Name:		Class:	

ST ANDREW'S JUNIOR COLLEGE

JC 2 Preliminary Exam (TUTOR'S COPY)

Chemistry **9647/02**

Higher 2 **31 August 2016**

Paper 2 **2 hours**

Candidates answer in the spaces provided on the question paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in dark blue or black pen.

You may use a soft pencil for any diagrams, graphs or rough working.

Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions.

You are reminded of the need for good English and clear presentation in your answers.

The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use:

Question	Marks
1	
2	
3	
4	
5	
6	
7	
Total (72 marks)	

This document consists of **27** printed pages (including this page) and **1** blank page.

1	A student found a bottle of solid benzoic acid in the school laboratory. She was tasked to determine the standard enthalpy change of neutralisation of benzoic acid. The standard enthalpy change of neutralisation is when one mole of water is formed between an acid and a base. $$H^+ (aq) + OH^- (aq) \rightarrow H_2O (l)$$ You may assume you are provided with the following: • **FA 1**, aqueous sodium hydroxide, NaOH • Solid benzoic acid • Polystyrene (styrofoam) cups • Apparatus normally found in a school laboratory Before carrying out the experiment, an aqueous solution of 2.00 mol dm^{-3} benzoic acid (**FA 2**) is first prepared. Subsequently, in separate experiments, different volumes of **FA 2** and **FA 1** are mixed while keeping the total volume of the reaction mixture constant. In each experiment, the temperature rise, ΔT, is to be determined. A graph of ΔT against volume of **FA 1** used is then plotted. Data from the graph can then be used to determine: • the ΔT_{max}, • the concentration of **FA 1**, • the enthalpy change of neutralisation between **FA 1** and **FA 2**. It is given that 4.18 J is required to raise the temperature of 1 cm^3 of any solution by 1 ^oC.		
	(a)	Write an equation to represent the standard enthalpy change of neutralisation between sodium hydroxide and benzoic acid. [1]	
		$C_6H_5COOH(aq) + NaOH(aq) \rightarrow C_6H_5COO^-Na^+(aq) + H_2O(l)$	
	(b)	**(i)**	Write a detailed plan to prepare 2.00 mol dm^{-3} solution of **FA 2**. [3]
		<u>To prepare 250.0 cm^3 of 2.00 mol dm^{-3} benzoic acid (**FA 2**)</u> Molar mass of $C_7H_6O_2$ = 122 g mol^{-1}	

1) Amount present in 250.0 cm^3 of 2.00 mol dm^{-3} solution = 61.0 g

2) Use a weighing balance to measure accurately 61.0 g (minimum 61.0 g or maximum 62.0 g) of solid $C_7H_6O_2$ in a clean and dry 3) weighing bottle. Record the mass of the solid and the weighing bottle.

4) Dissolve the solid 5) in a 100 cm^3 / 250 cm^3 beaker with 30 cm^3 of water.

6) Transfer the solution and washings 7) into a 250 cm^3 graduated flask/ volumetric flask and 8) make up to the mark dropwise with deionized / distilled water

9) Shake the solution to obtain a homogeneous solution and label it **FA 2**.

10) Reweigh the emptied weighing bottle. / Alternative: wash the weighing bottle in the procedure

if student calculate 61g but use an alternative value ignore

(ii) It is predicted that the maximum temperature change for the neutralisation would occur when the volume of **FA 1** mixed is between 25 cm^3 and 30 cm^3. The total volume of any mixture should be kept constant at 50 cm^3.

Write a detailed plan on how you could determine the temperature changes for the series of reactions between **FA 1** and **FA 2**.

Your plan should include details of:

- all essential experimental details,
- appropriate volumes of solutions to be used,
- a tabulation of the experimental data to be collected (including volumes used),
- how these measurements can be used to obtain the temperature change, ΔT

Procedure

1) Place a dry polystyrene cup into a 250 cm^3 beaker.

2) Use a 50 cm^3 / 100 cm^3 measuring cylinder/burette 3) to transfer 20 cm^3 of **FA 1** into the styrofoam cup labelled **FA 1**

4) Use a 50 cm^3 / 100 cm^3 measuring cylinder/burette 5) to transfer 30 cm^3 of **FA 2** into another styrofoam cup labelled **FA 2**

6) Use a thermometer 7) to measure the temperature of the **FA 1** and **FA 2** solution separately. Record as T_{FA1} and T_{FA2} respectively.

8) Transfer the contents of **FA 2** cup to the **FA 1** cup.

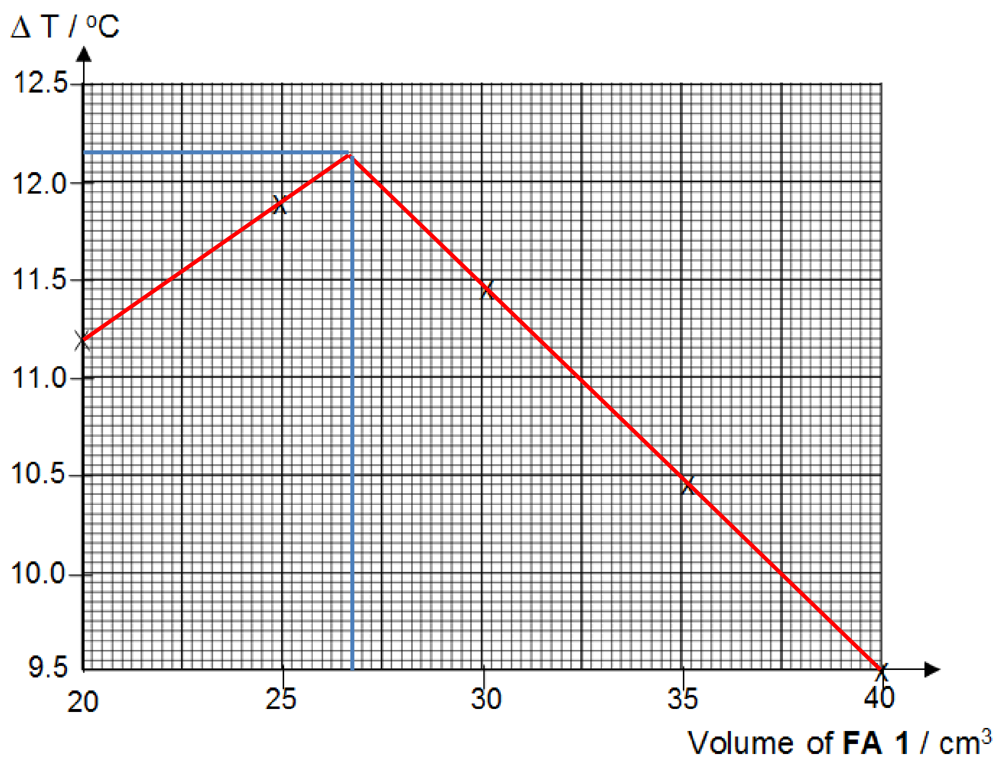
9) Stir the mixture gently using the thermometer provided.

10) Record the maximum/highest temperature reached. 11) Record as T_{max}. Wash and dry both the **FA 1** and **FA 2** styrofoam cups.

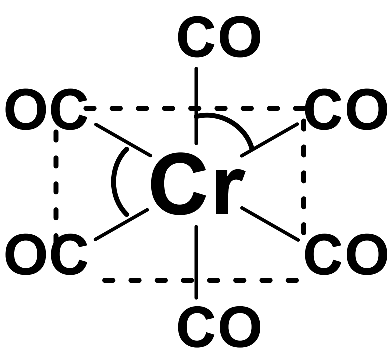
12) Repeat steps 1 to 8 for Mixtures 2 to 5

Tabulation:

Vol of **FA 1** / cm^3	Vol of **FA 2** / cm^3	Initial temperature of **FA 1** / °C	Initial temperature of **FA 2** / °C	Average temperature / °C	Highest temp / °C	ΔT, / °C
20.00	30.00					
25.00	25.00					
30.00	20.00					
35.00	15.00					
40.00	10.00					

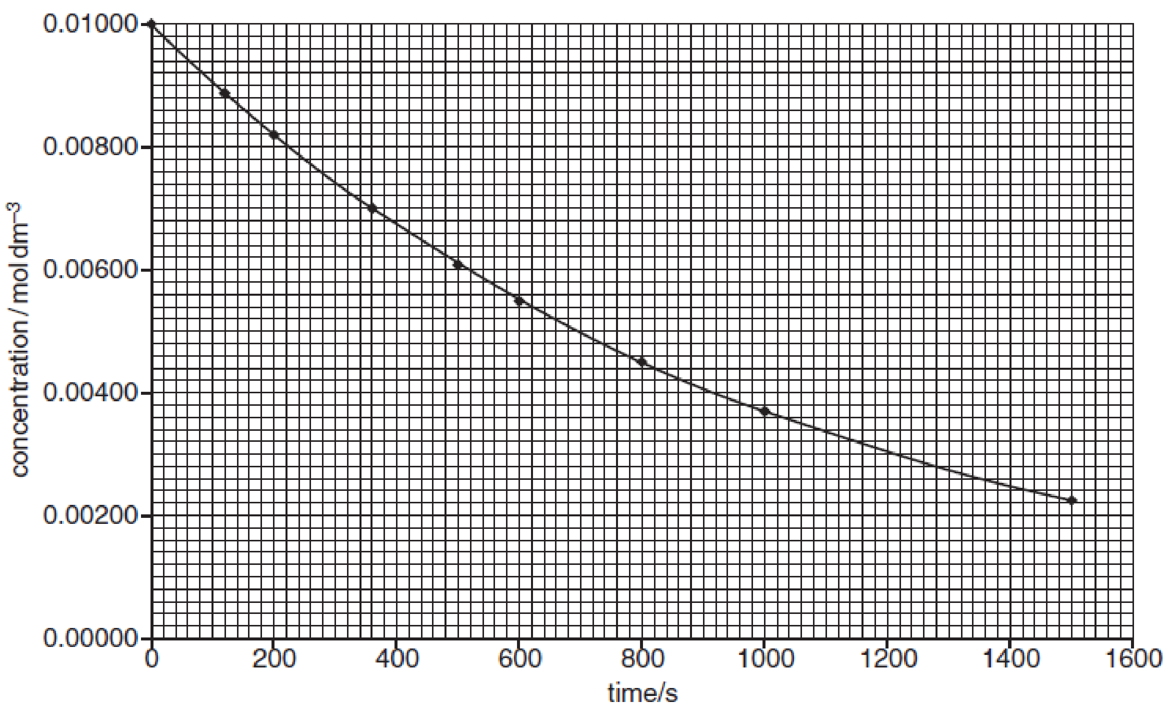
	(b)	**(iii)**	The following plots were plotted on a grid after another similar experiment was conducted. Draw suitable graphs through the plotted points. [1]
		 	
	(c)	By using the graph in **(b)(iii)**, calculate • the concentration of **FA 1**, given that the total volume of the mixture is 50 cm^3. • the enthalpy change of neutralisation for the reaction between **FA 1** and **FA 2**. [2]	
		Volume of **FA 1** (NaOH) used when temperature change is maximum = 26.50 to 26.80 cm^3 No of moles of benzoic acid used = (50-26.75)/1000 x 2.0 = 0.0465 mole NaOH ≡ benzoic acid No of moles of NaOH (**FA 1**) used = 0.0465 mole	

		Concentration of sodium hydroxide in **FA 1** = 0.0465/ 0.02675 = 1.738 mol dm^{-3} = 1.74 mol dm^{-3} From graph, maximum ΔT = 12.15 °C q when ΔT is highest = 50 × 4.18 × 12.15 = 2539 J No of moles of water formed = 0.0470 Enthalpy change of neutralisation between NaOH and benzoic acid = − 2539 /0.0465 = − 54.6 kJ mol^{-1}
		[Total: 12]

2	**(a)**	Chromium carbonyl, also known as chromium hexacarbonyl, is a chemical compound with the formula $Cr(CO)_6$. $Cr(CO)_6$ is zerocovalent, meaning that Cr has an oxidation state of 0. Draw the structure of the complex and state the shape and bond angle around the Cr atom in the complex.	
			 Shape: Octahedral Bond Angle: **90º**
			[2]
	(b)	Chromium hexacarbonyl undergoes the following ligand replacement reaction. $Cr(CO)_6 + PR_3 \longrightarrow Cr(CO)_5PR_3 + CO$	

Two separate experiments were carried out to study the rate of this reaction.

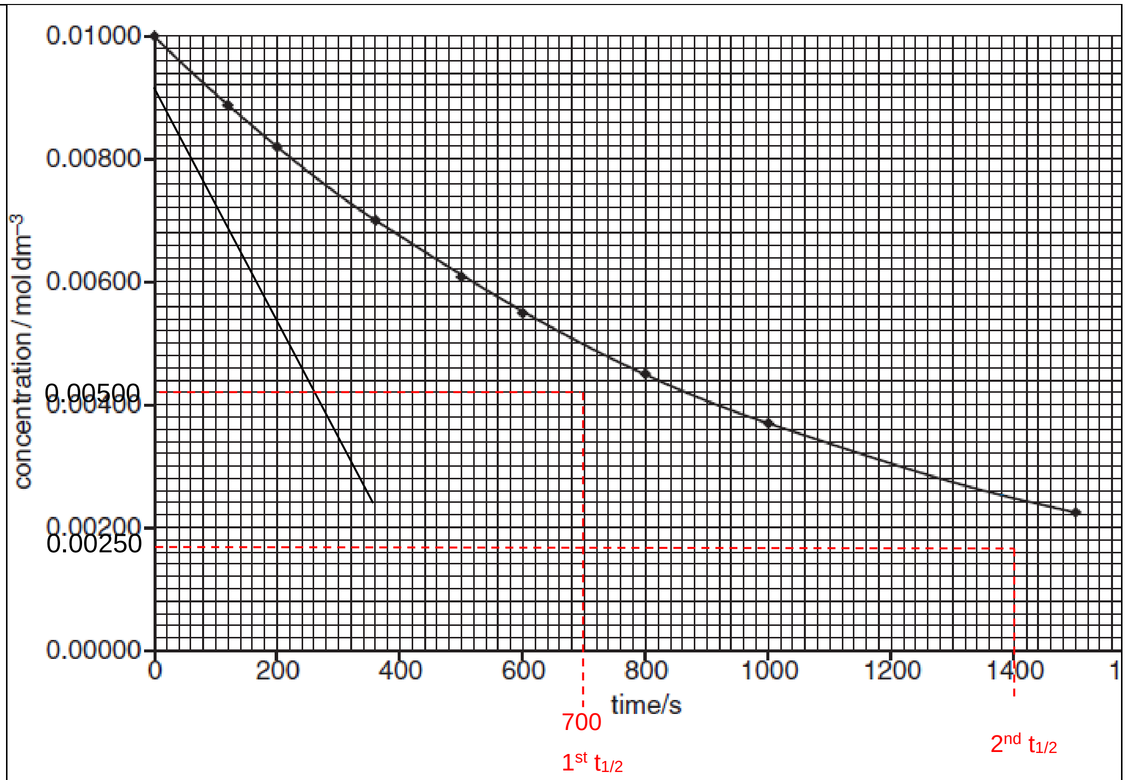
In the first experiment, the ligand PR_3 was in a large excess and $[Cr(CO)_6]$ was measured against time. The results are shown on the graph below.



In the second experiment, $Cr(CO)_6$ was in a large excess, and $[PR_3]$ was measured against time. The following results were obtained.

time / s	**$[PR_3]$ / mol dm^{-3}**
0	0.0100
120	0.0076
200	0.0060
360	0.0028

(i) On the graph, plot the data given in the table.



[1]

(ii) Use the graphs to determine the order of reaction with respect to $Cr(CO)_6$ and PR_3. In each case explain how you arrived at your answer.

$Cr(CO)_6$

At least 2 sets of half-life clearly labelled on the graph for experiment 1

$t_{1/2}$ = 700 s

the order of reaction with respect to $[Cr(CO)_6]$ is one.

PR_3

because (b) PR_3 graph is a straight line with a constant gradient or line shows a constant rate of reaction or no change in rate or shows a linear decrease the order of reaction with respect to $[PR_3]$ is zero.

[2]

(iii) Write the rate equation for the reaction, and calculate a value for the rate constant, stating the units of the rate constant.

			rate = k[$Cr(CO)_6$] $t_{1/2} \approx 700$ s $k = \ln 2 / t_{1/2} = 0.693/700 = 9.9 \times 10^{-4}\ s^{-1}$ OR alternative method using initial rate method. Initial Rate Method Gradient = (0.01 – 0.00099) / (0 - 800) = - 9.9×10^{-4} Take modulus and ignore the negative sign; hence rate is 9.9×10^{-4}.
			[3]
		(iv)	Two possible mechanisms for this reaction are given below. State the mechanism which is consistent with the rate equation you have written in **(b)(iii)** and explain your answer. **Mechanism A** $Cr(CO)_6 \rightarrow Cr(CO)_5 + CO$ slow $Cr(CO)_5 + PR_3 \rightarrow Cr(CO)_5PR_3$ fast **Mechanism B** $Cr(CO)_6 + PR_3 \rightarrow$ [OC- - -$Cr(CO)_4$- - -PR_3] $\rightarrow Cr(CO)_5PR_3 + CO$ (transition state)
			mechanism A is consistent because it has a slow step (Step 1) involving one mole / molecule of $Cr(CO)_6$
			[2]
			[Total: 10]

3 This question refers to compounds of calcium and barium.

(a) Oil paints contain traces of red Ca^{2+} and green Ba^{2+} ions which give them their characteristic red and green colours respectively. Oil painting is typically done on canvas. During the manufacturing process of canvas, hydrogen orthoperiodate ions, HIO_6^{4-}, is left on the canvas.

Orthoperiodate salts are formed when orthoperiodate ions, IO_6^{5-}, reacts with the Ca^{2+} and Ba^{2+} ions in the paint, causing the decolourisation of the red and green colour of the paint. The equations below show the formation of IO_6^{5-} and its salts.

$$HIO_6^{4-}\,(aq) \rightleftharpoons H^+\,(aq) + IO_6^{5-}\,(aq) \qquad K_a = 4.04 \times 10^{-6}\ \text{mol dm}^{-3}$$

$$5\,M^{2+}\,(aq) + 2\,IO_6^{5-}\,(aq) \rightarrow M_5(IO_6)_2\,(s) \qquad \text{where } M^{2+} \text{ is } Ca^{2+} \text{ or } Ba^{2+}$$

Relevant K_{sp} values are given in the table below :

Salt	$\boldsymbol{K_{sp}}$
$Ca_5(IO_6)_2$	4.0×10^{-9}
$Ba_5(IO_6)_2$	1.6×10^{-15}

The painting was stored in a display cabinet at a low pH environment. Over the weekend, the electrical supply of the display cabinet was disrupted which resulted in an increase of the environment's pH. It was found that the green portions of the painting were decolourised due to the formation of solid barium orthoperiodate, $Ba_5(IO_6)_2$.

Explain qualitatively why the green coloured areas of the painting were decolourised but not the red coloured areas when the pH increased.

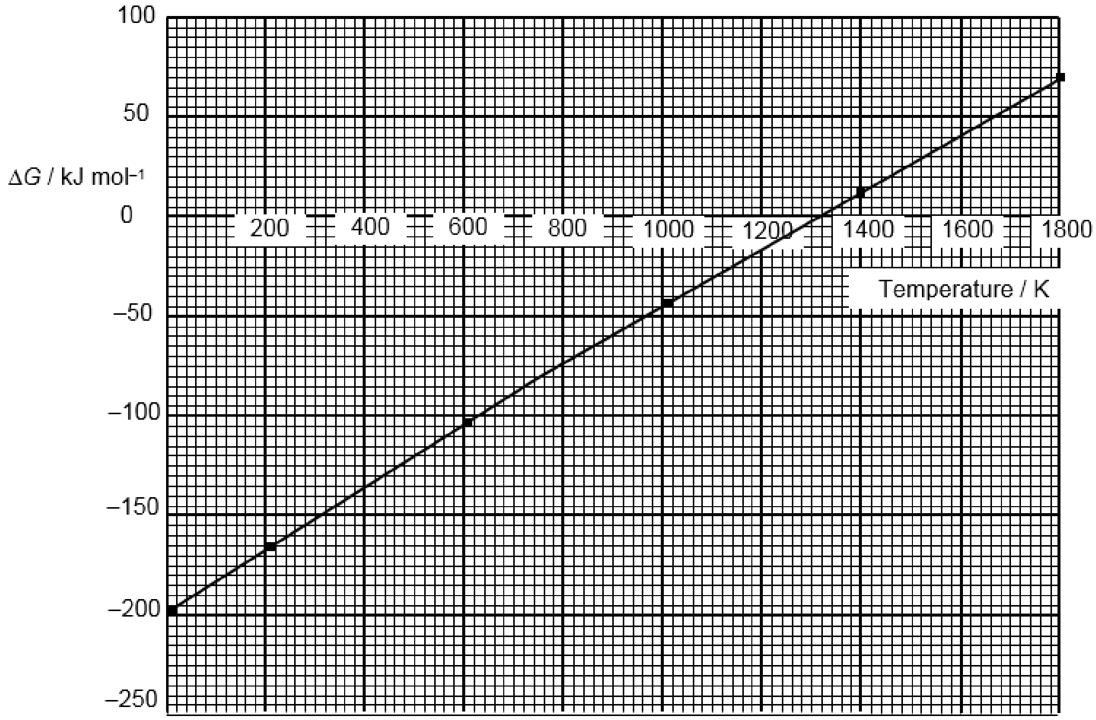
		When pH increases, $[H^+]$ decreases, resulting in the equilibrium shifting right to produce H^+ ions by LCP. Thus the concentration of IO_6^{5-} ions is high as the position of equilibrium shifts towards the right. Hence IP of $Ba_5(IO_6)_2$ is higher than that of its K_{sp} and hence the precipitate of barium orthoperiodate, $Ba_5(IO_6)_2$ forms and the green coloured area containing barium ions were decolourised However, $Ca_5(IO_6)_2$ has higher K_{sp} value and hence do not precipitates easily even with this increase in concentrations of IO_6^{5-} ions, the resulting ionic product of Ca^{2+} ions and IO_6^{5-} ions still does not exceeds the K_{sp}, hence the precipitate of $Ca_5(IO_6)_2$ is not formed and the red coloured area containing calcium ions is not being affected.	
			[3]

(b) ΔG, ΔH and ΔS are related by the following equation.

$$\Delta G = \Delta H - T\Delta S$$

The Ellingham diagram below shows how ΔG changes between 0 K and 1800 K for the following reaction.

$$CaO\ (s) + H_2O\ (l) \rightarrow Ca(OH)_2\ (s)$$



For the range of temperatures in the graph above, it can be assumed that the enthalpy change and the entropy change of the reaction remain approximately constant.

(i) Predict the sign of ΔS for the reaction, showing your reasoning.

The ΔS is negative as there is a decrease in the number of liquid molecules, and hence, the system becomes less disordered / there are lesser ways or arranging the particles in the system.

OR Based on the equation: ΔG = ΔH - TΔS; since the graph is a plot of the ΔG against T, rearranging the equation will give ΔG = (-ΔS)T + ΔH

which correspond to $y = (m)\,x + C$

Hence the gradient of the graph (m) is (-ΔS).

[Turn Over

			[2]
		(ii)	Using the graph, calculate ΔS.
			m = (-200 - 70/0 -1800) = 0.150 (0, -200) & (1800, 70) ΔS = - 0.150 kJ mol^{-1} K^{-1} *Based on the equation: ΔG = ΔH - TΔS; since the graph is a plot of the ΔG against T, rearranging the equation will give ΔG = (-ΔS)T + ΔH* *which correspond to y = (m) x + C* *Hence the gradient of the graph (m) is (-ΔS).*
			[1]
		(iii)	Using the graph, determine ΔH.
			ΔH = -200 kJ mol^{-1}
			[1]
		(iv)	Determine the temperature above which the reaction become non-spontaneous.
			1320K
		[1]	
		[Total: 8]	

4 The table below gives data about some physical properties of the elements calcium, copper and chromium.

Physical Property	**Calcium**	**Copper**	**Chromium**
Relative atomic mass	40.1	63.5	52.0
Atomic radius / nm	0.197	0.128	0.117
Density / g cm^{-3}	1.54	8.92	7.20
First Ionisation Energy / kJ mol^{-1}	590	745	653

(a) **(i)** Explain why the first ionisation energy of copper and chromium are both higher than that of calcium.

- Copper and chromium have more protons and hence higher nuclear charge than calcium.
- The additional electrons of the d-block metals are in the inner 3d subshell which provide relatively poor shielding for the outermost / valence / 4s electrons.
- Hence, the outermost / valence / 4s electrons of the copper and chromium are attracted more strongly to the nucleus, resulting in higher ionization energy.

[2]

(ii) Use relevant data from the table to explain qualitatively why the densities of copper and chromium are significantly greater than that of calcium.

Copper and chromium have larger atomic masses (63.5 & 52.0) than Ca (40.1) and have smaller atomic radii . This leads to smaller volume. Since density = $\frac{mass}{volume}$, hence the densities of copper and chromium are significantly greater than that of calcium.

[1]

(b) Chromium (III) nitrate is more acidic than chromium (II) nitrate. Explain with the aid of a relevant equation.

		A solution of Cr^{3+} is more acidic due to the higher charge density of the cation. $[Cr(H_2O)_6]^{3+}(aq) \rightleftharpoons [Cr(OH)(H_2O)_5]^{2+}(aq) + H^+(aq)$;
		[2]
	(c)	When a particular copper ore was reduced, an alloy was produced which was composed mainly of copper, but with gold and chromium impurities. It contained no other metal. In order to purify it, the alloy was made the anode of an electrolytic cell, with a pure copper cathode and aqueous copper (II) sulfate as the electrolyte. Explain, with reference to E^θ values, what happens to the gold and chromium impurities during this purification process. The electrode reaction for the standard Au^{3+}/Au half cell is Au^{3+} (aq) + 3e $\rightleftharpoons$ Au (s) E^θ = +1.50 V
		Cu^{2+} (aq) + 2e $\rightleftharpoons$ Cu (s) E^θ = + 0.34 V Cr^{3+} (aq) + 3e $\rightleftharpoons$ Cr (s) E^θ = – 0.74 V ; or Cr^{2+} (aq) + 2e $\rightleftharpoons$ Cr (s) E^θ = – 0.91 V ; ignore all other eqns Quoting of E values from data booklet - • Impurities with E^θ more positive than Cu like Au will fall off as anode sludge • When an electric current is applied, copper at the anode (+), together with Cr which are more easily oxidized than Cu due to their more negative E^θ values, are oxidized to their ions. Cu^{2+} and Cr^{3+}, then migrate to the cathode • At the cathode, only Cu^{2+} ions are reduced to Cu due to its more positive E^θ . Cr^{3+} remain as ions in the solution as they do not reduce to metals easily.
		[3]

	(d)	A current of 1.8 A was passed through the cell described in **(c)** for 17 minutes, and the electrodes removed, washed, dried and weighed. It was found that some mass was lost from the anode. After filtering it off and drying it, the deposit below the anode weighed 0.085 g. On adding an excess of hydroxide ions to the electrolyte, a grey-green precipitate was formed. Its mass was 0.304 g. (You may assume that negligible amount of copper ions remained in the electrolyte.)	
		(i)	Calculate the expected increase in mass of the cathode.
			Q = It = 1.8 x 17 x 60 = 1836 C Amt of Cu deposited = 1836/ (96500 x 2) = 9.51x 10^{-3} mol Mass of Cu deposited = expected increase in mass of cathode = 9.51x 10^{-3} mol x 63.5 = 0.604 g
			[2]
		(ii)	Identify the grey-green precipitate.
			grey-green precipitate: chromium (III) hydroxide OR $Cr(OH)_3$;
			[1]
		(iii)	It was found that the mass of copper removed from the alloy was 0.466 g. Calculate the masses of gold and chromium removed from the alloy. Hence calculate the total mass lost by the anode.
			Mass of gold removed = 0.0850 g Amt of $Cr(OH)_3$ = 0.304/ (52+3x17) = 0.00295 mol Mass of Cr removed = 0.00295 x 52.0 = 0.153 g Actual mass lost by anode =0.466 + 0.153 + 0.085 = 0.704 g
			[3]
			[Total: 14]

[Turn Over

5 (a) A student conducted an experiment to identify the trend in thermal stability of hydrogen halides. The reaction occurred according to the following equation:

$$2HX(g) \rightleftharpoons H_2(g) + X_2(g)$$

The approximate K_c values for the above equilibrium at 500°C is shown in the table below.

.

Temperature /°C	***K*c**		
	HC*l*	**HBr**	**HI**
500	10^{-13}	10^{-9}	10^{-5}

(i) Using the Data Booklet, explain the trend in thermal stability of hydrogen halides down the group.

	H – C*l*	**H – Br**	**H – I**
Bond energy/ kJ mol^{-1}	431	366	299

Quoting of bond energy values from data booklet

- Down the group, the size of the halogen increases, therefore the orbitals overlap becomes less effective .
- the bond strength becomes weaker, so H – X bond is more easily broken.
- Hence, the thermal stability of the hydrogen halides decreases down the group

[2]

(ii) Hence, deduce if the trend in **(a)(i)** agrees with the K_c data given above.

As Kc becomes more positive / increases, there are more products

Hence this agrees with (a)(i).

[1]

(b) A student conducted another experiment to distinguish between samples of sodium chloride and phosphorus pentachloride. It was found that red onion water can be used as an indicator. The table below shows the colour of the indicator at various pH.

pH	**Colour**
Less than 7	Red
7	Violet

(i) T To each unknown sample of chlorides, he added a few drops of red onion water. He recorded the colour of the indicator. Predict the identities of the chlorides.

Colour of red onion water	**Identity of chloride**
Red	**Phosphorus pentachloride**
Violet	**Sodium chloride**

[1]

(ii) With the aid of an equation, describe the action of water on phosphorus pentachloride.

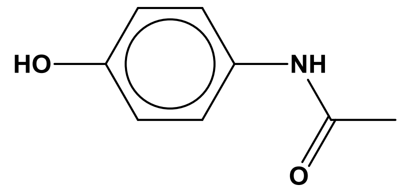
PCl_5 undergo hydrolysis readily in water to form a strongly acidic solution.

In excess water: $PCl_5\,(s) + 4H_2O\,(l) \rightarrow H_3PO_4\,(aq) + 5HCl\,(aq)$

[2]

[Total: 6]

6 Paracetamol is an effective analgesic discovered by Joseph von Mering in 1893. Its structure is as shown.

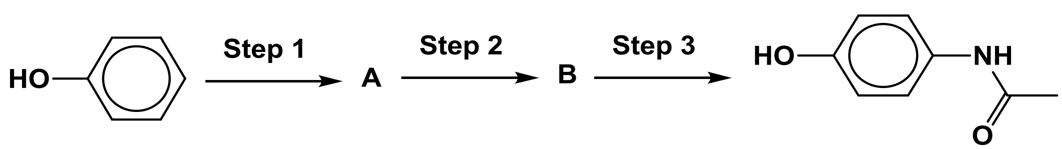


(a) Explain why all the carbon-carbon bonds in benzene are of the same length.

In benzene ring, the pi electrons / pi bonds are delocalized over the 6 C and hence, the C-C bond length are the same.

[1]

(b) **(i)** Paracetamol may be synthesised from phenol as shown.



State the reagents and conditions for steps **1** to **3**. Draw the structure of the intermediate product **B**.

[4]

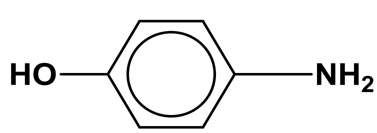
Reagents and conditions:

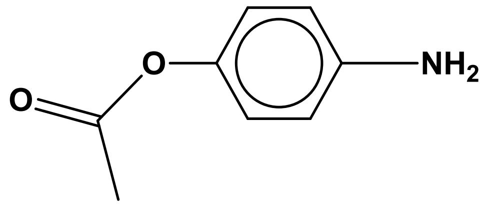
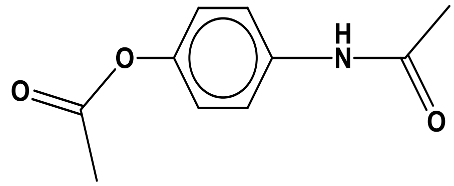
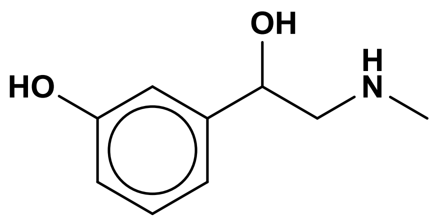
Step 1: HNO_3 (aq), room temperature

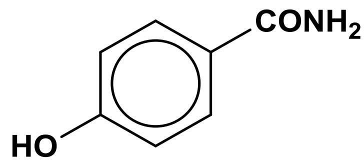
Step 2: Sn, conc. HC*l* heat, followed by (careful neutralisation with) NaOH; *if first part of step 2 is wrong, then no mark for second part even if second part is correct.*

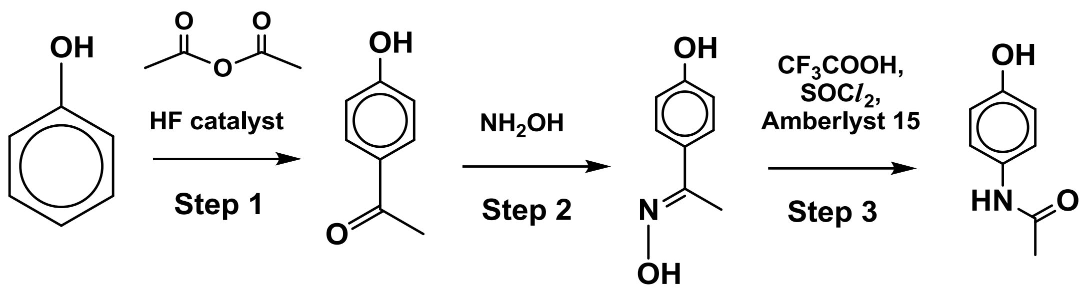
Step 3: CH_3COCl, room temperature

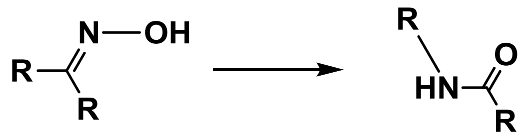
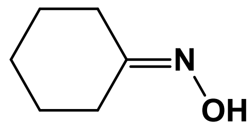
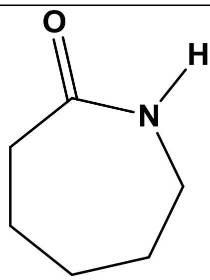
Structure of **B**

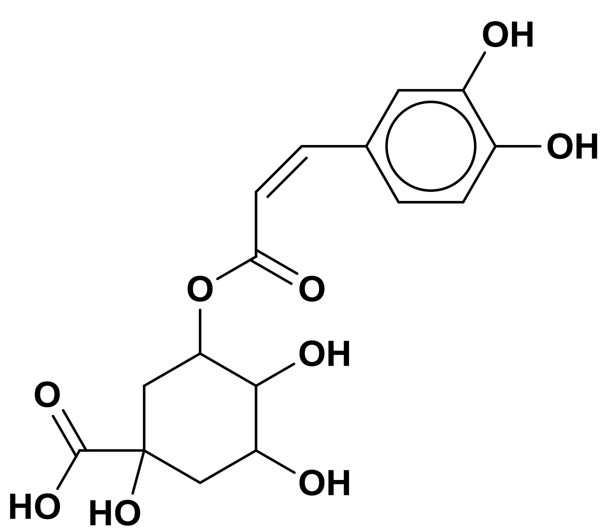


		(ii)	Based on **Step 3** of the given reaction scheme, draw the structure of a possible side-product.
			 or 
			[1]
		(iii)	Phenylephrine is a decongestant which may be taken with paracetamol when a person is suffering from cold. The structure of phenylephrine is as shown.  State and explain how the basicity of phenylephrine might compare with that of paracetamol.
			Phenylephrine is more basic than paracetamol. Paracetamol has an amide group, in which the lone pair of electrons on N is delocalised over O-C-N bond / into the benzene ring and therefore is unavailable to accept H^+. For phenylephrine, it has a primary amine. The 2 electron donating R groups makes the lone pair of electrons on N more available to accept H^+.
			[2]

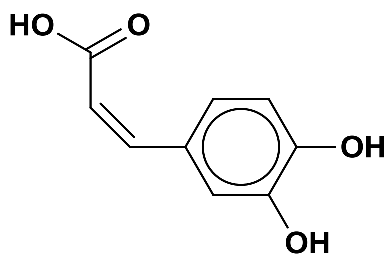
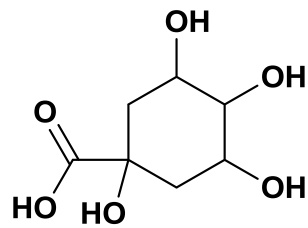
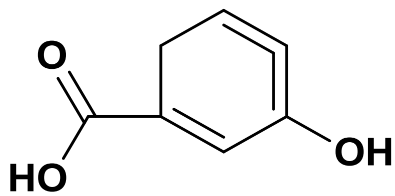
		(iv)	Suggest a simple chemical test to distinguish between paracetamol and compound **A**.  **Compound A**
			Add NaOH (aq) to each of the compound separately and heat. Insert a glass rod dipped with concentrated HC*l* into each test-tube. For compound A, a colourless pungent gas is evolved and forms white fume. For paracetamol, there is no evolution of colourless, pungent gas and hence, no white fumes is seen. OR Add NaOH (aq) to each of the compound separately and heat. For compound A, a colourless pungent gas is evolved and turns moist red litmus paper blue. For paracetamol, there is no evolution of colourless, pungent gas. The moist litmus paper remains red.
			[2]

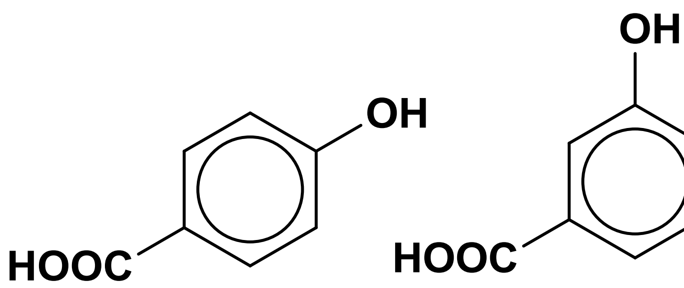
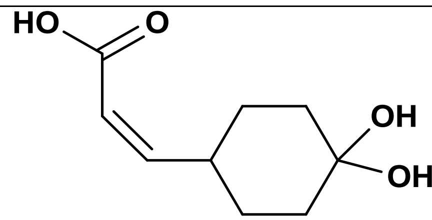
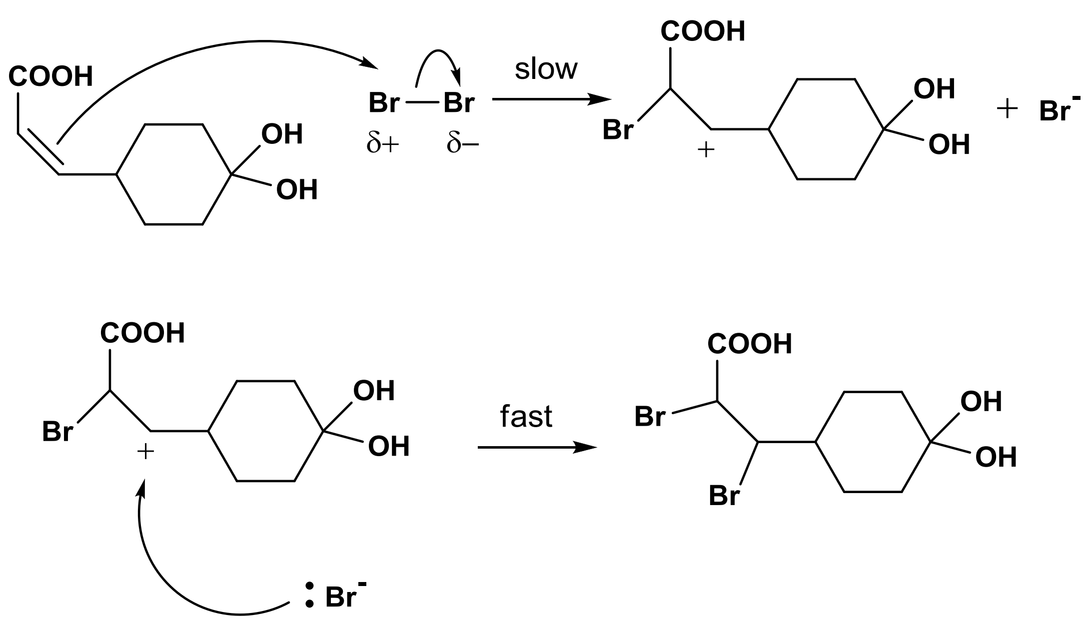
	(c)	**(i)**	Hoechst and Celanese discovered a simpler synthetic route for paracetamol as shown.  State the types of reaction for steps **1** and **2**.
			[2]
			Step 1: Electrophilic substitution Step 2: Condensation / Addition-elimination

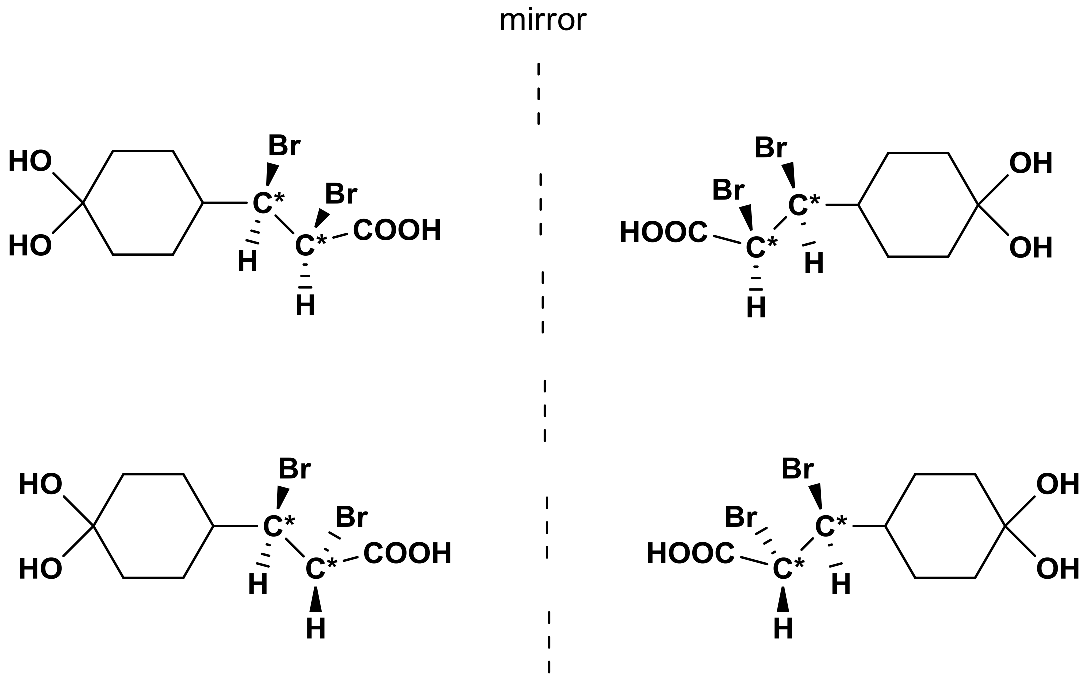
		(ii)	Step **3** is known as the Beckmann arrangement, where an oxime is converted into an amide.  **Oxime** **Amide** Draw the structure of the product formed when  undergoes the Beckmann arrangement.
			
			[1]
			[Total: 13]

7	Coffee beans contain chlorogenic acid, which is an antioxidant and an important biosynthetic intermediate. The structure of chlorogenic acid is as shown. 

[Turn Over

	(a)	State the number of moles of hot NaOH (aq) that will react with 1 mole of chlorogenic acid.
		[1]
		4 mol
	(b)	On heating with dilute acid, chlorogenic acid produces two compounds, **X** and **Y**.  Compound **X**  Compound **Y** When compound **Y** reacts with hot excess concentrated sulfuric acid, a product with a molecular formula of $C_7H_6O_3$ is formed. A student claims that the product formed has the following structural formula but the teacher disagrees.  Draw the correct structure of the product and explain what is wrong with the student's answer.

		The product formed is unstable as there is ring strain. Or sp hybridized C should have linear shape but this is not possible in a ring structure and hence it is unstable.  	
		[2]	
	(c)	 Compound **Z**	
		(i)	Compound **Z** reacts with Br_2 (*l*) at room temperature and in the dark. Describe the mechanism showing curly arrows, charges, dipoles and any relevant lone pairs.
			Electrophilic addition 
			[3]

		(ii)	The product of **(c)(i)** exists as a mixture of 4 stereoisomers. State the type of isomerism exhibited by the product and draw all the stereoisomers.
			Optical isomerism 
			[3]
			[Total: 9]

End of Paper