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

For Examiner's Use

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]

From *Data Booklet*,

		$E^\ominus$ / V
(1)	$Li^+ + e^- \prod Li$	– 3.04
(2)	$I_2 + 2e^- \prod 2I^-$	+0.54

$E^\ominus_{cell} = 0.54 - (-3.04) = +3.58$ V [1] with (+) sign

Cathode: $\frac{1}{2} I_2 + e \rightarrow I^-$ OR $I_2 + 2e \rightarrow 2I^-$ [1] with single arrow

Anode: $Li \rightarrow Li^+ + e^-$ [1] with single arrow

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

Cathode : positive
Anode : negative [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]

In the part (i) calculations, we have assumed that the concentrations of the ions are at 1 mol dm^{-3}, and conditions are at 25^{O}C and 1 bar but the working conditions of the button cell are <u>not at standard conditions.</u> [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]

		$E^\ominus$ / V
(1)	$Li^+ + e^- \prod Li$	– 3.04
(2)	$\frac{1}{2} I_2 + e^- \prod I^-$	+0.54

Overall eqn: $Li + \frac{1}{2} I_2 \rightarrow Li^+ + I^-$ $E_{cell} = E(I_2/I^-) - E(Li^+/Li)$

When current is drawn,

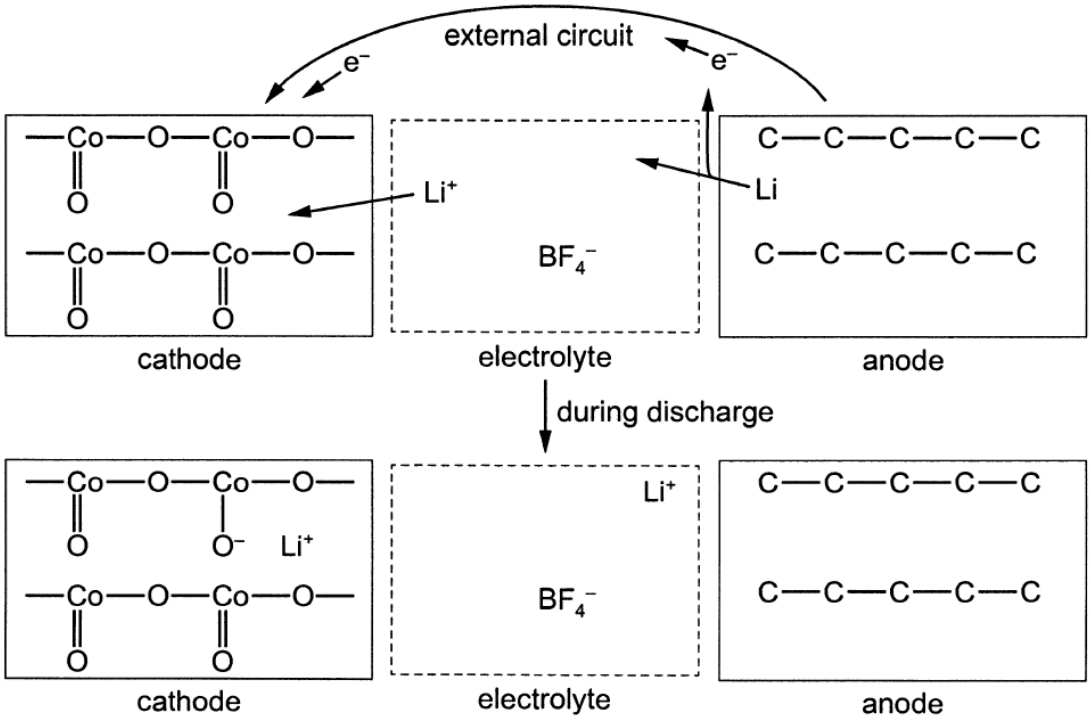
- Lithium oxidises to Li^+ by losing electrons. Mass of Li decreases.
- Iodine reduces to iodide ions by gaining electrons. Mass of iodine decreases.

- Since $[I^-]$ increases, POE of (2) shifts to the LEFT to remove the added I^-, causing $E(I_2/I^-)$ to be less positive, and hence E_{cell} will become less positive
- $[Li^+]$ increases, POE of (1) shifts to the RIGHT to remove the added Li^+, causing $E(Li^+/Li)$ to be less negative/more positive, and hence E_{cell} will become less positive

4 pt 3 mk; 3 pt 2 mk; 1 or 2 pts 1 mk

(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]

Lithium reacts explosively/vigorously/exothermically with water / gives off flammable hydrogen gas. Thus, a non-aqueous electrolyte is typically used.
$2Li(s) + 2H_2O(l) \rightarrow 2LiOH(aq) + H_2(g)$ [1] for explanation and eqn
(State symbols not required)

(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]

- Metallic bonds are present in Li, with Li^+ ions in a sea of delocalised electrons.
  In graphite, there are delocalised electrons between each layer of C atoms.
  Hence metallic bonding is formed between the Li atoms and C atoms in graphite.
  OR
  Metallic bonding exists between Li^+ ions and delocalised electrons between the layers of C atoms
- [1] for stating the type of bonding and explanation

Ionic bonding is formed between Li^+ and the O^- ions present in the CoO_2 lattice. [1]
(Refer to diagram of cathode during discharde. O^- ions are formed in the process.)

(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]

$Li^+ + e^- \rightarrow Li$

$Q = It = n_eF$

$$n_{Li} = n_e = \frac{I \times t}{F} = \frac{1.2 \times 60 \times 60}{96500}$$

$$m(Li) = \frac{1.2 \times 60 \times 60}{96500} \times 6.9 = 0.3089 = 0.309g$$

1 mk for calculation of n(Li); 1 mk for conversion to mass (allow ecf)

(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

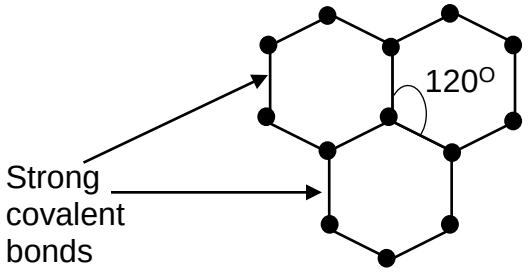
- the type of hybridisation of the carbon atoms
- the type of orbital overlap to form the bonds [3]

- Graphene has a giant covalent structure with each C atom covalently bonded to three other carbon atoms (trigonal planar geometry) to form hexagonal rings.

- Each carbon atom is sp^2 hybridised, and forms 3 σ bonds and 1 π bond.

- The σ bond is formed through head-on overlap between sp^2 hybrid orbital from an adjacent C atom. The π bond is formed through sideways overlap of the unhybridised p orbitals from an adjacent C atom.

- Diagram (should show at least 1 C that forms 3 sigma bonds):



4 pts 3 mks; 3 pts 2 mks; 1 or 2 pts 1 mk.
(deduct 1 mk overall if student drew graphite instead)

(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]

The C–C bond in graphene is stronger than that in diamond. [1]

This is due to the presence of both σ and π bonds in graphene, while there are only σ bonds present in diamond.
OR
greater s character / smaller p character of the sp^2–sp^2 overlap in graphene as compared to the sp^3–sp^3 overlap in diamond. [1]

(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]

- Graphite is the most stable allotrope/elemental form of carbon
- ΔH_f of elements = 0.

[1] for both pts

Comments:

Do not accept the following explanations

-"Graphite is considered as the elemental form of carbon" (Diamond is also an elemental form of carbon, and the statement does not explain that graphite is the most stable elemental form of carbon)

- "Carbon exists as graphite at standard conditions" (carbon also exists a diamond at standard conditions)

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

$\Delta S_{reaction} = S_{products} - S_{reactants}$

$= S_{graphite} - S_{diamond}$

$= 5.74 - 2.38$

$= + 3.36 \text{ J K}^{-1} \text{ mol}^{-1}$ [1] correct value, units and sign

(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]

Since $\Delta S > 0$, $-T\Delta S$ is always negative at all temperatures. [1]

and $\Delta H < 0$

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

$\Delta G < 0$ is spontaneous at all temperatures. [1]

(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]

No. The answer in (iii) only gives an indication if the reaction is feasible thermodynamically. Although the reaction is spontaneous, it has a high activation energy and takes place at a very slow rate. [1]

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[Total: 23]

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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]

- Since pH of human body is 7.4, to achieve an effective buffer, **7.4 = pK_a ± 1**
- The components of the buffer system is **$H_2PO_4^-$ and HPO_4^{2-}**

(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]

n / mol	NaOH	+	H_3PO_4 →	NaH_2PO_4	+	H_2O
Original	0.003		0.003	0		-
Change	– 0.003		– 0.003	+ 0.003		-
Final	0		0	0.003		-

n / mol	NaOH	+	NaH_2PO_4 →	Na_2HPO_4	+	H_2O
Original	x		0.003	0		-
Change	– x		– x	+x		-
Final	0		0.003 – x	x		-

Amount of NaOH needed = 0.003 + x

Let total volume be V dm^3

- 7.4 = 6.8 + log [x/V] / [(0.003 – x)/V] (ecf, based on species selected in part i, 1 mark as long as student can write the buffer formula correctly)
  x / (0.003 – x) = $10^{0.6}$
  x = 0.001194 – 3.981x
  x = 0.002397
- n(NaOH) = 0.003 + 0.002397 = 0.005397 mol (ecf)
- Volume of NaOH = 0.005397 / 0.150 = 36.0 cm^3 (ecf)

Each point 1 mark

(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) $H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$ $pK_{a1} = 6.1$
(3) $HCO_3^-(aq) \rightleftharpoons CO_3^{2-}(aq) + H^+(aq)$ $pK_{a2} = 10.3$

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

$7.4 = 6.1 + \log [HCO_3^-] / [H_2CO_3]$
$[H_2CO_3] / [HCO_3^-] =$ **1/20**

(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]

Any of the answers below

- The ratio of $[H_2CO_3]$ to $[HCO_3^-]$ is 1:20. The ideal ratio should be **1:1 for maximum effectiveness** OR **1:10 for effectiveness**
- There is **too little H_2CO_3**, the buffer has **limited capacity** to maintain pH especially when pH increases.
- The pH of human blood is 7.4, which is **out of effective range i.e. 6.1 ± 1** (or 10.3 ± 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]

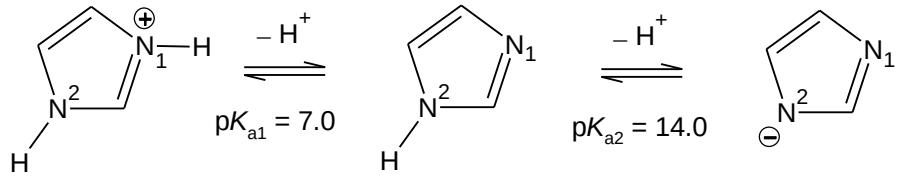
- **Position of equilibrium in (2) shifts left to reduce the added acid**.
- **Hence, concentration of H_2CO_3 increases**
  (H_2CO_3 produced in the blood travels to the lungs)
- **Position of equilibrium in (1) shifts left to reduce the increase in H_2CO_3**
- **CO_2 is produced**
- Heavy breathing helps to **expel/remove CO_2**
- Hence **concentration of H_2CO_3 is lowered** till the ratio becomes 1:20 again.

3 pts 1 mark

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

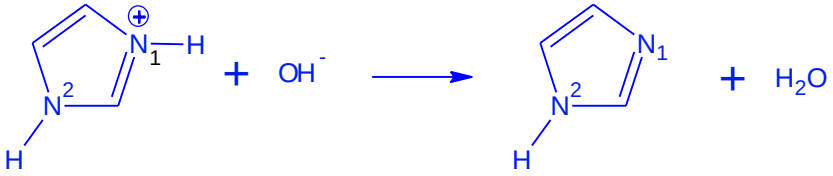
These are some properties of the imidazole group:

- 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.



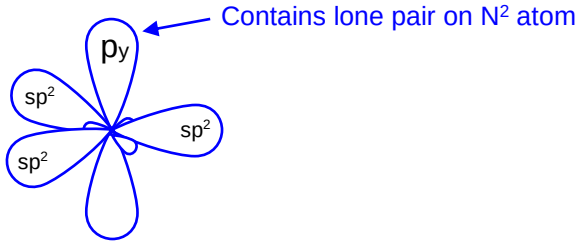
protonated imidazole | imidazole | deprotonated imidazole

(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]



Arrow should be irreversible sign

(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]

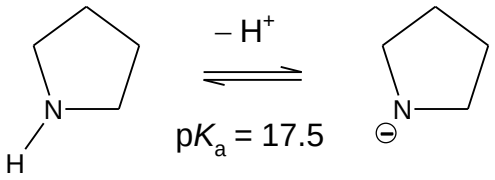


1 mark – correct drawing of sp^2 hybridisation
1 mark – correct labelling of the p orbital including the lone pair location

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

- Unhybridised **p orbital** on sp^2 hybridised **N^2 atom overlaps with the π orbitals** of the adjacent **double bonds** i.e. C=C and C=N.
- **Lone pair on N^2 atom is delocalised**, hence **not available for dative bonding with a proton / donation to empty orbital**

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



pyrrolidine

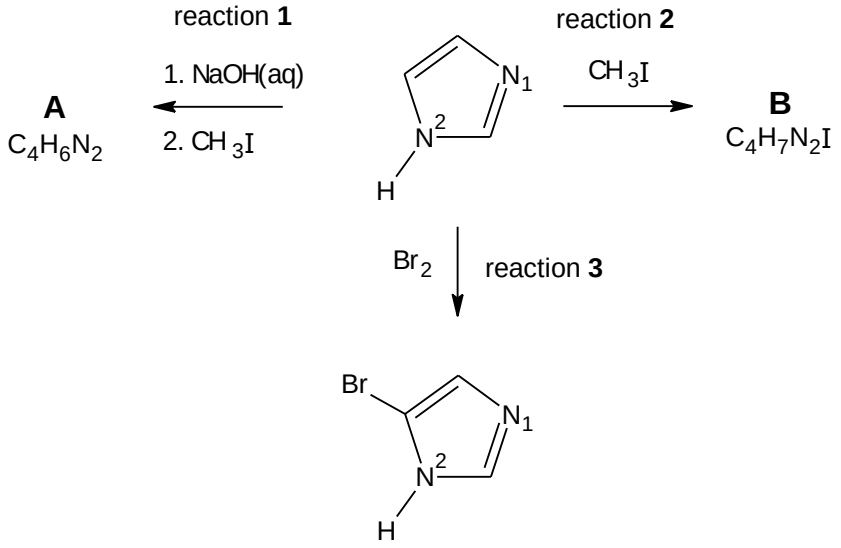
- For imidazole, the delocalisation (explained in previous part) also causes the **negative charge on N^2 atom in the conjugate base of imidazole to be dispersed over the ring**, hence **stabilising the conjugate base**.
  OR The **electronegative N^1 atom** further disperses the negative charge and stabilizes the conjugate base

- For pyrrolidine, the **electron donating alkyl groups** **intensify the negative charge** on N^2 atom, **destabilizing the conjugate bas**

(POE of acid dissociation lies more to the right for the more stable conjugate base)

1 point 1 mark

The reaction scheme below outlines some reactions that imidazole undergoes.



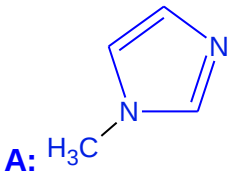
Due to the difference in basicity, the nitrogen atoms in imidazole have different nucleophilicities. Hence, the nitrogen atoms in imidazole reacts with CH_3I in a similar way but under different conditions in reactions **1** and **2**.

(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]

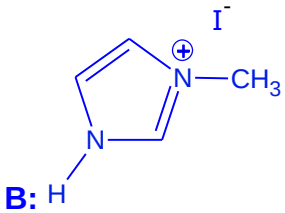
To convert **N^2 atom** into a **stronger nucleophile**.

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

A:



B:



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

- Br_2 **did not undergo electrophilic addition** with the C=C alkene bond
  OR
  Alkenes **undergo electrophilic substitution** with Br_2

- This is because the ring is **resonance-stabilised** (due to **delocalization of π electron cloud** around the planar ring) and hence prefers to undergo substitution so as to **preserve the resonance-stabilised structure**

[Total: 19]

For Examiner's Use

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]

- Volume of methanoic acid from one ant = $\frac{50}{100} \times 7.5 \times 10^{-6} = 3.75 \times 10^{-6}$ dm^3 [1]
- Number of ants to produce 1 dm^3 = $\frac{1}{3.75 \times 10^{-6}} = 2.667 \times 10^5 \approx 2.67 \times 10^5$ [1]

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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]

- ZnO acted as heterogeneous catalyst.
  HCOOH vapour molecules diffuse towards catalyst surface and become chemically adsorbed through formation of temporary bonds with neighbouring active sites.
- Such chemisorption involves the formation of weak temporary bonds between the molecules and the catalyst (using vacant and energetically accessible orbitals)
- The formation of these bonds cause the covalent bonds within the molecules to weaken, hence lowering the activation energy of the reaction.
  Eventually, the molecules dissociate, forming highly reactive intermediates which then combine to form the product.
- After reaction, the product molecules break free from the surface and diffuse away from the surface or product molecules desorb from the surface

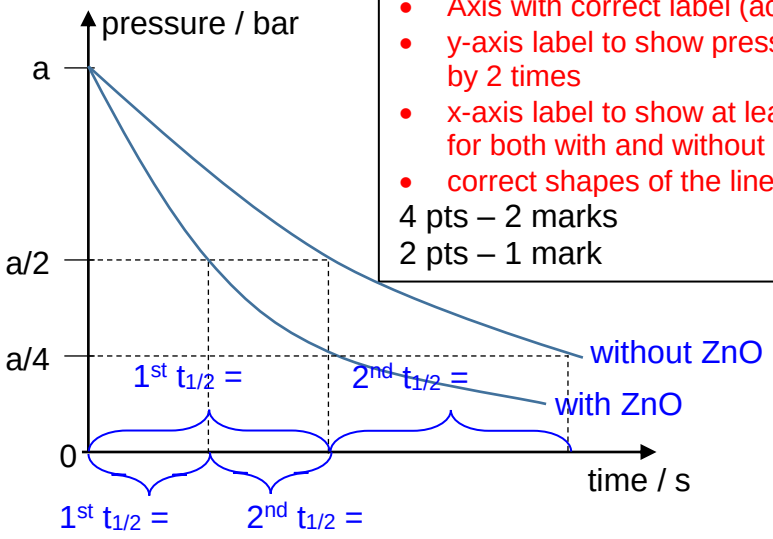
4 points (3 marks), 3 points (2 marks), 2 points (1 mark)

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

Half-life = 625/5 = 125 s

Accept if student provides the ans without showing the calculation.

(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]



- Axis with correct label (accept if no units)
- y-axis label to show pressure decreasing by 2 times
- x-axis label to show at least 2 half-lives for both with and without ZnO
- correct shapes of the lines

4 pts – 2 marks
2 pts – 1 mark

(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]

- At the end of reaction, total pressure = 0.8 × 2 = 1.6 bar (because 1 mol of methanoic acid vapour produces 2 mol of gases)

- $P = 1.6 \times 10^5$ Pa
- $V = 436 \times 10^{-6}$ m^3

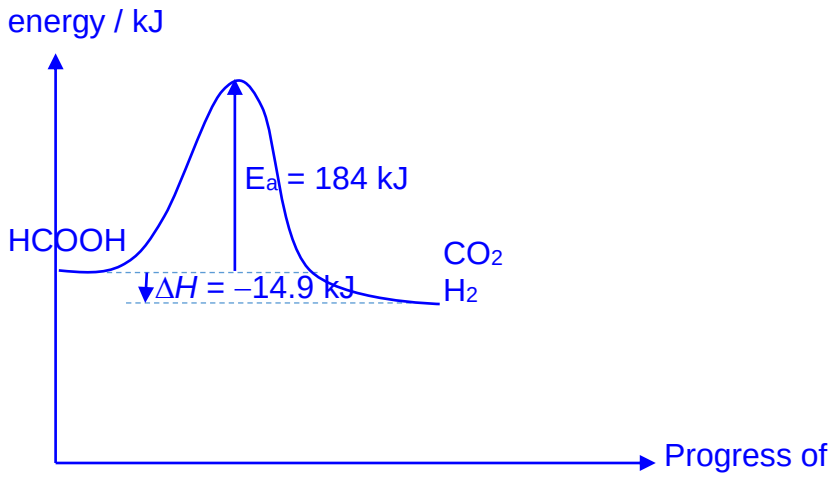
$PV = nRT$

$n = \frac{PV}{RT}$

- $n = \frac{1.6 \times 10^5 \times 436 \times 10^{-6}}{8.31 \times 838} = 0.0100$ mol

4 points correct – 2 marks
2 points correct – 1 mark

(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]



- Single step reaction pathway diagram
- Axis labelled correctly
- E_a and ΔH labelled correctly
- Reactants and products labelled correctly

4 points (2 marks), 2 points (1 mark)

(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]

The activation energies of both the forward and backward reactions do not differ very much. [1]

Student may calculate the E_a of the reverse reaction to illustrate the above.

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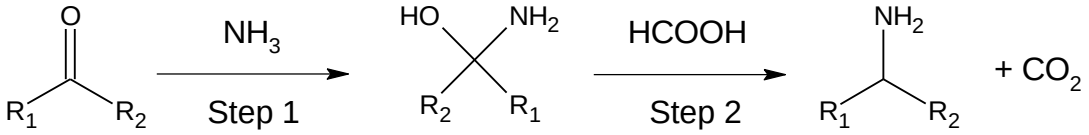
(c) The Leuckart reaction is the chemical reaction that converts carbonyl compounds to amines.

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.

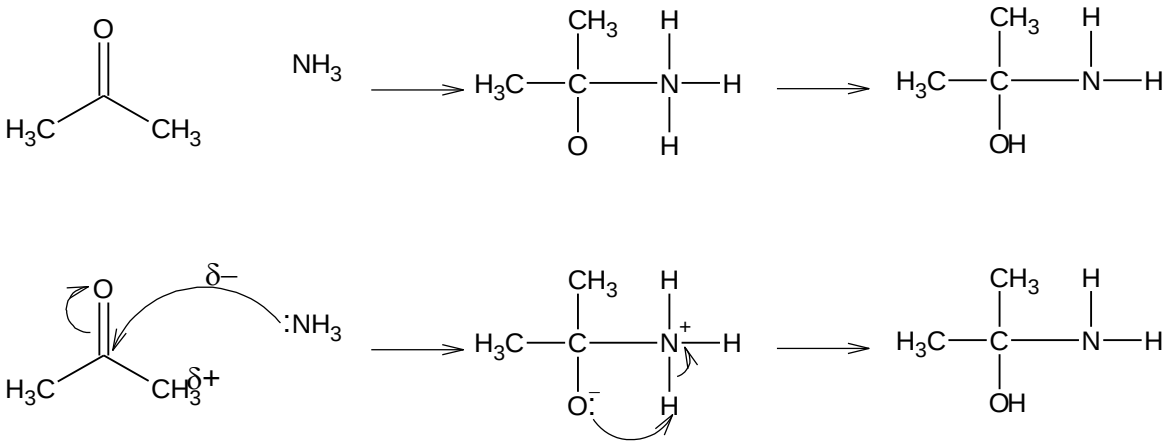


carbonyl compound intermediate

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

nucleophilic addition [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]



- Arrow from lone pair from NH_3 to carbonyl carbon
- Partial charges on C=O
- Arrow from δ+ C to δ– O
- – charge on O and + charge on N
- Arrow from lone pair of O^- to H attached to N
- Arrow from N–H bond to N

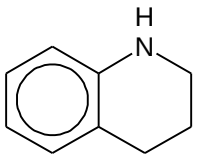
6 points (2 marks), 3 points (1 mark)

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

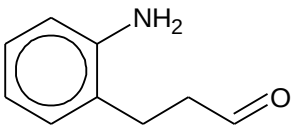
- HCOOH acted as a reducing agent.
- It undergoes oxidation as the oxidation number of C increases from +2 in HCOOH to +4 in CO_2.

2 points – 1 mark

(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]



Z



[1]

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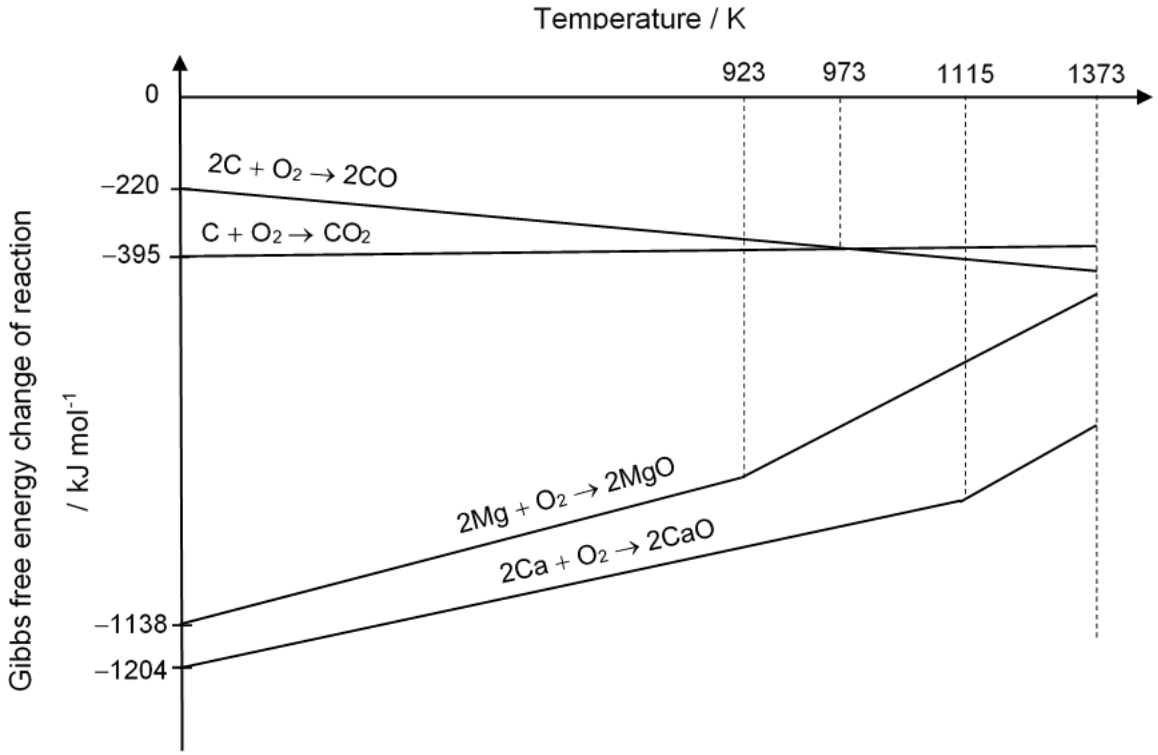
[Total: 18]

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]

Entropy is a measure of the disorder of a system.

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For Examiner's Use

(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]

$C(s) + O_2(g) \rightarrow CO_2(g)$

No change in the number of gaseous molecules, almost no change in entropy and hence the line is nearly horizontal.

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

$\Delta S = -\left(\frac{-395-(-220)}{973-0}\right)$ [1]

$= +0.1798$ kJ mol^{-1} K^{-1}

$= +180$ J mol^{-1} K^{-1} [1]

For Examiner's Use

(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]

- There is a positive gradient from 0 K to about 1373 K.
- Since there is a decrease in the number of gaseous molecules when Mg reacts with oxygen gas, there is a decrease in disorderliness of system, $\Delta S<0$. This decrease in disorderliness is shown by the positive gradient.
- The increase in gradient is slightly greater from 923 K to 1373 K. (This is because Mg starts melting at about 923 K) / The gradient increased at 923 K.
- From 0 K to about 923 K, it is solid Mg that is undergoing oxidation, i.e. $Mg(s) + O_2(g) \rightarrow MgO(s)$.
- From 923 K to 1373 K, it is liquid Mg that is undergoing oxidation, i.e. $Mg(l) + O_2(g) \rightarrow MgO(s)$.
- Since the change in state when liquid Mg reacts with oxygen to form MgO results in a larger decrease in disorderliness of the system, the change in entropy when liquid Mg undergoes oxidation/at 923 K to 1373 K is slightly more negative than that of solid Mg/at 0 K to 923 K.

Do not accept increasing gradient.
6 points – 3 marks
4-5 points – 2 marks
2-3 points – 1 mark

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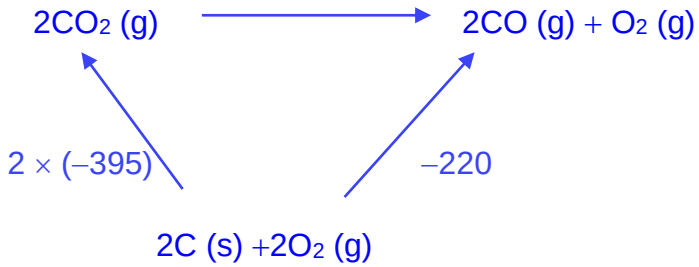
(d) In an effort to decrease the amount of greenhouse gases, the decomposition of CO_2 to CO and O_2 is a potential remedy.

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

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]



By Hess' Law,
$\Delta H = -2(-395) - 220 = +570$ kJ mol^{-1}

Correct energy cycle – 1 mark
2 x (-395) – 1 mark
Correct answer for ΔH – 1 mark

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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]

- Since the free energy change (ΔG) for the oxidation of Ca is more negative than that of Mg at all temperatures shown,
- the formation of oxide/forward reaction is more spontaneous for Ca than Mg.
- Since Ca is more likely to undergo oxidation, it is a stronger reducing agent.

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For Examiner's Use

(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]

- MgO is slightly soluble in water. Hence, MgO dissolves slowly in water to produce a slightly soluble $Mg(OH)_2$ solution that is slightly alkaline, about pH 8 (either slightly soluble in water or dissolves slowly)
- $MgO(s) + H_2O(l) \rightleftharpoons Mg(OH)_2(aq)$
- CaO reacts readily with cold water to produce soluble $Ca(OH)_2$ that is strongly alkaline, about pH 12.
- $CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq)$

Every 2 points – 1 mark

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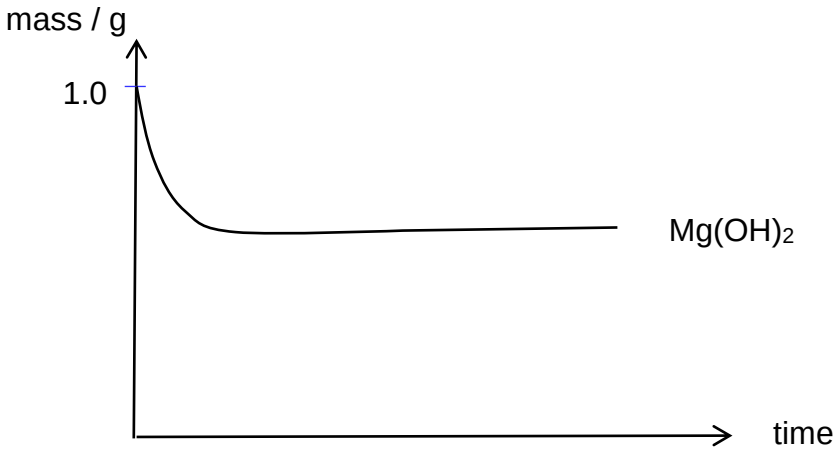
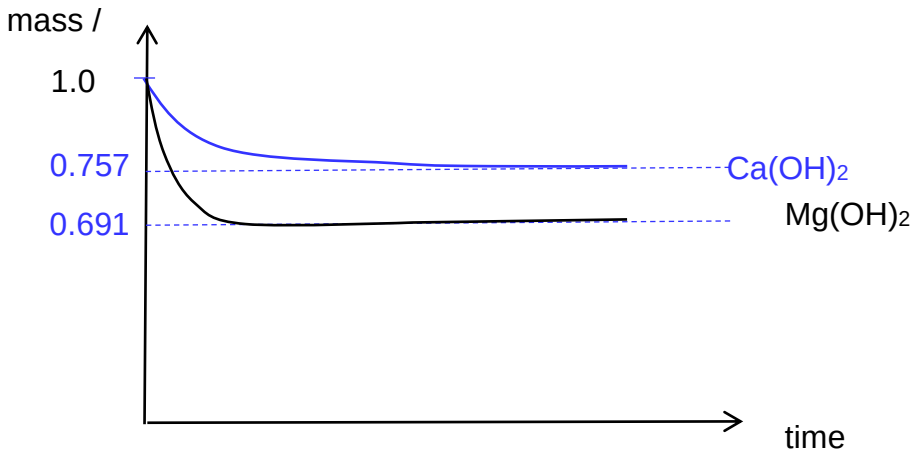
(g) Hydroxides of metals such as magnesium and calcium can be broken down into simpler substances upon strong heating.

(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. [1]





$M(OH)_2(s) \rightarrow MO(s) + H_2O(g)$

$n(Ca(OH)_2) = 1.00 / 74.1 = 0.01349$ mol
$n(Mg(OH)_2) = 1.00 / 58.3 = 0.01715$ mol

$m(CaO) = 0.01349 \times 56.1 = 0.757$ g
$m(MgO) = 0.01715 \times 40.3 = 0.691$ g

- Start graph at 1.0g
- Gradient for decomposition of $Ca(OH)_2$ is smaller and plateau later
- 0.691g of $Mg(OH)_2$ and 0.757g of $Ca(OH)_2$ as the final mass of the product

3 points – 3 marks
2 points – 2 marks
1 point – 1 mark

(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]

- As the initial slope of the graph is proportional to the initial rate of the decomposition reaction. The initial slope of the decomposition reaction of magnesium hydroxide steeper than that of calcium hydroxide.
- Both Mg^{2+} and Ca^{2+} cations have the same ionic charge. Since the ionic radius of Mg^{2+} (0.065nm) is smaller than the ionic radius of Ca^{2+} (0.099nm), Mg^{2+} has a larger charge density than Ca^{2+} and a higher polarising power.
- There will be greater distortion of the electron cloud of OH^- in $Mg(OH)_2$. Thus, the O-H bond in $Mg(OH)_2$ is weakened to a greater extent.
- Hence, it is easier to decompose $Mg(OH)_2$ compared to $Ca(OH)_2$, resulting in an increased in reaction rate for the decomposition of $Mg(OH)_2$.

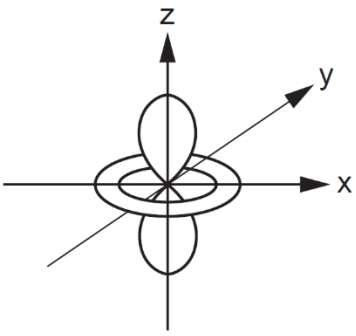
4 points – 2 marks
2-3 points – 1 mark

[Total: 20]

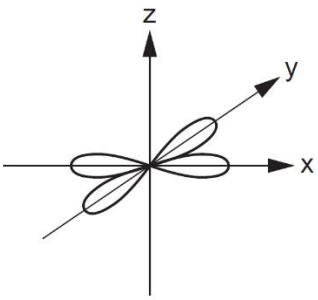
For Examiner's Use

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.

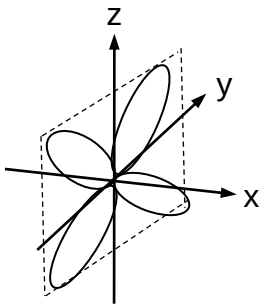
On **separate** diagrams, sketch and label **each** atomic orbital from the 3d subshell.[3]



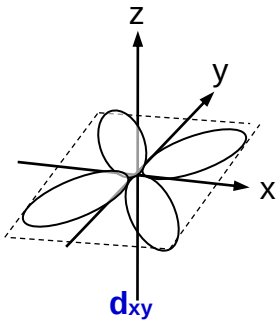
d_{z^2}



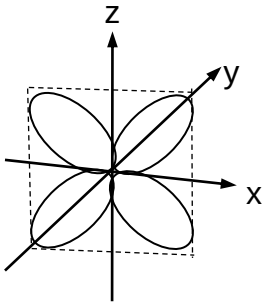
$d_{x^2 - y^2}$



d_{yz}



d_{xy}



d_{xz}

5 correct – 3 mk
4 correct – 2 mk
3 correct – 1 mk

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For Examiner's Use

(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]

$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$ [1]

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

Disproportionation [1]

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

- $n(MnO_2) = \dfrac{0.174}{54.9 + 2(16.0)} = 0.00200$ mol
- $n(Fe^{2+}) = \dfrac{20}{1000} \times 1.00 = 0.0200$ mol
- $n(KMnO_4) = \dfrac{1}{5}(0.0200) = 0.00400$ mol

3• [1] – ecf

Let the oxidation number of Mn in compound **E** be x.

[R]: Mn^{x+} + $(x - 4)\ e^-$ → Mn^{4+}

0.00200 0.00200(x – 4) 0.00200

n(electrons gained) = 0.00200(x – 4)

[O]: Mn^{x+} → Mn^{7+} + $(7 - x)\ e^-$

0.00400 0.00400 0.00400(7 – x)

n(electrons lost) = 0.004 (7 – x)

n(electrons gained) = n(electrons lost)

0.00200(x – 4) = 0.004 (7 – x)

x = +6 [1]

Or

Overall eqn: $(x - 4)Mn^{x+} + (7 - x)Mn^{x+} \rightarrow (7\text{-}x)Mn^{4+} + (x - 4)Mn^{7+}$

$\dfrac{n(Mn^{4+})}{n(Mn^{7+})} = \dfrac{7 - x}{x - 4} = \dfrac{0.00200}{0.00400} = \dfrac{1}{2}$

$x - 4 = 14 - 2x$

$3x = 18$

$x = 6$ [1]

Formula of **E** = K_2MnO_4 [1]

(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]

- $n(CO_2) = \frac{148}{24000} = 0.006166 \text{ mol} = n(MnCO_3)$
- $m(MnCO_3) = 0.006166 \times 114.9 = 0.7085 \text{ g}$
- $\%(MnCO_3) = \frac{0.7085}{2.00} \times 100 = 35.42$
- $= 35.4\%$ (3 sf)

2 – 3• [1]; 4• [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]

mass of crucible **and**
mass of crucible and ore (before heating) **and**
mass of crucible and ore residue after heating [1] – all

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

Repeat the heating, cooling and weighing to achieve 2 constant masses [1]

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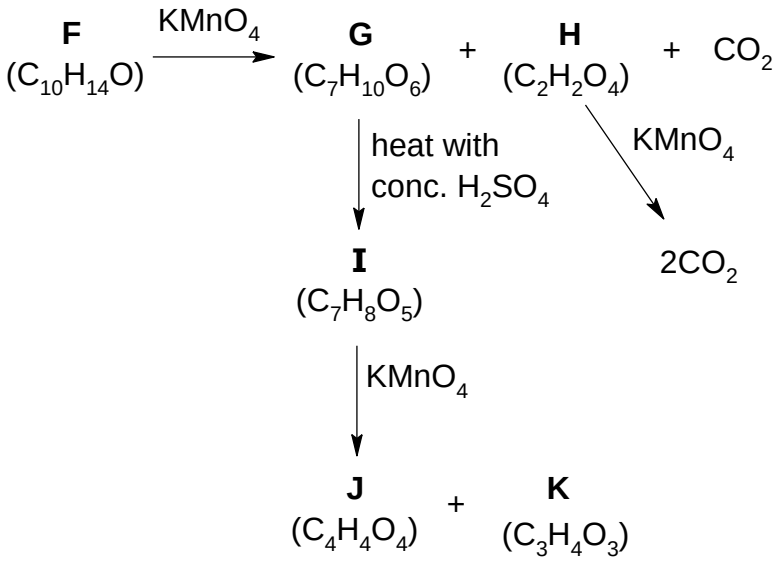
[Turn Over

(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]

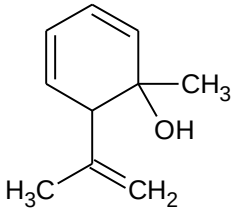
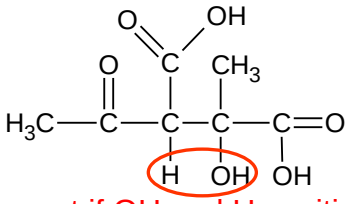
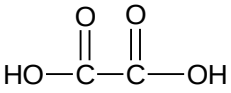
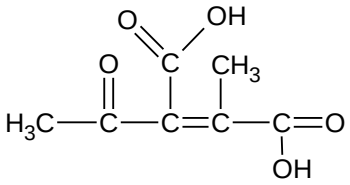
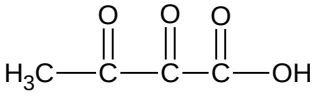
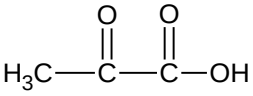
F contains tertiary alcohol as it undergoes reduction with Na but not oxidation with $K_2Cr_2O_7$. [1]

(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]

G contains methyl ketone group (CH_3CO–) as it undergoes oxidation with alkaline aqueous I_2. **G** contains 2 carboxylic acid group (–COOH) as it undergoes acid-base/neutralisation with 2 moles of NaOH(aq). [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]

F 	**G**  Accept if OH and H position
H 	**I** 
J 	**K** 

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[Total: 20]

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