Catholic Junior College

JC2 Preliminary Examination
Higher 2

CANDIDATE NAME

CLASS **2T**

CHEMISTRY **9729/02**

Paper 2 Structured Questions

Friday 23 August 2019

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your 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.

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

At the end of 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			
Paper 1			**30**
Paper 2	**Q 1**	**11**	
	Q 2	**18**	
	Q 3	**18**	
	Q 4	**10**	
	Q 5	**10**	
	Q6	**8**	**75**
Paper 3	**Q 1**	**22**	
	Q 2	**19**	
	Q 3	**19**	
	Q 4 / 5	**20**	**80**
Paper 4			**55**
Total			**240**
Total % and Grade			

This document consists of **19** printed pages and **1** blank page.

[Turn over

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

1 The Taj Mahal is an ivory-white marble monument in the Indian city of Agra. The famous building is becoming brown and green from environmental pollution. Acid rain accelerates the erosion of marble monuments. Marble consists primarily of calcium carbonate.

(a) You should refer to the following solubility product data to help answer the following questions.

Substance	$CaCO_3$	$CaSO_4$	$BaCO_3$	$BaSO_4$
Solubility product / $mol^2\,dm^{-6}$	1.69×10^{-8}	2.03×10^{-3}	8.28×10^{-9}	8.84×10^{-11}

The pollutant SO_2 dissolves in rainwater to form sulfuric acid. The sulfuric acid slowly converts calcium carbonate into solid calcium sulfate.

(i) Write an equation for the reaction between calcium carbonate and sulfuric acid.

.... [1]

(ii) By calculating the solubilities of calcium carbonate and calcium sulfate, deduce why acid rain accelerates the erosion of marble.

[3]

The lifespan of Taj Mahal can be extended by treatment with an aqueous mixture of barium hydroxide, $Ba(OH)_2$ and urea, $CO(NH_2)_2$. As this solution soaks into the porous marble, the urea slowly hydrolyses forming ammonia and carbon dioxide. The carbon dioxide released reacts with the barium hydroxide in the mixture forming barium carbonate.

(iii) Write an equation for the reaction between barium hydroxide and carbon dioxide.

.... [1]

(iv) By considering the reaction between surface barium carbonate and acid rain, explain how the erosion process can be slowed down.

....

....

.... [1]

(b) Group 2 carbonates undergo decomposition in the same way at different temperatures.

(i) Predict and explain the order of decomposition temperatures for the three carbonates, $MgCO_3$, $CaCO_3$ and $BaCO_3$.

....

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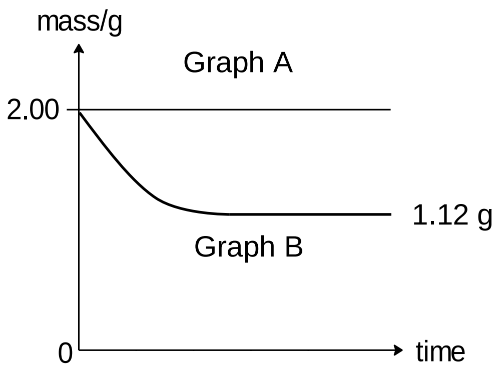
.... [3]

The graph given below shows the change in mass when 2.00 g of each $CaCO_3$ and $BaCO_3$ were heated separately at a temperature, T ^{o}C.



(ii) From the shapes of the graphs, identify $CaCO_3$ and $BaCO_3$ in the spaces provided below**.**

Graph A: ....

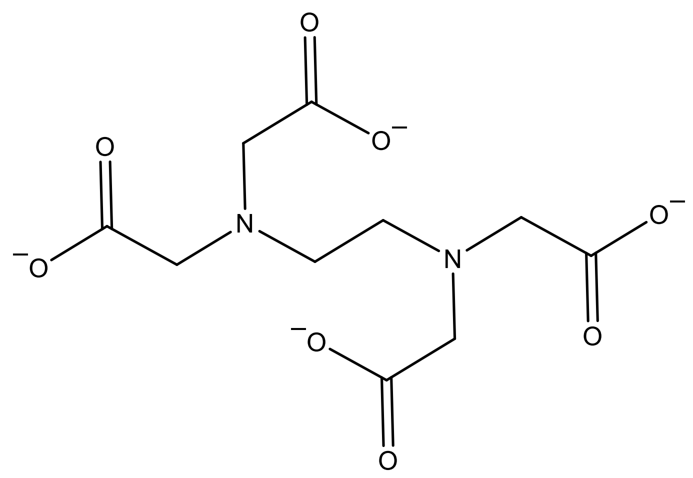
Graph B: ....

[1]

(iii) Sketch on the same axes, a graph that would be obtained by heating 2.00 g of magnesium carbonate, $MgCO_3$, at the same temperature, T ^{o}C. [1]

[Total: 11]

2 Hydrogen peroxide is a common bleaching agent used to whiten wood pulp during the manufacture of paper. Transition metal ions such as Fe^{3+}(aq), that are naturally present in wood pulp, would catalyse the decomposition of hydrogen peroxide, and hence reduce the bleaching efficiency. The wood pulp is therefore washed with a chelating agent such as EDTA to remove the transition metal ions before hydrogen peroxide is added.
[EDTA = $(^{-}O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2^{-})_2$]



EDTA

(a) **(i)** Any Fe^{3+}(aq) in the wood pulp would form a polydentate complex with EDTA. Give the formula of the complex formed. You may use the abbreviation 'EDTA' in your answer.

.... [1]

(ii) State the coordination number of the complex in **(a)(i)**.

.... [1]

(b) **(i)** H_2O and NH_3 are simple molecules. Explain why, at room temperature, H_2O is a liquid while NH_3 is a gas.

....

....

....

....

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.... [2]

(ii) While EDTA is a polydentate *ligand*, H_2O and NH_3 are examples of monodentate *ligands* in transition metal complexes. Explain what is meant by the term *ligand*.

....

....

.... [1]

(c) Consider the ion $[Cu(H_2O)_6]^{2+}$ present in an aqueous solution of copper(II) sulfate. When a central metal is surrounded by water ligands, it is known as an aqua complex. Addition of NH_3 to the copper(II) sulfate solution brings about a stepwise replacement of the water ligands by ammonia ligands such that the overall equation is shown below.

$$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$$

The stability constant, K_{stab}, for the above equilibrium is given as:

$$K_{stab} = \frac{[Cu(NH_3)_4(H_2O)_2\,]^{2+}}{[Cu(H_2O)_6{}^{2+}][NH_3]^4} = 1 \times 10^{13}\ mol^{-4}\ dm^{12}$$

In the above expression, the square brackets imply concentrations in mol dm^{-3}. Similar to the example shown above for $[Cu(H_2O)_6]^{2+}$, complexes of iron have values of K_{stab} which are measured against the relative stability of the aqua complex of iron.

The following table lists some iron complexes together with their colours and their stability constants.

aqueous complex	**colour**	K_{stab}
$[Fe(SCN)(H_2O)_5]^{2+}$	deep red	1×10^2
$[FeF_6]^{3-}$	colourless	2×10^{15}
Fe^{3+}(aq) complex with EDTA	yellow	x
$[Fe(CN)_6]^{3-}$	pale yellow	1×10^{31}

(i) Including equations where appropriate, use the data to explain

- why an addition of KSCN(aq) to a solution of Fe^{3+}(aq) produces a deep red solution.

....

....

....

.... [2]

- what is observed when KF(aq) is added to the deep red solution mentioned above.

....

....

....

.... [2]

(ii) Deduce if the value of ***x*****,** the K_{stab} of the Fe^{3+}(aq) complex with EDTA, is expected to be higher or lower than the K_{stab} value of $[FeF_6]^{3-}$.

....

.... [1]

(iii) Give the electronic configuration of Fe in $[Fe(CN)_6]^{3-}$(aq).

.... [1]

(iv) $[Fe(CN)_6]^{3-}$(aq) is a weaker oxidising agent than Fe^{3+}(aq). Explain this statement by quoting appropriate $E^{\ominus}$ values from the *Data Booklet*.

....

....

....

....

.... [2]

(d) **(i)** Carbon monoxide, CO, is a toxic gas. Draw the dot-and-cross structure of CO.

[1]

CO is also a ligand in iron pentacarbonyl, $Fe(CO)_5$. CO binds to the central metal via the carbon atom.

(ii) What is the oxidation state of iron in $Fe(CO)_5$?

.... [1]

(iii) Draw and name the shape of the complex, $Fe(CO)_5$.

[2]

(iv) When iron pentacarbonyl reacts with iodine in hexane solution, iron is oxidised and an octahedral complex, $Fe(CO)_4I_2$, is formed.

Isomerism can occur in $Fe(CO)_4I_2$ due to different positions of the ligands with respect to the central metal ion. Draw the two isomers of $Fe(CO)_4I_2$.

[1]

[Total: 18]

3 **(a)** Converting harmful greenhouse gases such as CO_2 into useful chemical commodities, such as methanol, CH_3OH, is gaining traction in green chemistry as it is economically viable and environment–friendly.

A mixture containing 1.0 mol of CO_2 and 3.0 mol of H_2 is allowed to reach *dynamic equilibrium* at 200°C and 55 bar. Under these conditions, 32% CO_2 is converted to methanol, CH_3OH.

$$CO_2\,(g) \;+\; 3H_2\,(g) \rightleftharpoons CH_3OH\,(g) \;+\; H_2O\,(g)$$

Calculate the equilibrium pressure of each gas and hence calculate the K_p value, with the units for this reaction at 200°C.

[4]

(b) Methanol reacts with carbon monoxide with the help of catalyst to produce ethanoic acid.

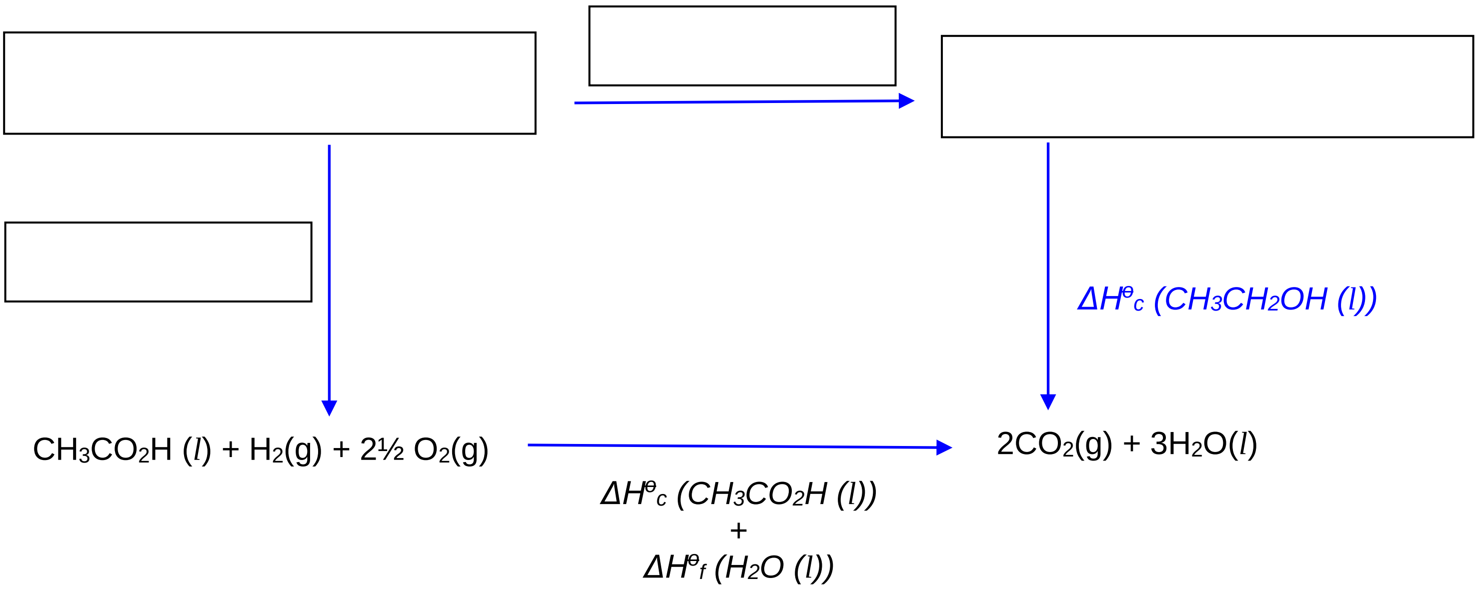
Define the term *standard enthalpy change of formation* of liquid ethanoic acid, CH_3CO_2H (*l*).

....

.... [1]

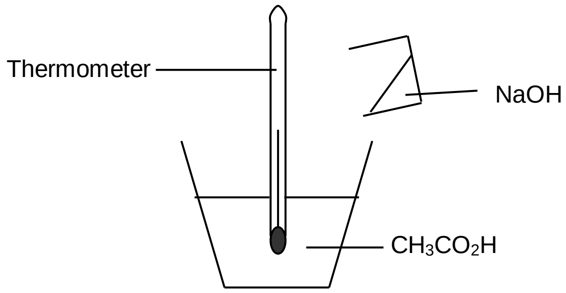
(c) Using the enthalpy change values given below, complete the energy cycle and calculate the standard enthalpy change of formation for ethanoic acid, CH_3CO_2H (*l*).

$\Delta H^\ominus_f$ (CH_3CH_2OH (*l*))	= – 278 kJ mol^{-1}
$\Delta H^\ominus_c$ (CH_3CH_2OH (*l*))	= – 1371 kJ mol^{-1}
$\Delta H^\ominus_c$ (CH_3CO_2H (*l*))	= – 876 kJ mol^{-1}
$\Delta H^\ominus_f$ (H_2O (*l*))	= – 286 kJ mol^{-1}



[4]

(d) The ethanoic acid, CH_3CO_2H can undergo neutralisation with sodium hydroxide, NaOH. A thermochemical experiment was carried out to determine the enthalpy change of neutralisation using the experimental set–up below.



The following results were obtained:

Volume of NaOH added / cm^3	50.0
Volume of CH_3CO_2H added / cm^3	50.0
Concentration of NaOH used / mol dm^{-3}	1.00
Concentration of CH_3CO_2H used / mol dm^{-3}	0.65
Initial temperature of CH_3CO_2H / ^oC	25.0
Highest temperature reached / ^oC	28.5
Specific heat capacity of water / J g^{-1} K^{-1}	4.18
Density of water / g cm^{-3}	1.00

(i) Use the results to determine the experimental enthalpy change of neutralisation.

[3]

(ii) The experiment described in **(d)(i)** was repeated using HC*l* instead of CH_3CO_2H, under the same conditions. The enthalpy change of neutralisation was found to be –57.9 kJ mol^{-1}. Apart from heat loss, suggest another reason for the discrepancy between this value and that calculated in **(d)(i)**.

....

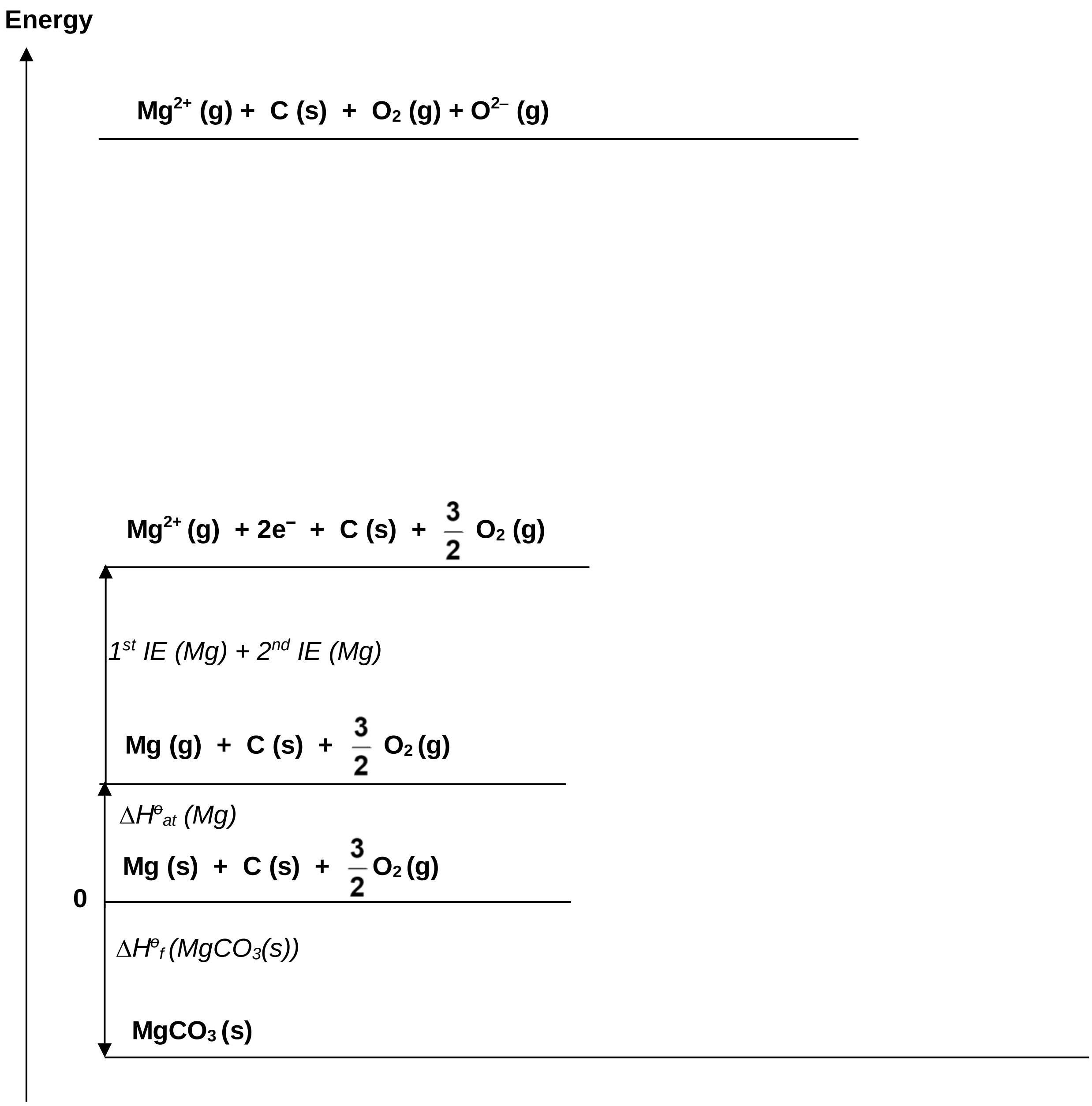
.... [1]

(e) Like many acids, ethanoic acid reacts with basic carbonates such as magnesium carbonate, $MgCO_3$ to release carbon dioxide.

Using the following data and relevant data from the *Data Booklet*, complete the following energy level diagram and use it to determine the standard enthalpy change of formation of magnesium carbonate, $MgCO_3$. [5]

lattice energy of $MgCO_3$ (s)	= –3208 kJ mol^{-1}
standard enthalpy change of atomisation of Mg (s)	= +147 kJ mol^{-1}
sum of 1st and 2nd electron affinity of oxygen	= +702 kJ mol^{-1}
standard enthalpy change of formation of CO_2 (g)	= –393 kJ mol^{-1}
standard enthalpy change of reaction below, $\Delta H^{\ominus}_r$	= –778 kJ mol^{-1}

$O^{2-}(g) + CO_2(g) \longrightarrow CO_3^{2-}(g)$



[Total: 18]

4 Dragons are able to breathe fire because the parasitic bacteria that live in their lungs produce flammable gases. If a dragon exhales sharply, the gas can ignite due to the friction against the rough walls of the larynx.

(a) The gas exhaled by a dragon contains 20 mole % of hydrogen sulfide, H_2S and 15 mole % of oxygen. The average volume of a dragon's lung is 5.1 m^3 and due to the high pressures experienced when a dragon exhales, the molar volume of the gas contained in their lungs is 15 $dm^3\ mol^{-1}$.

(i) Calculate the total amount of gas in moles contained in a dragon's lung.

[1]

(ii) Assuming the temperature of a dragon's lung is 40 ^{o}C and the gaseous mixture behaves ideally, use the ideal gas equation and your answer in **(a)(i)** to calculate the internal pressure in the lung experienced by a dragon.

[1]

(iii) The actual pressure in the dragon's lung is lower than the value calculated in **(a)(ii)**. Account for the discrepancy observed.

....

....

....

.... [1]

(iv) Write a balanced equation for the reaction that describes the burning of gas exhaled by the dragon. Hence, calculate the additional moles of oxygen required for the complete combustion of one exhalation of the dragon.

[3]

(b) The parasitic bacteria in the dragon's lung produces a protein molecule **A** which speeds up the formation of flammable gases.

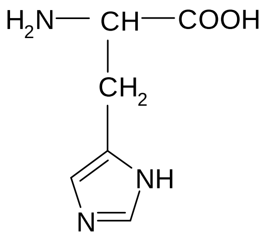
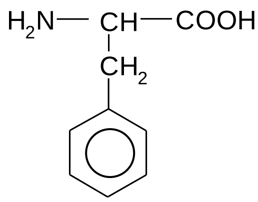
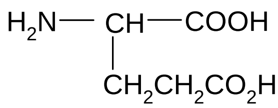
In the study of the structure of **A**, it was digested using two different enzymes. The fragments obtained were separated using electrophoresis. Analysis of the fragments from each digestion gave the following results:

Digestion using the first enzyme:	Digestion using the second enzyme:
his-phe-gly ser-pro-glu asp-gly thr-phe-leu	gly-asp-gly-thr pro-glu phe-leu-ser his-phe

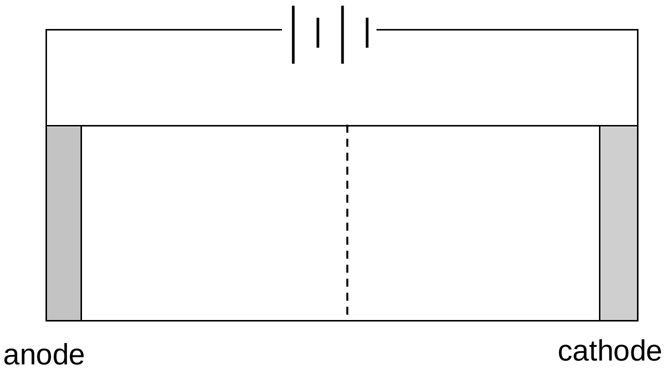
(i) Write out the amino acid sequence of the smallest polypeptide **A**.

.... [2]

(ii) A tripeptide, his-phe-glu, obtained from **A** was further hydrolysed. The resulting solution was added to an excess of a buffer solution of pH 6.5 and placed at the centre of the plate. A potential difference was then applied across the plate.

Amino acids	 his	 phe	 glu
Isoelectric point	7.58	5.48	3.10

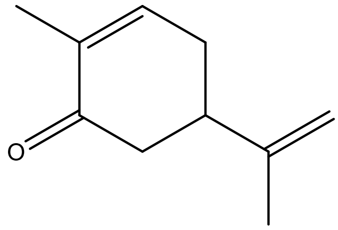
Indicate the relative positions of the amino acids on the diagram below.



[2]

[Total: 10]

5 Carvone is a chemical found naturally in essential oils extracted from the seeds of two common herbs, spearmint and dill.



Carvone

Two stereoisomers of carvone are responsible for the distinctively different flavor and smell of the two herbs.

(a) State the type of stereoisomerism carvone can exhibit.

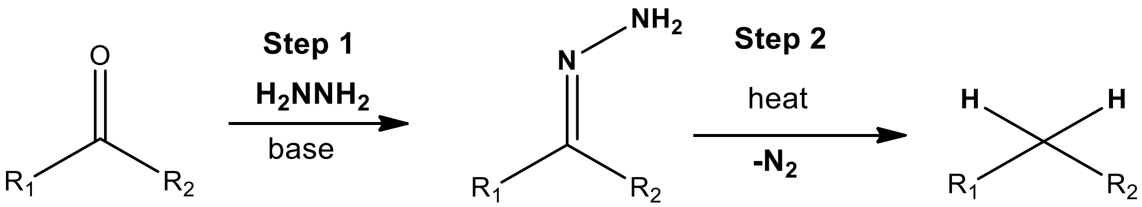
.... [1]

(b) Draw the two stereoisomers of carvone.

[1]

(c) Carvone undergoes reduction with different reagents and conditions to form different products. One notable reduction method is the ***Wolff-Kishner reduction*** whereby the ketone functional group in carvone reacts with hydrazine, N_2H_4, in the presence of a strong base to form limonene, $C_{10}H_{16}$, a major component in the oil of citrus fruit peels.

The general reaction sequence of the ***Wolff-Kishner reduction*** is shown below.

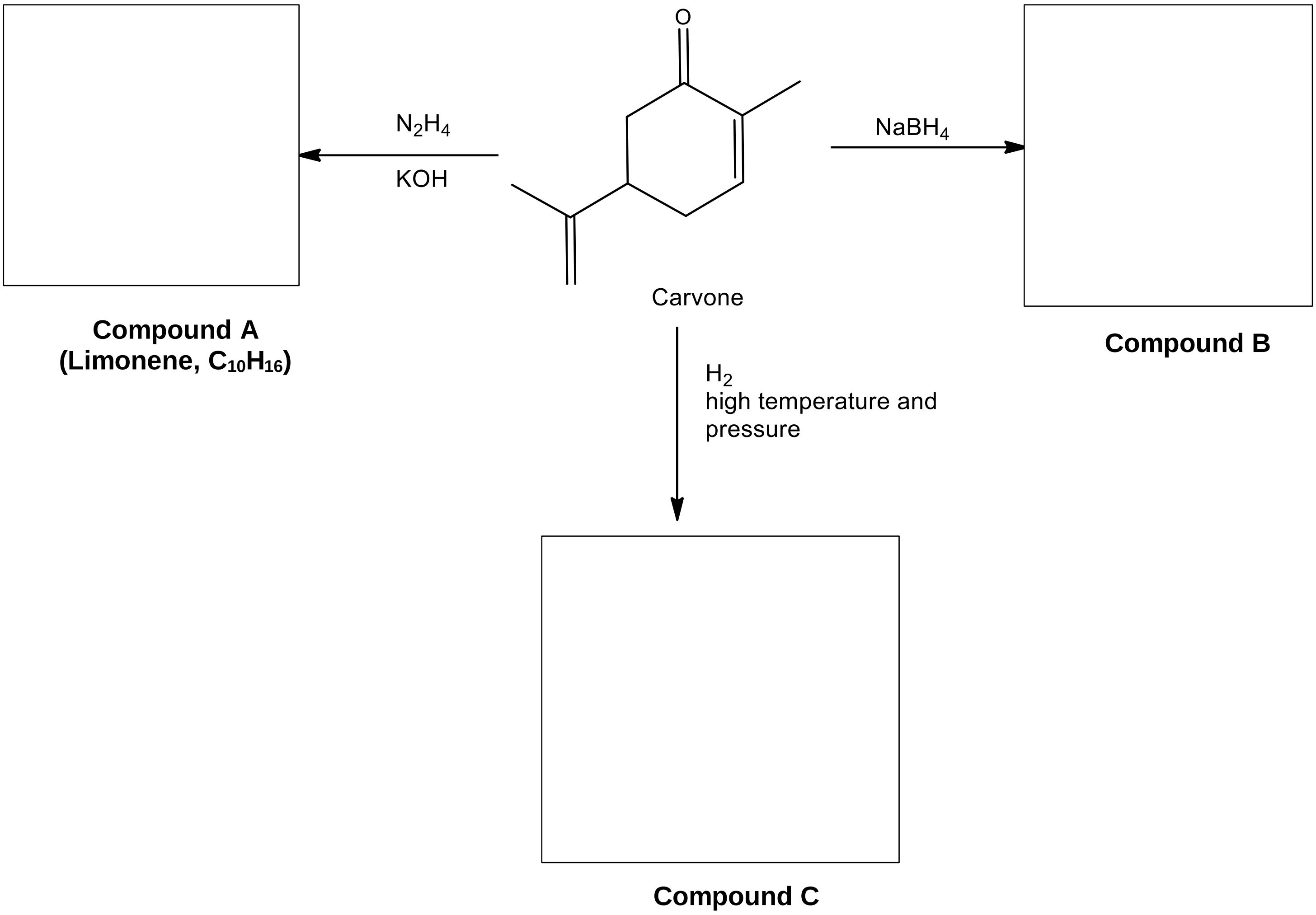


The ***Wolff-Kishner reduction*** is unsuitable for base-sensitive reactants.

(i) Suggest the type of reaction in **Step 1**.

.... [1]

(ii) The following reaction scheme shows the various reduction reactions of carvone. Suggest the structural formulae of compounds **A**, **B** and **C** in the boxes below.



[3]

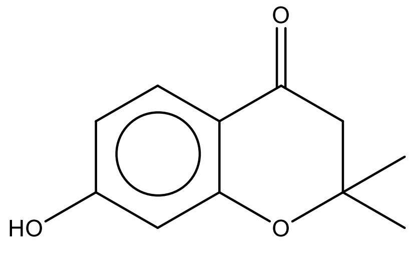
(iii) Suggest a simple chemical test that could distinguish between carvone and limonene. State the observations expected for each compound and the products (if any) that gives the observations.

Reagents and conditions: ....

	Observations:	Products:
Carvone		
Limonene		

[3]

(iv) Suggest a reason why the following compound is unlikely to undergo the ***Wolff-Kishner reduction*** despite the presence of a ketone functional group.



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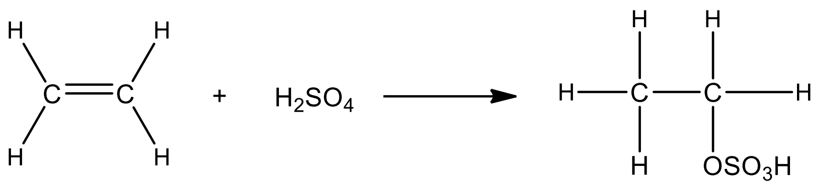
…………………….. [1]

[Total: 10]

6 When fuming sulfuric acid reacts with alkenes, electrophilic addition occurs to form alkyl hydrogensulfates. This is exemplified by the reaction involving ethene below.



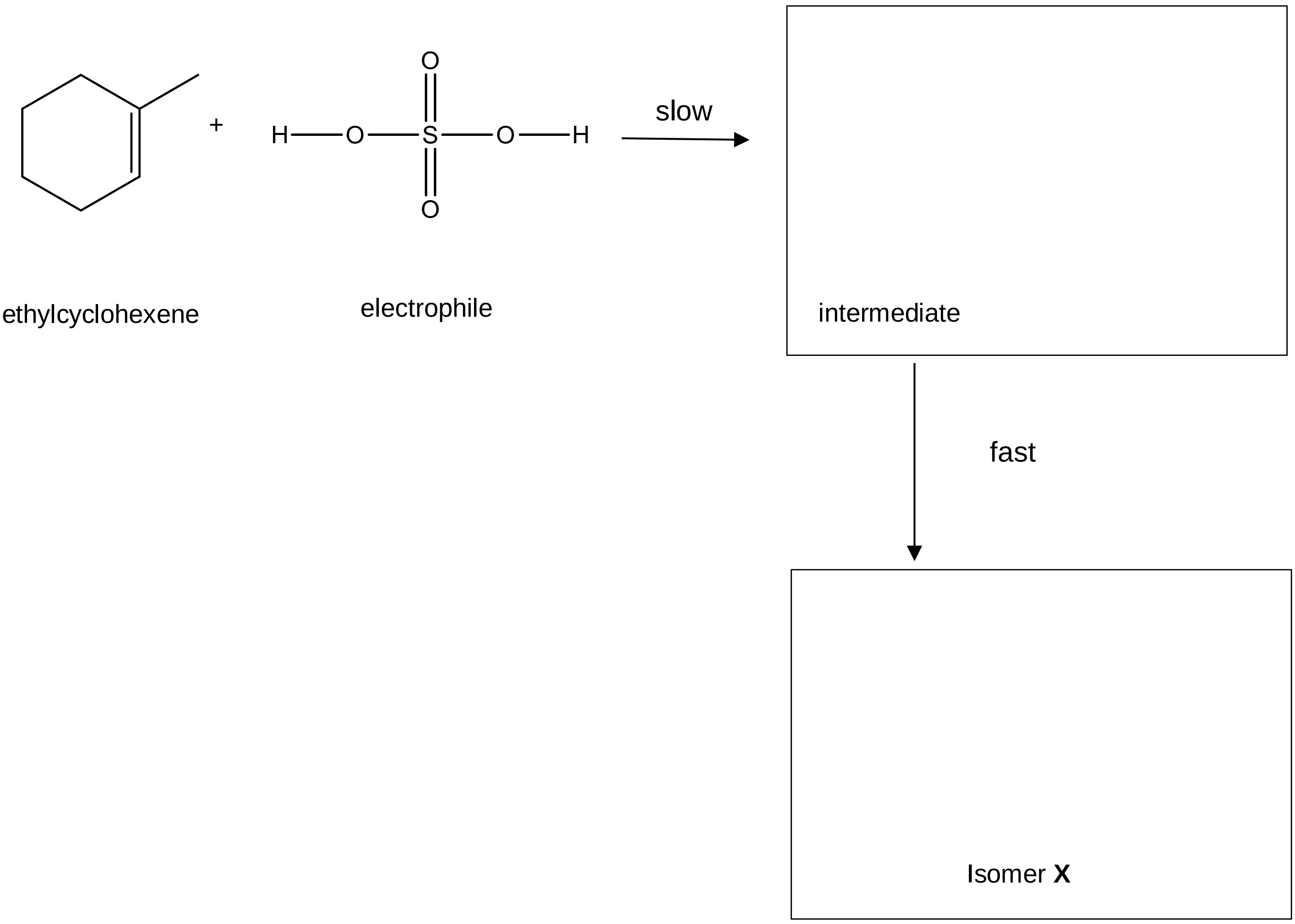
When 1-methylcyclohexene reacts with fuming sulfuric acid, a mixture of two isomers **X** and **Y** are formed, with isomer **X** being the major product.

(a) Name and define the type of isomerism exhibited by isomers **X** and **Y**.

....

....[2]

(b) Complete the following to suggest a mechanism for the reaction between 1-methylcyclohexene and sulfuric acid to form **X**. Show the structure of the intermediate, the movement of the electron pairs and the structure of **X**.



1-methylcyclohexene

electrophile

[4]

(c) Explain why benzene does not undergo addition reactions with fuming sulfuric acid.

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[Total: 8]

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