0.1 mol dm^{-3} aqueous acid solution was added to 25 cm^3 of a 0.1 mol dm^{-3} aqueous solution of an alkali.

The titration curve shown was obtained.



(a) Which titration would produce this curve?

(1)

☒ **A** ethanoic acid added to sodium hydroxide

☒ **B** hydrochloric acid added to sodium hydroxide

☒ **C** ethanoic acid added to ammonia

☒ **D** hydrochloric acid added to ammonia

(b) Which indicator would be **most** suitable for this titration?

(1)

		Indicator	pH range
☒	**A**	malachite green	0.2–1.8
☒	**B**	methyl yellow	2.9–4.0
☒	**C**	methyl red	4.2–6.3
☒	**D**	thymol blue	8.0–9.6

(Total for question = 2 marks)

Q15.

Sodium hydrogensulfate is a widely used acid, with applications that include removing limescale and as a food additive. Sodium hydrogensulfate is a weak acid because of the presence of the hydrogensulfate ion, HSO_4^-.

(a)(i) Write the equation for the dissociation of the hydrogensulfate ion in aqueous solution. State symbols are not required.

(1)

(ii) A solution of sodium hydrogensulfate has pH = 1.13

Calculate the concentration of this solution, in g dm^{-3}.

[pK_a of HSO_4^- = 1.92]

(5)

(iii) State the assumptions you have used in (a)(ii).

(2)

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(b) A solution containing sodium hydrogensulfate and sodium sulfate is a buffer that is used to preserve urine for steroid analysis.

(i) State what is meant by the term buffer.

(2)

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(ii) Calculate the pH of the buffer prepared by dissolving 0.750 mol of sodium hydrogensulfate and 0.500 mol of sodium sulfate in distilled water to make 1.00 dm^3 of solution.

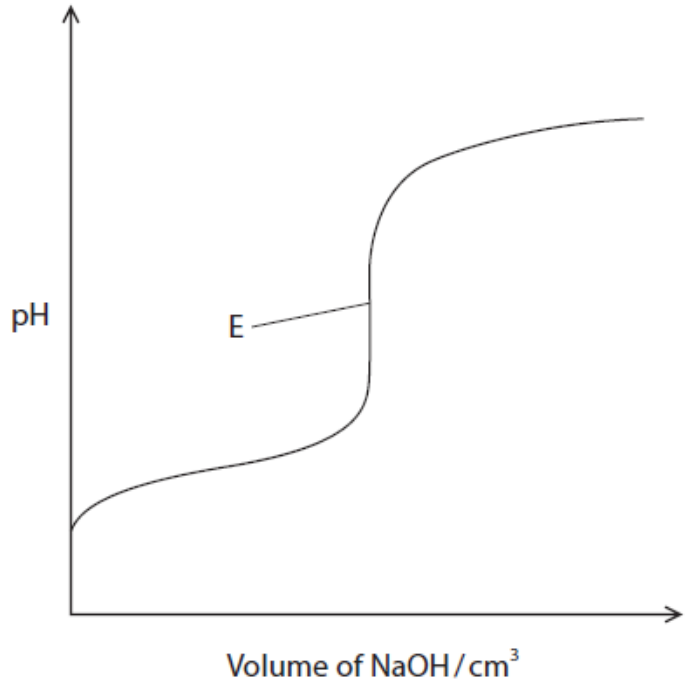
(3)

(iii) Separate samples of 0.00500 mol of hydrochloric acid are added to 1.00 dm^3 of distilled water and to the buffer in (b)(ii).

Calculate the pH **changes** that result in each case.
Assume that the volumes remain constant at 1.00 dm^3.

(4)

(c) The titration curve obtained from the addition of sodium hydroxide solution to a weak acid is shown. The equivalence point (E) of this titration occurred at pH = 8



Explain the observations that would be made if methyl orange (pK_{In} = 3.7) were used as the indicator for this titration.

(3)

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(Total for question = 20 marks)

Q16.

Answer the question with a cross in the box you think is correct ☒ . If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒ .

This question is about weak acids.

pK_a of ethanoic acid, CH_3COOH = 4.8

pK_a of chloroethanoic acid, $CH_2ClCOOH$ = 2.9

(a) What is the pH of a 0.100 mol dm^{-3} solution of chloroethanoic acid?

(1)

☐ **A** 0.27

☐ **B** 1.95

☐ **C** 2.90

☐ **D** 3.90

(b) Which is the acid-conjugate base pair in the reaction between ethanoic acid and chloroethanoic acid?

(1)

		Acid	Conjugate base
☒	A	CH_3COOH	CH_3COO^-
☒	B	CH_3COOH	$CH_3COOH_2^+$
☒	C	$CH_2ClCOOH$	CH_2ClCOO^-
☒	D	$CH_2ClCOOH$	$CH_2ClCOOH_2^+$

(Total for question = 2 marks)

Mark Scheme

Q1.

Question Number	Answer	Additional Guidance	Mark
(a)(i)	An answer that makes reference to the following point: • $HCOOH + KOH \rightarrow HCOOK + H_2O$	Allow $HCOO^- K^+$ / $HCOO^- + K^+$ Allow $HCOOH + OH^- \rightarrow HCOO^- + H_2O$ Allow Na in place of K Ignore state symbols even if incorrect Do not award HCOO – K	(1)

Question Number	Answer	Additional Guidance	Mark
(a)(ii)	• correct volume read off the graph (1) • correct concentration (1)	Example of calculation 22 (cm^3) This may be noted on the graph $25.0 \times 0.15/22.0 = 0.17045$ (mol dm^{-3}) Ignore SF except 1SF Allow TE on wrong volume Correct answer scores 2	(2)

Question Number	Answer	Additional Guidance	Mark
(a)(iii)	An answer that makes reference to the following points: • volume at half-neutralisation **(1)** • pH value at half-neutralisation **(1)** • calculation of K_a **(1)**	 11 cm^3 (Allow TE from volume in (a)(ii)) pH = 3.8 (± 0.1) (Hydrogen ion concentration = $10^{-3.8}$) $K_a = 1.5849 \times 10^{-4}$ / 0.00015849 ($mol\ dm^{-3}$) Correct answer with no working scores 3 Allow TE throughout Ignore SF If 3.9 used (Hydrogen ion concentration = $10^{-3.9}$) $K_a = 1.2589 \times 10^{-4}$ / 0.00012589 ($mol\ dm^{-3}$) If 3.7 used (Hydrogen ion concentration = $10^{-3.7}$) $K_a = 1.9953 \times 10^{-4}$ / 0.00019953 ($mol\ dm^{-3}$) Allow TE from wrong pH	**(3)**
	Alternative method 1 • pH at half-neutralisation **(1)** • p K_a value **(1)** • calculation of K_a **(1)**	 3.8 (± 0.1) 3.8 (± 0.1) $K_a = 10^{-3.8}$ $= 1.5849 \times 10^{-4}$ / 0.00015849 ($mol\ dm^{-3}$) Correct answer with no working scores 3 If 3.9 used Hydrogen ion concentration = $10^{-3.9}$ $= 1.2589 \times 10^{-4}$ / 0.00012589 ($mol\ dm^{-3}$) $= K_a$ If 3.7 used Hydrogen ion concentration = $10^{-3.7}$ $= 1.9953 \times 10^{-4}$ / 0.00019953 ($mol\ dm^{-3}$) $= K_a$ Allow TE from wrong pH for M2 and M3	

	Alternative method 2 (using pH of the methanoic acid at the start) • pH at the start **(1)** • convert pH into H^+ concentration **(1)** • calculation of K_a **(1)** 2.0 gives a value of 6.667×10^{-4} (mol dm^{-3}) 2.1 gives a value of 4.206×10^{-4} (mol dm^{-3}) 2.2 gives a value of 2.654×10^{-4} (mol dm^{-3}) 2.3 gives a value of 1.674×10^{-4} (mol dm^{-3}) 2.4 gives a value of 1.057×10^{-4} (mol dm^{-3}) 2.5 gives a value of 3.162×10^{-3} (mol dm^{-3})	2.3 Allow 2.0-2.5 Hydrogen ion concentration = $10^{-2.3}$ = 5.0119×10^{-3} / 0.0050119 (mol dm^{-3}) $K_a = \frac{(5.0119 \times 10^{-3})^2}{0.15}$ = 1.6746×10^{-4} / 0.00016746 (mol dm^{-3}) Correct answer with no working scores 3 Allow TE from wrong pH (i.e. not in the range of 2.0-2.5) Ignore SF	

Question Number	Answer	Additional Guidance	Mark
(b)	An answer that makes reference to the following points: • calculation of $[H^+]$ **(1)** • correct ratio **(1)**	Example of calculation $[H^+] = K_a \times \frac{[HA]}{[A^-]}$ OR $\frac{[H^+]}{K_a} = \frac{[HA]}{[A^-]}$ 2.5119×10^{-5} / 0.000025119 $\frac{[HA]}{[A^-]} = \frac{2.5118864 \times 10^{-5}}{1.3 \times 10^{-5}} = 1.9322:1$ Correct answer with no working scores 2 Allow just 1.9322 Allow rounding to 2:1 Ignore SF Reciprocal ratio correctly identified 0.5175:1 scores 2 Correct answer with no working scores 2 Allow Henderson-Hasselbach equation $pH = pKa - \log \frac{[HA]}{[A^-]}$ $4.6 = 4.8861 - \log \frac{[HA]}{[A^-]}$ **(1)** $\frac{[HA]}{[A^-]} = 1.9322:1$ **(1)** Allow just 1.9322 Ignore SF Reciprocal ratio correctly identified 0.5175:1 scores 2	**(2)**

Q2.

Question Number	Answer	Mark
	The only correct answer is B (4.17) *A is not correct because this is the −log of the concentration* *C is not correct because this is the −log of the K_a* *D is not correct because this is the −log of the K_a multiplied by the concentration*	(1)

Q3.

Question Number	Answer	Mark
	The only correct answer is B (13.43) *A is not correct because this is the −log [OH^-]* *C is not correct because it does not produce 2 x OH^-* *D is not correct because the −log [OH^-] has been added to* pK_w	(1)

Q4.

Question number	Answer	Mark
	The only correct answer is C (12.3) *A* *is incorrect because the concentration of hydroxide ions has been halved instead of doubled* *B* *is incorrect because the concentration of hydroxide ions has been taken as 0.01 mol dm^{-3}* *D* *is incorrect because this has been calculated using 0.1 mol dm^{-3} as the concentration of calcium hydroxide*	**(1)**

Q5.

Question number	Answer	Mark
	A approximately 6.5	1

Q6.

Question Number	Correct Answer	Mark
	The only correct answer is A (the dissociation of water is endothermic, so the concentration of hydrogen ions is higher at 100°C than it is at 25°C) ***B*** *is incorrect because at higher temperatures more hydrogen ions are present* ***C*** *is incorrect because the dissociation of water is endothermic* ***D*** *is incorrect because the dissociation of water is endothermic*	(1)

Q7.

Question Number	Correct Answer	Mark
(a)	**The only correct answer is D** (CH_3COCH_2I CHI_3) ***A*** *is incorrect because* CH_3I *is not formed in acidic conditions* ***B*** *is incorrect because* CH_3COCI_3 *is not formed in acidic conditions* ***C*** *is incorrect because* CH_3I *is not formed in alkaline conditions*	(1)

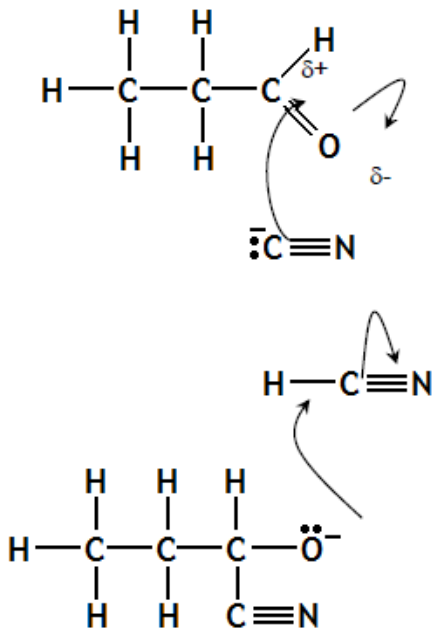
Question Number	Correct Answer	Mark
(b)	**The only correct answer is C** (2.5) ***A*** *is incorrect because the value of the pH has been divided by 3* ***B*** *is incorrect because the concentration of* H^+ *ions has been multiplied by 3 rather than divided* ***D*** *is incorrect because this value is adding 1/3 of 2 onto 2*	(1)

Q8.

Question Number	Answer	Mark
(a)	**The only correct answer is A** (colorimetry) ***B*** *is not correct because the solution would not go cloudy* ***C*** *is not correct because there is no base to titrate against* ***D*** *is not correct because starch is an indicator and would immediately turn blue-black*	(1)

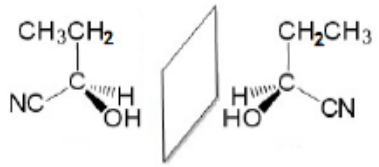
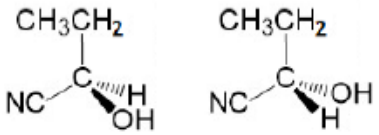
Question Number	Answer	Mark
(b)	**The only correct answer is B** (1.98) ***A*** *is not correct because the concentration of the acid has been increased three times* ***C*** *is not correct because the concentration of the acid has been decreased six times* ***D*** *is not correct because the pH has been multiplied by three*	(1)

Q9.

Question Number	Answer	Additional Guidance	Mark
(a)(i)	An answer that makes reference to the following points: Step 1 • lone pair of electrons on C of C≡N • curly arrow from anywhere on the C of C≡N to C in propanal including the charge • curly arrow from C=O bond to or just beyond O • dipole on C=O Step 2 • lone pair on O in intermediate Step 1 or Step 2 • curly arrow from the O (or minus charge) of intermediate to H of H-C≡N • curly arrow from H-C bond to C of H-C≡N	 All 7 points scores 4 marks 5 or 6 points scores 3 marks 3 or 4 points scores 2 marks 2 points scores 1 mark Ignore formula of products even if incorrect Ignore all dipoles on HCN Penalise dipoles on C-O in the intermediate	**(4)**

Question Number	Answer		Additional Guidance	Mark
(a)(ii)	An explanation that makes reference to the following points:			**(2)**
	• the value of K_a / dissociation is (very) small / the equilibrium lies (very) well to the left	**(1)**	Allow it is a (very) weak acid Allow it is partially dissociated	
	• so the concentration of CN^- ions is (very) low / there is a lack of CN^- ions	**(1)**	Allow a comment that all / most CN^- in the reaction come from KCN Ignore references to K_a of KCN Ignore references to rate of dissociation	

Question Number	Answer	Additional Guidance	Mark
(a)(iii)	An answer that makes reference to the following points: • (it increases the rate of reaction by) providing **CN^- ions** in the same phase/state **(1)** • and it / KCN / CN^- ion is regenerated in Step 2 (so overall is not used up in the reaction) **(1)**	Ignore incorrect phases Allow it is regenerated at the end (of the reaction) Ignore references to adsorbing and desorbing If no other mark is scored for it is in the same phase/state **and** is not used up (1) OR A homogeneous catalyst / KCN is in the same phase/state **and** speeds up the reaction/provides an alternative pathway with lower activation energy (1)	**(2)**

Question Number	Answer	Additional Guidance	Mark
(b)	• a three-dimensional diagram of 2-hydroxybutanenitrile showing at least one dotted bond **(1)** **and** at least one wedged bond which are next to each other **(1)** • the mirror image of the first structure	Allow just a three dimensional diagram of 2-hydroxybutanenitrile showing at least one dotted and one wedged bond Diagrams may show a mirror / plane of symmetry though this is not necessary  Allow diagrams that swap two of the four substituents e.g.  If not other marks are scored allow two tetrahedral structures which are mirror images that do not have wedged and dotted bonds scores (1) Ignore connectivity errors Allow TE in M2 for incorrect compounds	**(2)**

Q10.

Question Number	Answer	Additional Guidance	Mark
(a)(i)	• no effect / none / nothing / no change	Ignore references to rate	**(1)**

Question Number	Answer	Additional Guidance	Mark
(a)(ii)	An explanation that makes reference to the following points: • (equilibrium) yield (of sulfur trioxide / SO_3 / product) decreases • the equilibrium constant / K_p / K_c / K decreases (as temperature increases) **(1)** **and** because the (forward / right) reaction is exothermic / releases heat (energy) / ΔH is negative **(1)**	Allow less sulfur trioxide / SO_3 / product forms Ignore equilibrium position shifts to the left Ignore more reactants formed Allow the equilibrium constant / K_p / K_c / K decreases (as temperature increases) **and** because the reverse / backward / left reaction is endothermic / absorbs heat (energy) Allow K decreases because $\Delta S_{surroundings}$ / ΔS_{total} decreases / becomes less positive (as temperature increases and assuming ΔS_{system} is constant) Ignore reference to rate	**(2)**

Question Number	Answer	Additional Guidance	Mark
(a)(iii)	• expression for K_p	Example of expression for K_p: $K_p = \dfrac{p(SO_3(g))^2}{p(SO_2(g))^2 \text{ (x) } p(O_2(g))}$ Allow P / PP / pp etc for partial pressure and this can be inside the brackets Allow e.g. p^2SO_3 Ignore missing (g) / brackets around formulae Do not award square brackets	**(1)**

Question Number	Answer	Additional Guidance	Mark
(a)(iv)	• calculation of eqm moles (1) • calculation or expressions for 3 partial pressures (1) • substitution of values into K_p expression (1) • calculation of K_p **and** answer to 2 / 3 SF **and** units (1)	Example of calculation: SO_2: Initial mol 2.00; Eqm mol 2.00 – 1.60 = 0.40 O_2: Initial mol 1.00; Eqm mol 1.00 – 0.80 = 0.20 SO_3: Initial mol -; Eqm mol 1.60 Total mol at eqm: 0.40 + 0.20 + 1.60 = 2.20 Partial pressure /atm: $\frac{0.40 \times 5.00}{2.20} = 0.90909$; $\frac{0.20 \times 5.00}{2.20} = 0.45455$; $\frac{1.60 \times 5.00}{2.20} = 3.6364$ TE for partial pressures on eqm moles $K_p = \frac{3.6364^2}{0.90909^2 \times 0.45455}$ $= 35.2 / 35\ atm^{-1}$ TE on expression for K_p in (a)(iii) Allow answer from previous correct rounding to 2 or more SF e.g. 0.91 0.45 and 3.6 gives 34.8 Penalise incorrect rounding once only e.g. 0.909 to 0.9 Allow fractions in working but not in final answer Allow atm^- for units but do not allow any other units Allow correct units written in (a)(iii) if not written here Correct answer to 2 or 3 SF with units and no working scores (4)	(4)

Question Number	Answer	Additional Guidance	Mark
(b)(i)	• calculation of mass of H_2SO_4 in 1 dm^3 (1) • calculation of concentration of acid (1)	Example of calculation: mass of H_2SO_4 in 1 dm^3 concentrated acid = 0.985 x 1800 = 1773 (g) concentration of acid = $\frac{1773}{(2 \times 1.0) + 32.1 + (4 \times 16.0)}$ $= 18.073 / 18.07 / 18.1 / 18\ (mol\ dm^{-3})$ TE on mass of H_2SO_4 in 1 dm^3 Allow 98 for molar mass of H_2SO_4 giving 18.092 / 18.09 / 18.1 / 18 (mol dm^{-3}) Correct answer to 3 or more SF with no working scores (2) Do not award (2) for 18 unless 0.985 has been used in calculation	(2)

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Question Number	Answer	Additional Guidance	Mark
(b)(ii)	• calculation of $[H^+(aq)] / [H_3O^+(aq)]$	Example of calculation: $[H^+(aq)] / [H_3O^+(aq)] = 10^{-0.97}$ $= 0.10715 / 0.1072 / 0.107 / 0.11$ (mol dm^{-3}) Ignore SF except 1 SF Ignore incorrect units Correct answer with no working scores (1) Do not award 0.1 / 0.10 / 0.214	(1)

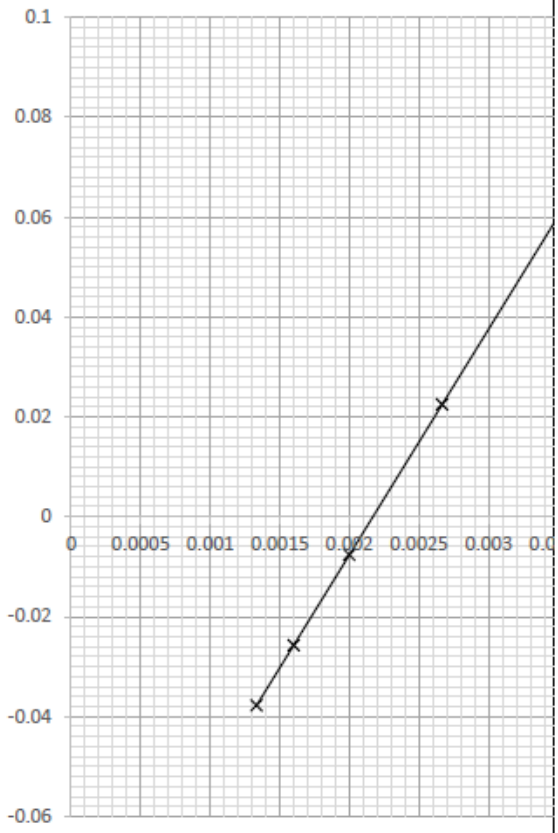
Question Number	Answer	Additional Guidance	Mark
(b)(iii)	An explanation that makes reference to the following points: **First equilibrium** • the first ionisation of sulfuric acid is complete **or** the equilibrium position of the first equation lies very far to the right (1) **Second equilibrium** • so $[H_3O^+(aq)]$ (from the second equilibrium) is very small (1)	Allow $[H^+(aq)]$ for $[H_3O^+(aq)]$ Ignore missing state symbols Allow high $[H_3O^+(aq)]$ from first equilibrium Allow acid fully dissociates in first equilibrium Ignore just acid fully dissociates Allow second equilibrium shifts to the left Allow second dissociation is suppressed / further dissociation is prevented	(2)

Question Number	Answer	Additional Guidance	Mark
(c)(i)	• $HSO_4^- + OH^- \rightarrow SO_4^{2-} + H_2O$ (1) • $SO_4^{2-} + H^+ \rightarrow HSO_4^-$ **or** $SO_4^{2-} + H_3O^+ \rightarrow HSO_4^- + H_2O$ (1)	Allow equations in either order Allow ⇌ provided equations written in directions shown Ignore state symbols even if incorrect Penalise non-ionic equations once only e.g. using HCl and NaOH Allow $HSO_4^- \rightarrow SO_4^{2-} + H^+$ **and** $H^+ + OH^- \rightarrow H_2O$ for M1	(2)

Question Number	Answer	Additional Guidance	Mark
(c)(ii)	• calculation of the concentration of SO_4^{2-} ions (1) • calculation of the concentration of HSO_4^- ions (1) • expression for K_a (1) • re-arrangement of expression **and** calculation of $[H^+]$ (1) • calculation of pH (1)	Example of calculation: $[SO_4^{2-}] = \frac{25.0 \times 0.150}{1000} \times \frac{1000}{100}$ $= 0.0375$ (mol dm^{-3}) Allow mol $SO_4^{2-} = 0.00375 / 3.75 \times 10^{-3}$ (mol) $[HSO_4^-] = \frac{75.0 \times 0.100}{1000} \times \frac{1000}{100}$ $= 0.075$ (mol dm^{-3}) Allow mol $HSO_4^- = 0.0075 / 7.5 \times 10^{-3}$ (mol) Do not award this mark if subtraction then done $K_a = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]} / 0.012 = \frac{[H^+] \times 0.0375}{0.075}$ Allow mol substituted into correct expression $[H^+] = \frac{K_a[HSO_4^-]}{[SO_4^{2-}]} = \frac{0.012 \times 0.075}{0.0375}$ $= 0.024$ (mol dm^{-3}) TE on expression, $[SO_4^{2-}]$ and $[HSO_4^-]$ or mol $pH = -\log[H^+] = -\log 0.024$ $= 1.6198 / 1.620 / 1.62 / 1.6$ TE on $[H^+]$ Ignore SF except 1 SF Correct answer without working scores (5) Allow alternative methods	(5)

Q11.

Question Number	Answer	Additional Guidance	Mark
(a)	• states or uses equation **(1)** • calculate $S^{\ominus}_{products}$ **(1)**	$\Delta S^{\ominus}_{system} = S^{\ominus}_{products} - S^{\ominus}_{reactants}$ $-98.0 = S^{\ominus}_{products} - ((0.5 \times 192) + (1.5 \times 131))$ $S^{\ominus}_{products} = 292.5 - 98$ $S^{\ominus}_{products}$ = (+)194.5 / 195 ($J\ K^{-1}\ mol^{-1}$) If units are given they must be correct Allow TE on incorrect $S^{\ominus}_{reactants}$ Comment Correct answer with no working scores (2) $S^{\ominus}_{products}$ = 63.5 scores max (1) $S^{\ominus}_{products}$ = 225 scores max (1)	**(2)**

Question Number	Answer	Additional Guidance	Mark
(b)	• 5 points plotted on the graph to within one square **(1)** • straight line of best fit passing through all points **(1)**		**(2)**

Question Number	Answer	Additional Guidance	Mark
(c)(i)	An answer that makes reference to the following points: • uses the line or points from the data to calculate the gradient **and** units	Example of calculation Gradient = $\frac{8.27 \times 10^{-2} - -0.76 \times 10^{-2}}{4.00 \times 10^{-3} - 2.00 \times 10^{-3}}$ = 45.15 kJ mol^{-1} Allow an answer between 42.0 – 48.0 Ignore SF except 1 SF	**(1)**

Question Number	Answer	Additional Guidance	Mark
(c)(ii)	An answer that makes reference to the following points: • enthalpy change of reaction / $\Delta_r H$ (of the Haber process)	 Allow $-\Delta_r H$ Allow enthalpy change / ΔH / $-\Delta H$	**(1)**

Question Number	Answer	Additional Guidance	Mark
(c)(iii)	An answer that makes reference to the following points: • value of T found either by reading from the graph the value of T when $\Delta S_{total} = 0$ or by calculation	 460 (K) Allow an answer between 440 - 480 $= \frac{\text{answer to (c)(i)}}{98}$ $= \frac{45150}{98} = 460.71$ / 460 (K) Or $= \frac{-\text{answer to (b)}}{-98}$ $= \frac{-45150}{-98} = 460.71$ / 460 (K) ALLOW TE on graph or on answer to (c)(i)	**(1)**

Question Number	Answer	Additional Guidance	Mark
(d)(i)	• total entropy, $\Delta S = R\ln K$ or $\ln K = \Delta S / R$ or $K = e^{\frac{\Delta S}{R}}$		**(1)**

Question Number	Answer	Additional Guidance	Mark
(d)(ii)	• calculation of ln K **(1)** • evaluation of K **(1)**	Example of calculation $-37.7 = 8.31 \times \ln K$ $\ln K = -4.5367$ $K = 0.01071 / 1.071 \times 10^{-2}$ Final answer with no working scores (2) Allow TE on M1 to M2 No TE on incorrect expression Ignore units Ignore SF except 1 SF	**(2)**

Question Number	Answer	Additional Guidance	Mark
(d)(iii)	An answer that makes reference to the following points: Either • (ΔS_{total} decreases because) ΔS_{system} (and ΔH) do not change with temperature (significantly) **(1)** • therefore $\Delta S_{surroundings}$ must decrease (so that (ΔS_{total} decreases) **(1)** • this is because $\Delta S_{surroundings} = -\Delta H/T$ (so as T increases $-\Delta H/T$ becomes less positive because ΔH is exothermic) **(1)** Or • the reaction is exothermic **and** so increasing temperature shits the equilibrium to the left / towards the reactants **(1)** • the value of K decreases • because ΔS_{total} is proportional to K / $S_{total} = R \ln K$ the value of ΔS_{total} decreases	Allow more negative / less positive Accept the backward reaction is favoured	**(3)**

Question Number	Answer	Additional Guidance	Mark
(d)(iv)	• overall conversion to ammonia is increased by recycling unused reactants	Allow remove the ammonia from the equilibrium / as it is formed Ignore references to catalysts, temperature and pressure	**(1)**

Question Number	Answer		Additional Guidance	Mark
(e)(i)	• formula of diammonium hydrogenphosphate • balanced equation	**(1)** **(1)**	$(NH_4)_2HPO_4$ $2NH_3 + H_3PO_4 \rightarrow (NH_4)_2HPO_4$ Allow multiples Allow ions for the product Allow for M2 $NH_3 + H_3PO_4 \rightarrow (NH_4)H_2PO_4$ Allow ions for the product No other TE Ignore state symbols even if incorrect	**(2)**

Question Number	Answer	Additional Guidance	Mark
(e)(ii)	• $NH_4^+ = NH_3 + H^+$ OR • $NH_4^+ + H_2O = NH_3 + H_3O^+$	Allow $\rightarrow$ instead of $\rightleftharpoons$ Do not award reactions reversed Allow $NH_4^+ + OH^- \rightarrow NH_3 + H_2O$ Allow $\rightleftharpoons$ instead of $\rightarrow$ Ignore state symbols even if incorrect	**(1)**

Question Number	Answer	Additional Guidance	Mark
(e)(iii)	An answer that makes reference to the following points: • the mixture contains a large amount/ (large) reservoir of **both** ammonium ions and ammonia / of NH_4^+ and NH_3 **(1)** **Either** • added H^+ reacts with ammonia to form ammonium ions / $H^+ + NH_3 \rightleftharpoons NH_4^+$ **Or** • added H^+ combines with OH^- ions in water to form water / $H^+ + OH^- \rightarrow H_2O$ **And** ammonia reacts with water to produce OH^- ions / $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ **(1)** • ratio of ammonium ions to ammonia hardly changes **(1)**	Do not award incorrect formulae such as NH_3^- in M1 and M2 but allow TE in M3 Ignore comments about acid / base in relation to NH_4^+ / NH_3 unless defined Allow $\rightarrow$ instead of $\rightleftharpoons$ Allow H_3O^+ Allow $\rightarrow$ instead of $\rightleftharpoons$ This marking point must include at least one ionic equation Allow remains constant Allow pH is unchanged / changes very little because added H^+ removed **and** change in concentration of NH_3 **and** NH_4^+ is small	**(3)**

Q12.

Question Number	Answer	Mark
(a)	**The only correct answer is B** (region **U**) ***A** is not correct because in region **T** there is only aqueous ammonia at the start of the titration* ***C** is not correct because in region **V**, the vertical part of the graph, represents the end-point of the titration* ***D** is not correct because in region **W** all the aqueous ammonia has been neutralised*	(1)

Question Number	Answer	Mark
(b)	**The only correct answer is A** (methyl red) ***B*** *is not correct because phenol red has a pH range of 6.8 to 8.4 and 8.4 is not in the vertical region* ***C*** *is not correct because phenolphthalein has a pH range of 8.2 to 10.0 and this is not in the vertical region* ***D*** *is not correct because thymol blue has a pH range of 1.2 to 2.8 and this is not in the vertical region*	(1)

Question Number	Answer	Mark
(c)	**The only correct answer is B** (5.8) ***A*** *is not correct because this is the approximate pH when excess hydrochloric acid has been added* ***C*** *is not correct because this is the approximate pH near the start of the end point when there is still excess aqueous ammonia* ***D*** *is not correct because this is the approximate pH of aqueous ammonia*	(1)

Q13.

Question Number	Correct Answer	Mark
	The only correct answer is D (phenolphthalein) ***A*** *is incorrect because the indicator needs a range contained between pH 8 and pH 11* ***B*** *is incorrect because the indicator needs a range contained between pH 8 and pH 11* ***C*** *is incorrect because the indicator needs a range contained between pH 8 and pH 11*	(1)

Q14.

Question Number	Answer	Mark
(a)	**The only correct answer is D** (hydrochloric acid added to ammonia) *A is not correct because it is a weak acid and strong base* *B is not correct because it is a strong acid and strong base* *C is not correct because it is a weak acid and weak base*	(1)

Question Number	Answer	Mark
(b)	**The only correct answer is C** (methyl red) *A is not correct because malachite green would change colour at about pH 1* *B is not correct because methyl yellow would change colour at about pH 3.5* *D is not correct because thymol blue would change colour at about pH 9*	(1)

Q15.

Question number	Answer	Additional guidance	Mark
(a)(i)	• correct equation	Examples of equations: $HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$ Or $HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$ Allow $HSO_4^- + H_2O \rightleftharpoons H^+ + SO_4^{2-}$ Or $HSO_4^- \rightleftharpoons H_3O^+ + SO_4^{2-}$ Accept $\rightarrow$ for $\rightleftharpoons$ Ignore state symbols even if incorrect.	1

Question number	Answer	Additional guidance	Mark
(a)(ii)	• expression for K_a **(1)** • calculation of K_a from pK_a and $[H^+]$ from pH **(1)** • rearrangement of expression for K_a and substitution of values and calculation of $[NaHSO_4]$ in mol dm^{-3} **(1)** • calculation of $M_r(NaHSO_4)$ **(1)** • calculation of $[NaHSO_4]$ in g dm^{-3} **(1)**	Example of calculation: $K_a = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]}$ or $K_a = \frac{[H^+]^2}{[HSO_4^-]}$ M1 is scored if implied in the calculation but if given must be correct Comment: Do not penalise SO_4^- for SO_4^{2-} $K_a = 10^{-1.92}$ (= 0.012023) **and** $[H^+] = 10^{-1.13}$ (= 0.074131) $[HSO_4^-] = \frac{0.074131^2}{0.012023} = 0.45709$ (mol dm^{-3})* $M_r(NaHSO_4) = 120.1$ Allow 120 $[NaHSO_4] = 120.1 \times 0.45709$ = 54.896(g dm^{-3})* (54.851 if 120 used) * These are obtained using unrounded intermediate values If $M_r(HSO_4^-) = 97.1$ is used 44.383 (g dm^{-3}) scores M5 Accept $[HSO_4^-] - [H^+] = 0.45709$ $[HSO_4^-] = 0.45709 + 0.074131$ = 0.53122 (mol dm^{-3}) = 63.799 (g dm^{-3}) TE at each stage Ignore SF except 1 SF COMMENT Correct answer with some working scores (5)	5

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Question number	Answer	Additional guidance	Mark
(a)(iii)	An answer that makes reference to the following: • hydrogensulfate (ion) dissociation / ionisation negligible **(1)** • $[H^+]$ only due to (dissociation / ionisation of) HSO_4^- / hydrogensulfate (ion) **(1)**	Comment: Do not penalise SO_4^- for SO_4^{2-} Allow $[HSO_4^-]_{equilibrium} = [HSO_4^-]_{initial}$ $[NaHSO_4]_{equilibrium} = [NaHSO_4]_{initial}$ Allow Slight / partial / incomplete / does not dissociate for 'negligible' (dissociation) Allow $[H^+]$ due to) dissociation / ionisation of water negligible Or dissociation / ionisation of water negligible Or $[SO_4^{2-}] = [H^+]$ Allow $[H_3O^+]$ for $[H^+]$ throughout Penalise omission of [] in discussion once only Penalise use of HA or 'weak acid' or A^- once only Ignore references to temperature	**2**

Question number	Answer	Additional guidance	Mark
(b)(i)	An answer that makes reference to the following: • a buffer resists change in pH **(1)** • on the addition of **small** amounts of acid and / or of alkali **(1)**	 Accept Maintains a **fairly** / **nearly** constant pH Allow withstands change in pH Allow large change or small change for change Do not award maintains constant pH Ignore references to the acid-salt ratio Allow H^+ for acid base / OH^- for alkali	**2**

Question number	Answer	Additional guidance	Mark
(b)(ii)	• substitution of values into K_a expression **(1)** • rearrangement of K_a expression **(1)** • calculation of pH to at least 1 dp **(1)**	Example of calculation: $K_a = \frac{[H^+][SO_4^{2-}]}{[HSO_4^{2-}]}$ $K_a = 10^{-1.92}$ (=0.012023) $= \frac{[H^+] \times 0.500}{0.750}$ $[H^+] = \frac{K_a \times 0.750}{0.500}$ (mol dm^{-3}) pH = −log(1.5 x 0.012023) (= −log 0 .018034) = 1.744 Ignore SF except 1 SF Correct answer with some working scores (3) TE at each stage but M3 dependent on some use of K_a **and** calculation of $[H^+]$ **and** value of pH < 7 Accept use of Henderson-Hasselbalch equation: $pH = pK_a + \log \frac{[SO_4^{2-}]}{[HSO_4^-]}$ or $\log \frac{[salt]}{[acid]}$ (1) $= 1.92 + \log \frac{0.500}{0.750}$ (1) = 1.7439 (1) TE on arithmetical errors If salt and acid reversed in H-H equation max 1 (M3 only for 2.0961) No TE on any other error in H-H equation (scores (0))	3

Question number	Answer	Additional guidance	Mark
(b)(iii)	• calculation of pH **and** change in pH for water **(1)** • calculation of new $[HSO_4^-]$ **and** calculation of new $[SO_4^{2-}]$ **(1)** • calculation of $[H^+]$ **(1)** • calculation of pH **and** change in pH for buffer **(1)** Use of H-H for M3 and M4 $pH = 1.92 + \log \frac{0.495}{0.755}$ (1) $= 1.92 + (-0.18334) = 1.7367$ from 1.7439 (1)	Example of calculation: pH (0.00500 mol dm^{-3} HCl) = $-\log(0.00500) = 2.30$ $\Delta(pH) = 7 - 2.30 = 4.70$ Accept changes from 7 to 2.3 If no other mark is scored in (b)(iii) pH = 2.3 scores 1 $0.750 + 0.00500 = 0.755$ (mol dm^{-3}) $0.500 - 0.00500 = 0.495$ (mol dm^{-3}) $[H^+] = \frac{K_a \times 0.755}{0.495} = \frac{0.012023 \times 0.755}{0.495}$ $= 0.018338$ (mol dm^{-3}) TE only on arithmetical errors and if at least one change in concentration calculated $pH = -\log(0.018338) = 1.737$ $\Delta(pH) = 1.744 - 1.737 = 0.007$ OR $\Delta(pH) = 1.74 - 1.737 = 0.003$ if rounded value given in (b)(ii) Accept changes from 1.744 / 1.74 to 1.737 Allow 1.74 to 1.74 (3 SF) / no change	**4**
		TE on M4 for arithmetical errors on correct method Allow TE if there has been some attempt at calculating a new $[H^+]$. In both cases final pH must be lower than the start pH of the buffer **and** $\Delta(pH) \leq 0.2$ Ignore SF	

Question number	Answer	Additional guidance	Mark
(c)	An explanation that makes reference to the following: • the colour of the methyl orange indicator will change from red to orange to yellow **(1)** • The volume of alkali added between the start of the indicator colour change and the formation of the end-point colour is large (compared with the volume used if the indicator change colour in the vertical section of the titration curve) **(1)** • the end-point (shown by the methyl orange) will occur (well) below the equivalence point **(1)**	Ignore just 'red to yellow' Allow There is only a gradual change in colour or the (indicator) colour changes slowly or there is no sharp change in colour or colour change will not occur on the addition of just a few drops of alkali Ignore just 'colour change of methyl orange occurs at 3.2-4.4'	3

Q16.

Question Number	Answer	Mark
(a)	**The only correct answer is B** (1.95) *A is not correct because pK_a has not been converted to K_a* *C is not correct because this is the pH of 0.100 mol dm^{-3} ethanoic acid* *D is not correct because the square root of K_a x $[CH_2ClCOOH]$ has not been used to calculate $[H^+]$*	**(1)**

Question Number	Answer	Mark
(b)	**The only correct answer is C** (Acid: $CH_2ClCOOH$, Conjugate base: CH_2ClCOO^-) *A is not correct because ethanoic acid has a higher pK_a than chloroethanoic acid so acts as a base in this reaction* *B is not correct because ethanoic acid has a higher pK_a than chloroethanoic acid so acts as a base in this reaction* *D is not correct because chloroethanoic acid loses a proton when it acts as an acid*	**(1)**