# Catholic Junior College

## JC2 Preliminary Examination

## Higher 2

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| **CANDIDATE NAME** |  |
| **CLASS** | **2T** |

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# CHEMISTRY **9729/02**

Paper 2 Structured Questions **Friday 23 August 2019**

**2 hours**

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

# WORKED SOLUTIONS

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 / $mol^2\,dm^{-6}$ | $1.69 \times 10^{-8}$ | $2.03 \times 10^{-3}$ | $8.28 \times 10^{-9}$ | $8.84 \times 10^{-11}$ |

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.

**$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2CO_3$**

**Or $CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2$**

[1]

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

**Calculate the solubility of $CaCO_3$, x:**

**$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$**

**$K_{sp}(CaCO_3) = [Ca^{2+}][CO_3^{2-}]$**

**$1.69 \times 10^{-8} = x^2$**

**$x = \underline{1.30 \times 10^{-4}}\ mol\ dm^{-3}$**

**Calculate the solubility of $CaSO_4$, y:**

**$CaSO_4(s) \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}(aq)$**

**$K_{sp}(CaSO_4) = [Ca^{2+}][SO_4^{2-}]$**

**$2.03 \times 10^{-3} = y^2$**

**$y = \underline{4.51 \times 10^{-2}}\ mol\ dm^{-3}$**

**Acid rain contains $H_2SO_4$, which converts $CaCO_3$ into $\underline{CaSO_4}$, which is more soluble in water.**

[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.

**$Ba(OH)_2 + CO_2 \rightarrow BaCO_3 + H_2O$**

[1]

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

**$BaCO_3 + H_2SO_4 \rightarrow BaSO_4 + CO_2 + H_2O$ or $BaCO_3 + H_2SO_4 \rightarrow BaSO_4 + H_2CO_3$**

**$BaCO_3$ can react with $SO_2$ / $H_2SO_4$ in the air to form a layer of barium sulfate, $BaSO_4$. $BaSO_4$ is the least soluble and hence, slow down the erosion process.**

[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 $BaCO_3$.

**Decomposition temperature: $MgCO_3 < CaCO_3 < BaCO_3$**

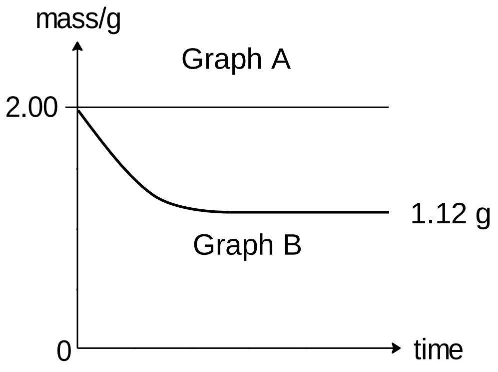
**Going down Group 2, size of cation increases from $Mg^{2+}$ to $Ba^{2+}$.**

Hence, **charge density and polarising power of cation decreases from $Mg^{2+}$ to $Ba^{2+}$.**

Therefore, **the ability of cation to distort the $CO_3^{2-}$ electron cloud**, weakening and break the C−O bond **decreases from $Mg^{2+}$ to $Ba^{2+}$**

Hence less energy is required to decompose $MgCO_3$ and the decomposition temperature is the lowest. [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 °C.



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

**Graph A:** $BaCO_3$

**Graph B:** $CaCO_3$

[1]

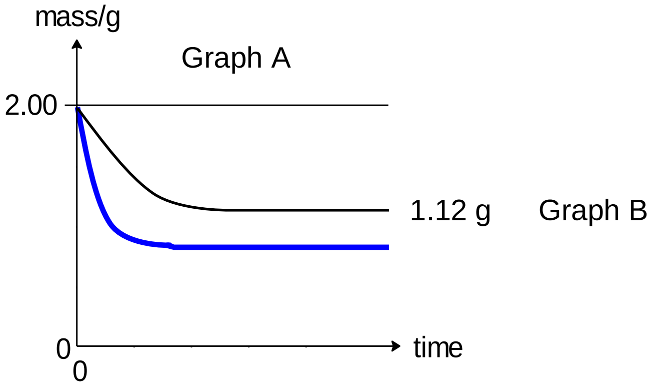
**$CaCO_3 \rightarrow CaO + CO_2$**

**Amount of $CaCO_3$ = 2.00 / 100.1 = $2.00 \times 10^{-2}$ mol**

**$CaCO_3 \equiv CaO$**

**Mass of CaO = $2.00 \times 10^{-2} \times 56.1$ = 1.12 g**

**(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 °C.



[1]

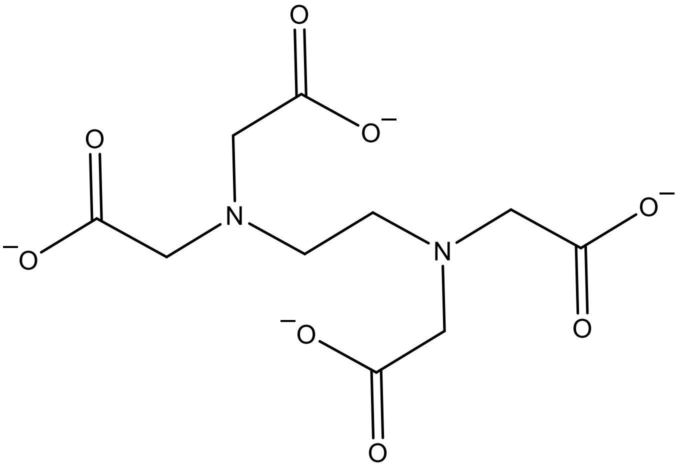
Shorter time to decompose + smaller residual mass

$CaCO_3 \rightarrow CaO + CO_2$
Amount of $CaCO_3$ = 2.00 / 100.1 = 0.0200 mol
$CaCO_3 \equiv CaO$
Mass of CaO = 0.0200 x 56.1 = 1.12 g

Amount $MgCO_3$ = 2.00 / 84.3 = 0.0237 mol
$MgCO_3 \equiv MgO$
Mass of MgO = 0.0237 x 40.3 = 0.955 g
$MgCO_3$ is less thermally stable than $CaCO_3$. Hence, $MgCO_3$ decompose completely faster.

[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.

**$[Fe(EDTA)]^-$** ..................................................................................................... [1]

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

**6** ..................................................................................................... [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.

**$H_2O$ is a liquid due to the presence of more extensive intermolecular hydrogen bonding in $H_2O$ than $NH_3$. On average, $H_2O$ can form two hydrogen bonds per molecule while $NH_3$ can only form one hydrogen bond per molecule. More energy is thus required to overcome the hydrogen bonds in $H_2O$.** ..................... [2]

**Alternative answer:**

**$H_2O$ is a liquid due to the presence of stronger intermolecular hydrogen bonding in $H_2O$ than $NH_3$. O is more electronegative than N hence H−O bond is more polar than H−N bond, thus a greater dipole moment of the H−O bond that makes the intermolecular hydrogen bonding stronger. More energy is thus required to overcome the hydrogen bonds in $H_2O$.**

**(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*.

**A ligand is an ion or molecule that has at least one lone pair of electrons that can be donated into the vacant orbitals in the central metal atom or ion to form a dative covalent bond.** [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 | $1 \times 10^2$ |
| $[FeF_6]^{3-}$ | colourless | $2 \times 10^{15}$ |
| $Fe^{3+}$(aq) complex with edta | yellow | $x$ |
| $[Fe(CN)_6]^{3-}$ | pale yellow | $1 \times 10^{31}$ |

**(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.

**When KCSN is added, the deep red $[Fe(SCN)(H_2O)_5]^{2+}$ is formed as ligand exchange / displacement takes place OR as position of equilibrium shifts right as shown by the higher $K_{stab}$ value**

**$[Fe(H_2O)_6]^{3+} + SCN^- \rightleftharpoons [Fe(SCN)(H_2O)_5]^{2+} + H_2O$** [2]

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

**When KF is added, the colourless $[FeF_6]^{3-}$ is formed.**

**(ligand exchange takes place. $[FeF_6]^{3-}$ is more stable than $[Fe(SCN)(H_2O)_5]^{2+}$ as seen by the larger $K_{stab}$ value.)**

**$[Fe(SCN)(H_2O)_5]^{2+} + 6F^- \rightleftharpoons [FeF_6]^{3-} + SCN^- + 5H_2O$** [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 $[FeF_6]^{3-}$.

**Higher because chelates tend to be more stable complexes, as the polydentate ligands are able to hold the metal cation more securely.** [1]

**(Lecture notes)**

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

**$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$ or $[Ar]\ 3d^5$** [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*.

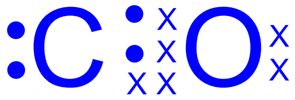
**$[Fe(H_2O)_6]^{3+}(aq) + e^- \rightleftharpoons [Fe(H_2O)_6]^{2+}(aq)$ $E^{\ominus} = +0.77$ V**

**$[Fe(CN)_6]^{3-}(aq) + e^- \rightleftharpoons [Fe(CN)_6]^{4-}(aq)$ $E^{\ominus} = +0.36$ V**

**The less positive $E^{\theta}$ value suggests that $[Fe(CN)_6]^{3-}$(aq) has a lower tendency to be reduced to $[Fe(CN)_6]^{4-}$.**

**(This indicates that $CN^-$ ligand better stabilises $Fe^{3+}$ than $H_2O$ ligand)** [2]

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



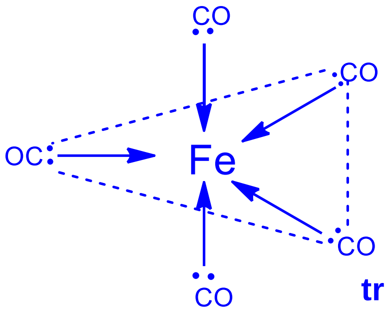
[1]

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 $Fe(CO)_5$?

**0** [1]

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

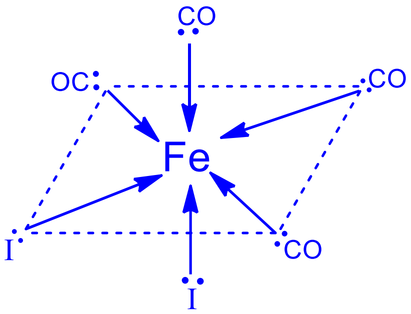


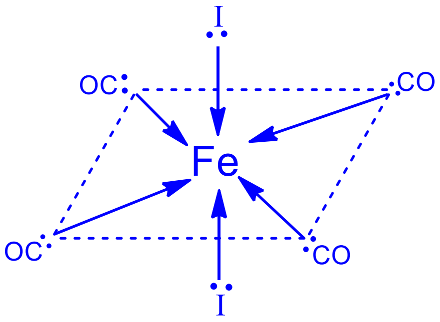
**trigonal bipyramidal**

[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 $Fe(CO)_4I_2$.





**$I^-$ ligand can be either be cis or trans position / $I^-$ ligand can be in opposite positions of the central metal or the same side of the central metal.**

[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]

| | **$CO_2$ (g)** + | **$3H_2$ (g)** $\rightleftharpoons$ | **$CH_3OH$(g)** + | **$H_2O$(g)** |
|---|---|---|---|---|
| Initial amount / mol | 1.0 | 3.0 | 0 | 0 |
| Change / mol | $-\frac{32}{100}\times 1.0 = -0.32$ | $-3(0.32) = -0.96$ | +0.32 | +0.32 |
| Equilibrium amount / mol | **0.68** | **2.04** | **0.32** | **0.32** |

Total amount of gaseous particles = 0.68 + 2.04 + 0.32 + 0.32 = 3.36 mol

$$P_{CH_3OH} = P_{H_2O} = \frac{0.32}{3.36}\times 55 = 5.238 \text{ bar}$$

$$P_{CO_2} = \frac{0.68}{3.36}\times 55 = 11.13 \text{ bar}$$

$$P_{H_2} = \frac{2.04}{3.36}\times 55 = 33.39 \text{ bar}$$

$$K_p = \frac{(P_{CH_3OH})\,(P_{H_2O})}{(P_{CO_2})(P_{H_2})^3}$$

$$= \frac{5.238 \times 5.238}{11.13 \times (33.39)^3} = \underline{\mathbf{6.62 \times 10^{-5}\ bar^{-2}}}$$

**(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]

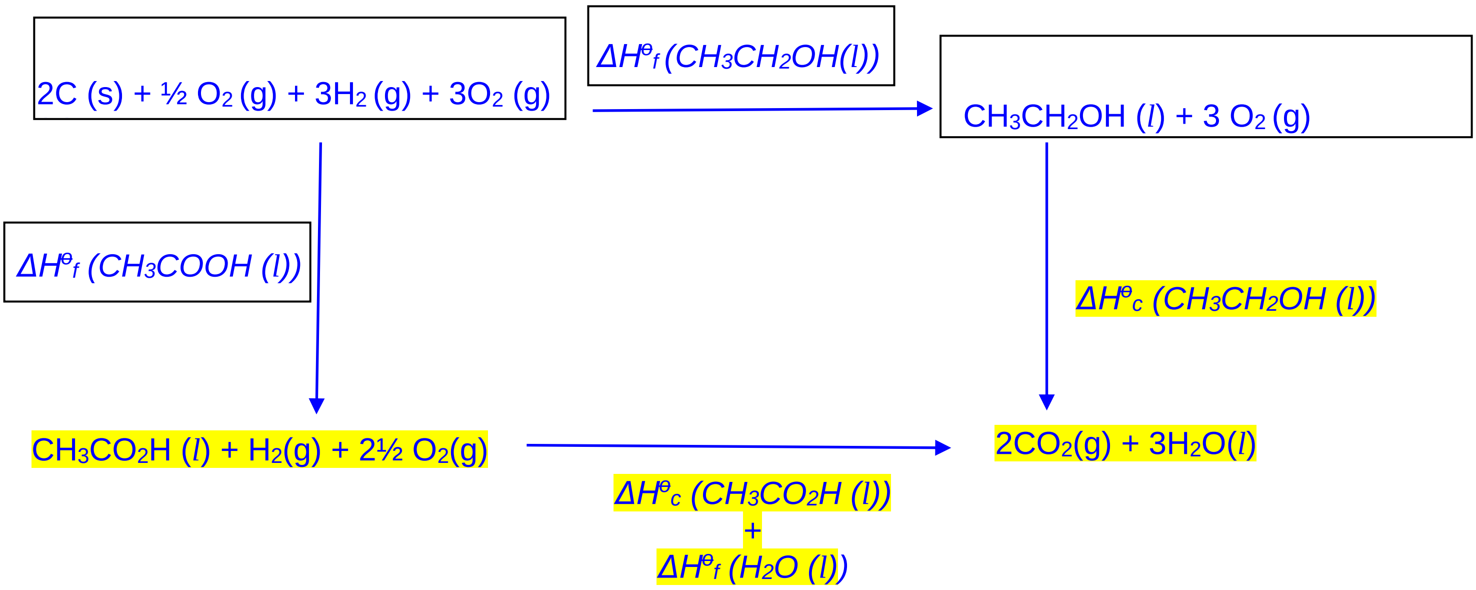
Standard enthalpy change of formation of liquid ethanoic acid is the **energy change** when **one mole of $CH_3CO_2H$ ($l$)** is **formed from its elements** (i.e. C (s), $H_2$ (g) and $O_2$(g)) **at standard conditions of 298K and 1 bar**.

**(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]

Given:

$2C(s) + \frac{1}{2}O_2(g) + 3H_2(g) \longrightarrow CH_3CH_2OH(l)$ $\Delta H^\ominus_f$ ($CH_3CH_2OH(l)$) = –278 kJ mol$^{-1}$
$CH_3CH_2OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$ $\Delta H^\ominus_c$ ($CH_3CH_2OH(l)$) = –1371 kJ mol$^{-1}$
$CH_3CO_2H(l) + 2O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l)$ $\Delta H^\ominus_c$ ($CH_3CO_2H(l)$) = – 876 kJ mol$^{-1}$
$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l)$ $\Delta H^\ominus_f$ ($H_2O(l)$) = – 286 kJ mol$^{-1}$



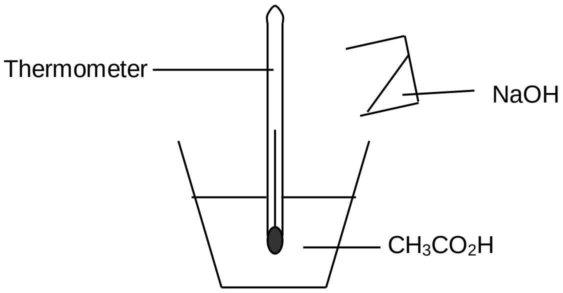
By Hess's Law,

**$\Delta H^\ominus_f$ ($CH_3CO_2H(l)$) +** $\Delta H^\ominus_c$ ($CH_3CO_2H$ ($l$)) **+** $\Delta H^\ominus_f$ ($H_2O$ ($l$)) **=** $\Delta H^\ominus_f$ ($CH_3CH_2OH$ ($l$)) + $\Delta H^\ominus_c$ ($CH_3CH_2OH$ ($l$))

**$\Delta H^\ominus_f$ ($CH_3CO_2H(l)$) = (–278) + (–1371) – (–876) – (–286)**

**= – 487 kJ mol$^{-1}$**

**(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 $CH_3CO_2H$ / °C | 25.0 |
| Highest temperature reached / °C | 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]

Heat absorbed by the solution, $Q = mc\Delta T = (100 \times 1.00)(4.18)(28.5 - 25.0)$
$= \mathbf{1463\ J}$

Assuming no heat loss to surroundings, i.e. 100% efficiency,

$$\Delta H_n = -\frac{Q'}{n_{H_2O}}$$

No. of moles of $CH_3CO_2H$ = $0.65 \times \frac{50}{1000}$ = 0.0325

No. of moles of NaOH = $1 \times \frac{50}{1000}$ = 0.0500

$\Rightarrow$ $CH_3CO_2H$ is the limiting reagent

Mole ratio: $CH_3CO_2H \equiv H_2O$

No. of moles of $H_2O$ formed = no. of moles of $CH_3CO_2H$ = **0.0325 mol**

$$\Delta H_n = -\frac{Q'}{n_{H_2O}} = \frac{-1463}{0.0325} = \underline{\mathbf{-45.0\ kJ\ mol^{-1}}}$$

**(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]

The value calculated in (d)(i) is less exothermic, as $CH_3CO_2H$, as a weak acid, only *dissociates partially* in solution.

**Some of the heat released** from the neutralisation is used to **promote further dissociation of $CH_3CO_2H$ molecules** (energy is used to break the O–H bonds in the remaining $CH_3CO_2H$ molecules to form more $H^+(aq)$ for neutralisation). Hence the overall enthalpy change is less exothermic.

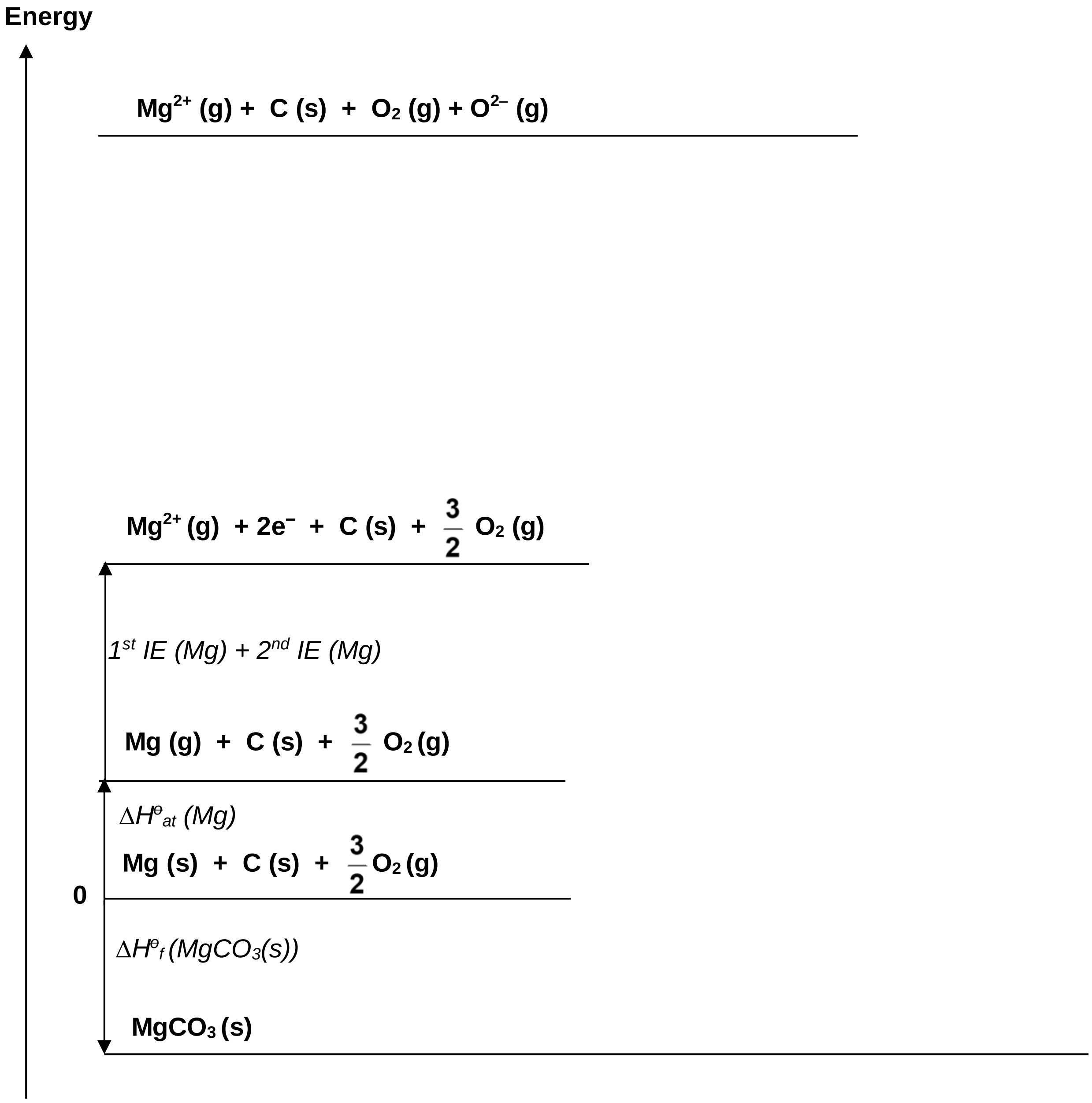
**(e)** Like many acids, ethanoic acid reacts with basic carbonates such as magnesium carbonate, $MgCO_3$ to release carbon dioxide.

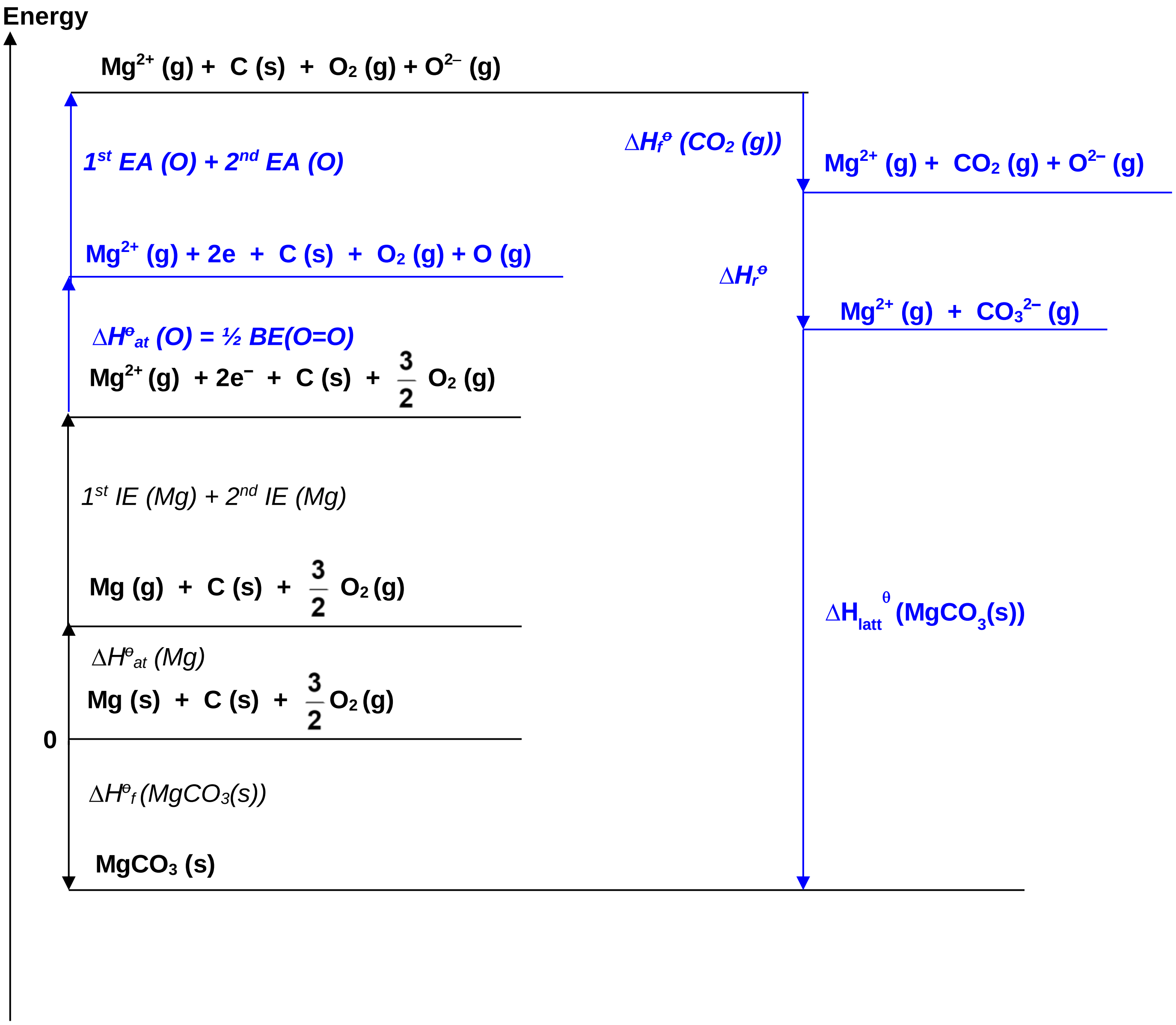
Using the following data and relevant data from the *Data Booklet*, complete the following energy level diagram and use it to determine the standard enthalpy change of formation of magnesium carbonate, $MgCO_3$.

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 $mol^{-1}$

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

[5]


Energy
$Mg^{2+}$ (g) + C (s) + $O_2$ (g) + $O^{2-}$ (g)
$Mg^{2+}$ (g) + $2e^-$ + C (s) + $\frac{3}{2}$ $O_2$ (g)
$1^{st}$ IE (Mg) + $2^{nd}$ IE (Mg)
Mg (g) + C (s) + $\frac{3}{2}$ $O_2$ (g)
$\Delta H^\ominus_{at}$ (Mg)
Mg (s) + C (s) + $\frac{3}{2}$ $O_2$ (g)
0
$\Delta H^\ominus_f$ ($MgCO_3$(s))
$MgCO_3$ (s)



By Hess' Law,

$\Delta H_f$ ($MgCO_3$ (s)) =

$\Delta H_{at}{}^{\theta}$(Mg) + 1st IE (Mg) + 2nd IE (Mg) + ½ BE(O=O) + 1st EA(O) + 2nd EA (O) + $\Delta H_f{}^{\theta}$($CO_2$) + $\Delta H_r{}^{\theta}$ + $\Delta H_{latt}{}^{\theta}$($MgCO_3$)

$\Delta H_f$ ($MgCO_3$ (s)) = +147 + 736 + 1450 + ½(496) + 702 + (–393) + (–778) + (–3208)

= **–1096 kJ mol$^{-1}$**

[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.

**Total amount of gas = $5.1 \times 10^3 / 15$**

**$= \underline{340}$ mol**

[1]

**(ii)** Assuming the temperature of a dragon's lung is 40 °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.

**Let p to be the internal pressure in the dragon's lung**

**$pV = nRT$**

**$p \times 5.1 = 340 \times 8.314 \times (40 + 273)$**

**$p = \underline{173 \times 10^3 \text{ Pa}}$**

[1]

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

The calculated value in part (a)(ii) is based on the assumption gases in the dragon's lung are ideal gases. However, they behave as real gases.

**There are <u>significant intermolecular forces of attractions between these gas molecules</u>. Hence, these gases exert smaller amount of force on the walls of the lung.**

The actual pressure is expected to be smaller than that calculated by ideal gas equation.

[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.

**$H_2S + (3/2)O_2 \rightarrow SO_2 + H_2O$**

**Amount of $H_2S$ gas = $\underline{340 \times 0.2 = 68}$ mol**

**Amount of $O_2$ gas contained in the dragon's lung = $\underline{340 \times 0.15}$**

**= $\underline{51}$ mol**

**$H_2S \equiv (3/2)O_2$**

**The amount of $O_2$ gas required for complete combustion**

**= 68 x 3/2 = 102 mol**

**The additional moles of $O_2$ required = $\underline{102 - 51 = 51}$ mol**

[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<br>ser-pro-glu<br>asp-gly<br>thr-phe-leu | gly-asp-gly-thr<br>pro-glu<br>phe-leu-ser<br>his-phe |

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

**From 2nd enzyme: gly−asp−gly−thr**

**From 1st enzyme: his-phe-gly asp-gly thr-phe-leu**

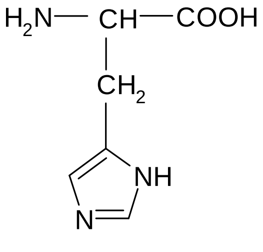
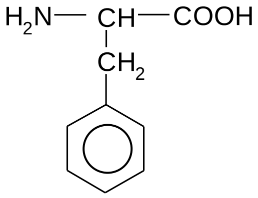
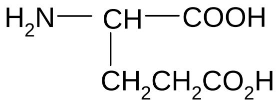
**From 2nd enzyme: his-phe phe-leu-ser**

**From 1st enzyme: ser-pro-glu**

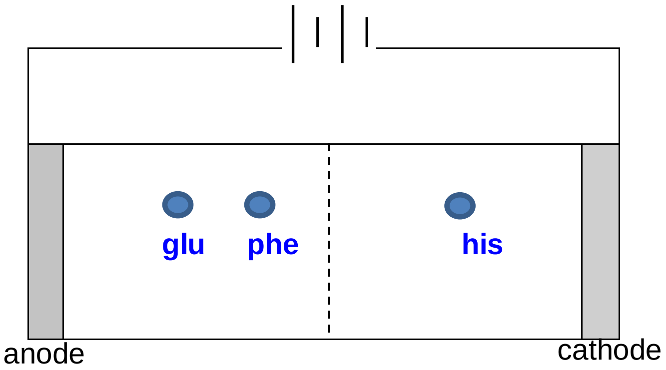
**his−phe−gly−asp−gly−thr−phe−leu−ser−pro−glu**

[2]

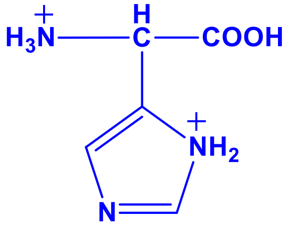
**(ii)** A tripeptide, his-phe-glu, obtained from **A** was further hydrolysed. The resulting solution was added to an excess of a buffer solution of pH 6.5 and placed at the centre of the plate. A potential difference was then applied across the plate.

| Amino acids | <br>his | <br>phe | <br>$H_2N-CH(CH_2CH_2CO_2H)-COOH$<br>glu |
|---|---|---|---|
| Isoelectric point | 7.58 | 5.48 | 3.10 |

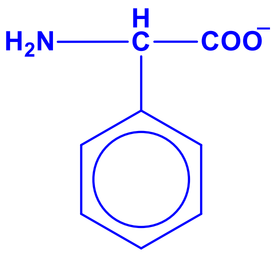
Indicate the relative positions of the amino acids on the diagram below.



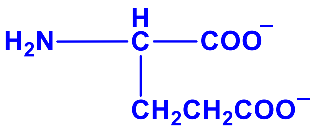
At pH 6.5,



his



phe



$H_2N-CH(CH_2CH_2COO^-)-COO^-$

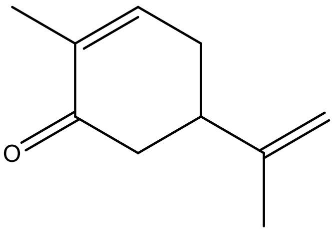
glu

[2]

Positively charged species will migrate to the cathode (negative electrode)
Negatively charged species will migrate to the anode (positive electrode)

[Total: 10]

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



Carvone

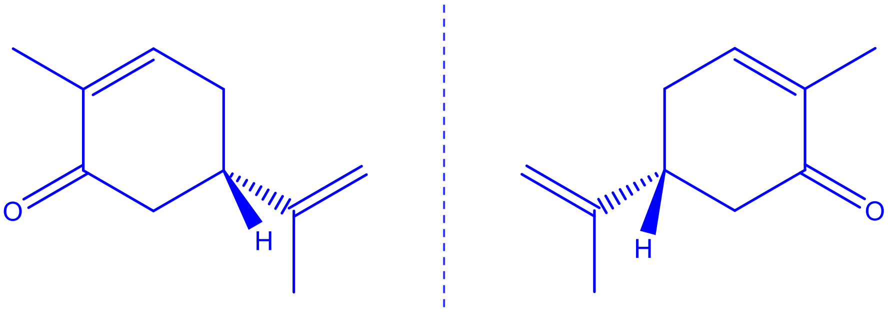
Two stereoisomers of carvone are responsible for the distinctively different flavor and smell of the two herbs.

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

**Optical isomerism / enantiomerism**

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

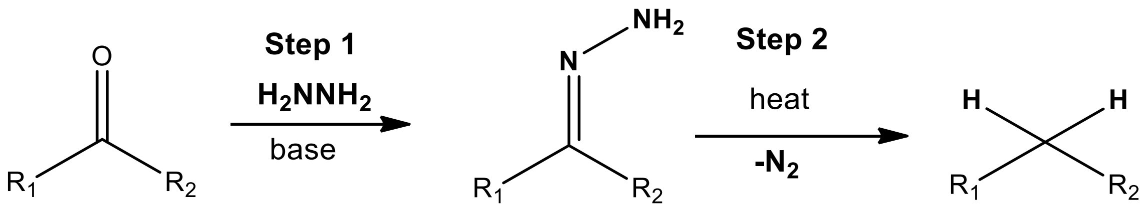
**(b)** Draw the two stereoisomers of carvone.



[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.

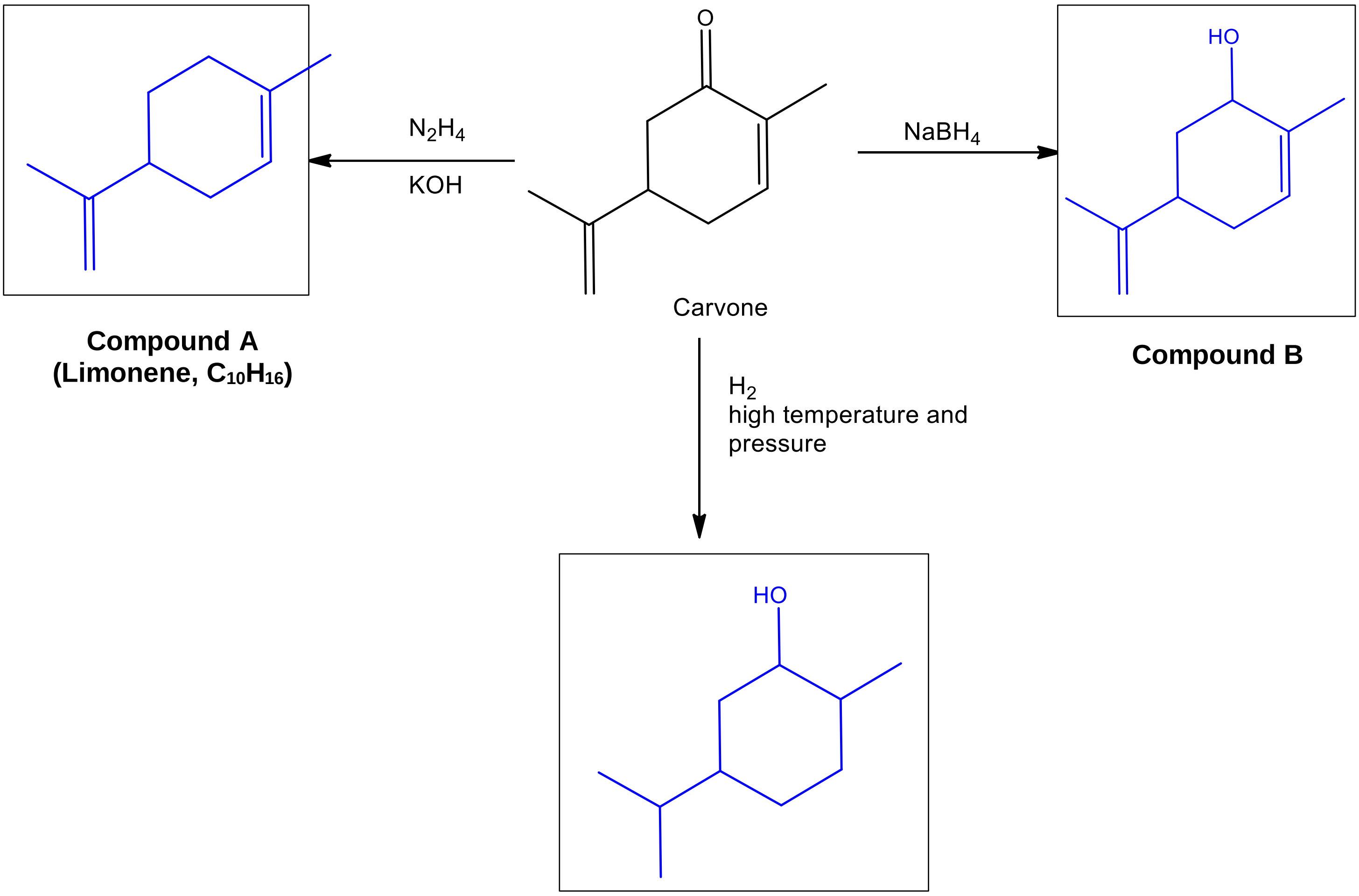


The ***Wolff-Kishner reduction*** is unsuitable for base-sensitive reactants.

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

Condensation / Addition-Elimination ..........[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.



**Compound A**
**(Limonene, $C_{10}H_{16}$)**

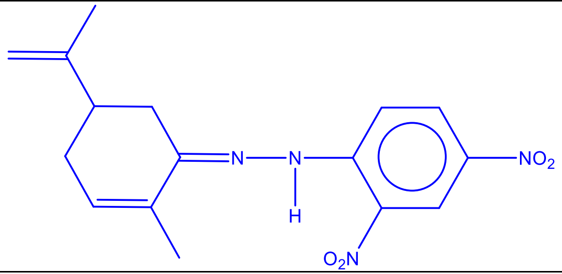
**Compound B**

**Compound C**

[3]

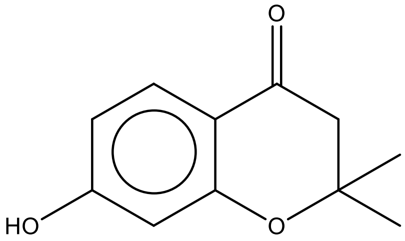
**(iii)** Suggest a simple chemical test that could distinguish between carvone and limonene. State the observations expected for each compound and the products (if any) that gives the observations.

Reagents and conditions: 2, 4-dinitrophenylhydrazine, heat ..........

| | Observations: | Products: |
|---|---|---|
| Carvone | **Orange ppt formed** |  |
| Limonene | **No orange ppt formed** | **N.A.** |

[3]

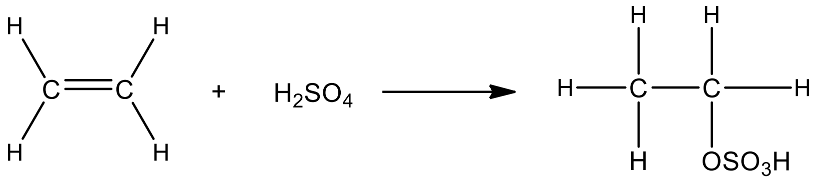
**(iv)** Suggest a reason why the following compound is unlikely to undergo the ***Wolff-Kishner reduction*** despite the presence of a ketone functional group.



**Presence of acidic phenolic group which would react with the base used in step 1** [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.



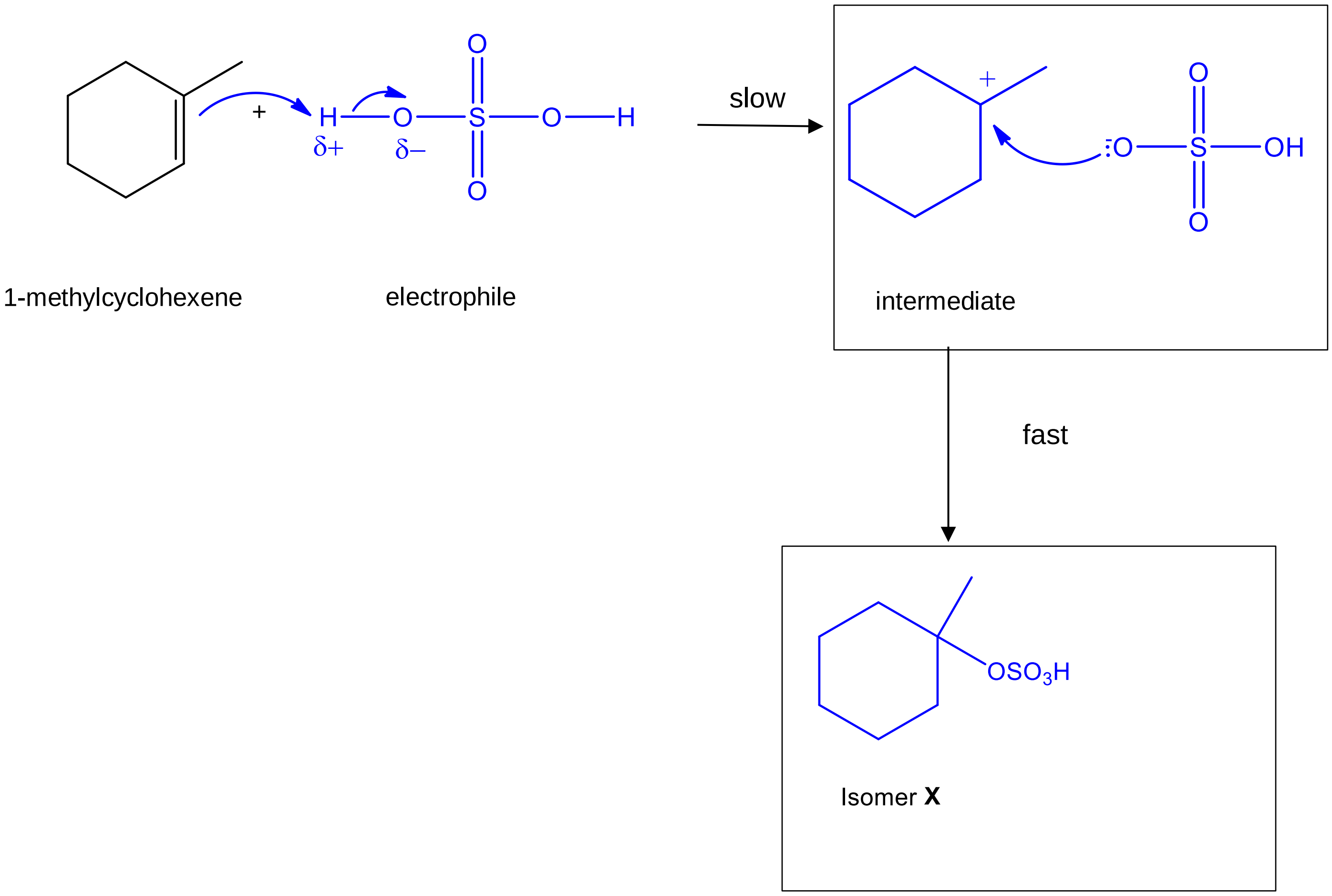
When 1-methylcyclohexene reacts with fuming sulfuric acid, a mixture of two isomers **X** and **Y** are formed, with isomer **X** being the major product.

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

**Positional/Constitutional isomerism**

**Constitutional isomers have the same molecular formula but different structural formula. In addition, positional isomers have the same substituents / functional groups, but at different positions (-$OSO_3H$).** [2]

**(b)** Complete the following to suggest a mechanism for the reaction between 1-methylcyclohexene and sulfuric acid to form **X**. Show the displayed structure of $H_2SO_4$, the structure of the intermediate, the movement of the electron pairs and the structure of **X**. [4]



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

**Benzene contains a ring of delocalised π electrons which leads to extra stability (resonance stability),**
**hence to maintain the stability of benzene, it would not undergo addition reaction which will lead to breaking the ring of delocalised π electrons and giving less stable products due to loss of resonance stability.** ........................ [2]

[Total: 8]