EUNOIA JUNIOR COLLEGE
JC2 Preliminary Examination 2019
General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME	

CIVICS GROUP	1	8	–			INDEX NUMBER		

CHEMISTRY

9729/02

Paper 2 Structured Questions

17 September 2019
2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, civics group, index number 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 the 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 2	
1	**/ 15**
2	**/ 20**
3	**/ 20**
4	**/ 20**
Total	**/ 75**

This document consists of **20** printed pages.

For Examiner's Use

1 The compounds of magnesium have important applications. Magnesium oxide is often used as a refractory material to line furnaces while magnesium chloride is used to de-ice roads and pavements in winter.

(a) (i) Explain why magnesium oxide has the formula MgO.

Each Mg atom has 2 valence electrons. **One Mg atom loses 2 valence electrons** to **one O atom** to achieve stable **octet configuration**.

.....[1]

Comments:
- Many candidates simply wrote "because it is formed from Mg^{2+} and O^{2-}", without explaining why the atoms form those ions in the first place (to achieve stable octet).
- "To form stable ions" is also not accepted as the ions are not stable!

(ii) State and explain the property that allows magnesium oxide to be used as a refractory material.

MgO has a **high melting point.** A **large amount of energy** is required to overcome the **strong electrostatic forces of attraction between oppositely charged ions**.

.....[1]

Comments:
- The term "ionic bonds" are not accepted.
- Some students did not know what a refractory material is.

(iii) Describe the action of water on magnesium oxide. Write an equation for any reaction that occurs, and suggest the pH of the solution formed.

MgO does **not** react very **vigorously** and it **dissolves sparingly in water** to form a **weakly alkaline** solution of **pH = 9.**

$MgO + H_2O \rightleftharpoons Mg(OH)_2$

.....[2]

Comments:
- This straightforward recall type question was surprisingly not well-answered.

For Examiner's Use

(iv) State and explain whether magnesium or calcium has a higher tendency to form oxides.

Down the group, the **atomic radius increases**. **Weaker electrostatic force of attraction** between the nucleus and valence electrons. Metal atoms **lose their valence electrons** to form M^{2+} cations **more easily**.

Hence, **Ca** has a ***greater tendency*** to be **oxidised** and form oxide than Mg.

.....

.....[2]

Comments:

- This straightforward recall type question was surprisingly not well-answered.
- Two common misconceptions involve arguments along the lines of stability of CaO (either involving charge density or lattice energy). However, candidates fail to appreciate that charge density explains why CaO does not undergo thermal decomposition readily, while lattice energy is about forming CaO from its gaseous ions (rather than atoms).

For Examiner's Use

(b) In an experiment, 40.0 cm^3 of aqueous magnesium chloride was titrated with 1.00 mol dm^{-3} sodium hydroxide. The reaction involves the precipitation of magnesium hydroxide.

$$MgCl_2(aq) + 2NaOH(aq) \rightarrow Mg(OH)_2(s) + 2NaCl(aq)$$

The pH change of the solution is given in Fig. 1.1.

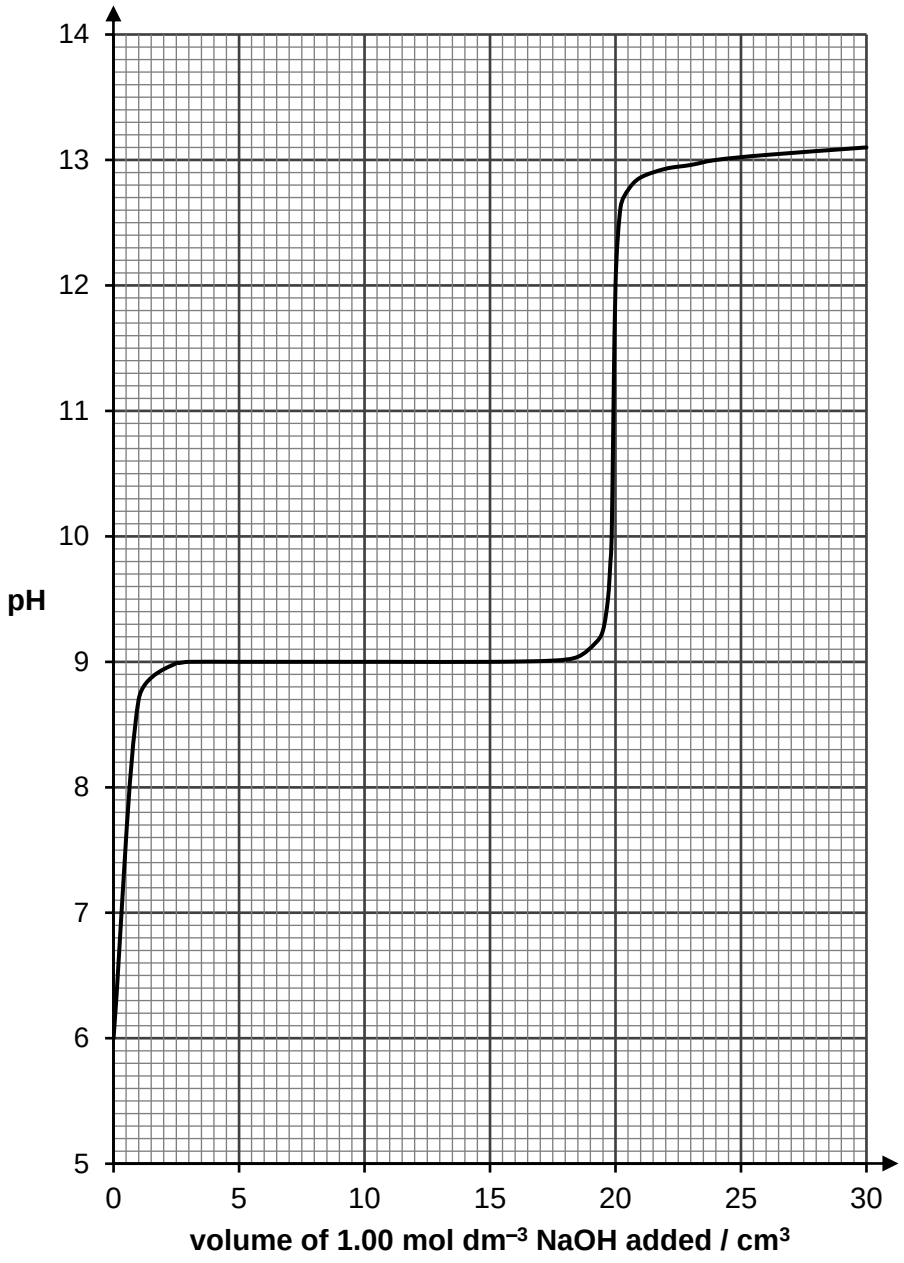

Fig. 1.1

For Examiner's Use

(i) Write an equation to illustrate the hydrolysis of the hydrated magnesium ion, $[Mg(H_2O)_6]^{2+}$.

$[Mg(H_2O)_6]^{2+}(aq) \rightleftharpoons [Mg(H_2O)_5(OH)]^{+}(aq) + \mathbf{H^+(aq)}$ .....[1]

Comments:
- This straightforward recall type question was surprisingly not well-answered. As the ion undergoes partial hydrolysis, the reversible arrow is required.

(ii) Using your answer to **(b)(i)**, write an expression for the acid dissociation constant, K_a, of the hydrated magnesium ion, $[Mg(H_2O)_6]^{2+}$.

$$\mathbf{K_a = \frac{[H^+][Mg(H_2O)_5(OH)^+]}{[Mg(H_2O)_6^{2+}]}}$$

[1]

Comments:
- The most common mistake was to put the charge outside of the square bracket, which represents concentration in the K_c expression)

(iii) Using Fig. 1.1, calculate the initial concentration of H^+.

From the graph, initial pH = 6
Initial $[H^+]$ = **1.00×10^{-6} mol dm^{-3}**

[1]

Comments:
- This was generally well-attempted.

(iv) Calculate the concentration, in mol dm^{-3}, of the aqueous $MgCl_2$.

$$n_{MgCl_2} = \frac{1}{2} n_{NaOH}$$

$$[MgCl_2] = \frac{\frac{1}{2} \times \left(1.00 \times \frac{20.0}{1000}\right)}{\frac{40.0}{1000}} = \mathbf{0.250\ mol\ dm^{-3}}$$

[1]

Comments:
- Some candidates did not notice the mole ratio.

For Examiner's Use

(v) Using your answer to **(b)(iii)** and **(b)(iv)**, determine the K_a for the hydrated magnesium ion, $[Mg(H_2O)_6]^{2+}$.

$$K_a = \frac{\left[H^+\right]^2}{\left[Mg(H_2O)_6^{2+}\right]_0 - \left[H^+\right]} = \frac{\left(1.00\times10^{-6}\right)^2}{0.250 - 1.00\times10^{-6}}$$
$$= \underline{\mathbf{4.00\times10^{-12}\ mol\ dm^{-3}}}$$

[1]

Comments:
- Some candidates did not know that the concentration of $[Mg(H_2O)_5(OH)]+$ ion is the same as that of H^+.

(vi) When 10 cm^3 of alkali have been added, calculate:

I. the hydroxide ion concentration,

pOH = 14 – 9 = 5
$[OH^-]$ = $\underline{\mathbf{1.00\times10^{-5}\ mol\ dm^{-3}}}$

II. the hydrated magnesium ion concentration.

$$\left[Mg^{2+}\right] = \frac{\frac{1}{2}\times\left(\frac{40}{1000}\times0.250\right)}{\frac{50}{1000}} = \underline{\mathbf{0.100\ mol\ dm^{-3}}}$$

[2]

Comments:
- For I, some candidates did not know that they are supposed to make use of the pH to calculate pOH.
- For II, many candidates did not know that they are supposed to make use of the initial amount.

(vii) Hence, calculate a value for the solubility product, K_{sp}, of magnesium hydroxide.

K_{sp} = $[Mg^{2+}][OH^-]^2$
= $0.100\times(10^{-5})^2$
= $\mathbf{1.00\times10^{-11}}\ mol^3\ dm^{-9}$

[1]

Comments:
- As error carried forward was allowed, this was generally well-attempted.

For Examiner's Use

(viii) Explain the constant pH observed when the volume of NaOH added is in the range of 5.0 cm^3 and 15.0 cm^3.

The **OH^-(aq) added is removed as solid $Mg(OH)_2$.**

$Mg^{2+}(aq) + 2OH^-(aq) \rightarrow Mg(OH)_2(s)$. This keeps **$[OH^-]$ constant** (pH is constant at 9). [1]

Comments:
- Majority of the candidates incorrectly assumed that there is a buffer solution without appreciating the type of reaction this is.

[Total: 15]

Comments:
- Average mark for Q2 lies between 10–11 marks. Highest score was 16.
- Refer to detailed comments for the respective parts below.

For Examiner's Use

2 At 1200 K, in the presence of a gold wire, dinitrogen oxide, N_2O, decomposes as follows.

$$2N_2O(g) \longrightarrow 2N_2(g) + O_2(g)$$

The rate of the reaction can be followed by measuring the total pressure, *p*, as it changes with time, *t*. In such an experiment, the total pressure increased as shown in Table 2.1.

Table 2.1

total pressure, *p* / kPa	25.0	27.5	30.0	32.5	34.0	35.0
time, *t* / s	0	1030	2360	4230	5870	7420
partial pressure of N_2O / kPa	25.0	20.0	15.0	10.0	7.00	5.00

(a) (i) Calculate the concentration of N_2O at the start of the reaction in mol dm^{-3}.

using $pV = nRT$

$$\frac{n}{V} = \frac{p}{RT} = \frac{25.0 \times 10^3 \text{ Pa}}{8.31 \text{ J K}^{-1} \text{ mol}^{-1} \times 1200 \text{ K}}$$
$$= 2.507 \text{ mol m}^{-3}$$
$$= \underline{\mathbf{2.51 \times 10^{-3} \text{ mol dm}^{-3}}}$$

[1]

Comments:
- Majority of the students made use of the correct formula to arrive at the $[N_2O]$ in mol m^{-3}.
- However, many did not know the conversion from **mol m^{-3} to mol dm^{-3}**, thus losing this mark (or they were unaware they need to convert, forgetting the units for V in the equation was in m^3.).

For Examiner's Use

(ii) Show that the partial pressure of N_2O at any time t is equal to $(75.0 - 2p)$ kPa.

Let q kPa be the partial pressure of O_2 at time t.

	$2N_2O(g)$	$\longrightarrow$	$2N_2(g)$	+	$O_2(g)$
initial partial pressure / kPa	25.0		0		0
Δ in partial pressure / kPa	$-2q$		$+2q$		$+q$
partial pressure at time t / kPa	$25.0 - 2q$		$2q$		q

total pressure at time $t = 25.0 - 2q + 2q + q$

$$p = 25.0 + q$$

$$q = p - 25.0$$

partial pressure of N_2O at time $t = 25.0 - 2q$ kPa

$$= 25.0 - 2(p - 25.0) \text{ kPa}$$

$$= 25.0 - 2p + 50.0 \text{ kPa}$$

$$= 75.0 - 2p \text{ kPa } (\textbf{shown})$$

[2]

Comments:

- It was surprising that a considerable no. of students were not able to prove/show this expression for partial pressure of N_2O.
- Most students were able to come out with the relevant ICE table but stopped short of arriving at the final expression.
- A number of students merely substitute the value of total pressure, p (for a particular time) into the expression and then obtain the value of partial pressure of N_2O to be the same as the table and concluding expression was thus correct.

(iii) Hence, complete Table 2.1 for the partial pressures of N_2O after 1030 s, 2360 s, 4230 s, 5870 s and 7420 s. [1]

Comments:

- Large majority of students were able to complete this part.
- Despite the expression given in the previous part, some students obtained incorrect values (common values seen were 5.00 and 0.00 respectively) for the last 2 columns (for p=34.0 and 35.0 [they thought reaction completed at this time.]). It seemed that these students had independently did this part of the table first right from the beginning of the qns without referring to the context given in (a)(ii).

(iv) Plot on the grid in Fig. 2.1, a graph of the partial pressure of N_2O against time, *t*, and hence determine the order of the reaction with respect to N_2O.

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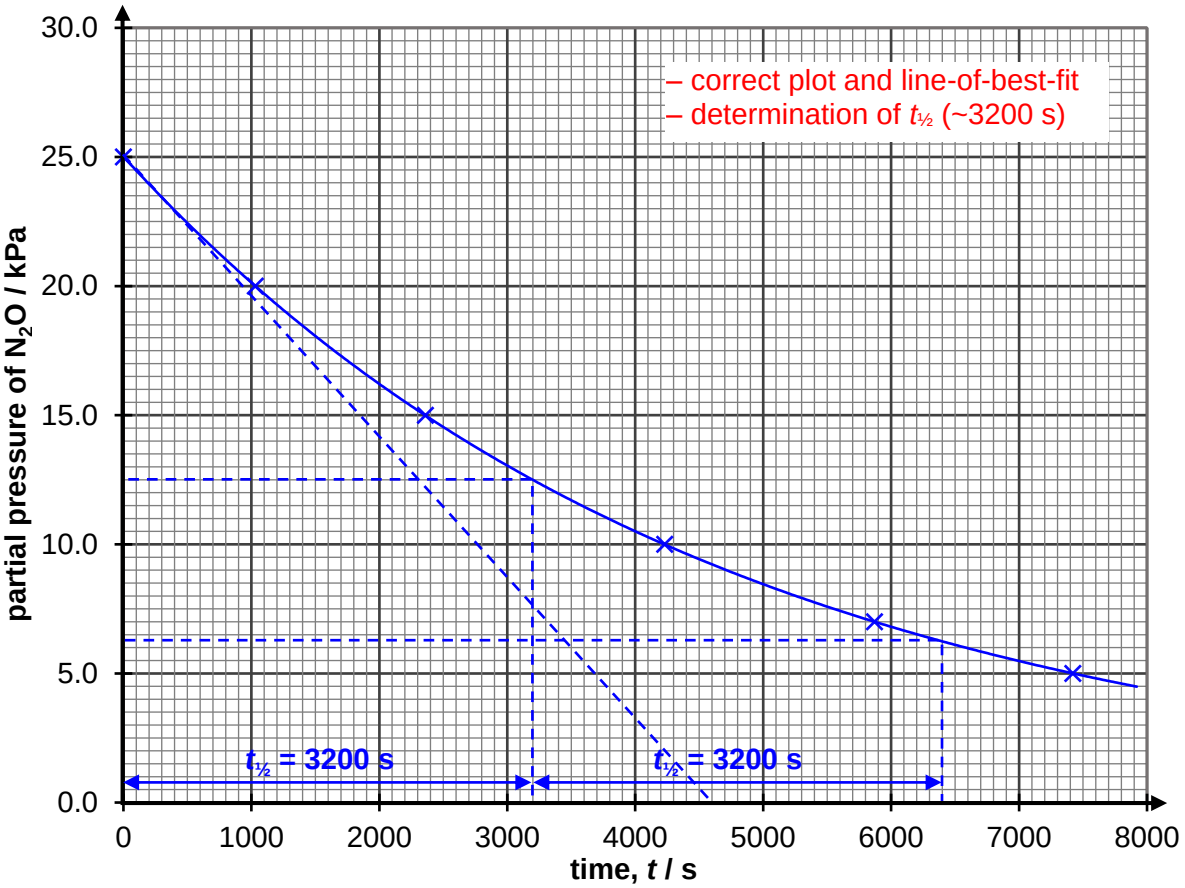

Fig. 2.1

Since the graph of partial pressure of N_2O against *t* has a **constant half-life of 3200 s** (must be shown on graph),
the order of the reaction with respect to N_2O is **1**.

[3]

Comments:

- Most students were able to obtain the best-fit curve with curve passing through all points.
- They were largely thus able to obtain constant or approx. constant half-lives (around 3200 s). **At least 2 half-lives should be shown (3 half-lives for practical).** For approx. constant half-lives to be concluded, the values should be within 200 s of each other.
- Some students misplotted the (1030, 20.0) and (5870, 7.00), thus affecting the quality of their half-live values. These students will still receive credit for showing their half-lives working clearly on the graph. However, they will be penalised 2m – the 1st mark for plotting and best-fit curve and the 3rd mark for concluding on half-lives and thereby the order. Often these students' half-lives values fall out of the 200s range to be considered approx. constant.

Comments (cont'd):

- For those students who incorrectly determine the last 2 partial pressure values for p=34.0 and p=35.0 (refer to 2nd bulleted point of comments given in **(a)(iii)**), they drew a best-fit straight line instead. They were penalised for the 1st mark for the best-fit curve and the 3rd mark for quality of $t_{1/2}$ and order of reaction (since they will conclude is zero order). They would still receive credit for showing relevant half-lives if they did (most often they did not since they obtained a constant gradient).
- **Students are to be reminded** that they need to show or indicate their half-lives working (construction lines to indicate where they used to determine their respective half-lives e.g. from 25 to 12.5 to 6.25 or 20 to 10 to 5 and their respective t values) and half-live values on the graph as reflected in the answers above. If the 2 half-lives values were different, they should evaluate the average half-live value and conclude on the order. They should not just draw construction lines, show some values like 3,200 and 6,400 on the graph (without indicating the 2 $t_{1/2}$ values) and then conclude since half-lives were constant, order=1. Markers will not interpret this for you since this qns is assessing your understanding of half-live concept.

For Examiner's Use

(v) Calculate the rate constant for the reaction, including its units.

using $k = \dfrac{\ln 2}{t_{\frac{1}{2}}}$

$$k = \frac{\ln 2}{3200}\ \text{s}^{-1}$$
$$= 2.166 \times 10^{-4}\ \text{s}^{-1}$$
$$= \underline{\mathbf{2.17 \times 10^{-4}\ s^{-1}}}$$

or

$$\text{initial rate of reaction} = \frac{2.51 \times 10^{-3}\ \text{mol dm}^{-3}}{4600\ \text{s}}$$
$$= 5.45 \times 10^{-7}\ \text{mol dm}^{-3}\ \text{s}^{-1}$$

substituting into the rate equation,

$$\text{rate} = k[\text{N}_2\text{O}]$$
$$5.45 \times 10^{-7} = k\left(2.51 \times 10^{-3}\right)$$
$$k = \underline{\mathbf{2.17 \times 10^{-4}\ s^{-1}}}$$

[1]

Comments:

- Both methods should obtain the same value and units.
- Most students used the 1st method to determine the rate constant. However, some thought there were no units for k (they wrote "no units") or gave incorrect units for k, failing to relate back to the 1st order wrt to N_2O which they earlier obtained.
- Students who used the 2nd initial rates method often failed to recognise the y-axis of their graph was in kPa and not in mol dm^{-3} s^{-1}. They then went on to make use of the rate equation dividing by $[N_2O]$ (which was in mol dm^{-3}) to obtain their k and still giving the units as s^{-1}. They failed to recognise the units of rate is in kPa and $[N_2O]$ is in mol dm^{-3}.
- Students who incorrectly determine the order from **(a)(iv)** was given credit for this part should they do the correct manipulations (with the correct units) based on error carried forward principle.

For Examiner's Use

(vi) When platinum is used instead of gold as the catalyst, the rate equation for the same reaction becomes

$$\text{rate} = \frac{k_2[N_2O]}{1 + b[O_2]}$$

where k_2 is the new rate constant and b is a constant.

Describe and explain how the rate of decomposition will change as the reaction proceeds.

As the reaction progresses, **concentration of the N_2O reactant decreases** as it is being **consumed**, hence the **rate would decrease**.

In addition, the **concentration of the O_2 product increases** as it is **formed**, hence the rate would **further decrease**.

.....[2]

Comments:
- Majority of the students were able to explain this part well, identifying both $[O_2]$ and $[N_2O]$.
- Some students focused only on $[O_2]$ or $[N_2O]$ in their explanation.

(b) N_2O is a linear molecule.

(i) Draw the dot-and-cross diagram of a N_2O molecule.

[1]

Comments:
- This part was poorly done. Many students placed the O as the central atom, forgetting a key principle in drawing dot-cross diagrams that the **central atom is usually the less electronegative atom** (though O has only 1 atom in this case).
- All structures with O as the central atom were penalised, even if they satisfy the octet and linear shape conditions.

For Examiner's Use

(ii) The standard enthalpy change of formation of N_2O is +82 kJ mol^{-1}.

Using data from the *Data Booklet*, determine a value for the bond dissociation energy of the nitrogen–oxygen bond in N_2O.

$$N{\equiv}N + \tfrac{1}{2}\,O{=}O \rightarrow N{\equiv}N{\rightarrow}O$$

$$+82 = \sum \text{B.E.}(\text{bonds broken}) - \sum \text{B.E.}(\text{bonds formed})$$

$$+82 = \text{B.E.}(N{\equiv}N) + \frac{1}{2}\text{B.E.}(O{=}O) - \text{B.E.}(N{\equiv}N) - \text{B.E.}(N{-}O)$$

$$= \frac{1}{2}(+496) - \text{B.E.}(N{-}O)$$

$$\text{B.E.}(N{-}O) = \underline{\textbf{+166 kJ mol}^{-1}}$$

[2]

Comments:

- This part was also poorly done. This was due to either using the incorrect formula (of bonds formed – bonds broken) or failing to express their equation for the formation of N_2O to be in terms of 1 mol of N_2O. Many made use of 2 N_2 + O_2 to give 2 N_2O equation and still took this enthalpy change to be +82.
- Students who obtained the incorrect structure for **(b)(i)** was given full credit should they show the correct manipulations based on error carried forward principle.
- Students are reminded that bond energy value has a "+" sign associated with the value. Those who omitted it were not penalised this time.

(iii) The activation energy of the uncatalysed (decomposition) reaction is 90 kJ mol^{-1} and of the catalysed reaction 40 kJ mol^{-1}. The energy profile diagram of the uncatalysed reaction is shown in Fig. 2.2.

On the same axes in Fig. 2.2, draw the energy profile diagram for the catalysed reaction and label all relevant enthalpy changes.

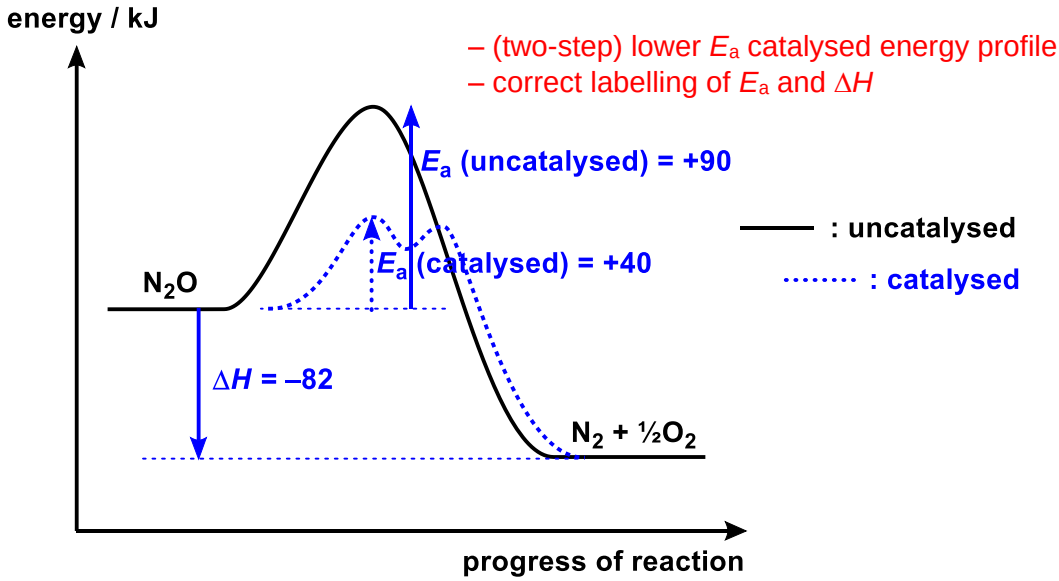

Fig. 2.2

[2]

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Comments:

- All students who attempted this qns recognised the lower activation energy for the catalysed route. There were some who drew the 2 humps for the catalysed route.
- Many did not label the exothermic enthalpy change of decomposition (and some labelled the formation reaction instead) and some did not label the uncatalysed route Ea (despite qns instructing them to label all enthalpy changes).
- Students are reminded that bond energy in **(b)(ii)** and above E_a values comes along with a "+" sign before it, though not penalised this time if not given.

(iv) Hence, explain why it is thermodynamically and kinetically not possible to make N_2O from its elements, even if a gold catalyst is present.

The formation of N_2O is **non-spontaneous** ($\Delta G > 0$) **at all temperature** as the **reaction is endothermic ($\Delta H > 0$) and leads to a decrease in entropy** ($\Delta S <$ 0) since there is a net consumption of gaseous molecules.

In addition, the **activation energy for the formation of N_2O** from N_2 and O_2 is **much higher than the activation energy for the exothermic decomposition of N_2O**, even in the presence of gold catalyst. Thus, any N_2O even if it is slowly formed, would **rapidly decompose** to give back N_2 and O_2.

.....[2]

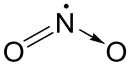
Comments:

- Most students were able to explain well for the thermodynamic part relating back to the entropy change and thus the Gibbs free energy, concluding that it will always be larger than zero and thus not spontaneous.
- However, for the kinetics part, many just relate to the fact that the activation energy was too high and as such will be a very slow reaction. They did not relate back to the Ea of the backward decomposition reaction (from part (b)(iii)). Students should relate back to the command word: "Hence, explain….". It serves to guide them their ans should relate back to the previous part.
- Considerable no. of students seem to be confused with regards to what does the terms thermodynamically and kinetically means or related to. These students relate thermodynamics to activation energy instead and kinetics to entropy change and Gibbs free energy instead.

For Examiner's Use

(c) Nitric acid production represents the largest source of N_2O in the chemical industry. Nitrogen monoxide, NO, an intermediate in the production of nitric acid, readily decomposes to N_2O and nitrogen dioxide, NO_2, at high pressures.

$$3NO(g) \longrightarrow N_2O(g) + NO_2(g)$$

NO_2 is in fact a radical with the following structure: 

(i) Given that $\Delta H_f^{\ominus}(NO) = +90 \text{ kJ mol}^{-1}$ and $\Delta H_f^{\ominus}(NO_2) = +33 \text{ kJ mol}^{-1}$. Together with the data given in **(b)(ii)**, calculate the standard enthalpy change for the decomposition of NO into N_2O and NO_2.

$$\begin{aligned}\Delta H_r^{\ominus} &= \sum \Delta H_f^{\ominus}(\text{products}) - \sum \Delta H_f^{\ominus}(\text{reactants}) \\ &= \Delta H_f^{\ominus}(N_2O) + \Delta H_f^{\ominus}(NO_2) - 3\Delta H_f^{\ominus}(NO) \\ &= +82 + 33 - (3 \times +90) \\ &= \underline{\mathbf{-155 \text{ kJ mol}^{-1}}}\end{aligned}$$

[1]

Comments:

- This part was generally well done.
- Students who got this wrong were usually due to either due to the incorrect formula they used (reactants – products instead) or forgetting the coefficient "3" for enthalpy change of formation of NO.
- Some students who did the above correct manipulation went on to divide by 3 to their value. They did so thinking Standard enthalpy change of decomposition of NO referred to only 1 mol of NO in the given equation. They are reminded that they should calculate any general enthalpy change of reaction (not within the scope of the definitions which they have learnt) based on the stoichiometric ratio as given by the equation.

(ii) Comment on the extent of deviation of the two gases, NO_2 and N_2O, from ideal gas behaviour under the following pressure conditions.

High pressure : Both gases **deviate similarly** from ideal gas behaviour. Under high pressure condition, deviation from ideal gas behaviour is due to the **volume occupied by the molecules being not negligible compared to the volume of the container**. Since NO_2 and N_2O are **similar in size**, the two gases will deviate similarly. [1]

For Examiner's Use

Low pressure : At low pressure, deviation from ideal gas behaviour is due to the **intermolecular attraction** between molecules. NO_2 has a **larger dipole moment** compared to N_2O. Hence, the **permanent dipole-permanent dipole attraction** between the NO_2 molecules are **stronger** than that between N_2O molecules, causing **NO_2 to deviate more from ideal gas behaviour**. .....[1]

Comments:

- This part was poorly done. Most compared both gases with reference to ideal gas rather than comparing the extent of deviation of NO_2 versus N_2O from ideal gas behaviour.
- For **High pressure**, students need to be reminded that the dominant factor or assumption they should be discussing should be regarding the assumption that volume of gas molecules being negligible as compared to the volume of gas/container being no longer valid since at high pressure, the **pV value for non-ideal gases in general is larger than that of ideal gas**. Students who gave the latter assumption about intermolecular forces of attraction being no longer negligible and concluding that NO_2 having stronger permanent dipole-permanent dipole (pd-pd) interactions than that of N_2O still receive full credit (though they should recognise that when molecules have significant intermolecular forces of attraction, this will result in the impact on the container i.e. pressure being lower. Thus, pV values will be lower than that of ideal gas and thus contradict experimental data).
- Students who did compare the size of NO_2 and N_2O did not realise the difference whether in terms of no of electrons (23 vs 22) or Mr (46 vs 44) was very small and as such their sizes were similar and thus should exhibit similar deviation from ideal gas.
- For **Low pressure**, since the volume of gas molecules being negligible as compared to the volume of gas/container, the key point/assumption to be mentioned is the difference in intermolecular forces of attraction between NO_2 and N_2O, resulting in the **pV values for non-ideal gases to be lower than that of ideal gas**. Students who incorrectly determine in **(b)(i)** the N_2O structure with O as the central atom (so 2 N=O bonds) and thus conclude that N_2O had intermolecular instantaneous dipole-induced dipole interactions (since it is non-polar) and weaker than the stronger intermolecular pd-pd interactions for NO_2 was given credit. It was annotated in their scripts that N_2O is actually polar but error carried forward due to their structure in **(b)(i)**.

[Total: 20]

For Examiner's Use

3 Tris, or tris(hydroxymethyl)aminomethane, is a white crystalline organic compound with the formula $(HOCH_2)_3CNH_2$. It is extensively used in biochemistry and molecular biology as a component of buffer solutions.

(a) State and explain whether Tris will be a stronger or weaker base compared to methylamine, CH_3NH_2.

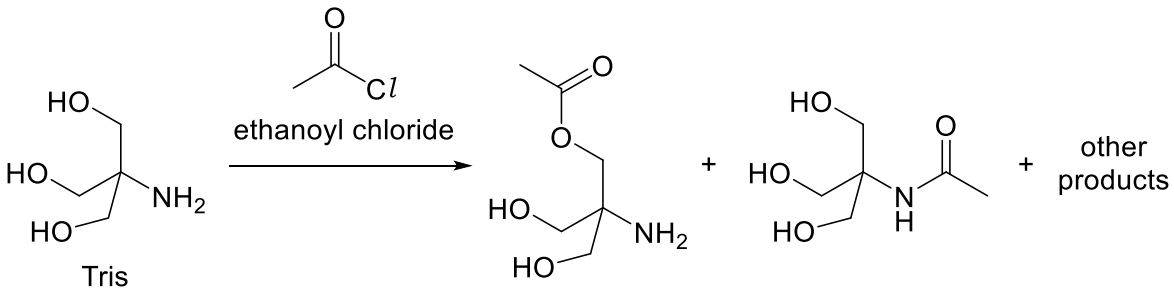
Weaker base. (with correct reason)

The **three OH groups** are **electron-withdrawing** due to the **highly electronegative** **oxygen** atoms, hence rendering the **lone pair of electrons on the nitrogen less available for donation to an acid**. [2]

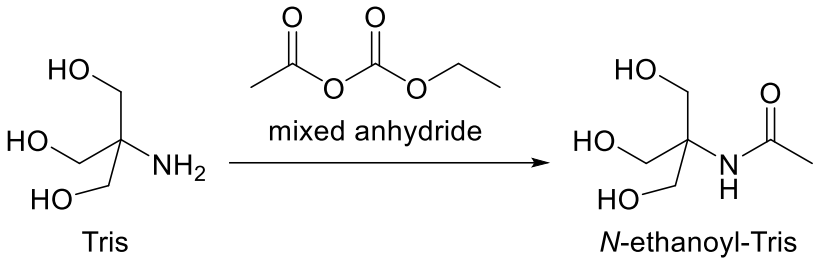
Comments:

- This part is poorly attempted. Many concluded wrongly that Tris is a stronger base because N atom in Tris is bonded to three larger electron donating alkyl groups and that increased the availability of the lone pair of electrons on N. The presence of the electron withdrawing OH group was overlooked.
- Some who have concluded that Tris is a weaker base but gave the wrong or contradicting reasons and were not awarded any mark.
- Those who have correctly concluded Tris is a weaker base but had some inaccuracy in the reason was awarded 1 mark. Some of the inaccuracy are as follows.
  - Presence of electron withdrawing groups intensify the negative charge on N (wrong! There is no negative charge on N)
  - Presence of electron withdrawing groups increase the lone pair on N (wrong! The no. of lone pair of electrons on N atom will not increase!)
- Many indicated that $(HOCH_2)$ group is electron withdrawing. Mark was not deducted for this, but it is more accurately to state the electron withdrawing group as the OH group.

When one mole of Tris is treated with one mole of ethanoyl chloride, a mixture of products is obtained, involving ethanoylation at both the nitrogen and oxygen atoms of Tris:



However, when one mole of Tris is treated with one mole of $CH_3CO_2CO_2CH_2CH_3$ (a mixed anhydride), *N*-ethanoyl-Tris is obtained cleanly in high yield:



(b) Suggest a likely explanation for the differences in selectivity observed using the two ethanoylating reagents.

As the C=O carbon in ethanoyl chloride is **more electrophilic / electron-deficient** than that in the mixed anhydride, it is **less selective** towards the **more nucleophilic amine nitrogen atom** compared to the alcohol oxygen atom.

or

As the C=O carbon in the mixed anhydride is **less electrophilic / electron-deficient** than that in ethanoyl chloride, it is **more selective** towards the **more nucleophilic amine nitrogen atom** compared to the alcohol oxygen atom. [2]

Comments:

- It can be seen that many candidates do not understand the question and end up describing the difference in selectivity instead of explaining why.
- Many only went as far as stating ethanoyl chloride is more reactive than the mixed anhydride without stating that the C=O carbon is more electron deficient than that in the mixed anhydride. Some incorrectly state that ethanoyl chloride is a better nucleophile!
- Many also failed to identify that the amine nitrogen atom is more nucleophilic than the alcohol oxygen atom. They simply state ethanoyl chloride is a better electrophile and hence can react with both the N and O atom in Tris. The full two marks cannot be given for this.

A Tris–HC*l* buffer can be prepared by dissolving solid Tris in a suitable volume of hydrochloric acid.

Tris has a pK_b of 5.93 at 25 ºC.

(c) (i) Explain whether Tris or hydrochloric acid should be used in excess.

Tris should be used in excess.

This is because a buffer is composed of a **weak base and its conjugate acid**,

thus there must be excess Tris, the weak base. [1]

Comments:

- While many correctly identified that Tris should be in excess, few were able to explain the need for both a weak base and its conjugate acid to be present to act as a buffer.
- Many answers incorrectly focused on why an excess of HC*l* would not give a buffer, rather than explain how a buffer is obtained.

For Examiner's Use

(ii) Explain how the Tris–HC*l* buffer works.

The mixture consists of a **large reservoir** of the **base** (Tris) and its **conjugate acid** ($TrisH^+$), and hence is able to remove **small amounts of acid and base added, respectively,** hence **maintaining the pH relatively constant**.

.....[2]

Comments:
- Many students did not realise that the question was simply asking them to define how a buffer works.
- Many answers failed to mention the need for a large reservoir of the base and its conjugate acid. A large number thought that HC*l* was the acid component of the buffer, failing to realise that the buffer must be made of a weak base and its conjugate acid (or vice versa), rather than a strong acid of HC*l*.
- A number of answers omitted to mention that the buffer was only able to remove small amounts of acid and base.
- Weaker answers repeated the terms given in the question, for example, by saying that the buffer buffers against pH changes, or completely omitted to explain that the removal of small amounts of acid and base added maintained a relatively constant pH.

(iii) Explain whether the hydrochloric acid can be replaced by ethanoic acid.

Yes. So long as there are **sufficient amounts** of the weak base and its conjugate acid (*or* weak acid and conjugate base) to remove the small amount of acid or base added.

.....[1]

Comments:
- This was poorly done.
- Majority thought that ethanoic acid being a weak acid would only partially dissociate, hence not be able to provide H^+ required to react with Tris to form sufficient conjugate acid. It should be noted that when H^+ from ethanoic acid has been reacted, more ethanoic acid would dissociate to form more H^+.
- Some thought that adding small amounts of ethanoic acid would convert the basic buffer to an acidic buffer, without realising that ethanoic acid would need to be in large excess of Tris for it to happen. (Since the acidic buffer would need to consist of the weak acid and its conjugate base)

For Examiner's Use

(iv) By means of an equation, show how the Tris–HC*l* buffer functions when a small amount of dilute sodium hydroxide is added.

$(HOCH_2)_3CNH_3^+ + OH^- \rightarrow (HOCH_2)_3CNH_2 + H_2O$ [1]

Comments:
- This was generally well done.
- Some thought that HC*l* which was added to the buffer would be able to react with NaOH, not realising that it would have already reacted with the basic Tris to form the conjugate acid (which would react with NaOH added).

(v) State the effective pH range of Tris buffer.

pK_a of conjugate acid = 14 – 5.93 = 8.07. Effective pH range is pK_a ± 1, so will be **7.07 to 9.07**. [1]

Comments:
- While many realised that the range was ± 1, many wrongly thought that they could use pK_b instead of pK_a.

(vi) Based on your answer to **(c)(v)**, suggest a reason why Tris is used extensively in biochemistry and molecular biology as a buffer.

The working range of Tris buffer **lies in the physiological pH** typical of most living organisms. [1]

Comments:
- Few students realised that the physiological pH lies within the working range of the buffer. Many related the use of Tris to the blood pH or working pH of enzymes which was not accepted.

For Examiner's Use

(vii) Determine the volume of 1.00 mol dm^{-3} hydrochloric acid that must be used to dissolve 5.00 g of Tris to obtain a buffer solution at pH 8.50.
[M_r of Tris = 121.0]

$$n_{\text{Tris solid}} = \frac{5.00}{121.0} = 0.04132 \text{ mol}$$

Let the buffer contains x mol of Tris and the volume of 1.00 mol dm^{-3} HCl be V dm^3,

$$K_a\left(\text{TrisH}^+\right) = \frac{\left[\text{H}^+\right]\left[\text{Tris}\right]}{\left[\text{TrisH}^+\right]}$$

$$10^{-(14-5.93)} = \frac{10^{-8.50}\left(\frac{x}{V}\right)}{\frac{0.04132 - x}{V}}$$

$$x = \frac{0.04132}{1+10^{-0.43}} = 0.03013$$

$$\text{Tris} + \text{HC}l \rightarrow \text{TrisH}^+\text{C}l^-$$

$$n_{\text{HC}l \text{ needed}} = n_{\text{TrisH}^+} = 0.04132 - 0.03013 = 0.01119 \text{ mol}$$

$$V = \frac{n_{\text{HC}l}}{\left[\text{HC}l\right]} = \frac{0.01119}{1.00} = \underline{\mathbf{0.0112 \text{ dm}^3}} = \underline{\mathbf{11.2 \text{ cm}^3}}$$

[3]

Comments:

- This was poorly done. Many students failed to realise that they were dealing with a buffer solution and applied equations for weak bases instead. Those who attempted to use the buffer equation often quoted the wrong Henderson Hasselbach (HH) equation, confusing pH with pOH, and pK_a with pK_b. Many did not correctly identify the base/acid species and the corresponding salt in the equation used.
- Many thought that the [acid] was the same as that of [HCl]. Those who were able to identify the correct species for the HH eqn did not realise that the amount of Tris at equilibrium would differ from the starting amount as some would have already reacted with the added HCl.

Tris is manufactured industrially by the exhaustive reaction of nitromethane, CH_3NO_2, with methanal under basic conditions to produce the intermediate $(HOCH_2)_3CNO_2$, which is subsequently reduced to give the final product:

$$\text{CH}_3\text{NO}_2 + 3\text{HCHO} \xrightarrow{\text{NaOH}} \left(\text{HOCH}_2\right)_3\text{CNO}_2 \xrightarrow{[\text{H}]} \left(\text{HOCH}_2\right)_3\text{CNH}_2$$

For Examiner's Use

(d) Nitromethane, CH_3NO_2, has a low pK_a of 10.2, which is comparable to that of phenol (pK_a = 9.95) and much more acidic compared to most alcohols (pK_a ~16).

(i) Explain why phenol is more acidic than most alcohols.

The **negative charge** of the phenoxide conjugate base is **delocalised into the benzene ring**, **dispersing the charge**, rendering the phenoxide ion **more stable** than alkoxide ions, hence phenol a stronger acid.

.....[1]

Comments:
- This was generally well done.
- Some answers mentioned that benzene was electron withdrawing, hence dispersing the negative charge. It should be noted that it is not sufficient to state as such since benzene can be either electron-donating or electron-withdrawing, depending on what it is attached to. Hence how benzene is electron-withdrawing in this case must be fully explained.
- Many answers omitted to explain how the charge was stabilised, with answers often left as the phenoxide ion being more stable.

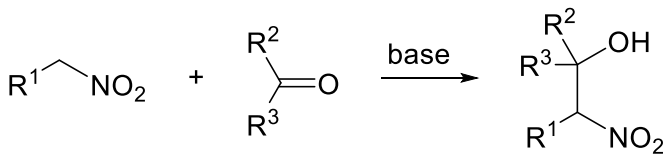
(ii) Suggest likely reasons for the low pK_a of nitromethane.

The negative charge on the conjugate base is stabilised by both **delocalisation into the NO_2**, as well as by the **electron-withdrawing (inductive) effect** of the highly electronegative N and O.

.....[1]

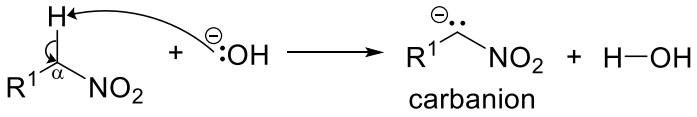
Comments:
- This was poorly done. Few realised that the H on CH_3NO_2 was acidic and could dissociate. Many answers attempted to explain the low basicity of nitromethane instead, or thought that the negative charge was on N.
- Most answers only gave either the mesomeric effect or inductive effect.

The first stage involves the Henry reaction, which is a classic carbon–carbon bond formation reaction between a nitroalkane and a carbonyl compound:

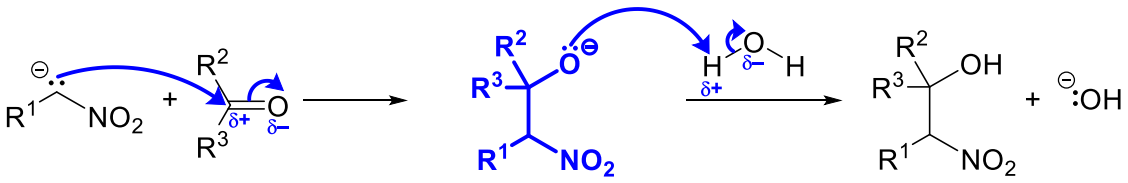


For Examiner's Use

(e) The Henry reaction begins with deprotonation of the acidic nitroalkane on the α-carbon forming a negatively charged carbanion:



Complete Fig. 3.1 to suggest a mechanism for the subsequent attack of the carbanion onto the carbonyl carbon, and protonation of the intermediate to give the 2-hydroxynitro product. Show the structure of the intermediate, all charges and relevant lone pairs, and show the movement of electron pairs by using curly arrows.



intermediate

Fig. 3.1

[3]

Comments:
- This was generally well done. Common mistakes include omission of partial charges of water and the C=O.

(f) Suggest a reagent for reduction of the intermediate, $(HOCH_2)_3CNO_2$, to give Tris.

Sn or Fe, concentrated HCl / $LiAlH_4$ / H_2 with Ni or Pt .....[1]

[Total: 20]

Comments:
- This was generally well done.

For Examiner's Use

4 (a) Caffeine is a stimulant drug that is the world's most widely consumed psychoactive drug. It is found naturally in tea leaves and coffee beans, but can also be synthesised in the laboratory. One method involves converting theobromine into caffeine *via* a two-step route shown in Fig. 4.1.

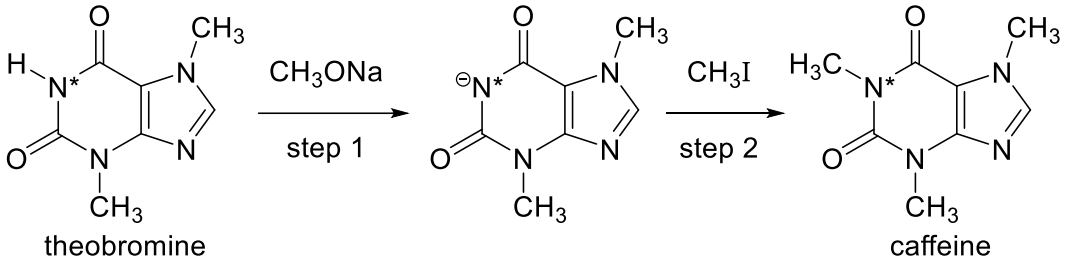


Fig. 4.1

(i) State the type of reaction in step 1.

Acid-base reaction .....[1]

Comments:
- Generally well done. However, some students gave it as "deprotonation", benefit of doubt was given.
- Some students gave all sorts of organic reaction mechanism thinking that the question is about Step 2.

(ii) Step 1 is necessary as the lone pair on the N* atom of theobromine is not available for reaction directly with CH_3I.

Suggest an explanation for this.

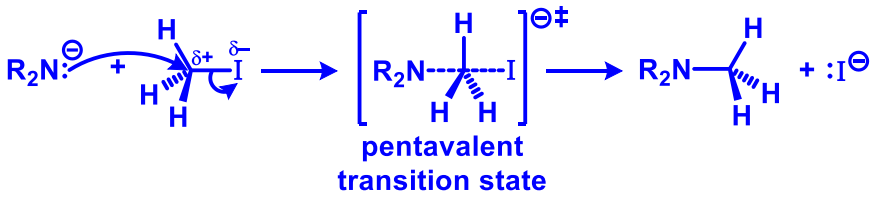
The lone pair on the N* atom **delocalises into the π-electron cloud of the adjacent C=O bond**. Hence it is unavailable for reaction.

.....[1]

Comments:
- Generally okay. Many students lack the appreciation of the importance of the π-electron cloud of the bond that allows for the delocalisation of the lone pair but credit was still given if idea of delocalisation into the C=O bond is present.
- Some students gave the reason of the lone pair being unavailable due to the presence of the electron-withdrawing O atom. This is insufficient.
- Some students gave vague reasoning that the lone pair was able to delocalise into the O atoms which is not possible without the C in the C=O bond.

(iii) Describe the mechanism for the reaction in step 2. You may represent the anionic intermediate as R_2N^-.

Bimolecular Nucleophilic Substitution / S_N2



[3]

Comments:

- This part was poorly attempted. Many students were unable to see that step 2 is an S_N2 reaction, with the anionic intermediate serving as the nucleophile and CH_3I as the electrophile. Also, many students who wrote S_N2 gave the wrong superscript/subscripts such as SN_2/S_{N2}/etc.
- Many students who gave the correct reaction were unable to completely complete the mechanism. Many omitted the correct arrows, charges, double dagger representing the transition state, the weakening bond in the transition state and all products.
- Students are reminded that 3D configuration should be observed for S_N2 reactions even though it is not a marking point.

(b) Caffeine can be extracted from an aqueous solution using liquid-liquid extraction, where the caffeine solute is partitioned between an aqueous phase (aq) and an organic phase (org). The resulting equilibrium for caffeine extraction may be written as:

$$\text{caffeine(aq)} \rightleftharpoons \text{caffeine(org)}$$

The ratio of the concentrations of caffeine in the two phases can be written as an equilibrium constant called the partition coefficient, K_D.

$$K_D = \frac{[\text{caffeine}]_{org}}{[\text{caffeine}]_{aq}}$$

Caffeine can be extracted using different organic solvents such as trichloromethane and benzene. After extraction, it can be purified further into white crystals.

The K_D of caffeine in benzene and trichloromethane are given in Table 4.1.

Table 4.1

solvent	K_D
benzene	0.450
trichloromethane	8.30

For Examiner's Use

(i) Using Table 4.1, determine which is the better solvent in extracting caffeine from the aqueous phase. Explain your answer with reference to the structure and bonding.

Trichloromethane is the better solvent as it has the **largest K_D value**. Both caffeine and trichloromethane are **both polar** but benzene is **non-polar**. Hence, caffeine and trichloromethane are able to interact strongly via **permanent dipole–permanent dipole interactions between the molecules**. Hence, trichloromethane is a better solvent than benzene.

.....[2]

Comments:

- This was poorly done in general. Many students were unable to comprehend the question correctly.
- Many students simply stated which is a better solvent without using information from the table. Also, many students chose the wrong solvent as they thought that caffeine is to be extracted into the aqueous phase when it should be **from** the aqueous phase.
- The explanation using the structure and bonding for why it is a better solvent was done very poorly. Many students were unable to identify correctly that caffeine is polar. Some students thought that trichloromethane is CCl_4 instead of $CHCl_3$. Therefore, indicating the wrong polarity of the molecule. Also, many students tried to explain that benzene has resonance structure/pi electrons etc. to explain its structure and bonding but this is not necessary. Students should be careful that with reference to structure and bonding in terms of chemical bonding, it is referring to in this case, simple molecules structures of the solvents, their polarity and hence the type of intermolecular forces of attraction that exists.
- Students who correctly identified that type of intermolecular forces of attraction between the solvents only did not answer the question. Ultimately, students must be able to explain why the solvents can interact well with the caffeine molecules and hence why which solvent is a better solvent.

For Examiner's Use

(ii) After the extraction, the solvent is removed to give crude solid caffeine. Suggest how you can purify the crude caffeine and describe how you can ascertain the purity of the caffeine thus obtained.

The caffeine can be purified via a single solvent **recrystallisation** using trichloromethane. To ascertain the purity, take a few crystals of caffeine and **determine its melting point** using a thiele tube/melting point machine. If the crystals melt at a **sharp and accurate** (compared to literature value) **melting point, it is pure**. If the crystals **gradually melt over a temperature range, it is not pure**. [2]

Comments:
- This part was poorly done. Many students were unable to identify the method in purifying organic compounds. Students are reminded to be familiar with laboratory knowledge from practicals.
- For students who attempted to explain how to ascertain purity of the compounds were not specific enough in their answers and hence did not get the credit.

Nowadays, liquid CO_2 is the preferred solvent used to extract caffeine even though it is non-polar.

(iii) Explain why caffeine is able to dissolve in liquid CO_2.

Although CO_2 is not polar, it has **polar C=O bonds**. Hence, the polar bonds is able to interact with the **polar bonds within caffeine via permanent dipole–permanent dipole interactions**, making caffeine soluble in liquid CO_2.

[1]

Comments:
- This part was poorly done. Even though the question stated that liquid CO_2 is non-polar, many students repeated this in their answer or even gave that CO_2 is polar.
- Many students were unable to appreciate that caffeine is a polar molecule and should be interacting with liquid CO_2 via permanent dipole-permanent dipole interaction due to the polar bonds present.
- Many students also reasoned that caffeine was able to undergo hydrogen bonding with liquid CO_2, which is not possible as the H atoms of caffeine are directly bonded to C, which is not electronegative enough to generate a $H^{\delta+}$ capable of hydrogen bonding.

For Examiner's Use

(iv) Compared to trichloromethane and benzene, suggest why liquid CO_2 is the preferred solvent in extracting caffeine.

Liquid CO_2 is **non-toxic/very volatile and easy to remove**.

.....[1]

Comments:

- This part was poorly attempted with many vague answers such as easier to obtain or less costly. To get the credit for easier to obtain, students must be able to explain that it is accessible from the atmosphere. Liquid CO_2 in reality is not easy to generate as it requires a very high pressure/low temperature which will result in a costly procedure.

(c) To determine the amount of caffeine in the organic extract described in **(b)**, the organic extract can be analysed spectrophotometrically, a method that measures the absorption of a specific wavelength of light in the ultraviolet–visible light region by the analyte, in this case, caffeine.

Prior to the determination of the caffeine content, a calibration plot using known concentrations of caffeine using trichloromethane as a solvent was prepared and analysed using a UV-Vis spectrophotometer. Fig. 4.2 shows the calibration plot from the analysis.

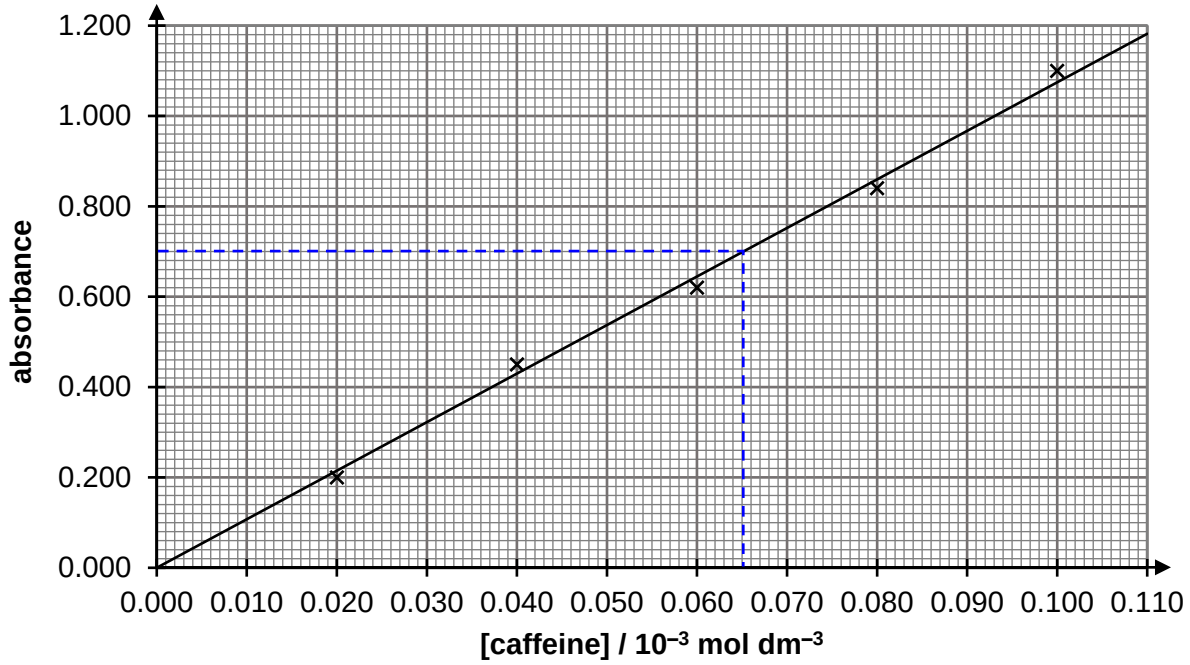


Fig. 4.2

For Examiner's Use

(i) State one assumption made when using spectrophotometry to determine the concentration of caffeine in a sample of tea leaves for example.

One assumption is that caffeine is the **only compound** in tea leaves which **absorbs light at the specific wavelength used** in the determination.

or other logical answers that indicate the absorption was due to caffeine only. [1]

Comments:
- This part was poorly attempted. There were incomplete or vague answers.
- Students were expected to show understanding that absorption was due to caffeine only

(ii) The organic phase extract was found to have an absorbance of 0.700.

Using Fig 4.2, determine the concentration of caffeine present in the extract.

6.50×10^{-5} mol dm^{-3} [1]

Comments:
- This part is well done in general.
- Common mistakes involved error in reading the graph. Also mis-interpret or missing out the "10^{-3}" in the x axis.

(iii) The caffeine was extracted using 0.050 dm^3 of trichloromethane and 0.500 dm^3 of water.

Using your answer in **(c)(ii)** and data from Table 4.1, determine the concentration of caffeine remaining in the aqueous phase in mol dm^{-3}.

$$[\text{caffeine}]_{org} = 6.50 \times 10^{-5} \text{ mol dm}^{-3},\ K_D(\text{trichloromethane}) = 8.3$$

$$[\text{caffeine}]_{aq} = \frac{[\text{caffeine}]_{org}}{K_D} = \frac{6.50 \times 10^{-5}}{8.3}$$

$$= 7.8313 \times 10^{-6} \text{ mol dm}^{-3}$$

$$= 7.83 \times 10^{-6} \text{ mol dm}^{-3}$$ [1]

Comments:
- This part is well done in general.
- E.c.f. was awarded.

For Examiner's Use

(iv) Hence, determine the total mass of caffeine originally present in the sample. (M_r of caffeine = 194.2)

$$\begin{aligned} \text{n(caffeine)} &= \left[0.065\times10^{-3}\times0.050\right]+\left[7.8313\times10^{-6}\times0.500\right] \\ &= 7.1656\times10^{-6}\ \text{mol} \\ \text{m(caffeine)} &= 7.1656\times10^{-6}\times194.2 \\ &= 1.3916\times10^{-3}\ \text{g} \\ &= \mathbf{1.39\times10^{-3}\,g} \end{aligned}$$

[1]

Comments:
- Common mistakes involved using the "Total Volume of 0.550 dm^3" for their calculations.
- Many students did not attempt this part.

(d) Instead of extracting caffeine using a single volume of solvent, it is possible to use successive volumes of solvent to extract caffeine from the sample.

The following equation gives $[\text{caffeine}]_n$, the concentration of caffeine *remaining* in V_{aq} dm^3 of aqueous phase, after extraction using n V_{org} dm^3 portions of organic solvent.

$$[\text{caffeine}]_n = \left(\frac{V_{aq}}{V_{org}K_D + V_{aq}}\right)^n [\text{caffeine}]_0$$

$[\text{caffeine}]_0$ is the original concentration of caffeine in the V_{aq} dm^3 of aqueous phase.

An investigation on the efficiency of caffeine extraction was performed using
- one 0.100 dm^3 portion,
- five 0.020 dm^3 portions, and
- ten 0.010 dm^3 portions

of trichloromethane, while keeping the total volume used constant (0.100 dm^3).

The initial concentration of caffeine in 0.100 dm^3 of the aqueous phase is 1.00×10^{-3} mol dm^{-3}.

(i) Using the equation above and data from Table 4.1, complete Table 4.2.

Table 4.2

number of portions of trichloromethane used	concentration of caffeine left in aqueous phase (mol dm^{-3})	% caffeine **not** extracted from aqueous phase
one 0.100 dm^3 portion	1.08×10^{-4}	10.8%
five 0.020 dm^3 portions	7.51×10^{-6}	0.751%
ten 0.010 dm^3 portions	2.37×10^{-6}	0.237%

[3]

Comments:
- This part was poorly done in general. Despite the example given, many were unable to use the equation to correctly calculate the concentration left as well as % not extracted.

For Examiner's Use

(ii) Comment on the efficiency of extracting caffeine using five 0.020 dm^3 successive portions of trichloromethane.

Using **more portions of trichloromethane** allows for **more caffeine to be extracted, thus making extraction more efficient**. [1]

Comments:
- This part was poorly done in general. Some students did not attempt this part at all.
- For students who mentioned data from the table were expected to compare the efficiency between using one portion and ten portions.

(iii) Extracting caffeine using too many successive portions of trichloromethane is not ideal. Suggest a reason for this.

When **excessive portions of trichloromethane** is used, the amount of caffeine extracted **diminishes and becomes less inefficient**. [1]

Comments:
- This part was poorly done in general. Some students did not attempt this part at all.

[Total: 20]