

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

Date – Morning/Afternoon

Version 2.0

Time allowed: 1 hour 30 minutes

You must have:

- the Data Sheet for Chemistry A

You may use:

- a scientific or graphical calculator



First name

Last name

StemUp Model Solution

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.
- Where appropriate, your answers should be supported with working. Marks may be given for a correct method even if the answer is incorrect.
- 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 **24** pages.

Answer **all** the questions.

1 Give chemical explanations for the following statements.

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

*Br₂ has more electrons, so stronger induced dipole-dipole interactions.....
(London forces) between molecules..... [1]*

(b) A carton of milk expands on freezing.

*In ice, hydrogen bonds hold the H₂O molecules further apart than in liquid.....
water (open lattice), so ice is less dense and takes up more space..... [1]*

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

*Potassium atoms have one more proton than argon atoms (atomic number.....
19 not 18); the table is in order of proton number..... [1]*

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

*Further substitution occurs, giving a mixture of products such as.....
1,1-dichloroethane and trichloroethanes, not just chloroethane..... [1]*

(e) Water has a concentration of approximately 56 mol dm⁻³.

*1 dm³ of water has a mass of 1000 g, so $n(\text{H}_2\text{O})$ in 1 dm³ = $1000 \div 18.0$
 $= 55.6 \approx 56$ mol, i.e. 56 mol dm⁻³..... [1]*

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

*The π bonds in benzene are delocalised; the π electrons are spread evenly.....
over all six carbon atoms of the ring..... [1]*

- (g) IR spectroscopy distinguishes ketones from carboxylic acids.

Carboxylic acids have a broad O-H absorption at 2500-3300 cm⁻¹ (as well as C=O), which ketones do not have. [1]

- (h) 1.323 g of N₂O(g) has a volume of 1.00 dm³ at 100 kPa and 400 K.

$n(\text{N}_2\text{O}) = 1.323 \div 44.0 = 0.0301 \text{ mol}$; $V = nRT/p = 0.0301 \times 8.314 \times 400 \div (100 \times 10^3) = 1.00 \times 10^{-3} \text{ m}^3 = 1.00 \text{ dm}^3$ [1]

- (i) 4.25 g of C₆H₅COOCH₃ contains 1.88×10^{22} molecules.

$M(\text{C}_6\text{H}_5\text{COOCH}_3) = 136 \text{ g mol}^{-1}$; number of molecules = $(4.25 \div 136) \times 6.02 \times 10^{23} = 1.88 \times 10^{22}$ [1]

- (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 (lower bond enthalpy), so it breaks more easily during hydrolysis. [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.

[6]

Use the first sample for the cation test and the second sample for the anion tests.

Cation test: add aqueous sodium hydroxide to sample 1, then warm gently.

Green precipitate means Fe^{2+} : $\text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe}(\text{OH})_2$

Pale pink/buff precipitate means Mn^{2+} : $\text{Mn}^{2+} + 2\text{OH}^- \rightarrow \text{Mn}(\text{OH})_2$

No precipitate, but on gentle warming a gas (ammonia) turns damp red litmus paper held over the opening of the tube blue, means NH_4^+ : $\text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_3 + \text{H}_2\text{O}$

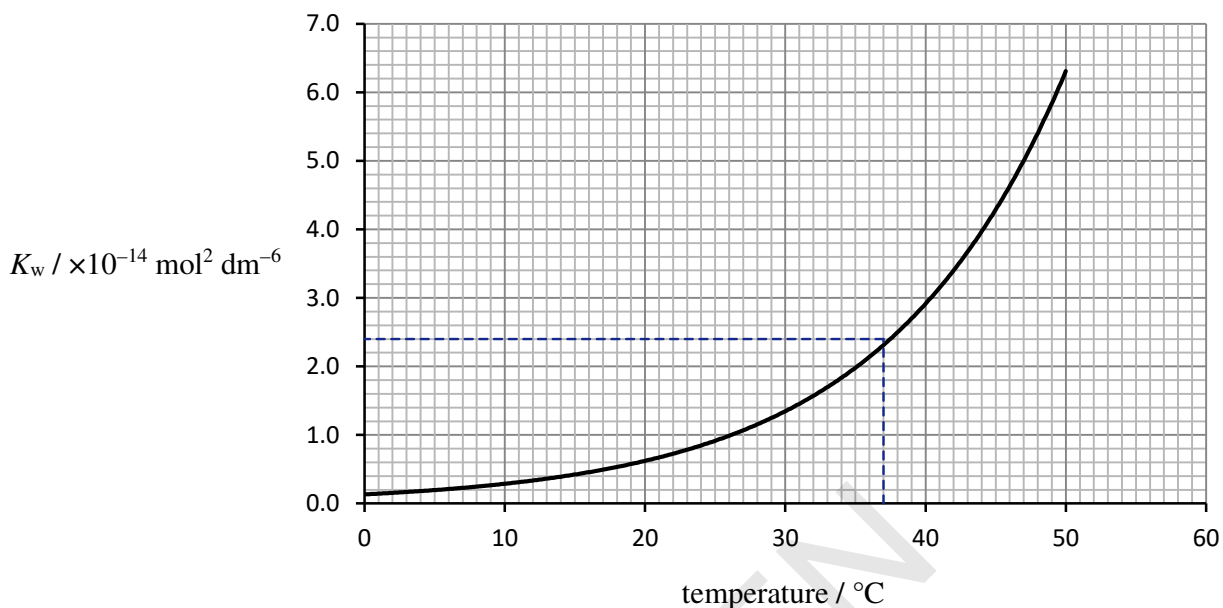
Anion tests on sample 2, in the order carbonate, then sulfate, then chloride.

This sequence is needed because carbonate would also give a white
 precipitate with Ba^{2+} (BaCO_3) and with Ag^+ (Ag_2CO_3), and sulfate can give
 a precipitate with Ag^+ (Ag_2SO_4), so these must be ruled out first.
 1. Add dilute nitric acid: effervescence (gas turns limewater milky) means
 CO_3^{2-} : $\text{CO}_3^{2-} + 2\text{H}^+ \rightarrow \text{CO}_2 + \text{H}_2\text{O}$
 2. If no effervescence, add aqueous barium nitrate: a white precipitate

Additional answer space if required.

means SO_4^{2-} : $\text{Ba}^{2+} + \text{SO}_4^{2-} \rightarrow \text{BaSO}_4$
 3. If no precipitate, add aqueous silver nitrate: a white precipitate means
 Cl^- : $\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl}$. Then add dilute aqueous ammonia: the precipitate
 dissolves, confirming chloride.
 Only one cation and one anion give a positive result, so the compound is
 identified, e.g. a green precipitate with NaOH and a white precipitate with
 $\text{Ba}(\text{NO}_3)_2$ means the compound is FeSO_4 .

- (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.

At 37 °C, from the graph $K_w = 2.4 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$

For pure water $[H^+] = [OH^-]$, so $K_w = [H^+]^2$

$[H^+] = \sqrt{(2.4 \times 10^{-14})} = 1.55 \times 10^{-7} \text{ mol dm}^{-3}$

$pH = -\log(1.55 \times 10^{-7}) = 6.81$

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.

$Co : N : H : Cl = 21.98/58.9 : 31.35/14.0 : 6.72/1.0 : 39.75/35.5$

$= 0.373 : 2.24 : 6.72 : 1.12$

$= 1 : 6 : 18 : 3$

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

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

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

..... $[\text{Co}(\text{NH}_3)_6]^{3+}$ [1]

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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.

(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]

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

..... 4 [1]

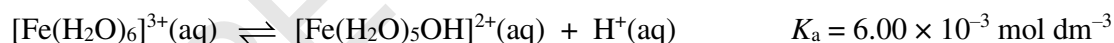
(b) $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ions take part in ligand substitution reactions.

An excess of aqueous potassium cyanide, $\text{KCN}(\text{aq})$, is added to an aqueous solution containing $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ 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.

..... $[\text{Fe}(\text{H}_2\text{O})_6]^{3+} + 6\text{CN}^- \rightarrow [\text{Fe}(\text{CN})_6]^{3-} + 6\text{H}_2\text{O}$ [2]

(c) The complex ion, $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, behaves as a weak Brønsted–Lowry acid in aqueous solution. The equation below represents the dissociation of aqueous $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ions, together with the K_a value.



(i) Write the expression for the acid dissociation constant, K_a , for $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$.

$$K_a = \frac{[[\text{Fe}(\text{H}_2\text{O})_5\text{OH}]^{2+}] [\text{H}^+]}{[[\text{Fe}(\text{H}_2\text{O})_6]^{3+}]} \quad [1]$$

(ii) Calculate the pH of a $0.100 \text{ mol dm}^{-3}$ solution of $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ to **two** decimal places.

$$[\text{H}^+] = \sqrt{K_a \times [\text{HA}]} = \sqrt{6.00 \times 10^{-3} \times 0.100} = 0.0245 \text{ mol dm}^{-3}$$

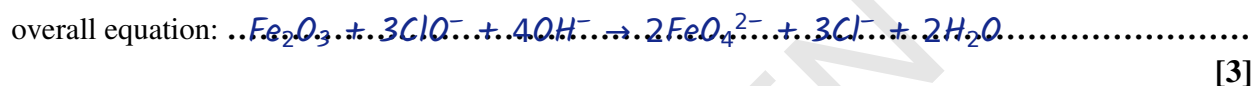
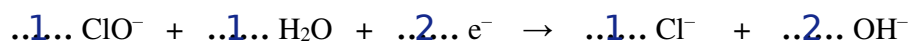
$$\text{pH} = -\log(0.0245) = 1.61$$

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.



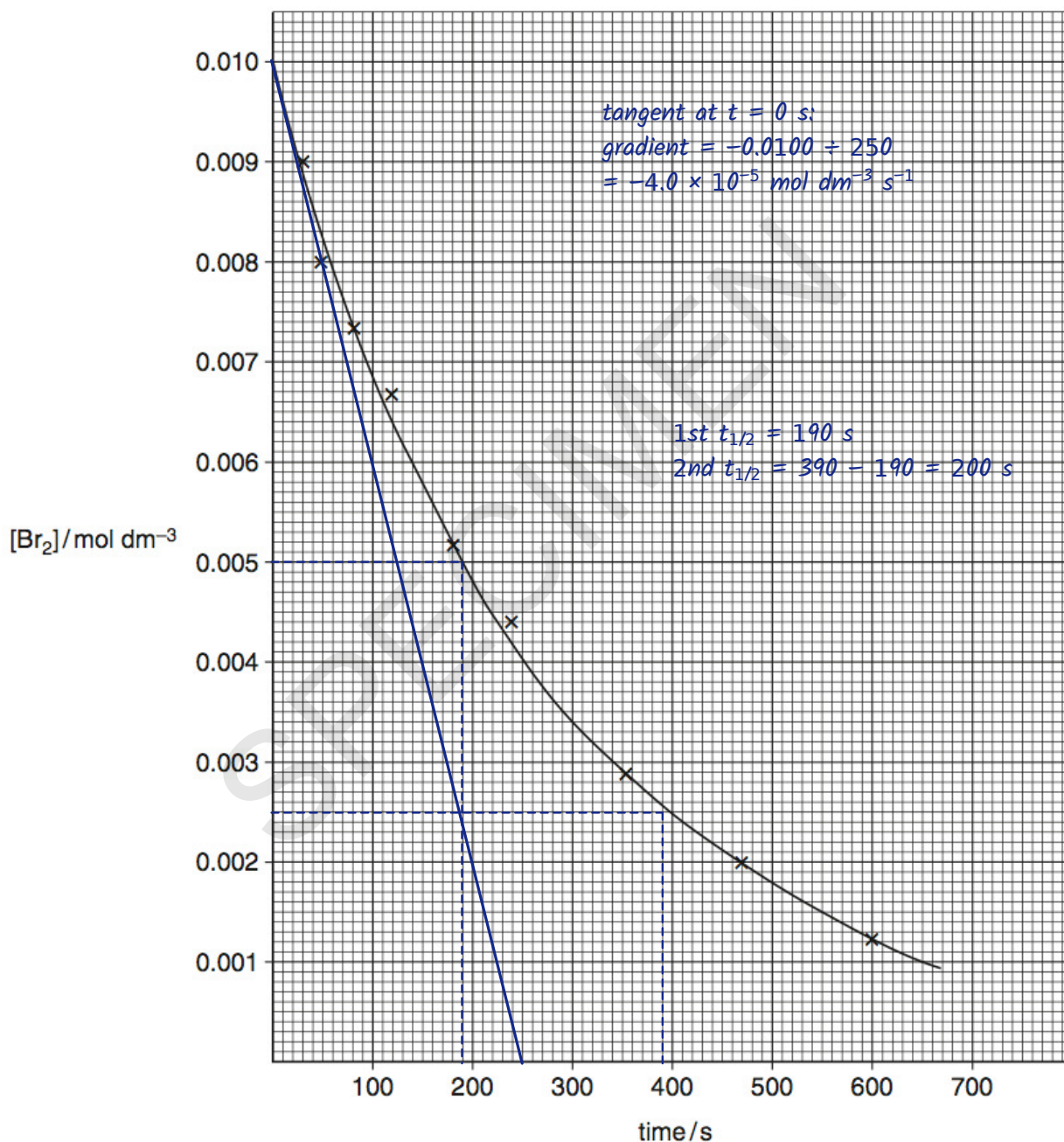
[3]

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



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.

..Use a colorimeter to measure the decrease in intensity of the orange/brown
..colour of bromine (absorbance) over time..... [1]

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

Measure the volume of CO_2 gas produced at regular time intervals, using a gas syringe. [1]

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

HCOOH is in such large excess that its concentration stays effectively constant, so it has no effect on the rate. [1]

- (d)* Using the graph, determine

- the initial rate of reaction
- the rate constant.

Your answer must show full working using the graph and the lines below as appropriate. [6]

Initial rate: I drew a tangent to the curve at $t = 0$ s (on the graph). It goes from $0.0100 \text{ mol dm}^{-3}$ at 0 s to 0 mol dm^{-3} at 250 s. gradient $= -0.0100 \div 250 = -4.0 \times 10^{-5}$, so initial rate $= 4.0 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$. Order: from the graph, $[\text{Br}_2]$ falls from 0.0100 to $0.0050 \text{ mol dm}^{-3}$ in 190 s, and from 0.0050 to $0.0025 \text{ mol dm}^{-3}$ in a further 200 s (190 s to 390 s). The half-life is constant (about 195 s, two values within 20 s), so the reaction is first order with respect to Br_2 . Rate equation: rate $= k[\text{Br}_2]$ (zero order in HCOOH , as it is in excess). Rate constant: $k = \text{initial rate} \div [\text{Br}_2] \text{ at } t = 0 = 4.0 \times 10^{-5} \div 0.0100 = 4.0 \times 10^{-3} \text{ s}^{-1}$. Check from half-life: $k = \ln 2 \div t_{1/2} = 0.693 \div 195 = 3.6 \times 10^{-3} \text{ s}^{-1}$, which agrees. So $k = 4.0 \times 10^{-3} \text{ s}^{-1}$.

Additional answer space if required.

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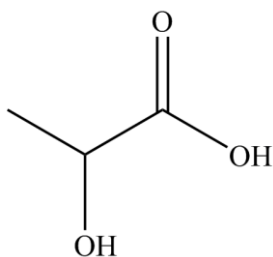
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5 This question is about organic acids.

(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.

$$M(\text{lactic acid, } C_3H_6O_3) = 90.0 \text{ g mol}^{-1}$$

$$n(\text{lactic acid}) = 1.125 \div 90.0 = 0.0125 \text{ mol}$$



$$n(H_2) = 0.0125 \div 2 = 6.25 \times 10^{-3} \text{ mol}$$

$$V = 6.25 \times 10^{-3} \times 24\,000 = 150 \text{ cm}^3$$

volume of H_2 = ...150.cm³..... [2]

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

A is $(CH_3CH(OH)COO)_2Mg$

.....C₆H₁₀O₆Mg..... [1]

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

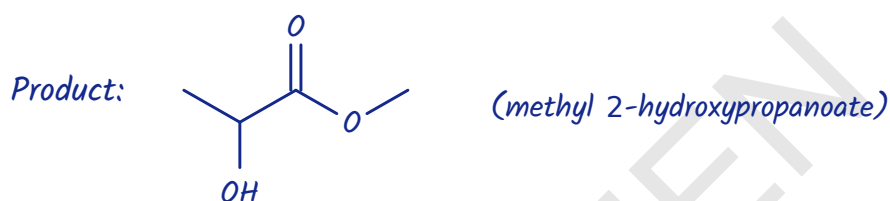
Do **not** include reactions with bases or metals.

For each reaction,

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

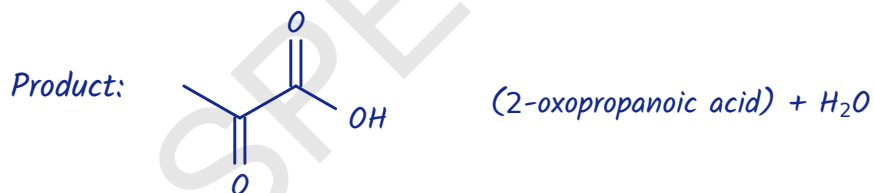
1. *COOH group: esterification*

Reagents/conditions: methanol, CH₃OH, with concentrated H₂SO₄ catalyst, heat under reflux



2. *secondary -OH group: oxidation*

Reagents/conditions: K₂Cr₂O₇ and dilute H₂SO₄ (acidified dichromate), heat under reflux

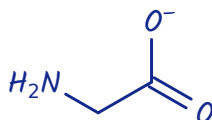


[4]

- (b) In basic conditions, α -amino acids form anions with the general formula, $\text{RCH}(\text{NH}_2)\text{COO}^-$. These anions can act as bidentate ligands.

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

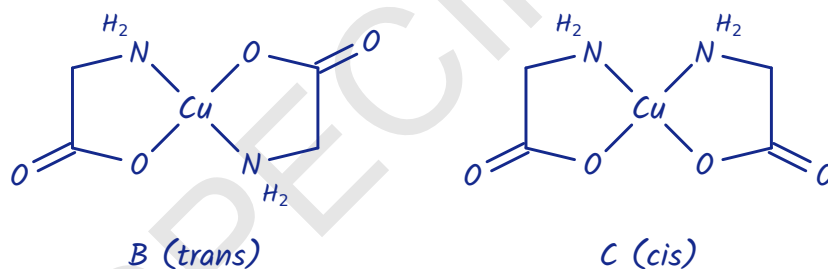
- (i) Draw the **skeletal** formula of the anion of glycine.



[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 ($\text{R} = \text{CH}_3$) would be expected to form more than two square planar stereoisomers with copper(II) ions.

Explain this statement.

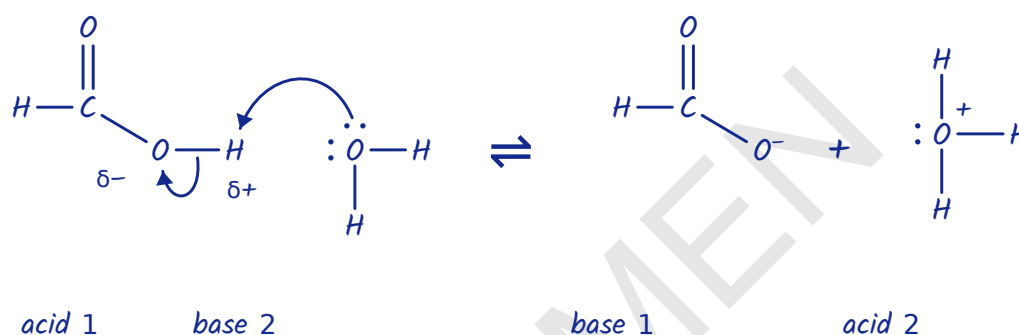
Alanine has a chiral C atom, so each ligand can be either optical isomer, giving extra stereoisomers on top of cis/trans.

[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.



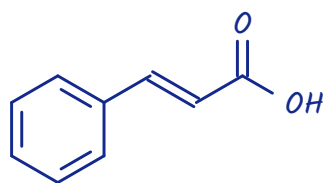
[2]

(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.



D: $C_6H_5CH=CHCOOH$ (3-phenylpropenoic acid), $C_9H_8O_2$

Electrophilic substitution means D contains a benzene ring; electrophilic addition means D contains an alkene $C=C$.

D is a monobasic acid with two O atoms, so it has one $COOH$ group.

$M_r = 148$: C_6H_5 (77) + $COOH$ (45) = 122, leaving 26 = C_2H_2 ($CH=CH$), so D is $C_9H_8O_2$ ($9 \times 12.0 + 8 \times 1.0 + 2 \times 16.0 = 148$).

^{13}C environments in $C_6H_5CH=CHCOOH$: $COOH$ (1), $CH=CH$ (2), ring C attached to the chain, ortho, meta and para C (4), total 7, matching the seven peaks.

[5]

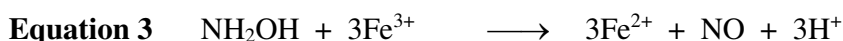
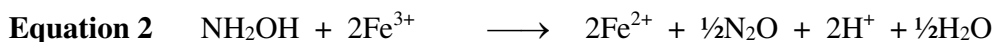
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6 Hydroxylamine, NH_2OH , is a strong reducing agent.

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.



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

The method is outlined below.

Stage 1 Using a pipette, add 25.0 cm^3 of $4.32 \times 10^{-2} \text{ mol dm}^{-3}$ 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 $0.0400 \text{ mol dm}^{-3}$ $\text{Fe}^{3+}(\text{aq})$.

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

Stage 3 Titrate the cooled mixture with $2.00 \times 10^{-2} \text{ mol dm}^{-3}$ $\text{KMnO}_4(\text{aq})$.

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

Explain your reasoning.

$$n(\text{NH}_2\text{OH}) = 4.32 \times 10^{-2} \times 25.0/1000 = 1.08 \times 10^{-3} \text{ mol}$$

Equation 3 needs the most Fe^{3+} (3 mol per mol NH_2OH):

$$n(\text{Fe}^{3+}) = 3 \times 1.08 \times 10^{-3} = 3.24 \times 10^{-3} \text{ mol}$$

$$\text{volume} = 3.24 \times 10^{-3} \times 1000 \div 0.0400 = 81.0 \text{ cm}^3$$

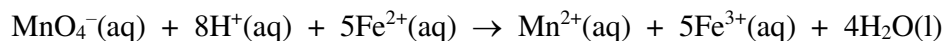
$$\text{volume} = \dots\dots\dots 81.0 \dots\dots\dots \text{ cm}^3$$

explanation: *..Fe³⁺ must be in excess whichever equation is correct, so the
..minimum volume is the maximum amount needed to react with all the
..NH₂OH, i.e. if Equation 3 is correct (greatest amount of Fe³⁺)*

[4]

- (b) In the student's titration, 21.6 cm^3 of $\text{KMnO}_4(\text{aq})$ is required to reach the end point.

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



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

$$n(\text{MnO}_4^-) = 2.00 \times 10^{-2} \times 21.6/1000 = 4.32 \times 10^{-4} \text{ mol}$$

$$n(\text{Fe}^{2+}) = 5 \times 4.32 \times 10^{-4} = 2.16 \times 10^{-3} \text{ mol}$$

$$\text{NH}_2\text{OH} : \text{Fe}^{2+} = 1.08 \times 10^{-3} : 2.16 \times 10^{-3} = 1 : 2$$

So 1 mol NH_2OH reduces 2 mol Fe^{3+} ; Equation 2 is correct.

[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 the reaction of NH_2OH with Fe^{3+} , ensuring the

reaction is complete

Without boiling the reaction is slow and incomplete, so less Fe^{2+} is

formed and less KMnO_4 is needed, so the titre is lower [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 the quantities (scale up, e.g. x5) and boil once, so.....
.there is enough solution for more than one titration; then titrate.....
.separate measured portions..... [1]

END OF QUESTION PAPER

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