



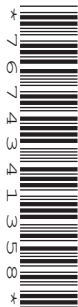
Oxford Cambridge and RSA

Wednesday 19 June 2019 – Morning

A Level Chemistry A

H432/03 Unified chemistry

Time allowed: 1 hour 30 minutes



You must have:

- the Data Sheet for Chemistry A
(sent with general stationery)

You may use:

- a scientific or graphical calculator



Please write clearly in black ink. **Do not write in the barcodes.**

Centre number

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Candidate number

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First name(s)

Last name

StemUp Model Solution

INSTRUCTIONS

- Use black ink. You may use an HB pencil for graphs and diagrams.
- 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. If additional space is required, use the lined page(s) at the end of this booklet. The question number(s) must be clearly shown.

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 These short questions are from different areas of chemistry.

(a) Explain why a CF_4 molecule has polar bonds but does **not** have an overall dipole.

*F is more electronegative than C, so each C-F bond is polar ($\text{C}^{\delta+}-\text{F}^{\delta-}$).
 CF_4 is tetrahedral (symmetrical), so the bond dipoles cancel: no overall dipole.* [2]

(b) Explain why a small proportion of molecules in water have a relative molecular mass of 20.

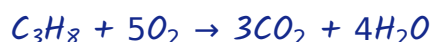
Some molecules contain heavier isotopes of H or O, e.g. ^2H (deuterium, D) or ^{18}O , which have more neutrons: D_2O has $M_r = (2 \times 2) + 16 = 20$. [1]

(c) What is the partial pressure of O_2 (in Pa) in a gas mixture containing 21% O_2 by volume and with a total pressure of $1.0 \times 10^5 \text{ Pa}$?

$$p(\text{O}_2) = 0.21 \times 1.0 \times 10^5$$

partial pressure of $\text{O}_2 = 2.1 \times 10^4 \text{ Pa}$ [1]

(d) What mass of carbon dioxide (in g) is formed by the complete combustion of 42.0 m^3 (measured at RTP) of propane?



$$n(\text{C}_3\text{H}_8) = 42.0 \times 10^3 \text{ dm}^3 \div 24.0 = 1750 \text{ mol}$$

$$\text{mass CO}_2 = 3 \times 1750 \times 44.0 = 231\,000 \text{ g}$$

mass = 231 000 g [2]

(e) A reaction is first order with respect to H^+ . At a pH of 1, the initial rate is $2.4 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$.

What is the initial rate at a pH of 3?

pH 1 $\rightarrow$ pH 3: $[\text{H}^+]$ falls from 10^{-1} to 10^{-3} , i.e. 100 times less

first order, so rate = $2.4 \times 10^{-3} \div 100$

initial rate = $2.4 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$ [1]

(f) What is the number of oxygen atoms in 4.26 g of P_2O_5 ?

$$n(P_2O_5) = 4.26 \div 142.0 = 0.0300 \text{ mol}$$

$$O \text{ atoms} = 5 \times 0.0300 \times 6.02 \times 10^{23}$$

number of oxygen atoms = 9.03×10^{22} [2]

- 2 Benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$, is added to some foods as a preservative.

A student prepares benzoic acid as outlined below.

Step 1 The student mixes 4.00 cm^3 of phenylmethanol, $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$, (density = 1.04 g cm^{-3}) with sodium carbonate and aqueous potassium manganate(VII), as an oxidising agent. The mixture is heated under reflux.

Step 2 The resulting mixture is cooled and then acidified with concentrated HCl . Impure crystals of benzoic acid appear.

Step 3 The student recrystallises the impure crystals to obtain 1.59 g of pure benzoic acid.

- (a) In **Step 1**, sodium carbonate, Na_2CO_3 , makes the reaction mixture alkaline.

Write an ionic equation to show how carbonate ions form an alkaline solution in water.



- (b) In **Step 2**, explain why the mixture must be acidified so that crystals of benzoic acid appear.

In the alkaline mixture the product is present as the soluble salt, benzoate ions ($\text{C}_6\text{H}_5\text{COO}^-$).

The acid protonates the benzoate ions: $\text{C}_6\text{H}_5\text{COO}^- + \text{H}^+ \rightarrow \text{C}_6\text{H}_5\text{COOH}$, forming benzoic acid, which is insoluble in cold water. [1]

- (c) Write the overall equation for the preparation of benzoic acid from phenylmethanol.

Use $[\text{O}]$ for the oxidising agent.



- (d) Calculate the percentage yield of benzoic acid.

Give your answer to **3** significant figures.

$$\text{mass of } \text{C}_6\text{H}_5\text{CH}_2\text{OH} = 4.00 \times 1.04 = 4.16 \text{ g}$$

$$\text{theoretical } n(\text{C}_6\text{H}_5\text{COOH}) = n(\text{C}_6\text{H}_5\text{CH}_2\text{OH}) = 4.16 \div 108.0 = 0.0385 \text{ mol}$$

$$\text{actual } n(\text{C}_6\text{H}_5\text{COOH}) = 1.59 \div 122.0 = 0.0130 \text{ mol}$$

$$\% \text{ yield} = (0.0130 \div 0.0385) \times 100$$

percentage yield = 33.8 % [3]

- (e) In **Step 3**, describe how the student can recrystallise the impure crystals to obtain pure benzoic acid.

Dissolve the impure crystals in the minimum volume of hot water (solvent).

Leave the solution to cool so that pure benzoic acid crystallises; the soluble impurities stay in solution.

Filter off the crystals under reduced pressure (Büchner funnel), wash with a little cold water and leave to dry.

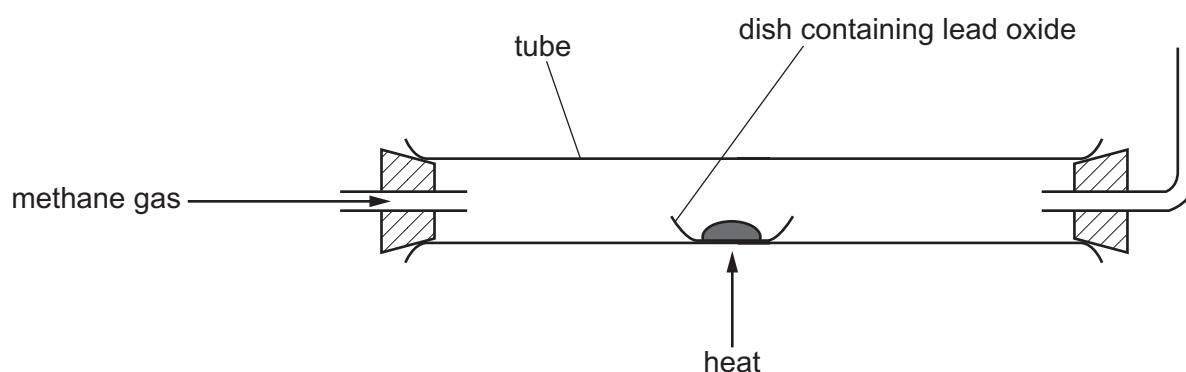
[2]

3 This question is about elements and compounds in Group 14 (Group 4) of the periodic table.

(a) There are four oxides of lead: PbO , PbO_2 , Pb_2O_3 and Pb_3O_4 .

A student carries out an experiment to identify an unknown lead oxide, which is one of the four oxides of lead shown above.

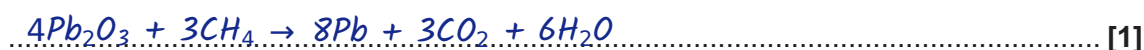
The student plans to reduce the unknown lead oxide to lead by heating the lead oxide in a stream of methane gas, CH_4 . The apparatus is shown below.



Student's method

- Weigh an empty dish.
Add the lead oxide to the dish and reweigh.
- Set up the apparatus and pass methane gas through the tube as shown.
Heat the dish for 10 minutes.
- Pass cold air through the tube to cool the dish and contents.
- Weigh the dish and contents.

(i) Write the equation for the reduction of Pb_2O_3 with CH_4 .



(ii) The student uses safety glasses and a lab coat.

State, with a reason, **one** other important safety precaution the student should take when carrying out this experiment.

Lead compounds (and the CO / gases produced) are toxic, so carry out the experiment in a fume cupboard.

[1]

- (iii) The student was not sure that all the oxygen had been removed from the lead oxide.

Suggest **two** modifications that the student could make to their method to be confident that all the oxygen had been removed. Explain your reasoning.

- 1 *Heat, cool and reweigh repeatedly until constant mass, to ensure all the lead oxide has reacted.*
- 2 *Cool the dish in a stream of methane (not cold air), so the hot lead cannot react with O₂ again.*

[2]

- (iv) The student makes suitable modifications to the method and repeats the experiment to obtain the accurate results shown below.

Mass of dish/g	8.364
Mass of dish + lead oxide/g	11.818
Mass of dish + lead at end of experiment/g	11.496

Calculate the empirical formula of the lead oxide.

$$\text{mass Pb} = 11.496 - 8.364 = 3.132 \text{ g}$$

$$\text{mass O} = 11.818 - 11.496 = 0.322 \text{ g}$$

$$\text{Pb} : \text{O} = 3.132 \div 207.2 : 0.322 \div 16.0$$

$$= 0.0151 : 0.0201 = 1 : 1.33 = 3 : 4$$

empirical formula = *Pb₃O₄* [2]

- (b) SiO₂ and CO₂ are oxides of other Group 14 (Group 4) elements.

Solid SiO₂ melts at 2156 °C. Solid CO₂ melts at -56 °C.

Suggest the type of lattice structure in solid SiO₂ and in solid CO₂ and explain the difference in melting points in terms of the types of force within each lattice structure.

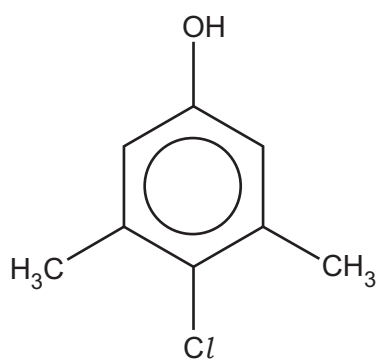
Structure in SiO₂(s) *giant covalent (lattice)*

Structure in CO₂(s) *simple molecular (lattice)*

Explanation *SiO₂: strong covalent bonds are broken. CO₂: weak London forces (induced dipole-dipole) between molecules are overcome. Covalent bonds in SiO₂ are stronger than intermolecular forces in CO₂, so more energy is needed.*

[4]

- 4 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-dimethylphenol [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 *Add universal indicator / pH paper; it turns orange-red (pH < 7),*

but there is no effervescence with Na_2CO_3 (it is too weak an acid to

react with carbonate). [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 cm³ 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.



$$K_a = [H^+][C_8H_8ClO^-] \div [C_8H_9ClO] \approx [H^+]^2 \div [C_8H_9ClO]$$

$$M(C_8H_9ClO) = 156.5 \text{ g mol}^{-1}$$

$$4.80 \text{ g per } 100 \text{ cm}^3 = 48.0 \text{ g dm}^{-3}$$

$$[C_8H_9ClO] = 48.0 \div 156.5 = 0.3067 \text{ mol dm}^{-3}$$

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

$$K_a = (7.244 \times 10^{-6})^2 \div 0.3067$$

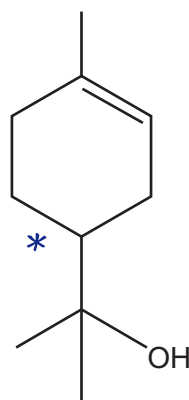
$$= 1.71 \times 10^{-10} \text{ mol dm}^{-3}$$

$$K_a = 1.71 \times 10^{-10} \text{ mol dm}^{-3} \text{ [5]}$$

(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]

(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.

It has a $C=C$ double bond, and each carbon of the $C=C$ is attached to two different groups (CH_3 and ring C ; H and ring C).
By CIP priority rules, the higher priority group on each C of the $C=C$ is the ring carbon. Both are on the same side, so it is the *Z* isomer.
The *E* isomer cannot exist; the ring carbons would be on opposite sides of the $C=C$, so the ring would be too strained to form; the ring locks the groups on one side.

[4]

(iii) α -Terpineol contains two functional groups.

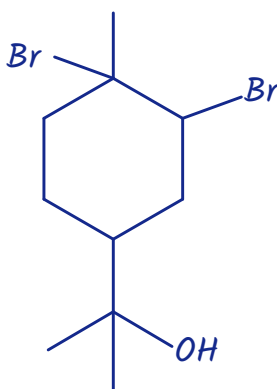
For each functional group, choose a reagent that reacts with that group **only**.
Draw the structures for the organic products of the reactions.

Show structures for organic compounds.

Reagent(s) *Br₂ (bromine, at room temperature)*

Name of functional group that reacts *alkene*

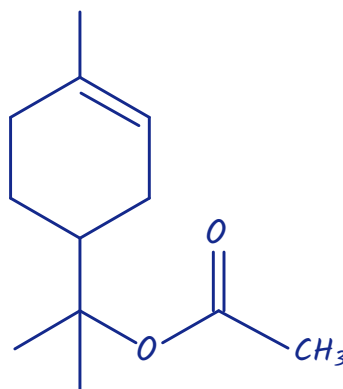
Structure of organic product



Reagent(s) *CH₃COCl (ethanoyl chloride)*

Name of functional group that reacts *(tertiary) alcohol*

Structure of organic product



[4]

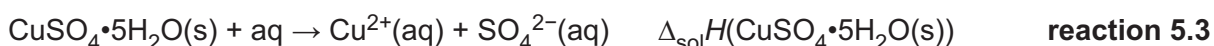
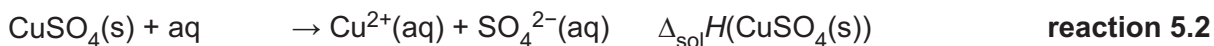
5 This question is about copper(II) sulfate, CuSO_4 , and sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$.

- (a) The enthalpy change of reaction, $\Delta_r H$, for converting anhydrous copper(II) sulfate to hydrated copper(II) sulfate is difficult to measure directly by experiment.



The enthalpy changes of solution of anhydrous and hydrated copper(II) sulfate can be measured by experiment. The reactions are shown below.

In the equations, 'aq' represents an excess of water.



Experiment 1

A student carries out an experiment to find $\Delta_{\text{sol}} H(\text{CuSO}_4(\text{s}))$ for **reaction 5.2**.

Student's method

- Weigh a bottle containing $\text{CuSO}_4(\text{s})$ and weigh a polystyrene cup.
- Add about 50 cm^3 of water to the polystyrene cup and measure its temperature.
- Add the $\text{CuSO}_4(\text{s})$, stir the mixture, and measure the final temperature.
- Weigh the empty bottle and weigh the polystyrene cup with final solution.

Mass readings

Mass of bottle + $\text{CuSO}_4(\text{s})/\text{g}$	28.04
Mass of empty bottle/g	20.06
Mass of polystyrene cup/g	23.43
Mass of polystyrene cup + final solution/g	74.13

Temperature readings

Initial temperature of water/ $^{\circ}\text{C}$	20.5
Temperature of final solution/ $^{\circ}\text{C}$	34.0

Experiment 2

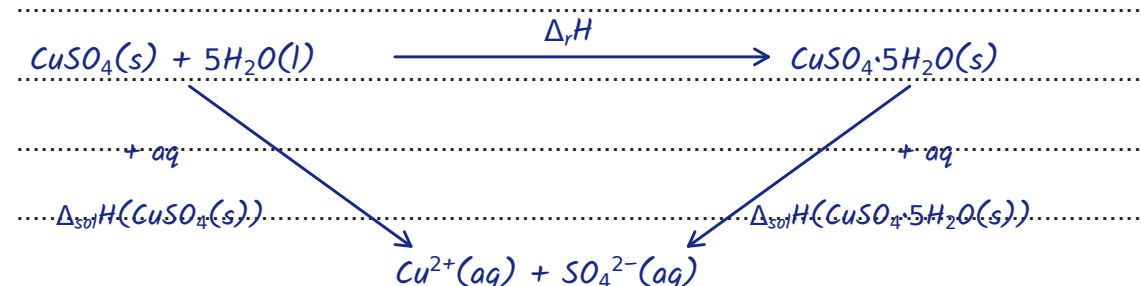
The student carries out a second experiment with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (**reaction 5.3**). The student uses the same method as in **Experiment 1**.

The student calculates $\Delta_{\text{sol}} H(\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s}))$ as $+8.43\text{ kJ mol}^{-1}$.

- (i)* Calculate $\Delta_{\text{sol}}H(\text{CuSO}_4(\text{s}))$ for **reaction 5.2** and determine the enthalpy change of **reaction 5.1**, Δ_rH .

Assume that the specific heat capacity, c , of the solution is the same as for water.

Show your working, including an energy cycle linking the enthalpy changes. [6]



$$\text{Mass of solution} = 74.13 - 23.43 = 50.70 \text{ g}; \Delta T = 34.0 - 20.5 = 13.5 \text{ }^\circ\text{C}$$

$$\text{Energy change } q = mc\Delta T = 50.70 \times 4.18 \times 13.5 = 2861 \text{ J} = 2.861 \text{ kJ}$$

$$\text{Mass of CuSO}_4 = 28.04 - 20.06 = 7.98 \text{ g, so } n(\text{CuSO}_4) = 7.98 \div 159.6 = 0.0500 \text{ mol}$$

The temperature rises, so reaction 5.2 is exothermic (negative sign):

$$\Delta_{\text{sol}}H(\text{CuSO}_4(\text{s})) = -2.861 \div 0.0500 = -57.22 \text{ kJ mol}^{-1}$$

$$\text{Hess' law, from the energy cycle: } \Delta_{\text{sol}}H(\text{CuSO}_4(\text{s})) = \Delta_rH + \Delta_{\text{sol}}H(\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s}))$$

Additional answer space if required

$$\Delta_rH = \Delta_{\text{sol}}H(\text{CuSO}_4(\text{s})) - \Delta_{\text{sol}}H(\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s})) = -57.22 - (+8.43)$$

$$\Delta_rH = -65.65 \text{ kJ mol}^{-1}$$

- (ii) The thermometer had an uncertainty in each temperature reading of $\pm 0.1^\circ\text{C}$.

The student calculates a 20% uncertainty in the temperature change in **Experiment 2**.

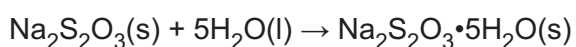
Calculate the temperature change in **Experiment 2**.

$$\text{uncertainty in } \Delta T = 2 \times 0.1 = \pm 0.2^\circ\text{C (two readings)}$$

$$\Delta T = 0.2 \div 0.20 = 1.0^\circ\text{C}$$

$$\text{temperature change} = \underline{1.0}^\circ\text{C [1]}$$

- (b) The standard enthalpy change of reaction, $\Delta_r H^\ominus$, and the standard free energy change, $\Delta G^\ominus$, for converting anhydrous sodium thiosulfate to hydrated sodium thiosulfate are shown below.



$$\Delta_r H^\ominus = -55.8 \text{ kJ mol}^{-1}$$

$$\Delta G^\ominus = -16.1 \text{ kJ mol}^{-1}$$

Standard entropies are given in the table.

Compound	$S^\ominus / \text{J K}^{-1} \text{ mol}^{-1}$
$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}(\text{s})$	372.4
$\text{H}_2\text{O}(\text{l})$	69.9

Determine the **standard** entropy, $S^\ominus$, of anhydrous sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3(\text{s})$.

Give your answer to **3** significant figures.

$$\Delta G = \Delta_r H - T\Delta S, \text{ with } T = 298 \text{ K}$$

$$-16.1 = -55.8 - 298\Delta S$$

$$\Delta S = (-55.8 + 16.1) \div 298 = -0.1332 \text{ kJ K}^{-1} \text{ mol}^{-1} = -133.2 \text{ J K}^{-1} \text{ mol}^{-1}$$

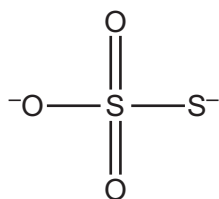
$$\Delta S = S(\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}) - [S(\text{Na}_2\text{S}_2\text{O}_3) + 5 \times 69.9]$$

$$-133.2 = 372.4 - 349.5 - S(\text{Na}_2\text{S}_2\text{O}_3)$$

$$S(\text{Na}_2\text{S}_2\text{O}_3) = 22.9 + 133.2 = 156.1$$

$$S^\ominus = \underline{+156} \text{ J K}^{-1} \text{ mol}^{-1} \text{ [4]}$$

- (c) Sodium thiosulfate contains the thiosulfate ion, $\text{S}_2\text{O}_3^{2-}$.
The displayed formula of $\text{S}_2\text{O}_3^{2-}$ can be shown as below.



thiosulfate ion

- (i) Predict the O–S–S bond angle and name of the shape of the thiosulfate ion.

Bond angle 109.5°

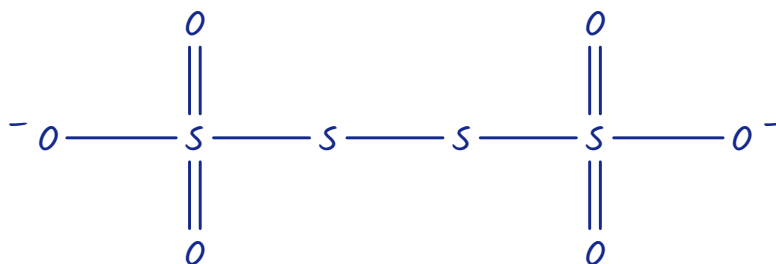
Name of shape tetrahedral

[1]

- (ii) In some of its reactions, the thiosulfate ion forms the tetrathionate ion, $\text{S}_4\text{O}_6^{2-}$.

The $\text{S}_4\text{O}_6^{2-}$ ion is a 'dimer' of $\text{S}_2\text{O}_3^{2-}$.

Draw a displayed formula for the $\text{S}_4\text{O}_6^{2-}$ ion.

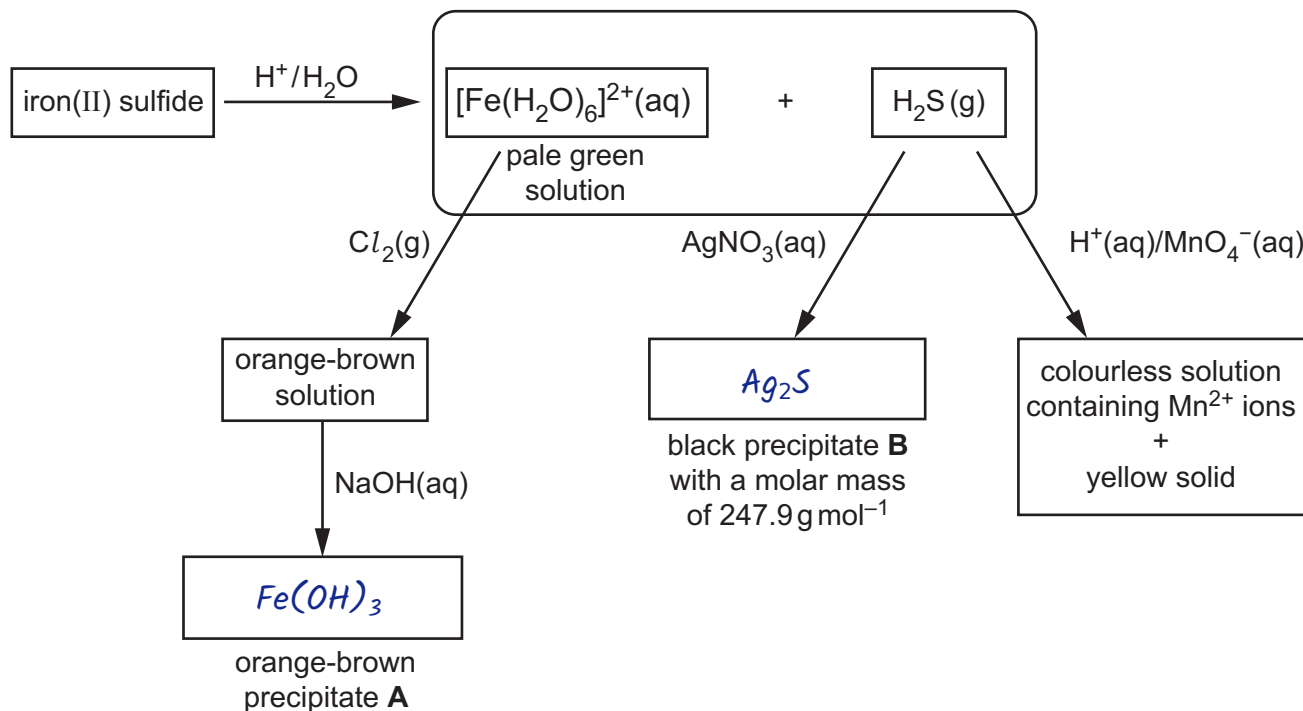


[1]

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6 This question is about reactions of iron compounds.

(a) A student carries out the reactions in the flowchart, starting with iron(II) sulfide.



(i) In the boxes, write the formulae of **A** and **B**. [2]

(ii) The student thinks that the reaction of iron(II) sulfide with $\text{H}^+/\text{H}_2\text{O}$ is a redox reaction.

Explain, with reasons, whether the student is correct.

The student is incorrect. Fe stays at +2 (FeS and $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$) and S stays at -2 (FeS and H_2S): no oxidation numbers change, so it is not redox.

..... [1]

(iii) Write the equation for the reaction of $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$ with $\text{Cl}_2(\text{g})$.

$2[\text{Fe}(\text{H}_2\text{O})_6]^{2+} + \text{Cl}_2 \rightarrow 2[\text{Fe}(\text{H}_2\text{O})_6]^{3+} + 2\text{Cl}^-$ [1]

(iv) Construct an equation for the reaction of $\text{H}_2\text{S}(\text{g})$ with $\text{H}^+(\text{aq})/\text{MnO}_4^-(\text{aq})$.

$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}; \quad \text{H}_2\text{S} \rightarrow \text{S} + 2\text{H}^+ + 2\text{e}^-$

$5\text{H}_2\text{S} + 2\text{MnO}_4^- + 6\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 5\text{S} + 8\text{H}_2\text{O}$

(b)* Compound **C** is a hydrated ionic compound with the empirical formula: $\text{FeH}_{18}\text{N}_3\text{O}_{18}$.

A student investigates the thermal decomposition of compound **C** as outlined below.

Stage 1

The student gently heats 0.00300 mol of compound **C** to remove the water of crystallisation. 0.486 g of water is collected, leaving 0.00300 mol of the anhydrous compound **D**.

Stage 2

The student strongly heats 0.00300 mol of compound **D**, which decomposes to form a solid oxide **E** (molar mass of 159.6 g mol^{-1}) and 270 cm^3 of a gas mixture, measured at RTP, containing gases **F** and **G**.

Stage 3

The student cools the 270 cm^3 gas mixture of **F** and **G**.

- Gas **F** is a compound that condenses to form 0.414 g of a liquid.
- Gas **G** remains and has a volume of 54 cm^3 , measured at RTP.
Gas **G** is tested and it relights a glowing splint.

Determine the formulae of **C**, **D**, **E**, **F** and **G**.

Show all your working and equations for the reactions.

[6]

Stage 1: $n(\text{H}_2\text{O}) = 0.486 \div 18.0 = 0.0270 \text{ mol}$; $0.0270 \div 0.00300 = 9$, so

C contains $9\text{H}_2\text{O}$.

$\text{FeH}_{18}\text{N}_3\text{O}_{18} - 9\text{H}_2\text{O} = \text{FeN}_3\text{O}_9$, so **D** is $\text{Fe}(\text{NO}_3)_3$ and **C** is $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$.

$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} \rightarrow \text{Fe}(\text{NO}_3)_3 + 9\text{H}_2\text{O}$

Stage 2: $M(\text{Fe}_2\text{O}_3) = (2 \times 55.8) + (3 \times 16.0) = 159.6 \text{ g mol}^{-1}$, so **E** is

Fe_2O_3 .

Stage 3: **G** relights a glowing splint, so **G** is O_2 ; $n(\text{O}_2) = 54 \div 24\,000 =$

0.00225 mol .

$n(\text{F}) = (270 - 54) \div 24\,000 = 216 \div 24\,000 = 0.00900 \text{ mol}$

$M(\text{F}) = 0.414 \div 0.00900 = 46.0 \text{ g mol}^{-1}$, so **F** is NO_2 ($14.0 + 32.0 = 46.0$).

$n(\text{D}) : n(\text{NO}_2) : n(\text{O}_2) = 0.00300 : 0.00900 : 0.00225 = 4 : 12 : 3$, so:

$4\text{Fe}(\text{NO}_3)_3 \rightarrow 2\text{Fe}_2\text{O}_3 + 12\text{NO}_2 + 3\text{O}_2$

C = $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, **D** = $\text{Fe}(\text{NO}_3)_3$, **E** = Fe_2O_3 , **F** = NO_2 , **G** = O_2

Additional answer space if required.

END OF QUESTION PAPER

This image shows a blank sheet of white paper designed for writing. It features a series of evenly spaced horizontal blue lines across its entire width. A single vertical blue line runs down the left side, creating a narrow margin. The paper is otherwise completely empty, with no text or markings.

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