

CANDIDATE NAME			 u.	_		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

# Answer all questions in the space provided.

1	Complete the energy level diagram in Fig. 1.1, showing the relative energy levels of orbitals i the $3^{rd}$ principal quantum shell.	in

energy

Fig. 1.1

(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
	bromine and krypton
	[3]

[Total: 6]

[2]

2	atta	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 n textiles, cosmetics, and food packaging.						
	Poly tetra	/(tetrai	fluoroethene), PTFE, is an early and popular example of PFAS made by polymerising ethene, $F_2C=CF_2$ .					
	(a)	(i)	State the shape and bond angle around the carbon atom in F <sub>2</sub> C=CF <sub>2</sub> .					
			[2]					
		(ii)	Carbon atoms in F₂C=CF₂ are sp² hybridised.					
			Explain what is meant by $sp^2$ hybridisation with reference to the carbon atom in $F_2C=CF_2$ .					
			[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 sp² carbon atom.					
			[1]					
	(b)	Expla	in why F₂C=CF₂ is a gas at room temperature whereas PTFE is a solid.					
		•••••	······································					
		•••••						
			[2]					
	(c)	In re-	cent years, scientific evidence indicates that PFAS pose health and environmental erns. Due to its persistence in the environment, it has been dubbed "forever chemicals".					
		Sugg	est why PFAS would last in the environment "forever".					
			[1]					

(d) The	e mechanism of	polymerisation	of PTFE consists	of four	separate	stages .	A to	D
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- A homolytic fission of an organic peroxide, RO-OR, produces two RO∙ radicals
- B RO• reacts with one F<sub>2</sub>C=CF<sub>2</sub> molecule to produce a new radical
- c repeated steps involving production of a series of new radicals to produce

$$RO-CF_2-CF_2-[CF_2-CF_2]_n-CF_2-CF_2$$

- two radicals combine to form RO-CF<sub>2</sub>-CF<sub>2</sub>-[CF<sub>2</sub>-CF<sub>2</sub>]<sub>(2n+2)</sub>-CF<sub>2</sub>-CF<sub>2</sub>-OR
- (i) This polymerisation can also be carried out using a non-symmetrical molecule such as CH<sub>2</sub>=CHC*l* to give poly(chloroethene).

Write equations to show the formation of RO–CHC*i*–CH<sub>2</sub>• and RO–CHC*i*–CH<sub>2</sub>-CHC*i*–CH<sub>2</sub>• in stages **B** and **C** of the polymerisation of CH<sub>2</sub>=CHC*i*.

(ii) Fig. 2.1 shows a section of poly(chloroethene), where R<sub>1</sub> and R<sub>2</sub> represent chlorinated alkyl chains.

$$RO-R_1$$
 \*  $R_2-OR$ 

Fig. 2.1

Explain why the carbon atom labelled with \* is chiral.

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

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.
		,
		[3]
	(b)	Two different mechanisms for the nucleophilic substitution of halogenoalkanes are called S <sub>N</sub> 1

- (b) Two different mechanisms for the nucleophilic substitution of halogenoalkanes are called S<sub>N</sub>1 and S<sub>N</sub>2. 2-bromopropane, a secondary bromoalkane, can undergo both S<sub>N</sub>1 and S<sub>N</sub>2.
  - (i) Draw a mechanism for the reaction between 2-bromopropane and OH<sup>-</sup> via S<sub>N</sub>2. Show relevant lone pairs and dipoles, and use curly arrows to indicate the movement of electron pairs.

(ii)	Using collision theory, explain how the rate of reaction varies as the concentration of 2-bromopropane increases.
	[2]
(iii)	An investigation of the kinetics of the nucleophilic substitution of 2-bromopropane with OHin a certain solvent is carried out. The overall rate equation of this nucleophilic substitution is found to be:
	rate = y [2-bromopropane] + z [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>(b)(i)</b> .

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

Table 3.1

expt	[2-bromopropane] / mol dm <sup>-3</sup>	[OH <sup>-</sup> ] / mol dm <sup>-3</sup>	initial rate / mol dm <sup>-3</sup> s <sup>-1</sup>
 1	0.10	0.10	7.1 × 10 <sup>-7</sup>
2	0.10	0.20	1.2 × 10 <sup>-6</sup>

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 <i>y</i> =	
z =	
units of z =	
	r 41

[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

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

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

compound

Table 3.3

	AgC <i>l</i>	1.77 × 10 <sup>-10</sup>	
	AgC <i>l</i> AgBr	5.35 × 10 <sup>-13</sup>	
			_
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•••••	••••••		***************************************
*******************	•••••	•••••	[3]
			[3]

value of K<sub>sp</sub>

ļ	Dica grou	licarboxylic acids are organic compounds that contain two carboxylic acid (–CO <sub>2</sub> H) functiona roups. Industrially, they are important precursors in chemical synthesis of useful compounds.		
	(a)	Maleic acid, HO₂CCHCHCO₂H, exhibits stereoisomerism. State the type of stereoisomerism present and explain how it arises.		
			[2]	
	(b)	Malei	ic acid ionises in two stages.	
			$HO_2CCHCHCO_2H \rightleftharpoons HO_2CCHCHCO_2^- + H^+ \qquad pK_{a,1} = 1.94$	
			$HO_2CCHCHCO_2^- \rightleftharpoons ^-O_2CCHCHCO_2^- + H^+ \qquad pK_{a,2} = 6.22$	
		Male in sea	ic acid can be used to make a buffer that is used to determine the amount of trace metals awater. 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 $^-O_2CCHCHCO_2^-$ .	
			[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.	
			[2]	

	(iv)	Deduce whether the above buffer is more effective in buffering against added acids or bases. Give your reasoning.
		[1]
(c)	Calci etha	ium ethanedioate, $CaC_2O_4$ , is found in kidney stones. At sufficiently high concentrations, nedioate ions react with the calcium ions in the kidney to form solids via equilibrium 1 below.
		$Ca^{2+}(aq) + C_2O_4^{2-}(aq) \rightleftharpoons CaC_2O_4(s) (1)$
	(i)	The solubility of calcium ethanedioate is $6.70 \times 10^{-3}  g  dm^{-3}$ at 25°C. Calculate the value of its solubility product.
	(ii)	The concentration of $Ca^{2+}(aq)$ in a sample of body fluids is $2.20\times 10^{-3}$ mol dm <sup>-3</sup> . Calculate the concentration of $C_2O_4{}^{2-}(aq)$ just before calcium ethanedioate begins to precipitate.
	(iii)	[1] By referring to equilibrium 1, suggest one way a person may try to reduce the formation of kidney stones. Explain your reasoning.
		[1]

(d) Maionic acid, HO<sub>2</sub>CCH<sub>2</sub>CO<sub>2</sub>H, is used as a precursor for the reaction scheme in Fig. 4.1.

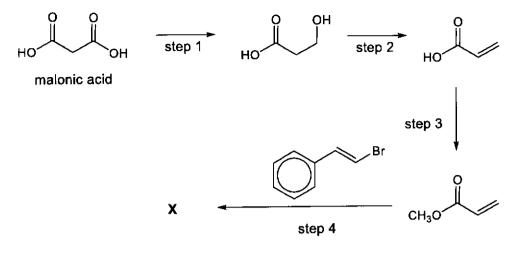


Fig. 4.1

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

(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.

$$R_1$$
—Br +  $R_2$  1. Pd catalyst  $R_1$   $R_2$  2. base  $R_2$ 

Fig. 4.2

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

**X**: ......

[Total: 15]

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5	(a)	(i)	The equation for the thermal decomposition of hydrogen halides is shown below
J	(a)	117	The equation for the theman decempediates of the angles of the

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

Describe the thermal decomposition of HC <i>l</i> , HBr and HI, giving observations where relevant, and explain any variation in their thermal stabilities.
••••••
***************************************
[3]
Using data from the Data Booklet, calculate the standard enthalpy change for the decomposition of 1 mole of HCI(g).

[2]

- (b) Dilute hydrochloric acid is frequently used in the chemistry laboratory. It is prepared via dilution of known volumes of concentrated HC*i* with suitable volumes of water, which allows for dilute solutions of different concentrations to be produced.
  - (i) "37% w/w HC*I*" is a concentrated HC*I* reagent from manufacturers. This label indicates that 100 g of the reagent contains 37 g of HC*I*.

Calculate the concentration, in mol  $dm^{-3}$ , of HCl in this reagent, given that its density is 1.2 g cm<sup>-3</sup>.

(ii)

(ii) Hence, calculate the volume, v cm³, of 37% w/w HCl which must be diluted with sufficient water to make 250 cm³ 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.
	[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.

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

Table 5.1

standard enthalpy change of formation of HCI(aq, 0.1 mol dm <sup>-3</sup> )	-167.2 kJ mol <sup>-1</sup>
standard enthalpy change for the reaction	-62.6 kJ mol <sup>-1</sup>
$HCI(g) \rightarrow HCI(conc, 37\% \text{ w/w})$	

(v) Two outlines for preparing 250 cm<sup>3</sup> of 0.100 mol dm<sup>-3</sup> hydrochloric acid are presented below.

#### Outline A

- 1. Transfer v cm³ of 37% w/w HCl into a 250 cm³ 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<sup>3</sup> of deionised water into a 250 cm<sup>3</sup> volumetric flask.
- 2. Slowly add v cm3 of 37% w/w HCl 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.

(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.

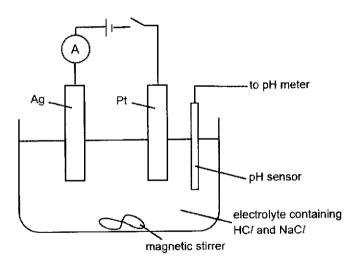


Fig. 5.1

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.

cathode: 
$$H^+(aq) + e^- \rightarrow \frac{1}{2} H_2(q)$$

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

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

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.

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

The procedure for the experiment is as follows:

- 1. Transfer 2.50 cm<sup>3</sup> of 0.100 mol dm<sup>-3</sup> HCI(aq) into a 250 cm<sup>3</sup> beaker.
- 2. Add 97.5 cm³ of 0.2 mol dm⁻³ NaCl(aq) into the beaker. (NaCl(aq) is added, instead of deionised water, to maintain sufficient electrical conductivity of the electrolyte.)
- 3. Construct the electrolytic setup in Fig. 5.1.
- 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.

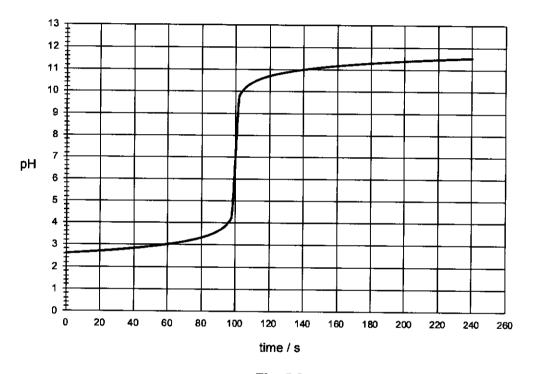


Fig. 5.2

(i) From Fig. 5.2, state the time taken to reach equivalence point, teq.

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

(iii)	Calculate the initial amount, in moles, of HCI 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 $1.60 \times 10^{-19}$ C.
	[1]
(v)	NaCl(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 $E^{\circ}$ values, explain why it is important that silver ions are prevented from reaching the cathode.
	[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 $t_{\rm eq}$ 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.

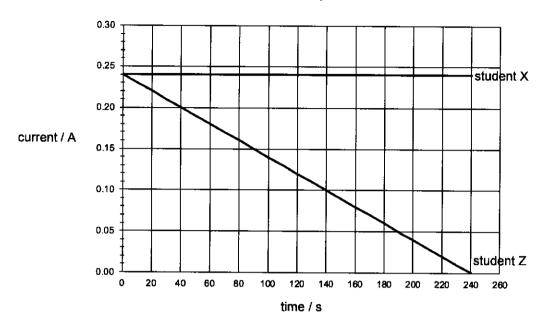


Fig. 5.3

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]

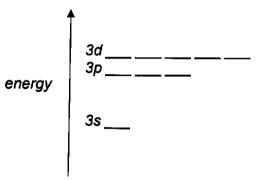
[Total: 23]

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## HWA CHONG INSTITUTION 2024 C2 H2 CHEMISTRY PRELIMINARY EXAMINATION SUGGESTED SOLUTIONS

#### Paper 2

1 (a)



[1] Correct number of orbitals for each subshell with labels

[1] Correct relative energy gap (bigger gap between 3s and 3p than 3p and 3d)

- (b) (i) First ionisation energy is the energy required to remove one mole of electrons from one mole of free gaseous atoms to form 1 mole of unipositively charged gaseous ions.
- (b) (ii) 1st IE of Se is lower than As [1/2] Selenium has a lower 1st IE than arsenic because selenium contains a paired electron in one of its p orbitals, thus it experiences inter-electron repulsion. So, less energy is required to remove the outermost electron in selenium compared to arsenic.
  - [1] Explains that inter-electron repulsion in p-orbital leads to lower 1st IE in Se compared to As.

1st IE of Kr is higher than Br [1/2]

Krypton has a higher 1st IE than bromine because krypton has a greater effective nuclear charge than bromine. This is inferred from the fact the krypton has a larger proton number / greater nuclear charge, and electrons are added to the same quantum shell / leading to a relatively constant shielding effect. Therefore, the attraction between the nucleus and the outermost electron is stronger, and more energy is required to remove the outermost electron in krypton than bromine.

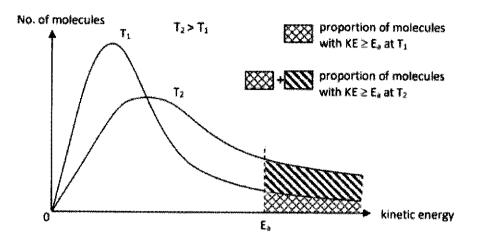
- [1] Uses effective nuclear charge to explain the stronger attraction between the outermost electron in Kr and the nucleus compared to that in Br, leading to higher 1st IE.
- 2 (a) (i) Trigonal planar [1], 120° [1]

- 2 (a) (ii) One 2s orbital is mixed with two 2p orbitals to give 3 hybridised sp<sup>2</sup> orbitals.
  - [1/2] correct type of atomic orbitals (2s and 2p)
    [1/2] correct number of atomic orbitals (1 and 2 respectively)
  - (a) (iii) The three sp<sup>2</sup> hybridised orbitals are degenerate and will be equally spaced apart in a trigonal planar arrangement to minimise repulsion.
    - [1/2] Indication of number of hybrid orbitals (state 'three' or 'trigonal planar')
      [1/2] Applying VSEPR Theory in the context of hybrid orbitals (i.e. hybrid orbitals will be equally spaced apart / minimise repulsion).
  - (b) PTFE has a greater number of electrons / larger electron cloud than F<sub>2</sub>C=CF<sub>2</sub> [1], thus it is more polarisable and has stronger dispersion forces than F<sub>2</sub>C=CF<sub>2</sub>. More energy is required to overcome the stronger dispersion forces in PTFE [1], and so it has a higher boiling point, and is a solid at room temperature while F<sub>2</sub>C=CF<sub>2</sub> is a gas.
  - (c) The C–C and C–F bonds in PFAS are very strong [1] and do not break/hydrolyse in typical environmental conditions.
  - (d) (i)  $RO \bullet + CHC_i = CH_2 \rightarrow RO CHC_i CH_2 \bullet [1]$  $RO - CHC_i - CH_2 \bullet + CHC_i = CH_2 \rightarrow RO - CHC_i - CH_2 - CHC_i - CH_2 \bullet [1]$
  - (d) (ii) The carbon atom is chiral because it has a tetrahedral geometry [1/2] and is bonded to four different groups [1/2].
  - (d) (iii) H C1C1 H H C1C1 H

    Type 1

    - Type 3 Fig. 1. Type 3
    - [1] Type 1; [1] Type 2 [1] Type 3 (any variation showing more random arrangement in the stereochemical arrangements)

3 (a)



#### [1] diagram, taking note of:

- axes
- · labels
- shape of graph (starts from intersection of axes).
- shaded areas (legend can be embedded in response)

[-0.5] for each error

At higher temperatures, there is a <u>higher proportion of molecules that have</u> <u>kinetic energies greater than or equal to E<sub>a</sub> [1] Hence, <u>frequency of effective collisions is higher [0.5]</u>, increasing rate of reaction [0.5].</u>

(b) (i)
$$\begin{array}{c}
CH_{3} \\
HO: \longrightarrow C \\
H^{\circ} \longrightarrow C \\
CH_{3}
\end{array}$$

$$\begin{array}{c}
CH_{3} \\
HO--C--Br \\
H CH_{3}
\end{array}$$

$$\begin{array}{c}
CH_{3} \\
HO-C--Br \\
CH_{3}
\end{array}$$

$$\begin{array}{c}
CH_{3} \\
CH_{3}
\end{array}$$

[2] Drawing of mechanism, inclusive of the following:

- Partial charges on C-Br atoms
- NO indication of slow or fast steps
- Balanced equations for the step of the mechanism (including balance of charge)
- Correct structure of transition state
- Lone pair on O atom of OH<sup>-</sup>
- Correct drawing and placement of curly arrows
- (b) (ii) When the concentration of 2-bromopropane increases, the number of 2-bromopropane molecules per unit volume increases / the 2-bromopropane molecules are closer [1]. This increases the frequency of effective collisions which in turn increases the rate of reaction [1]. [-0.5 for not mentioning effective collisions]

- 3 (b) (iii) Circle z [2-bromopropane][OH<sup>-</sup>]. [1]
  In the mechanism, <u>both</u> reagents / the 2-bromopropane and OH<sup>-</sup> are involved in the <u>rate-determining/only/slow step</u>.[1]
  - (b) (iv) rate = y [2-bromopropane] + z [2-bromopropane][OH<sup>-</sup>] From experiment 1,  $7.1 \times 10^{-7} = y(0.1) + z(0.1)(0.1)$ From experiment 2,  $1.2 \times 10^{-6} = y(0.1) + z(0.2)(0.1)$

Both equations – [1]

 $y = 2.20 \times 10^{-6}$ units of  $y = s^{-1}$  $z = 4.90 \times 10^{-5}$ units of  $z = mol^{-1} dm^3 s^{-1}$ 

## Each unit - [1] Each value - [0.5]

solubility of residue (if any) (c) (i) in concentrated in dilute observations compound aqueous ammonia aqueous ammonia soluble/partially insoluble 2-bromopropane cream ppt soluble [0.5] white ppt soluble [0.5] soluble 2-chloropropane [0.5]no ppt [0.5] iodobenzene

(c) (ii) When NH<sub>3</sub> is added, the Ag<sup>+</sup> forms the [Ag(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> complex. [1]

$$Ag^{+}(aq) + 2NH_{3}(aq) \rightleftharpoons [Ag(NH_{3})_{2}]^{+}(aq)$$

The formation of the [Ag(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> complex decreases [Ag<sup>+</sup>] [1],

The ionic product of  $[Ag^+][Cl^-]$  decreases to below  $K_{sp}$ . Hence, AgCl dissolves. **[0.5]** 

OR Hence position of equilibrium of  $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$  shifts rightwards to increase  $[Ag^+]$ , allowing AgCl(s) to dissolve.

However, as  $K_{sp}$  of AgBr is relatively lower, the addition of dilute NH<sub>3</sub>(aq) is insufficient to lower [Ag<sup>+</sup>] till the [Ag<sup>+</sup>][Br<sup>-</sup>] decreases to below that of the  $K_{sp}$  of AgBr. Hence, AgBr does not dissolve. [0.5]

4 (a) Cis-trans isomerism [1]

It occurs due to restricted bond rotation caused by the presence of the C=C bond [0.5] and different groups present on <u>each</u> carbon of the C=C. [0.5]

**4 (b) (i)** The pH of the buffer is at 6.5 which is higher than p $K_{a,1}$ . Hence the first proton would have <u>completely</u> dissociated at this point. [1]

(b) (ii) 
$$K_{a,2} = \frac{[-O_2CCHCHCO_2^-][H^+]}{[HO_2CCHCHCO_2^-]}$$
$$10^{-6.22} = (10^{-6.5}) \frac{[-O_2CCHCHCO_2^-]}{[HO_2CCHCHCO_2^-]}$$
$$\frac{[-O_2CCHCHCO_2^-]}{[HO_2CCHCHCO_2^-]} = 1.90546 \approx 1.91 (3 s.f.)$$

- (b) (iii)  ${}^-O_2CCHCHCO_2{}^- + H^+ \rightarrow HO_2CCHCHCO_2{}^-$  [1]  $HO_2CCHCHCO_2{}^- + OH^- \rightarrow {}^-O_2CCHCHCO_2{}^-$  [1]
- (b) (iv) The ratio calculated in (b)(iii) suggests higher concentration of the conjugate base (-O<sub>2</sub>CCHCHCO<sub>2</sub>-), hence the buffer removes acids more effectively. [1]

(c) (i) 
$$s = \frac{6.70 \times 10^{-3}}{128.1} = 5.230 \times 10^{-5}$$
 [1] 
$$K_{sp} = [Ca^{2+}][C_2O_4^{2-}] = s^2 = 2.735 \times 10^{-9} \approx 2.74 \times 10^{-9} \text{ mol}^2 \text{ dm}^{-6}$$
 [1]

(c) (ii) 
$$K_{sp} = [Ca^{2+}][C_2O_4^{2-}] = [C_2O_4^{2-}](2.20 \times 10^{-3}) = 2.735 \times 10^{-9}$$
  
 $[C_2O_4^{2-}] = 2.735 \times 10^{-9} \div (2.20 \times 10^{-3}) = 1.24 \times 10^{-6} \text{ mol dm}^{-3} [1]$ 

- (c) (iii) Drink more water to reduce the concentration of Ca<sup>2+</sup> and ethanedioate ions in your body. Position of equilibrium 1 will shift to the left and less solid is formed.
  - Reduce intake of foods high in ethanedioate ions (chocolate, spinach etc.) or Ca<sup>2+</sup>ions (e.g. milk, dairy product). Position of equilibrium 1 will shift to the left and less solid is formed
  - Increase the intake of acidic foods will lower the concentration of ethanedioate ions due to the formation of H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>. Position of equilibrium 1 will shift left and less solid is formed.
- (d) (i) step 1: one mole equivalent or limited LiA/H<sub>4</sub> (in dry ether) [1] step 2: excess concentrated H<sub>2</sub>SO<sub>4</sub>, heat [1] step 3: CH<sub>3</sub>OH, (a few drops of) conc H<sub>2</sub>SO<sub>4</sub>, heat [1]

5 (a) (i) HCl does not decompose even on strong heating. [0.5]
Strong heating of HBr yields brown fumes of Br<sub>2</sub>. [0.5]
Violet fumes of I<sub>2</sub> are obtained when a red-hot rod is plunged into a jar of HI. [0.5]

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The <u>thermal stability decreases</u> from HCl to HBr to HI. **[0.5]**As down Group 17, the H–X bond length increases and <u>bond strength</u> <u>decreases</u> **[0.5]** so less <u>energy</u> is needed to break the H–X bond. **[0.5]** 

5 (a) (ii) Bond broken: 1 × H–Cl: 431 kJ mol<sup>-1</sup>
Bond formed: ½ × H–H: ½ × 436 = 218 kJ mol<sup>-1</sup>
Bond formed: ½ × Cl–Cl: ½ × 244 = 122 kJ mol<sup>-1</sup>

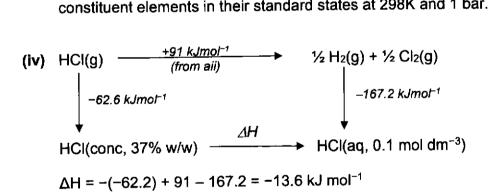
Standard enthalpy change of decomposition of HCI

= 431-218-122 = +91.0 kJ mol<sup>-1</sup>

[1] for correct bond energy values

[1] for correct coefficients and application of bond breaking/forming and final answer

- (b) (i) Volume of 100 g of conc HCl =  $100 \div 1.2 \div 1000 = 0.0833 \text{ dm}^3$  [1] Concentration of conc HCl =  $(37 \div 36.5) \div 0.0833 = 12.2 \text{ mol dm}^{-3}$  [1]
- (b) (ii) Number of moles of HCl required =  $250 \div 1000 \times 0.1 = 0.025$  mol Volume v =  $0.025 \div 12.2 = 0.00205$  dm<sup>3</sup> = 2.05 cm<sup>3</sup> [1]
- (b) (iii) It is the enthalpy change when 1 mole of a substance is formed from its constituent elements in their standard states at 298K and 1 bar. [1]



- [2] for energy cycle
- [1] for correct application of Hess Law and final answer
- (b) (v) As the dilution in (b)(iv) is exothermic, outline B is preferred as the heat liberated while diluting the concentrated acid is transferred to / absorbed by a larger volume of water/solution already in the flask, to avoid the temperature from rising too high. [1]
- (c) (i) t<sub>eq</sub> = 100 s [1]
- (c) (ii)  $Q = It = 0.24 \times 100 = 24.0 C [1]$
- 5 (c) (iii) Number of moles of HCI =  $2.50 \div 1000 \times 0.100 = 0.000250$  mol [1]

Number of moles of electrons passed = number of moles of H<sup>+</sup> = 0.000250 mol

$$F = Q / n_e = 24.0 \div 0.00025 = 96 000 C \text{ mol}^{-1}$$
 [1]

- (iv) L = F / e =  $96000 \div (1.60 \times 10^{-19}) = 6.00 \times 10^{23} \text{ mol}^{-1}$  [1]
- (c) (v)  $Ag^+ + e^- \rightleftharpoons Ag$   $E^e = +0.80 \text{ V} --(1)$   $E^e = 0.00 \text{ V} --(2)$

 $2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^ E^0 = -0.83 \text{ V} --(3)$ 

[0.5] for quoting the reduction potential for (1) and at least one of (2) and (3)

The reduction potential for  $Ag^+/Ag$  is <u>more positive</u> than for  $H^+/H_2$  and  $H_2O/H_2$ , [0.5] so silver ions will be preferentially reduced at the cathode [0.5]

so (1) will occur in addition to/instead of (2) and (3), so  $t_{eq}$  obtained may be too large/ $t_{eq}$  may not be obtainable/pH may not change.

[0.5] correct argument about the effect on the experiment

- (c) (vi) t<sub>eq</sub> obtained by student Y will be larger than expected because the <u>working pH range</u> of the given indicator (10.2 to 12.0) is <u>higher than</u> the <u>equivalence point pH of 7</u> (and also higher than the range of pH at the rapid change at the equivalence point). [1]
- (c) (vii) ratio = 0.500 or 1:2 or  $\frac{1}{2}$  [1]

Final pH = 10.7 [1] (accept 10.6 to 10.8)

