

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



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Please write cle	arly in	black	(ink.	Do no	ot writ	te in the barcodes.		
Centre number						Candidate number		
First name(s)								
Last name								

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.



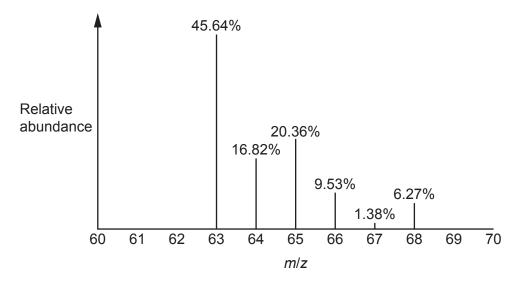
Answer all the questions.

ine	ese q	uestions are from different areas of chemistry.
(a)	Am	monia, NH ₃ , and ammonium nitrate, NH ₄ NO ₃ , are compounds of nitrogen.
	(i)	The boiling point of NH_3 is $-33^{\circ}C$.
		The boiling point of NH ₄ NO ₃ is 210 °C.
		Explain why there is a large difference in boiling points.
		[2]
	(ii)	Two students discuss the oxidation numbers in ammonium nitrate, $\mathrm{NH_4NO_3}$.
		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.

.....[1]

(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?

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

Give your answer to 2 decimal places.

relative atomic mass =[2]

(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	
2	
3	
4	

[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

are shown in the table.	
	[2]

(d)	Gly	vcine, H_2 NC H_2 COOH, is an α -amino acid.	
	(i)	Glycine reacts with NaOH to form the salt H ₂ NCH ₂ COONa.	
		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 ₂ NCH ₂ COONa H–N–H bond angle =°	
		HOOCCH ₂ NH ₃ C <i>l</i> H–N–H bond angle =°	
		explanation	
			[3]
	(ii)	Glycine reacts with aqueous copper(II) ethanoate to form copper(II) glycinate, Cu(H ₂ NCH ₂ COO) ₂ , and ethanoic acid. Copper(II) glycinate is a complex which exists as two square planar isomers.	i
		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	
		structures	
			[3]
			[~]

			6	
2	This	s que	estion is about redox reactions.	
	(a)	'Cal	lcium hypochlorite', $Ca(ClO)_2$, is an ionic compound used in 'bleaching po	owder'.
		The	$e^{-ClO^{-}}$ ion in $Ca(ClO)_2$ is the active ingredient that kills bacteria.	
		Cal	cium hypochlorite is prepared by reacting chlorine gas with calcium hydro	xide.
		2C <i>l</i>	$l_2(g) + 2Ca(OH)_2(s) \rightarrow Ca(ClO)_2(s) + CaCl_2(s) + 2H_2O(l)$	Equation 2.1
		(i)	420 dm ³ of chlorine, measured at RTP, is reacted with an excess of Ca(C	DH) ₂ .
			The solid products are dissolved in water to form 4.00 m³ of solution.	
			Calculate the concentration of $Ca(ClO)_2(aq)$ in this solution, in $moldm^{-3}$.	
			Give your answer to an appropriate number of significant figures and in	standard form.
			concentration =	moldm ⁻³ [3]
		(ii)	Calcium hypochlorite, $Ca(ClO)_2$, is heated. The $Ca(ClO)_2$ decomposes that $Ca(ClO_3)_2$. This is a disproportionation reaction.	to form CaCl ₂
			Write an equation for this decomposition and explain, using oxidation nuis a disproportionation reaction.	mbers, why this

$$CH_3CHO + 2H^+ + 2e^- \iff C_2H_5OH \qquad E^0 = -0.197V$$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \implies 2Cr^{3+} + 7H_2O \quad E^{\theta} = +1.33V$$

$$FeO_4^{2-} + 8H^+ + 3e^- \implies Fe^{3+} + 4H_2O \qquad E^{\theta} = +2.20V$$

Include overall equations.

(c)

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.

[5]
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($\rm II$) ions, a yellow precipitate and one other product.
Construct the equation for this reaction. State symbols are not required.

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.....[2]

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

Compound	Melting point/°C	Boiling point/°C	Density/gcm ⁻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 cm³ of pure 1-bromobutane.

(a)^	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]

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.

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

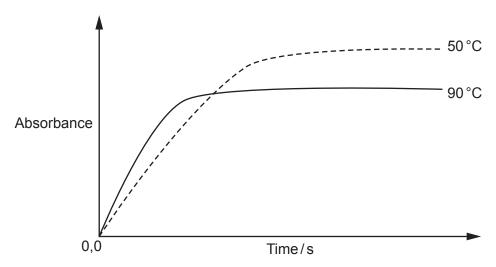
$$CoCl_4^{2-}(aq) + 6H_2O(I) \rightleftharpoons [Co(H_2O)_6]^{2+}(aq) + 4Cl^-(aq)$$
 Equilibrium 4.1 blue pink

- (a) The students are supplied with the equilibrium mixture in **Equilibrium 4.1** at room temperature.
 - One student heats 20 cm³ of the mixture to 50 °C.
 - The other student heats 20 cm³ 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:

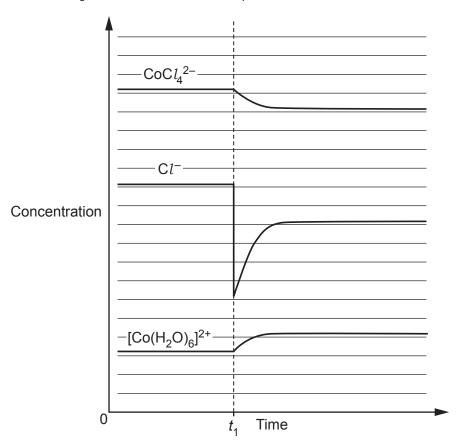
- Explain the different initial rates at 50 °C and 90 °C.
- Predict the sign of ΔH for the forward reaction in **Equilibrium 4.1**.

.....

(b) The students investigate how addition of aqueous silver nitrate, AgNO₃(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 .	
		[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.	
	·	[3]

- 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	∆ <i>H</i> / 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

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] Additional answer space if required.

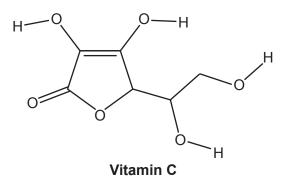
	14					
(b)	Internal combustion engines have historically used fuels obtained from crude oil as a source of power.					
	The environmental effects of fossil fuel use can be reduced by blending petrol with biof such as ethanol.					
	A fuel is being developed using a 1:1 molar ratio of octane and ethanol.					
	(i) Write the equation for the complete combustion of this fuel.					
		[1]				
	(ii)	Calculate the energy released, in kJ, by the complete combustion of 8.00 kg of this fuel.				
	$\Delta_{\rm c} H({\rm C_8 H_{18}}) = -5470{\rm kJmol^{-1}}; \ \Delta_{\rm c} H({\rm C_2 H_5 OH}) = -1367{\rm kJmol^{-1}}.$					
		energy released =kJ [3]				

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Turn over for the next question

- **6** A student carries out an investigation on vitamin C, C₆H₈O₆.
 - (a) The structure of vitamin C is shown below. Vitamin C is an optical isomer.



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

total number of optical isomers =[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.

 - (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.

Χ	=	 y =[2]

- (c) Vitamin C, $C_6H_8O_6$, is a weak acid ($K_a = 7.94 \times 10^{-5}$ (mol dm⁻³)), which is often referred to as ascorbic acid.
 - (i) In aqueous solution, vitamin C donates a proton to water:

$$\mathrm{C_6H_8O_6} \, + \, \mathrm{H_2O} \, \Longrightarrow \, \mathrm{C_6H_7O_6}^- \, + \, \mathrm{H_3O^+}$$

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

H₂O:

[2]

(ii) The student dissolves 0.150 mol of vitamin C in water and makes the solution up to 250 cm³ in a volumetric flask.

Calculate the pH of this solution of vitamin C.

Give your answer to 2 decimal places.

TURN OVER FOR QUESTION 6 PART (d)

(d) The label on a carton of orange juice lists the mass of vitamin C, in mg, in a typical serving of 150 cm³.

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

Vitamin C can be oxidised by iodine:

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

The student dilutes 150 cm³ of the orange juice with water to 250.0 cm³ 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 $\rm I_2(aq)$ is 22.50 $\rm cm^3.$

Determine the mass, in mg, of vitamin C in a 150 cm³ serving of the orange juice.

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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