## **Suggested Solutions**



# DUNMAN HIGH SCHOOL Preliminary Examination Year 6

# **H2 CHEMISTRY**

Paper 2 Structured Questions

9729/02 13 September 2022 2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

# **READ THESE INSTRUCTIONS FIRST**

Write your centre number, index number, name and class at the top of this page. Write in dark blue or black pen.

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

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

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

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

You may lose marks if you do not show your working or if you do not use appropriate units.

A Data Booklet is provided.

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

For Examiner's Use	
1	12
2	12
3	14
4	16
5	21
Total	75

This document consists of **18** printed pages.

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

**1** (a) Describe the thermal decomposition of the hydrogen halides HC*l*, HBr and HI and explain any variation in their thermal stabilities.

[3]

Hydrogen halides thermally decompose to give its constituent elements / show equation: 2HX  $\rightarrow$  H\_2 + X\_2.

HC*l* does not decompose even on strong heating. HBr decomposes on strong heating while HI decomposes readily in the presence of a hot rod.

Thermal stability decreases in the order HCl > HBr > HI as bond energy / bond strength of the H–X bond decreases from HCl to HBr to HI. As such, decreasing amount of energy is required to decompose the hydrogen halide from HCl to HI.

(b) Tert-butyl alcohol reacts with hydrogen chloride according to the equation shown.

$$(CH_3)_3COH + HCl \rightarrow (CH_3)_3CCl + H_2O$$

This reaction occurs in three steps.

- step 1 protonation of -OH group in  $(CH_3)_3COH$  to produce  $(CH_3)_3COH_2^+$  cation
- step 2 loss of H<sub>2</sub>O molecule from (CH<sub>3</sub>)<sub>3</sub>COH<sub>2</sub><sup>+</sup> to produce a carbocation
- step 3 chloride ion reacts with carbocation to produce (CH<sub>3</sub>)<sub>3</sub>CCl
- (i) Describe the mechanisms which occur in **steps 2 and 3**. Use curly arrows to show the movement of electrons and label the slow step.

[3]



(ii) An enantiomerically pure alcohol, where the carbon atom bonded to the –OH group is chiral, was used for the reaction in (b).

Use your answer in **(b)(i)** to deduce the stereochemical outcome of this reaction. Explain your reasoning.

[2]

The reaction will produce a racemic mixture / the product will be formed as a 50 : 50 mixture of enantiomers.

The carbocation intermediate is (trigonal) planar around the positively charged C atom. The chloride ion can attack the positively charged C atom from the top and bottom of the plane with equal probability.

Tert-butyl alcohol also reacts with solid phosphorus pentachloride,  $PCl_5$ , to produce  $(CH_3)_3CCl$ .

(iii) With the aid of a suitable equation, explain why the reaction is not carried out in aqueous medium.

[2]

 $PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$  $PCl_5$  hydrolyses in water and will not be available to undergo nucleophilic substitution with tert-butyl alcohol.

- (C) (CH<sub>3</sub>)<sub>3</sub>CC*l* is one of the two monochlorinated products of the reaction between an alkane, X, and chlorine gas in the presence of UV light.
  - (i) Draw the structure of the alkane, **X**, and state the IUPAC name of the other monochlorinated product.

[1]

Structure of Alkane, X:

Name of the other monochlorinated product: 1-chloro-2-methylpropane

(ii) The rate of formation of (CH<sub>3</sub>)<sub>3</sub>CC*l* is faster than that of the other monochlorinated product.

Suggest an explanation for the different rates of reaction.

[1]

 $(CH_3)_3CCl$  is formed from a tertiary radical intermediate,  $(CH_3)_3C\bullet$ , which is more stable than the primary radical intermediate,  $(CH_3)_2CHCH_2\bullet$ , that forms the other monochlorinated product,  $(CH_3)_2CHCH_2Cl$ .

[Total: 12]

2 (a) The following equilibrium occurs when ethanal is mixed with water.



Use relevant data from the *Data Booklet* to calculate the equilibrium constant, *K*, for the reaction.

 $\Delta G^{\ominus} = -RT \ln K$ (-0.282 x 10<sup>3</sup>) = -(8.31)(298)ln K ln K = 0.11388

 $K = e^{0.11388} = 1.12$ 

(b) The aldol reaction is a useful reaction that forms a carbon–carbon bond between two carbonyl compounds. For example, two ethanal molecules can be combined using the aldol reaction.

The carbonyl carbon,  $\mathbf{a}$ , of one ethanal molecule forms a covalent bond with a carbon atom,  $\mathbf{b}$ , of another ethanal molecule. Carbon atom,  $\mathbf{b}$ , must be adjacent to carbonyl carbon,  $\mathbf{c}$ .



(i) When different carbonyl compounds are used in an aldol reaction, a mixture of structural isomers is formed.

Suggest two possible structural isomers that can be formed if propanone, CH<sub>3</sub>COCH<sub>3</sub>, and propanal, CH<sub>3</sub>CH<sub>2</sub>CHO, are mixed.

[2]

[2]

### Any **two** of the following:



CH<sub>3</sub>CH<sub>2</sub>CH(OH)CH(CH<sub>3</sub>)CHO OH O H CH<sub>3</sub>COCH<sub>2</sub>C(OH)(CH<sub>3</sub>)CH<sub>3</sub> O HO

(ii) Both propanal and propanoic acid can be formed from propan-1-ol in the same reaction.

Describe the reagents and conditions needed to ensure that the reaction yields propanal as the major product.

[2]

Heat propan-1-ol with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, H<sub>2</sub>SO<sub>4</sub>(aq) with immediate distillation to collect mainly propanal as distillate.

(c) Some tin reagents are useful in organic chemistry.

Tin forms two chlorides,  $SnCl_2$  and  $SnCl_4$ .

(i) A mixture of these chlorides was found to contain 50.0% by mass of tin. Calculate the percentage by mass of  $SnCl_2$  in the mixture.

[3]

Relative formula mass of  $SnCl_2 = 189.7$ 

Relative formula mass of  $SnCl_4 = 260.7$ 

Percentage by mass of Sn in  $SnCl_2 = \frac{118.7}{189.7} \times 100 = 62.572\%$ 

Percentage by mass of Sn in SnC $l_4 = \frac{118.7}{260.7} \times 100 = 45.531\%$ 

Let y be the fraction of mass of SnCl<sub>2</sub> in the sample. y  $\left(\frac{62.572}{100}\right)$ +  $(1-y)\frac{45.531}{100} = \frac{50}{100}$ y = 0.26229

percentage by mass of  $SnCl_2$  in the sample = 0.26229 x 100 = 26.2%

(ii) Tin exists in +2 or +4 oxidation states in many of its compounds. Great care must be taken to ensure the correct oxidation state of tin is formed.

A student proposed the following preparation methods to prepare the two chlorides,  $SnCl_2$  and  $SnCl_4$ .

### Preparation method for SnCl<sub>2</sub>

Heating tin with hydrochloric acid produces hydrogen gas. Careful evaporation of the water and dehydration produces white solid  $SnCl_2$ .

#### Preparation method for SnCl<sub>4</sub>

Passing chlorine gas over heated tin produces colourless liquid SnCl<sub>4</sub> as the only product.

Explain if the preparation methods proposed above are feasible without reference to any calculation. Use relevant standard electrode potentials from the *Data Booklet*.

[3]

 $Sn^{2+}(aq) + 2e^{-} \rightleftharpoons Sn(s) \qquad E^{\ominus} = -0.14V$ 2H<sup>+</sup>(aq) + 2e<sup>-</sup> ⇔ H<sub>2</sub>(g)  $E^{\ominus} = 0.00V$ Sn<sup>4+</sup>(aq) + 2e<sup>-</sup> ⇔ Sn<sup>2+</sup>(aq)  $E^{\ominus} = +0.15V$   $E_{\text{H}^{+}/\text{H}_{2}}^{\Theta}$  is more positive than  $E_{\text{Sn}^{2+}/\text{Sn}}^{\Theta}$  but less positive than for  $E_{\text{Sn}^{4+}/\text{Sn}^{2+}}^{\Theta}$ . Hence H<sup>+</sup> can oxidise Sn to Sn<sup>2+</sup> to form SnCl<sub>2</sub> but cannot oxidise Sn<sup>2+</sup> to Sn<sup>4+</sup>.

 $Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$   $E^{\ominus} = +1.36V$ 

The preparation method of  $SnCl_4$  proposed is feasible.

 $E_{Cl_2/Cl^-}^{O}$  is more positive than both  $E_{Sn^{2+}/Sn}^{O}$  and  $E_{Sn^{4+}/Sn^{2+}}^{O}$ . Hence  $Cl_2$  can oxidise Sn to Sn<sup>4+</sup> to form SnCl<sub>4</sub>.

[Total: 12]

- 3 (a) Compound N,  $C_3H_4O_3$ , liberates a gas when treated with aqueous sodium carbonate.
  - (i) Identify the gas and state the functional group that is present in compound **N**.

[1]

Gas is carbon dioxide. Functional group: carboxylic acid / -COOH group

When 0.10 cm<sup>3</sup> of liquid compound **N** was dissolved in an inert solvent and an excess of sodium metal added, 15 cm<sup>3</sup> of gas was produced at 303 K and 1 atm. [Density of compound **N** = 1.093 g cm<sup>-3</sup>]

(ii) Calculate the ratio of the amount of compound **N** reacted to the amount of gas that is produced.

[1]

mass of  $N = 0.10 \times 1.093 = 0.1093$  g moles of N = 0.1093/88 = 0.0012420 mol

moles of gas =  $\frac{(101325)(15 \times 10^{-6})}{(8.31)(303)}$  = 0.00060362 mol

mole ratio of **N** : gas =  $0.0012420 : 0.00060362 \approx 2 : 1$ 

(iii) Use your answers in (a)(i) and (a)(ii) to suggest two possible structures of compound N. Explain your reasoning.

[3]

#### From **(a)(ii)**,

since mole ratio of **N** : H<sub>2</sub> gas  $\approx$  2 : 1, one mole of **N** undergoes <u>redox / acid-metal</u> reaction to produce 0.5 mole of H<sub>2</sub> gas. Hence, **N** contains <u>one carboxylic acid</u> (or one alcohol) group.

#### From (a)(i),

Since **N** already contains a carboxylic acid functional group, **N** must contain either a ketone or an aldehyde functional group to satisfy the molecular formula of  $C_3H_4O_3$ .

The two possible structures of **N** are:



Compound **N**,  $C_3H_4O_3$ , is formed as the only organic product when a neutral organic compound **M**,  $C_4H_8O_3$ , is heated with acidified KMnO<sub>4</sub>. **M** does not decolourise aqueous bromine.

- (iv) Use the information provided and your answer in (a)(iii) to
  - identify the structure of **N** and
  - deduce the structure of **M**.

Explain your reasoning and the chemistry of the reactions involved.

[3]

Since N is an oxidation product of M, N cannot contain an aldehyde group and thus N is:



Since M is a neutral organic compound, it cannot contain the carboxylic group and is likely to contain an ester functional group given that there are three oxygen atoms in its molecular formula.

Since N already contains three carbon atoms, M is a methyl ester and the remaining oxygen atom could be attributed to a ketone or secondary alcohol functional group.

Possible structures of M	Molecular formula
О О С-С H <sub>3</sub> C-О СН <sub>3</sub>	$C_4H_6O_3$
$ \begin{array}{c}                                     $	$C_4H_8O_3$

M has to contain a secondary alcohol functional group to satisfy the molecular formula of  $C_4H_8O_3$ . Therefore, M has undergone acid hydrolysis (of ester), followed by oxidation (of methanol and the secondary alcohol) to produce N (as the only organic product) with the liberation of  $CO_2$  gas when M is heated with acidified KMnO<sub>4</sub>.



(b) Phenylethene, C<sub>6</sub>H<sub>5</sub>CH=CH<sub>2</sub>, can be used to synthesise three different aromatic compounds **R**, **S** and **T** as shown in Fig. 3.1.



9



(i) State the reagents and conditions required for reaction I.

KMnO<sub>4</sub>(aq), NaOH(aq), cold

Compounds **S** and **T** have the following features.

- Each compound contains a disubstituted benzene ring.
- They have an identical substituent on their benzene rings.
- S has its substituents at positions 1 and 2 on the benzene ring.
- **T** has its substituents at positions 1 and 3 on the benzene ring.
  - (ii) Using the information provided and given that the same type of reaction is occurring in III and V, suggest structures for the intermediates **P** and **Q**.

Hence state the reagent and conditions required for reaction II.

P Q CH<sub>2</sub>CH<sub>3</sub> COOH

Reagent and conditions required for reaction II: H<sub>2</sub>, Ni, heat

(iii) Suggest and explain how the conditions for reactions III and V would differ despite the same type of reaction occurring.

[2]

[1]

[3]

A higher temperature is required for reaction V than III.

The  $-CO_2H$  group is deactivating while the  $-CH_2CH_3$  group is activating. The benzene ring in benzoic acid has a lower electron density and is a weaker nucleophile / less susceptible to electrophilic substitution compared to that in ethylbenzene.

[Total: 14]

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4 Hydrogen peroxide, H<sub>2</sub>O<sub>2</sub>, finds its applications in a diversity of fields. Amongst many uses, it is an important precursor for the synthesis of organic peroxides and polymers. As such the manufacture of hydrogen peroxide has been an important industrial process since the 20<sup>th</sup> century.

Today, most of the world's hydrogen peroxide is manufactured by the anthraquinone process. This process involves the two steps shown below.



- (a) Step 1 involves the adsorption of H<sub>2</sub> gas onto the surface of the palladium metal catalyst.
  - (i) State the property that palladium possesses that allows it to act as a catalyst in step 1, and explain how the adsorption of  $H_2$  gas onto palladium increases the rate of reaction.

[2]

Palladium has low-lying vacant / partially filled d orbitals.

The adsorption of  $H_2$  weakens the H–H bond, and allows it to break more readily, lowering the activation energy. Hence, rate of reaction increases.

(ii) A study of the kinetics of step 1 revealed that at low pressures, the rate of reaction increases with increasing pressure of  $H_2$ . However, at high pressures, increasing the pressure of  $H_2$  has no effect on the rate of reaction.

Explain these observations.

[2]

At low pressures, the surface of palladium has available active sites for  $H_2$  to adsorb as it is not saturated. Hence, the rate of reaction increases when the pressure of  $H_2$  is increased.

In contrast, at high pressures, the surface of palladium is saturated with  $H_2$  and there are no active sites for adsorption to occur / active sites are fully occupied with  $H_2$ . Hence, the rate of reaction is no longer affected by the increase in  $H_2$  pressure.

Although palladium and nickel belong to Group 10 of the Periodic Table, both elements have different ways of filling up their d orbitals. For palladium, it has a fully filled 4d subshell.

(iii) Draw, on the Cartesian axes provided in Fig. 4.1, the orbital from which the first electron of palladium is removed. Label the axes and orbitals clearly.

[1]



## Any one the following with correctly labelled axes and orbitals:



(iv) It is observed that the first ionisation energies of the Period 4 transition elements remain relatively invariant. Explain this observation.

[2]

- The first ionisation energy of Period 4 transition elements involves the removal of an electron from the 4s orbital.
- Across the transition elements, electrons are added to the penultimate 3d orbitals.
- As such, the increase in nuclear charge is cancelled out by the increase in shielding effect.
- Effective nuclear charge remains relatively constant. Hence, the energy required to remove the 4s electron remains relatively invariant.
- (b) At the end of step 1, anthrahydroquinone is extracted from the reaction mixture before reacting it with O<sub>2</sub> in step 2.

It is observed that step 2 follows the rate equation below.

rate = 
$$k$$
[anthrahydroquinone][O<sub>2</sub>]

In this step, a large excess of  $O_2$  is required to ensure that anthrahydroquinone is completely oxidised back to anthraquinone, producing hydrogen peroxide.

(i) Explain why the rate equation for step 2 can be rewritten as rate = k'[anthrahydroquinone].

[1] This is because  $O_2$  is in large excess and hence the concentration / pressure of  $O_2$  remains relatively constant throughout the reaction. As such, the rate equation can be rewritten as rate = k'[anthrahydroquinone] where  $k' = k[O_2]$  is a constant.

(ii) Hence sketch, on Fig 4.2, a labelled graph to show how the concentration of  $H_2O_2$  in step 2 will vary over time.

[2]



(iii) Step 2 was repeated with different initial pressures of O<sub>2</sub> and different initial concentrations of anthrahydroquinone.

Table 4.1 shows the initial quantities of reactants used for each experiment and the time required for the initial concentration of anthrahydroquinone to be halved for experiment 1.

expt	initial pressure of O <sub>2</sub> (g) / Pa	initial [anthrahydroquinone] / mol dm <sup>-3</sup>	time required for initial [anthrahydroquinone] to be halved / min
1	4 × 10 <sup>5</sup>	1.00	12.0
2	4 × 10 <sup>5</sup>	0.50	
3	8 × 10 <sup>5</sup>	1.00	

Table 4.1

Complete Table 4.1 and explain your answer.

[2]

## Table 4.1

expt	initial pressure of O₂(g) / Pa	initial [anthrahydroquinone] / mol dm <sup>-3</sup>	time required for initial [anthrahydroquinone] to be halved / min
1	$4 \times 10^{5}$	1.00	12.0
2	$4 \times 10^{5}$	0.50	12.0
3	8 × 10 <sup>5</sup>	1.00	6.0

Since  $t_{\frac{1}{2}} = \frac{\ln 2}{k'}$ , where  $k' = k[O_2]$ ,

changes in the concentration of anthrahydroquinone has no effect on the halflife of the reaction. Instead, doubling the initial pressure of  $O_2$  would halve the half-life of the reaction.

(c) At the end of step 2, the reaction mixture contains only anthraquinone and  $H_2O_2$ .  $H_2O_2$  can be separated out from the reaction mixture by adding water to the reaction mixture.

With reference to the bonding between relevant molecules, explain how the addition of water allows this to happen.

[2]

 $H_2O_2$  can form hydrogen bonding with the water molecules. Hence,  $H_2O_2$  will dissolve in water.

In contrast, anthraquinone has large non-polar benzene rings which will interfere with the hydrogen bonding it forms with water. Hence, anthraquinone will not dissolve in water but remain in the reaction mixture.

(d) Quinone and hydroquinone have similar structures to anthraquinone and anthrahydroquinone respectively.

The standard reduction potential of the quinone–hydroquinone system is +0.70 V.



An electrolytic cell was set up under standard conditions with a mixture of aqueous quinone and dilute sulfuric acid as the electrolyte and platinum rods as electrodes.

State the products formed at the anode and the cathode.

[2]

Possible oxidations at the anode: $O_2 + 4H^+ + 4e^- \rightleftharpoons H_2O$  $E^{\ominus} = +1.23 \text{ V}$  $S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$  $E^{\ominus} = +2.01 \text{ V}$ 

Since  $E^{\oplus}(O_2/H_2O)$  is less positive than  $E^{\oplus}(S_2O_8^{2-}/SO_4^{2-})$ ,  $H_2O$  will be preferentially oxidised to oxygen gas at the anode.

Possible reductions at the cathode:

$\begin{array}{c} \downarrow \\ \downarrow $	OH OH	<i>E</i> <sup>⊖</sup> = +0.70 V
$2H^+ + 2e^- \rightleftharpoons H_2$		<i>E</i> <sup>⊕</sup> = 0.00 V
$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$		$E^{\ominus} = -0.83 \text{ V}$

Since  $E^{\ominus}_{quinone/hydroquinone}$  is most positive, quinone will be preferentially reduced to hydroquinone at the cathode.

[Total: 16]

**5** (a) Glycine has the following structure.

O OH NH<sub>2</sub>

The p $K_a$  values of glycine are shown in Table 5.1.

Table 5.1

p $K_a$ of α–carboxyl group	p $K_a$ of $\alpha$ -amino group
2.30	9.60

(i) Glycine exists as a zwitterion at pH 5.95.

State what is meant by the term *zwitterion*.

[1]

[3]

A zwitterion is a species which is dipolar with no overall electrical charge.

(ii) A 15 cm<sup>3</sup> solution of 0.05 mol dm<sup>-3</sup> glycine is prepared in which glycine is fully protonated. The initial pH of this solution is 1.87.

Sketch the pH–volume added curve you would expect to obtain when  $11.25 \text{ cm}^3$  of 0.10 mol dm<sup>-3</sup> NaOH is added to this solution.

Use the information provided, and data from (a)(i) and Table 5.1 to label the various key points on the curve.

Show your working.



(iii) Write an equation to show the reaction occurring when 1.75 cm<sup>3</sup> of 0.10 mol dm<sup>-3</sup> NaOH is **further** added to the resulting solution in **(a)(ii)**.

Hence calculate the pH of the solution obtained.

[2]

Resulting solution in **(a)(ii)** is a buffer solution at maximum buffering capacity, containing equal concentrations of  $H_2NCH_2CO_2^-$  and  $H_3N^+CH_2CO_2^-$ .

When NaOH is added,  $H_3N^+CH_2CO_2^- + OH^- \rightarrow H_2NCH_2CO_2^- + H_2O$  New moles of salt,  $H_2NCH_2CO_2^- = 0.000375 + (\frac{1.75}{1000} \times 0.1) = 0.00055$  mol New moles of acid,  $H_3N^+CH_2CO_2^- = 0.000375 - (\frac{1.75}{1000} \times 0.1) = 0.0002$  mol  $pH = 9.60 + log10(\frac{0.00055/_{0.028}}{0.0002/_{0.028}}) = 10.0$  (3 sf)

(iv) Draw the structure of the predominant species of glycine at pH 10.0.

(v) Name the type of reaction occurring when **Q** is formed from two glycine molecules.



## [1]

[1]

#### Condensation

- (b) The presence of some amino acids has been linked to the precipitation of calcium ethanedioate (CaC<sub>2</sub>O<sub>4</sub>), a component of kidney stones, in the body. Research studies have been performed to better understand the effect of pH on the solubility of CaC<sub>2</sub>O<sub>4</sub>.
  - (i) Predict and explain the effect of pH on the solubility of  $CaC_2O_4$ .

[2]

When the pH decrease, the [H<sup>+</sup>] increases.  $C_2O_4^{2-}(aq)$  will react with H<sup>+</sup> causing the [ $C_2O_4^{2-}$ ] to decrease.

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

By Le Chateliers' Principle, the position of the equilibrium will shift to the right to increase the  $[C_2O_4^{2-}]$ .

Hence, the solubility of CaC<sub>2</sub>O<sub>4</sub> will increase with decreasing pH.

One research study on the effect of pH on the solubility of  $CaC_2O_4$  involves adding excess powdered  $CaC_2O_4$  to water that has its pH value adjusted. The suspension was filtered and the filtrate was titrated against acidified potassium manganate(VII) of a known concentration. The results are shown in Table 5.2.

experiment	pH of filtrate	volume of KMnO <sub>4</sub> added / cm <sup>3</sup>
1	1.56	30.00
2	1.76	24.55
3	2.45	13.40
4	3.20	8.00
5	5.37	3.70
6	6.16	3.50

Table 5.2

(ii) Construct balanced ion-electron equations for the reaction between CaC<sub>2</sub>O<sub>4</sub> and potassium manganate(VII) which produces a gas.

Hence write the overall equation for the reaction.

[2]

Reduction:  $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ Oxidation:  $C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$ Overall:  $2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$ 

(iii) Using the data in Table 5.2, comment on your prediction in (b)(i).

[2]

The prediction in (b)(i) is consistent with the data with the solubility of  $CaC_2O_4$  increasing with decreasing pH.

The data shows that as pH decreases, the volume of  $KMnO_4$  required to fully titrate ethanedioate increases. Since the ethanedioate ions originated from the dissolution of  $CaC_2O_4$ , the greater volume of  $KMnO_4$  required is indicative that more  $CaC_2O_4$  has dissolved.

(iv) In experiment 1, 200 cm<sup>3</sup> of the filtered solution was titrated against 0.00100 mol dm<sup>-3</sup> potassium manganate(VII).

Calculate the mass of Ca<sup>2+</sup>, in mg, present in the filtrate.

[2]

No. of moles of  $MnO_4^- = \frac{30}{1000} \times 0.001 = 3.00 \times 10^{-5}$  mol

No. of moles of  $C_2O_4^{2-} = \frac{5}{2} \times 3.00 \times 10^{-5} = 7.50 \times 10^{-5} \text{ mol}$ 

Since  $Ca^{2+} \equiv C_2O_4^{2-}$   $\Rightarrow$  No. of moles of  $Ca^{2+} = 7.50 \times 10^{-5}$  mol Mass of  $Ca^{2+} = 7.50 \times 10^{-5} \times 40.1 = 3.0075 \times 10^{-3}$  g = 3.01 mg (3 s.f.)

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[Turn over

- (c) Thermogravimetric analysis is an analytical technique used to determine a substance's thermal stability by monitoring the change in mass that occurs as a sample is heated at a constant rate.
  - (i) Calcium ethanedioate monohydrate, CaC<sub>2</sub>O<sub>4</sub>.H<sub>2</sub>O, has been used to calibrate equipment that performs thermogravimetric analysis because of its well-defined three-step decomposition process.

Complete the following equations which describe the decomposition process of  $CaC_2O_4$ . H<sub>2</sub>O. Include state symbols.

[2]

Step 1:  $CaC_2O_4.H_2O(s) \rightarrow CaC_2O_4(s) + H_2O(g)$ Step 2:  $CaC_2O_4(s) \rightarrow \underline{CaCO_3(s)} + \underline{CO(g)}$ Step 3:  $CaCO_3(s) \rightarrow \underline{CaO(s)} + \underline{CO_2(g)}$ 

(ii) A thermogram from a thermogravimetric analysis plots mass of carbonate against temperature.

Given the same initial mass of carbonate, state and explain how the thermogram of magnesium carbonate will differ from that of calcium carbonate in terms of

- the final mass of carbonate obtained,
- the temperature at which the mass of carbonate starts to change significantly.

[3]

Since both carbonates are of the same mass, the number of moles of magnesium carbonate (with a smaller relative formula mass) is greater than that of calcium carbonate. Hence, more moles and mass of carbon dioxide will be lost from magnesium carbonate, leading to a smaller final mass for magnesium carbonate.

Since the thermal stability of magnesium carbonate is lower than that of calcium carbonate due to  $Mg^{2+}$  having a higher charge density / polarising power than  $Ca^{2+}$ , less energy and a lower temperature is required for the thermal decomposition of magnesium carbonate to occur.

[Total: 21]