1. A solution of propanoic acid, CH_3CH_2COOH, has a pH of 2.89 at 25 °C.

What is $[H^+]$ in this solution?

A 1.7×10^{-6} mol dm^{-3}

B 4.6×10^{-4} mol dm^{-3}

[✓ **C**] 1.3×10^{-3} mol dm^{-3}

D 0.46 mol dm^{-3}

$pH = -\log_{10}[H^+]$

$[H^+] = 10^{-pH} = 10^{-2.89}$

$[H^+] = 1.288... \times 10^{-3}$ moldm^{-3}

$\therefore 1.3 \times 10^{-3}$ moldm^{-3}

Your answer C

[1]

2. A student investigates the reactions of two weak monobasic acids: 2-hydroxypropanoic acid, $CH_3CH(OH)COOH$, and butanoic acid, $CH_3CH_2CH_2COOH$.

(a) The student wants to prepare a standard solution of 2-hydroxypropanoic acid that has a pH of 2.19.

Plan how the student could prepare 250 cm^3 of this standard solution from solid 2-hydroxypropanoic acid.

In your answer you should provide detail of the practical procedure that would be carried out, including appropriate quantities and necessary calculations.

K_a for 2-hydroxypropanoic acid is 1.38×10^{-4} mol dm^{-3} at 25 °C.

$[H+] = 10^{-pH} = 10^{-2.19} = 6.46 \times 10^{-3}$ moldm^{-3}

$[CH_3CH(OH)COOH] = \frac{[H+]^2}{ka} = \frac{[6.46 \times 10^{-3}]^2}{1.38 \times 10^{-4}} = 0.0302$ moldm^{-3}

$0.0302 \times 250 \times 10^{-3} = 0.0755$ mol of 2-hydroxypropanoic acid

$0.0755 \times 90 = 6.80$g of 2-hydroxypropanoic acid

$\hookrightarrow 12+3+12+1+16+1+12+(16\times2)+1$

- Dissolve 6.80g of solid in less than 250 cm^3 distilled water in a beaker
- transfer the solution to a 250 cm^3 volumetric flask and ensure all solution is washed out of the beaker
- make solution up to 250 cm^3 with distilled water and ensure thorough mixing by inverting. **[8]**

(b) 2-Hydroxypropanoic acid is a slightly stronger acid than butanoic acid. The two acids are mixed together and an acid–base equilibrium is set up.

Suggest the equilibrium equation and identify the conjugate acid–base pairs.

$CH_3CH(OH)COOH + CH_3CH_2CH_2COOH \rightleftharpoons CH_3CH(OH)COO^- + CH_3CH_2CH_2COOH_2^+$

acid 1 base 2 base 1 acid 2

[2]

(c) To prepare a buffer solution, 75.0 cm³ of 0.220 mol dm⁻³ butanoic acid is reacted with 50.0 cm³ of 0.185 mol dm⁻³ sodium hydroxide.

K_a for butanoic acid is 1.5×10^{-5} mol dm^{-3} at 25 °C.

(i) Calculate the pH of 0.185 mol dm^{-3} sodium hydroxide at 25 °C.

Give your answer to **two** decimal places.

$pOH + pH = 14 \qquad pOH = -\log_{10}[OH^-]$

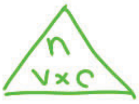
$pOH = -\log_{10}(0.185) = 0.73$

$14 - 0.73 = 13.27$

pH = 13.27 **[2]**

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

Give your answer to **two decimal places.**



Show **all** your working.

NaOH: $50 \times 10^{-3} \times 0.185 = 9.25 \times 10^{-3}$ mol

butanoic acid: $75 \times 10^{-3} \times 0.22 = 0.0165$ mol

$0.0165 - 9.25 \times 10^{-3} = 7.25 \times 10^{-3}$ mol of buffer

NaOH: $9.25 \times 10^{-3} \div 125 \times 10^{-3} = 0.074$ moldm^{-3}

buffer: $7.25 \times 10^{-3} \div 125 \times 10^{-3} = 0.058$ moldm^{-3}

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad [H^+] = 1.5 \times 10^{-5} \times \frac{0.058}{0.074} = 1.176 \text{ moldm}^{-3}$$

$pH = -\log_{10}(1.176) = 4.93$

$$[H^+] = K_a \times \frac{[HA]}{[A^-]} \qquad pH = -\log_{10}[H^+]$$

pH = 4.93 **[4]**

3. This question looks at ions and complexes.

(a)* You are provided with two boiling tubes containing solutions of the same ionic compound. The compound contains one cation and one anion from the lists below.

- cations: Fe^{2+}, Mn^{2+}, NH_4^+
- anions: Cl^-, CO_3^{2-}, SO_4^{2-}

Solutions of common laboratory reagents are available.

Plan a series of tests that you could carry out on the samples to identify the ionic compound. Your tests should produce at least one positive result for each ion.

For each test,

- include details of reagents, relevant observations and equations
- explain how your observations allow the ions to be identified.

You may include flowcharts or tables in your answer.

all tests conducted in separate boiling tubes

cation	test	result
Mn^{2+}	NaOH(aq)	pink ppt.
Fe^{2+}	NaOH(aq)	green ppt.
NH_4^+	NaOH(aq) and gentle heating	litmus paper turns blue

$Mn^{2+} + 2OH^- \rightarrow Mn(OH)_2$

$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$

$NH_4^+ + OH^- \rightarrow NH_3 + H_2O$

anion	test	result
CO_3^{2-}	HNO_3	effervescence
SO_4^{2-}	$Ba(NO_3)_2$	white ppt.
Cl^-	$AgNO_3$	white ppt.

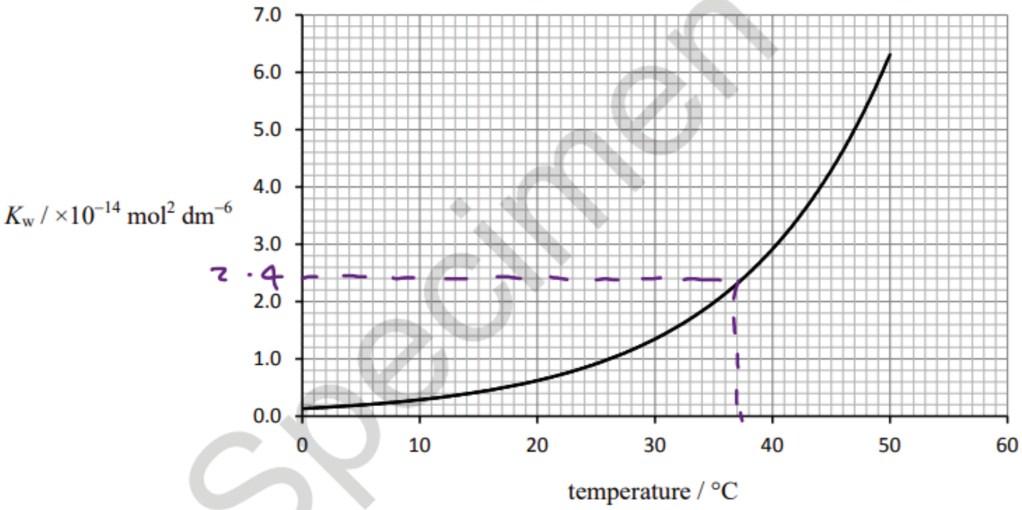
$Ag^+ + Cl^- \longrightarrow AgCl$ [add dilute NH_3 and ppt. dissolves]

$CO_3^{2-} + H^+ \longrightarrow H_2O + CO_2$ **[6]**

$SO_4^{2-} + Ba^{2+} \longrightarrow BaSO_4$

Cl^- test

(b) The dissociation of water is measured by the ionic product of water, K_w. The value of K_w varies with temperature as shown in the graph below.



Calculate the pH of water at body temperature, 37 °C.

$2.4 \times 10^{-14} = K_w$

$\sqrt{2.4 \times 10^{-14}} = [H^+] = 1.55 \times 10^{-7}$

$pH = -\log_{10}[H^+]$

$pH = -\log_{10} 1.55 \times 10^{-7} = 6.81$

pH = 6.81 **[3]**

(c) A complex of cobalt has the following composition by mass:

Co, 21.98%; N, 31.35%; H, 6.72%; Cl, 39.75%

(i) Calculate the empirical formula of this complex.

Co: $\frac{21.98}{58.9}$ $= 0.373$ $\frac{0.373}{0.373}$ $= 1$

N: $\frac{31.35}{14}$ $= 2.24$ $\frac{2.24}{0.373}$ $= 6$

H: $\frac{6.72}{1}$ $= 6.72$ $\frac{6.72}{0.373}$ $= 18$

Cl: $\frac{39.75}{35.5}$ $= 1.12$ $\frac{1.12}{0.373} = 3$

empirical formula = $CoN_6H_{18}Cl_3$ **[2]**

(ii) The formula of this cobalt complex can be expressed in form $[Co(L)_m]^{x+}(Cl^-)_n$

$n = 3$

so $x = 3$

Suggest the chemical formula of $[Co(L)_m]^{x+}$.

$[Co(NH_3)_6]^{3+}$ **[1]**

excluding Cl_3 and Co

$N_6H_{18} = (NH_3)_6$

4. This question looks at properties of iron compounds and iron ions in different oxidation states.

(a) Fe^{2+} and Fe^{3+} are the most common ions of iron.

$1s^2 2s^2 2p^6 3s^2 3p^6$ ~~$4s^2$~~ $3d^6$

filled first and lost first

(i) Write the electron configuration, in terms of sub-shells, for the Fe^{2+} ion.

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$ **[1]**

$3d^6$: [⇅] [↿] [↿] [↿] [↿]

(ii) How many orbitals contain an unpaired electron in an ion of Fe^{2+}?

4 **[1]**

(b) $[Fe(H_2O)_6]^{3+}$ ions take part in ligand substitution reactions.

forms $[Fe(CN)_6]^{3-}$

An excess of aqueous potassium cyanide, KCN(aq), is added to an aqueous solution containing $[Fe(H_2O)_6]^{3+}$ ions. A ligand substitution reaction takes place forming a complex ion that has a molar mass of 211.8 g mol^{-1}.

Write an equation for this ligand substitution reaction.

$[Fe(H_2O)_6]^{3+} + 6CN^- \rightarrow [Fe(CN)_6]^{3-} + 6H_2O$ **[2]**

(c) The complex ion, $[Fe(H_2O)_6]^{3+}$, behaves as a weak Brønsted–Lowry acid in aqueous solution. The equation below represents the dissociation of aqueous $[Fe(H_2O)_6]^{3+}$ ions, together with the K_a value.

$$[Fe(H_2O)_6]^{3+}(aq) \rightleftharpoons [Fe(H_2O)_5OH]^{2+}(aq) + H^+(aq) \qquad K_a = 6.00 \times 10^{-3} \text{ mol dm}^{-3}$$

(i) Write the expression for the acid dissociation constant, K_a, for $[Fe(H_2O)_6]^{3+}$.

$$ka = \frac{[[Fe(H_2O)_5OH]^{2+}][H^+]}{[Fe(H_2O)_6]^{3+}}$$ **[1]**

(ii) Calculate the pH of a 0.100 mol dm^{-3} solution of $[Fe(H_2O)_6]^{3+}$ to **two** decimal places.

$[H^+]^2 \leftarrow$ assume $[Fe(H_2O)_5OH]^{2+} = [H^+]$

$$ka = \frac{[H^+]^2}{[Fe(H_2O)_6]^{3+}}$$

$[H^+] = \sqrt{6 \times 10^{-3} \times 0.1} = 0.0245$ mol dm^{-3}

$-\log_{10}[H^+] = pH$

$pH = -\log_{10}[0.0245] = 1.61$

pH = 1.61 **[2]**

(d) Fe_2O_3 can be oxidised by ClO^- ions under alkaline conditions in a redox reaction.

Unbalanced half-equations for this reaction are shown below.

Balance the half-equations and construct an overall equation for the reaction.

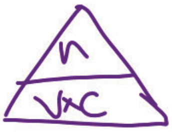
$$(\ldots\ ClO^- + \ldots\ H_2O + 2\ e^- \rightarrow \ldots\ Cl^- + 2\ OH^-) \times 3$$

$$\ldots\ Fe_2O_3 + 10\ OH^- \rightarrow 2\ FeO_4^{2-} + 5\ H_2O + 6\ e^-$$

overall equation: $Fe_2O_3 + 3ClO^- + 4OH^- \rightarrow 2FeO_4^{2-} + 3Cl^-$ $+ 2H_2O$ **[3]**

5. **HA** and **HB** are two strong monobasic acids.
25.0 cm^3 of 6.0 mol dm^{-3} **HA** is mixed with 45.0 cm^3 of 3.0 mol dm^{-3} **HB**.

What is the $H^+(aq)$ concentration, in mol dm^{-3}, in the resulting solution?



A 1.9

B 2.1

C 4.1

D 4.5

HA: $25 \times 10^{-3} \times 6 = 0.15 mol$

HB: $45 \times 10^{-3} \times 3 = 0.135 mol$

$$\frac{0.285 mol}{70 \times 10^{-3} dm^3} = 4.07 mol dm^{-3}$$

Your answer C **[1]**

6. This question is about the properties and reactions of ethanoic acid, CH_3COOH. Ethanoic acid is a weak acid with an acid dissociation constant, K_a, of $1.75 \times 10^{-5}\,mol\,dm^{-3}$ at 25 °C.

(a) A student uses a pH meter to measure the pH of a solution of CH_3COOH at 25 °C. The measured pH is 2.440.

Calculate the concentration of ethanoic acid in the solution.

$10^{-PH} = [H^+]$

Give your answer to **three** significant figures.

$[H^+] = 10^{-2.44} = 3.63 \times 10^{-3}\,mol\,dm^{-3}$

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

$[CH_3COOH] = \frac{[H^+]^2}{ka} = \frac{[3.63 \times 10^{-3}]^2}{1.75 \times 10^{-5}}$

$= 0.753\,mol\,dm^{-3}$

(3SF.)

concentration = 0.753 mol dm^{-3} **[3]**

(b) Ethanoic acid is added to another weak acid, fluoroethanoic acid, FCH_2COOH ($K_a = 2.19 \times 10^{-3}\,mol\,dm^{-3}$). An equilibrium is set up containing two acid-base pairs.

Stronger acid

Complete the equilibrium and label the conjugate acid-base pairs as **A1**, **B1** and **A2**, **B2**.

proton acceptor (base) proton donator (acid)

$CH_3COOH + FCH_2COOH \rightleftharpoons CH_3COOH_2^+ + FCH_3COO^-$

B2 A1 A2 B1

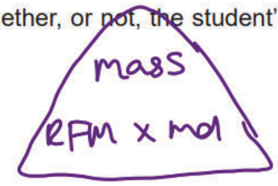
[2]

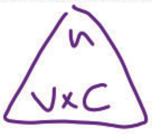
(c) The student plans to prepare a buffer solution that has a pH of 4.50. The buffer solution will contain ethanoic acid, CH_3COOH, and sodium ethanoate, CH_3COONa.

The student plans to add 9.08 g CH_3COONa to 250 cm^3 of 0.800 mol dm^{-3} CH_3COOH. The student assumes that the volume of the solution does not change.

(i) Show by calculation whether, or not, the student's experimental method would produce the required pH.

Show **all** your working.





$$\frac{9.08}{(12\times2)+3+((16\times2)+23)} = 0.111 \text{ mol of } CH_3COONa$$

$$0.111 \times 250\times10^{-3} = 0.443 \text{ moldm}^{-3}$$

$$Ka = \frac{[H^+][A^-]}{[HA]} = \frac{[H^+][0.443]}{[0.80]} = 1.75\times10^{-5}$$

$$[H^+] = 1.75\times10^{-5} \times \frac{[0.8]}{[0.443]} = 3.16\times10^{-5} \text{ moldm}^{-3}$$

$$-\log_{10}[H^+] = pH$$

$$-\log_{10}[3.16\times10^{-5}] = 4.50$$

[5]

(ii) When the student prepares the buffer solution, the volume of solution increases slightly.

Suggest whether the pH of the buffer solution would be the same, greater than, or less than your calculated value in **(c)(i)**.

Explain your reasoning.

same pH

Same ratio of $[HA]:[A^-]$

[2]

7. A buffer solution is prepared by mixing 200 cm^3 of 2.00 mol dm^{-3} propanoic acid, CH_3CH_2COOH, with 600 cm^3 of 1.00 mol dm^{-3} sodium propanoate, CH_3CH_2COONa.

K_a for CH_3CH_2COOH = 1.32×10^{-5} mol dm^{-3}

What is the pH of the buffer solution?

A 4.58

B 4.70

C 5.06

D 5.18

Your answer C

[1]

mol = vol (dm^3) × concentration (mol dm^{-3})

$$[A^-] = \frac{600\times10^{-3}\times1}{800\times10^{-3}} = 7.5\times10^{-3}$$ moldm-3

total volume

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

$$pH = -\log_{10}[H^+]$$

$$[HA] = \frac{200\times10^{-3}\times2}{800\times10^{-3}} = 5\times10^{-3}$$ moldm-3

$$1.32\times10^{-5} = \frac{[7.5\times10^{-3}][H^+]}{[5\times10^{-3}]}$$

$[H^+] = 8.8\times10^{-6}$ moldm-3

$pH = -\log_{10}[8.8\times10^{-6}] = 5.06$ (3sf.)

8. This question is about acids and bases found in the home.

(a) Ethanoic acid, CH_3COOH, is the acid present in vinegar.

A student carries out an experiment to determine the pK_a value of CH_3COOH.

- The concentration of CH_3COOH in the vinegar is $0.870\ mol\ dm^{-3}$.
- The pH of the vinegar is 2.41.

(i) Write the expression for the acid dissociation constant, K_a, of CH_3COOH.

$$Ka = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} \quad \hookrightarrow \frac{[H^+][A^-]}{[HA]}$$

[1]

(ii) Calculate the pK_a value of CH_3COOH.

Give your answer to **two** decimal places.

$$[H^+] = 10^{-pH} = 10^{-2.41} = 3.89 \times 10^{-3}\ mol\,dm^{-3}$$

assume $[H^+] = [A^-]$ because all H^+ ions must come from ethanoic acid

$$Ka = \frac{[3.89 \times 10^{-3}]^2}{[0.870]} = 1.74 \times 10^{-5}$$

$$pKa = -\log_{10} 1.74 \times 10^{-5} = 4.76$$

pK_a = 4.76 **[3]**

(iii) Determine the percentage dissociation of ethanoic acid in the vinegar.

Give your answer to **three** significant figures.

$$\%\ dissociation = \frac{[H^+]}{[HA]} \times 100$$

$$\frac{[3.89 \times 10^{-3}]}{[0.870]} \times 100 = 0.447\%$$

percentage dissociation = 0.447 % **[1]**

(b) Many solid drain cleaners are based on sodium hydroxide, NaOH.

- A student dissolves 1.26 g of a drain cleaner in water and makes up the solution to 100.0 cm^3.
- The student measures the pH of this solution as 13.48.

Strong base

Determine the percentage, by mass, of NaOH in the drain cleaner.

Give your answer to **three** significant figures.

$[H+] = 10^{-pH} = 10^{-13.48} = 3.31 \times 10^{-14}$ moldm^{-3}

$[OH^-] = \frac{kw}{[H+]} = \frac{1 \times 10^{-14}}{3.31 \times 10^{-14}} = 0.302$ moldm^{-3}

cm^3 → dm^3

$0.302 \times 100 \times \boxed{10^{-3}} = 0.0302$ mol

$0.302 \times \boxed{40} = 1.21$g

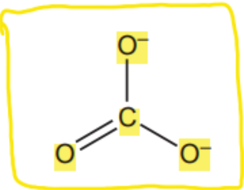
RFM of NaOH

$\frac{1.21}{1.26} \times 100 = 95.9\%$ (3sf)

percentage = 95.9 % **[4]**

(c) Sodium carbonate, Na_2CO_3, is a base used in washing soda.

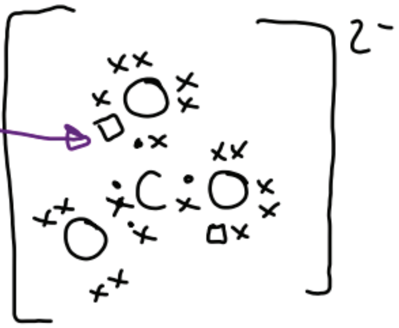
Na_2CO_3 contains the carbonate ion, CO_3^{2-}, shown below.



Structure to base dot and cross diagram from

Draw the '*dot-and-cross*' diagram for the carbonate ion.

Show outer electrons only and use different symbols for electrons from C and O, and any 'extra' electrons.



make the -ve sign "extra" electrons

[2]

9. The equation shows the dissociation of the acid H_3AsO_4 in water.

$$\underset{A1}{H_3AsO_4} + \underset{B2}{H_2O} \rightleftharpoons \underset{B1}{H_2AsO_4^-} + \underset{A2}{H_3O^+}$$

H_3AsO_4 and $H_2AsO_4^-$

H_2O and H_3O^+

Which pair is a conjugate acid–base pair?

~~**A**~~ H_3AsO_4 and H_2O

~~**B**~~ $H_2AsO_4^-$ and H_3O^+

~~**C**~~ H_3AsO_4 and H_3O^+

[✓ **D**] H_3O^+ and H_2O

Your answer D **[1]**

10. Healthy human blood needs to be maintained at a pH of 7.40 for the body to function normally.

(a)* Carbonic acid, H_2CO_3, is a weak acid which, together with hydrogencarbonate ions, HCO_3^-, acts as a buffer to maintain the pH of blood.

The pK_a value for the dissociation of carbonic acid is 6.38.

Explain, in terms of equilibrium, how the carbonic acid–hydrogencarbonate mixture acts as a buffer in the control of blood pH, and calculate the $[HCO_3^-] : [H_2CO_3]$ ratio in healthy blood. **[6]**

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

addition of H^+ causes $\rightleftharpoons$ to shift left
addition of OH^- causes $\rightleftharpoons$ to shift right

increase in H^+:

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

increase in OH^-:

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

$ka = 10^{-6.38} = 4.17 \times 10^{-7}$ moldm-3
$[H^+] = 10^{-7.40} = 3.98 \times 10^{-8}$ moldm-3
$pH = -\log_{10}[H^+]$ rearranged = $[H^+] = 10^{-pH}$
same equation used to convert pka => ka

Additional answer space if required

$$\frac{[HCO_3^-]}{[H_2CO_3]} = \frac{4.17\times10^{-7}}{3.98\times10^{-8}} \Rightarrow \text{ratio} : 10.47:1$$

(b) Red blood cells contain haemoglobin.

Explain using ligand substitutions:

- how haemoglobin transports oxygen around the body
- why carbon monoxide is toxic.

O_2 bonds with Fe^{2+} in haemoglobin and is replaced by H_2O or CO_2 and when required. The CO bond that forms is stronger than O_2 bond so CO is toxic.

[3]

11. This question is about weak acids.

The K_a values of three weak acids are shown in **Table 20.1**.

Weak acid	**K_a / mol dm^{-3}**
iodic(V) acid, $HIO_3(aq)$	1.78×10^{-1}
propanoic acid, $C_2H_5COOH(aq)$	1.35×10^{-5}
hydrocyanic acid, $HCN(aq)$	6.17×10^{-10}

Table 20.1

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

(a) Calculate the pH of 0.0800 mol dm^{-3} $C_2H_5COOH(aq)$.

Give your answer to **2** decimal places.

$1.35\times10^{-5} \times 0.08 = 1.08\times10^{-6} = [H+]^2$

$\sqrt{1.08\times10^{-6}} = 1.04\times10^{-3}$ moldm^{-3}

$pH = -\log_{10}[H+] = -\log_{10}[1.04\times10^{-3}] = 2.98$ (2dp.)

pH = 2.98 **[2]**

(b) A student adds a total of 45.0 cm^3 of 0.100 mol dm^{-3} NaOH(aq) to 25.0 cm^3 of 0.0800 mol dm^{-3} $C_2H_5COOH(aq)$ and monitors the pH throughout.

(i) Show by calculation that 20.0 cm^3 of NaOH(aq) is required to reach the end point.

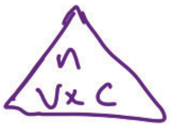
$0.08 \times 25\times10^{-3} = 0.002$ mol of C_2H_5COOH

$\frac{0.002}{0.1} = 0.02$ dm^3 = 20cm^3 of NaOH

[1]

(ii) Calculate the pH of the final solution.

Give your answer to **2** decimal places.



$n(OH^-)_{excess} = n(OH^-) - n(C_2H_5COOH)$

$(0.1 \times 45 \times 10^{-3})$ $(0.08 \times 25 \times 10^{-3})$

$n(OH^-)_{excess} = 0.0045 - 0.002 = 0.0025$ mol

$[OH^-] = \frac{0.0025}{70 \times 10^{-3}} = 0.0357$ moldm^{-3}

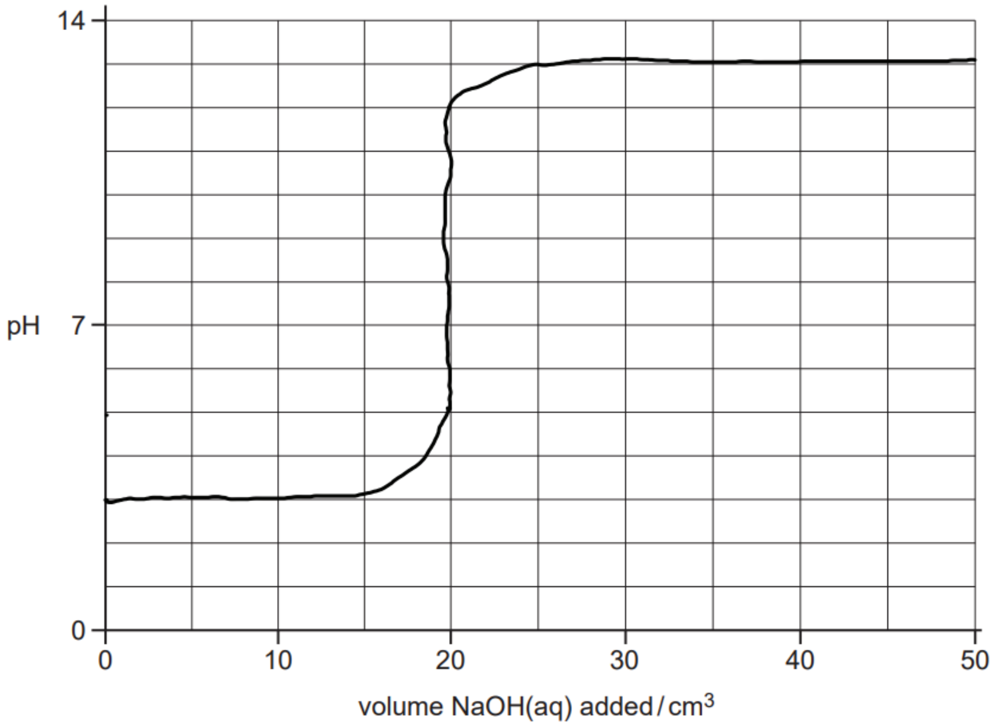
total volume = $45 + 25 = 70$ cm^3 $= 70 \times 10^{-3}$ dm^3

$pOH = -\log_{10}[OH^-] = -\log_{10}[0.0357] = 1.447$

$pH = 14 - pOH = 14 - 1.447 = 12.55$ (2dp.)

pH = 12.55 **[4]**

(iii) On the axes below, sketch a pH curve for the pH changes during the addition of 45.0 cm^3 of 0.100 mol dm^{-3} NaOH(aq) to 25.0 cm^3 of 0.0800 mol dm^{-3} C_2H_5COOH(aq).



[3]

(iv) The student considers using the four indicators in **Table 20.2** for the titration.

Indicator	**pH range**
Cresol red	0.2 – 1.8
Bromophenol blue	3.0 – 4.6
Cresol purple	7.6 – 9.2
Indigo carmine	11.6 – 14.0

Table 20.2

Explain which indicator would be most suitable for the titration.

cresol purple because pH range matches vertical section / equivalence point

[1]

(v) The student repeats the experiment starting with 25.0 cm^3 of 0.0800 mol dm^{-3} HCN(aq) and adding a total of 45.0 cm^3 of 0.100 mol dm^{-3} NaOH(aq).

Predict **one** similarity and **one** difference between the pH curve with $C_2H_5COOH(aq)$ and the pH curve with HCN(aq). Use the information in **Table 20.1**, and your answer to **(b)(iii)**.

Similarity End point of NaOH needed to neutralise

Difference HCN higher starting pH

[2]

(c) The student calculates the pH of 0.0800 mol dm^{-3} $HIO_3(aq)$. The student assumes that the equilibrium concentration of $HIO_3(aq)$ is the same as the initial concentration of $HIO_3(aq)$.

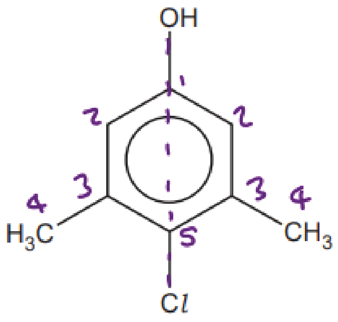
The student measures the pH, and finds that the measured pH value is different from the calculated pH value.

Explain why the measured pH is different from the calculated pH.

- HIO_3 dissociation is not negligable
- large Ka and HIO_3 is 'stronger' weak acid
- $[HIO_3]_{eq}$ is significantly lower than $[HIO_3]$ initial/undissociated

[1]

12. Dettol® is a disinfectant containing the antiseptic chloroxylenol, shown below.



chloroxylenol

(a) Chloroxylenol is a weak Brønsted–Lowry acid.

(i) What is the systematic name of chloroxylenol?

4 - chloro - 3,5- dimethyl phenol **[1]**

(ii) Predict the number of peaks in a ^{13}C NMR spectrum of chloroxylenol.

5 **[1]**

(iii) Name the functional group responsible for the acidity of chloroxylenol and describe a simple test which would confirm the presence of this group.

Functional group Phenol

Test indicator turns red / orange (pH < 7) and no reaction with Na_2CO_3

[2]

(iv) A student measures the pH of the contents in a bottle of Dettol® as 5.14.

The label on the bottle shows the percentage of chloroxylenol in Dettol® as 4.80% i.e. 100 cm^3 of Dettol® contains 4.80 g of chloroxylenol.

Assume the following:

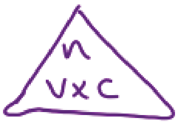
- Chloroxylenol is the only acidic component in Dettol®.
- Chloroxylenol is a weak monobasic acid.
- The density of Dettol® is 1.00 g cm^{-3}.

Write the equation, using molecular formulae, for the acid dissociation of chloroxylenol.

Calculate the acid dissociation constant, K_a, for chloroxylenol.

$$C_8H_9ClO \rightleftharpoons H^+ + C_8H_8ClO^-$$

$$RFM = (12 \times 8) + 9 + 35.5 + 16 = 156.5\ gmol^{-1}$$



$$Ka = \frac{[H^+]^2}{[HA]}$$

$$[H^+] = 10^{-pH}$$

$$\frac{4.8}{156.5} = 0.03067\ mol$$

$$\frac{0.03067}{100 \times 10^{-3}} = 0.3067\ moldm^{-3} = [HA]$$

$$[H^+] = 10^{-5.14} = 7.244 \times 10^{-6}\ moldm^{-3}$$

$$Ka = \frac{[7.244 \times 10^{-6}]^2}{[0.3067]}$$

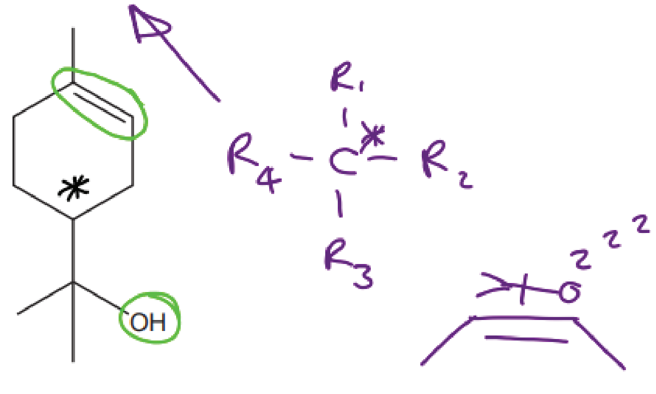
K_a = ...1.71 × 10^{-10}.............. mol dm^{-3} **[5]**

$$Ka = 1.71 \times 10^{-10}\ moldm^{-3}$$

(b) Dettol® contains other chemicals including α-terpineol, shown below.

(i) α-Terpineol is a chiral compound.

Show with an asterisk, (*), the chiral centre(s) in the structure of α-terpineol.



α-terpineol

[1]

E-asy chair

(ii) α-Terpineol meets the requirements for *E*/*Z* isomerism.
However, only one *E*/*Z* isomer of α-terpineol exists.

Explain

- why α-terpineol meets the requirements for *E*/*Z* isomerism
- whether α-terpineol is an *E*- or *Z*- isomer
- why only one *E*/*Z* isomer of α-terpineol exists.

• C=C double bond, each C attached to 2 different groups
• E/Z isomerism linked to high priority groups. Z- isomer groups are on the same side
• ring would be strained

[4]

(iii) α-Terpineol contains two functional groups.

For each functional group, choose a reagent that reacts with that group **only**.
Draw the structures for the organic products of the reactions.

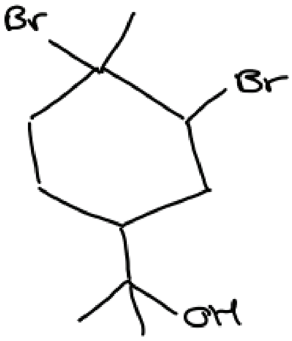
Show structures for organic compounds.

Reagent(s) Br_2

Name of functional group that reacts alkene

Structure of organic product

electrophilic addition mechanism

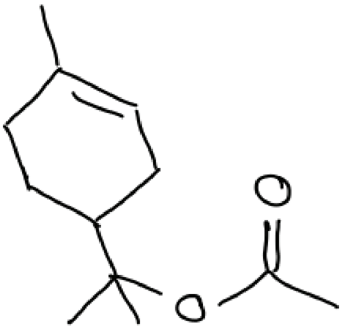


Reagent(s) CH_3COOH, H^+ catalyst

Name of functional group that reacts 3° alcohol

Structure of organic product

esterification



[4]

13. 20 cm^3 of 0.10 mol dm^{-3} hydrochloric acid is added to 10 cm^3 of 0.10 mol dm^{-3} sodium hydroxide.

What is the pH of the resulting mixture?

A 1.00

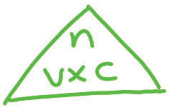
B 1.18

C 1.30

D 1.48

Your answer D

[1]



$20\times10^{-3} \times 0.1 = 2\times10^{-3}$ mol HCl

$10\times10^{-3} \times 0.1 = 1\times10^{-3}$ mol NaOH

$2\times10^{-3} - 1\times10^{-3} = 1\times10^{-3}$ mol excess H^+

$\frac{1\times10^{-3}}{(20+10)\times10^{-3}} = \frac{1}{30}$ moldm-3

$pH = -\log_{10}[H^+]$

$pH = -\log_{10}\left[\frac{1}{30}\right] = 1.48$

14. This question is about reactions and uses of the weak acids methanoic acid, HCOOH, and ethanoic acid, CH_3COOH.

(a) A student adds magnesium metal to an aqueous solution of ethanoic acid, CH_3COOH.
A redox reaction takes place.

Write the overall equation for this reaction and explain, in terms of oxidation numbers, which element has been oxidised and which element has been reduced.

Equation $\overset{0}{Mg} + 2\overset{-1}{\overbrace{CH_3COO}}\overset{+1}{H} \longrightarrow (\overset{-1}{\overbrace{CH_3COO}})_2\overset{+2}{Mg} + \overset{0}{H_2}$

Oxidation Mg : 0 ⟶ +2

Reduction H : +1 ⟶ 0

[3]

(b) The K_a values of HCOOH and CH_3COOH are shown in **Table 18.1**.

stronger acid

Weak acid	K_a **/ mol dm^{-3}**
HCOOH	1.82×10^{-4}
CH_3COOH	1.78×10^{-5}

3.74

4.75

pka = pH

pka = $-\log_{10}$ ka

Table 18.1

A student adds methanoic acid to ethanoic acid.

An equilibrium is set up containing two acid-base pairs.

Complete the equilibrium and label the conjugate acid-base pairs as **A1**, **B1** and **A2**, **B2**.

$HCOOH + CH_3COOH \rightleftharpoons HCOO^- + CH_3COOH_2^+$

A1 B2 B1 A2

[2]

$10^{-pH} = [H^+]$

$\frac{[H^+]^2}{[HA]} = Ka$

rearrange for $[HA] = [CH_3COOH]$

(c) Use **Table 18.1** to answer the following questions.

(i) The student measures the pH of $CH_3COOH(aq)$ as 2.72.

Show that the concentration of the $CH_3COOH(aq)$ is 0.204 mol dm^{-3}.

$10^{-2.72} = 1.905 \times 10^{-3}$ moldm^{-3} $= [H^+]$

$[CH_3COOH] = \frac{(1.905 \times 10^{-3})^2}{1.78 \times 10^{-5}} = 0.204$ moldm^{-3}

[2]

(ii) The student plans to make a buffer solution of pH 4.00 from a mixture of $CH_3COOH(aq)$ and sodium ethanoate, $CH_3COONa(aq)$.

The student mixes 400 cm^3 of 0.204 mol dm^{-3} $CH_3COOH(aq)$ with 600 cm^3 of $CH_3COONa(aq)$.

Calculate the concentration of $CH_3COONa(aq)$ needed to prepare this buffer solution of pH 4.00.

$10^{-pH} = [H^+]$

part (i) $[H^+]_{buffer} = 10^{-4} = 1 \times 10^{-4}$ moldm^{-3}

$= 400cm^3 = 0.4dm^3$

$\frac{0.204}{1} \times 0.4 = 8.16 \times 10^{-2} = [CH_3COOH]_{buffer}$

$= 1dm^3 = 1000cm^3$

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

$1.78 \times 10^{-5} = \frac{[1 \times 10^{-4}][CH_3COO^-]}{8.16 \times 10^{-2}}$

$[CH_3COO^-]_{buffer} = \frac{1.78 \times 10^{-5} \times 8.16 \times 10^{-2}}{1 \times 10^{-4}} = \boxed{1.5 \times 10^{-2}}$ moldm^{-3}

calculator answer

$\frac{\boxed{1.452...} \times 10^{-2} \times 1}{0.6} = 2.4 \times 10^{-2} = [CH_3COO^-]_{initial}$

opposite actions to part (i)

concentration = 2.4×10^{-2} mol dm^{-3} **[4]**

15. This question is about two different types of acid found in organic compounds, carboxylic acids and sulfonic acids, as shown in **Fig. 6.1**.

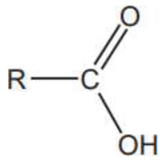
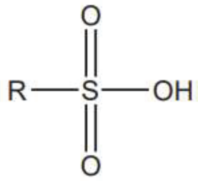
	
Carboxylic acid	Sulfonic acid

Fig. 6.1

(a) Complete **Table 6.1** to predict bond angles ***a*** and ***b*** and name the shapes which makes these bond angles in the functional groups of carboxylic acids and sulfonic acids.

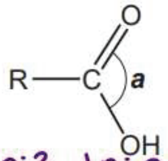
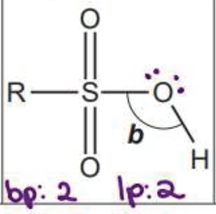
Type of acid	Acid	Bond angle	Name of shape
Carboxylic acid	 bp:3 lp:0	120°	trigonal planar
Sulfonic acid	 bp: 2 lp:2	104.5°	non-linear

Table 6.1

[2]

lone pairs repel more than bonded pairs

(b) Ethanoic acid, CH_3COOH, and methanesulfonic acid, CH_3SO_2OH, are both monobasic acids. The pK_a values are shown in the table.

Acid		**pK_a**
Ethanoic acid	CH_3COOH	4.76
Methanesulfonic acid	CH_3SO_2OH	–1.90

pka = pH

A student suggests that 1.0 mol dm^{-3} CH_3SO_2OH should have a lower pH value than 1.0 mol dm^{-3} CH_3COOH.

Write an equation, showing conjugate acid–base pairs, for the equilibrium of CH_3SO_2OH with water and explain, with reasons, whether the student is correct.

Label the conjugate acid–base pairs: **A1**, **B1** and **A2**, **B2**.

$$\underset{A1}{CH_3SO_2OH} + \underset{B2}{H_2O} \rightleftharpoons \underset{B1}{CH_3SO_2O^-} + \underset{A2}{H_3O^+}$$

acids: proton donors

bases: proton acceptors

CH_3SO_2OH is a stronger acid / dissociates more

student is correct CH_3SO_2OH has a lower **[4]**

pka / pH / higher ka / [H$^+$]

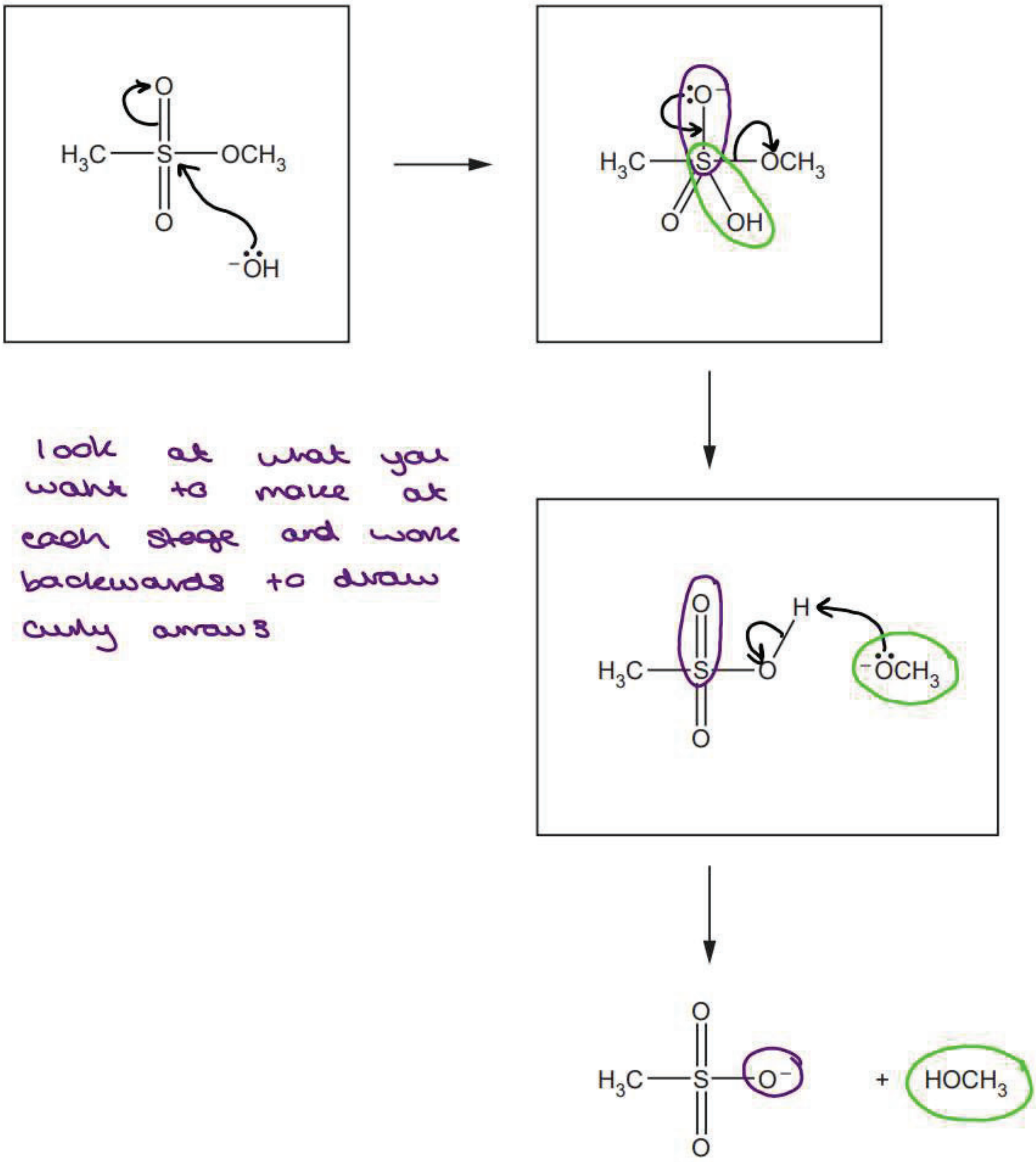
(c) Carboxylic acids and sulfonic acids both form esters.

Sulfonic acid esters can be hydrolysed by aqueous alkali.
The equation shows the alkaline hydrolysis of a sulfonic acid ester.

$CH_3SO_2OCH_3 + OH^- \rightarrow CH_3SO_2O^- + CH_3OH$

In the **3 boxes below**, add curly arrows to show the mechanism for this reaction.

In the first box, the hydroxide ion acts as a nucleophile.



look at what you want to make at each stage and work backwards to draw curly arrows

[4]