VICTORIA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME ………………………………………………………………..

CT GROUP ………………………………..

CHEMISTRY **9729/02**

Paper 2 Structured Questions **15 September 2022**

Candidates answer on the Question Paper. **2 hours**

Additional Materials: *Data Booklet*

READ THESE INSTRUCTIONS FIRST

Write your name and CT group in the space at the top of this page.
Write in dark blue or black pen.
You may use a HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

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

A Data Booklet is provided.

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

For Examiner's Use	
1	/ 25
2	/ 13
3	/ 12
4	/ 19
5	/ 6
Total	/ 75

This document consists of **18** printed pages.

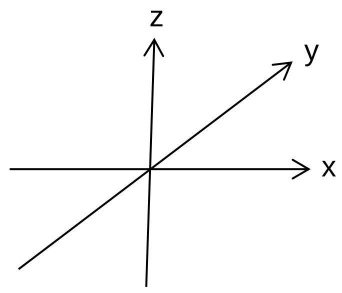
1 (a) The most common oxidation states of iron are +2 and +3.

(i) Iron(II) and iron(III) both contain electrons in all five 3d orbitals.

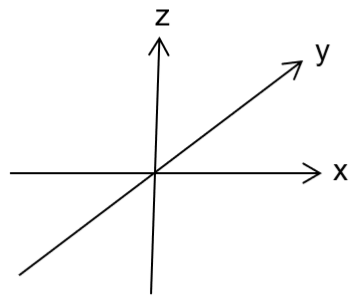
Sketch and label the shape of the following two 3d orbitals:

- one 3d orbital from the lower energy level in an octahedral complex
- one 3d orbital from the higher energy level in an octahedral complex

Use the axes below.



lower energy level



higher energy level

(ii) Explain why Fe^{2+}(aq) ions are coloured, whereas Zn^{2+}(aq) ions are colourless.

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[3]

(iii) Most naturally occurring samples of iron(II) oxide are found as the mineral wüstite. Wüstite has formula $Fe_{20}O_x$. It contains both Fe^{2+} and Fe^{3+} ions. 90% of the iron is present as Fe^{2+} and 10% is present as Fe^{3+}.

Deduce the value of *x*.

[1]

When aqueous solutions of $S_2O_8^{2-}$ and tartrate ions, $C_4H_4O_6^{2-}$, are mixed, the reaction proceeds very slowly. However, this reaction proceeds quickly in the presence of an Fe^{3+}(aq) catalyst. The overall equation for this reaction is as shown.

$$C_4H_4O_6^{2-} + 3S_2O_8^{2-} + 2H_2O \rightarrow 2CO_2 + 2HCO_2^{-} + 6H^{+} + 6SO_4^{2-}$$

(iv) State and explain the type of catalyst that Fe^{3+}(aq) functions in the above reaction.

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[1]

(v) Write two equations to show how Fe^{3+}(aq) functions as a catalyst in this reaction.

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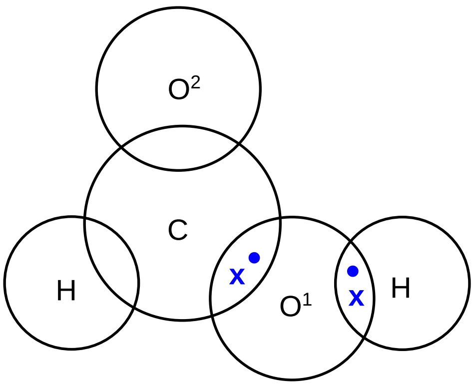
[2]

(b) (i) Complete the 'dot-and-cross' diagram below, drawing the outer electrons only, to show the bonding in methanoic acid, HCO_2H. The two oxygen atoms in HCO_2H are labelled O^1 and O^2 respectively.



[1]

(ii) The carbon atom in HCO_2H is sp^2 hybridised. Explain what is meant by sp^2 hybridisation with reference to the carbon atom in HCO_2H.

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[1]

(iii) Similar to carbon, oxygen atom can also undergo hybridisation. By considering the number of electron densities around oxygen atom labelled O^1, suggest the type of hybridised orbitals for the oxygen atom labelled O^1.

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[1]

(iv) Sketch a diagram to show how two sp^2 hybridised orbitals can form a sigma bond.

[1]

(c) Cyclohexane is immiscible with water. Iodine, I_2, can dissolve in both water and cyclohexane. The expression and numerical value for the partition coefficient, K_{pc}, of iodine between cyclohexane and water are given below.

$$K_{pc} = \frac{\text{concentration of } I_2 \text{ in cyclohexane}}{\text{concentration of } I_2 \text{ in water}} = 93.8$$

(i) 15.0 cm^3 of C_6H_{12} is shaken with 20.0 cm^3 of an aqueous solution containing I_2 until no further change is seen. It is found that 0.390 g of I_2 is extracted from water into the C_6H_{12}. Calculate the mass of I_2 that remains in the aqueous layer. Show your working.

[2]

(ii) Suggest how the value of K_{pc} of I_2 between hexa-2-one, $CH_3(CH_2)_3COCH_3$, and water would compare to the value given in **(c)**. Explain your answer.

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[2]

(d) Some data relating to calcium and oxygen are listed in Table 1.1.

Table 1.1

process	value / kJ mol^{-1}
first ionisation energy of oxygen	+1310
second ionisation energy of oxygen	+3390
first electron affinity of oxygen	–142
second electron affinity of oxygen	+844
enthalpy change for $\frac{1}{2}O_2(g) + 2e^- \rightarrow O^{2-}(g)$	+951
enthalpy change for $Ca(s) \rightarrow Ca^{2+}(g) + 2e^-$	+1933
lattice energy of CaO(s)	–3517

(i) Suggest why the first electron affinity of oxygen is negative.

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[1]

(ii) Suggest why the second electron affinity of oxygen is positive.

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[1]

(iii) Oxygen exists as O_2 molecules. Use relevant data from table 1.1 to calculate the bond energy of the O=O bond. Show your working.

[2]

(iv) Use relevant data from Table 1.1 to calculate the enthalpy change of formation of calcium oxide, CaO(s). Show your working.

[2]

(v) The lattice energy of lithium fluoride, LiF(s), is –1022 kJ mol^{-1}. Identify the factor that causes the lattice energy of calcium oxide to be more exothermic than that of lithium fluoride. Explain why this factor causes the difference in lattice energies.

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[2]

[Total: 25]

2 **(a)** Chlorine can be manufactured using the electrolysis of Na*Cl*(aq). At the cathode, H_2(g) and OH^-(aq) are produced. At the anode, the product mixture contains both Cl_2(g) and O_2(g). The mole ratio of each gas depends on the concentration of NaCl(aq).

(i) The half-equation for the cathode reaction is as shown.

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$$

Starting from **neutral** Na*Cl*(aq), write half-equations for the production of the following at the anode.

- O_2(g),
- Cl_2(g).

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[2]

(ii) Explain why the Cl_2(g) : O_2(g) mole ratio increases as concentration of Na*Cl*(aq) increases.

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[2]

(iii) Sodium chlorate(V) is prepared commercially by electrolysing Na*Cl*(aq) in a cell that allows the electrolytes at cathode and anode to mix. The cathode reaction is the same as that described in **(i)**. The equation for the anode reaction is as shown.

$$Cl^-(aq) + 6OH^-(aq) \rightarrow ClO_3^-(aq) + 3H_2O(l) + 6e^-$$

Calculate the mass of $NaClO_3$ that is produced when a current of 250 A is passed through the cell for 60 minutes.

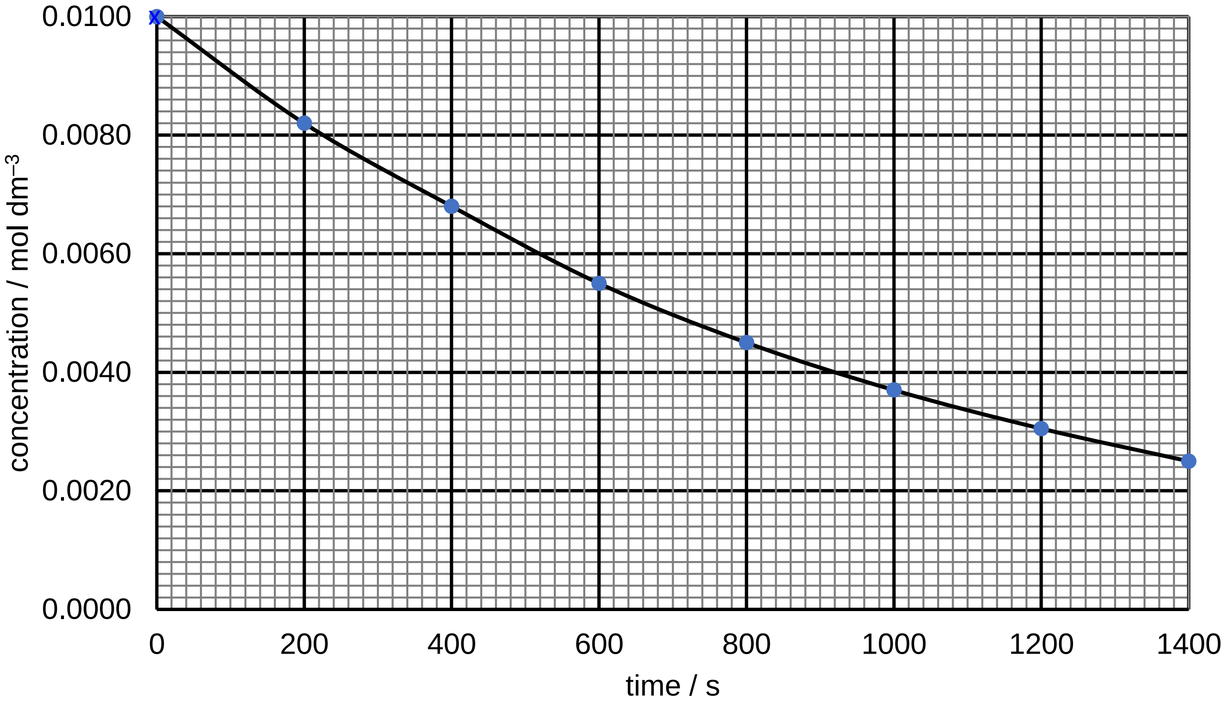
[2]

(b) Trimethylphosphine can act as a ligand, which can be represented as PR_3. Chromium hexacarbonyl undergoes the following ligand exchange reaction with PR_3 as shown below.

$$Cr(CO)_6 + PR_3 \rightarrow Cr(CO)_5PR_3 + CO$$

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 with time. The results are shown on the graph below whereby the y-axis represents the concentration of $Cr(CO)_6$.



In the second experiment, $Cr(CO)_6$ was in a large excess, and $[PR_3]$ was measured with time. Table 2.1 shows the results obtained.

Table 2.1

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

(i) Plot the data given in Table 2.1 on the graph above, using the same axis scales whereby the y-axis represents the concentration of PR_3. Draw the best–fit line through your points. [1]

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

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[2]

(iii) Define the term *rate equation*.

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[1]

(iv) Write the rate equation for the reaction and hence calculate a value for the rate constant including its units.

[3]

[Total: 13]

3 (**a**) The chemistry of some period 3 elements and their compounds are discussed here.

(i) Explain why the first ionisation energy of aluminium is lower than that of magnesium.

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[1]

Table 3.1 shows some information regarding three oxides, **E**, **F** and **G**.

Table 3.1

oxide	melting point / °C	electrical conductivity when molten
E	1713	very poor
F	24	nil
G	2072	good

(ii) These three oxides, in no particular order, are Al_2O_3, SiO_2 and P_4O_6. Identify **E**, **F** and **G**.

E: ………………… **F:** ……………….. **G:** …………………

[1]

(iii) With reference to structure and bonding, account for your answer in **(a)(ii)**.

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[3]

(iv) Suggest the pH values of the mixture formed when **E**, **F** and **G** are added separately to water. Write balanced equations for each of these reactions, where appropriate.

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[2]

(v) Aluminium oxide is *amphoteric*. With the aid of equations, explain the meaning of the term *amphoteric*.

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[2]

(b) The nitrates of strontium and barium decompose on heating, forming the same gaseous products.

Explain whether strontium nitrate would decompose at a higher or lower temperature than barium nitrate.

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[2]

(c) Hydrogen chloride is stable to heat while hydrogen iodide decomposes to hydrogen and iodine when heated with a red-hot steel. Explain why this is so.

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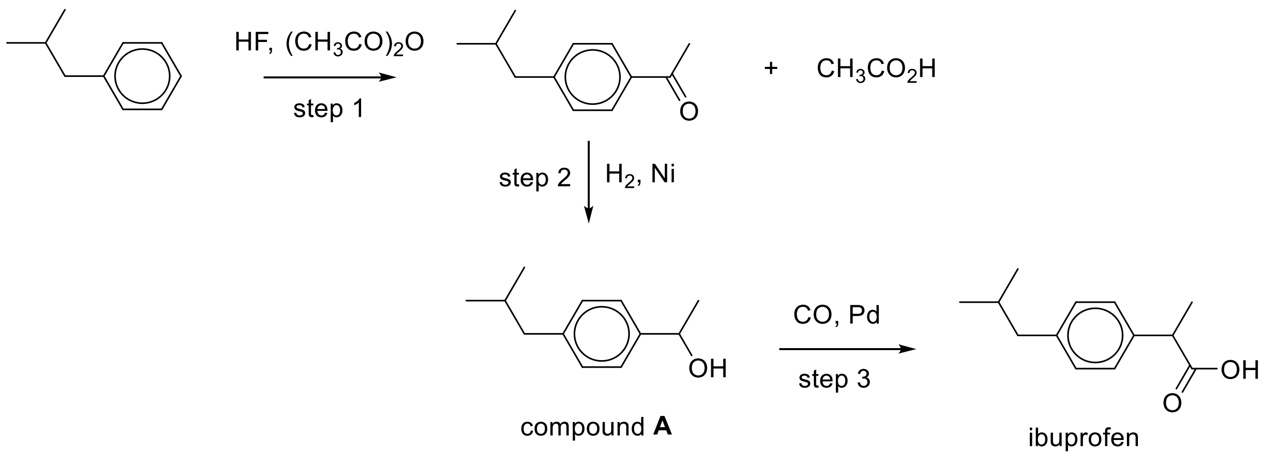
[1]

[Total: 12]

4 Ibuprofen, $C_{13}H_{18}O_2$, a non-steroidal anti-inflammatory drug, is used for the treatment of pain, fever and inflammation.

(a) The industrial synthesis of ibuprofen developed by BHC Company in the 1980s is shown below. This synthetic route proved to be highly successful in terms of its environmental friendliness.



An environmentally friendly chemical process is expected to have a high atom economy, indicating that a high proportion of the starting materials end up as part of the final product, hence reducing the amount of waste.

The atom economy of a process can be calculated using the formula:

$$\text{atom economy} = \frac{\text{molar mass of desired product}}{\text{sum of molar mass of all products}}$$

(i) Calculate the atom economy of the BHC Company process in the synthesis of ibuprofen.

[2]

(ii) Suggest the type of reaction in step 1.

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[1]

(iii) Outline a simple chemical test that could be carried out to distinguish compound **A** from ibuprofen.

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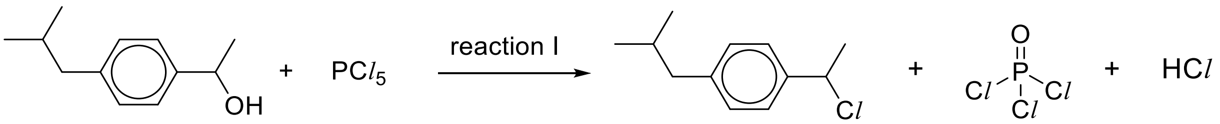
[2]

(iv) Ethanoic anhydride, $(CH_3CO)_2O$, used in step 1 could be regenerated by dehydrating ethanoic acid. In this reaction, 2 mol of ethanoic acid form 1 mol of ethanoic anhydride and 1 mol of water.

Determine the new atom economy if ethanoic acid formed in step 1 is reused in this synthesis.

[1]

(b) Instead of step 3 in **(a)**, compound **A** formed during the BHC Company process can react with PCl_5 to give compound **B** which then undergoes further reactions to yield ibuprofen.

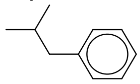


compound **A** compound **B**

The mechanism of converting compound **A** into compound **B** is thought to involve the following three steps.

- The initial nucleophilic attack on P by the lone pair of electrons on the oxygen atom in compound **A** to form a P−O bond together with a loss of Cl^-.
- This is followed by Cl^- acting as a base to abstract a proton.
- The third step involves a nucleophilic attack on a carbon atom by another Cl^- ion together with simultaneous P=O bond formation and P−C*l* bond cleavage to form the products.

(i) Use the information given above to write the three-step full mechanism for the reaction of compound **A** with PCl_5. Show relevant lone pairs and dipoles and use curly arrows to indicate the movement of electron pairs.

You may use R to represent the 

[3]

(ii) Considering the bonds formed in the products, suggest a reason why reaction I goes to completion.

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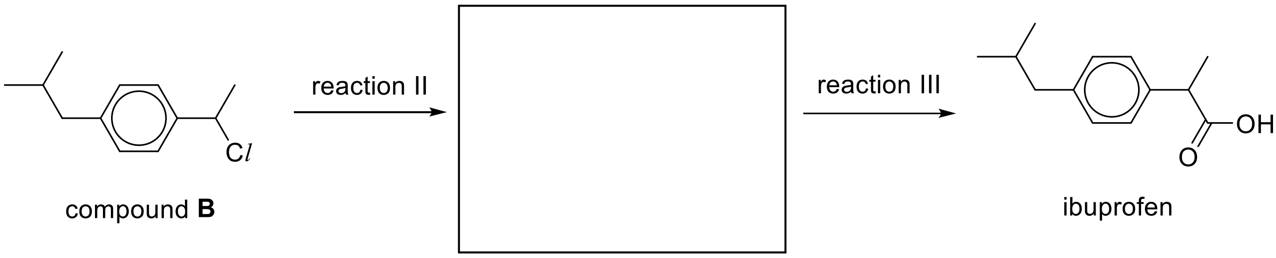
[2]

(iii) Complete the reaction scheme to show how ibuprofen could be synthesised from compound **B** in two steps. Draw the structure of the intermediate and state the reagents and conditions for each step.



intermediate compound

reaction	reagents and conditions
II	
III	

[3]

(c) When Group 2 salts of carboxylic acids are heated, it gives the metal carbonate and a carbonyl compound. For example, when calcium ethanoate is heated, it produces propanone.

$$(CH_3CO_2)_2Ca \rightarrow CaCO_3 + (CH_3)_2CO$$

When this reaction is carried out by heating a 1:1 molar mixture of calcium ethanoate and calcium methanoate, $(HCO_2)_2Ca$, a mixture of three carbonyl compounds is formed, all having $M_r < 60$.

(i) Suggest the structures of the three carbonyl compounds and the ratio in which they might be produced.

Structure of carbonyl compound			
Ratio			

[2]

(ii) Suggest **two** chemical tests that could be used to distinguish the three carbonyl compounds from each other. You should state what you would observe for each compound in each test.

Tests	Observations		
	Structure of compound 1	Structure of compound 2	Structure of compound 3

[3]

[Total: 19]

5(a) Table 5.1 shows some information about the elements, calcium, iron and copper.

Table 5.1

	calcium	iron	copper
Relative atomic mass	40.1	55.8	63.5
Atomic radius (metallic) / nm	0.197	0.126	0.128
Ionic radius (2+) / nm	0.099	0.076	0.069
Melting point / K	1112	1808	1358
Density / g cm^{-3}	1.54	7.86	8.93

(i) Describe the structure and bonding in calcium with the aid of a labelled diagram.

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[2]

(ii) Suggest why the atomic radii of iron and copper are both smaller than that of calcium.

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[2]

(iii) Use information from Table 5.1 to explain why the densities of iron and copper are significantly greater than that of calcium. [No calculations are required.]

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[2]

[Total: 6]