H

RAFFLES INSTITUTION
2019 YEAR 6 PRELIMINARY EXAMINATION

Higher 2

CANDIDATE NAME			
CLASS		INDEX NUMBER	

CHEMISTRY 9729/02

Paper 2 Structured Questions

17 September 2019
2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class and index number in the spaces provided 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 spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided. Do not write anything in it.

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

For Examiner's Use	
1	/ 8
2	/ 7
3	/ 16
4	/ 9
5	/ 15
6	/ 20
Total	/ 75

This document consists of **23** printed pages and **1** blank page.

1 Silicon dioxide is made up of the two most abundant elements on earth, and is the second most abundant mineral.

(a) Silicon dioxide is known to occur in as many as 12 different crystalline forms. Unlike SiO_2, silicon disulfide, SiS_2, lacks such variety in structures.

SiS_2 reacts quickly with liquid ammonia to form compound **X**, which has the following composition by mass.

Si 48.3%, N 48.1%, H 3.6%

Determine the empirical formula of **X**.

[1]

(b) Explain the difference in the first ionisation energies of silicon and phosphorus.

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Aluminium and phosphorus are adjacent to silicon in the Periodic Table yet their oxides behave differently as compared to silicon dioxide.

(c) Write equations to illustrate the acid-base behaviour of the oxides of aluminium and silicon.

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………………………………………………………………………………………….. [3]

(d) Explain, in terms of structure and bonding, why the melting point of P_4O_{10} is lower than that of SiO_2.

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[Total: 8]

2 A reaction is represented by the following equation.

$$xC(g) \rightleftharpoons yA(g) + B(g); \qquad \Delta H > 0$$

The reaction was studied by monitoring the amounts of C, A and B over time in a reaction vessel with a fixed volume of 2 dm^3.

The initial amounts of C, A and B used were 1.80 mol, 0.40 mol and 0.40 mol respectively. Fig. 2.1 shows the results that were obtained.

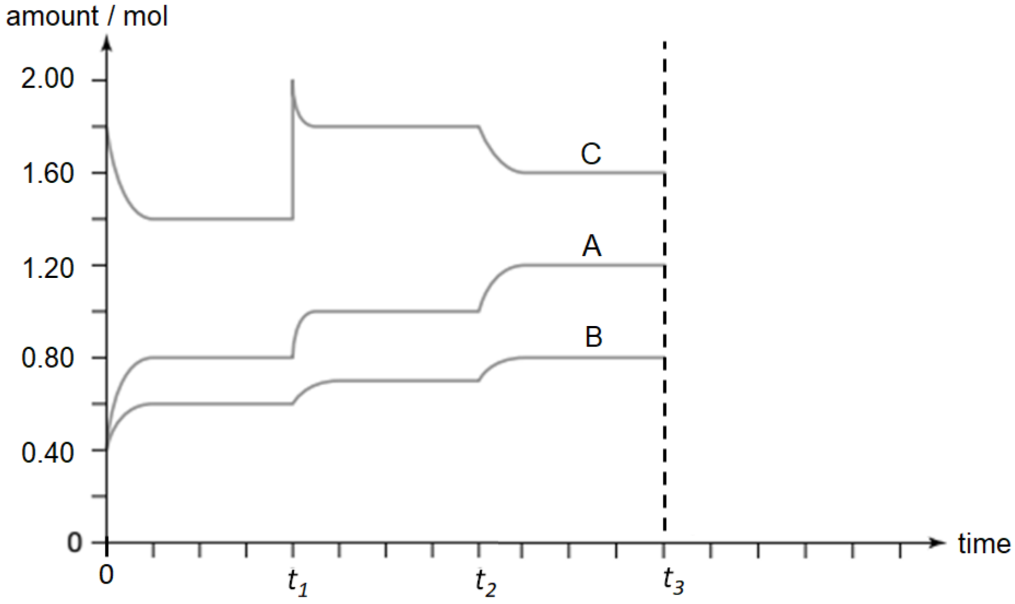


Fig. 2.1

(a) Determine the values of x and y in the above equation, showing clearly any calculations or reasoning.

[2]

(b) Calculate the equilibrium constant, K_c, immediately before time t_1. Include units in your answer.

[2]

(c) Based on the K_c value calculated in **(b)**, state whether the $\Delta G^\ominus$ of the reaction at the given temperature is less than, equal to or greater than zero.

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

(d) A change was made to the system at time t_2. State the change that was made.

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

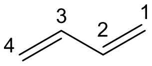
(e) At time t_3, an inert gas was added to the system at constant volume and temperature.

Sketch the effect of this change on the amounts of C, A and B in the space after the dotted vertical line on Fig. 2.1.

[1]

[Total: 7]

3 This question is about 1,3-butadiene.

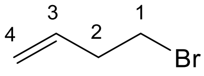
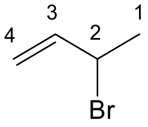
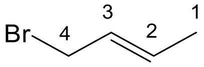
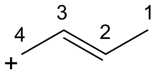


1,3-butadiene

1,3-butadiene undergoes an exothermic electrophilic addition reaction with an equimolar amount of HBr to produce a mixture of 1,2-addition and 1,4-addition products as shown in Table 3.1.

In this case, 1,2- and 1,4-addition refer to the positions of the carbon atoms in the diene at which H and Br atoms were added.

Table 3.1

type of addition	structure of product	% yield at 45 °C	structure of carbocation intermediate
1,2-addition	 **X**	0	
	 **Y**	15	Refer to your answer in **(b)**.
1,4-addition	 **Z**	85	

(a) State the total number of mono-brominated products, including stereoisomers, formed when 1,3-butadiene reacts with an equimolar amount of HBr at 45 °C.

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

(b) Describe the mechanism for the reaction between 1,3-butadiene and HBr to form compound **Y**. Show relevant lone pairs and dipoles, and use curly arrows to indicate the movement of electron pairs.

[2]

(c) In Table 3.1, draw the structure of the carbocation intermediate generated during the formation of compound **X**.

[1]

(d) **(i)** By considering the structures of the respective carbocation intermediates in Table 3.1, account for the percentage yield of each of the compounds stated below.

(1) compound **X**

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…………………………………………………………………………………………… [1]

(2) compound **Z**

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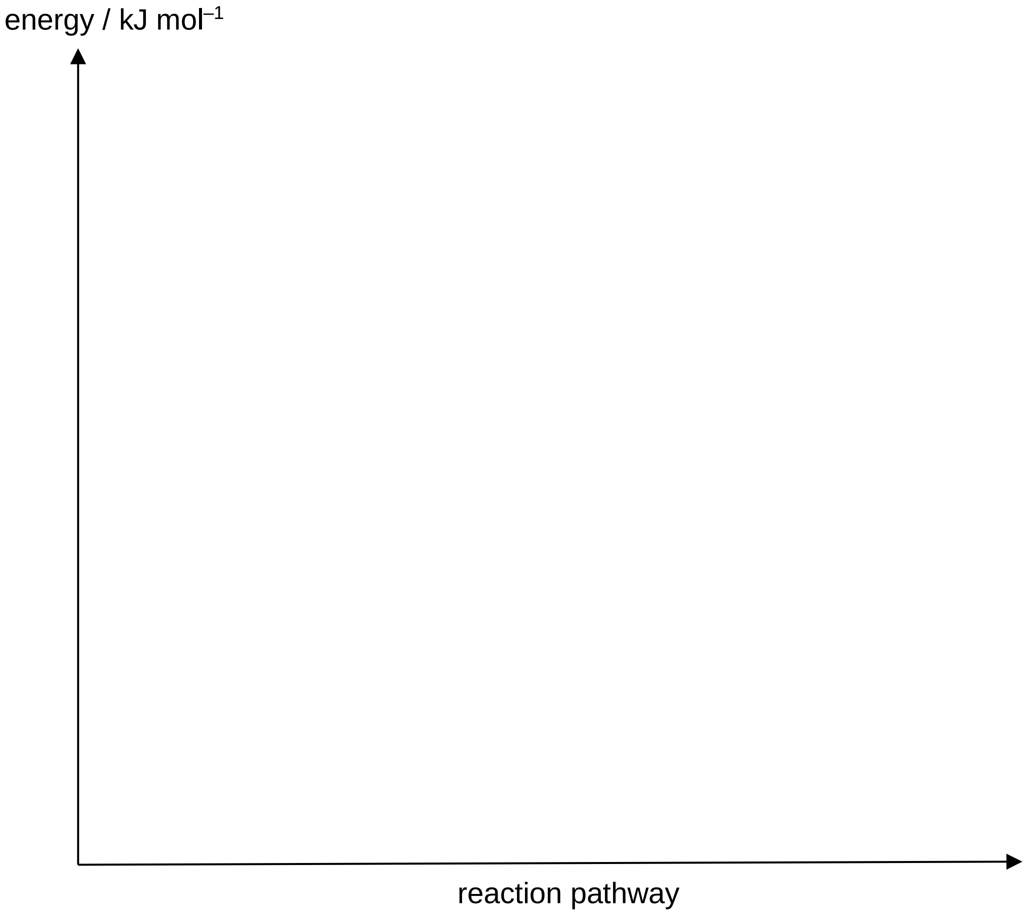
…………………………………………………………………………………………… [2]

(ii) **Y** is energetically more stable than **X**.

On the same axes, sketch **two** reaction pathway diagrams to illustrate the formation of compounds **X** and **Y** from 1,3-butadiene**,** labelling the reactants, intermediate and product for each diagram.

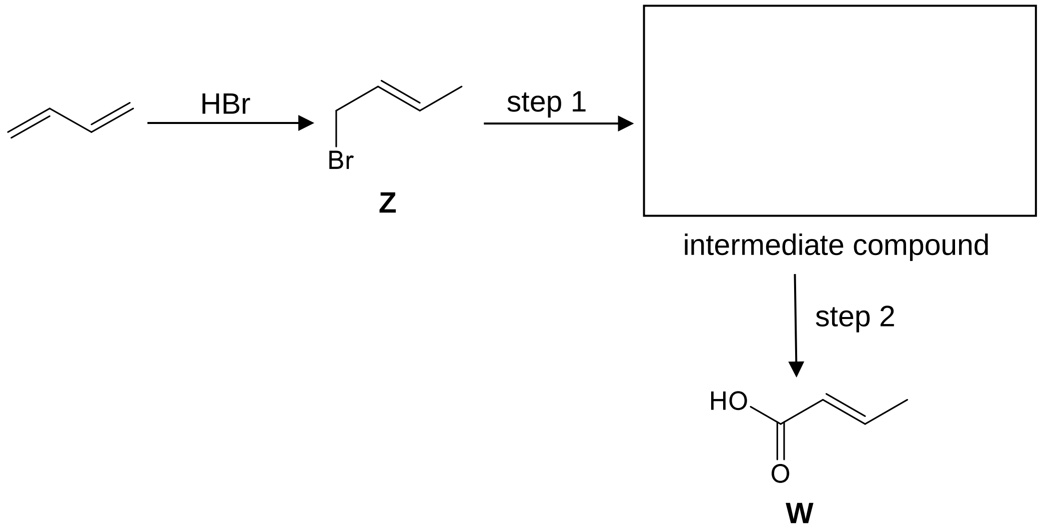


[3]

(e) Draw the structural formula of the major product formed when 1,3-butadiene reacts with an equimolar amount of aqueous bromine at 45 °C.

[1]

(f) **(i)** 1,3-butadiene can be used to synthesise compound **W** via the reaction scheme below.



Complete the reaction scheme above by drawing the structure of the intermediate compound in the box provided.

Suggest appropriate reagents and conditions for steps 1 and 2.

step 1: ………………………………………………………………………………………

step 2: ………………………………………………………………………………………

[3]

(ii) Describe a simple chemical test to distinguish **W** from 1,3-butadiene. Include any observations you would make.

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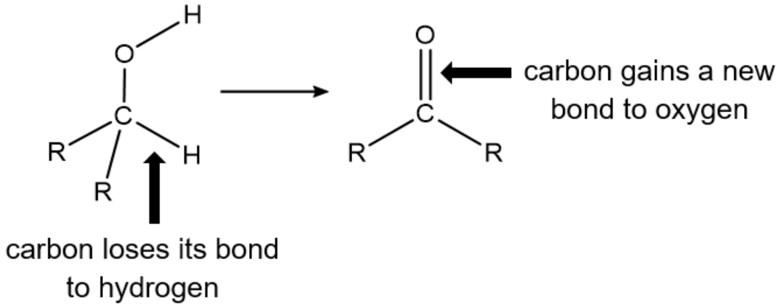
…………………………………………………………………………………………… [2]

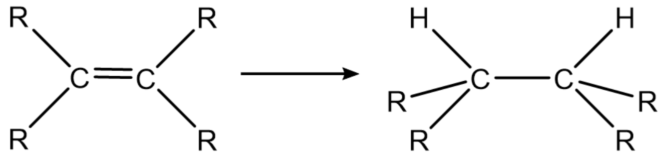
[Total: 16]

4 In organic chemistry, a heteroatom is an atom other than carbon or hydrogen. An example of a heteroatom is oxygen.

When a carbon atom in an organic compound loses a bond to a hydrogen and gains a new bond to a heteroatom (or to another carbon), the compound is **oxidised**.

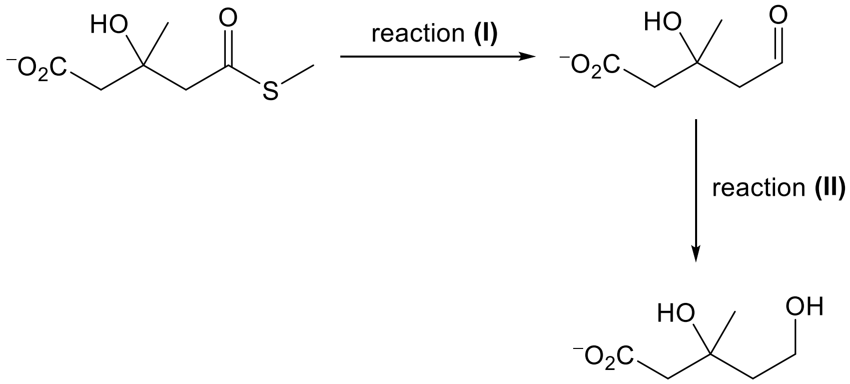


Conversely, when a carbon atom in an organic compound loses a bond to a heteroatom (or to another carbon atom) and gains a bond to a hydrogen, the compound is **reduced**, as shown by the following example.

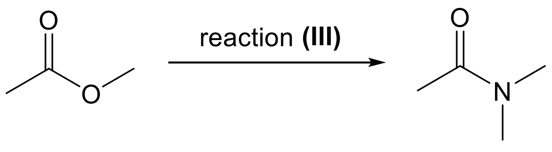


(a) **(i)** State which of the following three reactions are reduction reactions.

(1)



(2)



compound **A**

reduction reaction(s): ………………..……………………………………………….. [1]

(ii) For one of the reactions you chose in part **(a)(i)**, explain, in terms of the bonds lost and gained by the relevant carbon atoms, why the reaction is a reduction.

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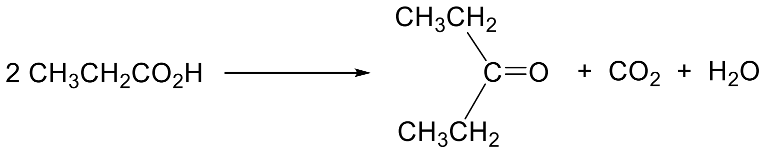
………………………………………………………………………………………… [1]

(iii) Give the structure of the product formed when compound **A** in **(a)(i)(2)** is reacted with $LiAlH_4$ in dry ether.

[1]

(b) The reduction of carboxylic acids produces aldehydes and primary alcohols. To produce ketones from carboxylic acids, a process known as ketonic decarboxylation can be used.

For example, the ketonic decarboxylation of propanoic acid to form pentan-3-one is shown below.



$$2\,CH_3CH_2CO_2H \longrightarrow (CH_3CH_2)_2C{=}O + CO_2 + H_2O$$

(i) The ketonic decarboxylation of compound **J** produces cyclopentanone. Give the structure of compound **J**.

[1]

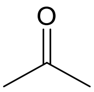
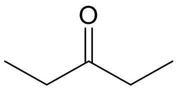
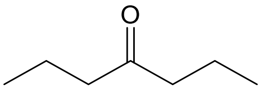
When ketonic decarboxylation was carried out using a 1:1 molar mixture of propanoic acid and ethanoic acid, a mixture of three ketones was formed.

(ii) Suggest the structures of the three ketones, and the ratio in which they might be produced.

[2]

Data regarding some ketones are given in Table 4.1.

Table 4.1

ketone	vapour pressure / mm Hg at 25 °C	boiling point / °C
	232	56.0
	35.8	102
	5.20	144

(c) The vapour pressure of a substance can be defined as the pressure exerted by the vapour of the substance in equilibrium with its liquid phase at a given temperature in a closed system.

(i) Explain why the vapour pressure of the above ketones decreases with increasing number of carbon atoms.

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(ii) Cyclopentanone has a boiling point of 130 °C.

By using relevant values from Table 4.1, calculate an approximate value for the vapour pressure of cyclopentanone.

[1]

[Total: 9]

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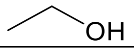
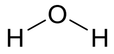
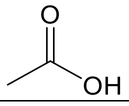
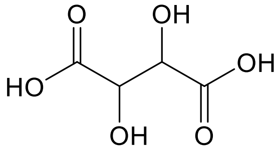
5 Wine contains many organic compounds, some of which are naturally occurring and some are products of fermentation. Data about some of these compounds and water are given in Table 5.1.

Table 5.1

compound	skeletal formula	pK_{a1}	pK_{a2}
ethanol		15.9	–
water		14.0	–
ethanoic acid		4.76	–
tartaric acid		2.98	4.34

(a) Explain the trend in the relative magnitudes of the pK_{a1} values in Table 5.1.

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(b) Tartaric acid (H_2T) is responsible for the tartness in wine.

In an experiment, 25.0 cm^3 of a solution of tartaric acid was titrated against a standard solution of KOH. It was found that 30.00 cm^3 of 0.100 mol dm^{-3} KOH was required to reach the second equivalence point.

$$2KOH(aq) + H_2T(aq) \longrightarrow K_2T(aq) + 2H_2O(l)$$

(i) Calculate the concentration of T^{2-} ions produced at the second equivalence point.

[1]

T^{2-} ions undergo hydrolysis to give an alkaline solution.

$$T^{2-} + H_2O \rightleftharpoons HT^- + OH^-$$

(ii) Using relevant data from Table 5.1, calculate the pH of the solution at the second equivalence point, ignoring the hydrolysis of HT^-.

[2]

(c) Potassium hydrogen tartrate, KHT, widely known as cream of tartar, is a powder that is often used in baking.

KHT is sparingly soluble in water.

$$KHT(s) \rightleftharpoons K^+(aq) + HT^-(aq)$$

The concentration of HT^- can be determined by titration.

$$HT^-(aq) + OH^-(aq) \longrightarrow T^{2-}(aq) + H_2O(l)$$

A sample of powdered KHT was added to 100 cm^3 of ***x*** mol dm^{-3} aqueous potassium nitrate. The mixture was allowed to reach equilibrium and then filtered. 25.0 cm^3 of the filtrate was then titrated with 0.0400 mol dm^{-3} sodium hydroxide. A titre volume of 20.00 cm^3 was obtained.

(K_{sp} of KHT = 2.11 x 10^{-3} mol^2 dm^{-6})

(i) Calculate the solubility of KHT in the potassium nitrate solution.

[2]

(ii) Hence, find the value of **x**.

[2]

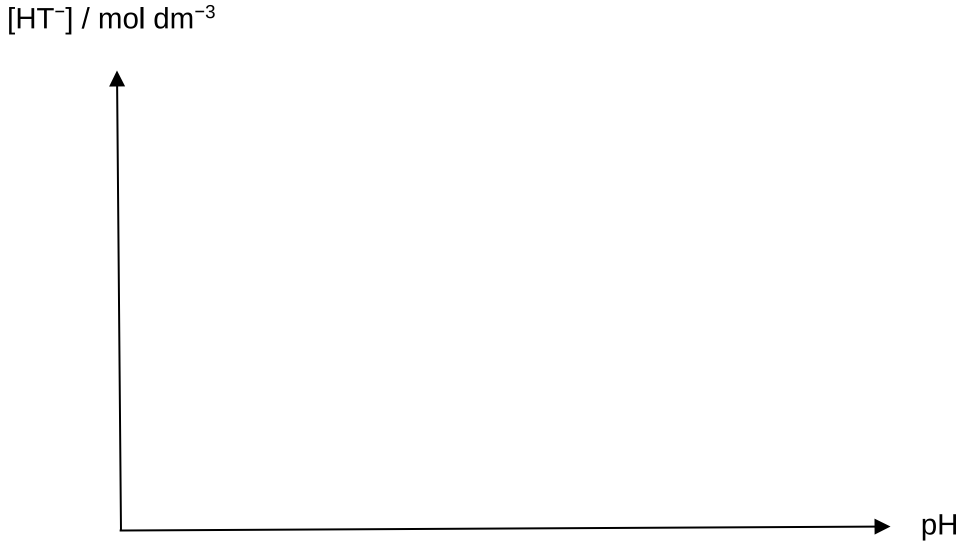
(d) The following equilibria exist for H_2T in a solution.

$$H_2T \rightleftharpoons H^+ + HT^- \quad \text{------- (1)}$$

$$HT^- \rightleftharpoons H^+ + T^{2-} \quad \text{------- (2)}$$

A solution of H_2T was prepared and its pH varied. It was found that the concentration of HT^- was maximal at pH 3.7.

Sketch a labelled graph of concentration of HT^- against pH and explain the shape of the graph with reference to the equilibrium equations.



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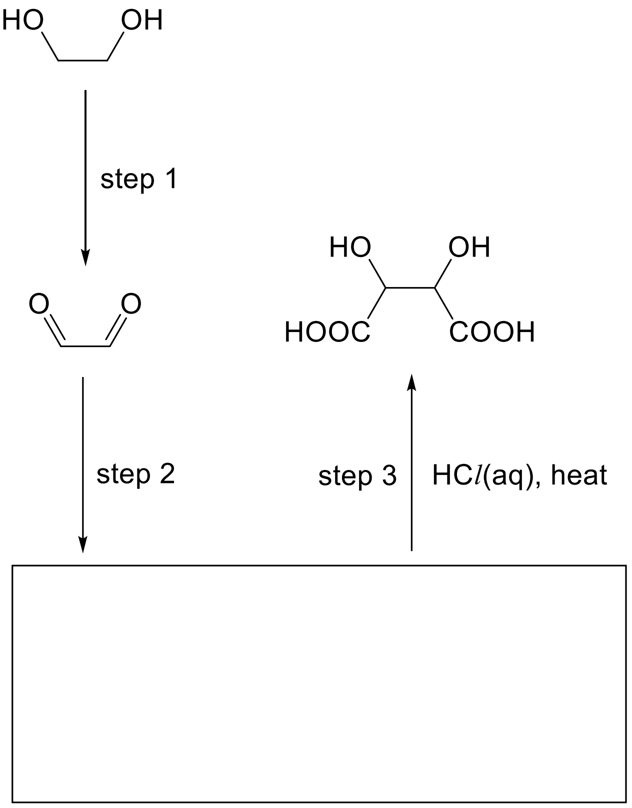
(e) Tartaric acid can be prepared from ethane-1,2-diol in 3 steps.



Identify the organic product from step 2 by drawing its structure in the box provided above.

Suggest reagents and conditions for steps 1 and 2.

step 1: ……………………………………………………………………………………………

step 2: ……………………………………………………………………………………………

[3]

[Total: 15]

6 **(a)** The aqueous solutions of two cobalt(II) salts are prepared and their colours are indicated in Table 6.1.

Table 6.1

aqueous solution	colour
$CoCl_2$	pink
$[Co(NH_3)_6]Cl_2$	yellow-brown

(i) Explain why an aqueous solution of $CoCl_2$ is coloured.

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……………………………………………………………………………………………. [3]

(ii) Explain why the two aqueous solutions have different colours despite both containing cobalt(II) salts.

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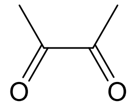
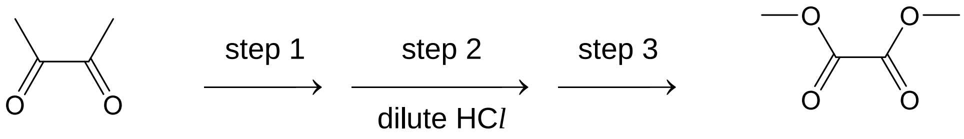
……………………………………………………………………………………………. [1]

(b) Butane-2,3-dione is one of the compounds responsible for the flavour of butter.



butane-2,3-dione

(i) The reaction scheme below shows the three-step conversion of butane-2,3-dione to dimethyl ethanedioate.



dimethyl ethanedioate

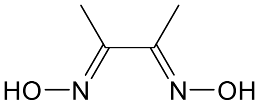
Suggest reagents and conditions for the following steps.

step 1: ………………………………………………………………………………………

step 3: ……………………………………………………………………………….......

[2]

Butane-2,3-dione reacts with a compound **P** to produce dimethylglyoxime ($C_4H_8N_2O_2$). The reaction which occurs is similar to that of butane-2,3-dione reacting with 2,4-dinitrophenylhydrazine.



dimethylglyoxime
$C_4H_8N_2O_2$

(ii) Identify compound **P**.

[1]

Dimethylglyoxime ($C_4H_8N_2O_2$) can be used to analyse nickel(II) compounds.

An excess of a solution of dimethylglyoxime is first added to an acidic solution of a nickel(II) compound. When aqueous ammonia is next added, a nickel(II) complex, $Ni(C_4H_7N_2O_2)_2$, is produced as a red precipitate.

$$[Ni(H_2O)_6]^{2+} + 2C_4H_8N_2O_2 + 2NH_3 \longrightarrow Ni(C_4H_7N_2O_2)_2 + 2NH_4^+ + 6H_2O$$

(iii) State and explain the role of ammonia in the above reaction.

…………………………………………………………………………………………….

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

(iv) Hence draw the structure of the ligand in the $Ni(C_4H_7N_2O_2)_2$ complex.

[1]

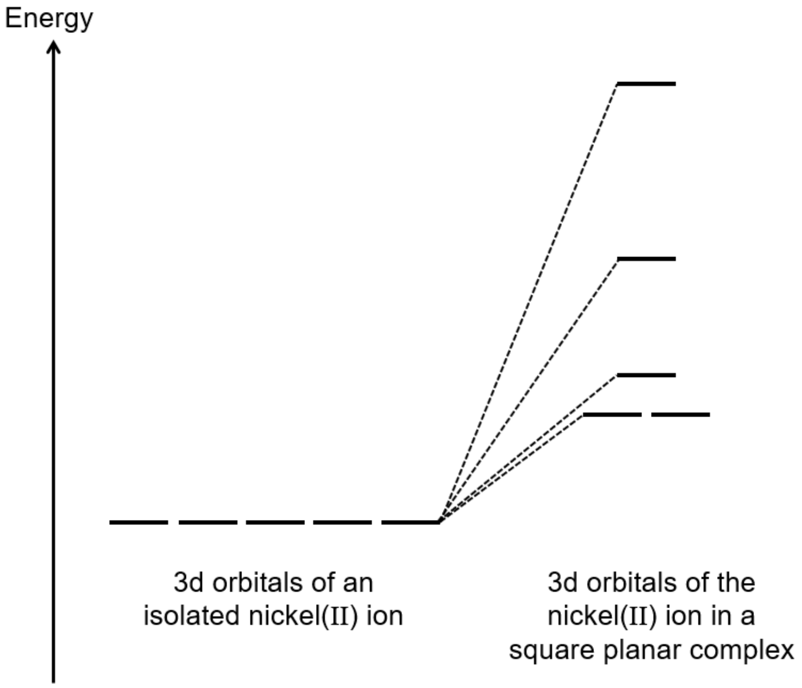
The $Ni(C_4H_7N_2O_2)_2$ complex is square planar in shape with respect to the nickel(II) ion. The coordination number of nickel in the complex is 4. The ligands in the complex are bidentate with the nitrogen atoms bonded to the nickel(II) ion. The –OH group in each ligand is involved in intramolecular hydrogen bonding.

(v) Draw the structure of the $Ni(C_4H_7N_2O_2)_2$ complex and label one of the two intramolecular hydrogen bonds clearly.

[2]

(vi) In the formation of a square planar complex, the ligands approach the central metal ion along the x and y axes.

The diagram below shows how the 3d orbitals of the nickel(II) ion in a square planar complex are split based on the crystal field theory.



State the identity of the 3d orbital with the highest energy in the nickel(II) ion in a square planar complex. Explain your answer.

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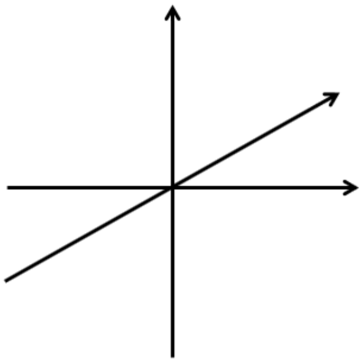
(vii) Label the Cartesian axes given below and use it to draw the shape of the 3d orbital identified in **(vi)**.



[1]

(c) Rhodium, platinum and palladium are transition metal catalysts used in catalytic converters in petrol-powered cars. They help to catalyse redox reactions which remove harmful pollutants such as carbon monoxide, unburnt hydrocarbons and nitrogen oxides, which are present in the exhaust fumes from a petrol engine.

(i) Construct a balanced equation for the reaction in which both CO and NO are removed from the exhaust gases by a catalytic converter.

.... [1]

(ii) The reaction in **(i)** is catalysed by rhodium in the catalytic converter.

Explain why rhodium is able to act as a heterogeneous catalyst.

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.... [1]

Describe how the rhodium catalyst speeds up the gaseous reaction in **(i)**.

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.... [3]

Rhodium compounds are used as homogeneous catalysts in the Monsanto process for the manufacture of ethanoic acid.

The Monsanto process is carried out in solution in methanol and involves the following series of steps.

step 1 $CH_3OH + HI \longrightarrow CH_3I + H_2O$

step 2 $CH_3I + [Rh(CO)_2I_2]^- \longrightarrow [(CH_3)Rh(CO)_2I_3]^-$

step 3 $[(CH_3)Rh(CO)_2I_3]^- \longrightarrow [(CH_3CO)Rh(CO)I_3]^-$

step 4 $[(CH_3CO)Rh(CO)I_3]^- + CO \longrightarrow [(CH_3CO)Rh(CO)_2I_3]^-$

step 5 $[(CH_3CO)Rh(CO)_2I_3]^- \longrightarrow [Rh(CO)_2I_2]^- + CH_3COI$

step 6 $CH_3COI + H_2O \longrightarrow CH_3COOH + HI$

(iii) Write an overall equation for the process.

.... [1]

[Total: 20]