



Oxford Cambridge and RSA

Friday 21 June 2024 – Morning

A Level Chemistry A

H432/03 Unified chemistry

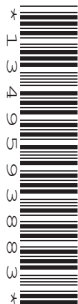
Time allowed: 1 hour 30 minutes

You must have:

- the Data Sheet for Chemistry A

You can use:

- a scientific or graphical calculator
- an HB pencil



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)

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Last name

StemUp Model Solution

INSTRUCTIONS

- Use black ink. You can use an HB pencil, but only for graphs and diagrams.
- Write your answer to each question in the space provided. If you need extra space use the lined pages at the end of this booklet. The question numbers must be clearly shown.
- Answer **all** the questions.
- Where appropriate, your answer should be supported with working. Marks might be given for using a correct method, even if your answer is wrong.

INFORMATION

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

ADVICE

- Read each question carefully before you start your answer.

1 This question is about acids, bases and salts.

(a) What is the pH of 1.00 dm^3 of $0.400 \text{ mol dm}^{-3}$ of NaOH(aq) at 298 K ?

$$[H^+] = K_w \div [OH^-] = 1.00 \times 10^{-14} \div 0.400$$

$$[H^+] = 2.50 \times 10^{-14} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log(2.50 \times 10^{-14}) = 13.60$$

$$\text{pH} = \dots 13.60 \dots [2]$$

(b) Water is added to 10.0 cm^3 of $0.750 \text{ mol dm}^{-3}$ HCl(aq) to produce 100 cm^3 of diluted HCl(aq) .

What is the pH of the diluted HCl(aq) ?

Give your answer to 2 decimal places.

$$[\text{HCl}] = 0.750 \times 10.0 \div 100 = 0.0750 \text{ mol dm}^{-3}$$

$$\text{pH} = -\log 0.0750 = 1.12$$

$$\text{pH} = \dots 1.12 \dots [1]$$

(c) A solution has concentrations of $0.300 \text{ mol dm}^{-3}$ $\text{CH}_3\text{COOH(aq)}$ and $0.100 \text{ mol dm}^{-3}$ $\text{CH}_3\text{COONa(aq)}$.

K_a for $\text{CH}_3\text{COOH} = 1.75 \times 10^{-5} \text{ mol dm}^{-3}$ at 298 K .

What is the pH of the solution at 298 K ?

Give your answer to 2 decimal places.

$$[H^+] = K_a \times [\text{CH}_3\text{COOH}] \div [\text{CH}_3\text{COO}^-]$$

$$[H^+] = 1.75 \times 10^{-5} \times 0.300 \div 0.100 = 5.25 \times 10^{-5} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log(5.25 \times 10^{-5}) = 4.28$$

$$\text{pH} = \dots 4.28 \dots [2]$$

- (d) A student is provided with hydrated copper(II) nitrate, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$.

The student needs to prepare a standard solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ with a concentration of $0.200 \text{ mol dm}^{-3}$. The student has access to usual laboratory apparatus and equipment.

Describe how the student would prepare 100.0 cm^3 of this solution, giving quantities, apparatus and method.

$$\text{Amount needed} = 0.200 \times 100.0 \div 1000 = 2.00 \times 10^{-2} \text{ mol}$$

$$M_r \text{ of } \text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O} = 63.5 + 2(14.0 + 48.0) + 3(18.0) = 241.5$$

$$\text{Mass needed} = 2.00 \times 10^{-2} \times 241.5 = 4.83 \text{ g}$$

Weigh out 4.83 g of the solid accurately into a weighing bottle using a 2 d.p.

balance, tip it into a beaker and reweigh the bottle to find the exact mass

transferred.

Dissolve the solid in a small volume of distilled water (about 50 cm^3 , less than

100 cm^3) in the beaker, stirring with a glass rod.

Transfer the solution to a 100.0 cm^3 volumetric flask using a funnel. Rinse the

beaker, glass rod and funnel with distilled water and add all the washings to the

flask.

Make up to the mark with distilled water, adding the last drops with a dropping

pipette so the bottom of the meniscus sits on the line.

Stopper the flask and invert it several times to mix thoroughly.

[5]

2 This question is about different areas of chemistry.

- (a) Hydrogen gas is manufactured by the chemical industry from the reversible reaction of methane and steam, shown below.



Average bond enthalpies are shown in the table.

Bond	H–H	O–H	C≡O
Average bond enthalpy / kJ mol^{-1}	+436	+464	+1077

- (i) Why do all average bond enthalpies have a positive value?

Bonds are being broken, and breaking a bond is endothermic; energy is always needed to break a bond. [1]

- (ii) Determine the C–H bond enthalpy, in kJ mol^{-1} , using the information above.

$$\text{bonds broken: } 4(\text{C}-\text{H}) + 2(\text{O}-\text{H}) = 4(\text{C}-\text{H}) + 2 \times 464 = 4(\text{C}-\text{H}) + 928$$

$$\text{bonds made: } 3(\text{H}-\text{H}) + 1(\text{C}\equiv\text{O}) = 3 \times 436 + 1077 = 2385 \text{ kJ}$$

$$\Delta H = \text{bonds broken} - \text{bonds made: } +195 = 4(\text{C}-\text{H}) + 928 - 2385$$

$$4(\text{C}-\text{H}) = 195 + 2385 - 928 = 1652 \text{ kJ}$$

$$\text{C}-\text{H} = 1652 \div 4 = +413 \text{ kJ mol}^{-1}$$

$$\text{C}-\text{H bond enthalpy} = \dots\dots\dots +413 \dots\dots\dots \text{ kJ mol}^{-1} \quad [3]$$

- (iii) Hydrogen gas is being considered as a household fuel to replace methane.

The enthalpy change of formation, $\Delta_f H$, for $\text{H}_2\text{O}(\text{l})$ is $-285.8 \text{ kJ mol}^{-1}$.

Determine the energy released when 60.0 m^3 of hydrogen is used as a household fuel at RTP.

Give your answer to 3 significant figures and in **standard form**.

$$n(\text{H}_2) = 60.0 \times 10^3 \text{ dm}^3 \div 24.0 \text{ dm}^3 \text{ mol}^{-1} = 2500 \text{ mol}$$

$$\text{energy released} = 2500 \times 285.8 = 714\,500 \text{ kJ}$$

$$\text{energy released} = \dots\dots\dots 7.15 \times 10^5 \dots\dots\dots \text{ kJ} \quad [2]$$

(b) Compound **A** is a chloride of a Period 3 element.

A student carries out the 2 steps below to find the formula of compound **A**.

Step 1 The student adds 5.00×10^{-4} mol of compound **A** to water.
A colourless solution is formed.

Step 2 The colourless solution reacts with exactly 60.0 cm^3 of $2.50 \times 10^{-2} \text{ mol dm}^{-3}$ $\text{AgNO}_3(\text{aq})$ to form a white precipitate.

(i) Write an ionic equation, with state symbols, for the reaction in **Step 2**.

$\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})$ [1]

(ii) Determine the formula of compound **A**.

$$n(\text{AgNO}_3) = 2.50 \times 10^{-2} \times 60.0 \div 1000 = 1.50 \times 10^{-3} \text{ mol}$$

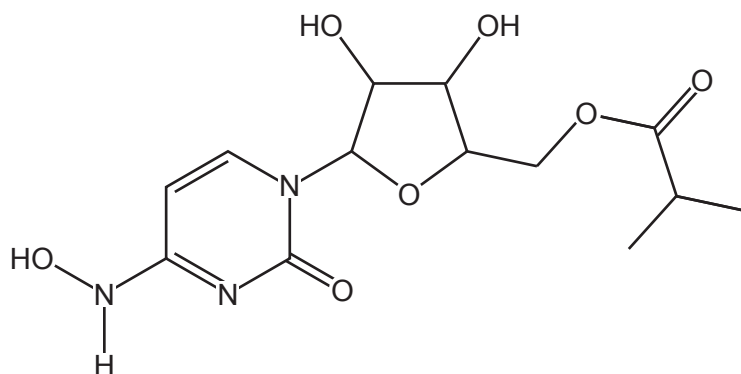
$$\text{so } n(\text{Cl}^-) \text{ released} = 1.50 \times 10^{-3} \text{ mol}$$

$$\text{ratio } A : \text{Cl} = 5.00 \times 10^{-4} : 1.50 \times 10^{-3} = 1 : 3$$

so **A** is XCl_3 ; the Period 3 element is aluminium

formula of **A** = ... AlCl_3 [3]

(c) Compound **B**, shown below, is an antiviral medicine.



compound B

(i) What is the molecular formula of compound **B**?

$C_{13}H_{19}N_3O_7$ [1]

(ii) How many chiral carbon atoms are there in one molecule of compound **B**?

4 [1]

(iii) A research chemist synthesises two related compounds, compound **C** and compound **D**, from compound **B**.

- In compound **C**, the N atoms in compound **B** had been replaced by P atoms.
- In compound **D**, the O atoms in compound **B** had been replaced by S atoms.

What is the difference between the relative molecular masses of compound **C** and compound **D**?

$$M_r \text{ of B, } C_{13}H_{19}N_3O_7 = 156.0 + 19.0 + 42.0 + 112.0 = 329.0$$

$$C, C_{13}H_{19}P_3O_7: M_r = 329.0 - 3(14.0) + 3(31.0) = 380.0$$

$$D, C_{13}H_{19}N_3S_7: M_r = 329.0 - 7(16.0) + 7(32.1) = 441.7$$

$$\text{difference} = 441.7 - 380.0 = 61.7$$

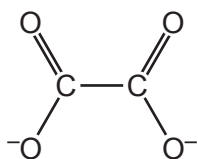
difference = ...61.7..... [2]

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Turn over for the next question

- 3 This question is about compounds and ions of iron(II) and iron(III) that contain ethanedioate ions, $\text{C}_2\text{O}_4^{2-}$.

(a) The $\text{C}_2\text{O}_4^{2-}$ ion, shown below, is an example of a bidentate ligand.



(i) Explain what is meant by the term **bidentate ligand**.

*A ligand that has two lone pairs of electrons (here on two O^- atoms),
so it forms two dative (coordinate) bonds to the central metal ion.*

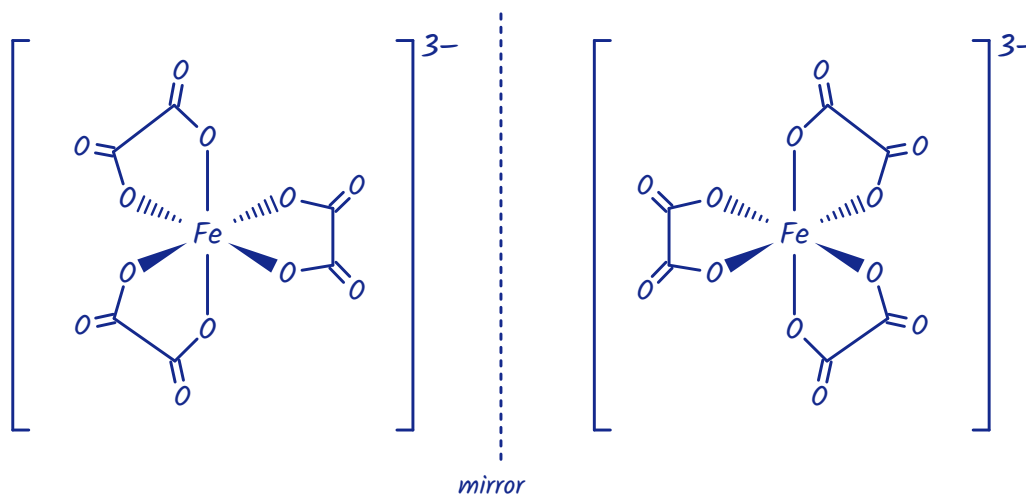
[2]

(ii) A complex ion **E** contains three $\text{C}_2\text{O}_4^{2-}$ ions bonded to an iron(III) ion in an octahedral shape.

Complex ion **E** exists as a mixture of two optical isomers.

Draw 3D diagrams to show the structures of the optical isomers of **E**.

Include any overall charge.



[3]

- (b) A student plans an investigation to find the number of waters of crystallisation, x , in a sample of hydrated iron(II) ethanedioate, $\text{FeC}_2\text{O}_4 \cdot x\text{H}_2\text{O}$.

The student decides to carry out a redox titration between solutions of iron(II) ethanedioate and potassium manganate(VII) in acidic conditions.

- (i) In the titration, both iron(II) ions and ethanedioate, $\text{C}_2\text{O}_4^{2-}$, ions are oxidised.

Construct half-equations for the oxidation of iron(II) and ethanedioate ions.

Oxidation of iron(II) ions



Oxidation of ethanedioate ions



[2]

- (ii) The student prepares a 250.0 cm^3 solution of iron(II) ethanedioate by dissolving 1.295 g of $\text{FeC}_2\text{O}_4 \cdot x\text{H}_2\text{O}$, in dilute sulfuric acid.

The student titrates 25.0 cm^3 samples of this solution with $0.0200\text{ mol dm}^{-3}$ KMnO_4 in the burette. The student carries out a trial, followed by three further titrations.

The diagrams show the initial burette readings and the final burette readings for the student's three further titrations.

Titration 1		Titration 2		Titration 3	
Initial reading	Final reading	Initial reading	Final reading	Initial reading	Final reading
					

All burette readings are measured to the nearest 0.05 cm^3 .

Complete the titration table.

	1	2	3
Final reading/ cm^3	23.55	45.40	22.75
Initial reading/ cm^3	1.90	23.55	1.20
Titre/ cm^3	21.65	21.85	21.55

[3]

- (iii) The uncertainty in each burette reading is $\pm 0.05\text{ cm}^3$.

Calculate the percentage uncertainty for the titre in **Titration 1**.

$$\% \text{ uncertainty} = (2 \times 0.05) \div 21.65 \times 100 = 0.46\%$$

percentage uncertainty = ...0.46..... % [1]

(iv)* In the titration, 5 mol of iron(II) ethanedioate reacts with 3 mol of manganate(VII) ions.

Analyse the student's results to find the number of waters of crystallisation, x , in the hydrated iron(II) ethanedioate, $\text{FeC}_2\text{O}_4 \cdot x\text{H}_2\text{O}$.

[6]

..Titres 1 and 3 (21.65 and 21.55 cm^3) are concordant, within 0.10 cm^3 . Titre 2

..(21.85 cm^3) is not concordant, so it is left out.

..Mean titre = $(21.65 + 21.55) \div 2 = 21.60 \text{ cm}^3$

.. $n(\text{MnO}_4^-) = 0.0200 \times 21.60 \div 1000 = 4.32 \times 10^{-4} \text{ mol}$

..5 mol FeC_2O_4 react with 3 mol MnO_4^- , so $n(\text{FeC}_2\text{O}_4)$ in 25.0 $\text{cm}^3 = 4.32 \times$

.. $10^{-4} \times 5/3 = 7.20 \times 10^{-4} \text{ mol}$

.. $n(\text{FeC}_2\text{O}_4)$ in 250.0 $\text{cm}^3 = 7.20 \times 10^{-4} \times 10 = 7.20 \times 10^{-3} \text{ mol}$

..Molar mass of $\text{FeC}_2\text{O}_4 \cdot x\text{H}_2\text{O} = 1.295 \div 7.20 \times 10^{-3} = 179.9 \text{ g mol}^{-1}$

..Molar mass of $\text{FeC}_2\text{O}_4 = 55.8 + 2(12.0) + 4(16.0) = 143.8 \text{ g mol}^{-1}$

..Mass of $x\text{H}_2\text{O}$ in 1 mol = $179.9 - 143.8 = 36.1 \text{ g}$

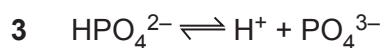
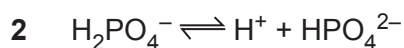
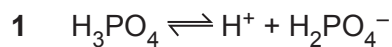
.. $x = 36.1 \div 18.0 = 2.0$, so $x = 2$ and the formula is $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$

Extra answer space if required.

4 This question is about the chemistry of compounds containing phosphorus.

(a) Phosphorus forms several acids including H_3PO_4 and H_3PO_3 .

H_3PO_4 is a tribasic acid. The equilibria for the dissociations are shown below.



(i) During the equilibria, H_2PO_4^- behaves both as an acid and as a base.

Explain this statement, using the equilibria 1, 2 and 3, as required.

In equilibrium 1 (reverse reaction), H_2PO_4^- acts as a base: it accepts a proton (H^+) to form H_3PO_4 .

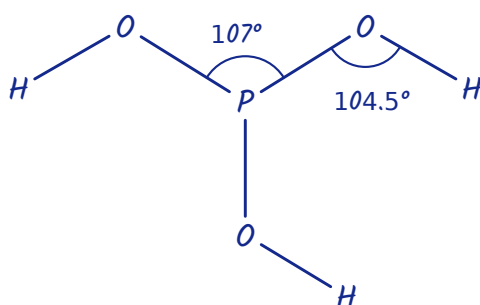
In equilibrium 2, H_2PO_4^- acts as an acid: it donates a proton (H^+) to form HPO_4^{2-} .

[2]

(ii) In a H_3PO_3 molecule, the O atoms are covalently bonded to the P atom. The H atoms are bonded to the O atoms.

Draw the structure of a H_3PO_3 molecule, showing all the bonds.

On your diagram, add the values for the O–P–O and P–O–H bond angles.



$$\text{O}-\text{P}-\text{O} = 107^\circ$$

$$\text{P}-\text{O}-\text{H} = 104.5^\circ$$

[3]

(iii) The systematic name of H_3PO_4 is phosphoric(V) acid.

What is the systematic name of H_3PO_3 ?

phosphoric(III) acid

[1]

(b) Phosphine, PH_3 , is a poisonous gas.

(i) Phosphine reacts with oxygen gas to form phosphorus(V) oxide and water.

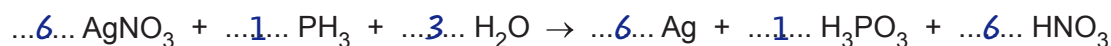
Write the equation for this reaction.



(ii) Aqueous silver nitrate, AgNO_3 , is reduced by PH_3 .

The unbalanced equation is shown below.

Balance the equation and use oxidation numbers to explain why this is a redox reaction.



Explanation *Ag is reduced: its oxidation number decreases from +1 in AgNO_3 to 0 in Ag.*.....

P is oxidised: its oxidation number increases from -3 in PH_3 to +3 in H_3PO_3

Oxidation and reduction take place at the same time, so it is a redox reaction......

..... [3]

- (c) When phosphorus(V) chloride, PCl_5 , and ammonium chloride are heated together, the compound $\text{P}_3\text{N}_3\text{Cl}_6$ is formed, together with HCl gas.

$\text{P}_3\text{N}_3\text{Cl}_6$ has a cyclic structure, like the Kekulé structure of benzene.

- (i) Write an equation for the reaction of PCl_5 and ammonium chloride to form $\text{P}_3\text{N}_3\text{Cl}_6$.



- (ii) Calculate the percentage by mass of P in $\text{P}_3\text{N}_3\text{Cl}_6$.

Give your answer to 2 decimal places.

$$M_r \text{ of } \text{P}_3\text{N}_3\text{Cl}_6 = 3(31.0) + 3(14.0) + 6(35.5) = 348.0$$

$$\% \text{ P} = 3(31.0) \div 348.0 \times 100 = 93.0 \div 348.0 \times 100 = 26.72\%$$

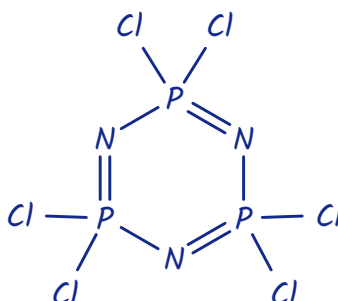
percentage by mass of P = 26.72% [2]

- (iii) Suggest **one** example of evidence that could show that $\text{P}_3\text{N}_3\text{Cl}_6$ has a Kekulé structure rather than a delocalised structure.

The P-N bond lengths would be different: shorter P=N double bonds alternating with longer P-N single bonds (a delocalised ring would have all P-N bonds the same length). [1]

- (iv) In a molecule of $\text{P}_3\text{N}_3\text{Cl}_6$ all the N and Cl atoms are bonded to P atoms.

Suggest a possible structure for a molecule of $\text{P}_3\text{N}_3\text{Cl}_6$.



[2]

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5 This question is about the analysis of organic compounds.

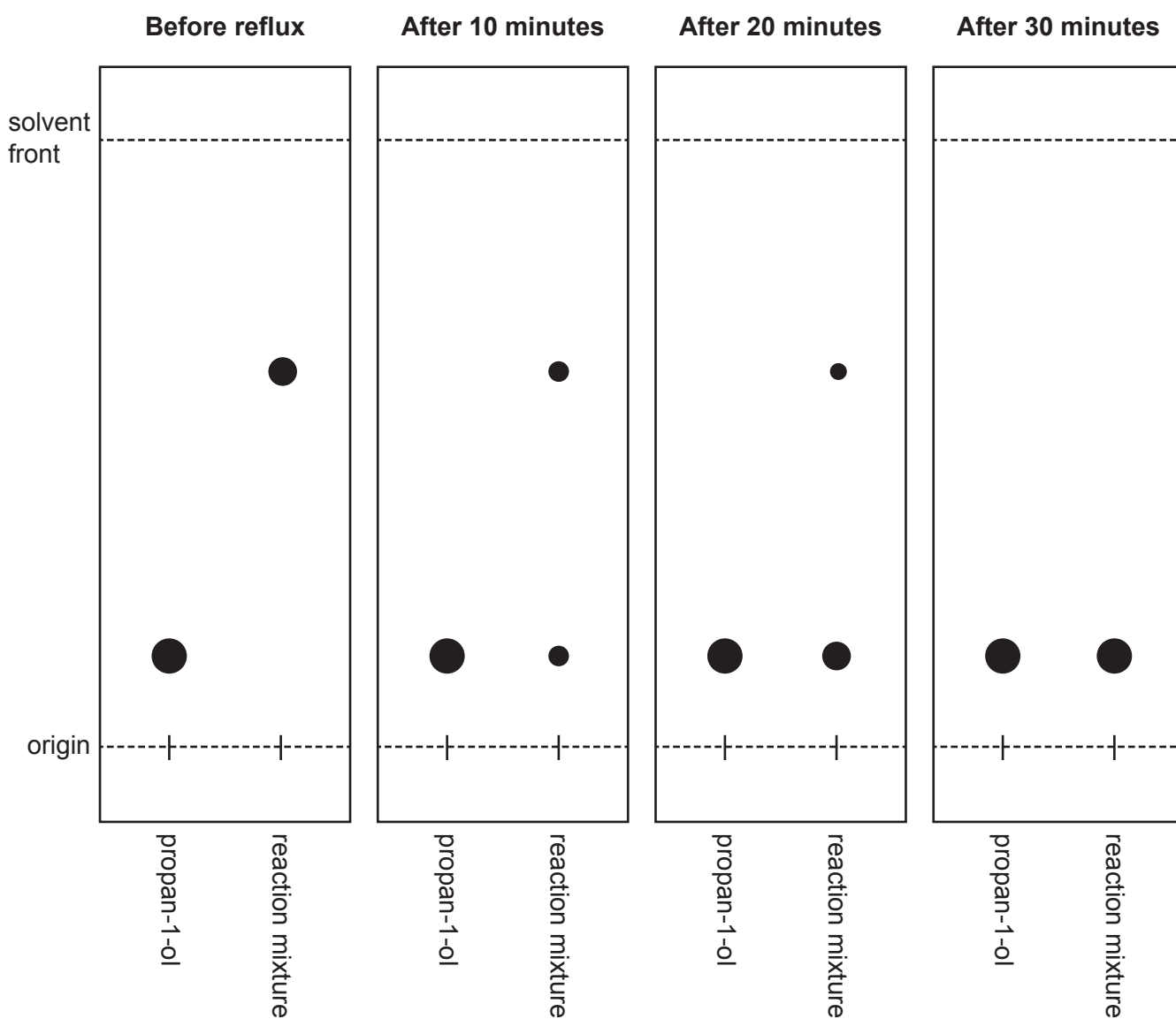
(a) A student investigates the alkaline hydrolysis of 1-bromopropane as outlined below.

Step 1 The student adds 1-bromopropane to an excess of aqueous potassium hydroxide, KOH(aq), in a pear-shaped flask.

Step 2 A TLC chromatogram is run using propan-1-ol and the reaction mixture.

Step 3 The reaction mixture is refluxed.
A TLC chromatogram of the reaction mixture is run every 10 minutes.

The TLC chromatograms are shown below.



- (i) Determine the R_f value of propan-1-ol.

Show your working.

distance moved by propan-1-ol = 1.4 cm

distance moved by solvent front = 9.1 cm

$$R_f = 1.4 \div 9.1 = 0.15$$

$$R_f = \dots 0.15 \dots [1]$$

- (ii) Write an equation for the alkaline hydrolysis of 1-bromopropane.

Show structures of organic compounds.



[1]

- (iii) A student investigates the alkaline hydrolysis of 1-chloropropane using the same method as for 1-bromopropane.

Predict, with reasons, how the appearance of the reaction mixture in the chromatogram produced after 20 minutes would be different when 1-chloropropane is used instead of 1-bromopropane.

Suggest why propan-1-ol is run alongside the reaction mixture.

After 20 minutes the propan-1-ol (lower, product) spot of the reaction mixture would be smaller and the 1-chloropropane (upper, reactant) spot would be bigger. This is because the C-Cl bond is stronger than the C-Br bond (higher bond enthalpy), so 1-chloropropane reacts more slowly (it is less reactive). Propan-1-ol is run alongside to show that the product spot is propan-1-ol, so it monitors the progress of the reaction and shows when the reaction has finished.

[3]

(b) Compounds **F**, **G**, **H** and **I** are structural isomers.

A student carries out test-tube tests on the compounds.
The student records the observations after carrying out each test.
These are shown in **Table 5.1**.

In **Table 5.1**, 2,4-dinitrophenylhydrazine has been abbreviated to 2,4-DNP.

Table 5.1

Compound	Test			
	2,4-DNP	Acidified dichromate(VI) reflux	Bromine water	Tollens' reagent
F	Orange solution	Green solution	Colourless solution	Colourless solution
G	Orange solution	Green solution	Orange solution	Colourless solution
H	Orange precipitate	Orange solution	Orange solution	Colourless solution
I	Orange precipitate	Green solution	Orange solution	Silver mirror

(i) Write the formula of the species causing the colours after refluxing with acidified dichromate(VI).

Green solution... Cr^{3+}

Orange solution... $\text{Cr}_2\text{O}_7^{2-}$

[2]

(ii)* The student is provided with further information about compounds **F–I**.

- They all have the molecular formula $C_5H_{10}O$.
- One of the compounds is alicyclic.
- The other compounds are unbranched.

Use this further information and the student's observations in **Table 5.1** to answer the following.

- How do the observations provide evidence for the possible functional groups in compounds **F–I**?
- Suggest a possible structure for each of the compounds **F–I**.

Show your reasoning.

[6]

2,4-DNP: H and I give an orange precipitate, so H and I have a carbonyl group

(aldehyde or ketone); F and G do not.

Dichromate: F, G and I turn it from orange to green ($Cr_2O_7^{2-}$ reduced to Cr^{3+}),

so they are oxidised: primary or secondary alcohols or an aldehyde. H is not oxidised, so H is a ketone.

Bromine water: only F decolourises it, so F has a $C=C$ bond; G, H and I are saturated.

Tollens': only I gives a silver mirror, so I is an aldehyde.

$C_5H_{10}O$ has one $C=C$, $C=O$ or ring. F is an unbranched unsaturated primary

alcohol, pent-4-en-1-ol. G is a saturated secondary alcohol, so its ring makes it

the alicyclic compound: cyclopentanol. H is the ketone pentan-2-one and I is the aldehyde pentanal (structures below).

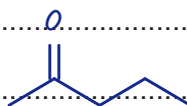
F:



G:



H:



I:



Extra answer space if required.

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