H

NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME							
CLASS	1	9			TUTOR'S NAME		
CENTRE NUMBER	S					INDEX NUMBER	

CHEMISTRY 9729/03

Paper 3 Free Response **16 September 2020**

2 hours

Candidates answer on the Question Paper

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, index number, name and class on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper. 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.

The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

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

For Examiner's Use	
1	/23
2	/19
3	/18
4 or 5	/20
Total	/80

Section A

Answer **all** questions in this section.

1 Lithium metal and its compounds have many uses, ranging from nuclear chemistry, batteries, air purification and pharmaceuticals.

(a) A button cell is a small single cell battery shaped like a button, with sizes typically 5 to 25 mm. Lithium-iodine button cells are widely used to power small portable electronics devices such as watches and calculators.

(i) Using appropriate data from the *Data Booklet*, calculate $E^{\ominus}_{cell}$ of a lithium-iodine button cell, and write the equations that take place at the cathode and anode. [3]

(ii) State the polarities of the cathode and anode. [1]

(iii) The actual voltage of a lithium-iodine button cell is +2.80 V. Suggest why this is different from the value you have obtained from **(i)**. [1]

(iv) After a current has been drawn for some time, the voltage of the button cell decreases.

- Describe how the masses of the lithium and iodine will have changed.
- Suggest why the voltage **decreases**. [3]

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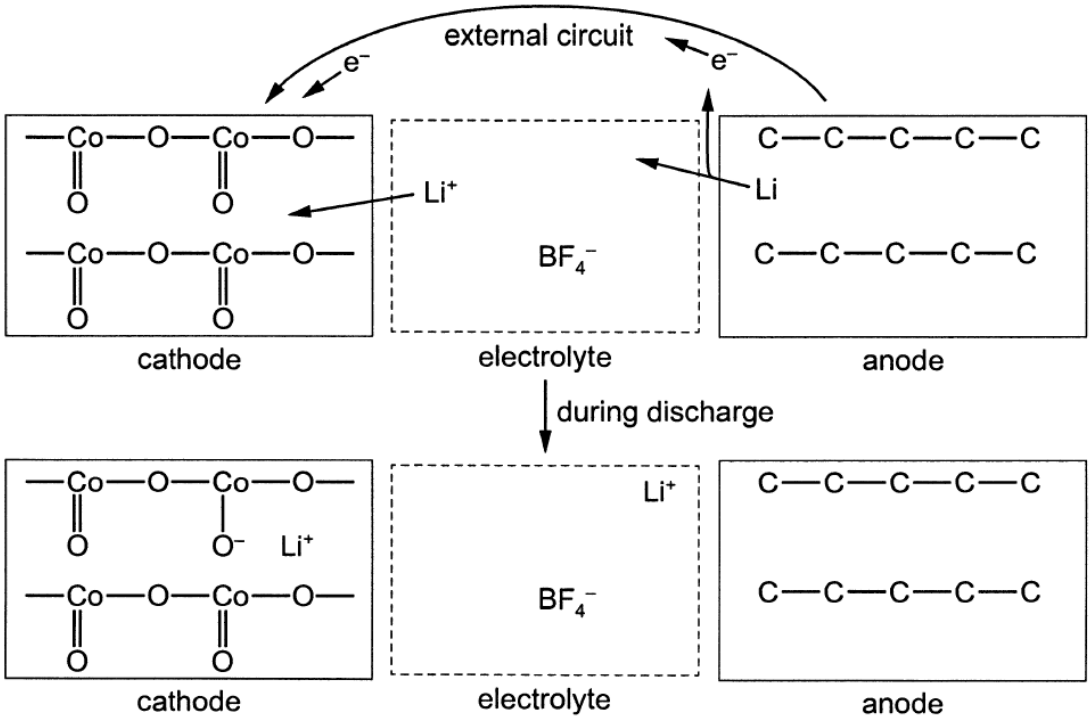
(b) Lithium is also used to make rechargeable batteries like the lithium-ion battery. A type of lithium-ion battery consists of a cathode made from cobalt oxide, CoO_2, and anode made from graphite with lithium atoms inserted between the layers; and an electrolyte of $LiBF_4$ dissolved in an organic solvent.

During discharge, Li atoms at the anode give up electrons to become Li^+ ions. The electrons travel round the external circuit, and are picked up by the cathode. A Li^+ ion from the electrolyte also moves to the cathode, and get inserted between the CoO_2 lattice. Cobalt is reduced from a +4 to +3 oxidation state in the process. This is illustrated in the following diagram in which C–C–C–C–C is a simplified representation of a layer of carbon atoms in graphite.



(i) For safety reasons, an organic solvent, rather than an aqueous solvent is used in this battery. Explain your answer with a suitable equation. [1]

(ii) Suggest the type of bonding between

- the lithium atoms and the layers of carbon atoms in graphite
- the lithium ions and the cobalt oxide lattice.

Explain your answers. [2]

(iii) During the charging process of the battery, lithium ions from the cathode are inserted into the anode. When charging is carried out at temperatures below 0 ^{O}C, the rate of reaction slows down, and lithium plating may occur instead. Lithium plating is the formation of metallic lithium around the anode and this results in a poorer battery performance.

Calculate the mass of lithium that will be deposited when a lithium-ion battery is charged for 1 hour at a current of 1.2 A, under conditions that results in lithium plating. [2]

(c) Latest research has found that replacing the graphite anode with graphene in lithium-ion batteries can help extend battery life.

(i) Graphene is a **single, one atom thick** layer of graphite. Describe the lattice structure of graphene with the aid of a labelled diagram.

Your answer should include

- the type of hybridisation of the carbon atoms
- the type of orbital overlap to form the bonds [3]

(ii) State and explain how you would expect the C–C bonds in graphene to differ in bond strength compared to that in diamond. [2]

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(d) Diamond and graphite are allotropes of carbon. The table below gives the thermodynamic data for diamond and graphite.

Allotrope	$\Delta H_f^\ominus$ / kJ mol^{-1}	$S^\ominus$ / J K^{-1} mol^{-1}
C(diamond)	+1.90	+2.38
C(graphite)	0	+5.74

(i) Explain why the standard enthalpy change of formation of graphite is 0 kJ mol^{-1}, while the standard enthalpy change of formation of diamond is +1.90 kJ mol^{-1}. [1]

(ii) Calculate the entropy change for the conversion of diamond to graphite. [1]

(iii) State whether the conversion of diamond to graphite is spontaneous at all temperatures. Explain using your answer from **(ii)**, and given that the standard enthalpy change of reaction for the conversion of diamond to graphite is exothermic. [2]

(iv) In daily life, we do **not** observe diamond converting to graphite. State and explain if your answer in **(iii)** agrees with this observation. [1]

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2 There are three major buffer systems that maintain pH in the human body: protein buffer system, phosphate buffer system and H_2CO_3 / HCO_3^- buffer system.

Tissue cells and vital organs of the body are extremely sensitive to even the slightest change in the pH environment. Hence it is important for the buffer systems to operate within its effective pH range i.e. pK_a ± 1. The pH of the healthy human body is maintained at 7.4, and any minor alterations from this pH can have severe implications.

(a) Phosphoric acid, H_3PO_4 is a weak triprotic acid that can be used to make phosphate buffers.

$$H_3PO_4(aq) \rightleftharpoons H_2PO_4^-(aq) + H^+(aq) \qquad pK_{a1} = 2.1$$
$$H_2PO_4^-(aq) \rightleftharpoons HPO_4^{2-}(aq) + H^+(aq) \qquad pK_{a2} = 6.8$$
$$HPO_4^{2-}(aq) \rightleftharpoons PO_4^{3-}(aq) + H^+(aq) \qquad pK_{a3} = 12.0$$

(i) Identify the two species of the phosphate buffer present in a healthy human body. Explain your answer. [1]

(ii) In an attempt to simulate the pH of a healthy human body system, a student adds 0.150 mol dm^{-3} NaOH to 25.0 cm^3 of 0.120 mol dm^{-3} H_3PO_4. Calculate the volume of NaOH that he should add in order to produce the buffer identified in **(i)**. [3]

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(b) The H_2CO_3 / HCO_3^- buffer system is the main buffer system which regulates pH in blood. The source of carbonic acid is dissolved carbon dioxide in blood.

(1) $H_2O(l) + CO_2(g) \rightleftharpoons H_2CO_3(aq)$
(2) $H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$ $\quad pK_{a1} = 6.1$
(3) $HCO_3^-(aq) \rightleftharpoons CO_3^{2-}(aq) + H^+(aq)$ $\quad pK_{a2} = 10.3$

(i) Calculate the ratio of $[H_2CO_3]$ to $[HCO_3^-]$ in the blood of a healthy human body. [1]

(ii) The H_2CO_3 / HCO_3^- buffer system is said to be quite ineffective in maintaining pH of the blood in a healthy human body. Suggest a reason for this. [1]

(iii) To compensate for the ineffectiveness of the H_2CO_3 / HCO_3^- buffer system, certain physiological processes help to counteract pH changes more quickly. Heavy breathing is one way to help counteract the acid produced in the muscles during exercise.

By referring to the equations above, explain how heavy breathing helps to maintain the pH of the human system during exercise. [2]

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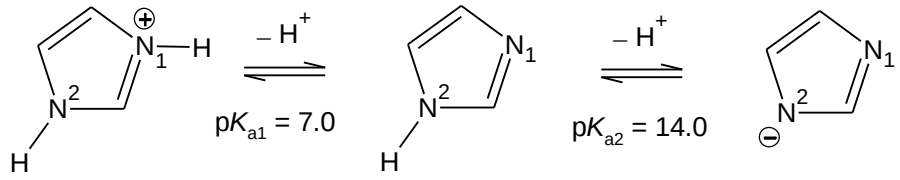
(c) Histidine is the key amino acid residue responsible for maintaining pH in haemoglobin. The histidine residue contains the imidazole functional group.

These are some properties of the imidazole group:

- In the planar imidazole ring, both nitrogen atoms are sp^2 hybridised.
- The N^1 atom is weakly basic but the N^2 atom is not.
- The N^2H group is weakly acidic and can be deprotonated in the presence of a very strong base.



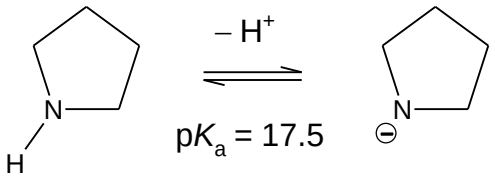
protonated imidazole | imidazole | deprotonated imidazole

(i) Write an equation to show how the imidazole group in haemoglobin reacts to maintain pH upon addition of base in the human body buffered at pH = 7.4 [1]

(ii) Draw a diagram to illustrate the orbitals around the N^2 atom in imidazole. On your diagram, identify and label the orbital which is likely to contain the lone pair of electrons on the N^2 atom. [2]

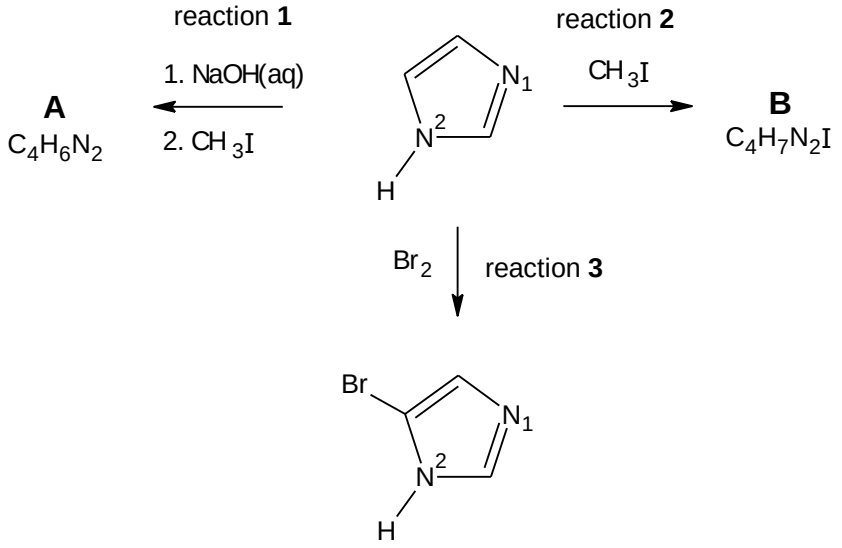
(iii) Hence, explain why the N^2 atom is **not** basic. [1]

(iv) Hence, explain why the N^2H group in imidazole is a stronger acid than the NH group in pyrrolidine. [2]



pyrrolidine

The reaction scheme below outlines some reactions that imidazole undergoes.



Due to the difference in basicity, the nitrogen atoms in imidazole have different nucleophilicities. Hence, the nitrogen atoms in imidazole reacts with CH_3I in a similar way but under different conditions in reactions **1** and **2**.

(v) Identify the N atom that reacted with NaOH in reaction **1** and explain why aqueous NaOH is required before reaction with CH_3I. [1]

(vi) Draw the structures of compounds **A** and **B**. [2]

(vii) Suggest what is unusual about reaction **3** and hence suggest an explanation for this anomaly. [2]

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3(a) Methanoic acid, HCOOH, was formerly known as formic acid because it is present in the sting of ants and the Latin name for ant is *formica*. It was first isolated in 1671 by John Ray who collected a large number of dead ants and extracted the acid from them by distillation.

At room temperature, pure methanoic acid is a liquid which is completely soluble in water.

When we are stung by a 'typical' ant, a solution of methanoic acid, **A**, is injected into our skin.

Solution **A** contains 50 % by volume of pure methanoic acid.

A 'typical' ant contains 7.5×10^{-6} dm^3 of solution **A**.

Calculate the number of ants required to produce 1 dm^3 of pure methanoic acid. [2]

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(b) HCOOH decomposes in the gas phase at elevated temperatures as follows:

$$HCOOH(g) \rightarrow CO_2(g) + H_2(g)$$

The decomposition reaction is determined to be first order.
The half-life of the decomposition reaction is 625 s.

When a small amount of solid ZnO is added to the reaction chamber, the rate of the reaction increases to 5 times its original value.

The progress of the reaction could be followed by measuring the partial pressure of methanoic acid vapour at regular time intervals.

(i) State the role of ZnO in the decomposition of methanoic acid vapour.
Outline the mode of action of ZnO in the decomposition of methanoic acid vapour. [3]

(ii) Calculate the half-life of the decomposition reaction when ZnO is added to the reaction mixture. [1]

(iii) Using your answer in **(ii)** and information above, sketch 2 graphs on the same axes to show how the partial pressure of methanoic acid vapour varies with time for the decomposition with and without ZnO. [2]

(iv) The pressure of methanoic acid vapour at the start of the reaction is 0.8 bar. The volume of the reaction chamber is 436 cm^3. The decomposition of methanoic acid vapour in the reaction chamber took place at 838 K.

Calculate the total amount of gases that occupy the reaction chamber at the end of the reaction. [2]

(v) Given that the enthalpy change and activation energy for the decomposition of methanoic acid vapour is -14.9 kJ mol^{-1} and +184 kJ mol^{-1} respectively, sketch the energy profile diagram for the decomposition reaction. [2]

(vi) With the aid of the energy profile diagram sketched in **(v)**, explain why the decomposition of methanoic acid vapour is likely to be reversible. [1]

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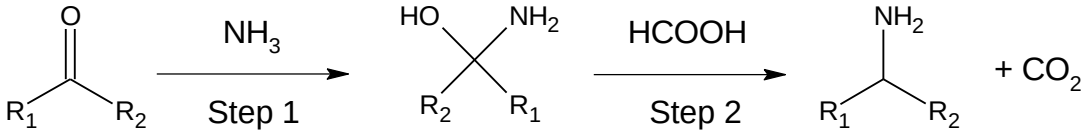
(c) The Leuckart reaction is the chemical reaction that converts carbonyl compounds to amines.

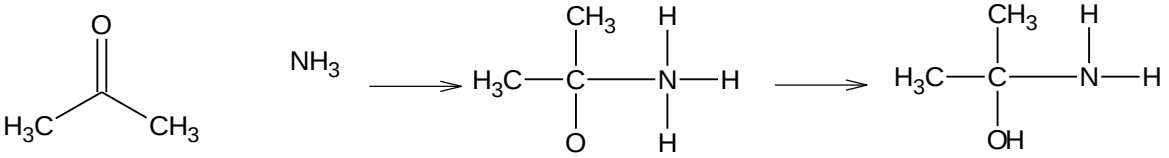
Ammonia reacts with the carbonyl compound to give an intermediate which further reacts with methanoic acid to give an amine as shown in the reaction scheme below.



carbonyl compound intermediate

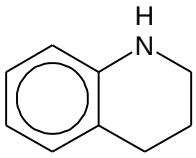
(i) State the type of reaction in step 1. [1]

(ii) Copy and complete the mechanism below for the reaction of ammonia with propanone, showing all charges and lone pairs and show the movement of electrons by curly arrows. [2]



(iii) Explain the role of HCOOH in Step 2 of the reaction scheme above. [1]

(iv) The following amine-containing compound, **Z**, can be synthesised using the reaction scheme shown above. Suggest the structure of the carbonyl compound with molecular formula $C_9H_{11}NO$ to synthesis **Z**. [1]



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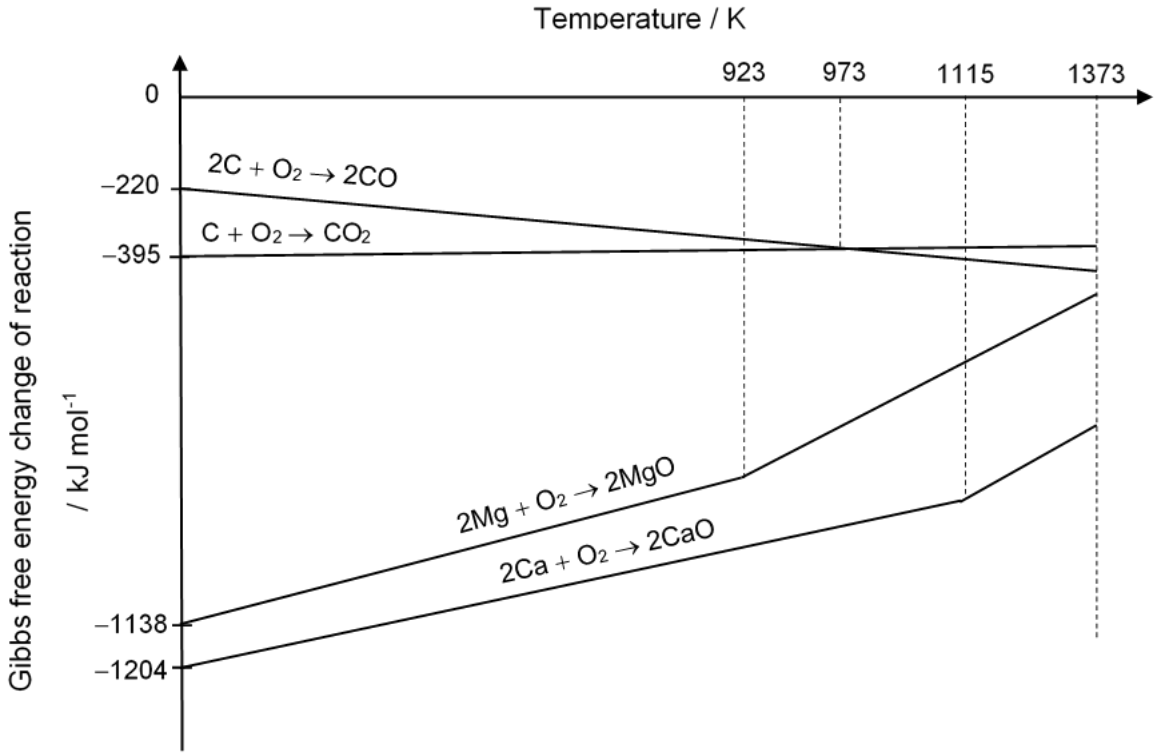
Section B

Answer **one** question from this section.

4 An Ellingham diagram is commonly used to show the variation in the free energy change of reaction with temperature. Since enthalpy change and entropy change are essentially constant with temperature unless a phase change occurs, the free energy versus temperature plot can be drawn as a series of straight lines. The graph showing the relationship between the Gibbs free energy change and the temperature of some oxides as well as the melting point of some elements are provided below.



Element	Melting point / K
Carbon	3823
Calcium	1115
Magnesium	923

Table 1

(a) The equation that relates the three thermodynamics factors, the *Gibbs free energy change*, the *enthalpy change of energy* and the *entropy change of energy* is known to be $\Delta G = \Delta H - T\Delta S$.

Define *entropy*. [1]

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(b) Given that the standard entropy change of energy is the negative gradient of each line in the Ellingham diagram,

(i) Explain why the gradient for oxidation of carbon to carbon dioxide is almost zero. [1]

(ii) Calculate the entropy change of the reaction, $2C + O_2 \rightarrow 2CO$, in J mol^{-1} K^{-1}. [2]

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(c) Using the Ellingham diagram and the information from Table 1, suggest an explanation for the shape of MgO graph from 0 K to 1373 K.

Your answer should include:

- the general shape of the graph
- the difference in the slope from 0 K to 923 K and 923 K to 1373 K. [3]

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(d) In an effort to decrease the amount of greenhouse gases, the decomposition of CO_2 to CO and O_2 is a potential remedy.

$$2CO_2 \rightarrow 2CO + O_2$$

Using the equation provided and the data from the Ellingham diagram on Page **22**, construct a suitable energy cycle to calculate the enthalpy change of the decomposition reaction. [3]

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(e) By using the Ellingham diagram on Page **22**, deduce which metal, Mg or Ca is the stronger reducing agent. [3]

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(f) A student studied the solubility of Group 2 oxides by adding the same of amount water to each of Group 2 oxide.

Describe the reactions of oxides of magnesium and calcium with water separately. Include relevant equations in your answer. [2]

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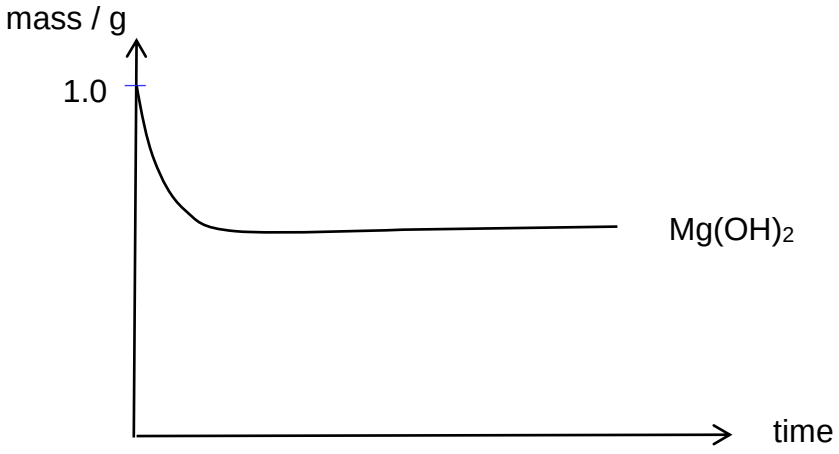
(g) Hydroxides of metals such as magnesium and calcium can be broken down into simpler substances upon strong heating.

(i) Copy the graph and sketch on the same axes as shown below, the graph that would be obtained if the experiment was carried out with 1.0 g of solid calcium hydroxide. Include the maximum mass after 1.0 g of both magnesium and calcium hydroxide has fully decomposed. [3]



(ii) Using relevant data from the data booklet, explain the initial slope of the graph of $Ca(OH)_2$ compared to $Mg(OH)_2$. [2]

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5(a) Manganese is found in the ore pyrolusite as manganese(IV) oxide, MnO_2. It was discovered in 1774 by Swedish chemist Johan Gottlieb Gahn when he heated pyrolusite with charcoal. Typical of transition elements, it exhibits variable oxidation states in compounds unlike s-block elements. Transition elements are d-block elements which form at least one stable ion with partially filled d orbitals.

On **separate** diagrams, sketch and label **each** atomic orbital from the 3d subshell.[3]

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(b) Heating a mixture of MnO_2 and KOH with oxygen from the air produces a green compound, **E**. **E** contains potassium, manganese and oxygen only.

On treatment with dilute acid, a sample of compound **E** reforms 0.174 g of MnO_2 and a purple solution of $KMnO_4$. Purple $KMnO_4$ is decolourised by the addition of 20.00 cm^3 of 1.00 mol dm^{-3} iron(II) sulfate.

(i) Write an ionic equation for the reaction between $KMnO_4$ and iron(II) sulfate. [1]

(ii) Identify the type of reaction that occurs when dilute acid is added to compound **E**. [1]

(iii) Calculate the oxidation number of manganese in compound **E** and hence deduce the formula of **E**. [3]

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(c) Rhodochrosite is the carbonate ore of manganese and does not contain hydroxide ions.

2.00 g of rhodochrosite produced 148 cm^3 of carbon dioxide under room conditions in its reaction with excess hydrochloric acid.

$$MnCO_3 + 2HCl \rightarrow MnCl_2 + H_2O + CO_2$$

(i) Calculate the percentage mass of $MnCO_3$ in rhodochrosite. Give your answer to three significant figures. [2]

A teacher suggested that the mass change from the thermal decomposition of a ground-up sample of rhodochrosite could be used to determine the percentage of carbonate in the sample. The teacher told the students to strongly heat a ground-up sample of the ore in a crucible.

(ii) State the measurements the students should make to determine the percentage mass of manganese carbonate in the sample of rhodochrosite. [1]

(iii) Explain how the students can ensure the results in **(ii)** are as accurate as possible. [1]

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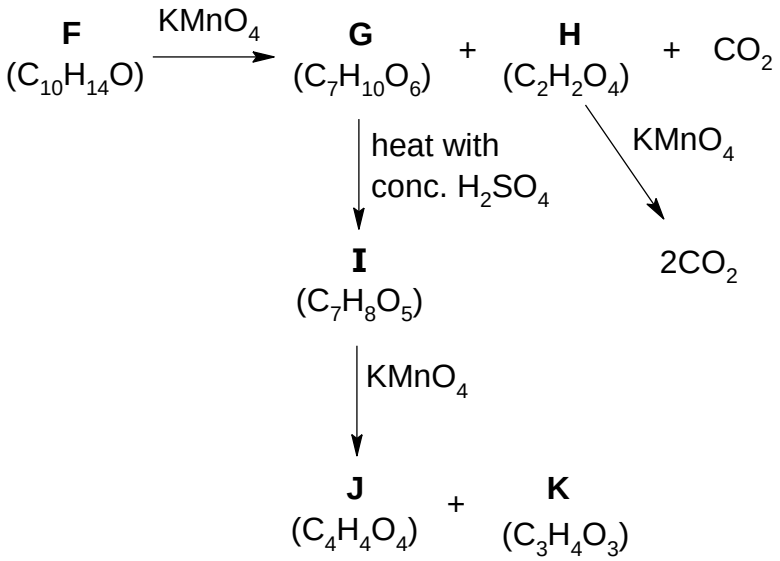
(d) Hot, concentrated potassium manganate(VII) oxidises several classes of organic compounds to ketones, carboxylic acids or carbon dioxide. By this means, the structures of compounds can be determined. Some compounds are easily oxidised, while others require longer heating.

The following scheme shows some reactions of compound **F**, and of its oxidation products.



(i) Compound **F** effervesces with sodium metal but does **not** react with warm acidified potassium dichromate(VI).

Explain these observations. [1]

(ii) Compound **G** gives yellow precipitate with alkaline aqueous iodine.
1 mole of **G** reacts with 2 moles of aqueous sodium hydroxide.

Explain these observations. [1]

(iii) Compounds **I**, **J** and **K** also give yellow precipitate with alkaline aqueous iodine. Hence, suggest the structures of compounds **F** to **K**. [6]

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