BP~773

Candidate Name: ____________________

Class	Adm No

H

millennia institute

2022 Preliminary Exams
Pre-University 3

H2 CHEMISTRY **9729/02**

Paper 2 Structured Questions

14 Sep 2022

2 hours

Candidates answer on the Question 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.

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

A Data Booklet is provided.

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.

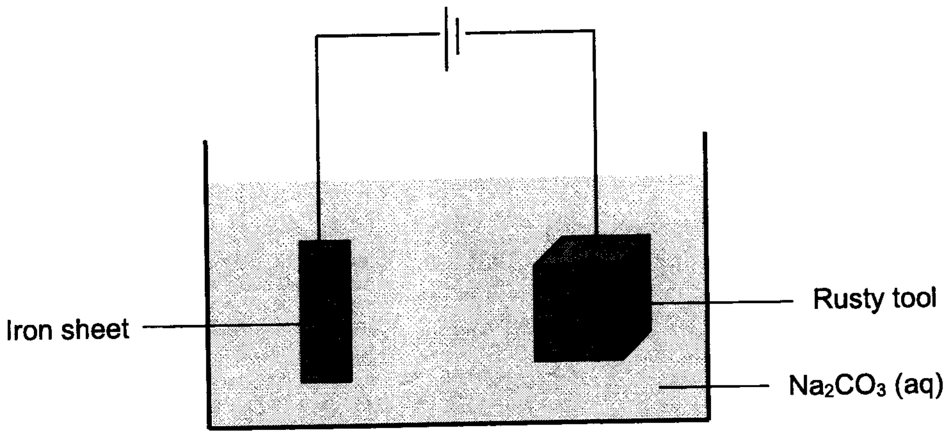
Question	1	2	3	4	5	Total
Marks	20	13	24	9	9	75

Answer all questions in the spaces provided.

1 Many household tools are made from stainless steel as it is highly resistant to corrosion and rust. Stainless steel contains iron, chromium, manganese, nickel, molybdenum, silicon and carbon which interacts with oxygen from water and air to form oxides. Of these elements, chromium has the highest resistance to corrosion.

Despite the high resistance, rusting still occurs in a humid environment. A 'Do-it-Yourself' (DIY) kit has been launched in the market to remove rust from household tools and the set-up is shown in **Figure 1.1**.

Figure 1.1



(a) **(i)** State if the iron sheet is the anode or the cathode.

....[1]

(ii) *Use of Data Booklet is relevant to this question.*
State and explain the observations found at the iron sheet electrode.

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....[2]

(iii) Suggest why carbonate ions from Na_2CO_3 electrolyte cannot be oxidised at the anode.

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(iv) A consumer saw the DIY kit and decided to purchase it and try out on his rusted dumbbell. He prepared the set up as shown in **Figure 1.1** with a 20 A power source and switched it on for 6 hours.

Determine the change in mass of the iron sheet.

[2]

(b) Fe_2O_3 is the main constituent of the rust found on household items. The standard electrode potentials involving the iron containing species can be found in **Table 1.1**.

Table 1.1

Half-equations	$E^\ominus$/V
$3Fe_2O_3 + H_2O + 2e \rightleftharpoons 2OH^- + 2Fe_3O_4$	–0.62
$Fe_2O_3 + 3H_2O + 6e \rightleftharpoons 2Fe + 6OH^-$	–0.88
$Fe_3O_4 + 4H_2O + 8e \rightleftharpoons 3Fe + 8OH^-$	–0.91

A layer was coated around the rusty tool after using the DIY kit.
With reference to the standard electrode potentials given in **Table 1.1**, explain fully whether the layer coated is iron.

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....[2]

(c) The metal alloy that made up the main components of stainless steel are transition metals.

(i) Define *transition metal.*

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....[1]

(ii) State a physical property of transition metals which makes them a suitable material used for household tools compared to main group metals.

....[1]

(iii) Iron(III) ions catalyse the reaction between I^- ions and $S_2O_8^{2-}$ ions through homogeneous catalysis.

Explain the term *homogeneous catalyst.*

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....[1]

(iv) By considering relevant $E^\ominus$ values from the Data Booklet, and using balanced equations, determine whether chromium(III) ions are suitable catalyst for the reaction between I^- ions and $S_2O_8^{2-}$ ions.

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(v) Describe the structure and bonding in the element chromium. Draw a diagram to illustrate your answer.

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....[2]

(d) Chromium(III) oxide has the same acid-base behaviour as aluminium oxide.

(i) State the type of oxide chromium(III) oxide exists as in terms of its acid-base behaviour.

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(ii) By quoting relevant data from the *Data Booklet*, explain why chromium(III) oxide and aluminium oxide have the same acid-base behaviour.

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(iii) *Use of Data Booklet is relevant to this question.*

Describe the observations when dilute NaOH is slowly added to the solution containing chromium(III) ions until in excess.

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[Total: 20]

2 **(a)** An aqueous solution of chlorine dioxide undergoes disproportionation in sodium hydroxide to form chlorate(V) ion, ClO_3^-, and hypochlorite ion, ClO^-. The reaction is catalysed by OBr^- ion.

$$4ClO_2(aq) + 4OH^-(aq) \xrightarrow{OBr^-} 3ClO_3^-(aq) + ClO^-(aq) + 2H_2O(l)$$

To study the kinetics of this reaction at 25 °C, initial rates were measured using various concentrations of ClO_2, OH^- and OBr^-.

experiment	$[ClO_2]$/ mol dm^{-3}	$[OH^-]$/ mol dm^{-3}	$[OBr^-]$ / mol dm^{-3}	initial rate/ mol dm^{-3} s^{-1}
1	0.02	0.05	0.01	2.30×10^{-3}
2	0.10	0.02	0.03	6.90×10^{-2}
3	0.02	0.10	0.01	4.60×10^{-3}
4	0.04	0.02	0.03	1.10×10^{-2}

(i) Explain, in terms of oxidation numbers, why this reaction is a disproportionation reaction.

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(ii) Determine the orders of reaction with respect to ClO_2, OH^- and OBr^-.

[3]

(iii) Hence, write the rate equation for the reaction.

....[1]

(iv) Calculate the rate constant, *k*, of the reaction and state its units.

[2]

(v) Determine the initial pH of an aqueous solution of the reaction mixture if the concentration of chlorine dioxide is 0.200 mol dm^{-3} and the concentration of OBr^- is 0.1 mol dm^{-3}, given that the initial rate of reaction is 1.45 mol dm^{-3} s^{-1}.

[2]

(b) With an appropriate sketch of the Maxwell-Boltzmann distribution, explain how a rise in temperature affects the rate of reaction.

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....[3]

[Total: 13]

3 Alpha hydroxy acids (AHA) have a general formula of RCH(OH)COOH. They are a group of plant and animal-derived acids used in a variety of skincare products and are known to tackle hyperpigmentation and signs of skin aging.

(a) **(i)** Explain why AHAs are generally water-soluble.

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....[2]

(ii) Glycolic acid, $CH_2(OH)COOH$, lactic acid, $CH_3CH(OH)COOH$, and mandelic acid, $C_6H_5CH(OH)COOH$, are examples of AHA.
Suggest, with reasoning, which of the three AHAs is the most soluble in water.

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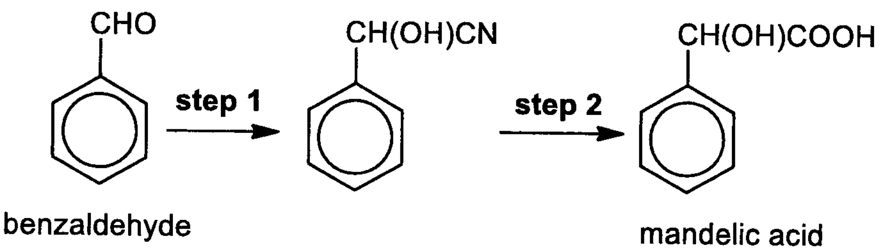
....[1]

(b) Mandelic acid can be synthesised in the laboratory from benzaldehyde by the following reactions.



(i) State the reagent and conditions used in **step 1**.

....[1]

(ii) State the type of reaction that occurs in **step 1** and **2**.

Step 1: ....

Step 2: ....

[2]

(iii) Describe the mechanism of the reaction in **step 1**. Show clearly all charges and the intermediate formed and use curly arrows to indicate the movement of electron pairs.

[3]

(iv) Predict, with reasoning, whether the product of **step 1** is able to rotate plane-polarised light.

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....[3]

(v) A scientist carrying out the synthesis of mandelic acid would like to check if all the reactants in **step 1** have been used up.

Devise a suitable chemical test which can help him verify if all the reactants in **step 1** have been used up and include observations in your answer.

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....[2]

(c) Glycolic acid is produced by plants during photorespiration and is recycled by conversion to glycine, H_2NCH_2COOH, within the cytoplasm. The same conversion can be done in the laboratory.

Devise a two-step synthetic route that converts glycolic acid to glycine in a laboratory. Include the reagents and conditions and the structure of the intermediate product. [3]

(d) A polypeptide made up of 10 amino acid residues is partially hydrolysed to give four smaller fragments. The four fragments are:

ala-gly-ser-gln
lys-trp-arg-pro
gln-his-lys
asp-ala-gly.

Deduce the sequence of the peptide chain.

[1]

(e) Amino acids can be neutral, positively or negatively charged, depending on the pH of the solution.

Amino acid exists as zwitterions at the isoelectric point.

(i) Define *zwitterion*.

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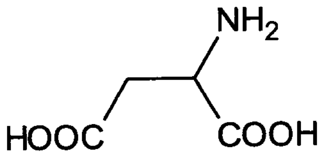
....[1]

(ii) Aspartic acid is an α-amino acid which has the R group $-CH_2COOH$.



Aspartic acid (asp)

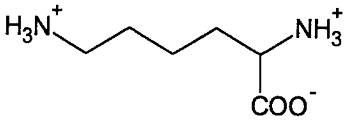
When fully protonated, the pK_a values of the acidic groups are 1.88, 3.65 and 9.60. Draw the fully protonated aspartic acid and assign the pK_a values.

[2]

(iii) Hence, draw the major species of aspartic acid at pH 5.

[1]

(iv) Aspartic acid was accidentally mixed with lysine at pH 5.



lysine at pH 5

Electrophoresis is a technique to separate the amino acids in an electric field. The sample was loaded onto an electrophoresis tank buffered at pH 5.0 and an electric field was applied.

On **Figure 3.1**, draw and label the relative positions of lysine and aspartic acid after the electrophoresis.

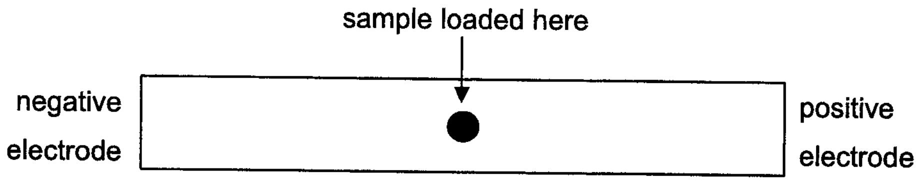


Figure 3.1

[2]

[Total: 24]

4 (a) Methane, CH_4 is the second major greenhouse gas after CO_2, exerting a significant influence on the climate and the chemistry of the atmosphere.

Biological methods have also been developed to produce methane from organic acids using bacteria. An example of this reaction where methane is produced from butanoic acid is shown below.

$$\_\_\_\ CH_3CH_2CH_2COOH(l) + \_\_\_\ H_2O(l) \rightarrow \_\_\_\ CH_4(g) + \_\_\_\ CO_2(g) \quad \Delta H_r$$

(i) Calculate the average oxidation state of C in each of the following carbon-containing compound.

C in $CH_3CH_2CH_2COOH$: ....

C in CH_4: ....

C in CO_2: .... [1]

(ii) Hence, or otherwise, balance the equation by filling in the stoichiometric coefficient in the above equation where methane is produced from butanoic acid in **(a)**. [1]

(iii) Using the thermochemical data shown in **Table 4.1**, draw a fully-labelled energy cycle to calculate the standard enthalpy change of reaction, ΔH_r in **(a)**.

Table 4.1

Standard enthalpy change of formation of liquid butanoic acid	–534 kJ mol^{-1}
Standard enthalpy change of combustion of carbon	–394 kJ mol^{-1}
Standard enthalpy change of combustion of hydrogen	–286 kJ mol^{-1}
Standard enthalpy change of formation of methane	–78.4 kJ mol^{-1}

[3]

(iv) Hence, predict the sign of ΔS for the reaction in **(a)** and explain the spontaneity of the reaction at high temperatures.

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....[2]

(b) Trouton's rule states that the entropy change of vapourisation for liquids such as benzene and hexane at their boiling points is almost the same value at around +85 to +88 $J\ K^{-1}\ mol^{-1}$.

However, the entropy change of vapourisation for butanoic acid is +130 $J\ K^{-1}\ mol^{-1}$.

Compare and explain the difference in the entropy change of vapourisation for butanoic acid and benzene.

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....[2]

[Total: 9]

5 Compounds **P**, **Q**, **R** and **S** are oxides or chlorides of Period 3 elements.

Table 5.1 shows some properties of the compounds.

Table 5.1

Compounds	**Melting point**	**Solubility in water**	**pH of solution**
P	High	Yes	13
Q	Low	Yes	2
R	High	Yes	6.5
S	High	No	

(a) Based on the information from **Table 5.1**, deduce the identities of compounds **P** and **R** and write the equations to justify the pH of the respective solutions.

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(b) **S** is only soluble in hot concentrated sodium hydroxide.

Identify compound **S** and write the equation for the reaction with hot concentrated sodium hydroxide.

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(c) When water is added to 0.0500 mol of **Q**, the resulting solution requires 0.250 mol of silver nitrate for complete reaction.
Identify compound **Q** and write the equations to show:

- its reaction with water
- the reaction between the resulting solution and silver nitrate

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....[3]

(d) The melting point of compound **P** is 1132 °C while that of potassium carbonate is 891 °C. Explain the difference in the melting points in terms of structure and bonding.

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[Total: 9]

END OF PAPER 2

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Class	Adm No

Candidate Name: ____________________

H

millennia institute

2022 Preliminary Examination
Pre-University 3

H2 CHEMISTRY **9729/03**

Paper 3 Free Response

19 September 2022

2 hours

Candidates answer on the Question 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 in the spaces 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. 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 / 6	
Marks	16	12	18	14	20	**80**

This question paper consists of **23** printed pages and **1** blank page.

Section A

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

1 **(a)** The Bunsen cell is an electrochemical cell built to provide electrical energy.

It consists of a zinc anode in dilute sulfuric acid, separated by a salt bridge from a carbon cathode in dilute nitric acid.

Nitrogen dioxide, NO_2, is the only gas formed from the reaction. At the anode, zinc decreases in size during the reaction.

(i) Draw a fully labelled diagram of the Bunsen cell. [3]

(ii) Use data from the *Data Booklet* to construct an overall equation for the reaction. [2]

(iii) Calculate the cell potential, E, for the reaction. [1]

(iv) The experimental E of the Bunsen cell is +1.9 V.

Use ideas about reversible reactions to suggest why the experimental E may differ from the calculated value in **(iii)**. [2]

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(b) Nitrogen dioxide, NO_2, and dinitrogen tetroxide, N_2O_4, exists at equilibrium as a mixture:

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

(i) Draw the 'dot-and-cross' diagram for N_2O_4. [1]

(ii) The standard enthalpy changes of formation for these gases are shown.

gas	NO_2	N_2O_4
$\Delta H_f^\ominus$ / kJ mol^{-1}	+33.2	+9.2

Calculate the standard enthalpy change for the reaction shown above. [1]

(iii) Explain why the sign of the value calculated in **(ii)** is as such. [1]

(iv) The standard entropy change for the reaction is –175.8 J mol^{-1} K^{-1}.

Explain why the value is negative. [2]

(v) Explain how the Gibbs free energy change, ΔG, of the reaction will vary with temperature. [2]

(vi) A sample of $NO_2(g)$ was sealed in a container. Its initial pressure was 1.00 bar. After reaching equilibrium, 0.351 bar of $N_2O_4(g)$ was formed.

Calculate the equilibrium constant, K_p, for this equilibrium. [1]

[Total: 16]

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[Turn over

2 (a) The copper(II) ion forms a coloured complex ion with six water molecules.

(i) Use your knowledge of VSEPR theory to name the shape of and state the bond angle in the complex. Explain your reasoning. [2]

(ii) Explain why the 3d orbitals of the copper(II) ion are split into 2 separate energy levels. [2]

The water molecules on the z-axis (axial ligands) can move further away from the copper(II) ion (Fig. 2.1), resulting in a further splitting of the orbitals into separate energy levels (Fig. 2.2). This is known as *Jahn–Teller distortion.*

As the new energy levels (Fig. 2.2) are close together, the electrons remain in their respective orbitals.

The complex is stabilised as the Cu^{2+} electrons now have a lower overall energy.

Jahn–Teller distortions will only be able to decrease the overall energy if the metal ion has an odd number of 3d electrons.

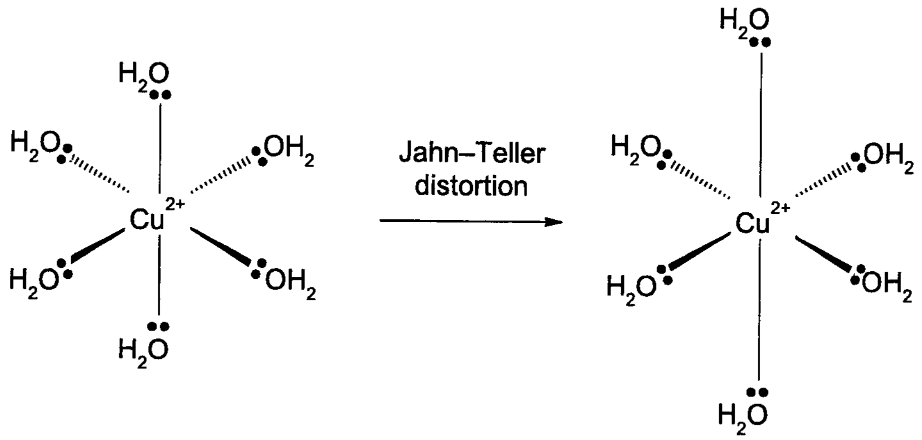

Fig. 2.1

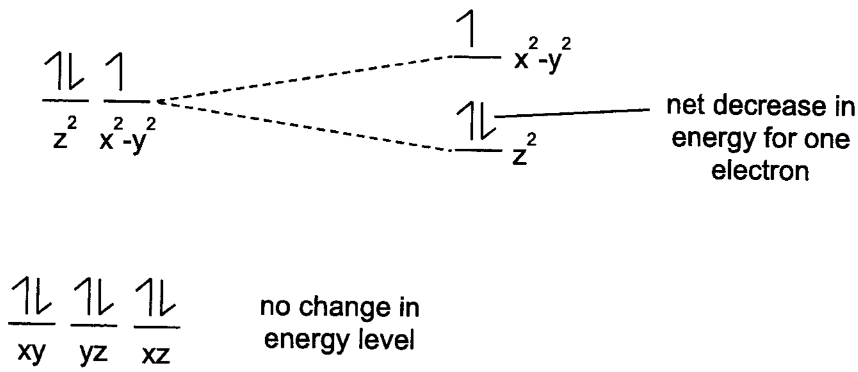

Fig. 2.2

(iii) Explain why the z^2 orbital is lower in energy after the further splitting. [1]

(iv) Predict if each of the ions will exhibit *Jahn–Teller distortion*:
1) Co^{2+}
2) Ni^{2+}.

Explain your reasoning. [2]

(v) Unlike complex ions of Cu^{2+}, complex ions of Cu^+ are not coloured.
Write the electronic configuration of Cu^+ and explain why its complex ions are not coloured. [2]

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(b) Use standard electrode potential data from the *Data Booklet* to calculate the standard Gibbs free energy change, $\Delta G^{\ominus}$, for the formation of the $[Cu(NH_3)_4]^{2+}$ complex ion from Cu^{2+}.

Hence, explain whether the reaction is feasible. [3]

[Total: 12]

3 (a) Phosphate buffered saline (PBS) is a solution that mimics the solute ion concentration of biological human cells.

PBS is prepared by dissolving 2.00 g of potassium dihydrogen phosphate, KH_2PO_4 (M_r = 136.1) and 1.42 g of disodium hydrogen phosphate, Na_2HPO_4 (M_r = 142.0), into water, then making up to 1.00 dm^3.

(i) Define the term *buffer solution*. [1]

(ii) PBS contains the ions produced from the dissociation of phosphoric acid, H_3PO_4 (Fig. 3.1). The successive pK_a of H_3PO_4 are 2.14, 7.20, and 12.37 respectively.

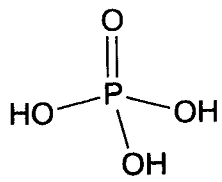

Fig. 3.1

Explain why the successive pK_a of H_3PO_4 increases. [1]

PBS contains the $H_2PO_4^-$(aq) and HPO_4^{2-}(aq) ions in equilibrium,

$$H_2PO_4^-(aq) \rightleftharpoons HPO_4^{2-}(aq) + H^+(aq) \qquad pK_a = 7.20$$

(iii) Calculate the pH of PBS. [3]

(iv) Write an ionic equation to show how PBS reacts with KOH(aq) [1]

(v) 100.0 cm^3 of PBS was reacted with different volumes of 0.0100 mol dm^{-3} KOH(aq) in separate experiments.

Calculate the pH of the solution formed when the following volumes of KOH(aq) are added to 100.0 cm^3 of PBS.

I 10.0 cm^3
II 200.0 cm^3 [6]

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(b) 'Hard water' contains a high concentration of calcium ions. PBS prepared using 'hard water' may appear cloudy due to precipitate formation.

Na_2HPO_4 and NaH_2PO_4 may react in a condensation reaction. Fixed proportions of Na_2HPO_4 and NaH_2PO_4 may be heated together to form sodium triphosphate, $Na_5P_3O_{10}$. The structure of $P_3O_{10}^{5-}$ is shown in **Fig 3.2**.

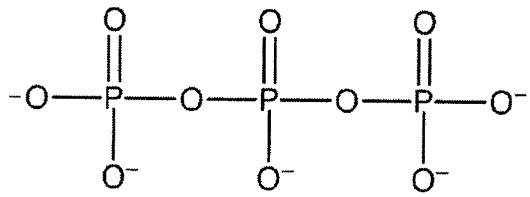

Fig 3.2

The $P_3O_{10}^{5-}$ ion consists of three phosphorus atoms linked together by oxygen atoms. It behaves as a tridentate ligand, binding to Ca^{2+} ions in a 1:1 ratio to form a soluble complex.

(i) Write a balanced chemical equation for the reaction to produce $Na_5P_3O_{10}$. [1]

(ii) State the shape of the $P_3O_{10}^{5-}$ ion about any of the P atoms. [1]

(iii) Draw the structure of the complex ion formed between the Ca^{2+} and $P_3O_{10}^{5-}$ ions. [1]

(iv) The numerical value of the K_{sp} of calcium phosphate is 2.07×10^{-33}. Since calcium phosphate is very insoluble in water, any small concentration of PO_4^{3-}(aq) present becomes significant.

The water used to prepare the PBS contains 5.06×10^{-5} g dm^{-3} of Ca^{2+}(aq).
The 1.00 dm^3 PBS contains 6.53×10^{-8} mol dm^{-3} of PO_4^{3-}(aq).

Calculate the minimum mass of $Na_5P_3O_{10}$ that must be dissolved into the 1.00 dm^3 PBS in order to prevent the precipitation of calcium phosphate. [3]

[Total: 18]

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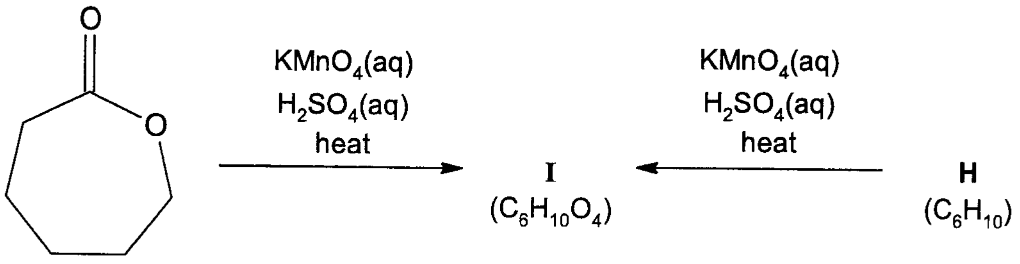
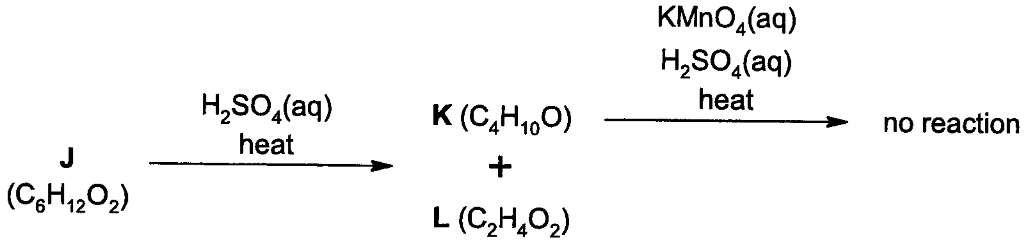
4 Potassium manganate(VII) is a potent oxidising agent that can take part in numerous reactions.

(a) **G** is a cyclic ester while **J** is a non-cyclic ester.



G



Suggest the structures of compounds **H**, **I**, **J**, **K** and **L**. [5]

(b) **A**, $C_6H_{10}O_5$, is a chiral compound that has wide uses in the manufacture of polymers.

When 1 mol of **A** is reacted with excess solid sodium carbonate at room temperature and pressure, 24 dm^3 of CO_2 is formed. **A** does not react with hot acidified potassium dichromate(VI) but reacts with excess hot concentrated H_2SO_4 to form **B**, $C_6H_8O_4$.

1 mol of **B** reacts completely with 2 mol of NaOH(aq). When **B** is heated with acidified $KMnO_4$(aq), **C**, $C_3H_4O_3$, and **D**, $C_3H_4O_4$, are formed.

C gives a yellow precipitate with warm aqueous alkaline iodine. Both **C** and **D** reacts with magnesium to give effervescence.

Deduce the structures of compounds **A**, **B**, **C** and **D** explaining the reactions described. [9]

[Total: 14]

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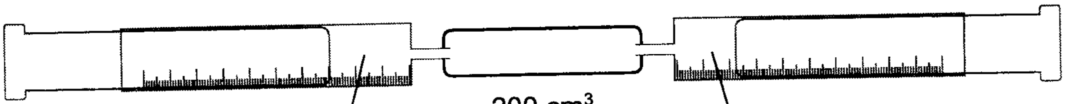
Section B

Answer **one** question from this section.

5 **(a)** The apparatus shown was used to produce 2-methylpropan-2-amine, $(CH_3)_3CNH_2$.



The volume occupied by the ethanol and its vapours can be taken to be insignificant.

(i) The two reactant gases were injected into the evacuated sealed tube at 293 K.

Calculate the total pressure after the two gases were mixed together.
Assume that there was no reaction taking place under these conditions. [2]

(ii) The reaction between $NH_3(g)$ and $(CH_3)_3CCl(g)$ would begin to take place when the system is subjected to heat.

Predict the predominant mechanism for the reaction.
Explain your reasoning. [2]

(iii) Outline the predominant mechanism for the reaction, showing clearly any lone pair, partial charges and the movement of electrons using curly arrows. [3]

(iv) Suggest a by-product of the reaction and how to minimise its formation. [2]

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(b) Fluorine gas is manufactured by electrolysing potassium hydrogen difluoride, KHF_2, dissolved in liquid hydrogen fluoride, HF, at –50°C and 1 atm.

(i) The HF_2^- ion further dissociates into two species.

A strong interaction forms between these two species.

Draw the two species, and label the interaction between them. [2]

(ii) Hydrogen fluoride can also dissociate, forming ions.

State and explain the *type* of acid-base behaviour exhibited by hydrogen fluoride. [1]

(iii) The only products of electrolysis were fluorine gas and hydrogen gas.

Write two half-equations to describe the discharge of ions at each electrode.
The electrodes can be taken to be inert. [1]

(iv) In one experiment, 355 g of KHF_2 and 145 g of HF were electrolysed.

Calculate the volumes of fluorine gas and hydrogen gas produced under the reaction conditions. [3]

(v) Explain which gas, fluorine gas or hydrogen gas, would have a more accurately calculated volume. [2]

(vi) Draw labelled diagrams to show the orbital overlaps in:
1) H_2
2) F_2
3) HF. [2]

[Total: 20]

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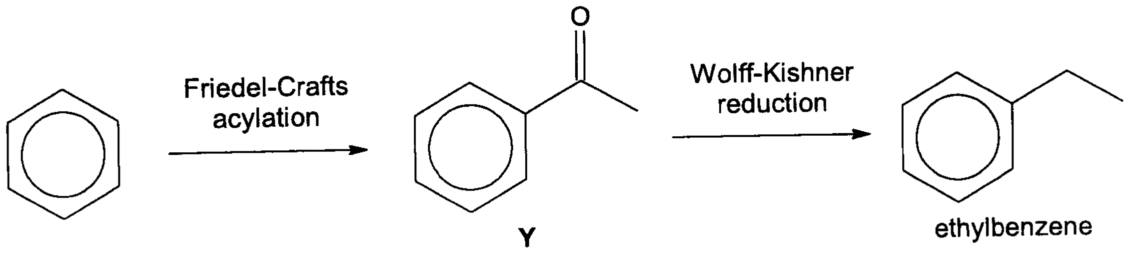
[Turn over

6 (a) Ethylbenzene can be produced from benzene using two consecutive reactions.



(i) The mechanism of Friedel-Crafts acylation in the first reaction shown above is the same as Friedel-Crafts alkylation using chloroethane as the reactant.

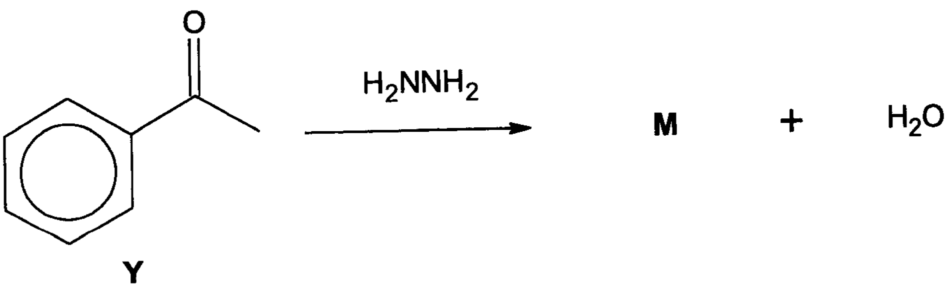
Outline the mechanism of Friedel-Crafts acylation to form **Y** above, showing clearly any lone pair, partial charges and the movement of electrons using curly arrows. [3]

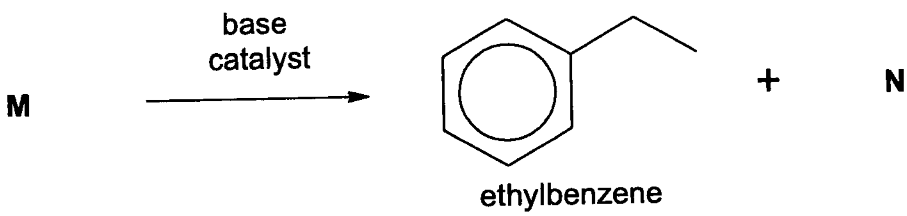
(ii) One advantage of Friedel-Crafts acylation over Friedel-Crafts alkylation is a higher percentage purity of the product. Whereas Friedel-Crafts alkylation often results in multi-substituted benzene rings, Friedel-Crafts acylation predominantly yields mono-substituted benzene rings.

Explain why Friedel-Crafts alkylation often results in multi-substituted benzene rings. [2]

(iii) The Wolff-Kishner reduction occurs in two steps.

In the first step, hydrazine, H_2NNH_2, reacts with **Y** in the same way as 2,4-dinitrophenylhydrazine.





Suggest the identity of **M** and **N** respectively. [2]

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(b) **(i)** State and explain the trend of atomic radii down the Group 2 elements. [2]

(ii) State and explain the trend of thermal stability of the Group 2 carbonates. [2]

(iii) 1.02 g of an unknown Group 2 carbonate, **X**CO_3, was strongly heated until a white solid of constant mass 0.505 g remained.

Determine the unknown element **X**. [3]

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(c) Uranium oxide, UO_2, reacts with hydrogen fluoride, HF, to form UF_4.
On adding fluorine, F_2, uranium fluoride, UF_6, is formed.

(i) Construct a balanced chemical equation for the overall reaction. [2]

(ii) Explain, using oxidation numbers, why the reaction is a redox reaction. [2]

There are two isotopes of uranium, ^{235}U and ^{238}U. While ^{238}U is much more abundant, only ^{235}U can be used to generate nuclear power.

Only samples of UF_6 containing at least 2% $^{235}UF_6$ can be used in nuclear reactors.

A sample of UF_6 has an average M_r of 351.95.

(iii) Calculate the percentage $^{235}UF_6$ in the sample. [1]

(iv) Hence determine if the sample can be used in nuclear reactors to generate power. [1]

[Total: 20]

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END OF PAPER 3

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Candidate Name: ____________________

Class	Adm No

H

millennia institute

Shift
Laboratory

2022 Preliminary Examinations
Pre-University 3

H2 CHEMISTRY **9729/04**

Paper 4 Practical

31 Aug 2022

2 hours 30 min

Candidates answer on the Question paper.

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.
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.
Qualitative Analysis Notes are printed at the back of the Question Paper.

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	1	2	3	4	Total
Marks	13	17	12	13	55

1 **Determination of amount of water of crystallization in $CuSO_4 \cdot nH_2O$**

Copper is a transition metal capable of exhibiting variable oxidation states. Compounds containing Cu^{2+} ions tend to be relatively stable.

Cu^{2+} ions react with excess potassium iodide, KI, to produce iodine, I_2, and a stable precipitate, CuI. To determine the concentration of Cu^{2+} via iodometric titration, all the Cu^{2+} ions are reduced to Cu^+ ions. A brown suspension, made up of an off-white precipitate of CuI in a brown solution of I_2, will be produced.

equation 1 $$2Cu^{2+} (aq) + 4I^- (aq) \rightarrow 2CuI (s) + I_2 (aq)$$

I_2 has a relatively low solubility in water. However, the presence of an excess of I^- ions in the reaction mixture allows the soluble tri-iodide ion, I_3^-, to form as shown by equation 2. This ensures that the I_2 formed as shown in equation 1 is fully dissolved.

equation 2 $$I_2 + I^- \rightarrow I_3^-$$

The I_3^- ions formed may be titrated against a standard solution of $Na_2S_2O_3$ as shown in equation 3.

equation 3 $$I_3^- + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 3I^-$$

The solution should be titrated immediately after addition of KI because the I_2 may be adsorbed onto the CuI precipitate, rendering the end-point less sharp.

You are provided with:

FA 1 is solid hydrated copper(II) sulfate, $CuSO_4 \cdot nH_2O$, where *n* is an integer

FA 2 is 0.10 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$

FA 3 is 1.00 mol dm^{-3} potassium iodide, KI

FA 4 is 10% potassium thiocyanate, KSCN

Starch indicator

The presence of thiocyanate ion, SCN^-, in the titration mixture near to the end-point will have an impact on the accuracy of the results. The procedure described is designed to improve on the accuracy.

In this experiment, you will determine the amount of water of crystallisation in 1 mol of $CuSO_4 \cdot nH_2O$. You will titrate **FA 1** against **FA 2**.

(a) Procedure

Preparation of solution of FA 1

1. Weigh accurately about 5.0 g of **FA 1** in a weighing bottle. Record your readings in an appropriate manner in the space provided below.
2. Transfer all the solid into a 250 cm^3 beaker. Dissolve this solid in about 100 cm^3 of deionised water.
3. Transfer the solution to a 250 cm^3 volumetric flask. Rinse the beaker with deionised water several times, adding each rinsing to the volumetric flask.
4. Make up the solution to 250 cm^3 with deionised water. Stopper, invert and shake well to obtain a homogenous solution. Label this solution as **FA 1 solution.**

Results

M1

[2] **M2**

(b) Titration

1. Fill the burette with **FA 2**.
2. Use a pipette to transfer 25.0 cm^3 of **FA 1** solution into a 250 cm^3 conical flask.
3. Use a measuring cylinder to add about 15 cm^3 of **FA 3** into this flask.
4. Titrate **FA 1** against **FA 2**. Near the end-point, when the brown suspension becomes pale yellow, add about 10 drops of starch solution.
5. Continue adding **FA 2** until the blue-black colour **just** disappears. Add 10 cm^3 of **FA 4** using a measuring cylinder.
6. Continue adding **FA 2** slowly. The end-point is reached when the **solution** first becomes colourless. The white precipitate remains.
7. Record your titration results in the space provided on page **4**. Make certain that your recorded results show the precision of your working.
8. Repeat the titration as many times as you think necessary to obtain consistent results.

(i) **Results**

M3
M4
[3] M5

(ii) From your titres, obtain a suitable volume of **FA 2** to be used in your calculations. Show clearly how you obtained this volume.

Volume of **FA 2** = ... [1] M6

(c) Calculations

(i) Calculate the amount of iodine, I_2, liberated from 25.0 cm^3 of **FA 1** solution.

amount of I_2 liberated from 25.0 cm^3 of **FA 1** solution =.......................................[1] M7

(ii) Hence, calculate the amount of copper(II) ions, Cu^{2+}, in 25.0 cm^3 of **FA 1** solution.

amount of Cu^{2+} in 25.0 cm^3 of **FA 1** solution = ... [1] **M8**

(iii) Determine the amount of $CuSO_4 \cdot nH_2O$ in 250 cm^3 of **FA 1** solution.

amount of $CuSO_4 \cdot nH_2O$ in 250 cm^3 of **FA 1** solution = ... [1] **M9**

(iv) Calculate the M_r of $CuSO_4 \cdot nH_2O$, and hence the value of n.
[A_r: H, 1.0; O, 16.0; S, 32.1; Cu, 63.5]

M_r of $CuSO_4 \cdot nH_2O$ = ... **M10**

value of n = ... [2] **M11**

(d) Starch forms a dark blue-black complex with the tri-iodide ion, I_3^-. The starch indicator is not added at the beginning of the titration as the resulting complex at high I_3^- concentration is relatively stable, dissociating only slowly.

Predict and explain the effect of adding the starch indicator at the start of the titration on the M_r of $CuSO_4 \cdot nH_2O$ determined in **(c)(iv)**.

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.... **M12**

....[2] **M13**

[Total: 13]

2 Investigation of the effect of concentration changes on the rate of a reaction

Iodate(V) ions, IO_3^-, also react with sulfite ions, SO_3^{2-}, in the presence of acid to produce iodine:

$$IO_3^-(aq) + SO_3^{2-}(aq) + H^+(aq) \rightarrow I_2(aq) + \text{other products}$$

The rate of this reaction is affected by the concentration of acid present in the reaction mixture. In the presence of starch, the iodine produced will give a dark blue colour. Therefore, the effect of the concentration of the acid on the initial rate of the reaction can be studied by measuring the time taken for a fixed amount of iodine to be produced.

You are also provided with:
FA 5 is 0.0500 mol dm^{-3} dilute sulfuric acid, H_2SO_4
FA 6 is 0.0400 mol dm^{-3} sodium sulfite, Na_2SO_3
FA 7 is 3.50 g dm^{-3} aqueous potassium iodate(V), KIO_3
Starch solution (from **Question 1**)

(a) You are required to perform a series of five 'iodine clock' experiments, by varying the concentration of acid and measuring the time, t, taken for the dark blue colour to appear.

- For each experiment, **solution 1** will contain the same volume of **FA 6** but a different volume of **FA 5**. You will need to ensure that the total volume of **solution 1** is kept constant at 50 cm^3 by adding deionised water as required.
- For each experiment, prepare **solution 2** as described in **(a)(i)**.

Note: Use separate measuring apparatus to prepare **solutions 1** and **2**.

For each experiment, you will note the volume of **FA 5**, $V_{FA\,5}$, and the time taken, t, for the reaction mixture to turn dark blue.

You will then calculate the following values to 3 significant figures:

- 1/t,
- lg(1/t),
- lg($V_{FA\,5}$).

In the space provided on page 9, prepare a table in which to record, to an appropriate level of precision:

- all volumes used to prepare **solution 1**,
- all values of t,
- all calculated values of 1/t, lg(1/t) and lg($V_{FA\,5}$).

(i) **Experiment 1**

Solution 1

- Pour 10.0 cm³ of **FA 6** to a 50 cm³ measuring cylinder and make up the volume to 50.0 cm³ by adding **FA 5**.

Solution 2

- Pour 10.0 cm³ of **FA 7** to a 10 cm³ measuring cylinder.

1. Transfer **solution 1** into a 100 cm³ beaker placed on a white tile.
2. Using a 10 cm³ measuring cylinder, add 5.0 cm³ of the starch indicator to the beaker.
3. Pour **solution 2** from the measuring cylinder **rapidly but carefully** into the beaker containing **solution 1**. Start the stopwatch immediately.
4. Stir the mixture using a glass rod.
5. Stop the stopwatch when the dark blue colour first appears.
6. Record the time taken, *t*, to the nearest second in your table.
7. Wash the beaker thoroughly with water and dry it.

(ii) **Experiment 2**

8. Prepare a different **solution 1** using 10.0 cm³ of **FA 6** and 10.0 cm³ of **FA 5**. Make up the volume to 50.0 cm³ by adding deionised water.
9. Prepare **solution 2** as described in **experiment 1** above.
10. Repeat steps 1 to 7.

(iii) **Experiment 3** to **5**

Choose **three** other suitable volumes of **FA 5**, between 10.0 cm³ and 40.0 cm³, for use in the remaining three experiments.

In each case,

- Use 10.0 cm³ of **FA 6**, together with your selected volume of **FA 5** and deionised water to prepare 50.0 cm³ of **solution 1**.
- Prepare **solution 2** as described in **experiment 1**.
- Determine the time taken, *t*, for the solution to turn dark blue.

Record all required volumes, time taken and calculated values in your table.

Results

M14
M15
M16
M17
M18

[5]

Graphical determination of order of reaction

In a series of experiments, where the same end-point (i.e. appearance of dark blue colour) is timed, while changing the concentration of one of the reactants and keeping the total volume of the mixture constant,

- 1/t can provide a measure of its initial rate,
- volume of the reactant that is changed in each experiment, can be used as a measure of its initial concentration.

Since the total volume of the reaction mixture is kept constant and only the concentration of **FA 5** has been changed, the rate equation, where ***m*** is the order of reaction with respect to H^+, can be simplified to

$$\text{rate} = k[H^+]^m$$

By taking logarithms of the factors in this equation and by substituting 1/t for rate and $V_{FA\,5}$ for concentration respectively,

$$\lg(1/t) = m \times \lg(V_{FA\,5}) + \lg k$$

Therefore, by plotting a graph of lg(1/t) against $\lg(V_{FA\,5})$, you will be able to draw a straight line of best-fit graph, where ***m*** is the gradient of the line.

(b) **(i)** Plot a graph of lg(1/t) on the *y*-axis against lg($V_{FA\ 5}$) on the *x*-axis. Draw the best-fit straight line, taking into account all of your plotted points.

[3] **M19** **M20** **M21**

(ii) From your graph, determine the value of ***m***, showing clearly all your working. Give your answer to 3 significant figures and hence state the order of reaction with respect to $[H^+]$.

m = ...

order of reaction with respect to $[H^+]$ = ...[1] **M22**

(c) This experiment is known to be very reliable. When it is performed carefully, it is possible to make a reaction mixture that changes colour after a specified time interval.

Use your graph to determine the volume of **FA 5** which would need to be added in **solution 1** so that the reaction mixture turns dark blue at **15 seconds**.

Show your working clearly.

M23

volume of **FA 5** required = ... [2] M24

(d) State and explain which experiment, from **experiments 1** to **5**, is likely to have the greatest error.

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....[1] M25

(e) Calculate the concentration of hydrogen ions, $[H^+]$, in mol dm^{-3}, that is present in the reaction mixture for **experiment 1** at time t = 0 s.

You may assume that the solutions are perfectly mixed and that the reaction has **not** started at t = 0 s.

M26

M27

$[H^+]$ = ... mol dm^{-3} [3] M28

(f) Suppose that the following mistake was made in the preparation of **solution 1** for **experiment 2**:

Kaleyn added 10.0 cm^3 of **FA 6** to the 50.0 cm^3 measuring cylinder and added **FA 5** up to the 30.0 cm^3 mark, instead of 20.0 cm^3 mark, on the measuring cylinder. After that, she made up the volume to 50.0 cm^3 by adding deionised water.

(i) State and explain how the value of t is affected for **experiment 2** described above.

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.... [1] **M29**

(ii) Suggest a modification to the experimental procedure to avoid this error.

....

.... [1] **M30**

[Total: 17]

3 **Planning**

Like iodine solution, many transition metal complex ions are coloured. It is possible to use this property to determine the concentration of a solution of a coloured complex ion. A few cm^3 of the solution is placed inside a machine, known as a spectrometer. This machine measures the amount of light that is absorbed when a specific wavelength of visible light is shone through a coloured solution. It does this by comparing the amount of light passing through the sample with the amount of light passing through the pure solvent. The amount of light absorbed is expressed as an *absorbance value.* The higher the concentration of the solution, the higher the absorbance value, i.e., the absorbance value is directly proportional to the concentration of the solution.

This technique can be used to determine the concentration of a solution of aqueous $[Ni(en)_3]^{2+}$. A series of known concentration of solution containing $[Ni(en)_3]^{2+}$ is prepared. A spectrometer is used to measure the absorbance of each solution. A graph of absorbance against concentration is then plotted. This graph is known as a calibration line.

The experiment is then repeated using a solution of unknown concentration. By comparing the absorbance of this solution with the calibration line, the concentration of $[Ni(en)_3]^{2+}$ in the unknown solution can be determined.

(a) Explain why transition metal compounds are often coloured.

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.... **M31**

....[2] **M32**

(c) Given that $[Ni(en)_3]^{2+}$ absorbs radiation of a wavelength of about 570 nm, use the information below to predict the colour of $[Ni(en)_3]^{2+}$.

Wavelength range (nm)	Colour	Complementary colour
400 - 450	Violet	Yellow
450 - 490	Blue	Orange
490 - 550	Green	Red
550 - 580	Yellow	Violet
580 - 650	Orange	Blue
650 - 700	Red	Green

.... [1] **M33**

(a) Using the information given above, you are required to write a plan to determine the concentration of $[Ni(en)_3]^{2+}$ in a solution of **X**.

You may assume that you are provided with:

- solution **X**, of unknown $[Ni(en)_3]^{2+}$ concentration less than 2 mol dm^{-3};
- a stock solution containing 5.00 mol dm^{-3} of $[Ni(en)_3]^{2+}$;
- access to a spectrometer and instructions for its use;
- graph paper;
- the apparatus and chemicals normally found in a school laboratory.

Your plan should include details of:

- the preparation of 100.0 cm^3 of 2.00 mol dm^{-3} aqueous $[Ni(en)_3]^{2+}$ from the stock solution;
- the preparation of a suitable range of diluted solutions of accurate concentrations;
- an outline of how the results would be obtained;
- a sketch of the calibration line you would expect to obtain;
- how the calibration line would be used to determine the concentration of $[Ni(en)_3]^{2+}$ in solution **X**.

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.... [9] M42

[Total: 12]

4 **Qualitative Analysis**

You are provided with two ionic solids, **FA 8** and **FA 9**.

Perform the tests described in the table below and record your observations in the table. In all the tests, the reagent should be added gradually until no further change is observed, with shaking after each addition. No additional or confirmatory tests for ions present should be attempted.

		observations with **FA 8**	observations with **FA 9**
(a)(i)	Add 1 cm^3 of dilute hydrochloric acid to ½ spatula of the solid sample in a test tube.		
(ii)	Add 2 cm^3 of silver nitrate solution to ½ spatula of the solid sample in a test tube. If need be, filter the resultant mixtures.		
(iii)	Add 1 cm^3 of potassium iodide solution to ½ spatula of the solid sample in a test tube. If need be, filter the resultant mixtures.		
(iv)	Add 1 cm^3 of aqueous iodine to ½ spatula of the solid sample in a test tube.		
(v)	Add 1 cm^3 of deionised water to ½ spatula of the solid sample in a test tube. To this resultant solution, add aqueous ammonia slowly, with shaking, until no further change is seen.		

[8]

M43
M44
M45
M46
M47
M48
M49
M50

(b) Suggest the identity of the cation and anion present in **FA 8**. Hence, write a balanced equation for the reaction occurring with **FA 8** in **(a)(ii)**.

cation: .... anion: **M51**

M52

equation: .... [3] **M53**

(c) Based on your observation in **(a)(iii)**, state the type of reaction undergone between potassium iodide and **FA 8**.

M54

.... [1]

(d) Based on your observation in **(a)(iv)**, state the role of **FA 9** in the reaction.

.... [1] **M55**

[Total: 13]

END OF PAPER

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Qualitative Analysis Notes

[ppt. = precipitate]

(a) Reactions of aqueous cations

cation	*reaction with*	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq),	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt. insoluble in excess	green ppt. insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt. insoluble in excess	off-white ppt. insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

ions	*reaction*
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, $Cl^-(aq)$	gives white ppt. with $Ag^+(aq)$ (soluble in $NH_3(aq)$)
bromide, $Br^-(aq)$	gives pale cream ppt. with $Ag^+(aq)$ (partially soluble in $NH_3(aq)$)
iodide, $I^-(aq)$	gives yellow ppt. with $Ag^+(aq)$ (insoluble in $NH_3(aq)$)
nitrate, $NO_3^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and Al foil
nitrite, $NO_2^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and Al foil; NO liberated by dilute acids (colourless NO $\rightarrow$ (pale) brown NO_2 in air)
sulfate, $SO_4^{2-}(aq)$	gives white ppt. with $Ba^{2+}(aq)$ (insoluble in excess dilute strong acids)
sulfite, $SO_3^{2-}(aq)$	SO_2 liberated with dilute acids; gives white ppt. with $Ba^{2+}(aq)$ (soluble in dilute strong acids)

(c) Test for gases

ions	*reaction*
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	"pops" with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	*colour of element*	*colour in aqueous solution*	*colour in hexane*
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple