OCR
Oxford Cambridge and RSA

A Level Chemistry A
H432/03 Unified chemistry
Sample Question Paper

Date – Morning/Afternoon
Time allowed: 1 hour 30 minutes

You must have:
- the Data Sheet for Chemistry A

You may use:
- a scientific calculator

First name	
Last name	
Centre number	Candidate number

INSTRUCTIONS
- Use black ink. You may use an HB pencil for graphs and diagrams.
- Complete the boxes above with your name, centre number and candidate number.
- Answer **all** the questions.
- Write your answer to each question in the space provided.
- Additional paper may be used if required but you must clearly show your candidate number, centre number and question number(s).
- Do **not** write in the bar codes.

INFORMATION
- The total mark for this paper is **70**.
- The marks for each question are shown in brackets **[ ]**.
- Quality of extended responses will be assessed in questions marked with an asterisk (*).
- This document consists of **20** pages.

Answer **all** the questions.

1 Give chemical explanations for the following statements.

(a) Bromine has a higher boiling point than chlorine.

Bromine has stronger London forces

[1]

(b) A carton of milk expands on freezing.

hydrogen bonds in ice hold H_2O molecules further apart than in water [1]

(c) Potassium is placed immediately after argon in the periodic table.

potassium atoms have one more proton than argon atoms [1]

(d) The reaction of ethane with chlorine under UV radiation is a poor method for preparing a high yield of chloroethane.

free radical substitution

further substitution occurs

[1]

(e) Water has a concentration of approximately 56 mol dm^{-3}.

water: $1\,dm^3 = 1000\,g$

$\frac{1000}{18} \approx 56$ mol $56/1 = 56\ mol\,dm^{-3}$ [1]

(f) The carbon–carbon bonds in benzene are all the same length.

π bonds in benzene are delocalised

[1]

(g) IR spectroscopy distinguishes ketones from carboxylic acids.

carboxylic acids have a broad O-H absorption at 2500-3300 cm^{-1} which ketones don't. **[1]**

(h) 1.323 g of $N_2O(g)$ has a volume of 1.00 dm^3 at 100 kPa and 400 K.

$1\ dm^3 = 1 \times 10^{-3}\ m^3$

$100\ kPa = 100 \times 10^3\ Pa$

$PV = nRT \rightarrow n = \frac{PV}{RT}$

$n = \frac{100 \times 10^3 \times 1 \times 10^{-3}}{8.314 \times 400} = 0.0301\ mol$ **[1]**

mass / mol x RFM

$0.0301 \times ((14 \times 2) + 16) = 1.323\ g$

(i) 4.25 g of $C_6H_5COOCH_3$ contains 1.88×10^{22} molecules.

mass / mol x RFM

$4.25 \div ((12 \times 8) + (1 \times 8) + (16 \times 2)) = 0.03125\ mol$

$0.03125 \times 6.023 \times 10^{23} = 1.88 \times 10^{22}$ **[1]**

A

avogadro's constant

(j) The rate of hydrolysis of 1-bromobutane is faster than that of 1-chlorobutane.

The C-Br bond is weaker than the C-Cl bond. **[1]**

2 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	+ve	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.

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

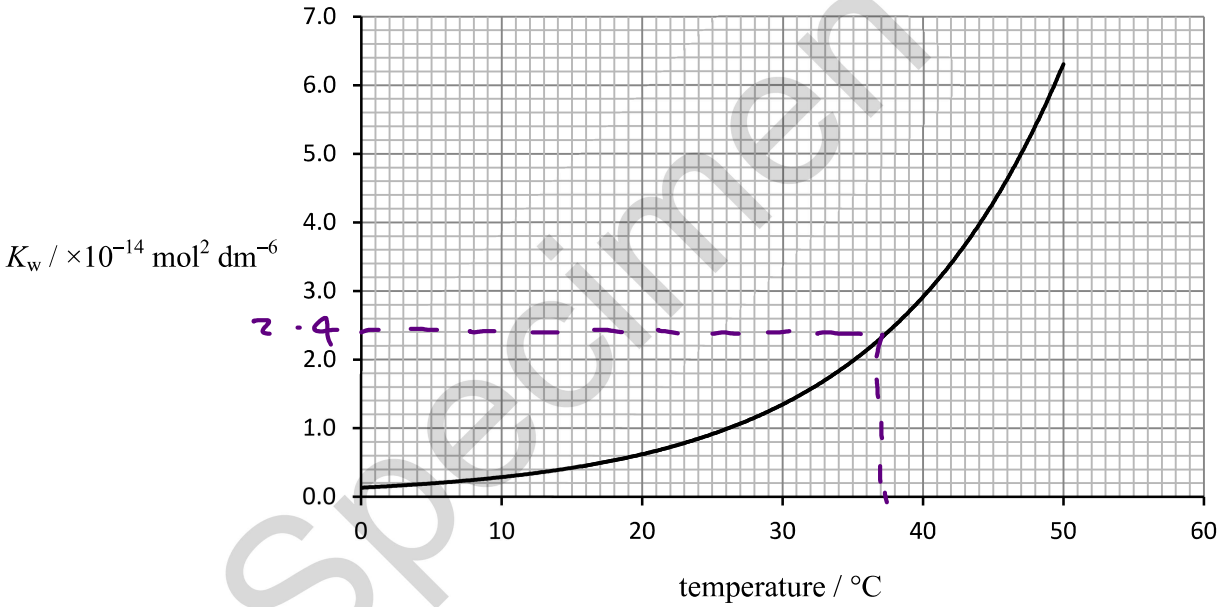
$CO_3^{2-} + H^+ \rightarrow H_2O + CO_2$

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

Cl^- test

[6]

(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: $\frac{21.98}{58.9} = 0.373$ $\quad \frac{0.373}{0.373} = 1$

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

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

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

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

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

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

$n = 3$ so $x = 3$

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

excluding Cl_3 and Co

$N_6H_{18} = (NH_3)_6$

3 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.

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

(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]

filled first and lost first

$3d^6$: ↑↓ | ↑ | ↑ | ↑ | ↑

(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 $[Fe(H_2O)_6]^{3+}$.

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

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

$K_a = \frac{[H^+]^2}{[Fe(H_2O)_6]^{3+}}$ ← assume $[Fe(H_2O)_5OH]^{2+} = [H^+]$

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

(..... ClO^- + ... H_2O + ..2.. e^- → ..... Cl^- + ..2.. OH^-) x 3

..... Fe_2O_3 + ..10.. OH^- → ..2.. FeO_4^{2-} + ..5.. H_2O + ..6.. e^-

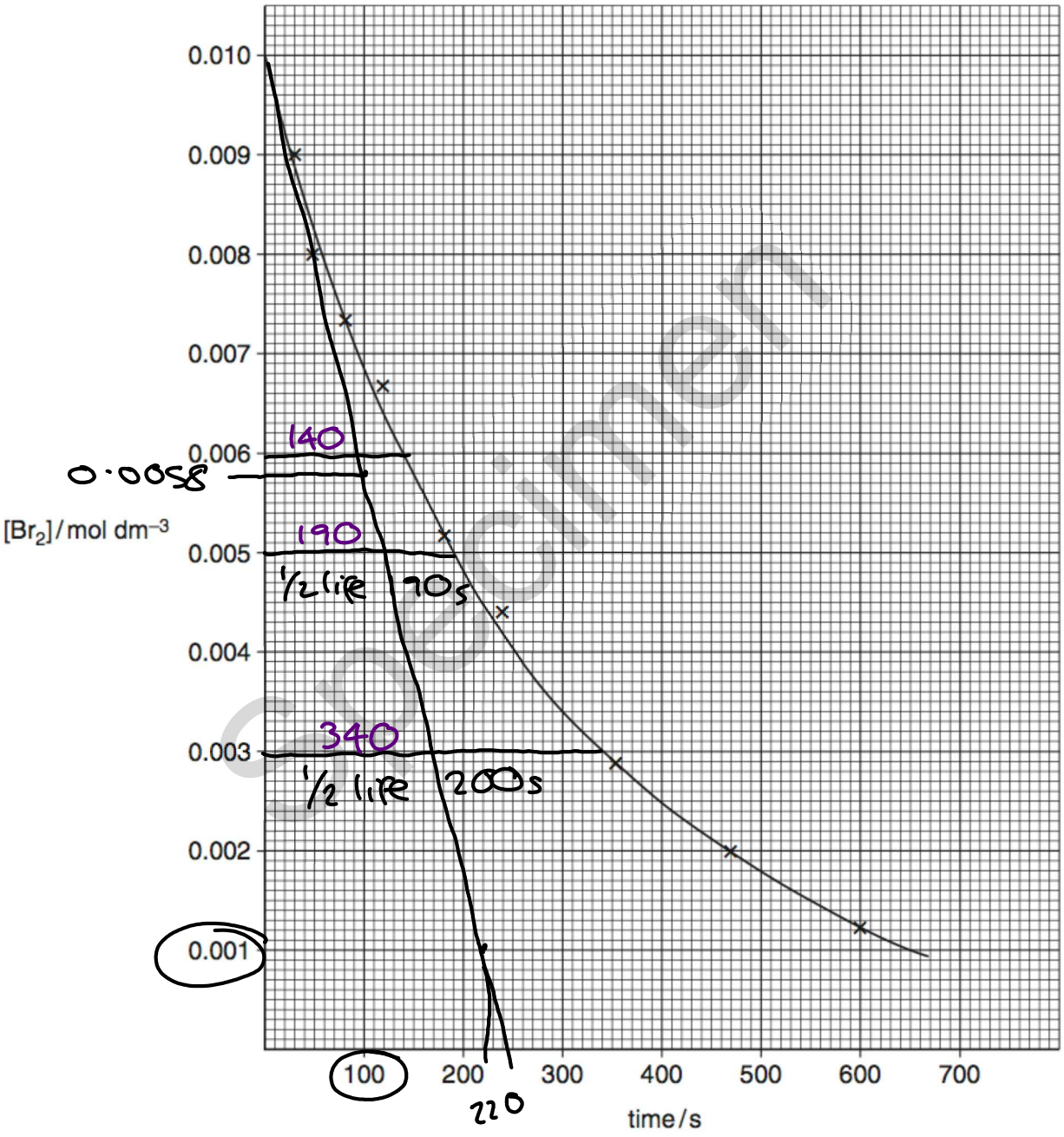
overall equation: $Fe_2O_3 + 3ClO^- + 4OH^- \rightarrow 2FeO_4^{2-} + 3Cl^- + 2H_2O$ **[3]**

4 Methanoic acid and bromine react as in the equation below.

$$Br_2(aq) + HCOOH(aq) \rightarrow 2H^+(aq) + 2Br^-(aq) + CO_2(g)$$

A student investigates the rate of this reaction by monitoring the concentration of bromine over time. The student uses a large excess of HCOOH to ensure that the order with respect to HCOOH will be effectively zero.

From the experimental results, the student plots the graph below.



(a) Suggest how the concentration of the bromine could have been monitored.

measure reduction of colour of bromine [1]

(b) Suggest a different experimental method that would allow the rate of this reaction to be followed over time.

measure volume of CO_2 produced

[1]

(c) Why would use of excess HCOOH ensure that the order with respect to HCOOH is effectively zero?

concentration of HCOOH would be constant

[1]

(d)* Using the graph, determine

- the initial rate of reaction
- the rate constant.

gradient of tangent at $t = 0$ s

Your answer must show full working using the graph and the lines below as appropriate.

$$\frac{0.0058 - 0.001}{220 - 100} = 4 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$$

divided concentration by time

Constant ½ life at 190 s

so Br_2 is 1st order

$$k = \frac{\text{rate}}{[Br_2]} = \frac{4 \times 10^{-5}}{0.01} = 4 \times 10^{-3} \text{ s}^{-1}$$

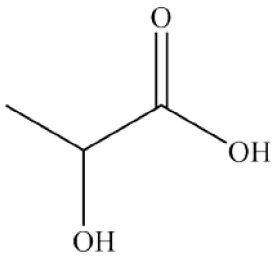
$$\frac{\text{mol dm}^{-3} \text{ s}^{-1}}{\text{mol dm}^{-3}}$$

concentration at $t = 0$ s

[6]

5 This question is about organic acids.

(a) Lactic acid, shown below, has two functional groups.



Lactic acid reacts with bases and with many metals.

- An aqueous solution containing 1.125 g of lactic acid is reacted with an excess of magnesium producing hydrogen gas.
- The excess magnesium is removed.
  The water is evaporated, leaving a white solid, **A**.

(i) Name the type of reaction of lactic acid with bases and with metals.

reaction with bases: neutralisation

reaction with metals: redox

[1]

(ii) Calculate the volume of $H_2(g)$ produced, measured at room temperature and pressure.

mass / mol × RFM

$\frac{1.125}{(12\times3)+(16\times3)+6} = 0.0125$ mol

$\frac{0.0125}{2} \times 24000 = 150\,cm^3$

$\frac{\text{Volume}}{24000} = \text{mol}$

x2 mol of lactic acid than H_2

volume of H_2 = 150 cm^3 **[2]**

(iii) What is the empirical formula of the white solid **A**?

$[C_3H_6O_3]^-$ ion of lactic acid

Mg^{2+} so x2 ions of lactic acid needed

$C_6H_{12}O_6Mg$ **[1]**

(iv) Predict **two** reactions of lactic acid, each involving a different functional group.

Do **not** include reactions with bases or metals.

For each reaction,

- state the type of reaction, the reagents and conditions
- draw the structures of any organic products formed.

COOH: esterification

CH_3OH, H_2SO_4

any alcohol

ester link $R_2-\overset{\overset{O}{\|}}{C}-O-R_1$

$CH_3(CHOH)COOCH_3$

2° OH: oxidation

$K_2Cr_2O_7$, H_2SO_4 + heat

$CH_3(CO)COOH$

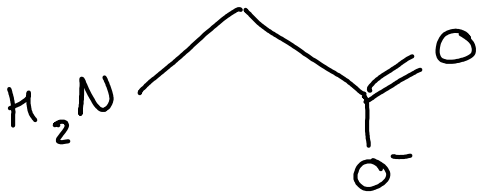
2° alcohol → ketone

[4]

(b) In basic conditions, α-amino acids form anions with the general formula, $RCH(NH_2)COO^-$. These anions can act as bidentate ligands.

Copper(II) ions can form a square planar complex with anions of the amino acid glycine (R = H). There are two stereoisomers of this complex, **B** and **C**.

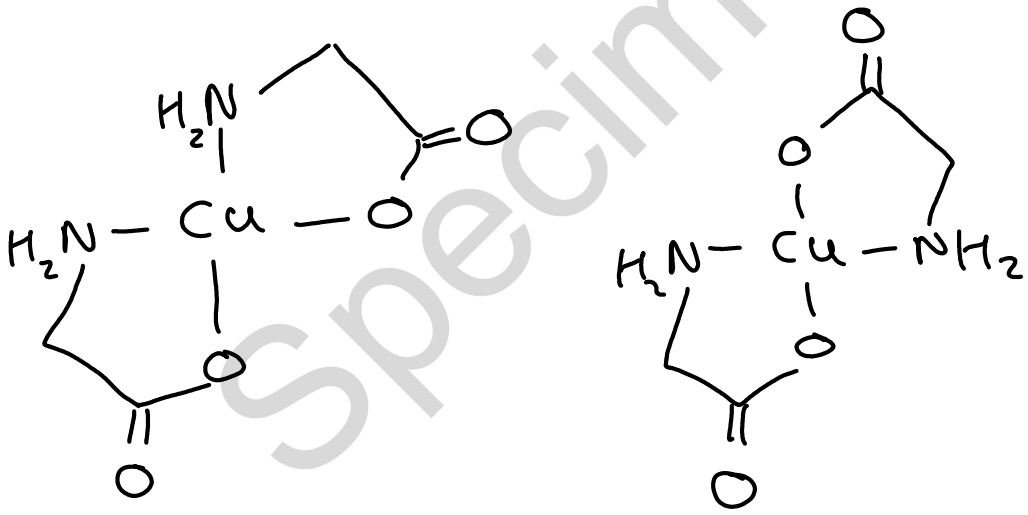
(i) Draw the **skeletal** formula of the anion of glycine.



[1]

(ii) Draw diagrams of stereoisomers **B** and **C**.

In your structures, show the ligands as skeletal formulae.



[2]

(iii) Anion ligands of the amino acid alanine (R = CH_3) would be expected to form more than two square planar stereoisomers with copper(II) ions.

Explain this statement.

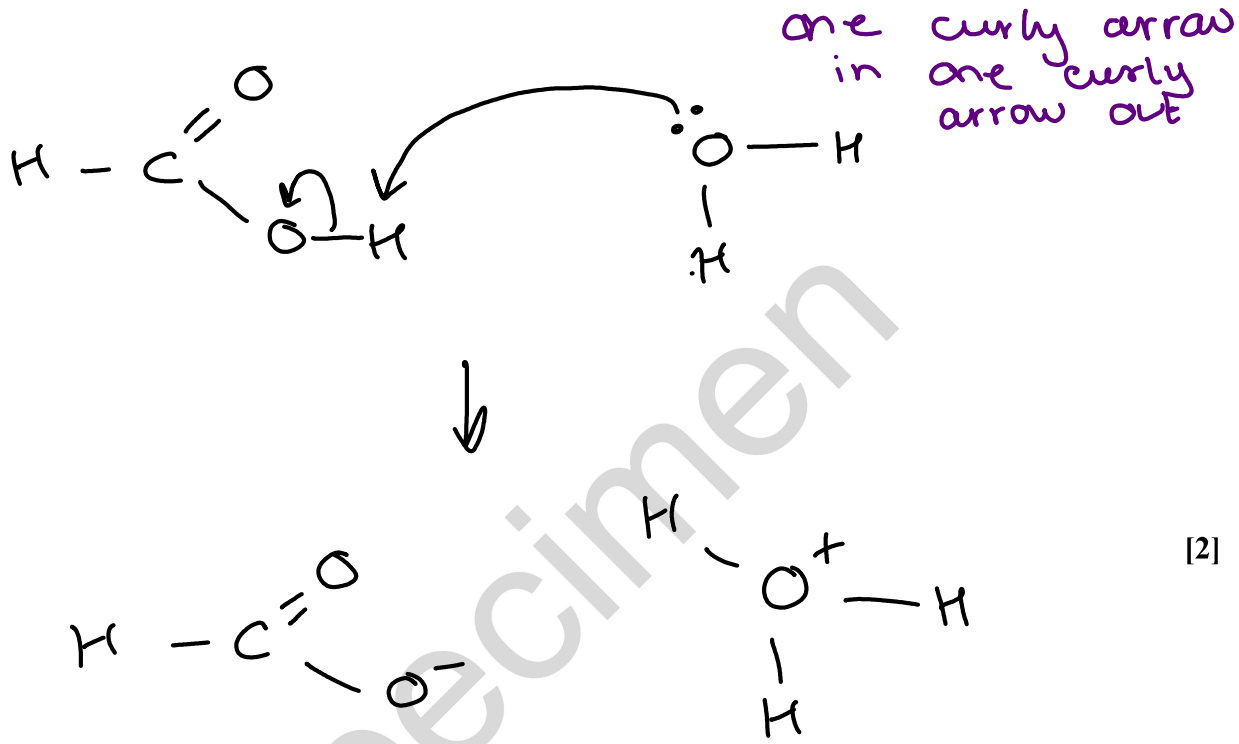
alanine has a chiral centre

..... **[1]**

(c) Methanoic acid is added to water. An acid–base equilibrium is set up containing two acid–base pairs.

Suggest a mechanism for the forward reaction in this equilibrium.

Your mechanism should use displayed formulae and curly arrows, and show all species present at equilibrium.



[2]

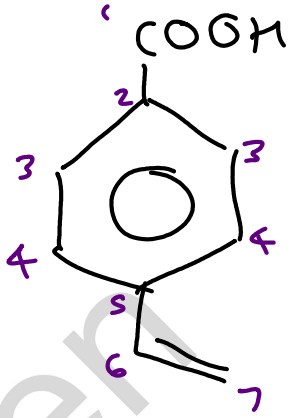
(d) Information about a monobasic organic acid **D** is shown below.

- **D** reacts by both electrophilic substitution and electrophilic addition.
- The molecular formula of **D** is $C_xH_yO_2$.
- The mass spectrum of **D** has a molecular ion peak at $m/z = 148$.
- The ^{13}C NMR spectrum of **D** contains seven peaks.

Determine and draw a possible structure for **D**.

Explain your reasoning from the evidence provided.

7 ^{13}C NMR peaks



electrophilic substitution = benzene ring

electrophilic addition = alkene (C=C)

molecular formula: $C_9H_8O_2$ (10), C=C, COOH (acid)

[5]

6 Hydroxylamine, NH_2OH, is a strong reducing agent.

When heated in aqueous solution, NH_2OH reduces Fe^{3+} ions to Fe^{2+} ions.

A student suggests the three possible equations for the reaction, shown below.

Equation 1 $NH_2OH + Fe^{3+} \longrightarrow Fe^{2+} + \frac{1}{2}N_2 + H^+ + H_2O$

Equation 2 $NH_2OH + 2Fe^{3+} \longrightarrow 2Fe^{2+} + \frac{1}{2}N_2O + 2H^+ + \frac{1}{2}H_2O$

assume 1 : 3 = molar ratio

Equation 3 $NH_2OH + 3Fe^{3+} \longrightarrow 3Fe^{2+} + NO + 3H^+$

The student plans to carry out an investigation to determine which equation is correct.

The method is outlined below.

n V K C

Stage 1 Using a pipette, add 25.0 cm^3 of 4.32×10^{-2} mol dm^{-3} NH_2OH to a conical flask. Add 10 cm^3 of 1 mol dm^{-3} H_2SO_4 to the conical flask followed by an excess of a solution containing 0.0400 mol dm^{-3} $Fe^{3+}(aq)$.

Stage 2 Boil the mixture for 5 minutes and allow to cool.

Stage 3 Titrate the cooled mixture with 2.00×10^{-2} mol dm^{-3} $KMnO_4(aq)$.

(a) Determine the minimum volume of 0.0400 mol dm^{-3} $Fe^{3+}(aq)$ that the student should plan to use in **Stage 1**.

Explain your reasoning.

$4.32 \times 10^{-2} \times 25 \times 10^{-3} = 1.08 \times 10^{-3}$ mol of NH_2OH

$1.08 \times 10^{-3} \times 3 = 3.24 \times 10^{-3}$ mol of Fe^{3+}

$\frac{3.24 \times 10^{-3}}{0.04} \times 1000 = 81.0 cm^3$

volume = 81.0 cm^3

explanation: minimum amount of Fe^{3+} required is maximum amount theoretically required to react with all NH_2OH.

[4]

(b) In the student's titration, 21.6 cm^3 of $KMnO_4(aq)$ is required to reach the end point.

The equation that takes place during the titration is shown below.

1 : 5 molar ratio

$$MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$$

Analyse the student's results to determine which of the three equations is correct.

Show **all** your working.

$21.6 \times 10^{-3} \times 2 \times 10^{-2} = 4.32 \times 10^{-4}$ mol of MnO_4^-

$4.32 \times 10^{-4} \times 5 = 2.16 \times 10^{-3}$ mol of Fe^{2+}

$NH_2OH : Fe^{2+}$

1.08×10^{-3} mol

$1.08 \times 10^{-3} : 2.16 \times 10^{-3}$

1 : 2

equation 2 only equation with a 1 : 2 ratio of $NH_2OH : Fe^{2+}$

[3]

(c) The student intends to repeat the procedure to check their results.

There is insufficient time for the student to repeat all three stages and the student decides to omit **Stage 2**, the boiling stage. Unfortunately the resulting titre is much less than the original titre.

The student rejects the results from the repeated procedure.

(i) Suggest the purpose of the boiling in **Stage 2** and reasons for the second titre being much less than the original titre.

Boiling speeds up reaction so there is less Fe^{2+}

so second titre is less than the original

[2]

(ii) The main reason for insufficient time is the need to boil and cool the mixture for each titration.

Suggest how the procedure could be modified so that **Stage 2** does not need to be carried out repeatedly.

Give your reasoning.

In Stage 1, increase quantities so that there is sufficient solution for more than one titration [1]

END OF QUESTION PAPER