HWA CHONG INSTITUTION
C2 Preliminary Examination
Higher 2

CANDIDATE NAME					**CT GROUP**	2	3	S		
CENTRE NUMBER	S					**INDEX NUMBER**					▨

CHEMISTRY **9729/02**

Paper 2 Structured Questions

28 August 2024

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your **name**, **CT group, centre number** and **index number** on all the work you hand in.

Write in dark blue or black pen.

You may use a HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

DO **NOT** WRITE ON ANY BARCODES.

Answer all questions in the spaces provided in the Question Paper.

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

A Data Booklet is provided.

No. of sheets of writing paper submitted (if any)	
For Examiner's Use	
1	**/ 6**
2	**/ 13**
3	**/ 18**
4	**/ 15**
5	**/ 23**
Deductions (s.f.)	
Deductions (units)	
Deductions (structures)	
Total	**/ 75**

This document consists of **18** printed pages and **2** blank pages.

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

1 **(a)** Complete the energy level diagram in Fig. 1.1, showing the relative energy levels of orbitals in the 3rd principal quantum shell.

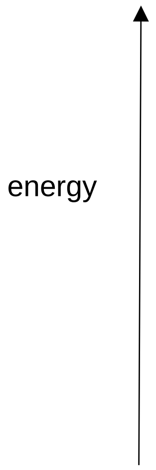

Fig. 1.1

[2]

(b) **(i)** Explain what is meant by the term *first ionisation energy.*

………

………[1]

(ii) Use your knowledge of the variation in first ionisation energy of the Period 3 elements (Na to Ar) to predict and explain how the first ionisation energy varies in each pair of elements.

- arsenic and selenium

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- bromine and krypton

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[3]

[Total: 6]

2 Polyfluoroalkyl substances (PFAS) is a group of compounds that have multiple fluorine atoms attached to an alkyl chain, giving these compounds waterproof properties, leading to widespread use in textiles, cosmetics, and food packaging.

Poly(tetrafluoroethene), PTFE, is an early and popular example of PFAS made by polymerising tetrafluoroethene, $F_2C=CF_2$.

(a) **(i)** State the shape and bond angle around the carbon atom in $F_2C=CF_2$.

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…………………………………………………………………………………………….. [2]

(ii) Carbon atoms in $F_2C=CF_2$ are sp^2 hybridised.

Explain what is meant by sp^2 hybridisation with reference to the carbon atom in $F_2C=CF_2$.

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

(iii) The shape of the carbon atom in $F_2C=CF_2$ depends on the arrangement of the hybridised orbitals.

Apply the principles of the VSEPR theory to explain how the hybridised orbitals are arranged in the second shell of the sp^2 carbon atom.

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

(b) Explain why $F_2C=CF_2$ is a gas at room temperature whereas PTFE is a solid.

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…………………………………………………………………………………………………...

………………………………………………………………………………………………..[2]

(c) In recent years, scientific evidence indicates that PFAS pose health and environmental concerns. Due to its persistence in the environment, it has been dubbed "forever chemicals".

Suggest why PFAS would last in the environment "forever".

…………………………………………………………………………………………………...

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

(d) The mechanism of polymerisation of PTFE consists of four separate stages **A** to **D**.

A homolytic fission of an organic peroxide, RO–OR, produces two RO• radicals
B RO• reacts with one $F_2C{=}CF_2$ molecule to produce a new radical
C repeated steps involving production of a series of new radicals to produce

$$RO–CF_2–CF_2–[CF_2–CF_2]_n–CF_2–CF_2\bullet$$

D two radicals combine to form $RO–CF_2–CF_2–[CF_2–CF_2]_{(2n+2)}–CF_2–CF_2–OR$

(i) This polymerisation can also be carried out using a non-symmetrical molecule such as $CH_2{=}CHCl$ to give poly(chloroethene).

Write equations to show the formation of
$RO–CHCl–CH_2\bullet$ and $RO–CHCl–CH_2–CHCl–CH_2\bullet$ in stages **B** and **C** of the polymerisation of $CH_2{=}CHCl$.

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…………………………………………………………………………………………………….. [2]

(ii) Fig. 2.1 shows a section of poly(chloroethene), where R_1 and R_2 represent chlorinated alkyl chains.

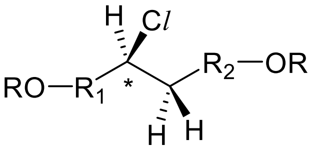

Fig. 2.1

Explain why the carbon atom labelled with * is chiral.

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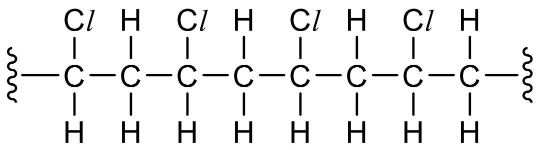
(iii) Fig. 2.2 shows four repeating units within poly(chloroethene).



$$\sim CHCl-CH_2-CHCl-CH_2-CHCl-CH_2-CHCl-CH_2 \sim$$

Fig. 2.2

The free radical polymerisation of poly(chloroethene) results in different stereochemical arrangements along the carbon chain.

The different arrangements can be classified into **three** types.

Types 1 and 2 result in polymers that have regular, crystal lattice structures with higher melting points.

Type 3 results in polymers that have poor packing and are unable to crystallise.

By considering Fig. 2.2 and your answers to **(d)(i)** and **(d)(ii)**, complete Fig. 2.3 by showing the positions of hydrogen and chlorine atoms for the three types of arrangements.

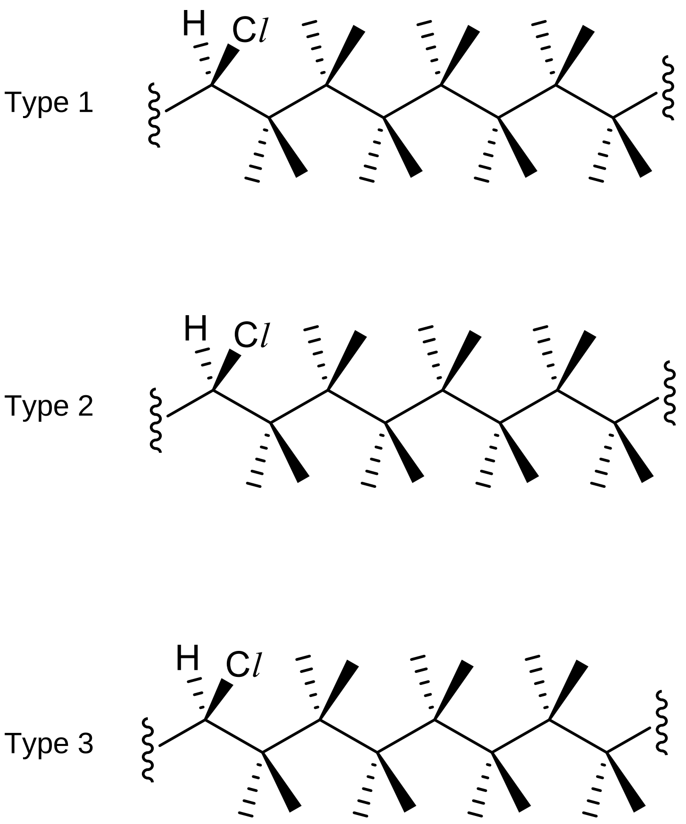


Fig. 2.3

[3]

[Total: 13]

3 **(a)** Explain, with the aid of a labelled Boltzmann distribution diagram, the effect on the rate of reaction by increasing temperature.

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……[3]

(b) Two different mechanisms for the nucleophilic substitution of halogenoalkanes are called S_N1 and S_N2. 2-bromopropane, a secondary bromoalkane, can undergo both S_N1 and S_N2.

(i) Draw a mechanism for the reaction between 2-bromopropane and OH^- via S_N2. Show relevant lone pairs and dipoles, and use curly arrows to indicate the movement of electron pairs.

[2]

(ii) Using collision theory, explain how the rate of reaction varies as the concentration of 2-bromopropane increases.

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....[2]

(iii) An investigation of the kinetics of the nucleophilic substitution of 2-bromopropane with OH^- in a certain solvent is carried out. The overall rate equation of this nucleophilic substitution is found to be:

$$\text{rate} = y\,[\text{2-bromopropane}] + z\,[\text{2-bromopropane}][OH^-]$$

where y and z are rate constants.

Circle the part(s) of the rate equation which corresponds to S_N2. Explain your answer with reference to the mechanism you have drawn in **(b)(i)**.

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....

....[2]

(iv) The results of two such experiments in **(b)(iii)** are recorded in Table 3.1.

Table 3.1

expt	[2-bromopropane] / mol dm^{-3}	[OH^-] / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	0.10	0.10	7.1×10^{-7}
2	0.10	0.20	1.2×10^{-6}

Use the results to calculate the values of *y* and *z* for the rate equation shown in **(b)(iii)**, stating their units.

y = ...

units of *y* = ...

z = ...

units of *z* = ...

[4]

(c) Excess acidified silver nitrate is added to the reaction mixture from **(b)(i)**, and a cream precipitate of AgBr is formed. The mixture is filtered and the AgBr residue is tested for its solubility in both dilute and concentrated aqueous ammonia. The results are recorded in Table 3.2.

2-chloropropane and iodobenzene are also separately heated with OH^-, and the above experiment is repeated for each compound.

(i) Complete Table 3.2 by stating the relevant observations for each test.

Table 3.2

compound	observations on adding acidified silver nitrate	solubility of residue (if any)	
		in dilute aqueous ammonia	in concentrated aqueous ammonia
2-bromopropane	cream ppt	insoluble	
2-chloropropane		soluble	
iodobenzene			

[2]

(ii) With reference to the K_{sp} values in Table 3.3, explain why AgC*l* is soluble in dilute aqueous ammonia while AgBr is insoluble in dilute aqueous ammonia.
You are not required to perform any calculations.

Table 3.3

compound	value of K_{sp}
AgC*l*	1.77×10^{-10}
AgBr	5.35×10^{-13}

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....[3]

[Total: 18]

4 Dicarboxylic acids are organic compounds that contain two carboxylic acid (–CO_2H) functional groups. Industrially, they are important precursors in chemical synthesis of useful compounds.

(a) Maleic acid, $HO_2CCHCHCO_2H$, exhibits stereoisomerism. State the type of stereoisomerism present and explain how it arises.

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………...[2]

(b) Maleic acid ionises in two stages.

$$HO_2CCHCHCO_2H \rightleftharpoons HO_2CCHCHCO_2^- + H^+ \qquad pK_{a,1} = 1.94$$

$$HO_2CCHCHCO_2^- \rightleftharpoons {}^-O_2CCHCHCO_2^- + H^+ \qquad pK_{a,2} = 6.22$$

Maleic acid can be used to make a buffer that is used to determine the amount of trace metals in seawater. The pH of the buffer solution was adjusted to 6.50 with sodium hydroxide.

(i) Explain why the predominant forms of maleic acid present in the above buffer are $HO_2CCHCHCO_2^-$ and ${}^-O_2CCHCHCO_2^-$.

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………...[1]

(ii) Calculate the ratio of the concentrations of ${}^-O_2CCHCHCO_2^-$ and $HO_2CCHCHCO_2^-$ present in the above buffer solution.

[1]

(iii) Write equations to show how the above buffer helps to maintain pH when a small amount of acid or base is added.

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………...[2]

(iv) Deduce whether the above buffer is more effective in buffering against added acids or bases. Give your reasoning.

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

(c) Calcium ethanedioate, CaC_2O_4, is found in kidney stones. At sufficiently high concentrations, ethanedioate ions react with the calcium ions in the kidney to form solids via equilibrium 1 below.

$$Ca^{2+}(aq) + C_2O_4^{2-}(aq) \rightleftharpoons CaC_2O_4(s) \text{ ---- } (1)$$

(i) The solubility of calcium ethanedioate is 6.70×10^{-3} g dm^{-3} at 25°C. Calculate the value of its solubility product.

[2]

(ii) The concentration of $Ca^{2+}(aq)$ in a sample of body fluids is 2.20×10^{-3} mol dm^{-3}. Calculate the concentration of $C_2O_4^{2-}(aq)$ just before calcium ethanedioate begins to precipitate.

[1]

(iii) By referring to equilibrium 1, suggest one way a person may try to reduce the formation of kidney stones. Explain your reasoning.

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

(d) Malonic acid, $HO_2CCH_2CO_2H$, is used as a precursor for the reaction scheme in Fig. 4.1.

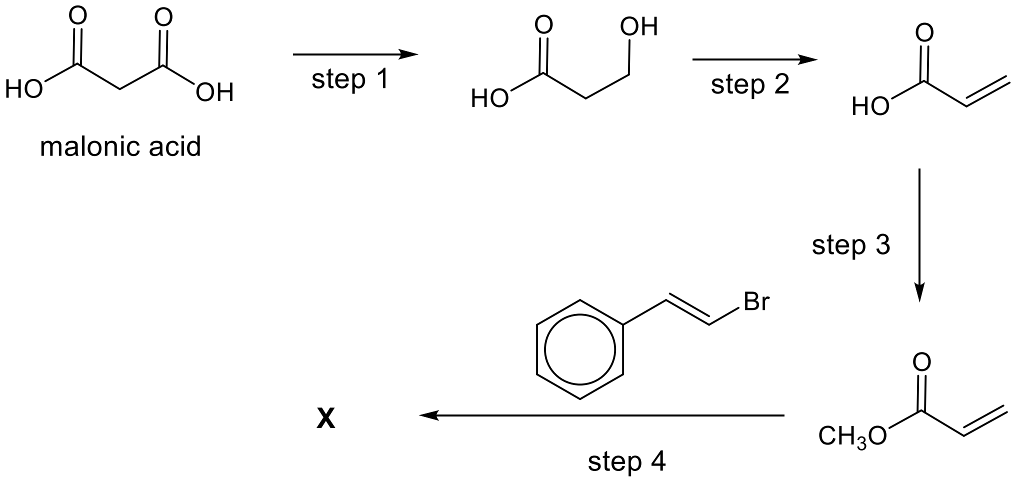

Fig. 4.1

(i) Give the reagents and conditions for steps 1 to 3.

step 1: ……………………………………………………………………

step 2: ……………………………………………………………………

step 3: …………………………………………………………………… [3]

(ii) The Heck reaction is the palladium-catalysed C–C bond formation between halogen compounds and alkenes. This reaction produces a *trans* alkene as the major product.

An example of the Heck reaction is shown in Fig. 4.2.

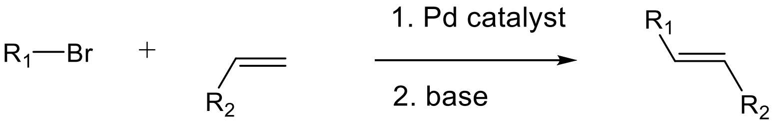

Fig. 4.2

In step 4 of Fig. 4.1, palladium catalyst and base were also added. Suggest the structure of **X.**

X: ……………………………………………….. [1]

[Total: 15]

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5 (a) (i) The equation for the thermal decomposition of hydrogen halides is shown below.

$$HX(g) \rightarrow \tfrac{1}{2}\,H_2(g) + \tfrac{1}{2}\,X_2(g)$$

Describe the thermal decomposition of $\text{HC}l$, HBr and HI, giving observations where relevant, and explain any variation in their thermal stabilities.

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(ii) Using data from the *Data Booklet*, calculate the standard enthalpy change for the decomposition of 1 mole of $\text{HC}l(g)$.

[2]

(b) Dilute hydrochloric acid is frequently used in the chemistry laboratory. It is prepared via dilution of known volumes of concentrated $\text{HC}l$ with suitable volumes of water, which allows for dilute solutions of different concentrations to be produced.

(i) "37% w/w $\text{HC}l$" is a concentrated $\text{HC}l$ reagent from manufacturers. This label indicates that 100 g of the reagent contains 37 g of $\text{HC}l$.

Calculate the concentration, in mol dm^{-3}, of $\text{HC}l$ in this reagent, given that its density is 1.2 g cm^{-3}.

[2]

(ii) Hence, calculate the volume, v cm^3, of 37% w/w HC*l* which must be diluted with sufficient water to make 250 cm^3 of 0.100 mol dm^{-3} hydrochloric acid.
If you were unable to obtain an answer in **(b)(i)**, use the value of 11.9 mol dm^{-3}.

[1]

(iii) Define the term *standard enthalpy change of formation* of a substance.

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

(iv) Using your answer in **(a)(ii)** and the information given in Table 5.1, calculate the standard enthalpy change for the following dilution, with the aid of an energy cycle.

$$\text{HC}l\text{(conc, 37\% w/w)} \rightarrow \text{HC}l\text{(aq, 0.1 mol dm}^{-3}\text{)} \qquad \Delta H < 0$$

Table 5.1

standard enthalpy change of formation of HC*l*(aq, 0.1 mol dm^{-3})	−167.2 kJ mol^{-1}
standard enthalpy change for the reaction HC*l*(g) → HC*l*(conc, 37% w/w)	−62.6 kJ mol^{-1}

[3]

(v) Two outlines for preparing 250 cm^3 of 0.100 mol dm^{-3} hydrochloric acid are presented below.

Outline A

1. Transfer v cm^3 of 37% w/w HC*l* into a 250 cm^3 volumetric flask. (volume v was calculated in **(b)(ii)**)
2. Slowly add deionised water into the volumetric flask and top up to the mark.

Outline B

1. Transfer 150 cm^3 of deionised water into a 250 cm^3 volumetric flask.
2. Slowly add v cm^3 of 37% w/w HC*l* into the volumetric flask.
3. Top up to the mark with deionised water.

Using the information provided about the dilution in **(b)(iv)**, explain whether outline A or B is preferred.

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(c) The following experiment, based on an approach known as coulometric titration, aims to determine a value for Faraday's constant and Avogadro's constant. Fig. 5.1 shows the electrolytic setup for the experiment. The electrolyte contains a known amount of dilute hydrochloric acid, which will be neutralised as the electrolysis proceeds.

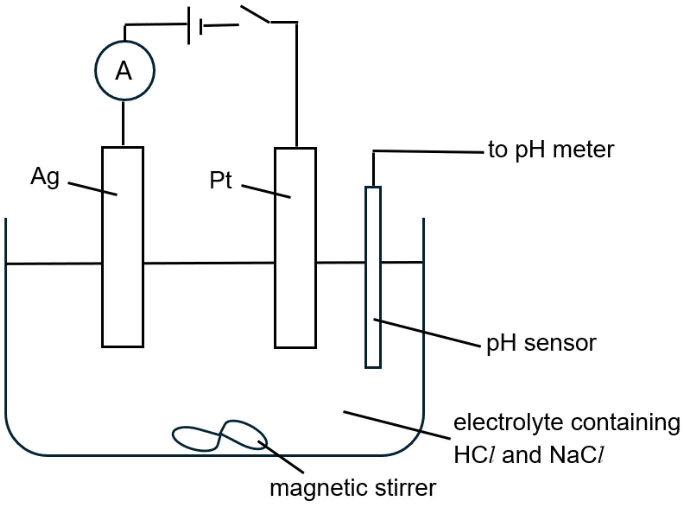

Fig. 5.1

When the switch is closed, the following reaction occurs at the inert Pt cathode before the known amount of dilute hydrochloric acid is completely used up, i.e. before the equivalence point is reached.

$$\text{cathode: } H^+(aq) + e^- \rightarrow \tfrac{1}{2} H_2(g)$$

Once the equivalence point is reached, the following reaction occurs at the cathode.

$$\text{cathode: } H_2O(l) + e^- \rightarrow \tfrac{1}{2} H_2(g) + OH^-(aq)$$

Overall, for every electron passed during the electrolysis, one $H^+(aq)$ ion is consumed from the electrolyte (before the equivalence point) or one $OH^-(aq)$ ion is produced (after the equivalence point). The electrolyte pH thus increases in a similar way to a conventional titration.

At the Ag anode, the following reaction occurs.

$$\text{anode: Ag(s)} \rightarrow \text{Ag}^+\text{(aq)} + \text{e}^-$$

The procedure for the experiment is as follows:

1. Transfer 2.50 cm^3 of 0.100 mol dm^{-3} HC*l*(aq) into a 250 cm^3 beaker.
2. Add 97.5 cm^3 of 0.2 mol dm^{-3} NaC*l*(aq) into the beaker. (NaC*l*(aq) is added, instead of deionised water, to maintain sufficient electrical conductivity of the electrolyte.)
3. Construct the electrolytic setup in Fig. 5.1.
4. Close the switch and start a stopwatch at the same time. Record the pH of the electrolyte indicated by the pH meter and the current indicated by the ammeter at regular time intervals.
5. Open the switch at time t = 240 s, which is beyond the equivalence point of the titration.

Student X carried out the experiment at a constant current of 0.24 A. Fig. 5.2 shows the variation of electrolyte pH with time obtained by student X.

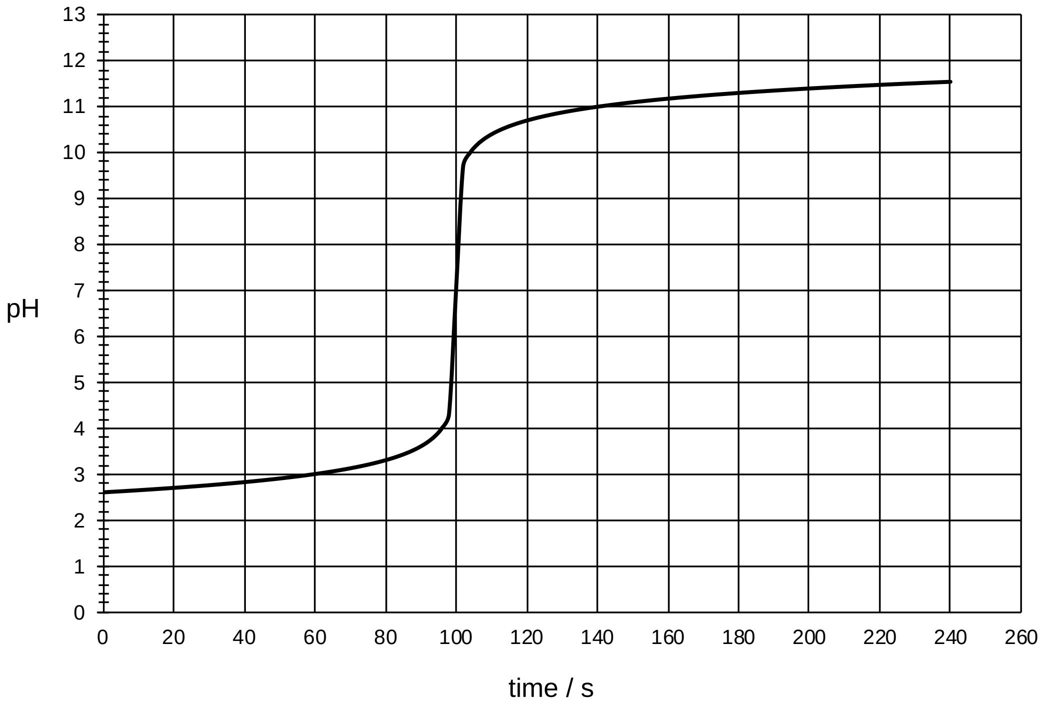

Fig. 5.2

(i) From Fig. 5.2, state the time taken to reach equivalence point, t_{eq}.

....[1]

(ii) Calculate the total quantity of charge that passed through the circuit up to time t_{eq}.

[1]

(iii) Calculate the initial amount, in moles, of HC*l* in the electrolyte. Hence, calculate a value for Faraday's constant.

[2]

(iv) Use your answer in **(c)(iii)** to find a value for Avogadro's constant, given that the electronic charge is 1.60×10^{-19} C.

[1]

(v) NaC*l*(aq) was added in step 2 to maintain electrical conductivity. Another reason was to prevent silver ions produced at the anode from reaching the cathode, by precipitating them as silver chloride.

With reference to relevant $E^\ominus$ values, explain why it is important that silver ions are prevented from reaching the cathode.

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………[2]

(vi) Student Y also carried out the experiment, but he did not use a pH meter. Instead, he added a few drops of an acid-base indicator (working range = 10.2 to 12.0) into the electrolyte, and recorded the time t_{eq} when the indicator changed colour.

By referring to Fig. 5.2, suggest whether the value of t_{eq} obtained by student Y will be smaller or larger than expected (if different from expected). Give your reasoning.

………

………[1]

(vii) Student Z also carried out student X’s experiment over 240 s, but controlled the applied current such that it decreased linearly during this time period. Fig. 5.3 shows the variation of current with time in the experiments conducted by both students on the same axes.

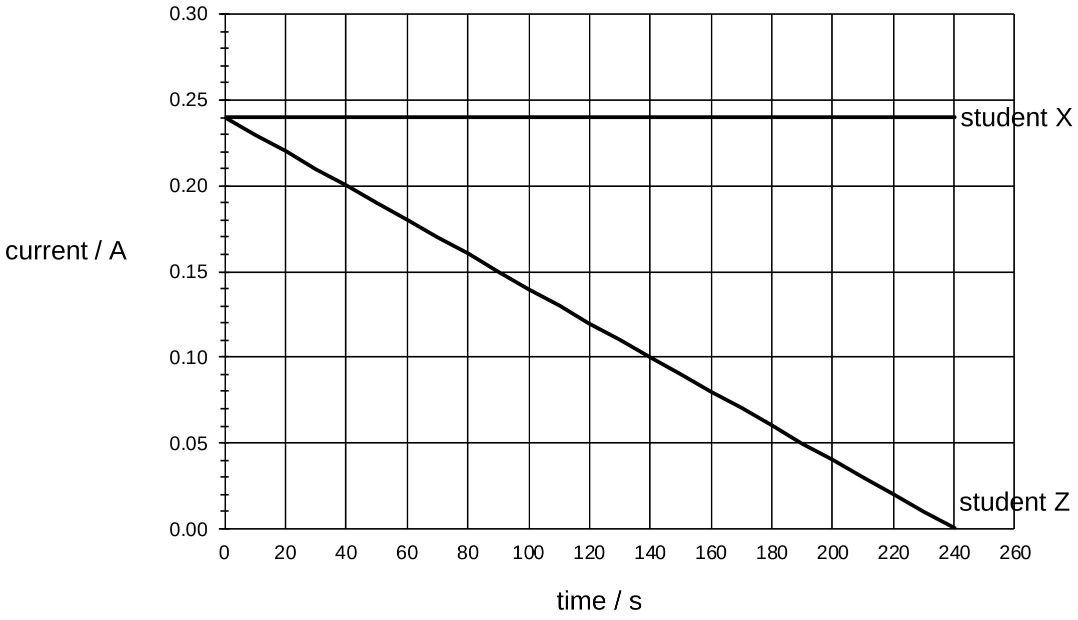

Fig. 5.3

Use Fig. 5.3 to suggest the value of the ratio of total charge passed in student Z’s experiment to the total charge passed in student X’s experiment. Hence, use Fig. 5.2 to suggest the final pH obtained in **student Z’s** experiment.

ratio: ………………………...

final pH: ………..…………… [2]

[Total: 23]

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