VICTORIA JUNIOR COLLEGE
JC 1 PROMOTIONAL EXAMINATIONS
Higher 2

CANDIDATE NAME .....

CT GROUP .....

# CHEMISTRY 9729//02

Paper 2 Structured Questions **30 September 2022**

Candidates answer on the Question Paper. **2 hours**

Additional Materials: Data Booklet

**READ THESE INSTRUCTIONS FIRST**

Write your index number, name and CT group in the spaces 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.

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

**Section B Free Response**
Answer the question in the spaces provided on the Question Paper.

A Data Booklet is provided.
The use of an approved scientific calculator is expected, where appropriate.
The number of marks is given in brackets [ ] at the end of each question or part question.

| For Examiner's Use | |
|---|---|
| S1 | /15 |
| S2 | /15 |
| E1 | /20 |
| E2 | /20 |
| Total | /70 |

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

## Section A: Structured Questions [30 marks]

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

**S1 (a)** The engine capacity of a car refers to the total volume of the combustion cylinders in the engine when the pistons are pushed out of the cylinders.

The following experiment was conducted using a test engine where the combustion cylinders have a total volume of 200 $cm^3$.

- Ethane gas, $CH_3CH_3$, was mixed with air and injected into the cylinders.
- The resultant fuel-air mixture (0.0280 mol) was then compressed and ignited.
- The pistons are pushed out during the combustion process to bring the volume of the cylinders to a maximum. The final pressure and temperature was recorded to be $1.23 \times 10^6$ Pa and 753 $^oC$ respectively.

**(i)** Using ideal gas equation, calculate the total number of moles of gaseous species in the cylinder after combustion of the fuel–air mixture.

[2]

**(ii)** Using your answer in **(a)(i)**, calculate the change in the total number of moles of gaseous species for the combustion process.

[1]

**(iii)** The complete combustion of 1 mol of ethane gas at 753 °C is represented by the following equation:

$$CH_3CH_3(g) + \frac{7}{2} O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$$

Using your answer in **(a)(ii)**, calculate the number of moles of $CH_3CH_3$ in the fuel-air mixture.

[2]

**(b)** In another experiment, liquid pentane, $CH_3(CH_2)_3CH_3$, was used as the fuel. The energy delivered by the test engine was found to be $2.80 \times 10^4$ kJ $h^{-1}$.

Additional data:

- Enthalpy change of combustion of liquid pentane = –3510 kJ $mol^{-1}$
- Density of liquid pentane = 0.626 g $cm^{-3}$
- Molar mass of pentane = 72.0 g $mol^{-1}$

**(i)** Calculate the total amount of energy delivered by the combustion of pentane when the test engine was kept running for two hours.

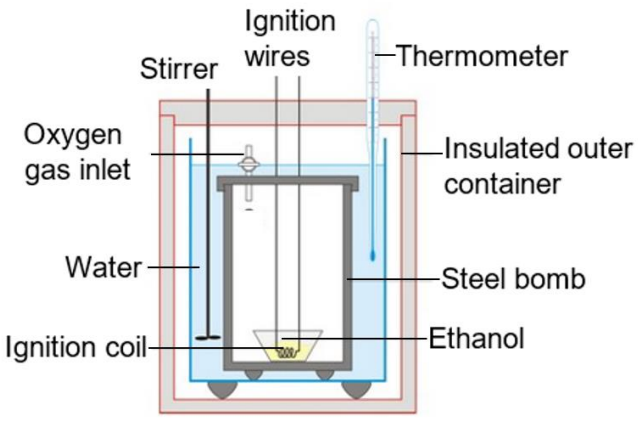
[1]

**(ii)** Calculate the volume of pentane (in $cm^3$) required needed to deliver the energy calculated in **(b)(i)**.

[2]

**(c)** The fuel energy value (in kJ $g^{-1}$) of a substance is the heat energy released when 1 g of that substance is combusted. It is known that ethanol, $C_2H_5OH$, has a fuel energy value of 23.3 kJ $g^{-1}$.

Liquid ethanol is commonly found in canisters used for portable gas stoves during camping trips. A camper found a left-over canister of ethanol and carried out an experiment to determine the mass of ethanol left in the canister. This was done using a bomb calorimeter as shown below:




In the bomb calorimeter, the bomb was filled with oxygen gas at high pressure and was immersed into a container filled with water. The liquid ethanol was then ignited using ignition wires. The maximum temperature of the water inside the calorimeter was measured.

Additional data:

| | |
|---|---|
| Mass of water used | 200 g |
| Change of temperature | 24.0 $^oC$ |
| Specific heat capacity of water | 4.18 J $g^{-1}$ $K^{-1}$ |
| Heat capacity of calorimeter (excluding water) | 19.3 J $K^{-1}$ |

**(i)** Write an equation for the standard enthalpy change of combustion of liquid ethanol, $C_2H_5OH(l)$.

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[1]

**(ii)** Using relevant data provided, calculate the mass of ethanol left in the canister.

[2]

**(d)** Tetracarbonylnickel, $Ni(CO)_4$, was first synthesised in 1890 by Ludwig Mond by the direct reaction of nickel metal with carbon monoxide. This pioneering work foreshadowed the existence of many other metal carbonyl compounds, including those of vanadium and chromium.

Some data for the synthesis of tetracarbonylnickel, $Ni(CO)_4$, are shown below:

| Equation | $\Delta H^{\ominus}$ / kJ mol$^{-1}$ | $\Delta S^{\ominus}$ / kJ K$^{-1}$ mol$^{-1}$ |
|---|---|---|
| $Ni(s) + 4CO(g) \rightarrow Ni(CO)_4(g)$ | –161 | –0.420 |

**(i)** Explain the significance of the sign of $\Delta S^{\ominus}$.

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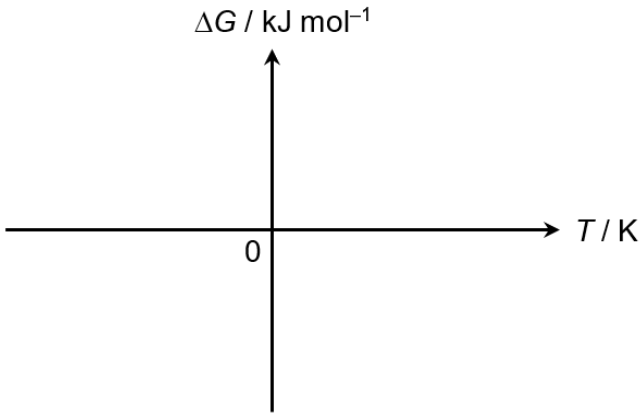
[2]

**(ii)** In the axes below, sketch a graph of the Gibbs' free energy change ($\Delta G$) versus temperature ($T$) for the synthesis of tetracarbonylnickel.

Labelling the ***y*-intercept** clearly with the correct value.




[2]

[Total: 15]

**S2 (a) (i)** Chlorine and bromine react with alkanes via the free-radical substitution mechanism.

Outline the mechanism of the reaction between methane and bromine to form bromomethane.

[3]

**(ii)** Light of a longer wavelength is lower in energy than light of a shorter wavelength.

Bromination of methane can be carried out with light of a longer wavelength (560–580 nm) while chlorination of methane can only be carried out with light of a shorter wavelength (430–490 nm). Use your answer from **(i)** to explain why.

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[2]

**(b)** During the process of chlorination, the relative rates of removing the first hydrogen atom from ethane and from methane are in the ratio of 270 : 1.

By considering the mechanism in **(a)(i)**, suggest why the rates of removing the first hydrogen atom are different for ethane and methane.

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[2]

**(c)** When propane reacts with chlorine in the presence of light, three isomeric products, each with the molecular formula $C_6H_{14}$, are formed in small amounts. Further analysis shows that they have different boiling points. One of them, **Q**, has a higher boiling point than the other two isomers.

**(i)** Draw the skeletal formulae of the three isomeric products, indicating clearly which one is **Q**.

[4]

**(ii)** Explain why **Q** has a higher boiling point than the other two isomers.

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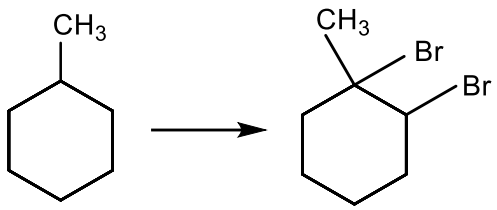
[2]

**(d)** Methylcyclohexane reacts with bromine to form a dibrominated product, **R**:




methylcyclohexane **R**

Compound **R** exists as a mixture of stereoisomers.
Draw the structure of each stereoisomer of **R**.

[2]

[Total: 15]

## Section B: Essay Questions [40 marks]

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

**E1** Carbon dioxide plays a vital role in the chemistry of seawater. When atmospheric carbon dioxide is dissolved in seawater, carbonic acid, $H_2CO_3$, a weak diprotic acid, is formed.

$$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

The dissociation of $H_2CO_3$ occurs in two steps and their corresponding p$K_a$ values are shown below.

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \qquad pK_{a1} = 6.37$$

$$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq) \qquad pK_{a2} = 10.3$$

An environmental technician collected a sample of seawater. The pH of the sample was found to be 3.68.

**(a) (i)** Calculate the concentration of $H_2CO_3$ in a 25.0 $cm^3$ portion of seawater. Assume that the second dissociation step of $H_2CO_3$ is negligible.

[2]

**(ii)** Calculate the pH of the resulting solution when 50.0 $cm^3$ NaOH(aq) of the same concentration as $H_2CO_3$(aq) in **(a)(i)** was added to completely neutralise the 25.0 $cm^3$ portion of seawater.

The equation for the complete neutralisation process is given below:

$$H_2CO_3(aq) + 2NaOH(aq) \rightarrow Na_2CO_3(aq) + 2H_2O(l)$$

[2]

**(iii)** Using your answers in **(a)(i)** and **(a)(ii)**, as well as the $pK_a$ values provided, sketch a graph to show how the pH of the solution changes as 50.0 $cm^3$ of NaOH(aq) in **(a)(ii)** is gradually added to 25.0 $cm^3$ portion of the seawater. Indicate clearly the corresponding volumes of NaOH(aq) in your graph.

[2]

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**(b)** Acid rain also plays a vital role in the chemistry of seawater. Limestone-rich soil that bound lakes and rivers protect them from acidification. Limestone, $CaCO_3$, dissolves sufficiently in lake water to form a $HCO_3^-$ / $CO_3^{2-}$ *buffer* capable of absorbing the incoming $H^+$ from acid rain.

$$H^+(aq) + CO_3^{2-}(aq) \rightarrow HCO_3^-(aq)$$

**(i)** Define the term *buffer*.

[1]

**(ii)** Calculate the pH of a sample of lake water given that the ratio of $[CO_3^{2-}]$ / $[HCO_3^-]$ is 0.958.

[2]

**(iii)** 22.0 $cm^3$ of 0.200 mol $dm^{-3}$ HC*l*(aq) was required to neutralise all the carbonate ions and hydrogencarbonate ions in a 25.0 $cm^3$ sample of lake water.

$$HCO_3^-(aq) + H^+(aq) \rightarrow CO_2(g) + H_2O(l)$$

$$CO_3^{2-}(aq) + 2H^+(aq) \rightarrow CO_2(g) + H_2O(l)$$

Using the ratio given in **(b)(ii)**, calculate the concentrations of carbonate ions and hydrogencarbonate ions in the lake.

[2]

**(c)** Carbon monoxide and nitrogen dioxide react according to the equation.

$$CO(g) + NO_2(g) \rightleftharpoons CO_2(g) + NO(g)$$

The rate equation for the reaction was found to be rate = k[CO][$NO_2$].

The kinetics of a mixture containing 1.0 mol $dm^{-3}$ each of CO and $NO_2$ was investigated at 298 K. The concentration of $CO_2$ was found to vary with time, t, as shown in ***Table 1.1***.

***Table 1.1***

| t / s | [CO] / mol $dm^{-3}$ | [$NO_2$] / mol $dm^{-3}$ | [$CO_2$] / mol $dm^{-3}$ | [CO][$NO_2$] / $mol^2$ $dm^{-6}$ | $\frac{\Delta[CO_2]}{\Delta t}$ / mol $dm^{-3}$ $s^{-1}$ |
|---|---|---|---|---|---|
| 0 | 1.0 | 1.0 | 0.000 | 1.000 | – |
| 5 | | | 0.500 | | $\frac{0.500 - 0.000}{5 - 0}$ = 0.100 |
| 10 | | | 0.690 | | |
| 15 | | | 0.784 | | |
| 20 | | | 0.840 | | |

**(i)** State the relationship of [$NO_2$] and [CO] at any time of the reaction.

[1]

**(ii)** Complete ***Table 1.1***, recording your answers to **3 decimal places**.

$\frac{\Delta[CO_2]}{\Delta t}$ will be used an approximation for the reaction rate at a particular time. The calculation at t = 5 s is shown for your reference.

[4]

**(iii)** Using the data in ***Table 1.1***, plot a suitable graph to confirm that the reaction shows overall second order kinetics.

[2]

**(iv)** Hence, determine the value of the rate constant, giving its units.

[1]

**(v)** If ***r*** is the rate of the reaction between CO and $NO_2$, write an expression in terms of ***r*** for the rate of the reaction when the partial pressures for both CO and $NO_2$ are doubled.

[1]

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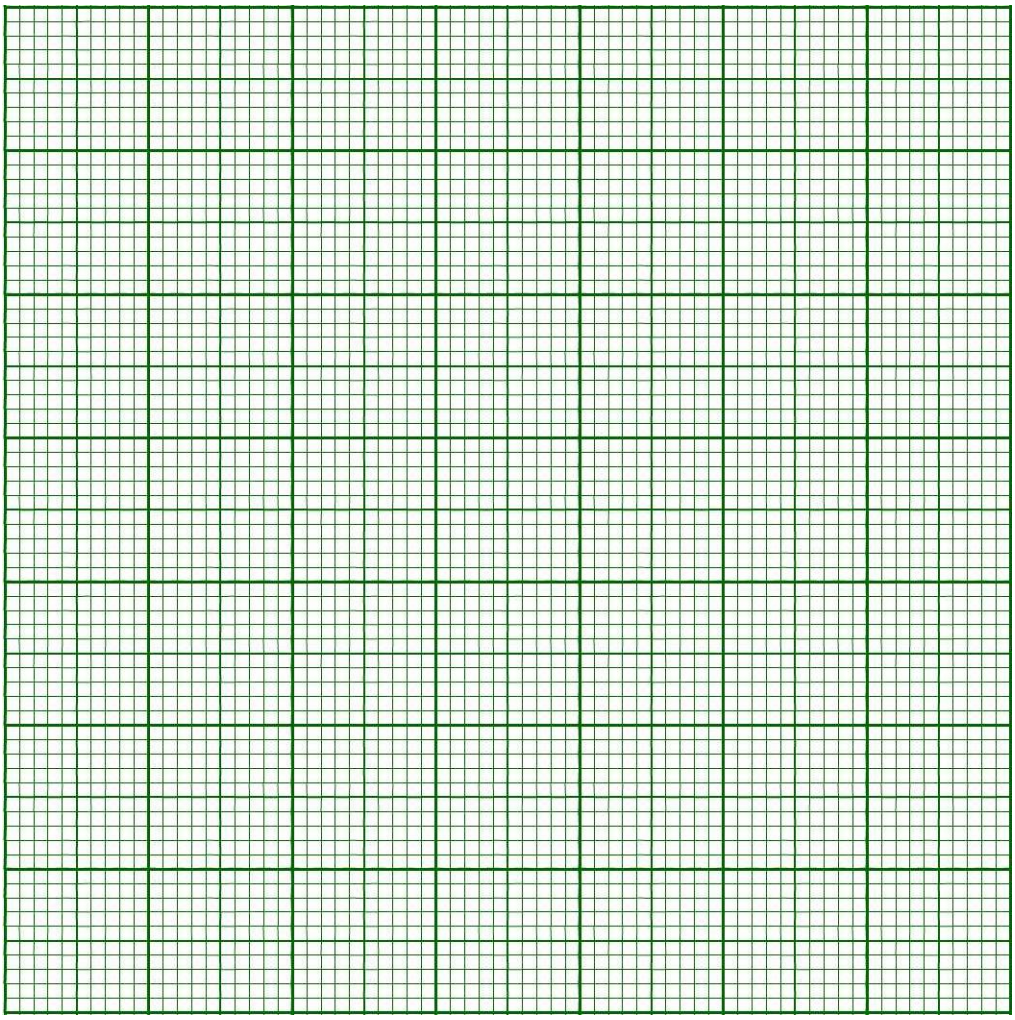

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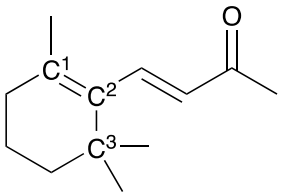
[Total: 20]

**E2** **(a)** Ionones are aroma compounds found in a variety of essential oils and are important fragrance chemicals used in perfumery.

β-ionone is characteristic of the scent of roses.




β-ionone

**(i)** State the hybridisation for $C^1$ and $C^3$.

[2]

**(ii)** Draw labelled diagrams to show how orbitals overlap between $C^1$ and $C^2$.

[2]

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**(b)** β-ionone has two C=C bonds. State and explain the possibility of cis-trans isomerism for each C=C bond.

[2]

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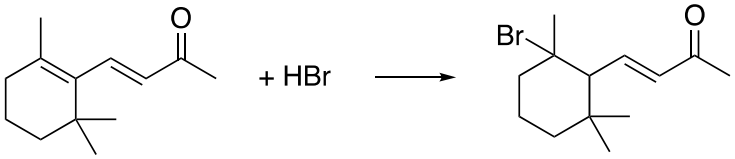
**(c)** When β-ionone undergoes electrophilic addition with equimolar amounts of hydrogen bromide, compound **A** is formed as one of the major products.

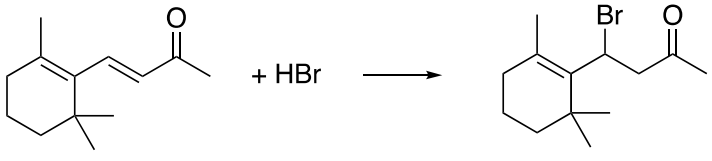



**A**

**(i)** Draw the mechanism for this reaction. Show all relevant charges, dipoles, lone pairs and curly arrows.

[2]

**(ii)** Compound **B** is one of the *minor* products.




**B**

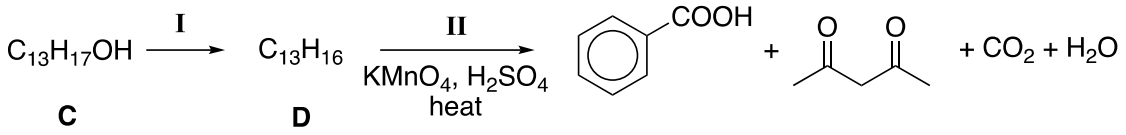
Draw the intermediate of this reaction.

[1]

**(iii)** By considering the relative stabilities of the intermediates formed, explain why compound **B** is a *minor* product.

[2]

**(d)** Compound **C** undergoes elimination to give compound **D** as the **only** organic product. Compound **D** is then heated with acidified $KMnO_4$ to give a mixture of products.




**C** **D**

Note: The reaction scheme above is not meant to be balanced.

**(i)** State the reagents and conditions for step **I**.

[1]

**(ii)** State the type of reaction for step **II**.

[1]

**(iii)** Deduce the structures of compound **C** and compound **D**.

[2]

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**(e)** Ethanol is manufactured by reacting ethene with steam. The reaction is reversible.

$$CH_2{=}CH_2(g) + H_2O(g) \rightleftharpoons CH_3CH_2OH(g) \qquad \Delta H < 0$$

**(i)** Write the expression for the equilibrium constant, $K_c$, for this reaction.

[1]

**(ii)** A mixture containing 2 mol of ethene and 1 mol of steam was heated at a constant temperature until equilibrium was established. Equilibrium was reached when 5% of the ethene had reacted. The volume of the vessel is 2.0 $dm^3$.

Calculate a value for the $K_c$ of this reaction.

[2]

**(iii)** Explain how a decrease in temperature will change the yield of ethanol.

[2]

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