

EUNOIA JUNIOR COLLEGE JC2 Preliminary Examination 2021 General Certificate of Education Advanced Level Higher 2

CANDIDATE NAME
CIVICS GROUP
CIVICS
CI

CHEMISTRY

Paper 2 Structured Questions

9729/02 16 September 2021 2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not use paper clips, highlighters, glue or correction fluid. Write your name, civics group, registration 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.

Answer all questions on the Question Paper

The number of marks is given in brackets [] at the end of each question or part question.

A Data Booklet is provided.

The use of an approved scientific calculator is expected, where appropriate.

For Examiner's Use	
Paper 2	
1	/15
2	/12
3	/13
4	/15
5	/20
Total	/75

1 Nitrosyl chloride, NOC*l* decomposes at temperatures above 100 °C to form nitrogen monoxide and chlorine as shown in the equation below.

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 $2NOCl(g) \rightarrow 2NO(g) + Cl_2(g)$

(a) A sample of NOC*l* was allowed to decompose at 127 °C and 147 atm. Assuming that NOC*l* behaves ideally, show that its initial concentration is 4.48 mol dm⁻³.

$$pV = nRT$$

[NOCl] = $\frac{n}{V} = \frac{p}{RT}$
= $\frac{147 \times 101325}{8.31 \times (127 + 273)}$
= 4480 mol m⁻³
= $\frac{4480}{1000}$ mol dm⁻³
= **4.48 mol dm⁻³**

[2]

Marker's Comments:

- Generally well done, but a number of students were not clear in showing the conversion of m⁻³ to dm⁻³. Some students thought that volume was calculated in cm⁻³ instead of m⁻³.
 - (b) A student pointed out that the assumption in (a) that NOC*l* behaves ideally is not valid. Suggest and explain **two** possible reasons why this may be so.

The pressure of NOCI is very high, causing the volume of each gas particle

becomes more significant relative to the total volume of the gas.

NOC1 has significant intermolecular forces of attraction as it is polar/has a

relatively large polarizable electron cloud. [2]

Marker's Comments:

- A significant number of students stated that NOC*l* was a large molecule, which led to its volume becoming significant. This is not accepted as NOC*l* only comprises 3 atoms and is not large enough for the assertion to hold.
- A number of students were still making the same mistake of stating that the volume of the <u>gas</u> (instead of <u>gas **particle**</u>) is significant compared to the volume of the container, without realising that the volume of the gas is the volume of the container.
- Some students tried to argue in terms of the temperature being too high/low, but 127 °C is neither too high or too low to attribute any deviation from ideality to.

(c) The change in the concentration of NOC*l* was monitored as the decomposition reaction occurred over time. The data obtained is shown in Fig. 1.1.

3



(i) Using Fig. 1.1, show that the reaction is second order with respect to NOC1.

rate at 4.00 mol dm⁻³ = $\left| \frac{4.40 - 1.00}{0.0 - 5.7} \right|$ = 0.5965 mol dm⁻³ h⁻¹ rate at 2.00 mol dm⁻³ = $\left| \frac{3.10 - 1.60}{0.0 - 10.0} \right|$ = 0.1500 mol dm⁻³ h⁻¹

Since the <u>rate increases</u> by $\frac{0.596}{0.150} \approx \frac{4 \text{ times}}{4 \text{ times}}$ when [NOC1] doubles, the reaction is second order with respect to NOC1.

Marker's Comments:

- This part was not well attempted. A large number of students argued that the reaction had to be second order since the graphs did not show zero or first order reaction. This is not acceptable as it is not conclusive. Zero, first and second are not the only possible orders of reaction.
- Many students tried to calculate rate using $\frac{1}{time}$, which is wrong. Rate $\approx \frac{1}{time}$ only when the reaction has proceeded to a small extent such that the average rate at that point is approximately equal to initial rate.
- Of the students who correctly made use of gradient to calculate the instantaneous rate at various concentrations of NOC *l*, the common mistakes made were:
 - Rate was given as a negative value.

- Tangents were not drawn correctly at the stated concentrations.
- Points chosen to calculate gradient were too close together.
- \circ Points were not accurately read e.g. the initial concentration is not 4.50 mol dm⁻³.

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(ii) Given that the rate equation is rate = $k[NOCl]^2$, calculate the rate constant of the reaction, stating its units clearly.

rate = $k [NOC l]^2$ 0.5965 = $k (4.00)^2$ $k = 0.0373 \text{ mol}^{-1} \text{ dm}^3 \text{ h}^{-1}$

[2]

Marker's Comments:

- Generally well done. ECF was given based on working in part (i).
 - (iii) A second experiment was conducted under the same conditions, but using half the initial concentration of NOC*1*.

On the axes provided below, sketch the graph that will be obtained using data from the second experiment, relative to that provided for the first experiment.



Marker's Comments:

• Poorly attempted. Most students did not realise that the shape of the graph should remain unchanged due to the rate constant, k, remaining unchanged.

(d) (i) Define half-life.

Half-life of a reaction is the time taken for the concentration/amount of a

reactant to decrease to half its initial value. [1]

Marker's Comments:

- A number of students lost the mark as they did not state that half-life applied to reactants, and instead merely referred to a "substance" in the definition.
 - (ii) The rate equation for the second-order decomposition of NOC*l* can also be represented in the following manner:

$$\frac{1}{\left[\text{NOC}l\right]_{t}} - \frac{1}{\left[\text{NOC}l\right]_{0}} = kt$$

where $[NOCl]_{t}$ = concentration of NOCl at time, t,

$$[NOCl]_{0}$$
 = original concentration of NOCl, and

k = rate constant

Using this equation, derive an expression for the half-life of the reaction.

$$\frac{1}{\left[\mathsf{NOC}l\right]_{t}} - \frac{1}{\left[\mathsf{NOC}l\right]_{0}} = kt$$

$$\frac{1}{\frac{1}{2}\left[\mathsf{NOC}l\right]_{0}} - \frac{1}{\left[\mathsf{NOC}l\right]_{0}} = kt_{\frac{1}{2}}$$

$$t_{\frac{1}{2}} = \frac{1}{k[\mathsf{NOC}l]_{0}}$$

[1]

For

Examiner's Use

Marker's Comments:

- Not well-attempted. Many students were not able to see the relationship between $[NOCl]_t$ and $[NOCl]_0$. Others did not understand the meaning of an "expression", and tried to work out the value of half-life.
- Of the students who managed to derive the expression, some left time as *t*, without realising that it has been defined to be a generic point in time.

(iii) Hence, state and explain whether the half-life of a second-order reaction will increase or decrease as the reaction proceeds.

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Since half-life is inversely proportional to the initial reference concentration of

the reactant, it will **increase** as the reaction proceeds. [1]

Marker's Comments:

- Students who were not able to derive the expression were unable to provide a complete and logical explanation and conclusion here.
 - (e) The reverse of the decomposition reaction can also occur such that NOC*l* is formed from NO and C*l*₂.

Given that a possible mechanism for the reaction is as shown below, suggest the rate equation for the reaction.

From slow step: rate = $k[Cl_2][N_2O_2]$ However, N_2O_2 is an intermediate.

From Step 1,

$$\mathcal{K}_{c} = \frac{[N_{2}O_{2}]}{[NO]^{2}}$$
rate = $k[Cl_{2}][N_{2}O_{2}]$
= $k[Cl_{2}](\mathcal{K}_{c}[NO]^{2})$
= $k'[Cl_{2}][NO]^{2}$, where $k' = k \times \mathcal{K}_{c}$

Marker's Comments:

• Most students gave the final rate equation without showing their working. While BOD was given and a mark was awarded for the rate equation,

[Total: 15]

[2]

2 During the 2000s, researchers looked into creating high-capacity rechargeable batteries Examiner's for use in energy storage in renewable energy generation. The zinc-cerium battery shown in Fig. 2.1 is one example of such a rechargeable battery involving redox flow.

proton-selective Zn(s) deposit membrane carbon electrode carbon electrode electrolyte electrolyte storage storage tank tank $Zn^{2+} \rightleftharpoons Zn \rightarrow Ce^{4+} \rightleftharpoons Ce^{3+}$ pump pump external load external circuit



The half-cells are made up of the following:

half-cell	electrolyte	electrode
Zn²+/Zn	Zn(CH ₃ SO ₃) ₂ (aq), CH ₃ SO ₃ H(aq)	carbon-based polymer (similar to graphite) with fine Zn metal particles on surface
Ce ⁴⁺ /Ce ³⁺	Ce(CH ₃ SO ₃) ₃ (aq), Ce(CH ₃ SO ₃) ₄ (aq), CH ₃ SO ₃ H(aq)	carbon-based polymer (similar to graphite)

The two electrolytes, consisting of methanesulfonic acid, CH₃SO₃H, and the respective salts, are separated by a proton-selective membrane.

- (a) During the discharge process, the Zn^{2+}/Zn half-cell undergoes oxidation.
 - (i) Identify the polarity of the electrodes for the half-cells during the discharge process.

Ce⁴⁺/Ce³⁺: positive Zn²⁺/Zn: negative [1]

(ii) Draw on Fig. 2.1 the direction of electron flow in the external circuit during the discharge process. [1] For

Use

These questions were done relatively well, where most students understood that during the

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Some specific comments:

discharge process, the battery acts as a galvanic cell.

Marker's Comments:

- (i) Several students confuse polarity of the electrodes with the nature of the electrodes which is different.
- (ii) Several students were unsure of the electron flow as they were confused between a galvanic cell (during discharge) and an electrolytic cell (during charging).
- (iii) Some students abbrievated positive and negative as pos and neg or +ve and ve. Spelling them out should be the way.
 - (iii) Write the overall equation for the reaction during the discharge process.

 $2Ce^{4+}(aq) + Zn(s) \rightarrow 2Ce^{3+}(aq) + Zn^{2+}(aq)$ [1]

(iv) Given that $E^{\oplus}(Ce^{4+}|Ce^{3+}) = +1.44 \text{ V}$, with the aid of the *Data Booklet*, calculate

the $\textit{E}_{cell}^{\ominus}$ for the reaction during the discharge process.

Zn(s) → Zn²⁺(aq) + 2e⁻ $E^{\ominus} = -0.76$ V $E^{\ominus}_{cell} = +1.44 - (-0.76) = \pm 2.20$ V

(v) Hence, calculate the standard Gibbs free energy in kJ mol⁻¹.

 $\Delta G^{\ominus} = -nFE_{cell}^{\ominus}$ = -(2)(96500)(+2.20) = -424600 J mol⁻¹ = -425 kJ mol⁻¹ (3 s.f.)

Marker's Comments:

These questions were generally well done across all students.

Some specific comments:

© EJC

- (i) Minority of students did not realise that a(iii) is in reference to the redox reation between Ce and Zn. Thus, including the methanesulfonate ion into the balanced equation is not necessary. Some did not balance based on the half equations as well.
- (ii) Some were not certain of calculate E_{cell}^{\ominus} using the equation $E_{red}^{\ominus} E_{oxi}^{\ominus}$, or misidentified the standard reduction potential value. Also, some recalled $\Delta G^{\ominus} = -nFE_{cell}^{\ominus}$ incorrectly.

[1]

[1]

- (b) Methanesulfonic acid dissociates fully in water. During the discharging process, the Examiner's Zn²⁺/Zn half-cell becomes more positive than the Ce⁴⁺/Ce³⁺ half-cell over time.
 - (i) Explain how the proton exchange membrane maintains electrical neutrality.

It allows for migration of H⁺ ions / protons from Zn²⁺/Zn tank to the Ce⁴⁺/Ce³⁺

tank to maintain electrical neutrality.

Marker's Comments:

This was weakly answered across all students. Students should note that proton exchange membranes facilitate proton (H⁺) movement only across the membrane and not generate protons. Also, the directionality of the proton movement from one half-cell to the other must be clear.

When a high concentration of methanesulfonic acid was used, it was found that cerium(III) methanesulfonate, $Ce(CH_3SO_3)_3$, precipitates out in the electrolyte.

(ii) Suggest the effect on E_{cell} when a higher concentration of methanesulfonic acid was used as the electrolyte. Explain your answer.

With an increase in the concentration of methanesulfonic acid, Ce(III)

methanesulfonate will precipitate out, resulting in a decrease in the

concentration of Ce³⁺(aq). The *E* for the cathode will be more positive than

+1.44 V, giving in a more positive E_{cell} compared to E_{cell}^{\ominus} = +2.40 V.

......[2]

Marker's Comments:

This was generally okay with students correctly identifying that the increase in methanesulfonic acid concentration will affect the concentration of Ce3+ which will affect $E(Ce^{4+}|Ce^{3+})$. Some students incorrectly identified the precipitate as Ce⁴⁺ based or tried to explain that the E value for methanesulfonate acid will be affected which is irrelevant to the context.

For

Use

(c) Although the zinc-cerium battery has potential in renewable energy storage, some side-reactions hinder its application.

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During the **charging process**, the electromotive force used is large enough to drive these side-reactions to be thermodynamically feasible.

Using relevant values from the *Data Booklet,* identify one side-reaction during the charging process and explain why it will occur.

Since $E^{\oplus}(H^+|H_2) = +0.00 \text{ V}$ is more positive than $E^{\oplus}(Zn^{2+}|Zn) = -0.76 \text{ V}$, H^+

can be reduced to H₂ in the Zn²⁺/Zn half-cell . or

Since $E^{\oplus}(O_2|H_2O) = +1.23 \text{ V}$ is less positive than $E^{\oplus}(Ce^{4+}|Ce^{3+}) = +1.44 \text{ V}$,

<u> H_2Q </u> can be oxidised to Q_2 in the Ce³⁺/Ce⁴⁺ half-cell. [2]

Marker's Comments:

This question was poorly attempted as many students argued based on a galvanic cell such that there is a redox reaction at cathode/anode of the half-cell and therefore calculating E_{cell} at the cathode/anode. This is conceptually wrong as during the charging process, the battery becomes an electrolytic cell.

Given the nature of the electrolytic cell, the side reactions involved will be related to preferential oxidation or reduction at the anode and cathode respectively. Students are expected to identify possible side reactions at these electrodes based on relevant *E* values.

Some students had a misunderstanding that more positive E value would be prefentially oxidised and vice versa for a negative E value. Also, students should be clear with terms like more positive /less positive instead of increase /decrease which is not clear.

- (d) Suggest
 - (i) why the carbon-based polymer can be used as a suitable material for the electrode for the Ce³⁺/Ce⁴⁺ half-cell.

The carbon-based polymer is a good electrical conductor / inert.

......[1]

(ii) why the zinc-cerium battery has a short lifespan, by considering the possible reactions occurring at the Zn²⁺/Zn half-cell.

The Zn electrode will be corroded over time by the acidic electrolyte.

.....[1]

- (i) This question was well done.
- (ii) This question was poorly done as many students identified that either the Zn runs out (which is inpractical since this is a battery) or that Zn will be oxidised (which is the nature of the reaction to begin with). Very few students were able to identify that the acidic nature of the electrolyte can corrode the Zn electrode via an acid-metal reaction.

[Total: 12]

For Examiner's

Use

3 Double indicator acid-base titrations are used in scenarios where there is more than one end-point to a titration. Hence, it can also be used to determine the composition of mixtures of acids, as well as the pH of buffer solutions formed from polyprotic acids.

A typical example of a polyprotic acid is carbonic acid, where:

$$\begin{split} &H_2 \text{CO}_3(\text{aq}) + H_2 \text{O}(l) \rightleftharpoons H_3 \text{O}^+(\text{aq}) + \text{HCO}_3^-(\text{aq}) \qquad \text{p} K_{\text{a1}} = 6.36 \\ &\text{HCO}_3^-(\text{aq}) + H_2 \text{O}(l) \rightleftharpoons H_3 \text{O}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \qquad \text{p} K_{\text{a2}} = 10.3 \end{split}$$

(a) Explain why the value of pK_{a2} is higher than that of pK_{a1} .

It is more difficult to lose a proton due to the stronger electrostatic force of

attraction between the increasing negatively charged anion and the proton.

.....[1]

Marker's Comments:

(a) The answer here alludes to a comparison of the ratio of the backward rate constant to forward rate constants (essentially, K_a is similar to K_c). The stronger electrostatic force of attraction between the increasingly negatively charged anion and proton hints at a more significant lowering of the activation energy of the backward reaction, and hence leads to a smaller p K_{a2} than p K_{a1} .

Common misconceptions included the following:

- Erroneous definitions pertaining to the donation of an electron instead of a proton.
- Simply relating the stability of the conjugate base at each dissociation step with the dissociation constant (This is in error, because each dissociation step is likely to be endothermic, i.e., the products will be of a higher energy level than the reactants. The correct way would be to consider ΔG of the dissociation step instead.)

A buffer solution was prepared by mixing Na₂CO₃ and NaHCO₃. To determine the pH of the buffer solution, a double-indicator titration was performed with 25.0 cm³ of the buffer against 0.200 mol dm⁻³ HC*l* using phenolphthalein (p K_{In} = 9.3) as an indicator for the first end-point.

After the first end-point was attained, methyl orange (p $K_{In} = 3.7$) was then added as the second indicator to the same solution to determine the second end-point.

The first end-point occur at 16.90 cm³. An additional titre volume of 19.20 cm³ was required to reach the second end point.

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The reaction between CO_3^{2-} ions and HC1 occurs in two stages, with HCO3 as the Examiner's intermediate product.

$$\mathrm{CO}_3^{2-}(\mathrm{aq}) + \mathrm{H}^+(\mathrm{aq}) \rightarrow \mathrm{HCO}_3^-(\mathrm{aq})$$

 $\mathrm{HCO}_3^-(\mathrm{aq}) + \mathrm{H}^+(\mathrm{aq}) \rightarrow \mathrm{H}_2\mathrm{CO}_3(\mathrm{aq})$

(b) (i) Calculate the concentration of CO_3^{2-} present in the buffer solution initially.

$$n_{\text{CO}_{3}^{2-}} = n_{\text{HC}l} \text{ reacted at the first end-point}$$
$$= \frac{16.90}{1000} \times 0.200 = 3.38 \times 10^{-3} \text{ mol}$$
$$\left[\text{CO}_{3}^{2-}\right] = \frac{3.38 \times 10^{-3}}{\frac{25.0}{1000}}$$
$$= 0.1352$$
$$\approx 0.135 \text{ mol dm}^{-3}$$

[1]

[1]

For

Use

(ii) Hence or otherwise, calculate the volume of hydrochloric acid used to fully react with the HCO_3^- present in the buffer solution initially.

 $\textit{n}_{\rm HCl}$ required to react with $\rm CO_3^{2-}$ at the second end-point $=2n_{\rm max}=2\times0.1352\times$ ___25

$$= 2 \Pi_{CO_{3}^{2^{-}}} = 2 \times 0.1332 \times \frac{1000}{1000}$$

$$= 6.76 \times 10^{-3} \text{ mol}$$
volume of HC*l* required to react with CO₃^{2^{-}} = $\frac{6.76 \times 10^{-3}}{0.200}$

$$= 0.0338 \text{ dm}^{3}$$

$$= 33.80 \text{ cm}^{3}$$
volume of HC*l* required to react with HCO₃⁻ = 36.10 - 33.80
$$= \frac{2.30 \text{ cm}^{3}}{2.30 \text{ cm}^{3}}$$
Alternatively,
19.20 - 16.90 = 2.30 \text{ cm}^{3}

(iii) Using your answer to (b)(ii), calculate the concentration of HCO₃ present in the buffer solution.

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$$n_{\text{HCO}_{3}^{-}} = n_{\text{HC}l} = \frac{2.30}{1000} \times 0.200 = 4.60 \times 10^{-4} \text{ mol}$$
$$\left[\text{HCO}_{3}^{-}\right] = \frac{4.60 \times 10^{-4}}{\frac{25.0}{1000}} = \frac{0.0184 \text{ mol dm}^{-3}}{1000}$$
[1]

(iv) Hence, calculate the initial pH of the buffer solution.

$$pH = pK_{a2} + lg \frac{[CO_3^{2-}]}{[HCO_3^{-}]}$$

= 10.3 + lg $\frac{0.1352}{0.0184}$
= 11.2 [1]

(v) Calculate the pH of the mixture attained at the second equivalence point.

At the second equivalence point, the solution comprises H₂CO₃ only

$$n_{H_{2}CO_{3}} = n_{CO_{3}^{2-}} + n_{HCO_{3}^{-}} = 3.38 \times 10^{-3} + 4.60 \times 10^{-4}$$

= 3.84 × 10⁻³ mol
$$[H_{2}CO_{3}] = \frac{3.84 \times 10^{-3}}{25.0 + 36.10} = 0.06284 \text{ mol dm}^{-3}$$

$$[H^{+}] = \sqrt{K_{a1} \times [H_{2}CO_{3}]}$$

= $\sqrt{10^{-6.36} \times 0.06284}$
= 1.656 × 10⁻⁴ mol dm⁻³
pH = -lg(1.656 × 10^{-4})
= **3.78** [3]

(vi) By considering the initial concentrations of Na_2CO_3 and $NaHCO_3$, calculate the volume of HC*l* to be added to 25.0 cm³ of the buffer to produce a resultant mixture with a pH of 10.3.

Since pH = p
$$K_{a2}$$
 = 10.3

$$\begin{bmatrix} CO_3^{2-} \end{bmatrix} = \begin{bmatrix} HCO_3^{-} \end{bmatrix} = \frac{0.1352 + 0.0184}{2}$$
= 0.0768 mol dm⁻³
volume of HC*l* added = $\frac{(0.1352 - 0.0768) \times \frac{25.0}{1000}}{0.200}$
= 7.30 × 10⁻³ dm³
= 7.30 cm³

[2]

For

Examiner's Use

It was important to understand that there were different concentrations of CO_3^{2-} and HCO_3^{-} present in the initial buffer. Hence, students must recognise the following concepts:

The initial pH of the buffer will not be the equivalent of the pK_a value. As HCO₃⁻ is the conjugate acid of CO₃²⁻ (in the initial buffer solution), the pH of the buffer

solution would be given by $pK_{a2} + Ig \frac{[CO_3^{2-}]}{[HCO_3^{-}]}$. There would also be no necessity for

the $[HCO_3^-]$ to be greater than the $[CO_3^{2-}]$.

The first equivalence point was achieved when all the CO₃²⁻ was protonated to HCO₃⁻. Subsequently, all the new HCO₃⁻ formed and those that were present initially in the buffer was acidified to form carbonic acid. Hence, the additional titre volume would definitely exceed the volume required to reach the first end-point. This difference can be attributed to the amount of HCO₃⁻ present initially.

(b)(i) This was generally well-attempted by most students, as long as they understood that the first titre volume correlated with the concentration of CO_3^{2-} present in 25.0 cm³ of the buffer solution used in the titration. The term "initially" would further suggest that concentration of CO_3^{2-} was to be taken with respect to the initial buffer solution, and hence the division by 0.025 dm³ in the second step (after finding the total amount of acid used).

(b)(ii)&(iii) Please refer to point 2 of the concepts shared in the first paragraph. Note also the required significant figure or decimal points for the calculation.

(b)(iv) Students may need to pay attention to the use of the correct pK_a used, and that HCO_3^- and CO_3^{2-} are the acid and conjugate base/ salt respectively. As this is a buffer solution, the concentrations of HCO_3^- , CO_3^{2-} and H^+ are not necessarily equivalent, and students can use either the Henderson-Hasselbalch or substitute the correct values into the corresponding K_a expression to solve for the pH of the buffer.

(b)(v) Students are reminded to check the calculation for the volume of the resultant mixture, which is 61.10 cm^3 . As the resultant mixture is slightly acidic due to salt hydrolysis, students, students can consider the dissociation of the acidic salt (as the only acid species present) to determine the resultant pH (instead of using the buffer equation, where the values of H⁺, H₂CO₃ and HCO⁻₃ are not known exactly).

(b)(vi) This question was generally poorly attempted. The ratio of the [salt]:[acid] can be adjusted by adding acid or base, and affects the pH solution of a buffer. As the resultant mixture had a pH of 10.3 that corresponded to pK_{a2} , the concentrations of HCO₃⁻ and CO₃²⁻

were equivalent. This then implied that the concentration of either species was to be half that of the total amount of acid and conjugate base present, which could be used as the starting point to solve the question.

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For

Examiner's (c) Using the information provided in the question as well as your answers from (b)(iv) -(b)(vi), sketch a graph to show the pH changes that occur when 50.00 cm³ of 0.200 mol dm⁻³ HCl is added to 25.0 cm³ of the initial buffer solution.

For

Use



Marker's Comments:

(c) Most students were able to draw the correct shape for the graph, which comprised two regions of rapid change around the two equivalence points, and two regions of buffer. However, most students did not indicate the corresponding pK_a values at the points where [salt]=[acid].

There were also a handful of students who mistakenly assumed that the resultant pH at the equivalence point was equivalent to the indicator's pK_{In} , where there was actually no such relationship. The fact that we can use different indicators to find out the equivalence point in a titration also proves the idea that the resultant pH of the mixture at equivalence point is independent of the indicator used (do not that the end point of a titration is very slightly different from the equivalence point). Students may refer to Q2(b)(v), which illustrates the necessary calculations involved in the determination of the equivalence point in a weak base-strong acid titration. These calculations are independent of the indicator used.

(d) Explain why ethanoic acid cannot be used in place of hydrochloric acid for this titration.

Ethanoic acid is a weak acid and there will be no sharp increase of pH that is typically found along with the end-point, hence there is no indicator that can be used to produce a distinct colour change to identify the end-point. [1]

(d) In titration (or a lot of measurements made during experiments), it would be important to be able to precisely identify an end-point such that the measurement of a physical quantity could be made consistently. For titration, it was the distinct colour change of an indicator that took place within the region of rapid pH change. This region of rapid pH change would not be present for weak acid-weak base titrations. For weak acid-strong base or strong acid-weak base titrations, this region of rapid pH change would still be present.

A lot of students shared that the use of a weaker acid led to an increase in titre value and made titration difficult. This was wrong on two aspects: (**I**) that it was the concentration of the acid that determined the titre value, and (**II**) the total volume used was inconsequential although it may constitute a different percentage uncertainty.

[Total: 13]

For Examiner's Use 4 Compound U was developed in the drug discovery process for an anaesthetic.



(a) The following synthetic scheme shows the synthesis of compound U.



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(iii) Suggest why bromination cannot be carried out in step I.

Bromination cannot be carried out in step I as the NO₂ group in nitrobenzene

is **<u>3-directing</u>**, hence the Br⁺ electrophile will not be directed at the 2-position

to form the product.

-[1]
- (iv) Describe the mechanism for the reaction in step III.



[3]

For

Examiner's Use

Marker's Comments:

(a) Although (i) and (iii) were generally well-attempted, candidates were unable to score full credit for (ii) and (iv) even though the answers were relatively straightforward. Candidates are advised to revise their organic chemistry content <u>thoroughly</u>.

Common errors included the following:

- Missing or extra atoms in the structures of R, S or reagents
- Using the wrong reducing agent for the reduction of nitrobenzene, or forgetting that <u>concentrated</u> HC*l* has to be used
- Attempting to carry out step II using carboxylic acid, which will result in an acidbased reaction instead of the desired nucleophilic acyl substitution
- Using ammonia or methylamine instead of ethylamine for step II
- Forgetting to name the mechanism, or indicate the slow step
- Unbalanced equations in the mechanism

(b) During the process of drug discovery, the following four compounds, W to Z, were also developed.

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Describe three simple chemical tests that could be carried out in sequence to distinguish between compounds W, X, Y and Z. State the expected observations for each test.

Test 1: Add Tollens' reagent to separate samples of the 4 compounds. or Add iodine, NaOH,

heat or Add neutral iron(III) chloride

Observations: No ppt observed for Z, silver mirror observed for W, X and Y. or ye low ppt

for Z; no ppt for W, X and Y or violet colouration for Z; solution remains yellow for W,X,Y

Test 2: Add. Fehling's solution to separate samples of W, X and Y.

Observations: Brick-red ppt will be observed for W and Y, no brick-red ppt for X.

Test 3: Add. Br2(ag) to separate samples of compounds W and Y.....

Observations: . Decolouration of orange Br2 (and a white ppt) will be observed for

Y: no decolouration for W.

[6]

(b) Few candidates were able to score full credit. Many candidates gave the wrong observations for correct chemical tests, or identified the wrong test even though their expected observations were correct. There were also candidates who used 2 reagents (in the same test) that reacted with each other e.g. hydrolysis using dilute acid before adding Na. Candidates are advised to revise their organic chemistry content thoroughly.

Common misceptions included the following:

- Mistaking 2,4-DNPH to give a negative observation for aldehydes
- Confusion about purpose of Tollen's reagent and Fehling's reagent
- Mistaking that hydrolysis of **W** will produce a volatile amine—the substituted phenylamine will have a higher boiling point than phenylamine, a liquid!
- Not recognising that **Y**, a substituted phenylamine, will give a positive test with aqueous Br₂. In fact, the alkyl group on the N atom increases the electron-density on N and activates the benzene ring towards electrophilic substitution further.

Besides conceptual errors, a number of candidates did not answer to the question:

- not stating the <u>observations</u> e.g. "no reaction" (without stating the expected observations)
- not specifiying the observations for the negative test.
- Not distinguishing between all 4 compounds e.g. using Tollen's reagent in Test 1 and iron(III) chloride in Test 2-- As both of these are used to distinguish Z from the other 3 compounds, the description for test 2 cannot be awarded any mark as it serves the same purpose as Test 1. Candidates should use Test 2 to differentiate the other 3 compounds from each other instead.

Also, Any gas evolved should also be tested and observations included.

[Total: 15]

For Examiner's Use 5 Organometallic chemistry is the study of compounds containing, and reactions involving, Examiner's metal-carbon bonds. In addition, other bonds such as metal-nitrogen and metal-halogen bonds, are also of interest.

For

Use

Common examples of organometallic compounds are

⊖ Li[⊕] R-Mg-X R-Pb-R R-Cu-R organomagnesium organocuprate organolead (Grignard reagents) (Gilman reagents)

where R = alkyl groups; X = Cl, Br or I

- (a) Tetraethyllead, $(C_2H_5)_4Pb$, is an example of an organolead compound, that for much of the 20th century was the chief antiknock agent for automotive gasoline, or petrol.
 - (i) State and explain the shape of the tetraethyllead molecule.

Since there are only <u>4 Pb–C</u> σ <u>bond pairs and no lone pairs</u> around the central

Pb atom, tetraethyllead will be tetrahedral in shape. [2]

Marker's Comments:

- Generally well done.
- Many candidates did not mention that there are no lone pairs, which was not penalised based on benefit-of-the-doubt. However, candidates are reminded that for predicting shape of molecules using VESPR, they should always provide the number of σ bond pairs and lone pairs around the central atom.

In the car engine, tetraethyllead burns to deposit solid lead and lead(II) oxide, PbO, which destroy the engine. Hence, lead scavengers such as 1,2-dibromoethane and 1,2-dichloroethane are used in conjunction with tetraethyllead, forming gaseous lead(II) bromide and lead(II) chloride in the engine instead.

(ii) Explain why $PbCl_2$ and $PbBr_2$ are more volatile than PbO.

Due to the much larger anionic radius and lower anionic charge of Ct and

Br⁻ compared to O²⁻, less energy is required to overcome the weaker ionic

bonds in PbCl₂ and PbBr₂ leading to **lower boiling points** compared to PbO.

.....[2]

- Generally not well done.
- Many candidates thought that PbCl₂ and PbBr₂ are covalent molecules due to the high charge density of Pb²⁺. However, if candidate check the *Data Booklet*, they will notice that ionic radius of Pb²⁺ = 0.120 nm, which is almost double that of Mg²⁺ = 0.065 nm and larger than that of Ca²⁺ = 0.099 nm. In other words, Pb²⁺ will have a very low charge density and the bonding in PbCl₂ and PbBr₂ should be predominantly ionic.
- For candidates who notice that PbO, PbC l_2 and PbBr₂ are ionic, and used the expression $|a^+a^-|$

for lattice energy, L.E. $\propto \left| \frac{q^+ q^-}{r_+ + r_-} \right|$, to argue for the higher volatility of PbCl₂ and PbBr₂,

many did not mention that **both** the q^- and r_- of O^{2-} being larger and smaller than that of the halide respectively. Unless candidate mention that the product of charges is a more significant factor, otherwise candidate will be penalised.

- Many candidates also used the term lattice energy is larger / smaller. Unless the candidate explicitly mention it is the **magnitude** of the lattice energy, otherwise, they are expected to be use the term *more exothermic* or *less exothermic* in the comparison of thermochemical quantities.
- Many candidates also mentioned more energy is needed to "overcome lattice energy". Candidate should understand that lattice energy is exothermic as it is the energy given out when an ionic lattice is formed from the gaseous ions. Hence one does not overcome lattice energy. More energy is needed to overcome the stronger / weaker ionic bonds between the oppositely charged ions instead.

Organometallic compounds tend to act as carbon-based nucleophiles.

(b) With reference to the bonding in organometallic compounds, suggest why they tend to act as carbon-based nucleophiles.

<u>Carbon</u> is <u>more electronegative</u> than the metals. Hence the metal–carbon bond

is polarised in such a way that the carbon carries the partial negative (δ -) charge,

hence rendering the carbon nucleophilic / Lewis basic. [1]

Marker's Comments:

- Poorly attempted.
- Most candidates fail to understand the term *carbon-based nucleophiles*, which if they look at the later parts should also come to realise that the question is looking at the alkyl (R) groups functioning as nucleophiles.
- Also, many fail to pick up from the opening paragraph that there are metal–carbon bonds in organometallic compounds.
- Many candidates argued that the R groups being electron-donating groups intensifying the electron density on the metal atom, making the metal a nucleophile instead.

Examiner's Use

For

Both Gilman reagents and Grignard reagents act as carbon-based nucleophiles, adding Examiner's across double bonds. However, the addition product with cyclohex-2-en-1-one differs for the two reagents.

For

Use



Nonetheless, Gilman reagent does not react with cyclohexene.



(c) (i) Explain why Gilman reagent does not react with cyclohexene.

The carbon-based nucleophile of Gilman reagent is repelled by the electron-

<u>rich</u> π -**electron cloud** of the **C=C**, hence R₂CuLi does not add across C=C.

...... [1]

Marker's Comments:

- Moderately well done.
- Many candidates mentioned that there is no region of electron-deficiency in cyclohexene which is correct. However, having no inherent region of electron-deficiency does not mean that reaction cannot take place. *E.g.* in the reaction of C=C with Br–Br for example. The Br-Br bond inherent is non-polar and does not have any region of electrondeficiency. However, when it approaches the electron-rich C=C, the Br-Br bond is

polarised giving Br - Br and reaction ensues between the C=C and the δ + Br.

- A number of candidates also mentioned that there is no C=O to induce a region of electron-deficiency in cyclohexene. Same argument as above, the C=O is not necessary to induce the electrophilic site, although with the C=O, the electron-deficient site is inherently present.
- So long as candidate mention that C=C is electron-rich, benefit-of-the-doubt is awarded that they understand that the electron-rich C=C will repel the nucleophilic reagent hence no reaction.

(ii) With the aid of a suitable diagram, explain why Gilman reagent reacts with carbon-3 of cyclohex-2-en-1-one but not carbon-2, using the concept of electronegativity and delocalisation in your answer.

For Examiner's Use



Due to the much higher electronegativity of oxygen compared to carbon,

and the **delocalisation of the** π -electrons of **C=C** into the **C=O** shown above,

carbon-3 will attain a partial positive (δ +) charge, while carbon-2 is neutral.

Hence, the carbon-based nucleophile of Gilman reagent will attack carbon-3,

but not carbon-2.

......[2]

Marker's Comments:

- Poorly attempted. This question is adapted from the idea in 2018 GCE A-Level Paper 3 Question 1(e)(ii).
- Many students argue that C-1 being bonded to the electronegative O is highly electrophilic. However, many went on argue that this carbon will then induce a dipole in the neighbouring C-2 and C-3 by drawing electrons from C-3 towards C-2, hence C-2 will carry a partial negative charge (δ–), while C-3 carry have a partial positive charge (δ+). However, in this case, it is not a simple case of inductive effect. Rather, the pair of *π* electrons in the C=C is *delocalised* into the C=O, hence imparting a positive charge on C-3 and a negative charge on O as shown in the resonance structure.
- The net result is that C-1 and C-3 are both electron-deficient, with a partial positive charge. Note that the resonance structures shown above *do not exist*. The structure of cyclohex-2-en-1-one is that of an *average* structure of the three resonance structures.
- The question asked to use the concept of *electronegativity* and *delocalisation*. The high electronegativity of O explains why the C=C π bond is delocalised into the C=O and not the C=O π bond being delocalised into the C=C (*i.e.* the pair of π electrons in the C=O bond 'moving towards' the C=C, which will impart a positive charge on the O and a negative charge on C-3 instead).
- Some candidates also incorrectly mentioned a *lone pair* being delocalised, although it is the pair of π electrons in the C=C. Some candidates also mentioned it is the π electrons on C-2, again not realising that the π electrons is in the π bond between C-2 and C-3.
- There are also candidates who thought that the C=C reacts like a usual C=C in giving a carbocation intermediate, failing to recognise that it is a nucleophilic R⁻ from Gilman reagent attacking C-3 instead.

For Examiner's Use

(iii) With reference to the structure of the cyclohex-2-en-1-one and the relative polarity of the metal–carbon bonds, suggest why Gilman reagent reacts preferentially with carbon-3 of cyclohex-2-en-1-one but Grignard reagent reacts with carbon-1, the carbonyl carbon.

As carbon-3 is further away from the electronegative oxygen than carbon-

1. the partial positive (δ+) charge on carbon-3 is lesser than that on

carbon-1...Since.magnesium.is.less.electronegative/.more.electropositive.

than copper, the carbon atom in the Mg-C bond has a larger partial negative.

(b-) charge than that in Cu-C. Hence, the more nucleophilic R group in

Grignard reagent favours the more electrophilic carbon-1, while the less.

nucleophilic R group in Gilman reagent favours the less electrophilic carbon-3.

.....[2]

Marker's Comments:

- Poorly attempted.
- Many candidates thought that the C=C in cyclohex-2-en-1-one being electron-rich, will be attacked by an electrophilic alkyl group, and hence argue that the Cu–C in Gilman reagent is polarised in such a way to generate an electrophilic R⁺. However, this whole question is about carbon-based nucleophiles.
- Many candidates incorrectly argue that the Mg–C bond is less polar than the Cu–C bond.
- Many candidates also mentioned about the electronegativity of the X in Grignard reagent or the Li in Gilman reagent. However, the carbon-based nuclephile originates from the metal-carbon bond between the Mg or Cu and the R group.

Another reaction where Gilman reagents and Grignard reagents give different product is in their reaction with acyl chlorides.



Gilman reagents react with acyl chloride to give ketones, while Grignard reagents react to give tertiary alcohols.

(d) (i) State the type of reaction undergone by the acyl chloride with Gilman reagent.

Nucleophilic (acyl) substitution [1]

- Generally well-attempted.
- Condensation is accepted too.
- However, there were a handful of responses which only mention substitution. Candidates are reminded that there should always be a descriptor on the nature of the reagent as being electrophilic / nucleophilic / free-radical.

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(ii) The reaction with Grignard reagents involves another type of reaction. State this second type of reaction.

Nucleophilic addition [1]

Marker's Comments:

- Generally not well-attempted.
- Many candidates gave reduction as the answer, seeing that it involves a C=O becoming a C-OH. Although indeed, the oxidation number of the original acyl carbon decreases (from +2 to +1). Just like in (d)(i), when the Cl is replaced by a R group, the oxidation number of the acyl carbon is decreased (from +3 to +2). However, we do not use reduction to describe the type of reaction. In cases where the mechanism involves a [electrophilic / nucleophilic] [addition / substitution] reaction, candidates are reminded to give the mechanism when asked for the type of reaction.
 - (iii) Draw the skeletal formula of the product obtained when 3-methylpentanoyl chloride reacts with the Grignard reagent, CH₃CH₂MgBr.



[1]

Marker's Comments:

- Generally not well-attempted.
- Candidates are reminded to read the question carefully. The question asked for the *skeletal* formula, for which all C and H (bonded to C) must not be shown.
- Many candidates also have missing/extra carbon atoms in their answers, which could be due to carelessness or they were not able to draw the structure of 3-methylpentanoyl chloride correctly in the first place.
- Another commonly seen mistake in candidates who forgot to 'convert' the CH₃CH₂ group from the Grignard reagent into skeletal form is to draw the bond to the already saturated CH₃ carbon instead of the CH₂ carbon in the ethyl group.

Gilman reagents are also effective nucleophiles for substitution reactions with organyl halides, in what is known as the Corey-House synthesis, as shown below. Grignard reagents, on the other hand, perform very poorly in this reaction.

For Examiner's Use



 $R'-X \xrightarrow{R_2CuLi} R'-R$ organyl halide dry ether

- where R = methyl, 1°, 2°, 3° alkyl, aryl, alkenyl R' = methyl, 1°, cyclic 2° alkyl, aryl, alkenyl X = Br or I
- (e) (i) What evidence suggest an S_N 2-type mechanism in the Corey-House synthesis?

Only methyl, primary and cyclic secondary alkyl halide reacts in the Corey-

House synthesis, but **not tertiary halide**.

.....[1]

Marker's Comments:

- Generally not well-attempted.
- Most candidates just mentioned that a primary organyl halide can be the substrate, hence it is S_N2. Actually a primary carbocation although not the most stable, is still possible to be formed. So simply being a primary organyl halide substrate does not exclude the possibility of a S_N1 mechanism.
- Based on benefit-of-the-doubt, so long as candidates mention two out of the three possible methyl, primary or (cyclic) secondary organyl halide as substrate, it is taken to mean that tertiary organyl halide cannot be used as the substrate, which will suggest a S_N2-type mechanism.
 - (ii) The S_N2-type mechanism in the Corey-House synthesis can be established by using the following cyclic secondary bromide as an organyl halide substrate.



State the observation which will confirm a S_N 2-type mechanism.

An **inversion of configuration** will be observed about the C–Br α -carbon.

.....[1]

Marker's Comments:

- Generally not well-attempted.
- Most candidates fail to realise that there are two chiral centres in the substrate, but the reaction will only affect the chiral centre at the α-carbon containing the C–Br bond. The C–CH₃ chiral centre will not be affected.

• Only an inversion of configuration will take place at the $\alpha\mbox{-}carbon$ to give

- Many candidates mentioned of rotating plane-polarised light in the opposite direction. However, due to the C–CH₃ chiral centre, the direction of the optical rotation may not be affected.
- Candidates are reminded that even in a normal S_N2 substitution reaction, if the halide is replaced by another nucleophile, e.g. CN or OH, the optical rotation may not necessary be in the opposite direction either. Only in **enantiomers** (all four substituents are exactly the same) then is the optical rotation by the same degree in the opposite direction.
- Inversion of configuration is simply describing the change in the 3-dimensional structure about the chiral centre. It does not say anything about the optical rotation.

The Corey-House synthesis is believed to proceed via first *oxidative addition* of the organyl halide to give a square planar copper-containing intermediate, which then undergoes *reductive elimination* to provide the product, R'–R.



Marker's Comments:

- Moderately well-attempted.
- Oxidation state is the same as oxidation number. A handful of candidates gave the copper species instead.
- Candidate should realise that in the Cu–X and Cu–C bonds, the X and C are the more electronegative atom and hence will be assigned the –1 oxidation number. This leaves the Cu with the positive oxidation number, taking into account the overall –1 charge of the two species.

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For

Examiner's

Use

R

 CH_3

(ii) With reference to (f)(i), suggest why the second step is known as *reductive elimination*.

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The second step involves the lost of two alkyl groups from the Cu centre, with

decrease in oxidation state of the Cu centre by 2 units.

......[2]

Marker's Comments:

- Generally well well-attempted.
- Some candidates did not explain the term *elimination*. Accepted if candidates mentioned the elimination of R-R', or that two products originate from one 'reactant', *i.e.* the opposite of addition.
- A handful of candidates incorrectly discussed using the next step forming R–Cu and LiX instead of the labelled reductive elimination step.

Unlike the reaction of organyl halides with aqueous sodium hydroxide, where aryl and alkenyl halides are unreactive, alkenyl and aryl bromide and iodide reacts readily with Gilman reagents. For example,



an alkenyl bromide

(g) Explain why alkenyl halides are unreactive towards aqueous sodium hydroxide.

The lone pair of electrons on the halogen is delocalised into the C=C, imparting

partial double bond character to the C-X bond, strengthening the bond, making

substitution difficult. [1]

Marker's Comments:

- Generally not well-attempted.
- Candidates were not sure what the question is asking in general.
- For those candidates who discussed about the strengthening of the C–X bond, the usage of terminology is often erroneous or incomplete.
- Instead of lone pair of electrons delocalising, candidates mentioned the p orbital delocalising into the C=C.
- The reason for the strengthening, which is the partial double bond character imparted, was also commonly left out.

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[Total: 20]