



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.

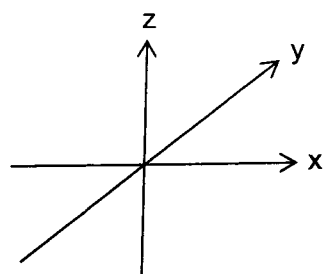
1 (a) The most common oxidation states of iron are +2 and +3.

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

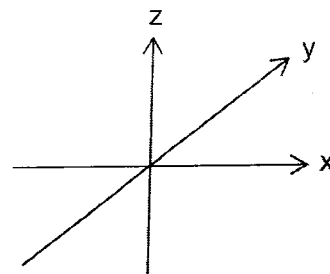
Sketch and label the shape of the following two 3d orbitals:

- 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 $\text{Fe}^{2+}(\text{aq})$ ions are coloured, whereas $\text{Zn}^{2+}(\text{aq})$ ions are colourless.

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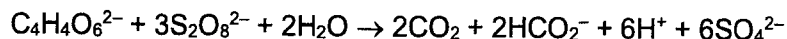
[3]

(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.



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

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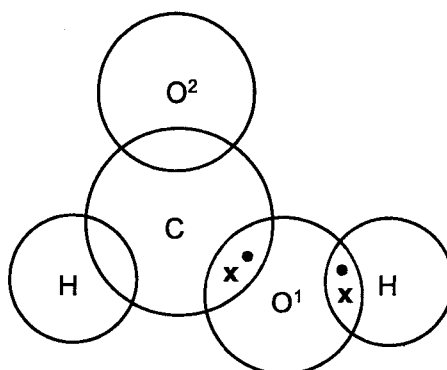
[1]

(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 O¹, suggest the type of hybridised orbitals for the oxygen atom labelled O¹.

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[1]

- (iv) Sketch a diagram to show how two sp² hybridised orbitals can form a sigma bond.

[1]

- (c) Cyclohexane is immiscible with water. Iodine, I₂, 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 cm³ of C₆H₁₂ is shaken with 20.0 cm³ of an aqueous solution containing I₂ until no further change is seen. It is found that 0.390 g of I₂ is extracted from water into the C₆H₁₂. Calculate the mass of I₂ 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 $-1022 \text{ kJ mol}^{-1}$. 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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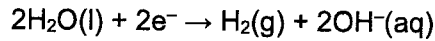
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[2]

- 2 (a) Chlorine can be manufactured using the electrolysis of $\text{NaCl}(\text{aq})$. At the cathode, $\text{H}_2(\text{g})$ and $\text{OH}^-(\text{aq})$ are produced. At the anode, the product mixture contains both $\text{Cl}_2(\text{g})$ and $\text{O}_2(\text{g})$. The mole ratio of each gas depends on the concentration of $\text{NaCl}(\text{aq})$.

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



Starting from **neutral** $\text{NaCl}(\text{aq})$, write half-equations for the production of the following at the anode.

- $\text{O}_2(\text{g})$,
- $\text{Cl}_2(\text{g})$.

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[2]

- (ii) Explain why the $\text{Cl}_2(\text{g}) : \text{O}_2(\text{g})$ mole ratio increases as concentration of $\text{NaCl}(\text{aq})$ increases.

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[2]

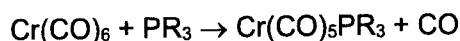
- (iii) Sodium chlorate(V) is prepared commercially by electrolysis $\text{NaCl}(\text{aq})$ in a cell that allows the electrolytes at cathode and anode to mix. The cathode reaction is the same as that described in (i). The equation for the anode reaction is as shown.



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

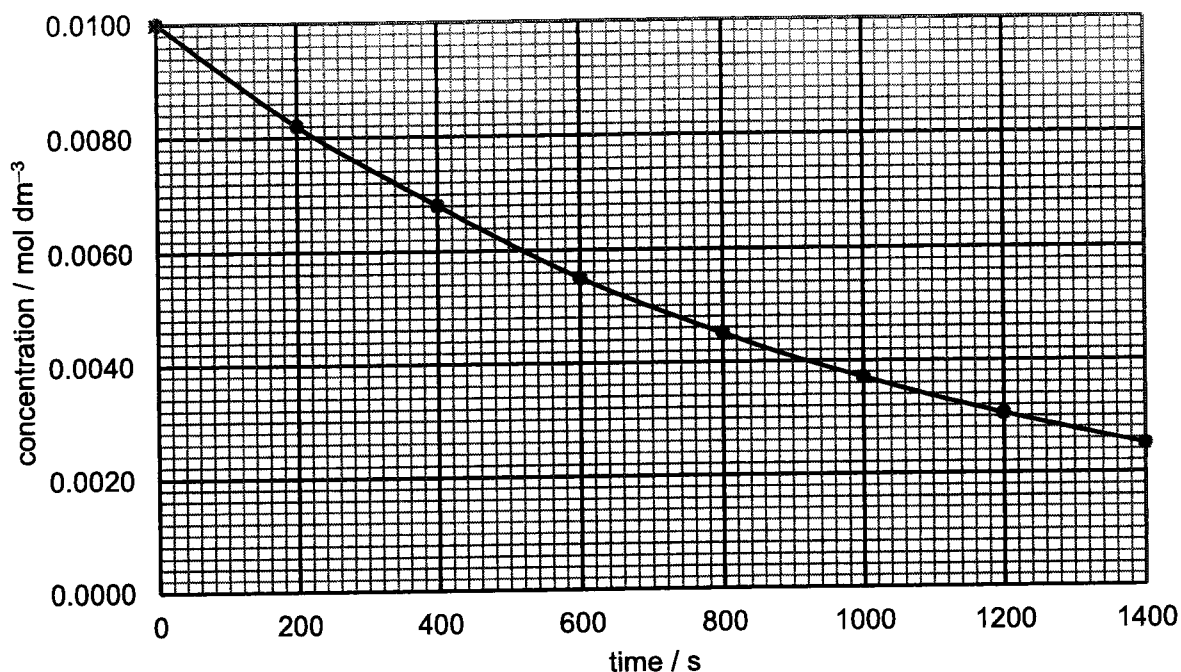
[2]

- (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.



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 $[\text{Cr}(\text{CO})_6]$ was measured with time. The results are shown on the graph below whereby the y-axis represents the concentration of $\text{Cr}(\text{CO})_6$.



In the second experiment, $\text{Cr}(\text{CO})_6$ was in a large excess, and $[\text{PR}_3]$ was measured with time. Table 2.1 shows the results obtained.

Table 2.1

time / s	$[\text{PR}_3] / \text{mol dm}^{-3}$
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 $\text{Cr}(\text{CO})_6$ 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.

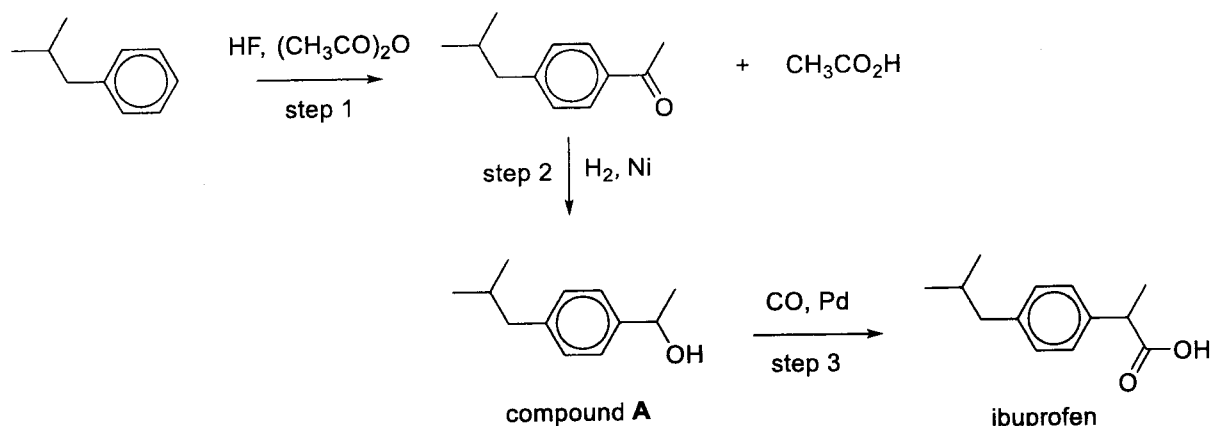
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[1]

[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.

[1]

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

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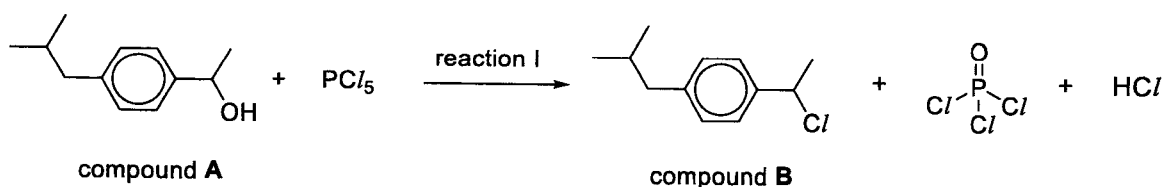
[2]

- (iv) Ethanoic anhydride, $(\text{CH}_3\text{CO})_2\text{O}$, 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.

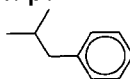


The mechanism of converting compound **A** into compound **B** is thought to involve the following three steps.

- 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–Cl bond cleavage to form the products.

14

- (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 1 goes to completion.

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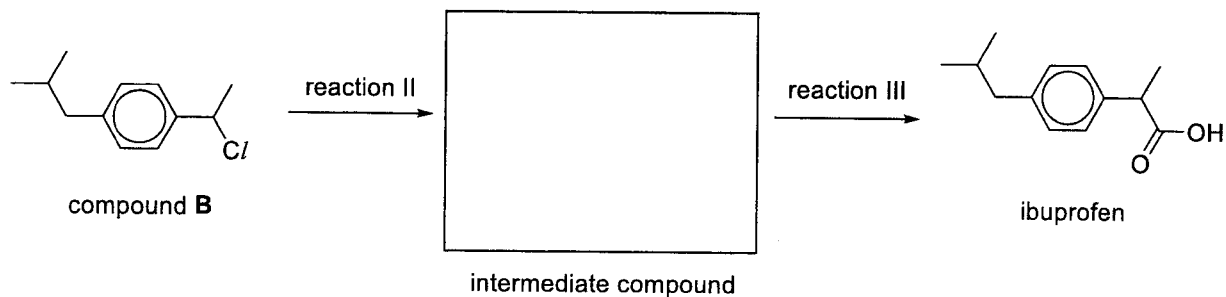
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[2]

- (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.



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.



When this reaction is carried out by heating a 1:1 molar mixture of calcium ethanoate and calcium methanoate, $(\text{HCO}_2)_2\text{Ca}$, 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]



VICTORIA JUNIOR COLLEGE
 JC 2 PRELIMINARY EXAMINATION
 Higher 2

CANDIDATE
 NAME

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CHEMISTRY

9729/03

Paper 3 Free Response

19 September 2022

Candidates answer on the Question Paper.
 Additional Materials: Data Booklet

2 hours

READ THESE INSTRUCTIONS FIRST

Write your name and CT group on all the work you hand in.
 Write in dark blue or black pen.
 You may use a soft 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. If additional space is required, you should use the pages at the end of this booklet. The question number must be clearly shown.

Section A

Answer **all** questions.

Section B

Answer **one** question.

A Data Booklet is provided.

The use of an approved scientific calculator is expected, where appropriate.

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

For Examiner's Use		
Section A	1	/ 18
	2	/ 22
	3	/ 20
Section B	4 OR 5	/ 20
Total		/ 80

This document consists of **26** printed pages.

Section A

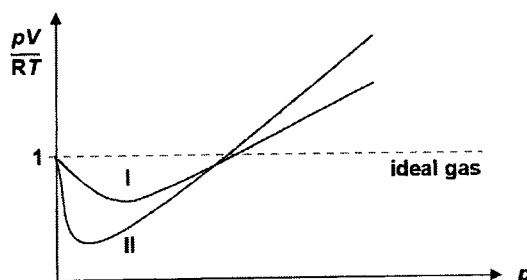
Answer **all** the questions in this section.

- 1 (a) (i) Under what conditions of temperature and pressure would you expect the behaviour of a real gas to be most like that of an ideal gas? [1]
- (ii) Barium ethanedioate, BaC_2O_4 , decomposes on heating to produce a mixture of two different gases, **A** and **B**, and an oxide only.

Neither gas **A** nor gas **B** is an ideal gas. They have the following boiling points.

gas	boiling point / °C
A	-191.5
B	-78.5

The graph below shows the variation of $\frac{pV}{RT}$ with pressure, p , for 1 mol each of gas **A** and gas **B** at constant temperature. Identify the graph that corresponds to gas **A** and explain your choice.



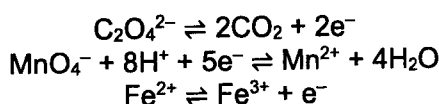
[2]

- (iii) Free volume, V , refers to the volume of space between gas molecules. For an ideal gas, the free volume is essentially the same as the volume of the container. This can be calculated using the ideal gas equation, $pV = nRT$.

The pressure of a 72 g gaseous sample containing gas **A** and gas **B** in a container of volume 400 cm^3 is measured to be $3.36 \times 10^7 \text{ Pa}$ at 527 °C .

Using the ideal gas equation, calculate the free volume of this gaseous sample in cm^3 . Assume the gaseous sample has an average $M_r = 36$. [2]

- (iv) Explain why the volume you have calculated in (a)(iii) differs from that of the volume of the container. [1]
- (v) An impure sample of barium ethanedioate, BaC_2O_4 , of mass 0.500 g, is added to 50.0 cm^3 of $0.0200 \text{ mol dm}^{-3}$ acidified MnO_4^- (aq) and heated. A redox reaction takes place and all BaC_2O_4 are reacted. The resulting solution is titrated with Fe^{2+} (aq). The end-point is reached when 30.40 cm^3 of $0.0500 \text{ mol dm}^{-3}$ Fe^{2+} (aq) has been added.



Calculate the percentage by mass of BaC_2O_4 in the 0.500 g impure sample. Show your working. [M_r : BaC_2O_4 , 225.3] [4]

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- (b) The elements of Group 14 can form monoxides and dioxides. The monoxides are unstable and will disproportionate into their element and dioxide. The equations for the disproportionation reactions are given in **Table 1.1**, together with some thermodynamic data for the reactions.

Table 1.1

disproportionation equation	$\Delta S^\circ / \text{J mol}^{-1} \text{K}^{-1}$	$\Delta H^\circ / \text{kJ mol}^{-1}$	$\Delta G^\circ / \text{kJ mol}^{-1}$
$2\text{CO(g)} \rightarrow \text{C(s)} + \text{CO}_2\text{(g)}$	-176	-173	-120
$2\text{SiO(g)} \rightarrow \text{Si(s)} + \text{SiO}_2\text{(s)}$	-363	-712	-603
$2\text{GeO(s)} \rightarrow \text{Ge(s)} + \text{GeO}_2\text{(s)}$	-13.6	-127	-123
$2\text{SnO(s)} \rightarrow \text{Sn(s)} + \text{SnO}_2\text{(s)}$	-9.20	-9.10	-6.36
$2\text{PbO(s)} \rightarrow \text{Pb(s)} + \text{PbO}_2\text{(s)}$	-4.00	+157	+158

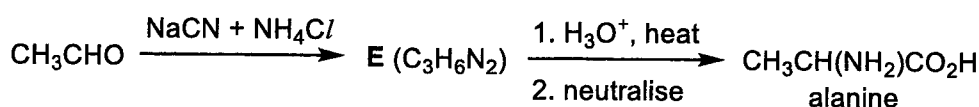
- (i) Explain why the entropy change for the disproportionation of SiO(g) is much more negative than that for CO(g). [1]
- (ii) Explain why the entropy change for the disproportionation of PbO(s) is close to zero. [1]
- (iii) Use data from Table 1.1 to deduce the temperature above which the disproportionation of CO(g) becomes unfavourable. [1]
- (iv) Explain why CO(g) does not spontaneously disproportionate at room temperature. [2]
- (v) Carbon monoxide, CO, is a gas at room temperature and pressure. It contains a coordinate bond. Explain what is meant by a *coordinate bond*. [1]
- (vi) Dicarbon monoxide, C₂O, is extremely reactive and is not encountered in everyday life. It is found in dust clouds in space and analysis has shown that the central atom is carbon with no unpaired electrons while the other carbon atom has a lone pair of electrons. Draw the structure of dicarbon monoxide, stating its shape and bond angle. [2]
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- 2 (a) Alanine, $\text{CH}_3\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$, is an amino acid that is used to make proteins. Its $\text{p}K_a$ values are 2.34 and 9.87.

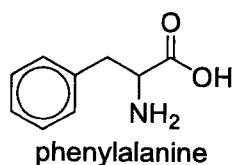
- (i) Sketch a graph to show how the pH of the solution would change during the gradual addition of 25.0 cm^3 of $0.100 \text{ mol dm}^{-3}$ NaOH to 10.0 cm^3 of $0.100 \text{ mol dm}^{-3}$ fully protonated alanine. Label the $\text{p}K_a$ values in your sketch. [2]
- (ii) From the following list of indicators, suggest an indicator that could be used to detect the first end-point of the titration. Explain your answer.

indicator	pH at which colour changes
malachite green	0 – 1
thymol blue	1 – 2
bromophenol blue	3 – 4.6
thymolphthalein	9 – 10

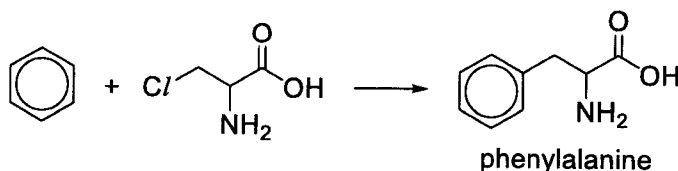
Alanine can be synthesised by a general reaction shown below. [2]



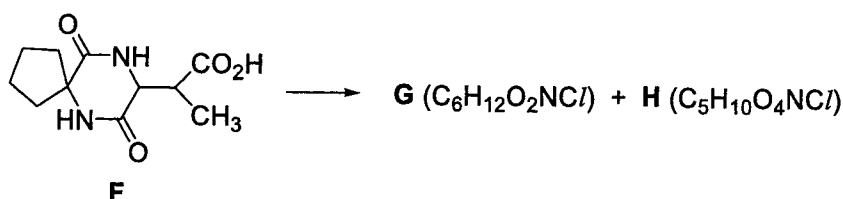
- (iii) Suggest the structure of compound E. [1]
- (iv) Suggest the structure of the starting material needed to synthesise phenylalanine by the above general reaction.



- (v) Phenylalanine can also be synthesised by reacting benzene and a halogen derivative, $\text{ClCH}_2\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$, in the presence of aluminium chloride. Suggest the mechanism for this reaction. Show all charges and the movement of electron pairs using curly arrows. [1]



- (vi) Compound F undergoes a reaction when heated in aqueous hydrochloric acid to produce two compounds, G and H. [3]



Suggest the type of reaction that has occurred. Draw the structures of compounds G and H. [3]

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(c) Silver chloride, AgCl , is sparingly soluble in water. The numerical value of the solubility product, K_{sp} , for silver chloride is $1.80 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$ at $25 \text{ }^\circ\text{C}$.

(i) Solid AgCl is stirred at $25 \text{ }^\circ\text{C}$ with $5.00 \times 10^{-3} \text{ mol dm}^{-3} \text{ AgNO}_3$ until no more AgCl dissolves. Calculate the concentration of chloride ions in this solution. [1]

(ii) Silver ions and thiosulfate ions react in a molar ratio 1:2 to form a soluble complex in aqueous solution. Explain, with the aid of relevant equations, how the solubility of silver chloride would be affected when solid sodium thiosulfate is added to an aqueous solution of silver chloride at $25 \text{ }^\circ\text{C}$. [2]

(iii) $7.00 \times 10^{-5} \text{ mol}$ of solid silver chloride is added to 2.50 dm^3 of aqueous sodium thiosulfate. $1.88 \times 10^{-5} \text{ mol}$ of silver chloride remained undissolved after equilibrium has been established. Determine the concentration of silver ions that has been used to form the silver-thiosulfate complex in the solution. [2]

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[Total: 22]

- 3 (a) Compound **A** has a molecular formula of $C_{12}H_{16}O$.

Ozone can be used to convert a $C=C$ bond into two $C=O$ bonds. Under certain conditions, ketones and/or carboxylic acids are formed, as shown in **Figure 3.1**. Ozone has **no** reaction with benzene.

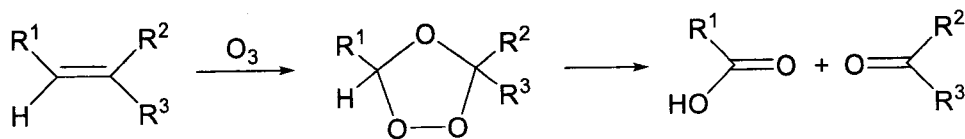


Figure 3.1

Compound **A** reacts with an excess of ozone under similar conditions to form two organic compounds, **B**, $C_9H_{10}O$, and **C**, $C_3H_6O_3$.

Compounds **A**, **B** and **C** form a yellow precipitate with alkaline aqueous iodine but only compound **B** forms an orange precipitate with 2,4-dinitrophenylhydrazine.

When compound **B** is reacted with concentrated HNO_3 and concentrated H_2SO_4 , two possible mono-nitro compounds can be formed but only **D** is formed in practice.

Compound **C** has a chiral centre and effervesces with aqueous sodium carbonate. When warmed with concentrated H_2SO_4 , **C** forms **E**, $C_6H_8O_4$.

- (i) Explain what is meant by a *chiral centre*. [1]
- (ii) Suggest possible structures of **A**, **B**, **C**, **D** and **E**. For each reaction, state the *type of reaction* described and explain what the information tells you about the functional groups present in each compound. [9]

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- (b) (i) When white anhydrous CuSO_4 is dissolved in liquid ammonia at -40°C , a deep blue solution **F** is formed.

Solid NaOH is then added to solution **F**, and the ammonia solvent is allowed to evaporate leaving behind a solid residue. Heating the residue to 220°C produces a mixture of two solids. When water is added to this mixture, one of the solids remains as a black solid **G**.

Solid **G** dissolves in $\text{HNO}_3(\text{aq})$ on warming without the evolution of gas to give a pale blue solution.

Suggest the chemical formulae of the compounds **F** and **G**. [2]

- (ii) When water is added to the white anhydrous CuSO_4 , the solid dissolves to give a blue solution. The solution changes to a yellow-green colour when concentrated NH_4Cl is added to it. Concentrating the solution produces green crystals of an ammonium salt with the empirical formula $\text{CuN}_2\text{H}_8\text{Cl}_4$.

State the type of reaction occurring and give the chemical formula of the ammonium salt formed. Explain these observations with the aid of an equation. [3]

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- (c) **Figure 3.2** shows the octahedral geometry of a transition metal complex with six monodentate ligands, L.

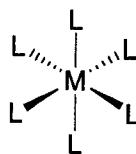


Figure 3.2

With reference to an octahedral complex, the *cis-trans* configuration is defined as follows:

Cis configuration:

Same groups of atoms are on the same side of the central metal atom, i.e. 90° from each other.

Trans configuration:

Same groups of atoms are on directly opposite sides of the central metal atom i.e. 180° from each other.

$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ is an octahedral complex. Similar to organic molecules, this complex can exist as a pair of *cis-trans* isomers.

Using the information above, draw the 3-dimensional structures of the *cis-trans* isomers of $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ and label the configuration. [2]

- (d) Radium was discovered in the ore, pitchblende, by Marie Curie in 1898. The metal was first isolated in 1910.

The metal was obtained by first reacting the radium present in the pitchblende to form insoluble radium sulfate which was converted into aqueous radium bromide. This solution was then electrolysed using a mercury cathode and a carbon anode. The radium formed react vigorously with water to form an alkaline solution.

- (i) Write an equation, with state symbols, for the reaction of radium with water. [1]
- (ii) State and explain if the reaction will be more or less vigorous than the reaction of barium with water. [2]

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Section B

Answer **one** question from this section.

- 4 (a) With reference to $E^\ominus(X_2|X^-)$ values from the *Data Booklet*, describe the relative reactivity of the halogens Cl_2 , Br_2 and I_2 as oxidising agents. [2]

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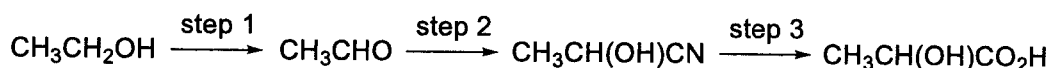
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- (b) Lactic acid, $CH_3CH(OH)CO_2H$, was first isolated in sour milk. It is also formed in our body during anaerobic respiration.

- (i) Lactic acid exhibits stereoisomerism. State the type of stereoisomerism and draw the pair of stereoisomers. [2]

Lactic acid can be synthesised from ethanol as shown below.



- (ii) State the reagents and conditions for steps 1 and 2. [2]
- (iii) Describe the reaction mechanism for step 2. Show all relevant charges, dipoles, lone pairs and electron movement using curly arrows. [2]
- (iv) State and explain how K_a of lactic acid would compare to that of propanoic acid. [2]

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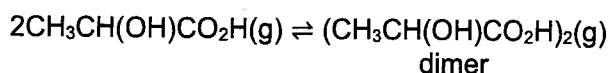
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- (c) Lactic acid undergoes dimerisation by forming two hydrogen bonds between two molecules.



In a container, 6.65 bar of lactic acid undergoes dimerisation at 127 °C. The total pressure of the gas mixture at equilibrium is found to be 3.52 bar.

- (i) Calculate the partial pressures of lactic acid and its dimer, in bar, at equilibrium. [2]
(ii) Write the K_p expression for this equilibrium and calculate its value in bar^{-1} . [2]

The Gibbs free energy change for this reaction is related to K_p by the following equation.

$$\Delta G = -RT \ln K_p$$

In the above equation, ΔG is in J mol^{-1} , T is in K and K_p is in bar^{-1} .

- (iii) Calculate the Gibbs free energy change of the dimerisation [1]
(iv) The entropy change for the dimerisation is $-30.0 \text{ J K}^{-1} \text{ mol}^{-1}$.

Calculate the enthalpy change of the dimerisation. Hence, estimate the strength of hydrogen bond in the dimer in kJ mol^{-1} . [2]

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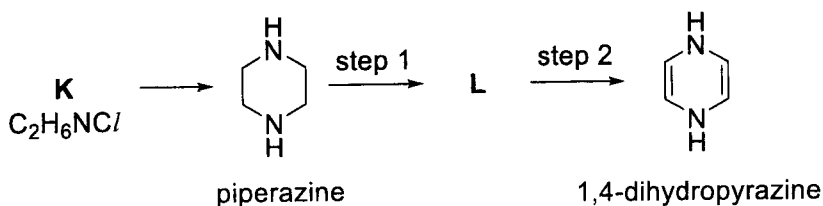
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- 5 (a) Piperazine, $C_4H_{10}N_2$ was used as an anti-parasites drug in the early 20th century. It can be synthesised from an organic compound **K**, C_2H_6NCI under suitable conditions. Piperazine can be used to prepare 1,4-dihydropyrazine via a two-step pathway as shown below.



- (i) Suggest and explain if 1,4-dihydropyrazine can exhibit *cis-trans* isomerism. [1]
- (ii) Suggest the structures of compounds **K** and **L**. [2]
- (iii) State the reagents and conditions for steps 1 and 2. [2]
- (iv) The preparation of 1,4-dihydropyrazine from piperazine in the above pathway gives a very low yield. Suggest which step in the pathway contributed to this low yield. Explain your answer. [1]
- (v) State and explain how the K_b of piperazine would compare to that of diethylamine, $(CH_3CH_2)_2NH$. [2]
- (vi) The two pK_b values of piperazine are 5.35 and 9.73 respectively.

A buffer solution is prepared by adding 11.2 g of piperazine into 100 cm³ of 1.00 mol dm⁻³ hydrochloric acid solution.

Calculate the pH of this buffer solution. [3]

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- (b) In order to function properly, the human body needs to maintain a blood pH between 7.35 and 7.45. Large deviations from this pH range are extremely dangerous. pH values greater than 7.8 or less than 6.8 often result in death. Blood contains large amounts of carbonic acid and hydrogencarbonate which help to maintain the blood pH. Describe, with the aid of equations, how the pH of blood is controlled by carbonic acid and hydrogencarbonate. [2]

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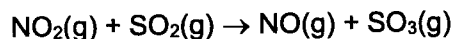
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- (c) The reaction between NO_2 and SO_2 is a key stage in the formation of acid rain.



The initial rate of this reaction was measured for different concentrations of reactants and the rate equation was obtained as shown.

$$\text{rate} = k[\text{NO}_2][\text{SO}_2]^2$$

- (i) Explain if the reaction between NO_2 and SO_2 is an elementary step reaction. [1]
- (ii) NO_2 is produced in the car engine when the temperature of the engine is very high. Write an equation to show how NO_2 is removed by the catalytic converter. [1]
- (iii) The catalyst in the catalytic converter functions as a heterogeneous catalyst. Outline the mode of action of the heterogeneous catalyst. [2]
- (iv) Explain, with the aid of a labelled Boltzmann distribution diagram, the effect of catalyst on the rate constant of a reaction. [3]

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VICTORIA JUNIOR COLLEGE
PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME

CT GROUP

CHEMISTRY

9729/04

Paper 4 Practical

29 Aug 2022

Candidates answer on the Question Paper.

2 hours 30 minutes

Additional Materials: As listed in the instructions below

READ THESE INSTRUCTIONS FIRST

Write your name and CT group on all the work you hand in.

Give details of the practical shift and laboratory where appropriate, in the boxes provided.

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 spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.

You may lose marks if you do not show your working or if you do not use appropriate units.

Qualitative Analysis Notes are printed on pages 13 and 14.

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.

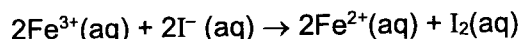
Shift	
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For Examiner's Use	
1	/ 9
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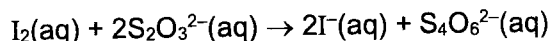
This document consists of **14** printed pages.

Answer **all** the questions in the spaces provided.

- 1 In acidic solutions, iron(III) ions are reduced by iodide ions to form iron(II) ions. The iodide ions are oxidised to iodine.



The rate of this reaction can be investigated by using starch indicator, which turns blue-black in the presence of iodine. Sodium thiosulfate is added to the reaction mixture to react with iodine as it is formed. The blue-black colour is seen when all the thiosulfate has reacted.



You will investigate how the rate of reaction is affected by changing the concentration of the iodide ions.

FA 1 is 0.050 mol dm⁻³ potassium iodide, KI.

FA 2 is 0.050 mol dm⁻³ acidified iron(III) chloride, FeCl₃.

FA 3 is 0.0050 mol dm⁻³ sodium thiosulfate, Na₂S₂O₃.

FA 4 is starch indicator.

(a) Experiment 1

1. Use the burette **labelled FA 1** to transfer 10.00 cm³ of **FA 1** into a 250 cm³ conical flask.
2. Use a 25 cm³ measuring cylinder to transfer 10 cm³ of deionised water into the conical flask.
3. Use the burette **labelled FA 3** to transfer 20.00 cm³ of **FA 3** and a 50 cm³ measuring cylinder to transfer 10 cm³ of **FA 4** to the same conical flask.
4. Use a 10 cm³ measuring cylinder to measure 10 cm³ of **FA 2**.
5. Add this **FA 2** into the same conical flask and start timing immediately.
6. Swirl the mixture once and place the conical flask on the white tile.
7. Stop timing as soon as the solution turns **intense** blue-black.
8. Record the time taken, **t**, to the nearest second.
9. Wash out the conical flask and stand it upside down in a beaker to drain for use again.

Experiment 2

10. Repeat Experiment 1 but use 20.00 cm³ of **FA 1** instead of 10.00 cm³ in step 1 and use 0.0 cm³ of deionised water instead of 10.0 cm³ in step 2.

Experiments 3 to 5

11. Carry out **three** further experiments to investigate how the reaction time changes with different volumes of potassium iodide, **FA 1**.
The combined volume of **FA 1** and deionised water must always be 20 cm³.
Do not use a volume of **FA 1** that is less than 6 cm³.

In the space on the next page, prepare a table to record the following for each of the five experiments.

- **V**, Volume of **FA 1** used,
- Volume of water used,
- **t**, Reaction time, to the nearest second,
- **Vt**
- **V²t**

Keep solutions FA 1, FA 3 and FA 4 for use in Question 2.

Results

[4]

- (b) V is the volume of FA 1 used in cm^3 and t is the time taken in seconds. On your table above, compute the values of Vt and V^2t for each experiment, to 2 significant figures.

[1]

- (c) The rate of the reaction in this investigation can be calculated using the following formula: **rate = 1 / reaction time**. Explain why this is so.

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

- (d) Deduce the order of reaction with respect to iodide ions. Explain your answer by referring to your calculated values of Vt and V^2t .

.....
.....
.....
..... [2]

- (e) Another student investigated the effect of concentration of iron(III) ions on the rate of this reaction. The student carried out another experiment, **Experiment 6**, and the rate is compared to that of **Experiment 1**. Suggest the volumes the student could use for **Experiment 6**.

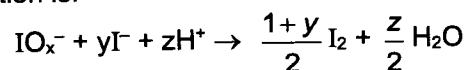
reagent	volume / cm ³
FA 1	
FA 2	
FA 3	
FA 4	
deionised water	

[1]

[Total: 9]

- 2 In this experiment you will determine the formula of the ion, IO_x^- . To do this, you will first react IO_x^- ions with an excess of iodide ions, I^- to form iodine, I_2 .

The equation for this reaction is:



where x, y and z are all integers.

The amount of iodine produced will then be determined by titration with thiosulfate ions.

In addition to **FA 1**, **FA 3** and **FA 4** used in question 1, you are also provided with the following.

FA 5 is a solution containing $0.00600 \text{ mol dm}^{-3} \text{ IO}_x^-$ ions.

FA 6 is 1.0 mol dm^{-3} sulfuric acid, H_2SO_4 .

(a) Dilution of FA 5

1. Pipette 25.0 cm^3 of **FA 5** into the 250 cm^3 volumetric flask.
2. Make the solution up to the mark using deionised water.
3. Shake the flask thoroughly.
4. Label this diluted solution of IO_x^- as **FA 7**.

Titration

1. Pipette 25.0 cm^3 of **FA 7** into a conical flask.
2. Using the burette labelled **FA 1**, transfer 10.00 cm^3 of **FA 1** into the same conical flask.
3. Using a measuring cylinder, transfer 10 cm^3 of **FA 6** into the same conical flask.
4. Titrate the mixture in the conical flask against **FA 3** in the burette labelled **FA 3** until the solution turns yellow.
5. Add 10 drops of **FA 4** into the conical flask.
6. Continue the titration until the blue-black colour just disappears.
7. Carry out as many titrations as you deem necessary to obtain consistent results.
8. In the space provided on the next page, prepare a table to record all your burette readings and the volume of **FA 3** used in each titration.

Results

[5]

- (b) (i) From your titration results, obtain a suitable volume of **FA 3** to be used in your calculations. Show clearly how you obtained this volume.

volume of **FA 3** = cm³ [1]

- (ii) Calculate the amount of iodine formed when 25.0 cm³ of **FA 7** reacts with 10.00 cm³ of **FA 1**. Show your working.

amount of iodine = mol [1]

- (iii) Calculate the amount of IO_x^- in 25.0 cm³ of **FA 7**. Show your working.

amount of IO_x^- = mol [1]

- (iv) Using your answer in (b)(ii) and (b)(iii), determine the value of y . Show your working.

$y = \dots\dots\dots$ [1]

- (v) Using your answer in (b)(iv), determine the value of z . Hence, determine the value of x .

$z = \dots\dots\dots$ and $x = \dots\dots\dots$ [1]

- (c) (i) The maximum error in the volume dispensed by the pipette is $\pm 0.06 \text{ cm}^3$.
Calculate the maximum percentage error in measuring the volume of **FA 5** used.

[1]

- (ii) A student suggested that a more accurate value of x can be determined if a 10.0 cm^3 pipette is used to measure the volume of **FA 6** rather than the measuring cylinder.

State whether you agree with this student. Explain your answer.

.....

 [1]

[Total: 12]

- 3 **FA 8** is a solid of Group 1 metal hydrogencarbonate, LHCO_3 . When it is heated, carbon dioxide and steam are produced.

In this experiment you will determine the relative atomic mass of the metal **L** in **FA 8** using gravimetric analysis.

(a) Gravimetric Analysis

1. Weigh and record the mass of a dry boiling tube.
2. Transfer all the **FA 8** from the container into the boiling tube.
3. Reweigh and record the total mass of the boiling tube and **FA 8**.
4. Heat the boiling tube gently for approximately one minute and then strongly for another four minutes.
5. Leave the boiling tube to cool on a wire gauze for at least five minutes.
6. After cooling, reweigh the boiling tube and its contents.
7. Repeat the heating, cooling and weighing process until you are satisfied that the decomposition is complete. The residue is **FA 9**, keep the residue for use in **3(b)**.
8. Record your results in an appropriate form in the space below.

Results

[4]

- (b) (i) Pour 1 cm depth of dilute hydrochloric acid into a test-tube. Add a spatula measure of the residue, **FA 9** to the acid.

Record all your observations and identify any gas formed.

.....

 [1]

- (ii) Use your observation in (b)(i) to identify the anion in **FA 9**. Assume that all the LHCO_3 has decomposed.

Anion in **FA 9** is [1]

- (iii) Hence, write a balanced equation for the thermal decomposition of LHCO_3 . Include state symbols.

..... [1]

- (iv) Calculate the amount of carbon dioxide given off in your experiment. Show your working.

amount of CO_2 = mol [1]

- (v) Hence, determine the relative atomic mass of metal **L**. Show your working.

relative atomic mass of metal **L** = [1]

- (c) (i) In another experiment, a student used a crucible with lid instead of a boiling tube for the heating and it was found that the results obtained were more accurate. Suggest why the crucible with lid can give a better result.

.....

 [1]

- (ii) Another student conducted a different experiment to determine the A_r of **L** by measuring the volume of carbon dioxide formed in the following reaction.



Suggest which method would give a more accurate determination of the A_r of **L**.

.....

 [1]

[Total: 11]

4 Qualitative Analysis

- (a) **FA 10** is a solid of a metal dioxide, MO_2 .

Solution **S** is an acidic solution of sodium ethanedioate, $\text{Na}_2\text{C}_2\text{O}_4$.

You will perform tests to identify the element **M** in **FA 10**.

Perform the tests (i) and (ii) described in **Table 4.1** and record your observations in the table. The volume given below are approximate and should be estimated rather than measured.

Test and identify any gases evolved.

Table 4.1

tests		observations
(i)	Transfer all the solution S into a boiling tube and add one spatula of FA 10 to the boiling tube. Warm the boiling tube cautiously. Leave the boiling tube to cool for about one minute and then filter the mixture into a test-tube.	
(ii)	To a 1 cm depth of filtrate from (a)(i) in a test-tube, add NaOH(aq) . Leave to stand.	
(iii)	Aqueous hydrogen peroxide is added to an equal volume of $\text{H}_2\text{SO}_4(\text{aq})$ in a test-tube, followed by addition of one spatula of FA 10 . The mixture is filtered into another test-tube. Leave the filtrate to stand.	Vigorous effervescence of O_2 which rekindles a glowing splint. A black/brown residue and a colourless filtrate obtained. The filtrate remains colourless.

[4]

- (b) (i) Consider your observations in (a)(ii), give the name of element **M** in **FA 10**. Explain your answer.

M is

.....

 [2]

- (ii) In (a)(i), the reaction between **FA 10** and ethanedioate occurred under acidic conditions. Write a balanced equation for this reaction.

..... [1]

- (iii) The filtrate obtained in (a)(i) turned pale yellow on standing.

Compare the role of **FA 10** in (a)(i) and (a)(iii). Explain your answer with reference to your observations in both tests.

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 [2]

- (c) **FA 11**, **FA 12** and **FA 13** are organic compounds with the molecular formulae C_7H_6O , C_3H_6O and C_2H_6O (not necessarily in any order).

Each compound has **only one** of the functional groups: alcohol, aldehyde and ketone.

- (i) Perform the tests described in **Table 4.2** and record your observations in the table. If there is no observable change, write **no observable change**.

Prepare the Tollens' reagent using the following procedure.

Place a 2 – 3 cm depth of silver nitrate in a test-tube, add aqueous sodium hydroxide drop by drop until a small amount of brown precipitate is formed and then add aqueous ammonia drop by drop with shaking until the precipitate just dissolves. This is Tollens' reagent.

Table 4.2

test	observations		
	FA 11	FA 12	FA 13
Add 1 cm depth of Tollens' reagent to test-tube containing 1 cm depth of each sample and place each test-tube in a hot water bath.			

[1]

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- (ii) Using only the bench reagents provided, suggest **one additional** chemical test that can help you identify the functional group present in each compound. Describe the test in the space provided in **Table 4.3**.

Perform the test and record the observations in **Table 4.3**.

Table 4.3

test	observations		
	FA 11	FA 12	FA 13

[2]

- (iii) Based on your observations in (c)(i) and (c)(ii), suggest the structures of the organic compounds present in **FA 11**, **FA 12** and **FA 13**.

FA 11 is

FA 12 is

FA 13 is

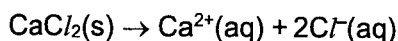
[3]

[Total: 15]

5 Planning

Self-heating food packaging is an active packaging with the ability to heat food contents without external heat sources or power. Packets typically use an exothermic chemical reaction. These packages are useful for military operations, during natural disasters or whenever conventional cooking is not available. These packages are often used to prepare main courses such as meat dishes, which are more palatable when hot.

The source of the heat is initiated by pressing on the heat pack. The heat pack is manufactured with the heating agent (anhydrous calcium chloride) separated from water by a thin breakable membrane. When pressure is applied on the packaging, a rod pierces the membrane, allowing the water and anhydrous calcium chloride to mix. The resulting reaction releases energy and thus warms the food surrounding it. The enthalpy change of solution for this dissolution process is approximately $-83.0 \text{ kJ mol}^{-1}$.



- (a) Plan an investigation to determine the enthalpy change of solution when anhydrous calcium chloride is dissolved in deionised water using a non-graphical method.

You may assume that you are provided with:

- approximately 120 cm^3 of deionised water
- approximately 10 g of anhydrous calcium chloride
- a thermometer
- Styrofoam cup
- common apparatus in the laboratory

In your plan, you should include brief details of:

- calculation of a suitable mass of calcium hydroxide you would use for a temperature rise of about $12 \text{ }^\circ\text{C}$ to $14 \text{ }^\circ\text{C}$;
- the apparatus you would use;
- the quantities of reagents you would use;
- the procedure you would follow and the measurements you would make (you may find it useful to label measurements in your plan as **M1**, **T1** etc.);
- how you would ensure that a **reliable** value of the enthalpy change of solution is obtained.

Assume that 4.18 J of heat energy raises the temperature of 1.0 cm^3 of the mixture by $1.0 \text{ }^\circ\text{C}$.

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Qualitative Analysis Notes

[ppt. = precipitate]

(a) Reactions of aqueous cations

cation	reaction with	
	NaOH(aq)	NH₃(aq)
aluminium, Al ³⁺ (aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH ₄ ⁺ (aq)	ammonia produced on heating	–
barium, Ba ²⁺ (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), Cu ²⁺ (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), Fe ³⁺ (aq)	red–brown ppt. insoluble in excess	red–brown ppt. insoluble in excess
magnesium, Mg ²⁺ (aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn ²⁺ (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, Zn ²⁺ (aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

anion	reaction
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, Cl^- (aq)	gives white ppt. with Ag^+ (aq) (soluble in NH_3 (aq))
bromide, Br^- (aq)	gives pale cream ppt. with Ag^+ (aq) (partially soluble in NH_3 (aq))
iodide, I^- (aq)	gives yellow ppt. with Ag^+ (aq) (insoluble in NH_3 (aq))
nitrate, NO_3^- (aq)	NH_3 liberated on heating with OH^- (aq) and Al foil
nitrite, NO_2^- (aq)	NH_3 liberated on heating with OH^- (aq) and Al foil; NO liberated by dilute acids (colourless $\text{NO} \rightarrow$ (pale) brown NO_2 in air)
sulfate, SO_4^{2-} (aq)	gives white ppt. with Ba^{2+} (aq) (insoluble in excess dilute strong acids)
sulfite, SO_3^{2-} (aq)	SO_2 liberated 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, NH_3	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