2022 VJC H2 Chemistry Promo Exam Paper 2 [Suggested Answers]

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 1.23×10^6 Pa and 753 °C 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.

pV = nRT
$(1.23 \times 10^6)(200 \times 10^{-6}) = n(8.31)(753 + 273)$
n = 0.0289 mol

Examiner's Comments:
Generally well done. Students need to be careful to substitute the correct value (1.23 not 1.20, or 8.31 not 8.13) for calculation.

[2]

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

Change in number of moles of gaseous species
= 0.0289 – 0.0280
= $+8.53 \times 10^{-4}$ mol

Examiner's Comments:
Generally well done too.

[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.

Change in number of moles of gaseous species / 1 mol CH_3CH_3 combusted
= (2 + 3) – (1 + 3.5)
= +0.5 mol
0.5 mol change in gaseous species / 1 mol CH_3CH_3 combusted
= 8.53×10^{-4} mol change in gaseous species / x mol CH_3CH_3 combusted
No. of moles of CH_3CH_3 in the fuel-air mixture
= x

$= 8.53 \times 10^{-4} \div 0.5$
$= 1.71 \times 10^{-3}$ mol

Examiner's Comments:
Many students failed to appreciate that the answers for (a)(ii) is the change of volume during combustion. Hence many went to try to calculate using ICE box method with 2 unknown parameters (that was not required at all) and in the end couldn't solve the question.

[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 2.80×10^4 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.

Energy delivered $= 2.80 \times 10^4 \times 2$
$= 5.60 \times 10^4$ kJ [OR 5.60×10^7 J]

Examiner's Comments:
Overall, the question was well done.

[1]

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

ΔH_c of pentane = – Energy delivered ÷ Amount of pentane
–3510 = – 5.60×10^4 ÷ Amount of pentane
Amount of pentane = 5.60×10^4 ÷ 3510
= 16.0 mol

Mass of pentane = 16.0×72.0
= 1150 g

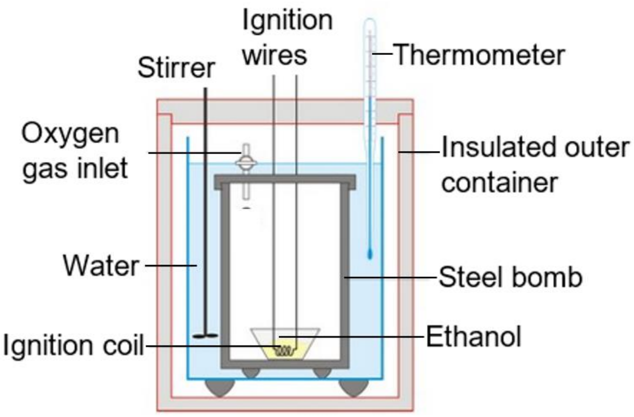
Volume of pentane = 1150 ÷ 0.626
= 1840 cm^3

Examiner's Comments:
Generally quite well done. Some students made careless mistakes in (i) calculating amount of pentane from the ΔH_c data, and (ii)calculating volume of pentane from amount of pentane.

[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 °C
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, $C_2H_5OH(l)$.

$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$
Balanced equation showing complete combustion of 1 mol of ethanol
Correct state symbols

Examiner's Comments:
Common mistakes:
-H_2O liberated should exist as liquid state and not gaseous state as ΔH_c of liquid ethanol is measured at standard condition of 298K and 1 bar.
-It should be 3 mol H_2O and not 7/2 mol of H_2O reacted.

[1]

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

Heat released from combustion of ethanol
= Heat absorbed by water + calorimeter
= $mc_{water}\Delta T + C_{calorimeter}\Delta T$
= (200 × 4.18 × 24.0) + (19.3 × 24.0)
= 20500 J
= 20.5 kJ

The mass of ethanol left
= 20.5 / 23.3
= 0.880 g

OR
The mass of ethanol left
= 20500 / 23300
= 0.880 g

Examiner's Comments:
Common mistakes:
-Heat absorbed by calorimeter was left out in the calculation or calculated wrongly.
- ΔT term was wrongly expressed in (24 + 273) K. Do not add 273Kto 24 °C, the unit of ΔT in °C is the same as the one in K since ΔT refers to temperature difference.
-Misinterpreted fuel energy in terms of kJ mol^{-1} instead of kJ g^{-1} (as given in the question). As such, some students assumed 0.880 represents the amount of ethanol burnt and calculated the mass of ethanol burnt wrongly by multiplying 0.880 by the M_r of ethanol.
-Mass of ethanol burnt was calculated wrongly as (1–0.880)g. However, 0.880 g is indeed the mass of ethanol left as this is the mass of ethanol burnt which heats up water and calorimeter by 24 °C. Anyway, initial mass of ethanol was also not given to be 1 g.

[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 $\Delta S^{\ominus}$.

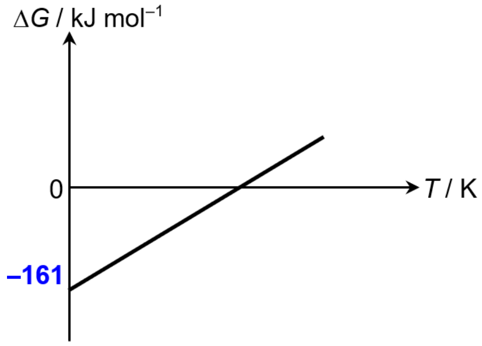
The sign of $\Delta S^{\ominus}$ is negative. This is due to a decrease in number of moles of gas particles in the reaction, leading to less ways of arranging the particles. Thus the system is becoming less disordered and entropy decreases.

Examiner's Comments:
Common mistakes:
-Many students did not explain the reasons behind why ΔS is negative. Indeed, many students wasted time to explain the significance of positive ΔS, which was not required in the question here as ΔS given in the question is negative.
-Many students also misinterpreted the question by explaining how negative ΔS contributed to the sign of ΔG under different temperatures using $\Delta G = \Delta H - T\Delta S$ to predict the spontaneity of the reaction, which was not asked in the question.

[2]

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

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



Straight line showing positive gradient
Correct labelling of y-intercept at –161 kJ mol^{-1}

Note:
$\Delta G = \Delta H - T\Delta S \Rightarrow \Delta G = (-\Delta S)T + \Delta H$
Graph is a straight line with positive gradient of ($-\Delta S$) and a negative y-intercept of ΔH. Also note that T in K cannot be negative value.

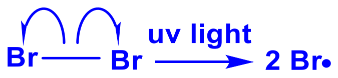
Examiner's Comments:
Generally quite well done.

[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.

Free-radical substitution
Initiation:



Propagation:
$CH_4 + Br\bullet \rightarrow \bullet CH_3 + HBr$
$\bullet CH_3 + Br_2 \rightarrow CH_3Br + Br\bullet$

Termination:
$2Br\bullet \rightarrow Br_2$
$2\bullet CH_3 \rightarrow CH_3CH_3$
$Br\bullet + \bullet CH_3 \rightarrow CH_3Br$

Examiner's Comments:
Some common mistakes were using CH_3 (methyl), CH_3CH_3 (ethane) instead of CH_4.
In the initiation step, students need to draw half arrow to represent homolytic fission of bromine molecule to form bromine radical.
Propagation leads to the formation of radical, not electrophile (e.g. CH_3+). Students need to be clear of what are the compounds formed for each step. Formation of hydrogen radical is not possible in the propagation step too.
There is no need for description of the mechanism. Students will only waste time in doing so.

[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.

Br–Br bond is weaker than C*l*–C*l* bond since Br atom is larger resulting in poorer overlapping of orbitals. Thus less energy is needed to break the Br–Br bond in the initiation stage.

Examiner's Comments:
The explanation is straight forward and systematic.
The use of wrong concepts for explanation that include the use of intermolecular forces of attraction or comparison of size of molecules (instead of size of atom). There is also no need to give detailed description of how a covalent bond is formed by the electrostatic forces of attraction between the bonding electrons and the nucleus. Many students hence did not explain why the bond energy for bromine is weaker.

[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.

•CH_2CH_3 radical is more stable than •CH_3 radical as the –CH_3 group exerts electron-donating inductive effect, which increases the electron density of the carbon with the unpaired electron. As a result, the first hydrogen is removed more readily from ethane to form the •CH_2CH_3 radical in the first propagation step.

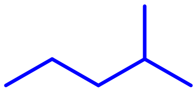
Examiner's Comments:
Poorly done. Many candidates fail to recognise that the rate of removing the H should be explained by stability of the alkyl radical rather than the number of H atoms that can be replaced (probability factor). Other mistakes, which pertain to use of wrong terminology, include:
- comparing stability of the starting alkane / final product rather than that of the intermediate
- describing the intermediate as carbocation rather than free radical
- mentioning that the charge is dispersed when a free radical is electrically neutral with ZERO charge.

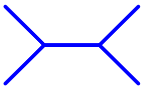
[2]

(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**.

Q





Examiner's Comments:

Fairly well done.Common conceptual error:

- Students don't realise that the C_6H_{14} product is formed in the termination stage and based on its molecular formula, must necessarily be formed from the combination of two 3-carbon alkyl radicals. The only two possible alkyl radicals formed in the propropation stage are either $CH_3CH_2\dot{C}H_2$ or $CH_3\dot{C}HCH_3$, which when combined in various ways, will give rise to the three products above. Other products, like $CH_3CH_2CH(CH_3)CH_2CH_3$ or $(CH_3)_3CCH_2CH_3$ are not possible.

Other errors:

- Including chlorine atom in the structure when the given molecular formula obviously corresponds to a hydrocarbon with NO chlorine atoms or any atom other than carbon and hydrogen
- Drawing partial or non-skeletal formulae
- Showing one C more or less
- Drawing 2 structures which are actually rotated versions of each other and hence are the same

[4]

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

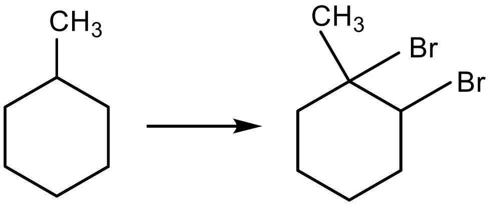
All three molecules have simple molecular structures.
Q is a straight-chain molecule where the other two isomers are branched. There is greater surface area of interaction between molecules of Q, leading to stronger (OR greater extent of) instantaneous dipole–induced dipole interactions. Hence, more energy is required to break the intermolecular forces in Q, leading to a higher boiling point.

Examiner's Comments:

Well done but mistakes pertaining to terminology are not uncommon. These include:
- describing Q as a linear rather than straight chain molecule, which gives the wrong impression that the actual shape of the molecule is linear.
- describing Q as having a longer carbon chain than the other isomers, giving the wrong impression that Q has more carbon atoms.
- using the more general (and hence vague) term of "intermolecular forces" rather than instantaneous dipole–induced dipole interactions.

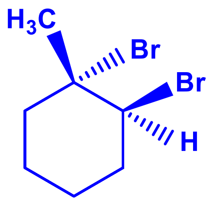
[2]

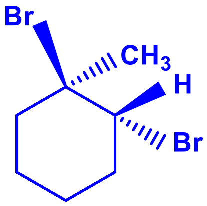
(d) Methylcyclohexane reacts with bromine to form a dibrominated product, **R**:

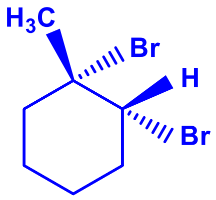


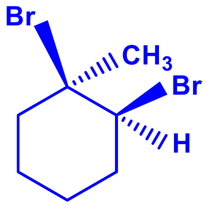
methylcyclohexane **R**

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









Examiner's Comments:
Very poorly done. Common errors:
- Not using the wedge / hashed bonds around one or both chiral carbons, thus not showing the spatial arrangement at all
- Drawing the wrong structure, e.g. inserting an extra C between the ring C and the –CH_3 group, breaking up the ring in some fashion, missing out one of the Br atoms
- Drawing a whole slew of structural isomers when question mentions "STEREOisomers"

The correct approach would be first to recognise that there are 2 chiral centres, hence giving rise to a total of $2^2 = 4$ stereoisomers. A simple way to draw the stereoisomers would be to start by showing the tetrahedral arrangement around EVERY chiral centre with the use of 2 normal line bonds, one wedge and one hashed bond. It's highly advisable that the normal line bonds be used for bonds within the ring. Then to get the other stereoisomers, just swap, for each chiral centre successively, the two groups attached to the wedge and hashed bonds.

[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 pK_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.

General Comments for E1:

For questions involving calculations, students are reminded to adhere to the following:

- ***Write clear working statements for each calculation step***
- ***Include units for each calculation step***
- ***Leave answers to appropriate significant figures i.e. 3 s.f. unless otherwise stated***

(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.

Method 1:

$$K_{a1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$$

$$[H_2CO_3] = \frac{[H^+]^2}{K_{a1}} = \frac{(10^{-3.68})^2}{10^{-6.37}}$$

$$= \underline{0.102 \text{ mol dm}^{-3}}$$

OR Method 2:

$$pH = -\lg\sqrt{K_{a1} \times [H_2CO_3]}$$

$$3.68 = -\lg\sqrt{10^{-6.37} \times [H_2CO_3]}$$

$$[H_2CO_3] = \underline{0.102 \text{ mol dm}^{-3}}$$

Examiner's Comments:

This was meant to be a straightforward part. Surprisingly, it was poorly done. Common mistakes include incorrect conversion of pK_{a1} to K_{a1}, incorrect conversion of pH to [H^+], using the wrong K_a expression i.e. using K_{a2} instead of K_{a1}, and wrongly applying the buffer equation when the system involved is a weak acid.

[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:

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

The resulting solution contains CO_3^{2-} i.e. a weak base:

$$[CO_3^{2-}] = \frac{50.0 \times 0.102 \times \frac{1}{2}}{75.0}$$

$$= 0.0340 \text{ mol dm}^{-3}$$

$$pK_b \text{ of } CO_3^{2-} = pK_{b2}$$

$$= 14.0 - 10.3$$

$$= 3.70$$

$$pOH = -\lg\sqrt{K_{b2} \times [CO_3^{2-}]}$$

$$= -\lg\sqrt{10^{-3.70} \times 0.0340}$$

$$= 2.58$$

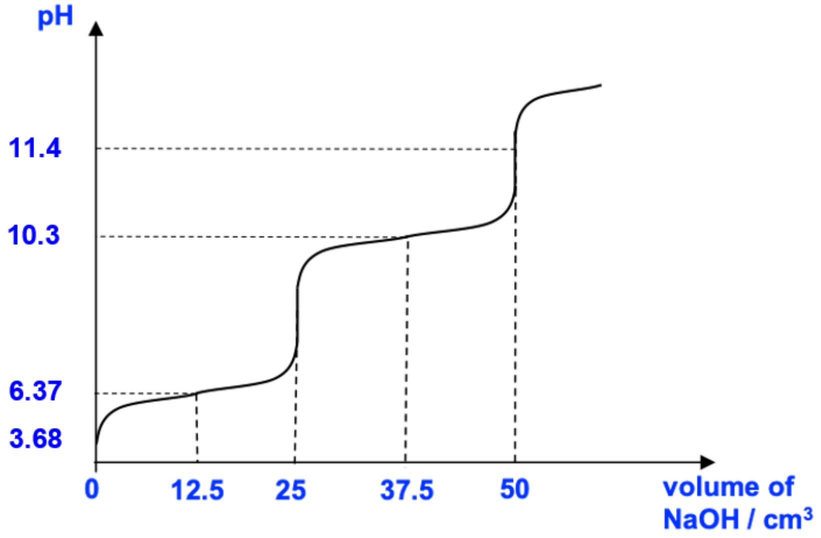
pH = 14.0 – 2.58 = <u>11.4</u>

<u>Examiner's Comments</u>:

This part was also poorly done. Even though the question stem tried to guide students by using the phrase "complete neutralisation", many students fail to recognise that this part of the question involves salt hydrolysis. Many wrongly deduced that NaOH was in excess. For those who were able to identify that $[CO_3^{2-}]$ was the contributor to the pH of the resulting solution, a significant number incorrectly applied K_{b1} instead of K_{b2} in the calculations.

[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.



<u>Examiner's Comments</u>:

There were very few complete answers for this part. Most students either did not draw the correct shape indicating two neutralisation points and/or did not highlight the pH at the two maximum buffer points.

[2]

(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*.

A buffer is a solution capable of <u>maintaining a fairly constant pH</u> when a <u>small amount of acid or base is added</u> to it.

<u>Examiner's Comments</u>:
Again, this was meant to be a straightforward part. Unfortunately, many students fail to score the maximum mark for this part. It is wrong to say that "pH does not change" or "pH remains constant". It is also wrong to leave out the phrase "small amount" of acid or base because a buffer is no longer effective when too much acid or base is added.

[1]

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

Using the acidic buffer formula,

$$\begin{aligned} pH &= pK_{a2} + \lg\frac{[CO_3^{2-}]}{[HCO_3^-]} \\ &= 10.3 + \lg 0.958 \\ &= \underline{10.3} \end{aligned}$$

<u>Examiner's Comments</u>:
Again, this was meant to be a straightforward part. Yet, many students fail to score the maximum mark for this part. Common mistakes include using the wrong pK_a i.e. K_{a1} instead of K_{a2}, writing the K_a expression wrongly, or recalling the buffer formula wrongly.

[2]

(iii) 22.0 cm^3 of 0.200 mol dm^{-3} $HCl(aq)$ 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.

Amount of H^+ used $= (22.0/1000) \times 0.200$
$= 4.40 \times 10^{-3}$ **mol**

Let w be the amount of HCO_3^-.
The amount of CO_3^{2-} will be 0.958w mol.

Based on the stoichiometry of equations,

Amount of H^+ required = w + (2 x 0.958w)
= 2.916w
= 4.40 x 10^{-3} mol

w = 1.51 x 10^{-3} mol
Hence,
[HCO_3^-] = w ÷ 25/1000
= 1.51 x 10^{-3} ÷ 25/1000
= 6.04 x 10^{-2} mol dm^{-3}

[CO_3^{2-}] = 0.958w ÷ 25/1000
= 0.958 x 1.51 x 10^{-3} ÷ 25/1000
= 5.79 x 10^{-2} mol dm^{-3}

Examiner's Comments:
Not well done. Many students didn't know how to proceed. A significant number of students also incorrectly divided 4.40 x 10^{-3} by 3 even though the ratio of [HCO_3^-] : [CO_3^{2-}] is not 1 : 1.

[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.

[NO_2] = [CO] at any time
[Or [NO_2] and [CO] decrease at the same rate]

Examiner's Comments:
This part was generally well done.

[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.

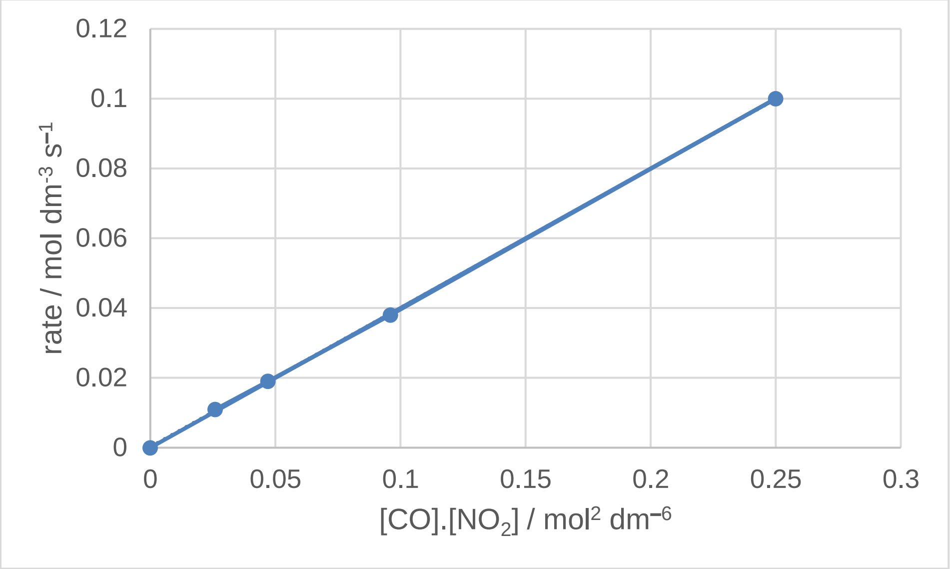
Table 1.1

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**	**0.500**	0.500	**0.250**	$\frac{0.500 - 0.000}{5 - 0}$ = 0.100
10	**0.310**	**0.310**	0.690	**0.096**	$\frac{0.690 - 0.500}{10 - 5}$ **= 0.038**
15	**0.216**	**0.216**	0.784	**0.047**	$\frac{0.784 - 0.690}{15 - 10}$ **= 0.019**
20	**0.160**	**0.160**	0.840	**0.026**	$\frac{0.840 - 0.784}{20 - 15}$ **= 0.011**

Examiner's Comments:
The [CO], [NO_2] and [CO].[NO_2] columns were generally well done. For $\frac{\Delta[CO_2]}{\Delta t}$, a significant number of students calculated each value by using t = 0 as the reference point. Take note that $\frac{\Delta[CO_2]}{\Delta t}$ is intended to be used as an estimate for instantaneous rate. For instantaneous rate, estimates should be determined over a "small time interval". This will ensure that the average rate over the small time interval is as close as possible to the instantaneous rate. When determined over a large time interval, the average rate will be very different from the instantaneous rate. Finally, many students also fail to follow the instructions given to leave their answers to 3 d.p.

[4]

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



Labelled axis of rate or $\frac{\Delta[CO_2]}{\Delta t}$ against [CO].[NO_2]

Graph passes through the origin

Points are correctly plotted

Examiner's Comments:
Very poorly done. Very few students showed an awareness that an overall second order reaction can only be proved using a rate vs [CO].[NO_2] graph. The line must also pass through the origin to reflect a second order reaction.

[2]

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

k = gradient
= 0.400 mol^{-1} dm^3 s^{-1}

Examiner's Comments:
The word "hence" meant that students were supposed to use the graph in c(iii) to solve for "k". However, since c(iii) was not well done, flexibility was given for students to calculate "k" using the rate equation.

[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.

rate = k[CO][NO_2]
When [CO] and [NO_2] both doubles, rate quadruples.
Thus, new rate = 4r

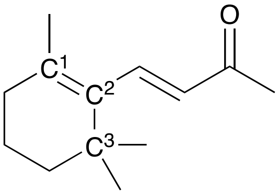
Examiner's Comments:
This was meant to be a straightforward question. However, many students seemed to overlook this part of the question due to their struggles in the preceding parts. Students are encouraged to check every part of the question to avoid losing marks that they could have easily scored.

[1]

[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

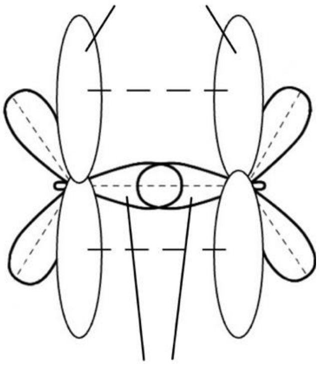
(i) State the hybridisation for C^1 and C^3.

C^1: <u>sp^2</u>
C^3: <u>sp^3</u>

<u>Examiner's Comments</u>:
Generally well done

[2]

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



Correct drawing (shape and angle) wrt to each bond
Complete labels

<u>Examiner's Comments</u>:
Poorly done with most students missing out detailed labels. Students should learn to properly label their diagrams

[2]

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

The C=C in the side-chain can exhibit cis-trans isomerism as the <u>C=C leads to restricted rotation</u> and there are <u>2 different groups attached on each alkene C</u>.

The C=C bond within the <u>ring is unable to form the trans isomer due to ring strain</u>.

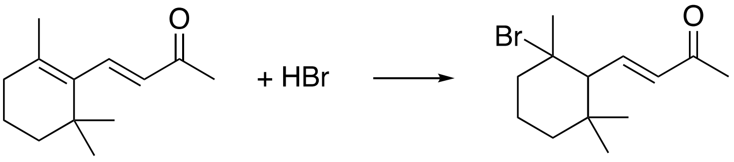
<u>Examiner's Comments</u>:
Generally well done for students who have done proper consolidation.

Most students could state whether or no cis-trans isomerism exists for each C=C bond. However explanation is mostly incomplete, some even with slight conceptual error.

1. *Cis-trans isomerism exists because of restricted rotation, hence when the two groups swap they cannot turn back. Some students freely used the phrase "free to rotate" to suggest the groups swapping showing incomplete understanding.*
2. *Cis-trans (or any related isomerism) exists AS LONG AS the two GROUPS (not molecules!!) attached to each C are different. They don't have to have a same group on each side*
3. *Double bond "in a ring" is insufficient as an answer. The ring strain which prevents the trans isomer from existing is important.*

[2]

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

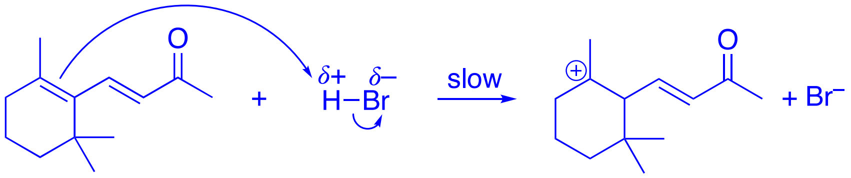


A

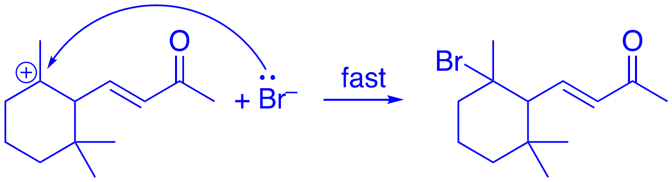
(i) Draw the mechanism for this reaction. Show all relevant charges, dipoles, lone pairs and curly arrows.

Electrophilic addition

Step 1: δ+ H attacks electron rich C=C to form a carbocation



Step 2: Br⁻ attacks carbocation to form A.

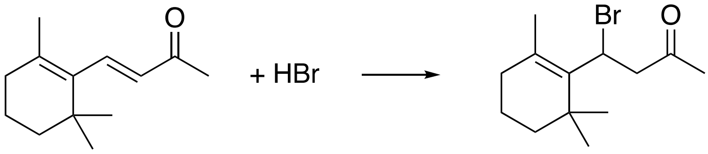


Correct intermediates
Balanced equations
Correct curly arrows
Correct dipoles & lone pairs

Examiner's Comments:
Generally well done for students who have done proper consolidation.
Note that starting point of the ARROW ALWAYS STARTS FROM the BOND or LONE PAIR (not the atom) and that DIPLOES & LONE PAIRS MUST BE SHOWN

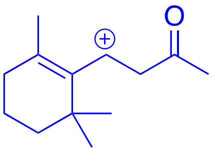
[2]

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



B

Draw the intermediate of this reaction.



Examiner's Comments:
Generally well done for students who have done proper consolidation.

[1]

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

Compound A is formed via a 3° carbocation, while B is formed via a 2° carbocation. The 3° carbocation has more alkyl groups which exert greater electron-donating inducting effect. Hence, this disperses the positive charge on the carbocation to a greater extent, making the carbocation more stable and leading to the formation of compound A as the major product.

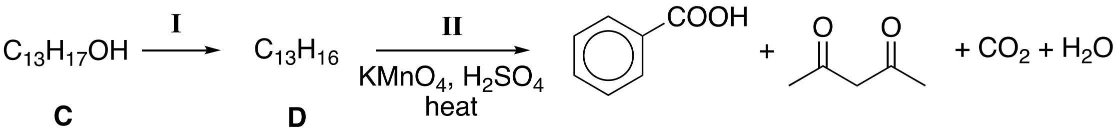
OR
The carbocation of compound B is closer to the electron withdrawing ketone group hence experience greater electron-withdrawing inductive effect. Hence this intensifies the positive charge on the carbocation to a greater extent, making the carbocation less stable and leading to the formation of compound B as the minor product.

Examiner's Comments:
Generally well done for students who have done proper consolidation.
Common errors:

1. ***"Markovnikov's rule" is insufficient as an answer. The explanation leading up to it needs to be explained.***
2. ***Poor phrasing e.g, compound B is more stable is not correct as an explanation. As mentioned the question stated "stability of the intermediates", it should be the cation that should be referred to.***

[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.



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

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

excess concentrated H_2SO_4, heat

<u>Examiner's Comments:</u>
Generally well done for students who have done proper consolidation.

[1]

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

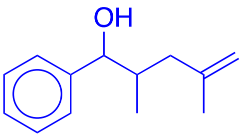
Oxidative cleavage

<u>Examiner's Comments:</u>
Generally well done for students who have done proper consolidation.
Students need to know that "oxidation" is an incomplete answer. It is different from oxidative cleavage.

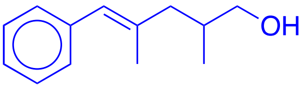
[1]

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

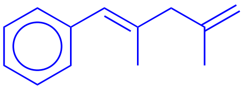
C:



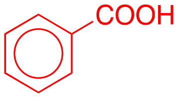
or



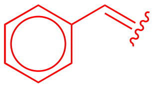
D:



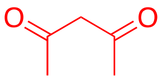
<u>Examiner's Comments:</u>
Generally poorly done.
The thought process is to work backwards from the 3 fragments from the oxidative cleavage of D:



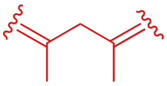
comes from



fragment



comes from



fragment

CO_2 comes from terminal alkene $=CH_2$
Putting these 3 together will give you D.
There are 4 possible alcohols that could give D
But only 2 can give ONLY D, as there is only 1 side for elimination to take place.

[2]

(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.

$$K_c = \frac{[CH_3CH_2OH]}{[CH_2{=}CH_2][H_2O]}$$

Examiner's Comments:
Generally well done for students who have done proper consolidation.
Common mistake: writing K_c in terms of Partial Pressure. K_c =/= K_p

[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.

	$CH_2{=}CH_2(g)$	+	$H_2O(g)$	$\rightleftharpoons$	$CH_3CH_2OH(g)$
Initial / mol	**2**		**1**		**0**
Change / mol	**–0.1**		**–0.1**		**+0.1**
Equilibrium / mol	**1.9**		**0.9**		**0.1**
Equilibrium / mol dm^{-3}	**0.95**		**0.45**		**0.05**

$$K_c = \frac{[CH_3CH_2OH]}{[CH_2{=}CH_2][H_2O]}$$

$$= \frac{0.05}{0.95 \times 0.45}$$

$$= 0.117$$

Examiner's Comments:
Generally well done for students who have done proper consolidation.
Key note: CHANGE FOLLOWS STOICHIOMETRIC RATIO.

[2]

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

By Le Chatelier's Principle, as temperature decrease, position of equilibrium will shift to the right to favour the exothermic forward reaction to increase temperature. Hence the yield of ethanol will increase.

Examiner's Comments:
Generally well done for students who have done proper consolidation.
Some students' answers were incomplete and missed out the part about POE shift.

[2]

[Total: 20]