Class Adm No

Candidate Name: _____

H

millennia institute

2024 Preliminary Examination
Pre-University 3

H2 CHEMISTRY **9729/03**

Paper 3 Free Response **13th Sep 2024**

2 hours

Candidates answer on separate paper.

Additional materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not turn over this question paper until you are told to do so

Write your name, class and admission number on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper. If additional space is required, you should use the page at the end of this booklet. The question number must be clearly shown.

Section A
Answer **all** questions.

Section B
Answer **one** question.

A Data Booklet is provided.
The use of an approved scientific calculator is expected, where appropriate.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

Question	A			B	**Total**
	1	2	3	4 / 5	
Marks	/19	/23	/18	/20	/**80**

Section A

Answer **all** the questions in this section.

1 The halogens are elements in Group 17 of the Periodic Table. The name “halogen” translates to “salt producer”, due to their tendency to form salts readily in the presence of Group 1 metals such as sodium.

(a) **(i)** Citing relevant data values, state and explain the trend of reactivity of the halogens as oxidising agents. [3]

(ii) Outline a procedure to demonstrate the relative reactivities of chlorine and bromine, given only the following reagents to choose from:

$Cl_2(aq)$ $Cl^-(aq)$ $Br_2(aq)$ $Br^-(aq)$

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(b) Gaseous PCl_3 and PCl_5 exist in an equilibrium.

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

At 250 °C, the K_c for this equilibrium has a value of 26.0.

(i) A sample of solid PCl_5 is added into a sealed 2 dm^3 container at 250 °C, and the solid quickly sublimes. After equilibrium was established, there was found to be 0.20 mol of Cl_2.

Determine the initial mass of solid PCl_5 added. [4]

(ii) In a modified experiment, some Na(s) was present in the container initially before addition of solid PCl_5 (all other conditions were kept the same).

Explain the effect of this on the position of equilibrium, and the value of K_c. [3]

(iii) In the solid state, PCl_5 exists as an ionic solid, with $[PCl_6]^-$ as the anion.

Identify a formula unit of the ionic solid. [1]

(iv) Describe how PCl_5 acts as a base in the formation of $[PCl_6]^-$, writing an equation to explain your answer. [1]

(v) Unlike PCl_5, PI_5 does not exist.

Suggest an explanation for why this is the case. [1]

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(c) A 25.0 cm^3 sample of water contains chlorine, Cl_2, and monochloramine, NH_2Cl.

The amounts of chlorine and monochloramine in this sample can be analysed using the DPD-FAS titration method, where DPD serves as the indicator and Fe^{2+} the titrant.

The concentration of chlorine is determined first:

Step 1:
Excess of indicator DPD (colourless) is added to the 25.0 cm^3 sample, turning the indicator magenta and reducing Cl_2.

$$\underset{\text{colourless}}{DPD} + Cl_2 \rightarrow \underset{\text{magenta}}{DPD^{2+}} + 2Cl^-$$

Step 2:
The resultant mixture is then titrated against Fe^{2+}.

$$DPD^{2+} + 2Fe^{2+} \rightarrow DPD + 2Fe^{3+}$$

From the same mixture, the concentration of monochloramine is determined next:

Step 3:
A small amount of catalyst is added, catalysing the reduction of NH_2Cl.

$$DPD + NH_2Cl + 2H^+ \rightarrow DPD^{2+} + NH_4^+ + Cl^-$$

Step 4:
The resultant mixture is then titrated against Fe^{2+}, same as Step 2.

$$DPD^{2+} + 2Fe^{2+} \rightarrow DPD + 2Fe^{3+}$$

When 0.0010 mol dm^{-3} of Fe^{2+} was used as the titrant, the titres obtained at the end of Steps 2 and 4 are 15.00 cm^3 and 5.00 cm^3 respectively.

(i) Calculate the amount of Cl_2 in the 25.0 cm^3 water sample. [1]

(ii) Calculate the amount of NH_2Cl in the 25.0 cm^3 water sample. [1]

(iii) Hence, determine the total concentration of Cl atoms (in g dm^{-3}) in the water sample. [2]

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[Total: 19]

2 (a) Compound **A**, $C_5H_8O_2$, is neutral. An orange precipitate is observed when 2,4-dinitrophenylhydrazine is added to it, but no precipitate is observed when Fehling's reagent is added.

1 mol of **A** reacts with acidified $KMnO_4$ to produce CO_2 gas and a single organic product **X**. **A** also turns orange acidified $K_2Cr_2O_7$ green, forming another organic product **Y**.

Effervescence of a gas that forms a white precipitate when bubbled through aqueous $Ca(OH)_2$ is observed when $Na_2CO_3(s)$ is separately added to both organic products **X** and **Y**.

A also reacts with PCl_5 to form **B**, C_5H_7OCl. Addition of HCN with trace NaOH(aq) to **B** results in the formation of **C**.

Deduce the structures of compounds **A**–**C**. [6]

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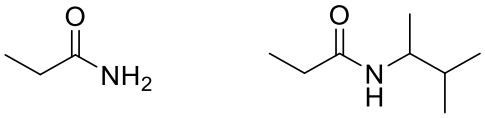
(b) Suggest a chemical test to distinguish between the following compounds.



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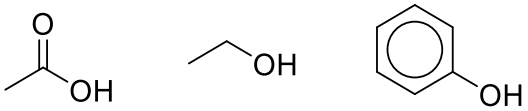
(c) Rank the following compounds in order of increasing acid strength, explaining your answer.



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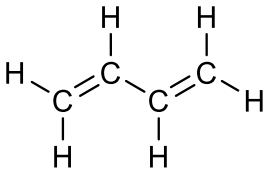
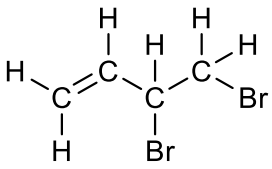
(d) Double bonds are said to be conjugated when adjacent p-orbitals of one π bond can align with the p-orbitals of another π bond. Buta-1,3-diene is an example of one such compound with conjugation between its two C=C bonds.

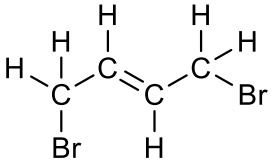


buta-1,3-diene

When 1 mol of Br_2 in CCl_4 is added to 1 mol of buta-1,3-diene, electrophilic addition occurs and products **E** and **F** are formed in an approximate ratio of 50:50.



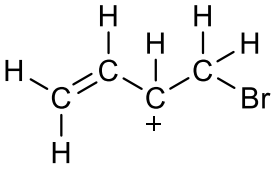
E



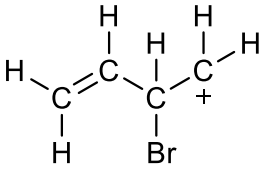
F

(i) Draw a suitable diagram to illustrate the conjugation of the two C=C bonds in buta-1,3-diene. [1]

(ii) Although two carbocation intermediates could have led to the formation of **E**, one is preferred over the other.



preferred intermediate



Explain why this intermediate is preferred. [2]

(iii) The carbocation intermediate leading to the formation of **F** is produced from the same preferred intermediate in **(ii)**.

By means of suitable curly arrow(s), show the production of the carbocation intermediate leading to the formation of **F**. [1]

(iv) Draw all the stereoisomers of **E**. [1]

(v) Draw all the stereoisomers of **F**. [1]

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(e) Aldehydes have different solubilities in water.

aldehyde	formula	solubility in water
ethanal	CH_3CHO	very soluble
pentanal	$CH_3(CH_2)_3CHO$	slightly soluble

(i) By means of a suitable diagram, illustrate why ethanal is very soluble in water. [2]

(ii) Explain why pentanal is **slightly** soluble in water. [2]

(iii) Explain whether the boiling point of ethanal is higher or lower than that of water. [2]

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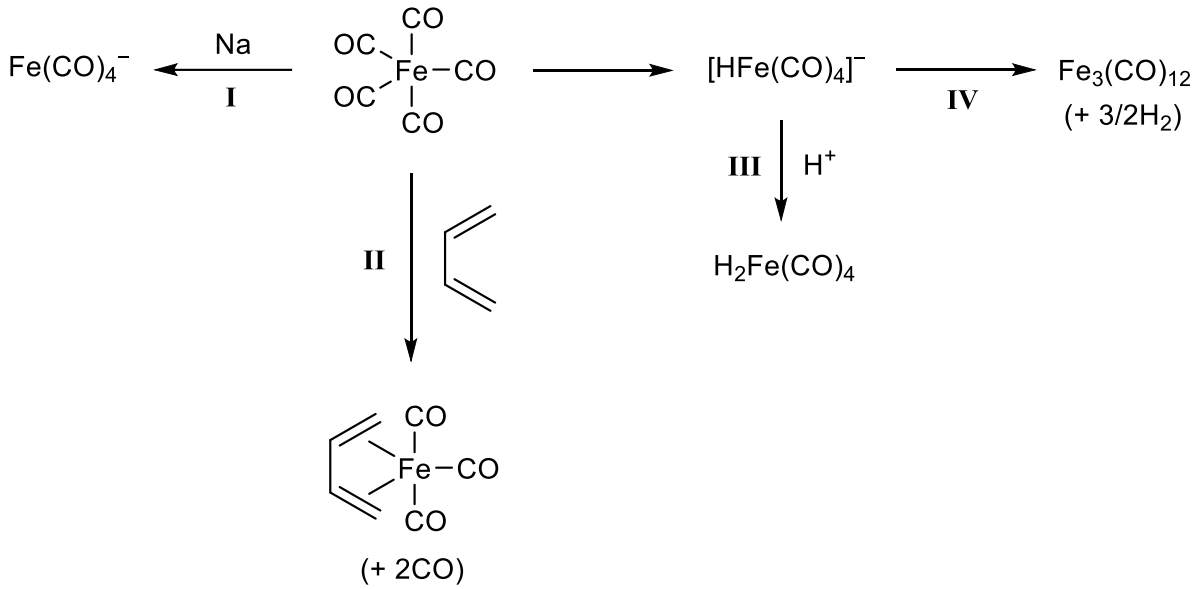
3 (a) Carbon monoxide, CO, is a poisonous, neutral gas that is colourless and odourless. It is also a common ligand in metal complexes. Iron pentacarbonyl, $Fe(CO)_5$, is one such example.

The reaction scheme below shows some reactions involving $Fe(CO)_5$.



(i) Determine the oxidation state of the Fe atom in $Fe(CO)_5$. [1]

(ii) The $[HFe(CO)_4]^-$ complex contains a hydride ion, H^-, and the $H_2Fe(CO)_4$ complex contains a H_2 ligand.

Given that $H_2Fe(CO)_4$ is still a penta-coordinate complex, draw the structure of $H_2Fe(CO)_4$. [1]

(iii) Identify the type of reactions taking place for Steps **I–IV** in the reaction scheme, focusing on the iron complex. [4]

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(b) CO reacts with oxygen to form CO_2, a known pollutant.

To tackle the harmful effects of CO_2 on the environment, two possible approaches are to

1) Cut down on CO_2 emissions, such as from the burning of fossil fuels, and to
2) Capture CO_2 from the atmosphere.

(i) In some countries, environmentally-friendly electrolysis factories directly utilise electricity generated from windmills to carry out the chemical reactions.

Identify how energies are changed from one form to another in one such electrolysis factory. [1]

To capture CO_2 from the atmosphere, a device called a "humidity-swing" can be used. It consists of a polymeric membrane with key organic functional groups on the carbon chain.

The functional groups, together with H_2O from the atmosphere, enable the reversible collection of CO_2.

(ii) Write an equilibrium equation for the reaction of CO_2 with H_2O. Include state symbols in your answer. [1]

(iii) Suggest a possible functional group that enables the collection of CO_2. [1]

(iv) Explain the harmful effects of CO_2 on the environment. [2]

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(c) A student carries out an electrolysis experiment at home using a high voltage battery as the power source, metal nails as the electrodes, and dilute sulfuric acid as the electrolyte.

The electrolysis set up is shown in Fig. 3.1.

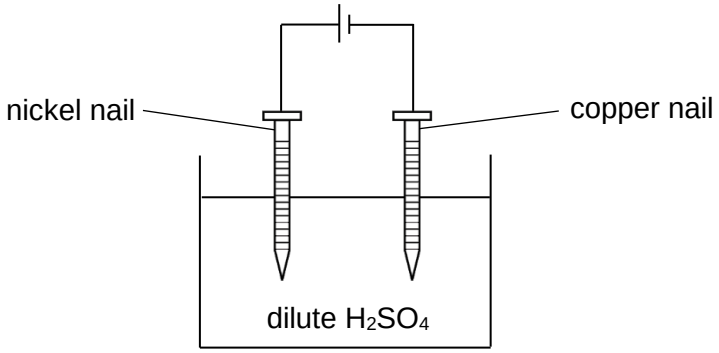

Fig. 3.1

The electrode reactions that took place are as follows.

At nickel anode: $Ni \rightarrow Ni^{2+} + 2e^-$
At copper cathode: $2H^+ + 2e^- \rightarrow H_2$

(i) With reference to relevant electrode reactions from the *Data Booklet* for **all** species present in the electrolysis set up, explain why the above electrode reactions have taken place preferentially. [4]

(ii) Given that the high voltage battery generates an average current of 2 A, determine the amount of H_2 gas produced in one day. [2]

(iii) The actual amount of H_2 gas produced in one day from the electrolysis reaction is lower than the value calculated in **(ii)**.

Suggest a likely reason for this. [1]

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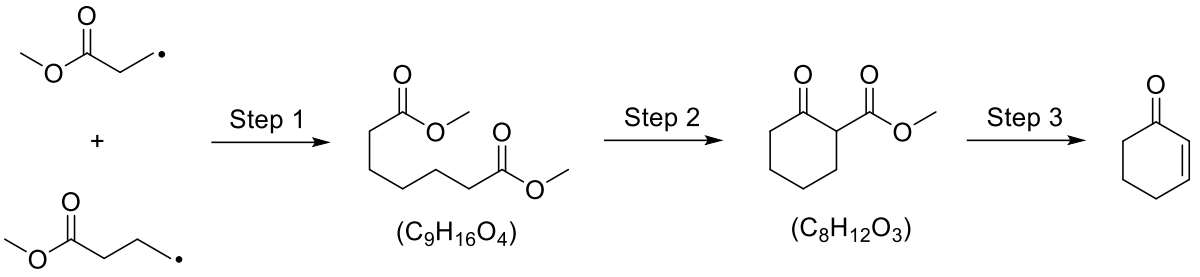
Section B

Answer **one** question from this section.

4 **(a)** A 3-step reaction scheme is as shown.



Identify the *types of reaction* that are occurring in Steps 1, 2 and 3. [3]

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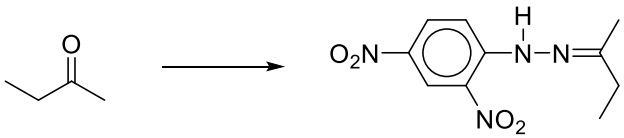
(b) For each of the reactions below, state the reagents and conditions required:

(i)



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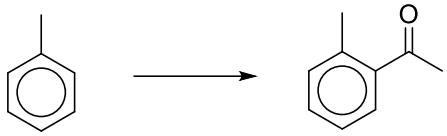
(ii)



[1]

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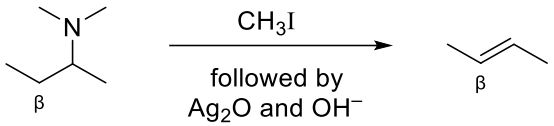
(c) The Hoffman Degradation reaction converts amines into alkenes. An example of this reaction is shown below, with the beta (β) carbon labelled.



The reaction mechanism consists of 2 steps:

- In step 1, CH_3I acts as the electrophile, reacting with the tertiary amine to form a quaternary ammonium cation and I^-.
- In step 2, a hydroxide ion then removes a proton from the beta carbon of the quaternary ammonium cation, forming a C=C bond and releasing a tertiary amine in the process.

(i) Define the term *electrophile*. [1]

(ii) Draw the mechanism of the Hoffman Degradation reaction shown above, including relevant charges, dipoles, and curly arrows in your answers. [3]

(iii) Suggest the structure of another carbon-containing product from this reaction. [1]

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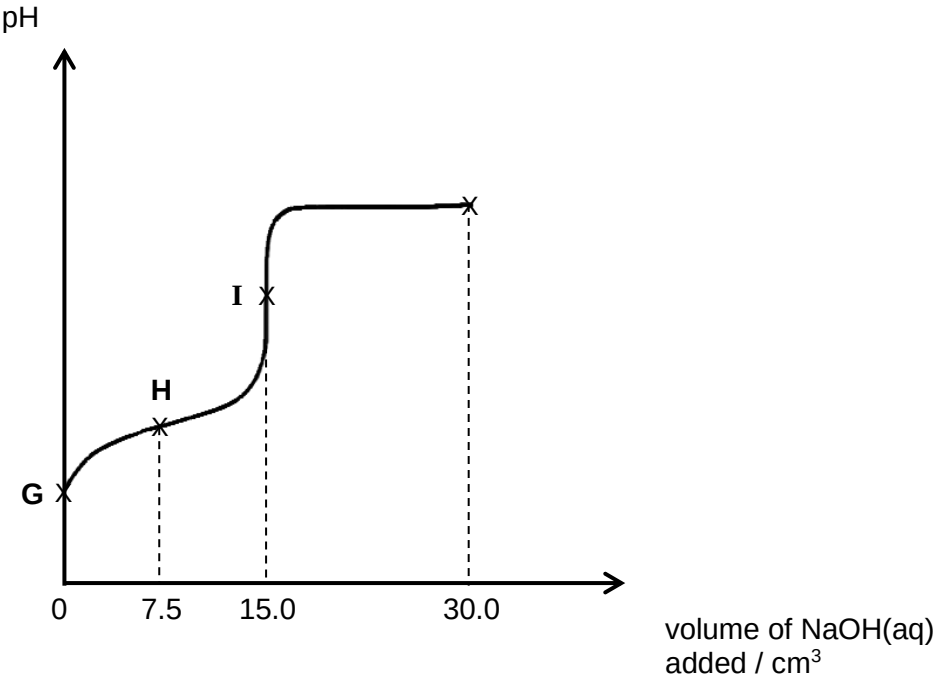
(d) 25.0 cm^3 of a 0.100 mol dm^{-3} monoprotic acid, HA, was titrated against NaOH(aq) to obtain the following pH curve. The pK_a value associated with HA is 3.75.



(i) Calculate the pH at point **G**. [1]

(ii) Representing the acid as HA, identify the two species present in high concentration at point **H**. [1]

(iii) Hence, write two chemical equations to explain the shape of the pH curve at point **H**. [2]

(iv) Determine the pH at point **I**. [2]

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(e) SO_4^{2-}(aq) was added dropwise to a 1 dm^3 solution containing 0.10 mol dm^{-3} Pb^{2+}(aq) and 0.20 mol dm^{-3} Sr^{2+}(aq) ions. After some time, $PbSO_4$ and $SrSO_4$ are precipitated.

The K_{sp} values of $PbSO_4$ and $SrSO_4$ are 6.30×10^{-7} and 3.20×10^{-7} respectively.

(i) Determine the concentration of SO_4^{2-} in the solution when $PbSO_4$ just begins to precipitate. [2]

(ii) Calculate the $[Sr^{2+}]$ remaining when $PbSO_4$ just begins to precipitate. [1]

(iii) Hence, determine the mass of $SrSO_4$ precipitated when $PbSO_4$ just begins to precipitate. (M_r of $SrSO_4$ = 183.7) [1]

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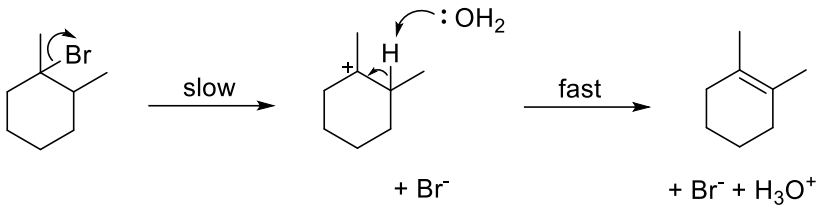
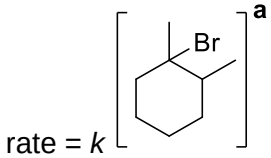
5 (a) Tertiary alkyl halides in ethanolic solvents can undergo elimination reactions to form alkenes. The 2-step reaction mechanism of a tertiary alkyl halide is as follows:



The generic rate equation for the above reaction is:



(where **a** and **b** are the respective orders of reactions)

(i) Determine the values of **a** and **b** based on the reaction mechanism given. [1]

(ii) Explain how you arrived at your answer in **(i)**. [1]

(iii) An experiment is conducted to verify the values of **a** and **b**.

Based on your answer in **(i)**, sketch the corresponding rate-concentration graphs that would be obtained for the tertiary alkyl bromide and water. [1]

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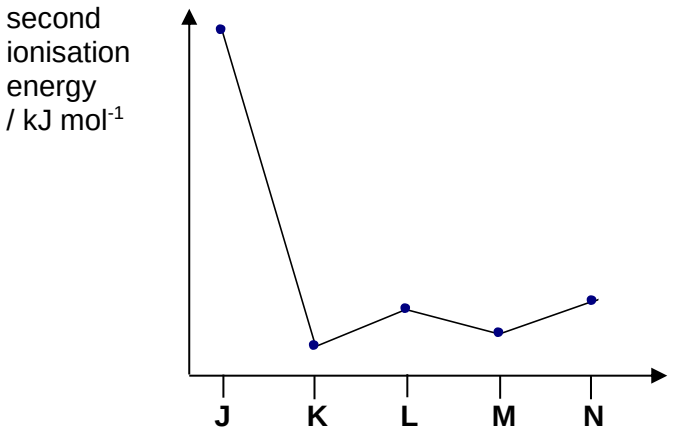
(b) The second ionisation energies of consecutive Period 3 s-block and p-block elements **J**–**N** are given in the graph below.



(i) Define *second ionisation energy*. [1]

(ii) Identify element **L** and write the equation to describe its second ionisation energy. [1]

(iii) By considering the electronic configurations of $\mathbf{J}^+$ and $\mathbf{K}^+$, explain the drastic decrease in second ionisation energy between element **J** and **K**. [2]

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(c) *Hess' Law* is frequently used to determine the enthalpy change of reactions that cannot be carried out simply via experiment.

(i) Define *Hess' Law*. [1]

(ii) The *enthalpy change of hydration* of an ion is defined as the energy released when 1 mol of the gaseous ion dissolves in an infinite volume of water.

Suggest why an "infinite volume of water" is required to determine the enthalpy change of hydration. [1]

(iii) Suggest why the standard enthalpy change of hydration of an ion is difficult to determine with an experiment. [1]

(iv) To determine the standard enthalpy change of solution of solid LiC*l*, an experiment was conducted by dissolving 1.00 g of the solid into 20.0 cm^3 of water (assume "infinite"). The temperature of the solution increased from 298 K to 308 K.

Calculate a value for the standard enthalpy change of solution of solid LiC*l*. [2]

(v) The lattice energy of LiC*l* is –830 kJ mol^{-1}.

Draw an energy cycle to determine a value for the sum of standard enthalpy changes of hydration of Li^+ and Cl^-. [3]

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(d) Magnesium reacts with steam but not cold water, while calcium reacts even in cold water.

(i) Without reference to any data values, explain the difference in reactivities of magnesium and calcium with water. [2]

The reactivities of magnesium sulfate and calcium sulfate can be compared by determining their thermal decomposition temperatures. In this reaction, O_2, SO_2 and SO_3 gases are evolved.

(ii) It is known that the ratio of O_2:SO_2 gas evolved is 1:2.

Write a balanced chemical equation for the thermal decomposition of magnesium sulfate. [1]

(iii) Explain whether magnesium sulfate or calcium sulfate has a higher thermal decomposition temperature. [2]

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