Oxford Cambridge and RSA

Thursday 23 June 2022 – 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 | | | | | | Candidate number | | | | |

First name(s) _____

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.

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Answer **all** the questions.

1 These questions are from different areas of chemistry.

(a) Ammonia, NH_3, and ammonium nitrate, NH_4NO_3, are compounds of nitrogen.

(i) The boiling point of NH_3 is –33 °C.

The boiling point of NH_4NO_3 is 210 °C.

Explain why there is a large difference in boiling points.

NH_3 is simple molecular (simple covalent); only weak intermolecular forces (hydrogen bonds) have to be broken between the molecules. NH_4NO_3 is ionic, made of NH_4^+ and NO_3^- ions. Ionic bonds are much stronger than intermolecular forces, so much more energy is needed to break them, giving a much higher boiling point.

[2]

(ii) Two students discuss the oxidation numbers in ammonium nitrate, NH_4NO_3.

One student claims that the two nitrogen atoms have the same oxidation number. The other student disagrees and claims that the nitrogen atoms have different oxidation numbers.

Explain with reasons which student is correct.

The second student is correct. In NH_4^+ the nitrogen has an oxidation number of −3, but in NO_3^- the nitrogen has an oxidation number of +5, so they are different.

[1]

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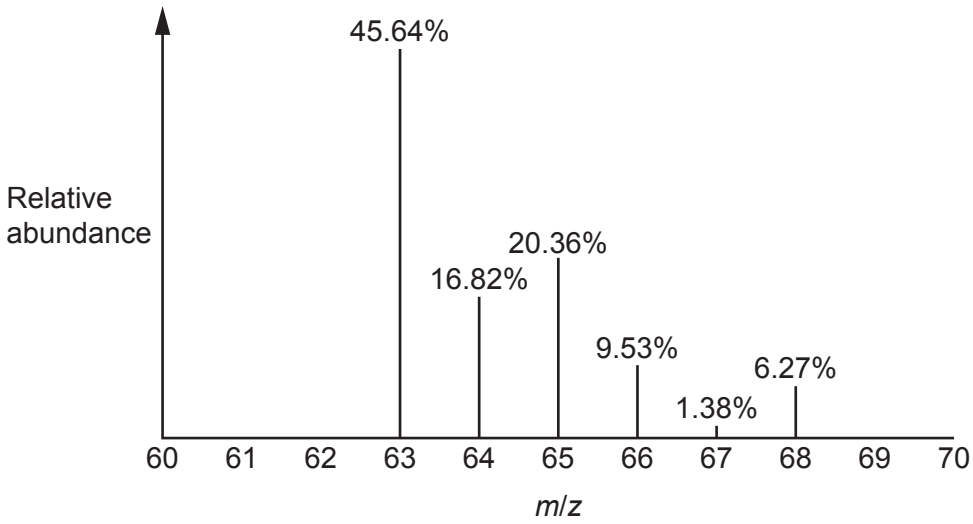
(b) Brass is an alloy of copper and zinc.

The mass spectrum of a sample of brass is shown below.



The peaks at m/z = 63 and m/z = 65 are from the ^{63}Cu and ^{65}Cu isotopes of copper.

The remaining four peaks are from isotopes of zinc.

(i) What are the percentage compositions of copper and zinc in the brass sample?

Cu = ...66..... % Zn = ...34..... % **[1]**

(ii) Calculate the relative atomic mass of zinc in the sample of brass.

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

Zn: total abundance = 16.82 + 9.53 + 1.38 + 6.27 = 34

(64 × 16.82) + (66 × 9.53) + (67 × 1.38) + (68 × 6.27) = 2224.28

A_r(Zn) = 2224.28 ÷ 34 = 65.42

relative atomic mass = ...65.42..... **[2]**

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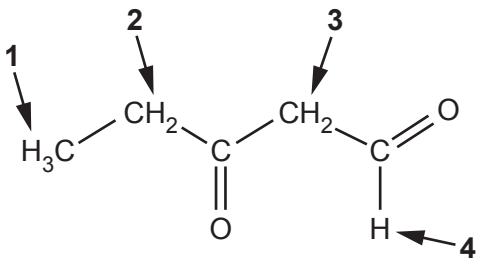
(c) The structure of an organic compound is shown below.

The protons are in four different environments, which are labelled **1**–**4**.



(i) Fill in the table to predict the splitting patterns in the **proton** NMR spectrum of the organic compound.

Proton environment	Splitting pattern
1	*triplet*
2	*quartet*
3	*doublet*
4	*triplet*

[2]

(ii) The table shows the chemical shifts for the peaks in the **proton** NMR spectrum at proton environments **2** and **3**.

Proton environment	**2**	**3**
Chemical shift, δ	2.5 ppm	3.6 ppm

Suggest why the peaks for proton environments **2** and **3** have the chemical shifts which are shown in the table.

Environment 2: the CH_2 protons are adjacent to one C=O group (H–C–C=O), which deshields them, giving 2.5 ppm.

Environment 3: the CH_2 protons are between two C=O groups (the ketone C=O and the aldehyde C=O on both sides), so they are deshielded more, giving a higher shift of 3.6 ppm. **[2]**

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(d) Glycine, H_2NCH_2COOH, is an α-amino acid.

(i) Glycine reacts with NaOH to form the salt H_2NCH_2COONa.

Glycine reacts with HCl to form the salt $HOOCCH_2NH_3Cl$.

The salts have different H–N–H bond angles.

State the different H–N–H bond angles and explain why they are different.

H_2NCH_2COONa H–N–H bond angle = ...107.....°

$HOOCCH_2NH_3Cl$ H–N–H bond angle = ...109.5.....°

explanation In H_2NCH_2COONa the N of NH_2 has 3 bonded pairs and 1 lone pair; the lone pair repels more, so 107°.

In $HOOCCH_2NH_3Cl$ the N of NH_3^+ has 4 bonded pairs and no lone pair, so 109.5°.

..... **[3]**

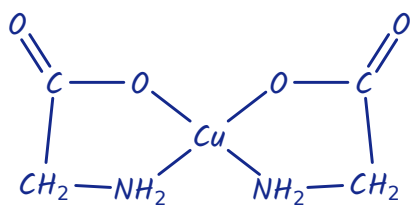
(ii) Glycine reacts with aqueous copper(II) ethanoate to form copper(II) glycinate, $Cu(H_2NCH_2COO)_2$, and ethanoic acid. Copper(II) glycinate is a complex which exists as two square planar isomers.

Write an equation for this reaction and draw the structures of the two square planar isomers of the complex $Cu(H_2NCH_2COO)_2$.

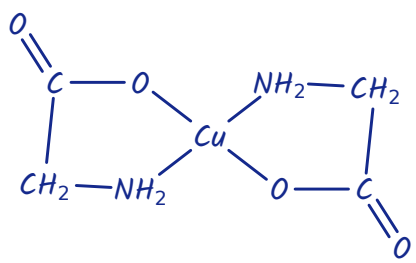
equation

$2H_2NCH_2COOH + Cu(CH_3COO)_2 \rightarrow Cu(H_2NCH_2COO)_2 + 2CH_3COOH$

structures



cis isomer



trans isomer

[3]

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2 This question is about redox reactions.

(a) 'Calcium hypochlorite', $Ca(ClO)_2$, is an ionic compound used in 'bleaching powder'.

The ClO^- ion in $Ca(ClO)_2$ is the active ingredient that kills bacteria.

Calcium hypochlorite is prepared by reacting chlorine gas with calcium hydroxide.

$$2Cl_2(g) + 2Ca(OH)_2(s) \rightarrow Ca(ClO)_2(s) + CaCl_2(s) + 2H_2O(l)$$ **Equation 2.1**

(i) 420 dm^3 of chlorine, measured at RTP, is reacted with an excess of $Ca(OH)_2$.

The solid products are dissolved in water to form 4.00 m^3 of solution.

Calculate the concentration of $Ca(ClO)_2(aq)$ in this solution, in mol dm^{-3}.

Give your answer to an **appropriate** number of significant figures and in standard form.

$n(Cl_2) = 420 \div 24.0 = 17.5$ mol

$n(Ca(ClO)_2) = 17.5 \div 2 = 8.75$ mol

$4.00\ m^3 = 4000\ dm^3$, so $c = 8.75 \div 4000 = 0.0021875$

(3 s.f.)

concentration = 2.19×10^{-3} mol dm^{-3} **[3]**

(ii) Calcium hypochlorite, $Ca(ClO)_2$, is heated. The $Ca(ClO)_2$ decomposes to form $CaCl_2$ and $Ca(ClO_3)_2$. This is a disproportionation reaction.

Write an equation for this decomposition and explain, using oxidation numbers, why this is a disproportionation reaction.

equation $3Ca(ClO)_2 \rightarrow 2CaCl_2 + Ca(ClO_3)_2$

explanation Chlorine is both reduced and oxidised in the same reaction:

Cl is reduced from +1 in ClO^- to −1 in $CaCl_2$.

Cl is oxidised from +1 in ClO^- to +5 in ClO_3^-.

[3]

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(b) A student analyses the redox reactions shown below. State symbols have been omitted.

$CH_3CHO + 2H^+ + 2e^- \rightleftharpoons C_2H_5OH$ $E^\ominus = -0.197\,V$

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$ $E^\ominus = +1.33\,V$

$FeO_4^{2-} + 8H^+ + 3e^- \rightleftharpoons Fe^{3+} + 4H_2O$ $E^\ominus = +2.20\,V$

The student concludes that different ions containing chromium can act as oxidising or reducing agents.

Using the terms oxidising agent and reducing agent, and ideas about electrode potentials and equilibrium, explain how the student is correct.

Include overall equations.

$Cr_2O_7^{2-}$ is an oxidising agent with C_2H_5OH (it oxidises C_2H_5OH): $E^\ominus$ for $Cr_2O_7^{2-}/Cr^{3+}$ (+1.33 V) is more positive than for CH_3CHO/C_2H_5OH (−0.197 V), so the $Cr_2O_7^{2-}/Cr^{3+}$ equilibrium shifts right and the CH_3CHO/C_2H_5OH equilibrium shifts left. E_{cell} = 1.527 V.

$Cr_2O_7^{2-} + 8H^+ + 3C_2H_5OH \rightarrow 2Cr^{3+} + 7H_2O + 3CH_3CHO$

Cr^{3+} is a reducing agent with FeO_4^{2-} (it reduces FeO_4^{2-}): $E^\ominus$ for $Cr_2O_7^{2-}/Cr^{3+}$ is less positive than for FeO_4^{2-}/Fe^{3+} (+2.20 V), so the $Cr_2O_7^{2-}/Cr^{3+}$ equilibrium shifts left and the FeO_4^{2-}/Fe^{3+} equilibrium shifts right. E_{cell} = 0.87 V.

$2Cr^{3+} + 2H^+ + 2FeO_4^{2-} \rightarrow Cr_2O_7^{2-} + H_2O + 2Fe^{3+}$

[5]

(c) A student bubbles hydrogen sulfide gas, $H_2S(g)$, through an acidified solution containing manganate(VII) ions, $MnO_4^-(aq)$.

A redox reaction takes place, forming aqueous manganese(II) ions, a yellow precipitate and one other product.

Construct the equation for this reaction. State symbols are not required.

$5H_2S + 2MnO_4^- + 6H^+ \rightarrow 2Mn^{2+} + 5S + 8H_2O$ **[2]**

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3 Information about 1-bromobutane and butan-1-ol is shown in the table.

Compound	Melting point / °C	Boiling point / °C	Density / g cm^{-3}
1-bromobutane	–113	102	1.268
butan-1-ol	–90	118	0.810

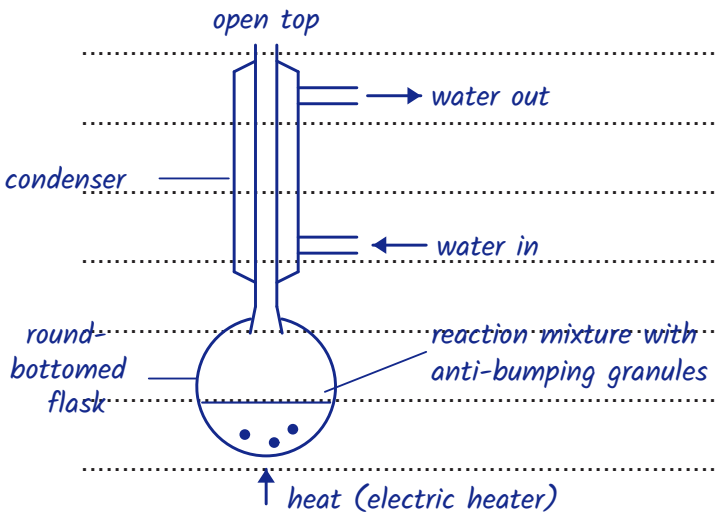
A student prepares a sample of 1-bromobutane by refluxing 9.25 g of butan-1-ol with sodium bromide and sulfuric acid.

After reflux, the reaction mixture is purified.

The student obtains 6.10 cm^3 of pure 1-bromobutane.

(a)* Draw a diagram to show how the student would have carried out the reflux and calculate the percentage yield of 1-bromobutane that the student obtains.

Describe how the student could have obtained pure 1-bromobutane from the reaction mixture obtained after reflux. **[6]**



Percentage yield: n(butan-1-ol) = 9.25 ÷ 74.0 = 0.125 mol

mass of 1-bromobutane = 6.10 × 1.268 = 7.735 g; n(C_4H_9Br) = 7.735 ÷ 136.9 = 0.0565 mol

1 : 1 ratio, so % yield = (0.0565 ÷ 0.125) × 100 = 45.2%

Purification: pour the mixture into a separating funnel, add water, stopper and shake, releasing the pressure. Allow the layers to separate.

1-bromobutane is denser than water (1.268 g cm^{-3}), so it is the bottom layer; run off the lower organic layer.

Wash it with aqueous sodium hydrogencarbonate to remove acid, then with

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water, again keeping the lower layer.

Dry the organic layer by adding anhydrous $MgSO_4$ (or $CaCl_2$) and swirling until the liquid is clear, then filter (decant) off the drying agent.

Redistil the dried liquid, collecting the fraction that boils at 102 °C (about 100 to 104 °C), which is pure 1-bromobutane; unreacted butan-1-ol boils at 118 °C so stays behind.

Additional answer space if required.

(b) Butan-1-ol reacts with sodium bromide and sulfuric acid to form 1-bromobutane by nucleophilic substitution.

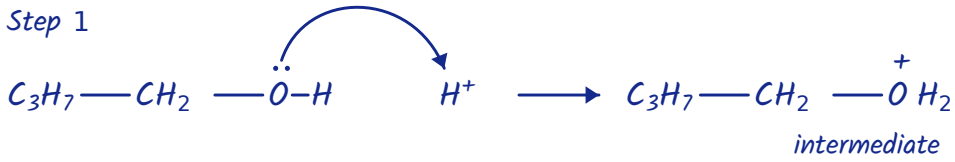
The mechanism for this reaction takes place by two steps.

Step 1 The oxygen atom of the alcohol group accepts a proton to form a positively-charged intermediate.

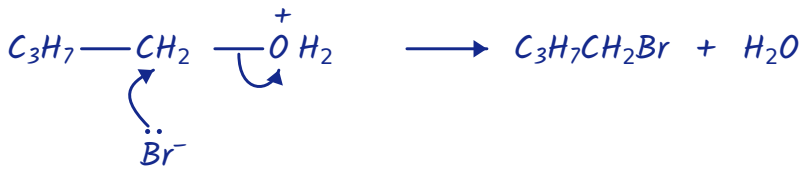
Step 2 Bromide ions react with the intermediate from **Step 1** by nucleophilic substitution to form 1-bromobutane.

Show both steps in this mechanism.

Step 1



Step 2



[4]

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4 Two students plan to investigate **Equilibrium 4.1**, shown below.

$CoCl_4^{2-}(aq) + 6H_2O(l) \rightleftharpoons [Co(H_2O)_6]^{2+}(aq) + 4Cl^-(aq)$ **Equilibrium 4.1**

blue pink

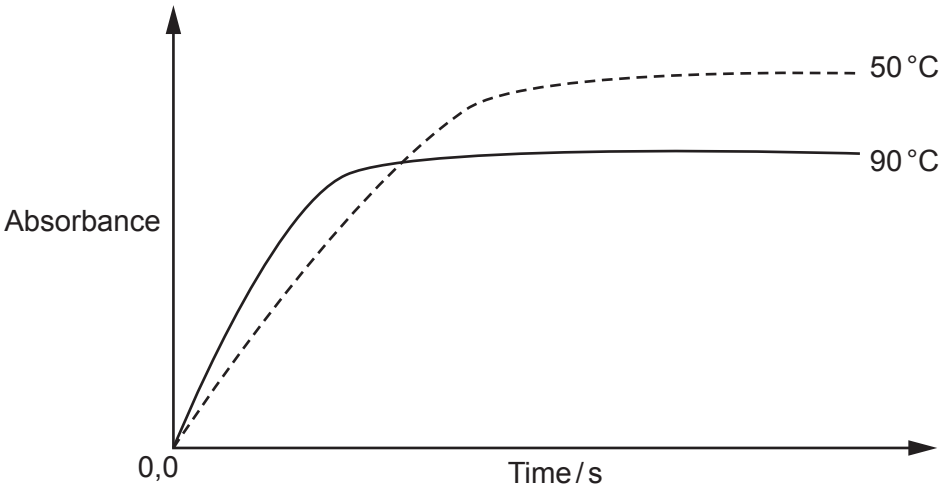
(a) The students are supplied with the equilibrium mixture in **Equilibrium 4.1** at room temperature.

- One student heats 20 cm^3 of the mixture to 50 °C.
- The other student heats 20 cm^3 of the mixture to 90 °C.

The students use colorimetry to observe how the colour of the equilibrium mixture changes over time.

- The colorimeter is set up so that the greater the absorbance, the greater the concentration of $[Co(H_2O)_6]^{2+}$.
- The initial absorbance is set to zero.
- The absorbance is recorded every 30 seconds.

The students plot the graph below from the results of the experiment.



Use the graph and relevant chemical theory to answer the following. Include all reasoning:

- Explain the different initial rates at 50 °C and 90 °C.
- Predict the sign of ΔH for the forward reaction in **Equilibrium 4.1**.

At 90 °C the initial rate is faster (steeper initial gradient): the particles have more kinetic energy, so collisions are more frequent and more particles have energy greater than the activation energy, E_a.

At 90 °C the final absorbance is lower, so the equilibrium $[Co(H_2O)_6]^{2+}$ is lower: the higher temperature shifts the equilibrium to the left (the endothermic direction).

So ΔH for the forward reaction is negative (exothermic). **[4]**

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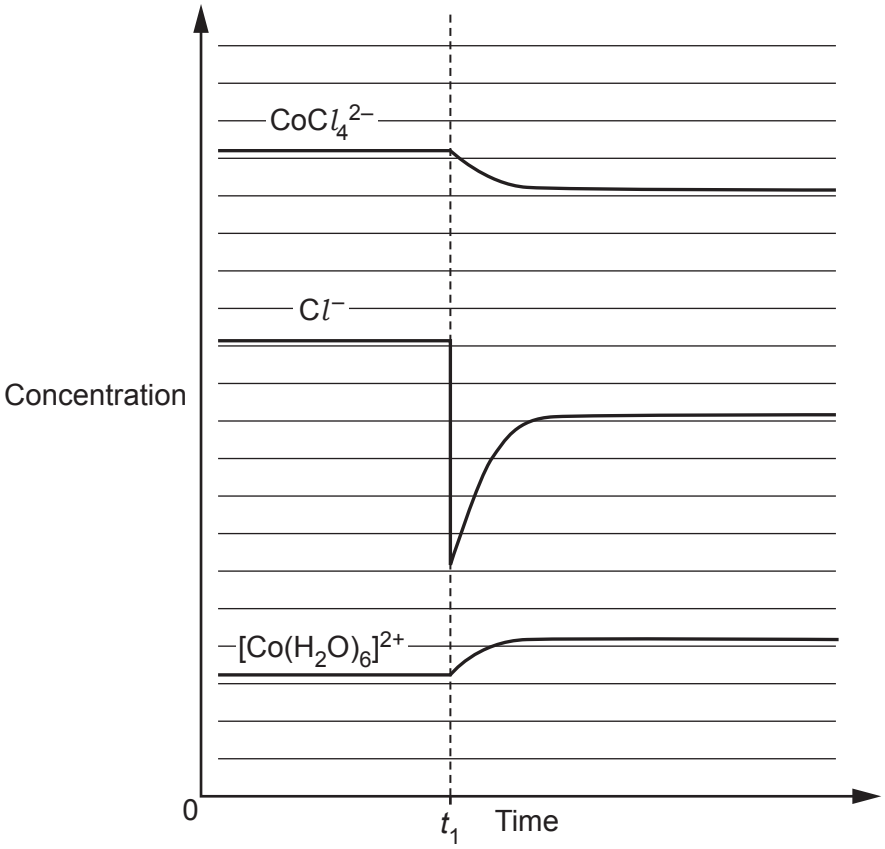
(b) The students investigate how addition of aqueous silver nitrate, $AgNO_3(aq)$, affects the equilibrium position in **Equilibrium 4.1**.

The graph shows the changes in the equilibrium concentrations of $CoCl_4^{2-}$, Cl^- and $[Co(H_2O)_6]^{2+}$ after addition of the $AgNO_3(aq)$.

The $AgNO_3(aq)$ is added at time = t_1.



(i) Explain why the Cl^- concentration drops sharply at time = t_1.

Cl^- ions react with the Ag^+ ions from $AgNO_3$ to form a precipitate of silver chloride: $Ag^+ + Cl^- \rightarrow AgCl$

[1]

(ii) Explain the changes in concentration of $CoCl_4^{2-}$, Cl^- and $[Co(H_2O)_6]^{2+}$ after time = t_1. Refer to **Equilibrium 4.1** in your answer.

$[Cl^-]$ is lowered, so the equilibrium shifts to the right to oppose the change: $[CoCl_4^{2-}]$ decreases and $[Co(H_2O)_6]^{2+}$ increases.

$[Cl^-]$ increases by 4 times the change in $[CoCl_4^{2-}]$ (or $[Co(H_2O)_6]^{2+}$), as $4Cl^-$ form per $CoCl_4^{2-}$ in the equation.

[3]

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5 This question is about energy changes.

(a)* A student plans to determine the enthalpy change of hydration of calcium ions.

The student finds the information below from data tables.

Enthalpy change	ΔH / kJ mol^{-1}
Lattice enthalpy of calcium chloride	–2223
Enthalpy change of hydration of chloride ions	–378

The student carries out an experiment to find the enthalpy change of solution of calcium chloride.

Student's method:

- Weigh a bottle containing calcium chloride and weigh a polystyrene cup.
- Add water from a measuring cylinder to the polystyrene cup and measure its temperature.
- Add the calcium chloride, stir the mixture, and measure the maximum temperature of the final solution.
- Weigh the empty bottle and weigh the polystyrene cup with the final solution.

Mass readings

Mass of bottle + calcium chloride / g	27.45
Mass of empty bottle / g	18.17
Mass of polystyrene cup / g	21.24
Mass of polystyrene cup + final solution / g	127.84

Temperature readings

Initial temperature of water / °C	21.0
Maximum temperature of final solution / °C	39.5

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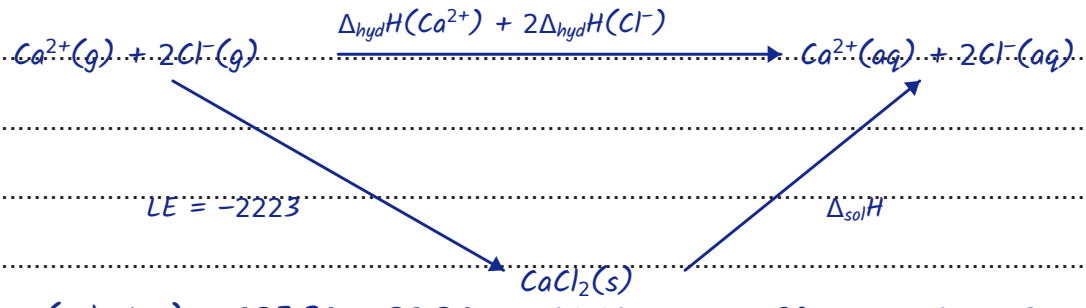
Calculate the enthalpy change of solution of calcium chloride and determine the enthalpy change of hydration of calcium ions.

Show your working, including an energy cycle linking the energy changes.

Assume that the density and specific heat capacity, *c*, of the solution are the same as for water. **[6]**



m(solution) = 127.84 − 21.24 = 106.60 g; ΔT = 39.5 − 21.0 = 18.5 K

q = mcΔT = 106.60 × 4.18 × 18.5 = 8243 J = 8.243 kJ

$m(CaCl_2)$ = 27.45 − 18.17 = 9.28 g; $n(CaCl_2)$ = 9.28 ÷ 111.1 = 0.08353 mol

The temperature rises, so it is exothermic: $\Delta_{sol}H(CaCl_2)$ = −8.243 ÷ 0.08353 = −98.7 kJ mol^{-1}

From the cycle: $\Delta_{hyd}H(Ca^{2+}) + 2\Delta_{hyd}H(Cl^-) = LE + \Delta_{sol}H$

$\Delta_{hyd}H(Ca^{2+})$ = −2223 + (−98.7) − (2 × −378)

Additional answer space if required.

$\Delta_{hyd}H(Ca^{2+})$ = −1566 kJ mol^{-1}

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(b) Internal combustion engines have historically used fuels obtained from crude oil as a source of power.

The environmental effects of fossil fuel use can be reduced by blending petrol with biofuels such as ethanol.

A fuel is being developed using a 1:1 molar ratio of octane and ethanol.

(i) Write the equation for the complete combustion of this fuel.

$2C_8H_{18} + 2C_2H_5OH + 31O_2 \rightarrow 20CO_2 + 24H_2O$ **[1]**

(ii) Calculate the energy released, in kJ, by the complete combustion of 8.00 kg of this fuel.

$\Delta_c H(C_8H_{18}) = -5470\,kJ\,mol^{-1}$; $\Delta_c H(C_2H_5OH) = -1367\,kJ\,mol^{-1}$.

$M(C_8H_{18}) = 114.0$ and $M(C_2H_5OH) = 46.0\ g\ mol^{-1}$

1 mol C_8H_{18} + 1 mol C_2H_5OH has a mass of 160 g

8000 ÷ 160 = 50 mol C_8H_{18} + 50 mol C_2H_5OH

energy = (50 × 5470) + (50 × 1367)

= 273500 + 68350 = 341850 kJ

energy released = 341850 kJ **[3]**

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Turn over for the next question

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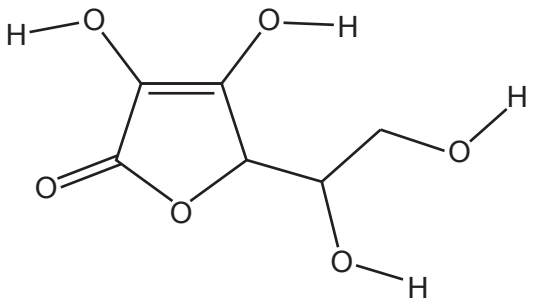
6 A student carries out an investigation on vitamin C, $C_6H_8O_6$.

(a) The structure of vitamin C is shown below. Vitamin C is an optical isomer.



Vitamin C

What is the total number of optical isomers with the structure of vitamin C?

total number of optical isomers = ...4..... **[1]**

(b) Vitamin C is extremely soluble in water. This means that vitamin C is removed rapidly from the body. 'Vitamin C ester' is available in tablet form as a less soluble source of vitamin C which stays in the body for longer.

(i) Suggest why vitamin C is extremely soluble in water.

Vitamin C has many (4) OH groups, so it forms many hydrogen bonds with water molecules.

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

(ii) A 'vitamin C ester' tablet contains an ester with the molecular formula $C_{22}H_{38}O_7$.

This ester can be prepared by reacting vitamin C with a long chain carboxylic acid, C_xH_yCOOH, in the presence of an acid catalyst.

Vitamin C and the long chain carboxylic acid react in a 1:1 molar ratio.

Determine *x* and *y* in the formula of this carboxylic acid.

ester + H_2O = vitamin C + acid

acid = $C_{22}H_{38}O_7 + H_2O - C_6H_8O_6 = C_{16}H_{32}O_2$

$C_{16}H_{32}O_2 = C_{15}H_{31}COOH$

x = ...15..... *y* = ...31..... **[2]**

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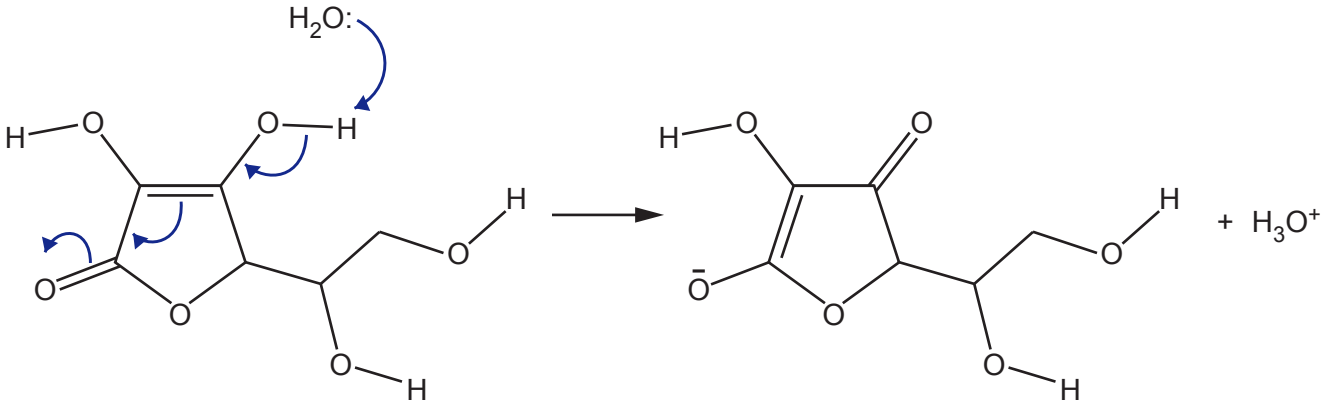
(c) Vitamin C, $C_6H_8O_6$, is a weak acid (K_a = 7.94 x 10^{-5} (mol dm^{-3})), which is often referred to as ascorbic acid.

(i) In aqueous solution, vitamin C donates a proton to water:

$$C_6H_8O_6 + H_2O \rightleftharpoons C_6H_7O_6^- + H_3O^+$$

Add curly arrows to the diagram to suggest the mechanism for this process.



[2]

(ii) The student dissolves 0.150 mol of vitamin C in water and makes the solution up to 250 cm^3 in a volumetric flask.

Calculate the pH of this solution of vitamin C.

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

[vitamin C] = 0.150 × (1000 ÷ 250) = 0.600 mol dm^{-3}

$[H^+] = \sqrt{(K_a \times [HA])} = \sqrt{(7.94 \times 10^{-5} \times 0.600)}$

$[H^+] = 6.90 \times 10^{-3}$ mol dm^{-3}

$pH = -\log(6.90 \times 10^{-3}) = 2.16$

pH = ...2.16..... **[3]**

TURN OVER FOR QUESTION 6 PART (d)

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(d) The label on a carton of orange juice lists the mass of vitamin C, in mg, in a typical serving of 150 cm^3.

The student carries out an investigation to check the vitamin C content in the orange juice.

Vitamin C can be oxidised by iodine:

$C_6H_8O_6(aq) + I_2(aq) \longrightarrow C_6H_6O_6(aq) + 2I^-(aq) + 2H^+(aq)$

The student dilutes 150 cm^3 of the orange juice with water to 250.0 cm^3 in a volumetric flask.

The student then titrates 25.0 cm^3 volume of this solution with 9.60×10^{-4} mol dm^{-3} iodine solution, $I_2(aq)$.

The mean titre of $I_2(aq)$ is 22.50 cm^3.

Determine the mass, in mg, of vitamin C in a 150 cm^3 serving of the orange juice.

$n(I_2) = 22.50 \times (9.60 \times 10^{-4}) \div 1000 = 2.16 \times 10^{-5}$ mol

1 : 1 ratio, so n(vitamin C) in 25.0 cm^3 = 2.16×10^{-5} mol

n(vitamin C) in 250.0 cm^3 = $10 \times 2.16 \times 10^{-5} = 2.16 \times 10^{-4}$ mol

(this is all the vitamin C in the 150 cm^3 serving)

$M(C_6H_8O_6) = (6 \times 12.0) + (8 \times 1.0) + (6 \times 16.0) = 176.0$ g mol^{-1}

mass = $2.16 \times 10^{-4} \times 176.0 = 0.0380$ g = 38.0 mg

mass of vitamin C in the 150 cm^3 serving of orange juice = ...38.0..... mg **[4]**

END OF QUESTION PAPER

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ADDITIONAL ANSWER SPACE

If additional space is required, you should use the following lined page(s). The question number(s) must be clearly shown in the margin(s).

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