WORKED SOLUTIONS FOR 2018 H2 CHEM PRELIM PAPER 1

Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10
D	С	С	В	А	В	A	D	D	С

Q11	Q12	Q13	Q14	Q15	Q16	Q17	Q18	Q19	Q20
D	D	D	С	A	В	С	С	A	A

Q21	Q22	Q23	Q24	Q25	Q26	Q27	Q28	Q29	Q30
A	D	В	В	A	В	В	A	С	A

1	Answer: D
	No. of moles of water = 0.133/18 = 0.00739
	No. of moles of NH ₃ = 18.50/1000 x 0.2 = 0.0037
	Ratio of NH_3 to water is 1: 2
	Therefore, x : y (i.e. N to O) of oxide is also 1:2
2	Answer: C
	Option A: Since silver chloride and silver iodide has the same number of ions, the solubility is
	directly proportional to the K_{sp} . Hence silver iodide is precipitated before silver chloride.
	When silver iodide precipitates, chloride ions are still in solution and have not precipitated
	yet. Hence, the concentration of chloride ions is still 1 mol dm ⁻³ .
	Option B: Let solubility of HgI ₂ be x, hence K_{sp} = 4x ³ . x = 6.50 $ imes$ 10 ⁻⁸ mol dm ⁻³
	Option C: The solubility of AgC l = 1 x 10 ⁻⁵ mol dm ⁻³ , AgI = 2.88 x 10 ⁻⁸ mol dm ⁻³ . AgI is less
	soluble than HgI.
	Option D: For HgI ₂ K _{sp} = $[Hg^{2+}][I]^2$, hence units is (mol dm ⁻³) ³ = mol ³ dm ⁻⁹
3	Answer: C
	The yellow precipitate remained in step 2 because IP of AgI > Ksp of AgI.
4	Answer: B
-	From the first 2 properties 0 has to be a main group metal
	Hence, ontion C and D are incorrect
	$\frac{1}{2}$
	Since it was obtained by removing electrons from the same orbital, u has to be either a metal
	In Group 1 or 2.

5	Answer: A
	Option A: The empirical formula: Cr, 15.5%; S, 38.1%; N, 29.2%
	Cr : S : N = 0.298 : 1.19 : 2.09 = 1: 4 : 7
	From K to N, there should be no change in oxidation state and merely a ligand exchange.
	In N, the coordination number is 6 and the oxidation number of Cr = +3. Given that there is
	one cation NH4 ⁺ , hence the overall charge is -1. Thus, There are 4SCN ⁻ ligands to make the
	overall charge -1.
	Option B: The conversion of L to M is also an acid base reaction where L is CrO ₄ ²⁻ and M is
	Cr_2O7^2 .
	Option C: K is Na ₃ [Cr(OH) ₆] (ag). K is not a solid unlike the formula given in option C.
	Option D: H_2O_2 is an oxidising agent in the conversion of K to L as the oxidation number of Cr.
	increases from $+3$ to $+6$
6	Answer: B
U	Answer. D Option A: Berullium chloride is a simple covalent molecule while magnesium chloride is an
	option A. Deryllium chloride is a simple covalent molecule while magnesium chloride is an
	id id intersections then the strong ionic hands in magnesium shlaride
	Id-Id interactions than the strong ionic bonds in magnesium chloride.
	Option B: The E*value for M ^{2*} / M is more negative down the group, indicating M is more easily
	oxidised hence its reducing power increases down the group.
	Option C: Ba ²⁺ has a smaller charge density than Mg ²⁺ and distorts electron cloud of $CO_3^{2^-}$ to
	smaller extent, hence C – O bond is weakened to a smaller extent and more energy is required
	to decompose BaCO ₃ . Hence, less CO ₂ is given off when $BaCO_3$ is decomposed.
	Option D: Ba and Mg are both metallic with strong electrostatic forces of attraction between
	metal cation and sea of delocalised electrons. The number of electrons in the sea of
	delocalised electrons would be the same as both lose 2 valence electrons per atom. Ba ²⁺ has
	a smaller charge density so the metallic bonds are weaker and less energy required to break
	them. Barium should have a lower melting point.
7	Answer: A
	The process of liquefaction is making the molecules of gas come closer together via
	pressurisation. If the intermolecular forces between the molecules are stronger, the pressure
	required would be less. Since NH_3 has hydrogen bond and is stronger than instantaneous
	dipole-induced dipole in CH ₄ , pressure needed for NH_3 would be less than CH ₄ .
8	Answer: D

	$pH = pK_a + lg [Na_2HPO_4] / [NaH_2PO_4]$
	Hence, $7.4 = 6.7 + \log [Na_2HPO_4] / [NaH_2PO_4]$
	7/10 = lg [Na ₂ HPO ₄]/ [NaH ₂ PO ₄]
	$[Na_2HPO_4]/[NaH_2PO_4] = 5$
	Hence, the answer can be C or D. However, since the $([HPO_4^{2-}] + [H_2PO_4^{}]) = 0.30$, thus D is
	the answer.
9	Answer: D
	Statement 1: False. No aldehyde is present.
	Statement 2: False. Only one mole of yellow precipitate is formed when one mole of CPA is
	subjected to iodoform test.
	Statement 3: False. Cl forms a partial double bond with C=C. Hence it does not undergoes
	hydrolysis with AgNO₃
10	Answer: C
	Since total pressure is 3 atm and the mole ratio between Q_2 and R_2 is 2:1, their respective
	partial pressure is 2 atm and 1 atm.
	$2Q_2(g) + R_2(g) \longrightarrow 2Q_2R(g)$
	Initial: 2 1 0
	change: -2x -x +2x
	equilibrium: $2 - 2x$ $1 - x$ $2x$
	Total pressure of gas at equilibrium = (2-2x)+(1-x) +2x = 3-x
	According to guestion.
	2x/(3-x) = 0.20
	x = 0.273 atm
	Thus,
	partial pressure of $Q_2 = 2 - 2(0.273) = 1.454$ atm
	partial pressure of $R_2 = 1 - 0.273 = 0.727$ atm
	partial pressure of $Q_2R = 2 \times 0.273 = 0.546$ atm
	$K_p = (0.546)^2 / [(1.454)^2(0.727)] = 0.194 \text{ atm}^{-1}$
11	Answer: D
	$Co^{3+} + e \rightleftharpoons Co^{2+} + 1.89$
	$Fe^{3+} + e \rightleftharpoons Fe^{2+} + 0.77$
	$S_2O_8^{2^-} + 2e \Rightarrow 2SO_4^{2^-} + 2.01$
	$I_2 + 2e \Rightarrow 2I^- + 0.54$

Statement 1:

Step 1: $2Co^{2+}(aq) + S_2O_8^{2-}(aq) \rightarrow 2Co^{3+}(aq) + 2SO_4^{2-}(aq)$

Step 2: $2I^{-}(aq) + 2Co^{3+}(aq) \rightarrow I_{2}(aq) + 2Fe^{3+}(aq)$

 E_{cell}^{\ominus} for step 1: 2.01 – 1.89 = +0.12 V

 E_{cell}^{\ominus} for step 2: 1.89 – 0.54 = +1.35 V

Statement 2:

 $S_2O_8^{2-}$ is a stronger oxidising agent than Fe³⁺ as it is more easily reduced due a more positive reduction potential +2.01 vs + 0.77 V.

Statement 3:

 E_{cell}^{\ominus} for step 1: 0.77 – 0.54 = +0.23 V

 E_{cell}^{\ominus} for step 2: 2.01 – 0.77 = +1.24 V

12 Answer: D

Option A: C atom with * is sp³ hybridised in the reactant. Nucleophilic substitution ($S_N 2$) mechanism as it is a primary RX. There is no intermediate. The product is formed via a transition state (C atom with * will not be sp³ hybridised anymore because it is bonded to 5 groups).

Option B: C atom with * is sp^3 hybridised in the reactant. Nucleophilic substitution (S_N1) mechanism as it is a tertiary RX. Intermediate is a carbocation where the C atom with * is sp^2 hybridised.



Option C: C atom with * is sp^2 hybridised in the reactant. Electrophilic substitution mechanism. The C atom with * in the intermediate is sp^3 hybridised.









Option D: Cl is more electronegative than Br, hence the negative charge on O is less available to accept H⁺ when Cl is attached to the ring compared to Br.

21 Answer: A

Hydrogen bond is only formed between HF and NH_3 when dissolve in water. The other 3 energy change involved breaking and forming of other kinds of bonds (e.g. covalent bond) and not the hydrogen bond.

22 Answer: D

Option A: Co has more protons than Ca, hence the nuclear charge is higher than Ca. Co also has more electrons than Ca but the increase in shielding effect is minimal. Although the additional 2 electrons in Co are added in an inner sub-shell, they still provide a relatively poor shielding for the outermost 4s electrons. Hence, the valence 4s electrons in Co experiences a greater effective nuclear charge and are attracted more strongly to the nucleus than those in Ca, resulting in a smaller radius.

Option B: Cobalt should have higher conductivity than calcium due to more delocalised electrons from 3d and 4s.

Option C: Cobalt should have higher m.p than calcium. For cobalt, both 3d and 4s electrons are delocalised to form a 'sea' of electrons for strong metallic bonding. Hence, strong electrostatic forces holding the metallic cations (which has a larger cationic charge and smaller cationic radius) together.

Option D: While the size of the atom, measured by the metallic radius, decreases slightly from scandium to zinc, the relative atomic mass increases considerably. This results in an increase in density from scandium to zinc. The d-block metals are, in general, denser than the s-block metals.

23 Answer: B

Statement 1: lodoform test is an oxidation reaction. Alcohol is oxidised to a carboxylic acid (carboxylate).

Statement 2: Acid-base reaction occurs in the last step where CI_3^- acts as base to accept H⁺ from OH in RCOOH (which acts as acid).

Statement 3: There is no addition reaction taking place.

24 Answer: B





Statement 1: HBr is a bronsted acid as it donates a proton. Hence the **product formed** (bromide ion) is a conjugate base.

Statement 2: $N_2H_5^+$ is the Bronsted acid in **Reaction 2 as it donates a proton**.

Statement 3: Since the POE lies to the right for both reactions, HBr is a stronger acid than $N_2H_5^+$ from Reaction 1 as it prefers to donate a proton. Likewise for Reaction 2 where $N_2H_5^+$ is a stronger acid than NH_4^+ .

Statement 4: N_2H_4 is the Lewis base in **Reaction 1** as it donates a lone pair of electrons for dative bonding to a proton from HBr.

~ END OF PAPER ~

Class

ST ANDREW'S JUNIOR COLLEGE



JC2 PRELIMINARY EXAMINATION

Chemistry (9729)

12 September 2018 2 hours

Paper 2 Structured Questions

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS:

Write in dark blue or black pen.You may use an HB pencil for any diagrams or graphs.Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper. The use of an approved scientific calculator is expected, where appropriate. A Data Booklet is provided.

At the end of the examination, fasten all your work securely together. The number of marks is given in brackets [] at the end of each question or part question.

For Examiner's use:

Question	1	2	3	4	5	Total
Marks	19	20	10	7	19	75

This document consists of **20** printed pages (including this page).

Answer **all** the questions.



	(ii)	Based on the diagram above, suggest why the sign of ΔS is negative for						
		the reaction.	[1]					
		The 2 reactants and GOx must come together to form one large entity.	. OR					
		There is a decrease in number of (gaseous) particles.						
		Hence, the products are less disordered than the reactants.						
		Examiners' comments:						
		Candidates are required to use the diagram to obtain their answer, as direct						
		by the question. Hence, it is insufficient to just give the concluding stateme						
		of products are less disordered or less ways of arrangement, as	such					
	statements are too general.							
	(iii)	Sketch a graph showing how the rate of this GOx-catalysed reaction						
		varies with the concentration of glucose.	[1]					
		rate 🛉						
		►[glucose]						
	Exam	iners' comments:						
	The n	nost common incorrect answer shows only a first order reaction, without						
	show	ing the saturation of the GOx enzymes as indicated by the zero order						
 	reacti	ion at higher [glucose].						
(c)	The c	overall equation can be re-expressed to show the change in functional						
	group).						
		$C_5H_{11}O_5CHO + O_2 + H_2O \longrightarrow C_5H_{11}O_5COOH + H_2O_2$						
		glucose gluconic acid						
	Calcu	late the enthalpy change of reaction for the conversion of glucose into						
	gluco	nic acid. Use relevant data from the <i>Data Booklet</i> .	[2]					

Bonds formed in product: C=O, C-O, O-H + 2O-H + O-O

 $\Delta H = (410 + 496) - (360 + 460 + 150) = -64.0 \text{ kJ mol}^{-1}$

Examiners' comments:

(i)

Some candidates attempted to break and form the unchanged portion of glucose and gluconic acid, $C_5H_{11}O_5$, which led to erroneous answers. Other common errors include the exclusion of BE in O_2 , H_2O and/or H_2O_2 .

(d) Experiments were done to determine the kinetics of the reaction.

In the first investigation, the following reaction mixture was prepared.

initial [glucose] = $5.00 \times 10^{-3} \text{ mol dm}^{-3}$

initial [GOx] = $1.00 \times 10^{-2} \text{ mol dm}^{-3}$

initial $[O_2] = 1.00 \times 10^{-2} \text{ mol dm}^{-3}$

The following results in **Table 1** were obtained.

Table 1

40	$[r]_{u}$
US	[giucose] / moi am °
0	5.00 x 10 ⁻³
10	3.40 x 10 ^{−3}
20	2.50 x 10 ^{−3}
30	1.80 x 10 ^{−3}
60	6.00 x 10 ⁻⁴

To determine the order of reaction with respect to [glucose], use these data to plot a suitable graph on the grid below.



Candidates should mark two $t_{1/2}$ clearly on the graph with \triangleleft using a ruler.

In the second and third investigations, the concentrations of oxygen and GOx were changed, but the initial [glucose] was kept the same as before. The following results in **Table 2** were obtained.

Table	e 2
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Investigation	Initial [O ₂]	Initial [GOx]	Initial rate
	(mol dm⁻³)	(mol dm⁻³)	(mol dm ⁻³ s ⁻¹)
1	1.00 x 10 ⁻²	1.00 x 10 ⁻²	Y
2	5.00 x 10 ⁻³	1.00 x 10 ⁻²	2.00 x 10 ⁻⁴
3	5.00 x 10 ⁻³	2.50 x 10 ⁻³	5.00 x 10 ⁻⁵

(iii) Use your graph in (d)(i) to determine the initial rate Y, showing all your working and drawing clearly on your graph. Hence, use the information in Table 2 to determine the orders of reaction with respect to [O₂] and [GOx]. Explain your reasoning.

 $\mathbf{Y} = (5.0 \times 10^{-3} - 1.0 \times 10^{-3}) = 2.00 \times 10^{-4}$

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Using investigation 1 and 2, when $[O_2]$ is halved, the <u>initial rate remains</u> the same. Hence, the reaction is <u>zero order with respect to $[O_2]$.</u>

[3]

Using investigation 2 and 3, when [GOx] decreases 4 times, the initial rate decreases 4 times. Hence, the reaction is <u>first order with respect to</u> [GOx].

Examiners' comments:

Rate does not have a negative sign.

Most candidates have difficulties determining the order of reaction with respect to $[O_2]$. Since $[O_2]$ is doubled, the initial rate should (1) stay the same $\approx 2.00 \times 10^{-4}$ if it is zero order, (2) double $\approx 4.00 \times 10^{-4}$ if it is first order or (3) quadruple

	≈ 8.00) X 1	0 ⁻⁴ if it is secon	d order. Hence, candidates should round off their		
	nump	erto	2.00 X 10 +, 4.00	7×10^{-1} or 8.00 $\times 10^{-1}$, whichever that is closest.		
	Some	cand	lidates were car	eless in recognising the indices, which led them to		
	incorr	ectly	think that the [G	D _x] increases 2.5X from investigation 2 to 3.		
(e)	GOx	can b	e used in a bios	ensor to convert glucose present in body fluids into		
	glucor	nic a	cid. The amount	t of hydrogen peroxide produced is then reduced		
	electro	ocher	nically to determ	ine the amount of glucose present.		
	A 0.1	cm ³	of blood sample	from a patient was tested to diagnose if he was at		
	risk of diabetes. The diagnosis is based on the concentration of glucose in the					
	blood.					
	Condition [glucose] in blood (x 10 ⁻³ mol dm ⁻³)					
			Normal	less than 5.6		
			Pre-diabetes	5.6 - 6.9		
			Diabataa	More then 6.0		
			Diabeles			
 	The b	iosen	sor gave a curre	nt of 1.01 mA for 1 min. (1000 mA = 1A)		
	(i)	Calc	ulate the numbe	r of moles of hydrogen peroxide produced. Hence,		
		diag	nose the condition	on of the patient.	[3]	
		H ₂ O	$_2$ + 2H ⁺ + 2e ⁻ \rightarrow	2H ₂ O		
		Amt	of charge = 1.01	X 10 ⁻³ X 60 = 0.0606 C		
		Amt	of e ⁻ = 0.0606 /	96500 = 6.2798 X 10 ⁻⁷ mol		
		Amt	of $H_2O_2 = 6.279$	8 X 10 ⁻⁷ / 2 = 3.14 X 10 ⁻⁷ mol (3sf)		
		Amt	of glucose = am	t of $H_2O_2 = 3.14 \times 10^{-7} \text{ mol}$		
		[gluo	cose] = 3.14 X 10	$0^{-7} / (0.1 \times 10^{-3}) = 3.14 \times 10^{-3} \text{ mol dm}^{-3}$		
	The <u>patient is normal</u> .					
		Exa	miners' commen	ts:		
		A fe	ew candidates a version given.	hought 1.01 mA was 1001 A, despite the unit		

		More students did not realised the mole ratio of $e^{-}:H_2O_2$ was 2:1.	
		Some candidates missed out the second part of the question, which	
		required them to calculate the [glucose] to diagnose the condition of the	
		patient.	
	(ii)	Before the test, the blood sample has to be treated to remove some	
		components present. Suggest why a treated blood sample was	
		necessary for the biosensor to give an accurate reading.	[1]
		The blood has to be treated to remove some components that can be	
		reduced or oxidised by the biosensor or GOx .	
		Examiners' comments:	
		Some candidates gave general answer like "impurity present", without	
		suggesting how the impurity would affect the accuracy of the reading.	
		Most candidates thought components in the blood would react with	
		glucose and therefore affecting the biosensor reading. However, any	
		reaction of blood components with glucose would have happened	
		anyway and the purpose of the biosensor is supposed to detect whatever	
		amount of glucose that is (left) in the blood.	
		[Total	: 19]
I			



			[2]	
	Туре	of bonding: Within each C_{60} molecule, there is strong <u>covalent bonds betw</u>	<u>ween</u>	
	carbo	on atoms.		
	Desc	ribe lattice structure: C ₆₀ exists as a regular lattice of simple covalent molec	cules	
 	with <u>i</u>	nstantaneous dipole-induced dipole interactions between C ₆₀ molecules.		
	Exan	niners' comments:		
	Some	e candidates wrongly identified the bonds as "covalent bonds between		
	mole	cules" while many others omitted to describe the lattice as "id-id		
	intera	actions <u>between molecules</u> or <u>intermolecular</u> id-id interactions".		
(b)	0.144	I g of C_{60} was placed in a 100 cm ³ container of hydrogen gas at 20 °C and		
	1.00	× 10° Pa.		
	The r	eaction occurred as shown in the equation.		
		$C_{60}(s) + xH_2(g) \rightarrow C_{60}H_{2x}(s)$		
	Wher	When all the C_{60} had reacted, the pressure was found to be 2.21 × 10 ⁴ Pa at the		
	same	e temperature.		
	(i)	Calculate the amount, in moles, of C_{60} that reacted.	[1]	
		Amount of C ₆₀ = 0.144 / 720 = <u>2 × 10⁻⁴</u> mol		
	(ii)	Calculate the amount, in moles, of hydrogen gas that reacted with C_{60} .	[2]	
		pV = nRT		
		$\therefore \Delta n = (p1 - p2)V / RT$		
		$\Delta n = (1.00 \times 10^5 - 2.21 \times 10^4).100 \times 10^{-6} / 8.31 \times 293 = \underline{0.00320} \text{ mol}$		
	(iii)	Use your answers from (i) and (ii) to deduce the molecular formula of		
		the hydrocarbon, $C_{60}H_{2x}$.	[2]	
 		C_{60} :H ₂ = 2.00 × 10 ⁻⁴ : 0.00320 = 1:16		
		X = 16		
		C ₆₀ H ₃₂		
		•		
 (c)	(i)	Graphite is another allotrope of carbon. State the type of hybridisation		
		and draw the arrangement of the hybrid orbitals about each C atom.	[2]	
		sp ²		

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	(ii)	Graphite is a go orbital overlap,	ood conductor of electricity. Explain, with reference to how graphite has a high electrical conductivity.	[2]
		The unhybridis	ed <u>p orbitals</u> on each carbon are overlapping sideways.	
		This <u>side-on o</u>	verlap results in the formation of a π -electron cloud.	
		The π electrons	s are delocalised and account for the high electrical	
		conductivity of	graphite.	
		Examiners' comments:		
		Many candidates did not talk about the side-on overlap. Many candidates also		
		omitted the typ	pe of orbital involved. Some candidates mentioned "mo	obile"
		electrons which	h are not as accurate as "delocalised".	_
(c)	(iii)	ii) The values for the enthalpy change of combustion of graphite and		
		diamond are given in the table below.		
		Substance	Enthalpy change of combustion / kJ mol ⁻¹	
		Graphite	-394	
		Diamond	-396	
		The products o	of the combustion reactions of graphite and diamond are	
		carbon dioxide	and water.	
		Suggest why	the enthalpy change of combustion of graphite is less	
		exothermic tha	n that of diamond.	[1]
	The C	The C-C bonds in graphite are stronger than that in diamond. (or words to the effect,		ect,
	e.g. g	e.g. graphite is energetically more stable than diamond / has lower energy content)		ent)
(d)	Silico	Silicon is another element in Group 14 which shows the same kind of bonding and		and
	struct	ure as diamond.		
	(i)	When silicon re	eacts with magnesium, Mg ₂ Si forms. Mg ₂ Si is thought to	
		contain the Si ⁴⁻	ion. Compare and explain the difference between the	
		atomic and ani	onic radii of silicon.	[2]

	The number of protons in both the atom and its anion is the same, he	ence
	nuclear charge remains constant. The anion has more electrons and he	ence
	there is an increase in electronic repulsion / valence electrons are	less
	strongly attracted to the nucleus, resulting in larger anionic radius in	Si ^{4–}
	when compared to Si.	
(ii	Suggest why the second ionisation energy of silicon is lower than that of	
	aluminium.	[2]
	A <i>l</i> ⁺ : [Ne]3s ²	
	Si ⁺ : [Ne]3s ² 3p ¹	
	The second electron to be removed from Si is in the p orbital which is	
	further away from the nucleus than the s orbital and it faces additional	
	shielding effect from the 3s electrons. Less energy required to remove it.	
(ii) Solid Mg ₂ Si reacts with dilute hydrochloric acid to form gaseous SiH ₄ and	
	a solution of magnesium chloride only. Write an equation, including state	
	symbols, to show the reaction of solid Mg_2Si with dilute hydrochloric acid.	[1]
	$Mg_2Si(s) + 4HCl (aq) \rightarrow SiH_4(g) + 2MgCl_2(aq)$	
(iv) Describe the reaction, if any, of NaC l and SiC l_4 with water, relating any	
	differences to their bonding. Give relevant equations for any reactions	
	and suggest the pH values of each resulting solution.	[3]
	As covalent character of chlorides increases, the more complete the hydro	lysis
	/ the more acidic the solution is.	
	NaCl dissolves in water to form a neutral solution of <u>pH 7</u> . SiCl ₄ underg	goes
	complete hydrolysis to form an acidic solution of <u>pH 2</u> .	
	$SiCl_4(l) + 2H_2O(l) \rightarrow SiO_2(s) + 4HCl(aq)$	
	[Total	20]

3 Hydrocarbons that contain other elements are known as heterocompounds. A special class of heterocompounds are thiols. Thiols are sulfur analogs of alcohols and have the general formula R-SH. Its structure is similar to that of an alcohol, but with sulfur in place of oxygen. One such example is CH₃SH.
 (a) State the bond angle about the oxygen atom in CH₃OH and explain if the bond angle is bigger than the bond angle about the sulfur atom in CH₃SH.

	;o; ;s;	
	H CH ₃ H CH ₃ 105° <105°	
	Both CH_3OH and CH_3SH have 2 bond pairs of electrons and 2 lone pairs of	
	electrons around O and S stoms respectively. In CH ₃ OH, oxygen has a greate	<u>r</u>
	electronegativity than sulfur in CH₃SH.	
	The bond pair of electrons are more strongly attracted to oxygen , resulting	in
	greater repulsion between the bond pairs in CH ₃ OH.	
	Hence, the <u>H-S-C bond angle in CH₃SH is less than 105⁰</u>	
	Examiners' comments:	
	Many candidates did not mention the words" bond pair" and this resulted in	
	vague answers which were not given credit.	
(b)	Thiols can be converted to produce compounds called disulfides. This type of	
	reaction is common in protein structures where it forms disulfide linkages	
	(-S-S-) between two thiols as shown in the following equation:	
	2 RS-H → R-S-S-R + H ₂	
	Based on the above equation, suggest two disulfide products that could be	
	formed when $HOCH_2CH_2SH$ and $HOCH_2CH(CH_3)SH$ are reacted.	
		[1]
	Any two of the three below:	
	HOCH ₂ CH ₂ S-SCH ₂ CH ₂ OH,	
	$HOCH_2CH_2S$ - $SCH(CH_3)CH_2OH$,	
	HOCH ₂ CH(CH ₃)S-SCH(CH ₃)CH ₂ OH	
	Examiners' comments:	
	Some candidates drew two enantiomers instead.	
(C)	Ditniothreitoi (DII) is an organic molecule with molecular formula, $C_4S_2O_2H_{10}$.	nas
	both the functional group of an alcohol and a thiol. The structure of DTT is given be	elow.
	∧ [™] ∕ ^{SH}	

DTT	can be oxidised under suitable conditions to form product \mathbf{X} with molec	ular	
form	formula, C ₄ S ₂ O ₂ H ₈ .		
 (i)	Draw the structural formula of product X .	[1]	
	HS OH HS O		
	Examiners' comments: Many candidates oxidised both secondary alcohols instead of one only. resulted in an oxidation product which did not fit the molecular formula give the question.	This ven in	
(ii)	Product X can then undergo nucleophilic addition with hydrogen cyanide under suitable conditions. Suggest the conditions for this reaction to take place and hence, describe the mechanism of the reaction, In your answer you should show all charges and lone pairs and show the movement of electrons by curly arrows.	[3]	
Conc NaO OR NaCl	ditions: Trace amount of NaOH (aq) or NaCN (aq), 10 – 20 °C H + HCN → Na ⁺ + CN ⁻ + H ₂ O N → Na ⁺ + CN ⁻		





Iron salts, usually iron(II) sulfate, catalyses the decomposition of aqueous hydrogen peroxide to water and oxygen. The reaction mechanism involves OH and HO₂ free radicals. The reaction mechanism is given below. Fe²⁺ + H₂O₂ → Fe³⁺ + HO● + OH⁻ Fe³⁺ + H₂O₂ → Fe²⁺ + HOO● + H⁺
Define *free radical*. [1]
Free radical is an atom or group of atoms having an <u>unpaired / single / lone / odd electron</u>.
(b) Draw the dot-and-cross diagram for HO₂ free radical. [1]











[Please Turn Over



	Amount of KOH = 0.75 x 0.020 = 0.015 mol	
	Mole ratio of KOH : HVA - I = 2 : 1	
	Amount of HVA - I = 0.015 / 2 = 0.0075 mol	
	[HVA - I] = 0.0075 / 0.025 = <u>0.300</u> mol dm ⁻³	
(ii)	Using the first pK_a value, calculate the initial pH at point A .	[2]
	$K_a = 10^{-3.7} = 1.995 \times 10^{-4}$	
	$\mathcal{K}_a = [\mathbf{H}^+]^2 / [\mathbf{H}\mathbf{V}\mathbf{A} - \mathbf{I}]$	
	$[H^+] = (1.995 \times 10^{-4} \times 0.300)^{1/2} = 7.736 \times 10^{-3} \text{ mol dm}^{-3}$	
	pH = −lg(7.736 x 10 ⁻³) = <u>2.11</u>	
(iii)	State the pH at point B and hence, explain the significance of point B .	[2]
	pH = 5.3	
	It has equal concentrations of salt and acid. OR It has equal ability to	
	remove small amount of H^+ and OH^- . OR Maximum buffer capacity.	
(iv)	Write an equation to show that pH at point C is more than 7.	[1]
	$C_9H_8O_4^{2-} + H_2O \rightleftharpoons C_9H_9O_4^{-} + OH^{-}$	
	[Total	: 19]

~ END OF PAPER ~

Section A

Answer all the questions in this section.

1 Electrosynthesis in organic chemistry is the synthesis of compounds in an electrolytic cell using inert electrodes. One important process is the Kolbe reaction. The Kolbe reaction is the decarboxylative dimerization of two carboxylate ions. Alkanes can be formed at the anode by the following reaction.



(a) Explain why alkanes are generally unreactive. [1]

Alkanes have C-C and C-H bonds which are strong and non-polar.

- (b) (i) Calculate the volume of carbon dioxide produced when a steady current of 5A is passed through the electrolyte for 32 minutes at standard temperature and pressure. [2] $Q = It = 32 \times 60 \times 5 = 9600 \text{ C}$ Amt of CO₂ = Amt of e = Q/F = 9600/(96500) = 0.09948 mol Vol of CO₂ collected = 0.09948 x 22.7 = 2.26 dm³
 - (ii) Methanoate ions undergo the Kolbe reaction to form only 2 gases. Using the axes given below, sketch the variation of pV/RT against p for one mole of **each** gas at the same temperature. Briefly explain your answer.

[2]





 CO_2 deviates more from ideal behaviour because it experiences <u>stronger</u> instantaneous dipole-induced dipole interactions / intermolecular forces between the molecules compared to H₂ which has a smaller electron cloud.

(c) The cathodic reaction for the Kolbe reaction can be represented by the

following half equation: $2H_2O + 2e \rightarrow H_2 + 2OH^{-1}$.

Write an overall equation for the Kolbe reaction involving ethanoate ions.

Hence, calculate ΔG^{Θ} for the Kolbe reaction given that the E^{Θ}_{cell} value for the reaction is +2.28 V. [2]

 $2CH_3COO^- \rightarrow CH_3-CH_3 + 2CO_2 + 2e$

 $2H_2O + 2e \rightarrow H_2 + 2OH$

Overall: $2CH_3COO^+ 2H_2O \rightarrow CH_3-CH_3 + 2CO_2 + H_2 + 2OH^-$

 $\Delta G^{\Theta} = - nFE = - (2)(96500)(2.28) = -440 \text{ kJ mol}^{-1}$

- (d) The reaction mechanism of the Kolbe reaction involves a 4-step reaction mechanism as described below:
 - Step 1: Dissociation of carboxylic acid to form a carboxylate ion.
 - Step 2: Oxidation of carboxylate ion to form a carboxyl radical, RCOO.
 - **Step 3**: Decomposition of the carboxyl radical to form carbon dioxide gas and an alkyl radical, R•.
 - Step 4: Formation of a covalent bond between two alkyl radicals.
 - (i) Using ethanoic acid as a starting reagent, suggest suitable equations for Steps 1, 2 and 4 on how ethane can be produced using the Kolbe reaction.

[3]

2

Step 1: $CH_3COOH \rightarrow CH_3COO^- + H^+$

Also accept "CH₃COOH + H₂O \rightarrow CH₃COO⁻ + H₃O⁺".

Step 2: $CH_3COO^- \rightarrow CH_3COO^{\bullet} + e$

Step 4: $CH_3 \bullet + CH_3 \bullet \rightarrow CH_3CH_3$ (accept C_2H_6 also)

(ii) The decomposition of the carboxyl radical to form carbon dioxide gas and an alkyl radical, R•, in Step 3 can be represented by the following equation: RCOO• → CO₂ + R•

Outline the mechanism of this step by copying the diagram below and include relevant curly half arrows.



(e) In another separate experiment, a new alkane A, C₆H₁₂, was produced. When reacted with bromine under ultraviolet light, A produced only one isomeric monobromo compound, B, which does not have a chiral centre. Draw the skeletal formulae of A and B.



[2]



(f) (i) Using monohalogenoethane, C₂H₅X, as examples, describe and explain the relative reactivities of chloro- and bromo-compounds in hydrolysis reactions.
 The hydrolysis of C₂H₅X will increases in reactivity (C₂H₅Cl < C₂H₅Br). This is because the bond length / bond energy of C-Cl <C-Br, hence, it is most difficult to overcome C-Cl bond > C-Br bond.

(ii) Halogenoalkanes such as chlorofluoroalkanes, CFCs, were once used as refrigerant fluids and aerosol propellants. In many applications, they have now been replaced by alkanes. This is because CFCs contribute to the destruction of the ozone layer. Explain how CFCs destroy the ozone layer and suggest one potential hazard of using alkanes instead of CFCs.
 CFCs produce <u>chlorine radicals</u>, which in turn initiate the chain reaction breaking down ozone molecules, O₃ to O₂.
 Alkanes are flammable.

Examiners' comments:

From 2010 A-level P3 – CFCs' involvement in the destruction of the ozone layer is because ultraviolet radiation from the sun in the stratosphere photolyses their molecules to generate chlorine radicals (not fluorine radicals) which initiate a chain reaction of destruction of ozone molecules. The replacement of CFCs by alkanes has a danger because alkanes are readily flammable.

(iii) Halogenoalkanes can react with lithium to give organolithium compounds.

These organolithium compounds can react with carbonyl compounds to form alcohols.



(R is alkyl, R' and R" are either alkyl or H)

Using the above reaction sequence, deduce the structure of a suitable bromoalkane, R-Br, and a suitable carbonyl compound to synthesise hexan-2-ol. [2] Ethanal, 1-bromobutane

OR Bromomethane, Pentanal

[Total: 19]

[2]
- 2 Wastewater has to be treated carefully to remove all harmful contaminants before it can be released into water bodies.
- (a) Industrial wastewater contains high levels of heavy metal ions. Electrocoagulation is used to remove heavy metal ions from wastewater. In this method, heavy metal ions are oxidised to form hydroxides, so that they can coagulate easily and be removed easily in subsequent steps.

A sample of wastewater containing Fe²⁺ is treated by electrocoagulation.

 $4Fe^{2+}$ (aq) + 10H₂O (*l*) + O₂ (g) $4Fe(OH)_3$ (s) + 8H⁺ (aq)

(i) By considering the interaction it forms with water, explain why Fe²⁺ cannot be [1] easily removed from wastewater.

It forms <u>ion-dipole interaction with water</u>. Hence, it is soluble in water and cannot be easily removed.

OR

It forms <u>dative bond with water</u> to form a soluble complex of $[Fe(H_2O)_6]^{2+}$. Hence it cannot be easily removed.

- (ii) State a suitable physical method to remove Fe(OH)₃ from the wastewater. [1] filtration
- (iii) Using Le Chatelier's Principle, suggest why the wastewater has to be kept [1] alkaline for a more effective removal of Fe²⁺.
 As [OH⁻] is high / [H⁺] is low, the position of the equilibrium shifts right to increase [H⁺]. Hence, more Fe²⁺ would be oxidised/removed as Fe(OH)₃.
- (iv) With an appropriate sketch of the Boltzmann distribution, explain how an [3] increase in temperature would affect the rate of removal of Fe²⁺.

No of particles with Energy, E



When T increases, the <u>KE of the reacting particles increases</u>. Hence, there are <u>more particles with $E \ge E_a$ and the frequency of effective collision increases</u>. The <u>rate</u> of removal of Fe^{2+} would <u>increase</u>.

(b) Ammonia is a toxic substance present in wastewater from the mining industry. Nitrification is a common biological treatment method to convert ammonia into less toxic nitrate.

 NH_3 (aq) + 2O₂ (g) $\rightarrow NO_3^-$ (aq) + H⁺ (aq) + H₂O (l)

(i) Write the expression for the equilibrium constant, K_c , for this reaction given that [1] K_c has units of mol⁻¹ dm³.

 $K_c = [NO_3^{-}][H^+] / [NH_3] [O_2]^2$

(ii) 12 mol of oxygen gas was pumped into 1000 dm³ of wastewater containing 5 [3] mol of NH₃. After nitrification, the resulting treated wastewater had a pH of 4.2. Calculate the value of K_c. Leave your answer to 3 significant figures.

	NH ₃ (aq)	+ 2O ₂	1	NO₃⁻(aq)	H⁺(aq)	H ₂ O	
Initial conc	0.005	0.012		0	0		
1							
mol dm ⁻³							
Eqm conc /	0.005 - 10 ^{-4.2}	$0.012 - 2 \times 10^{-4.2}$		10 ^{-4.2}	10 ^{-4.2}		
mol dm⁻³	= 0.0049369	=					
		0.011873					
$K_c = (10^{-4.2})^2 = 5.72 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ (3sf)}$							
(4.9369 X 10 ⁻³)(1.1873 X 10 ⁻²) ²							

(iii) State how the K_c in (ii) would change when the amount of NH₃ in wastewater is [1] increased to 10 mol.

 K_c would remain the same.

(iv) The nitrification process was carried out at room temperature. It was observed [2] that the outer surface of the reaction vessel was cold after some time.
 By considering the effect of temperature on the equilibrium, suggest and explain how you can change the reaction temperature to increase the conversion of ammonia.

The (forward) <u>reaction is endothermic</u>. Hence, we can <u>increase the temperature</u> to shift the equilibrium position right, <u>so as to absorb the excess heat</u>, which allows more NH_3 to be converted.

(v) Construct a suitable energy cycle using the following equations to show how the [3] enthalpy change of reaction, ΔH_r , can be determined.



(c) Wastewater treatment plants that treat pharmaceutical wastewater produces sludge that contains a high amount of organic substances. These organic substances can be combusted to harness energy for other processes. Tonalide, C₁₈H₂₆O, is one such organic compound found commonly in sludge. It has a melting point of 54.5°C.



tonalide

(i) Write an equation which describes the standard enthalpy change of combustion [1] of tonalide.

 $C_{18}H_{26}O(s) + 24O_2(g) \rightarrow 18CO_2(g) + 13H_2O(l)$

- (ii) The enthalpy change of combustion of tonalide is -865 kJ mol⁻¹. [2] Given that the combustion is 70% efficient, determine the amount of energy that can be harnessed from the combustion of sludge, which contains 900 g of tonalide.
 Amt of tonalide = 900 / (18 X 12.0 + 26 X 1.0 + 16.0) = 3.4883 mol Amt of heat released (100%) = 865 X 3.4883 = 3017.4 kJ Amt of energy harnessed (70%) = 3017.4 X 0.7 = 2110 kJ (3sf)
- (iii) The sign of the entropy change of combustion of tonalide is positive. Briefly [1] explain the effect of temperature on the spontaneity of combustion of tonalide. $\Delta G = \Delta H - T\Delta S$ $T\Delta S > 0$ $\Delta H < 0$ ΔG becomes more negative at higher temperatures. Hence, the combustion is more feasible. OR

 ΔG is always negative at all temperatures. Hence, the combustion is <u>feasible</u> at all temperatures.

[Total: 20]

3 Geraniol, C₁₀H₁₈O, is commonly used in perfumes and food flavourings.



It is produced from geranyl diphosphate as shown in the following equation.



<u>OPP</u> is a **bulky group** which creates <u>steric hindrance</u> for the nucleophile to attack the carbon bonded to OPP / <u>transition state</u> <u>is unstable</u>.

OR

OPP is negatively charged so it repels the approaching nucleophile (H_2O) .

- (iii) State the role of water in reaction II. [1] It acts as a <u>Bronsted-Lowry / Lewis base</u> (as it accepts H⁺ to form H_3O^+) or <u>nucleophile</u>.
- (iv) The following compound can be synthesised from geraniol. [4]



Propose a reaction scheme for this synthesis.



Step 1: KMnO₄, H₂SO₄ (aq), heat Step 2: NaBH₄ or Hydrogen / Nickel, heat Step 3: concentrated sulfuric acid, heat

(v) Explain what is meant by constitutional isomers and draw a [2] constitutional isomer of geraniol that will form a yellow precipitate with alkaline aqueous iodine.

They are compounds with the <u>same molecular formula</u> but <u>different</u> <u>structural formulae</u>



OR Any other structure with same molecular formula with R-CO(CH₃) or R-CH(OH)CH₃

- (b) Geranyl diphosphate can be synthesised using P_4O_{10} .
 - (i) Write an equation for the reaction of P_4O_{10} in water and describe [2] the effect of the resulting solution on universal indicator solution.

 $P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$

Universal indicator will turn red / orange.

(ii) Naturally occurring phosphorus contains the isotopes ³¹P, ³²P and [2] ³³P. Explain the term isotopes and calculate the relative atomic mass of phosphorus given that the relative abundance of each isotope is 91.1 %, 7.9% and 1.0 % respectively.

Isotopes are <u>elements</u> with the <u>same atomic number / same</u> <u>number of protons</u> but <u>different mass number / due to different</u> <u>number of neutrons</u>.

relative atomic mass = (0.911 x 31) + (0.079 x 32) + (0.01 x 33) = 31.1

(c) Geraniol is a by-product of the metabolism of sorbic acid, C₅H₇COOH. Sorbic acid and its salt are used to prevent growth of mould and fungi and to regulate the pH in food and drinks. With the aid of relevant equations, explain how the pH of food and drinks can be regulated through the use of sorbic acid and its salt.

[3]

C₅H₇COOH + OH⁻ → C₅H₇COO⁻ + H₂O C₅H₇COO⁻ + H⁺ → C₅H₇COOH

A <u>large reservoir</u> of acid and salt will help to remove a <u>small amount of</u> <u>base and acid</u> respectively to ensure that the <u>pH remains</u> **relatively/almost** constant/resists pH changes.

(d) Another constitutional isomer of geraniol is compound X. X does not react [5] with 2,4-dinitrophenylhydrazine. X produces effervescence when sodium metal is added to it. When hot acidified K₂Cr₂O₇ is added to X, orange solution remains. On addition of aqueous bromine to X, the orange solution decolourises and compound Y is formed. X reacts with hot acidified KMnO₄ to form compound Z only. When Z is reacted with excess concentrated H₂SO₄ at 170 °C, the following product is obtained.



X, **Y** and **Z** are all able to rotate the plane of polarised light. Suggest the identities of **X**, **Y** and **Z**, explaining your reasoning.

Observations	Deductions
X does not react with 2,4-DNPH.	X is not an aldehyde or ketone / not a carbonyl compound.
X produces effervescence when Na added.	Redox. Gas is H ₂ . X contains hydroxyl group (or – OH group or alcohol).
Orange solution remains when hot $K_2Cr_2O_7$ added to X .	X contains tertiary alcohol.
On addition of aqueous bromine to X , the orange solution turns colourless.	 X undergoes electrophilic addition. X contains C=C (or alkene).
X reacts with hot acidified KMnO ₄ to produce Z only.	Oxidation X is a cyclic compound
Z reacts with excess concentrated H_2SO_4 at 170 °C.	Elimination
X , Y and Z are all able to rotate the plane of polarised light.	All 3 compounds have chiral carbon.

Structures





[Total: 21]

Examiners' comments:

For structure Y, 2 Br atoms should not be added across the C=C bond as the reagent used is aqueous Br_2 . Answer should reflect the major product.

Section B

Answer **one** question in this section.

- 4 Transition elements and its compounds have various applications, such as in materials, catalysis and even in nature. An example of a transition element which has many uses and is widely researched on is copper.
 - (a) Explain what is meant by the term *transition element*. [1]
 It is a <u>d-block element</u> which forms <u>one or more stable ions</u> with <u>partially filled d</u> subshells.
 - (b) (i) Plastocyanin is a copper-containing protein found in vascular plants. The shape around Cu²⁺ in plastocyanin is tetrahedral and can be represented by the following simplified structure. The amino acids found around Cu²⁺ act as ligands.



Define the term *ligand*.

[1]

It is an **ion or molecule** which contains <u>at least 1 atom bearing a lone pair of</u> <u>electrons</u> which can be <u>donated into a low-lying vacant orbital of a central</u> <u>metal atom or ion</u> by forming a <u>dative bond</u>.

- (ii) Plastocyanin is commonly involved in electron transfer and this results in the formation of Cu⁺ complex which has a deep blue colour.
 State the electronic configuration of Cu⁺. [1]
 1s²2s²2p⁶ 3s² 3p⁶ 3d¹⁰
- (iii) The deep blue colour seen is considered to be unusual.
 Suggest a reason why this is so. [1]
 The <u>d orbitals in Cu⁺ are completely filled</u> and therefore, <u>no d-d transition</u> can occur and the complex should not be coloured.

- (c) Azurite is a copper containing mineral that is deep blue in colour. The formula of azurite is Cu₃(CO₃)₂(OH)₂ and it can be inferred that azurite contained copper(II) carbonate and copper(II) hydroxide, which are sparingly soluble salts.
 - (i) To prepare small crystals of azurite in the lab, a few drops of copper(II) sulfate solution can be added into a saturated solution of sodium carbonate and leave to stand overnight.

With reference to the preparation method as described, write an equation to suggest how OH⁻ may be produced from a saturated solution of sodium carbonate. [1]

 $CO_3^{2-} + H_2O = HCO_3^{-} + OH^{-}$

(ii) A student wishes to determine the percentage of azurite in a rock sample. He proposes to do so by performing a direct titration with dilute sulfuric acid. Suggest an explanation why the proposed method is not ideal. [1] The solid is <u>insoluble</u> and <u>cannot be directly titrated</u>. OR

The solid hydroxide and carbonate (especially) will be <u>too slow to react</u> with the sulfuric acid.

OR

The end-point will not be accurately determined.

(iii) Another student proposed the following method which is ideal in determining the percentage of azurite in a rock sample.

Step 1: Add 7.00 g of the rock sample to 130 cm^3 of 0.550 mol dm⁻³ sulfuric acid. The resulting solution was topped up to 250 cm³ using deionised water.

Step 2: 25.0 cm³ of the solution required 15.55 cm³ of 0.200 mol dm⁻³ sodium hydroxide for complete reaction.

Azurite reacts with sulfuric acid according to the following equation.

 $Cu_3(CO_3)_2(OH)_2 + a H_2SO_4 \rightarrow a CuSO_4 + b H_2O + c CO_2$

Complete the balancing of the above equation by deducing values for **a**, **b** and **c**. Hence, calculate the percentage of azurite in the rock sample.

[3]

 $Cu_3(CO_3)_2(OH)_2 + 3 H_2SO_4 \rightarrow 3 CuSO_4 + 4 H_2O + 2 CO_2$

Amount of NaOH = Amount of excess $H_2SO_4 = \frac{1}{2} \times \frac{15.55}{1000} \times 0.2 = 1.55 \times 10^{-3} \text{ mol}$

Amount of excess H_2SO_4 in 250 cm³ = 10 x 1.55 x 10⁻³ = 0.0155 mol

Amount of H_2SO_4 reacted with azurite = $(130/1000 \times 0.55) - 0.0155$ = 0.05595 mol Amount of azurite = 0.05595 / 3 = 0.01865 mol Mass of azurite = 0.01865 x 344.5 = 6.42 g % azurite in rock sample = 6.425 / 7 x 100% = 91.8% (to 3 sf)

(iv) Using your knowledge on the thermal decomposition of carbonates and given that Cu(OH)₂ thermally decomposes to form CuO and H₂O, write an equation for the thermal decomposition of azurite.

Using the equation written and appropriate molar mass values, calculate the percentage loss in mass upon strongly heating a sample of azurite until no further changes. [3]

Cu₃(CO₃)₂(OH)₂ → 3 CuO + H₂O + 2 CO₂ Mass of azurite in 1 mol = 344.5 g Mass of H₂O in 1 mol = 18 g Mass of CO₂ in 2 mol = 2 x 44 = 88 g % loss in mass = (18+88) / 344.5 x 100% = 30.76% \approx 30.8% (to 3 sf)

(v) In another instance, a student tried to synthesise azurite by adding copper(II) nitrate solution slowly to a solution containing 0.100 mol dm⁻³ sodium carbonate solution and 0.100 mol dm⁻³ potassium hydroxide solution. Calculate the concentration of Cu²⁺ required to begin precipitating CuCO₃ and Cu(OH)₂ respectively. Hence, state which compound precipitates first assuming that there is a negligible change in volume.

 K_{sp} of CuCO₃ = 7.08 x 10⁻⁹ mol² dm⁻⁶ K_{sp} of Cu(OH)₂ = 4.8 x 10⁻²⁰ mol³ dm⁻⁹

When Cu(OH)₂ first precipitates, $[Cu^{2+}] = 4.8 \times 10^{-20} / (0.1)^2 = 4.8 \times 10^{-18} \text{ mol dm}^{-3}$ When CuCO₃ first precipitates, $[Cu^{2+}] = 7.08 \times 10^{-9} / 0.1 = 7.08 \times 10^{-8} \text{ mol dm}^{-3}$ Cu(OH)₂ will precipitate first. [3]

(vi) When sufficient ammonia is added to copper(II) hydroxide precipitate, the precipitate dissolves. Explain this observation with the aid of relevant equations.

[2]

[3]

 $[Cu(H_2O)_6]^{2+}(aq) + 2OH^-(aq) - Cu(OH)_2(s) + 6H_2O(l) ---- eqm (1)$ blue solution blue precipitate

When \underline{excess} aqueous NH_3 is added, $\underline{\text{ligand exchange}}$ occurs to form a deep blue solution.

 $[Cu(H_2O)_6]^{2+} + 4NH_3 \longrightarrow [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O ---- eqm (2)$ deep blue solution

The formation of $[Cu(NH_3)_4(H_2O)_2]^{2+}$ decreases the concentration of $[Cu(H_2O)_6]^{2+}$ causing **position of equilibrium (1) to shift to the left in order to replenish** $[Cu(H_2O)_6]^{2+}$. Hence, blue ppt of Cu(OH)₂ dissolves, forming the deep blue solution.

(d) Copper metal is obtained from copper ore and is widely used in electrical wiring. To prevent short circuit, the metal used must have high purity. Outline how the impure copper ore is purified industrially to remove impurities such as zinc and silver metals.

Impure copper ore can be purified using electrolysis. The impure copper is placed at the anode, while pure copper is used as the cathode. The electrolyte used is aqueous CuSO₄.

When an electric current is applied, copper at the **anode (+)**, together with Zn are oxidised to their ions owing to their relatively less positive E° values. Hence, Cu^{2+} and Zn^{2+} then migrate to the cathode / remain in solution.

Ag will not be oxidised as it has a relatively positive E° values and it falls off the electrode and accumulate at the bottom as anodic sludge.

At the cathode, only Cu^{2+} ions are reduced to Cu, which is deposited on the pure copper electrode, due to its more positive E^{e} .

Zn²⁺ remain as ions in the solution as they do not reduce to metals easily.

[Total: 20]

- 5 Iron is an important transition element and the second most abundant metal in Earth's crust. Iron containing compounds have various uses and the element itself can also be found in a number of proteins within living things. Iron and its compounds have been widely researched on as they are relatively cheap and non-toxic.
 - (a) Haemoglobin is a protein found in red blood cells. Within haemoglobin, it contains an Fe²⁺ ion which has an octahedral shape as it is surrounded by five nitrogen-containing ligands and one oxygen-containing ligand, which is H₂O in deoxyhaemoglobin and O₂ in oxyhaemoglobin.
 - A species with unpaired electrons is paramagnetic and can be attracted by an externally applied magnetic field. On the other hand, a species with no unpaired electrons is diamagnetic and is unaffected by a magnetic field.
 Oxyhaemoglobin is found to be diamagnetic. Based on the information provided and using the diagram below, show the electronic distribution of the 3d electrons of Fe²⁺ in oxyhaemoglobin.



(ii) In both oxyhaemoglobin and deoxyhaemoglobin, the 3d orbitals are no longer degenerate as they are split into two different energy levels.
 Explain this observation. Using the Cartesian axes like those shown below, draw a fully labelled diagram of one of the 3d orbitals which has a lower energy level.



18

In octahedral complexes, the lone pair of electrons on the 6 ligands <u>approach Fe²⁺</u> <u>along the axes</u>. This results in <u>electronic repulsion</u>, which causes the energy level of $3d_{x^2-y^2}$ and $3d_{z^2}$ to be higher.



Either one:

(iii) Explain why oxyhaemoglobin is red. [2]
 When a <u>d electron from the lower energy d orbital absorbs light energy (visible light with wavelength corresponding to this energy gap)</u>, it is promoted to the higher energy d orbital and this is d-d transition.
 The red colour seen is complementary to the colour absorbed / red colour is not absorbed.

(iv) The complementary colours are shown using the following colour wheel.



The wavelength of each colour component in visible light is as provided.

Colour	Purple	Blue	Green	Yellow	Orange	Red
Wavelength	380 - 450	450 - 495	495 - 570	570 - 590	590 - 620	620 – 750
/ nm						

Oxyhaemoglobin is bright red while deoxyhaemoglobin is blue. Given that the wavelength of light is inversely proportional to energy, state and explain if water or oxygen causes a larger energy gap between the 3d orbitals.

O₂ causes a larger energy gap between the 3d orbitals.

[2]

Oxyhaemoglobin absorbs green colour which is of lower wavelength / higher energy than the orange colour that deoxyhaemoglobin absorbs.

(v) Fe²⁺ complex in oxyhaemoglobin does not have an overall charge. The structure is as shown.



State the charge around the N atom labelled (1) and the bond angle around the N atom labelled (2).

[2]

Charge around N(1): 1– Bond angle around N(2): 120°

- (vi) Besides Fe²⁺, Fe³⁺ may also exist in haemoglobin. Explain why Fe can have variable oxidation states in haemoglobin. [1]
 The <u>energy of 3d and 4s electrons are close in proximity</u>. Hence, the electrons in 3d and 4s orbitals may be shared or lost to give variable oxidation states.
- (vii) Each polypeptide chain in haemoglobin is made up of more than 100 amino acid residues. The general structure of an amino acid is as shown below.



In each chain, histidine, leucine and glycine amino acids can be found.

Amino acid	R group
Histidine	
Leucine	-CH ₂ CH(CH ₃) ₂
Glycine	-H

Draw the structural formula of a tripeptide with the sequence histidine-leucineglycine at pH 2. [2]



(viii) Haemoglobin can undergo complete hydrolysis non-enzymatically. State the reagents and condition for this to occur. [1]
 (6 mol dm⁻³) concentrated HC/ (Any mineral acid), prolonged heating / several hours (for 24h)

(b) To detect for the presence of blood in a crime scene, an organic compound named luminol may be used. Luminol uses iron in haemoglobin to catalyse the decomposition of hydrogen peroxide, which eventually leads to a blue glow to indicate the presence of blood. The synthetic route for luminol is as shown.



State the role of $Na_2S_2O_4$. Reducing agent

[Total: 20]

[1]

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Write your n Give details Write in dark You may use Do not use s	Write your name and class on all the work you hand in. Give details of the practical shift and laboratory in the boxes provided above. Write in dark blue or black pen. You may use a soft pencil for any diagrams or graphs. Do not use staples, paper clips, highlighters, glue or correction fluid.					
Answer all the use of a You may lo se Qualitative A	ne questions in the spaces provided on the Question Pape n approved scientific calculator is expected, where approp se marks if you do not show your working or if you do analysis Notes are printed on pages 16 and 17.	r. vriate. not use approp i	riate units.			
At the end of the examination, fasten all your work securely together. The number of marks is given in the brackets [] at the end of each question or part question.						
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Answer all the questions in the spaces provided.

1 Determination of percentage by mass of sodium carbonate in a mixture of sodium carbonate and sodium hydrogen carbonate

The complete reaction between sodium carbonate and hydrochloric acid can be represented as shown: $Na_2CO_3 + 2HCl \rightarrow 2NaCl + CO_2 + H_2O$

However, when sodium carbonate is titrated against hydrochloric acid, it reacts with hydrochloric acid in two separate stages.

When a mixture of sodium carbonate and sodium hydrogen carbonate is titrated against hydrochloric acid using thymolphthalein indicator, the blue colour of the indicator is discharged when sodium carbonate is partially neutralised as represented by *reaction 1*.

Screened methyl orange is then added and a further quantity of hydrochloric acid is necessary to bring about a colour change when **reaction 2** is complete. This further amount of acid reacts with both the sodium hydrogen carbonate formed in **reaction 1** as well as the sodium hydrogen carbonate present initially in the mixture.

(a) In this experiment, you will determine the amount of Na₂CO₃ and NaHCO₃ in **FA 1** by following the procedures below.

FA 1 is a solution containing sodium carbonate, Na_2CO_3 and sodium hydrogen carbonate, $NaHCO_3$.

FA 2 is an aqueous solution containing 0.50 mol dm⁻³ of hydrochloric acid, HC*l*.

- 1. Pipette 25.0 cm³ of **FA 1** into a conical flask.
- 2. Add 5 drops of thymolphthalein indicator and titrate **FA 1** against **FA 2** in a burette.
- 3. When the blue colour is discharged, note and record the burette reading in the table provided on page 3. This end-point may not be easily seen. Therefore, you are advised to put a white tile under your conical flask to help you. If you are unsure if the blue colour has discharged or not, you may also add a few more drops of thymolphthalein to the solution.

Do not discard this mixture!

(The volume of **FA 2** required to reach the first end-point need not be consistent but it should not exceed 15 cm^3 .)

- 4. Add 3 drops of screened methyl orange to this mixture and **continue** the titration until the second end-point is reached. Record the final burette reading in the same table provided on page 3.
- 5. Perform sufficient titrations to obtain consistent results for the **second end-point**, which is the total volume of **FA 2** required.

Results

	1	2	3	
Final burette reading (with screened methyl orange) / cm ³	30.80	40.50	30.60	
Final burette reading (with thymolphthalein) / cm ³	12.50	22.10	12.30	
Initial burette reading / cm ³	0.00	10.00	0.00	
Total volume of FA 2 used to reach the second end-point / cm^3	30.80	30.50	30.60	
Place a tick for the consistent results			▼	

accuracy of total volume of FA 2
 2 marks for 30.60 cm³ ≤ average titre volume ≤ 30.90 cm³
 1 mark for 30.30 cm³ ≤ average titre volume < 30.60 cm³
 or 30.90 cm³ < average titre volume ≤ 31.20 cm³

- 2 dp for all burette readings
- correct sequence for burette readings + putting ticks for two total volume of FA 2 that are within 0.10 cm³
- (b) *x* is the average volume of **FA 2** required to reach the first end point.

y is the average **further** volume of **FA 2** required to reach the second end-point.

From your 2 consistent titration results, calculate **x** and **y**.

 $x = (12.10 + 12.30) / 2 = 12.20 \text{ (cm}^3)$ Do note that the 2 x values need not be consistent

 $y = (40.50 - 22.10) + (30.60 - 12.30) = \frac{18.40 + 18.30}{2} = 18.35 \text{ (cm}^3)$

• correct calculations of x and y from the results in (a), in 2 dp

Examiners' comments:

• Students tend to make mistake in the calculation of y, rather than x.

x =[2] y =

[4]

Using \boldsymbol{x} , calculate the amount, in moles, of Na₂CO₃ in 25.0 cm³ of **FA 1**.

(C)

(i)

ecf from (b) No of moles of HC l = 12.20/1000 x 0.50 = 6.10 x 10 ⁻³ mol No of moles of Na ₂ CO ₃ = 6.10 x 10 ⁻³ mol									
		Number of moles of Na ₂ C	:O ₃ =						
			[1]	I					
(c)	(ii)	Using y, calculate the total amount, in moles, of NaHCO ₃ i ecf from (b) No of moles of HC <i>l</i> = $18.35/1000 \times 0.50 = 9.18 \times 10^{-3}$ mol Total no of moles of NaHCO ₃ = 9.18×10^{-3} mol	n the reaction mixture.						
		Total number of moles of NaHC	CO ₃ =[1]	I					
(d)	From your answers in (c), calculate the amount, in moles, of NaHCO ₃ in 25.0 cm ³ of FA 1 . No of moles of NaHCO ₃ formed from Na ₂ CO ₃ = 6.10×10^{-3} mol								
	No of moles of NaHCO ₃ in FA 1 = $9.18 \times 10^{-3} - 6.10 \times 10^{-3}$								
	i.e (c)	= 3.08 x 10 ⁻³ mol							
		Number of moles of NaHC	CO3 =[1]	l					
(e)	Calcul and Na [<i>A_r:</i> Na	ate the percentage by mass of sodium carbonate in FA 1 a ₂ CO ₃ . a, 23.0; H, 1.0; C, 12.0; O, 16.0]	, which is a mixture of NaHCC	13					
	Mass	of NaHCO₃ in FA 1 = 3.08 x 10 ⁻³ x 84.0 = 0.259 g	i.e ((d) x 84)						
	Mass of Na ₂ CO ₃ in FA 1 = $6.10 \times 10^{-3} \times 106.0 = 0.647$ g i.e ((c)(i) x 106)								
	•	correct calculation of mass of NaHCO ₃ and Na ₂ CO ₃							
	% by r	mass of Na ₂ CO ₃ in FA 1 = 0.647 / (0.647 + 0.259) x 100%	= 71.4 %						
	•	correct calculation of % by mass of Na ₂ CO ₃							

(f) A student decides to carry out the same experiment in (a) by using a pH meter to determine the percentage by mass of Na₂CO₃ in the mixture.

Given that pK_b of CO_3^{2-} = 3.68 and pK_b of HCO_3^- = 7.62, sketch a graph to show how the pH of the mixture changes as HC*l* is added. You may use your titre values in any set of experiments obtained in **(a)** for the volume of HC*l* at the two equivalence points.

[2]



OR



- correct shape in the right direction with correct axes and unit
- correct labelling of volumes at MBCs, pH at MBCs, 2 equivalence volumes using any set of titre volumes (including x and y)

Examiners' comments:

- Students tend to have difficulty sketching the graph.
- For those who managed to sketch the correct graph, they did not get the full marks due to the lack of labels for volume at MBC and inconsistent choice of values for volume at 1st and 2nd equivalence points.

Planning

- (g) Unlike Group 2 carbonates, solid sodium carbonate, Na₂CO₃, does **not** decompose on heating with a Bunsen burner. However, for solid sodium hydrogencarbonate, NaHCO₃, it will form sodium carbonate, steam and carbon dioxide when heated.
 - (i) Write an equation, with state symbols, to represent the thermal decomposition of sodium hydrogen carbonate.

```
\begin{array}{l} 2 \text{ NaHCO}_3(s) \rightarrow \text{Na}_2\text{CO}_3(s) \ + \ H_2\text{O}(g) \ + \ \text{CO}_2(g) \\ \\ \textbf{Mole ratio 1}: \frac{1}{2}: \frac{1}{2}: \frac{1}{2}: \frac{1}{2} \text{ is acceptable} \end{array}
```

```
......[1]
```

(g) (ii) Given the above information, you are to devise a plan to determine the percentage by mass of NaHCO₃ in a solid mixture of NaHCO₃ and Na₂CO₃.

You may assume you are provided with

- a boiling tube
- a pair of tongs
- 10 g of NaHCO₃ and Na₂CO₃ solid mixture
- a heat resistant mat
- equipment normally found in a school or college laboratory

In your plan, you should include details of:

- procedure you would follow, including the apparatus you would use and the safety precautions to take,
- measurements you would take,
- a brief outline of how the results can be used to determine the percentage by mass of NaHCO₃ in the mixture. You may make assumptions for the masses involved and use appropriate molar mass values to solve this.
 [A_i: Na, 23.0; H, 1.0; C, 12.0; O, 16.0]

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[6]
Procedure
1. Weigh the dry empty boiling tube using a weighing balance.
2. Place 10 g (or any mass as defined) of sample powder in the boiling tube and
weigh again. Record the mass reading.
3. Using the tongs provided, gently heat the boiling tube with the sample using a Bunsen
burner for about 2-3 minutes, before strongly heating the tube for another 5 minutes.
4. Cool the boiling tube on a heat resistant mat before weighing the tube and
sample. Record the mass reading.

5. Repeat the heat-cool-weigh process till consistent mass is obtained.

Point to note:

• Tongs, weighing balance, boiling tube and heat resistant mat must be appropriately used

For safety precaution, any 1 of the following is accepted:

- Ensure that the **tongs is positioned nearer to the mouth of the boiling tube** so that it would not be burnt/too hot to hold during heating.
- Tilt the boiling tube (about angle of 45°), <u>direct the mouth of the boiling tube</u> <u>away</u> from you and your neighbour as you start heating gently.
- Move the boiling tube up and down to ensure even heating of the solid. This will also prevent contents from spurting due to intensive heating at one spot.
- Using the tongs provided, <u>gently heat</u> the boiling tube with the sample using a Bunsen burner for about 2-3 minutes, <u>before strongly heating</u> the tube for another 5 minutes.

 $\begin{array}{l} \underline{\text{Treatment of results:}} \\ \text{Let the mass of solid mixture used be 10 g} \\ \text{Let the final mass (of Na_2CO_3) obtained be y g} \\ \text{Mass of H}_2\text{O and CO}_2 = (10 - y) g \\ \text{Mass of 1mol of H}_2\text{O and 1 mol of CO}_2 = 18.0 + 44.0 = 62.0 g \\ \text{Amount of H}_2\text{O and CO}_2 \text{ evolved} = 2(10 - y) / 62.0 \text{ mol} \\ &= \text{amount of NaHCO}_3 \\ \text{OR} \end{array}$

Amount of H₂O and CO₂ evolved = (10 - y) / 62.0 mol Amount of NaHCO₃ = 2(10 - y) / 62.0 mol

Mass of NaHCO₃ = $[2(10 - y) / 62] \times 84 \text{ g}$ % by mass = $\frac{84(x-y)}{31 \times 10} \times 100\%$

[Total: 20]

Examiners' comments:

- Students should try to answer the planning question, instead of leaving it blank.
- There were a number of students who did not understand the requirement of the question and therefore, ended up proposing inappropriate experimental methods, such as the use of gas collection or titration. These students also failed to recognise that other apparatus, such as gas syringe, were not provided.

2 Determination of n in the complex ion formula [Cu(NH₃)_n]²⁺

Many transition metal ions possess the ability to form complexes with ligands, which can either be organic or inorganic molecules/ions.

In this experiment, you will determine the value of *n* in the formula $[Cu(NH_3)_n]^{2+}(aq)$, which is the complex ion formed when aqueous NH₃ is added to Cu²⁺(aq).

Different volumes of CuSO₄ solution and aqueous ammonia are mixed and the corresponding temperature changes are measured.

FA 3 is 0.5 mol dm⁻³ CuSO₄ solution **FA 4** is 2.0 mol dm⁻³ aqueous ammonia

(a) Measure and record the temperatures of the given solutions FA 3 and FA 4.



• Temperatures should be recorded to 1 dp

(b) Carry out the following procedures and prepare a table for your results on **page 8**. Your table should include i) $V_{FA 3}$, ii) $V_{FA 4}$, iii) $T_{initial}$, iv) T_{max} , v) temperature rise, ΔT and vi) colour of solution and precipitate (if any).

Procedures:

Experiment 1

- Measure 9.00 cm³ of **FA 3** from a burette into a boiling tube.
- Add into the boiling tube 1.00 cm³ of **FA 4** from another burette.
- Note the temperature rise while stirring to ensure that you do not miss the highest temperature reached. Record this temperature as *T*_{max}.
- Note and record the colour of precipitate (if any) and the colour of solution observed.
- Discard the content in the boiling tube and wash the boiling tube thoroughly. Wipe the thermometer dry for use in **experiment 2**.

Experiment 2

- Measure 8.00 cm³ of **FA 3** from a burette into the boiling tube.
- Add into the boiling tube 2.00 cm³ of **FA 4** from another burette.
- Note the temperature rise while stirring to ensure that you do not miss the highest temperature reached. Record this temperature as T_{max} . Note and record the colour of precipitate (if any) and the colour of solution observed.
- Discard the content in the boiling tube and wash the boiling tube thoroughly. Wipe the thermometer dry for use in subsequent experiments.

Experiments 3 - 9

Perform 7 more experiments, each time reducing the volume of **FA 3** by 1.00 cm^3 but increasing the volume of **FA 4** by 1.00 cm^3 such that the total volume of solution is kept constant at 10.00 cm^3 .

The weighted average initial temperature, T_{intial} , of **FA 3** and **FA 4** can be calculated by using the formula:

$$T_{\text{initial}} = \frac{(V_{\text{FA}3} \times T_{\text{FA}3}) + (V_{\text{FA}4} \times T_{\text{FA}4})}{V_{\text{FA}3} + V_{\text{FA}4}}$$

[5]

where V_{FA3} and V_{FA4} are the volumes of FA 3 and FA 4 in the mixture

 T_{FA3} and T_{FA4} are the temperatures of FA3 and FA4 measured in (a)

Calculate $T_{initial}$ for each experiment and include it in your table of results.

	V _{FA 3} / cm ³	<i>V_{FA 4}</i> / cm ³	T _{initial} / °C	Τ _{max} / ° C	∆T / °C	Observation
1	9.00	1.00	27.5	28.4	0.9	(pale) blue ppt
2	8.00	2.00	27.4	28.9	1.5	(pale) blue ppt
3	7.00	3.00	27.3	29.4	2.1	(pale) blue ppt
4	6.00	4.00	27.2	29.4	2.2	(pale) blue ppt
5	5.00	5.00	27.1	29.7	2.6	(pale) blue ppt in deep blue solution
6	4.00	6.00	27.0	29.3	2.3	Deep blue solution
7	3.00	7.00	26.9	28.9	2.0	Deep blue solution
8	2.00	8.00	26.8	28.5	1.7	Deep blue solution
9	1.00	9.00	26.7	27.9	1.2	Deep blue solution

correct header with units

• correct decreasing V_{FA 3} and increasing V_{FA 4} in 2 dp

• 1 dp for T_{max} , $T_{initial}$ and ΔT

• correct calculation of $T_{initial}$ and ΔT

• observations changing from (pale) blue ppt to (deep / dark) blue solution. There should not be any ppt in the last 2 experiments. Examiners' comments:

- Students should follow the headers as given by the question, instead of coming up with their own.
- The header "colour of solution and ppt" and the corresponding observations proved to be a difficulty for a number of students.
- Students should recognise that the values for *T*_{max}, *T*_{initial} and ∆T should be recorded to 1 dp as the number of decimal places cannot be more precise than what the thermometer can read.
- Students should also note down the burette readings to 2 dp, according to the precision of instrument used.
- (c) Plot a graph of temperature rise, ∆T, against volume of **FA 4**. Your plot should consist of **two** best-fit **straight lines**.



• Axes labelled correctly with units + min and max points cover more than half the space in both directions + no awkward scale

[3]

- points plotted correctly to within half a small square
- 2 lines of best fit with intersection



- (d) (i) Show on your graph how the volume of **FA 4** that corresponds to the highest temperature rise can be determined.
 - Students should draw a vertical line from x-axis to the point of intersection or show coordinates at the point of intersection
 - Correct reading of point to within 1/2 small square for volume of FA 4

Volume of **FA 4** with highest temperature rise = cm³

Hence, calculate the volume of **FA 3** that corresponds to this volume of **FA 4**. Volume of **FA 3** = $10.00 - 4.95 = 5.05 \text{ cm}^3$

- correct calculation of volume of FA 3
- accuracy for n [(see (c)(iv)) should be 3.51 < n < 4.49

4.95

(ii) Calculate the amount, in moles, of aqueous ammonia in the volume of **FA 4** with the highest temperature rise.

```
Amount of NH_3 = 4.95 / 1000 \times 2.0 = 9.90 \times 10^{-3} \text{ mol}
```

Amount of NH₃(aq) = [1]

(iii) Calculate the amount, in moles, of Cu²⁺ ions in the volume of **FA 3** that you have determined in (i).

Amount of Cu^{2+} = 5.05 /1000 x 0.5 = 2.53 x 10⁻³ mol

Amount of Cu²⁺(aq) = [1]

(iv) Calculate the number of moles of NH_3 bonded with one mole of Cu^{2+} ions in the solution and hence, deduce the value of n in the formula $[Cu(NH_3)_n]^{2+}$.

Amount of NH₃ = 9.90×10^{-3} mol NH₃ : Cu²⁺ = 9.90×10^{-3} : 2.53×10^{-3} = 3.91 : 1 n = 4

n should be rounded off to the nearest whole number

[1]

n =

(e) The graph of ΔT against volume of NH₃ should theoretically look like the one below, with a combination of two straight lines with different positive gradients before the change in temperature starts to decrease.



With reference to the observations that you have recorded in the table on page 8, explain, with the aid of two relevant equations, why the graph is a combination of two straight lines with different positive gradients.

There were **two reactions** which produces different amount of heat / different enthalpy change of reaction.

 $[Cu(H_2O)_6]^{2+} + 2OH^- \rightarrow Cu(OH)_2 + 6H_2O$ OR Cu²⁺ + 2OH⁻ \rightarrow Cu(OH)₂

 $Cu(OH)_2 + 4NH_3 \rightarrow [Cu(NH_3)_4]^{2+} + 2OH^- OR Cu^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4]^{2+} OR$ $[Cu(H_2O)_6]^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4]^{2+} + 6H_2O$

Examiners' comments:

• This question was poorly attempted. A lot of students did not provide the 2 equations as required and often overlooked the hint given, which was to interpret the observations noted from their results.

(f) Suggest an improvement that you will make to this experiment to improve the accuracy of the results obtained.



Use a rubber bung with a hole (for the thermometer to be inserted) to cover the boiling tube immediately after the two reagents are mixed so as to prevent heat loss to surrounding. OR

Dry the boiling tube before each experiment so that the residual water will not add on to the total volume of solution and cause a lower temperature rise.

OR

Mix the solutions in a Styrofoam cup (with a lid) / use of draught-free environment to prevent heat loss to the surrounding.

Examiners' comments:

- Some students proposed the use of fumehood to prevent heat loss to surroundings, which is inappropriate because the vacuum pump inside the fumehood will affect the temperature reading (unless it is switched off).
- There were a few students who proposed the use of graphical method to determine the maximum T and hence, ∆T at point of mixing. This answer was not accepted as it was too tedious to do so for this experiment, as well as there was no usage of stopwatch to take note of the timing.

Planning

(g) Chromium cations can also form complexes. A student was given a solid which has a formula of either [Cr(H₂O)₅C*l*]C*l*₂ or [Cr(H₂O)₄C*l*₂]C*l*. The relative formula mass of the compound is 248.5.

When dissolved in water, the chloride ions not involved in the complex ion would be liberated into the solution.

 $[Cr(H_2O)_5Cl]Cl_2(s) \rightarrow [Cr(H_2O)_5Cl]^{2+}(aq) + 2Cl^{-}(aq)$ $[Cr(H_2O)_4Cl_2]Cl(s) \rightarrow [Cr(H_2O)_4Cl_2]^{+}(aq) + Cl^{-}(aq)$

To determine the formula of the solid given, a student prepared a 250 cm³ of standard solution using 29.80 g of the given solid. He then determined the amount of free chloride ions by titrating 25.0 cm³ of the standard solution against 0.3 mol dm⁻³ silver(I) nitrate solution while using some potassium chromate(VI) as an indicator. When silver(I) nitrate solution was added, a white precipitate of AgC*l* was formed.

 $Ag^{+}(aq) + Cl^{-}(aq) \rightarrow AgCl(s)$

When all the free chloride ions had precipitated, a red-brown precipitate of silver chromate(VI) was formed to signify that the end-point had been reached.

 (i) The teacher commented that the student should have reduced the mass of solid used by half for the preparation of standard solution.
 Explain, with the aid of suitable calculations, why 29.80 g is not a suitable mass to be used.

[2]

Amount of solid in 250 cm³ = 29.80 / 248.5 = 0.1199 mol If solid has formula [Cr(H₂O)₅C*l*]C*l*₂, Amount of C*l*⁻ in 25.0 cm³ = 0.1199 x 25.0/250 x 2 = 0.02398 mol Amount of AgNO₃ needed = (0.02398 / 0.3) x 1000 = 79.9 cm³ Since the volume required is more than a burette full or > 50.00 cm³, the mass is not suitable.

Examiners' comments:

Some students assumed the species to be [Cr(H₂O)₄Cl₂]Cl and wrongly concluded that the 40.0 cm³ needed was too big. Students should appreciate that the titre volume should be from 10.00 cm³ to 40.00 cm³ in order to have a relatively small percentage error.

(g) (ii) You are to describe how the student should prepare the standard solution by using his teacher's proposal.

In your answer, include

- the procedures involved in the preparation of the standard solution,
- the apparatus and equipment used to prepare the standard solution.

Procedure

Using a <u>weighing balance</u>, weigh accurately about 14.90 of the unknown solid. Tip/transfer the solid into a <u>small beaker</u> and <u>reweigh the emptied weighing</u> <u>bottle</u>.

Add some deionised water to dissolve the solid.

Transfer the solution into a 250.0 cm³ volumetric flask carefully and top up

to the mark using deionised water.

Stopper and shake well to obtain a homogeneous solution.

Examiners' comments:

 Some students gave shocking answer, such as the addition of solids directly into the volumetric flask. Others wrongly named the volumetric flask or use inappropriate apparatus, such as conical flask and round bottom flask.

[2]

3 Identifying cations in an unknown sample

(a) You are given FA 5, which is an aqueous solution containing two cations and one anion. One of the cations is Cu²⁺. The other cation can be found from the list in the Qualitative Analysis Notes provided on page 16.

Perform the tests described in Table 3.1. Record your observations in the table. In all the tests, the reagent should be added gradually until no further change is observed, with shaking after each addition. Test and identify any gases evolved. No additional or confirmatory tests for ions present should be attempted.

Table 3.1

	Tests	Observations	
1.	To 1 cm depth of FA 5 , add 2 cm depth of FA 1 (from question 1).	 Green solution turned brown which eventually turned yellow-green. Effervescence / Bubbling / Gas is observed. The gas formed white ppt with Ca(OH)₂(aq). The gas is CO₂. Examiners' comments: Some students did not identify the gas despite noting the effervescence. Others did not know how to spell "effervescence". 	
2.	Add about 3 cm ³ of dilute aqueous ammonia to 1 cm ³ of FA 5 . Filter the mixture and note the appearance of both the filtrate and residue. Add dilute sulfuric acid dropwise to the filtrate till in excess.	 Reddish-brown ppt is formed. The solution turned from (dark) green to dark blue. The residue is brown (can accept reddish-brown) and the filtrate is (deep / dark) blue. Light) blue ppt is formed upon dropwise addition of H₂SO₄. Ppt dissolves to form a very light blue / colourless solution in excess H₂SO₄. Examiners' comments: A large number of students wrongly concluded that the ppt was green, before eventually turning into brown upon standing in air. Majority of the students did not note down the formation of light blue ppt, which is Cu(OH)₂, when H₂SO₄ was added dropwise to the filtrate. 	
3.	Add a spatula of solid potassium iodide to	The filtrate is green / yellow, residue contains	
----	--	---	--
	3 cm^3 of FA 5. Filter the mixture and note	black and off-white ppt.	
	the appearance of the filtrate.		
		2 immiscible layers are formed. The top layer	
	Add 1 cm ³ of hexane to the filtrate and	is pink / violet / purple in colour and the	
	shake well.	bottom layer is green / yellow.	
		 Examiners' comments: A large number of students were not being precise in their observations, as they did not mention the formation of 2 immiscible layers and did not account for the colour of each layer. 	

[5]

- (b) Consider your observations in Table 3.1.
 - (i) State the other cation which is present in FA 5.
 [1]
 Fe³⁺
 Examiners' comments:

 A large number of students wrongly concluded the cation to either be Fe²⁺ or Cr³⁺.
 - (ii) **FA 5** turns Universal Indicator paper red. With reference to this and your observations in test 1, write an ionic equation to represent the reaction between **FA 1** and **FA 5**.

......[1]

2 H⁺ (aq) + CO₃^{2–} (aq) \rightarrow CO₂ (g) + H₂O (l) **OR**

 H^+ (aq) + HCO_3^- (aq) $\rightarrow CO_2$ (g) + H_2O (l)

(iii) With reference to test 3, suggest the identity of the species which was responsible for the observations seen when hexane was added to the filtrate. Hence, suggest the property of FA 5.

......[2]

I₂

FA 5 is oxidising / can be reduced.

Examiners' comments:

• This question was poorly attempted and this suggested that the students did not understand what happened in test 3.

Planning

- (c) FA 5 also contains an anion. To determine the identity, a student heated FA 5 with A*l* and NaOH(aq). A gas was evolved and it turned moist red litmus paper blue.
 - (i) Based on the observations given, state the possible identities of the anions.

[1]

 NO_3^- and NO_2^-

Examiners' comments:

- This question was meant to be an easy one but some students did not understand what was the chemical test carried out.
- (ii) You are provided with the reagents NaOH(aq), NH₃(aq), HNO₃(aq) and AgNO₃(aq).

Suggest a test to confirm the identity of the anion in FA 5. State the expected observations.

DO NOT carry out the test.

Test:

Expected observation for each of the possible anions in (i).

.....

.....[2]

Add HNO₃ (aq) (dropwise) to **FA 5**.

If brown gas is observed, NO₂-is present.

If no brown gas is seen, NO₃-is present.

Examiners' comments:

- Some students proposed the use of AgNO₃ which was inappropriate.
- Others proposed the addition of nitric acid to the products obtained from the reaction of FA 5 with A*l* and NaOH(aq), which was chemically wrong as the products are no longer nitrate or nitrite.

[Total: 12]

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Qualitative Analysis Notes

[ppt. = precipitate]

(a) Reactions of aqueous cations

Cotion	reaction with			
Callon	NaOH(aq)	NH₃(aq)		
aluminium,	white ppt.	white ppt.		
Al³⁺(aq)	soluble in excess	insoluble in excess		
ammonium,	ammonia produced on heating	-		
NH₄⁺(aq)				
barium, Ba²⁺(aq)	no ppt. (if reagents are pure)	no ppt.		
calcium, Ca ²⁺ (aq)	white ppt. with high [Ca ²⁺ (aq)]	no ppt.		
chromium(III), Cr ³⁺ (aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess		
copper(II), Cu²⁺(aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution		
iron(II), Fe ²⁺ (aq)	green ppt. turning brown on contact with air insoluble in excess	green ppt. turning brown on contact with air insoluble in excess		
iron(III),	red-brown ppt.	red–brown ppt.		
Fe ³⁺ (aq)	insoluble in excess	insoluble in excess		
magnesium,	white ppt.	white ppt.		
Mg ²⁺ (aq)	insoluble in excess	insoluble in excess		
manganese(II), Mn²⁺(aq)	off-white ppt. rapidly turning brown on contact with air insoluble in excess	off-white ppt. rapidly turning brown on contact with air insoluble in excess		
zinc,	white ppt.	white ppt.		
Zn²⁺(aq)	soluble in excess	soluble in excess		

(b) Reactions of anions

ion	reaction	
carbonate, CO ₃ ^{2–}	CO ₂ liberated by dilute acids	
chloride, C <i>l</i> ⁻ (aq)	gives white ppt. with Ag⁺(aq) (soluble in NH₃(aq))	
bromide, Br⁻(aq)	gives pale cream ppt. with Ag⁺(aq) (partially soluble in NH₃(aq))	
iodide, I⁻(aq)	gives yellow ppt. with Ag⁺(aq) (insoluble in NH₃(aq))	
nitrate, NO₃⁻(aq)	NH_3 liberated on heating with $OH^-(aq)$ and Al foil	
nitrite, NO₂⁻(aq)	NH ₃ liberated on heating with OH ⁻ (aq) and A <i>l</i> foil NO liberated by dilute acids (colourless NO \rightarrow (pale) brown NO ₂ in air)	
sulfate, SO₄²⁻(aq)	gives white ppt. with Ba ²⁺ (aq) (insoluble in excess dilute strong acids)	
sulfite, SO ₃ ^{2–} (aq)	SO ₂ liberated on warming with dilute acids; gives white ppt. with Ba ²⁺ (aq) (soluble in dilute strong acids)	

(c) Tests for gases

gas	test and test result	
ammonia, NH₃	turns damp red litmus paper blue	
carbon dioxide, CO ₂	gives a white ppt. with limewater	
	(ppt. dissolves with excess CO ₂)	
chlorine, Cl ₂	bleaches damp litmus paper	
hydrogen, H ₂	"pops" with a lighted splint	
oxygen, O ₂	relights a glowing splint	
sulfur dioxide, SO ₂	turns aqueous acidified potassium manganate(VII) from purple to colourless	

(d) Colour of halogens

Halogen	colour of element	colour in aqueous solution	colour in hexane
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br ₂	reddish brown gas / liquid	orange	orange-red
iodine, I ₂	black solid / purple gas	brown	purple