NAME		Class	

ST ANDREW'S JUNIOR COLLEGE

JC2 Preliminary Examination

H2 Chemistry (9729) **18 September 2019**

Paper 3 Free Response **2 hours**

Additional Materials: Data Booklet, Answer Booklet

READ THESE INSTRUCTIONS:

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.

Section A

Answer **all** questions. Marks **[60]**

Section B

Answer **one** question. Marks **[20]**

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.

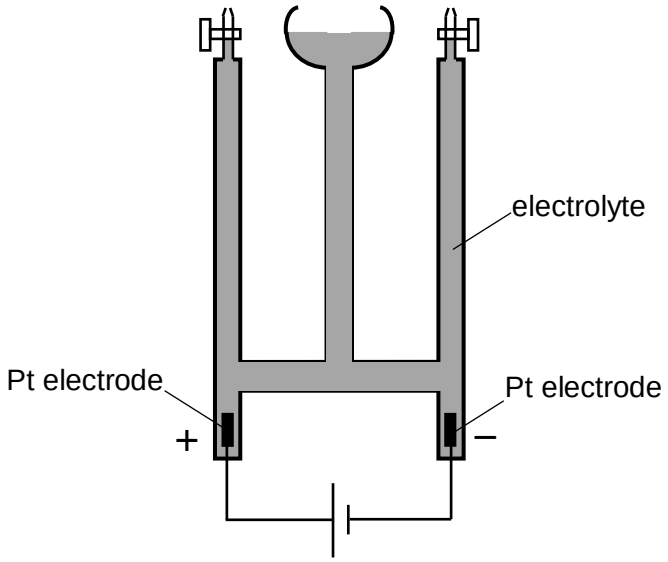
This document consists of **14** printed pages.

Section A

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

1 (a) Use of the Data Booklet is relevant to this question.

The Hoffmann voltameter is used to electrolyse concentrated iron (III) chloride solution. The setup of the Hoffmann voltameter is shown below.



(i) Describe the observations at the cathode and anode. Explain your answer with the aid of suitable ion-electron equations. **[2]**

(ii) State the difference in the observations at the anode when dilute aqueous iron (III) chloride solution is used instead. Explain your answer using relevant E^{θ} data. **[2]**

(b) The electrolysis of a hot aqueous solution of Na**X** yielded a reddish brown gas, $\mathbf{X_2}$, at the anode and hydrogen gas at the cathode. The red litmus paper turned blue when dipped into the solution at the cathode.

(i) Suggest the identity of the reddish brown gas $\mathbf{X_2}$. **[1]**

(ii) Write an ion-electron equation for the reaction at the cathode. **[1]**

(iii) Some of the $\mathbf{X_2}$ dissolved in the alkaline medium to form $\mathbf{X^-}$ and $\mathbf{XO_3^-}$ ions. Write a balanced equation to represent the reaction of $\mathbf{X_2}$ in alkaline medium. **[1]**

(iv) Describe a chemical test, which does **not** involve silver nitrate, that could distinguish between sodium chloride and sodium iodide. **[2]**

(c) Describe and explain how the thermal stability of the hydrogen halides varies down Group 17. **[2]**

(d) When methylcyclopentane is treated with a small quantity of chlorine in the presence of ultraviolet light, 4 mono-chlorinated constitutional isomers are produced. Draw the structures of the isomers and state the ratio in which they are formed. **[3]**

(e) $SiCl_4$ reacts readily with water to form a solution of pH 2. However, SiO_2 does not react with water and only reacts with hot concentrated alkali such as NaOH.

(i) Explain why $SiCl_4$ reacts readily with water, but SiO_2 only reacts with hot concentrated NaOH. Use relevant equations to explain your answer. **[3]**

(ii) Using $Cl_2(g)$ as an example, define the term *bond energy*. **[1]**

(iii) Construct an energy level diagram to calculate the enthalpy change of formation of $SiCl_4$.

Your diagram should include relevant data from the *Data Booklet* together with the following data: **[3]**

Enthalpy change of atomisation of Si = +338 $kJmol^{-1}$

Enthalpy change of vapourisation of $SiCl_4$ = +29 $kJmol^{-1}$

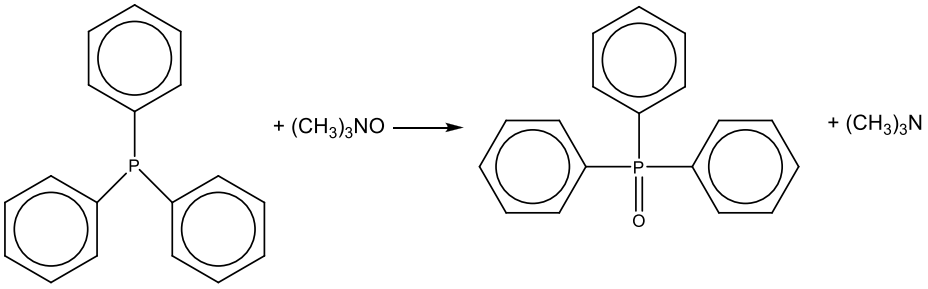
[Total: 21 marks]

2 **(a)** Phosphorus-containing compounds can react in various ways: as an acid, as a base, as an electrophile, as a nucleophile, as an oxidising agent and as a reducing agent.

Study the following reactions and decide in which way the phosphorus-containing compound is reacting in each case. Explain your answers fully.

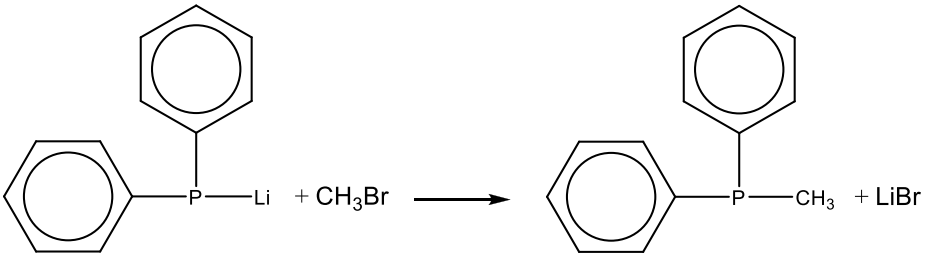
(i) $H_3PO_4 + H_2O \rightarrow H_2PO_4^- + H_3O^+$ **[1]**

(ii)



[1]

(iii)



[1]

(b) 2-chloropropanoyl chloride, **W**, can be obtained from propanoic acid by heating it with Cl_2 and PCl_5.

Reaction **1** :

$CH_3CH_2CO_2H(l) + Cl_2(g) + PCl_5(s) \rightarrow CH_3CHClCOCl(l) + 2HCl(g) + POCl_3(l)$

W

$\Delta H > 0$

(i) Explain the different reactivities of the two chlorine atoms in **W** towards water. **[2]**

(ii) Explain fully why the pH of an aqueous solution of 2-chloropropanoyl chloride is 1.0 while that of an aqueous solution of propanoic acid of the same concentration is greater than 1.0. **[2]**

(iii) **W** can be used to produce sweet-smelling **Z**, $C_6H_8O_4$, via compounds **X** and **Y**, as shown in Fig. 2.1

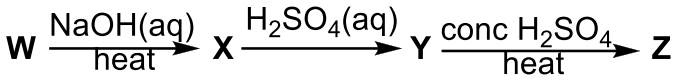
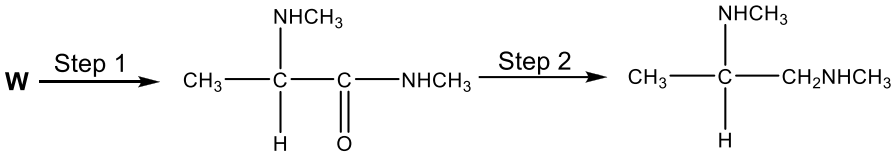


Fig. 2.1

Suggest structures for compounds **X**, **Y** and **Z** in Fig. 2.1. **[3]**

(iv) **W** can undergo the following reaction scheme.



State the reagents and conditions for Steps 1 and 2. **[2]**

(v) **V** is an isomer of **W**.

V rotates the plane of polarised light. It gives a positive test with 2,4-dinitrophenylhydrazine.

Draw the displayed formula of **V**, identifying the chiral carbon. **[1]**

(vi) Use the table of characteristic values for infra-red absorption frequencies in the *Data Booklet* to answer this question.

Infra-red adsorption frequencies can be used to identify functional groups in organic compounds. For example, propanol shows absorptions at 970–1250cm^{-1} and 3580–3620 cm^{-1}.

Use the table to suggest how infra-red absorption frequencies can be used to distinguish 2-chloropropanoyl chloride from propanoic acid. **[1]**

(vii) Given that reaction **1** is endothermic, explain why the reaction will only take place with heating. **[2]**

[Total : 16 marks]

3 There are 2 isomers of 2-methylbutanoic acid, $CH_3CH_2CH(CH_3)COOH$ (M_r 102.0) ; one of the isomers is sweet-smelling and the other has a stinky odour.

(a) **(i)** State the stereoisomerism exhibited by 2–methylbutanoic acid and how it arises. **[2]**

(ii) Hence, explain why the isomers have different smells. **[1]**

(b) Suggest a 2 stage synthesis of 2–methylbutanoic acid from 2–bromobutane. State reagents and conditions needed for each step, and show clearly the structure of any intermediate compounds. **[3]**

(c) Safety regulations set by many countries state that a factory would be fined, if stinky smelling compounds reached unsafe levels. The factory would have to stop production and undergo cleansing.

When 2–methylbutanoic acid was synthesised using 2–bromobutane in a factory, both the sweet-smelling and the stinky isomers were obtained in equal proportions.

(i) The M_r of 2–methylbutanoic acid in the liquid phase is 204.0.
With the aid of a diagram, explain the above. **[2]**

(ii) 2–methylbutanoic acid has a relatively low boiling point of 176 ^{o}C at 1 atm, and hence vaporises easily. This poses a problem when adhering to safety regulations.

In a factory, during the synthesis of 2–methylbutanoic acid, the workers did not seal the chemical container properly.

Given that the enthalpy change of vaporisation of 2–methylbutanoic acid is +59.1 kJ mol^{-1}, use the following equation (Clausius–Clapeyron Equation) to determine the vapour pressure of 2–methylbutanoic acid in the factory at night when the temperature was 30.2 ^{o}C.

$$\ln P = \frac{\Delta H_{vaporisation}}{R}\left(\frac{1}{T_{b.p.}} - \frac{1}{T}\right)$$

P = vapour pressure in atm at temperature T K

$\Delta H_{vaporisation}$ = enthalpy change of vaporisation of the substance in J mol^{-1}

R = universal gas constant

$T_{b.p.}$ = boiling point of the substance in K at 1 atm

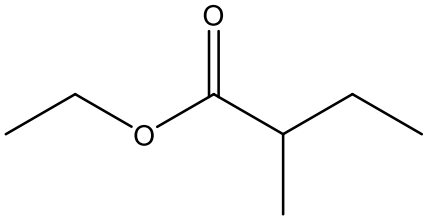
[2]

(iii) Safety protocols dictated that stinky smelling substances above 300 ppm (parts per million) is considered a safety hazard and likely to be fined. Based on your answers in **(a)(i)** and **(c)(ii)**, and given that the pressure in the factory is 1 atm, determine whether the factory would be fined.

[2]

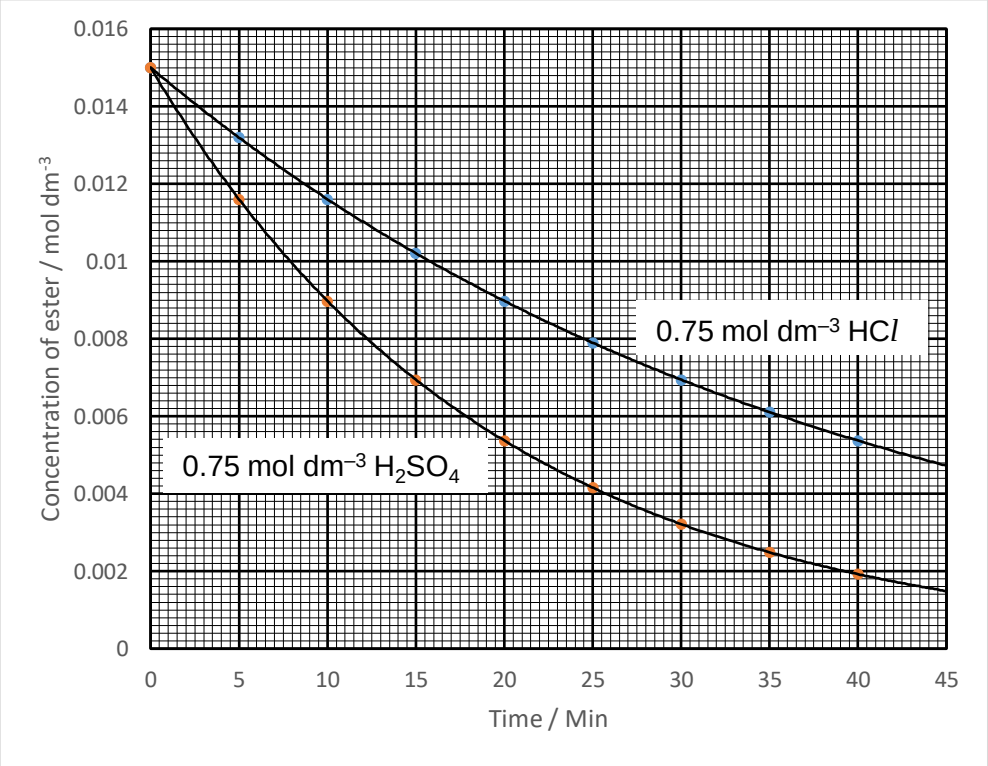
[1 x 10^{-6} atm in 1 atm = 1 ppm]

(d) Ethyl 2–methylbutanoate is an ester which is commonly found in citrus fruits, such as pineapple and oranges. It is commonly used as the starting material to form the sweet–smelling 2–methylbutanoic acid via hydrolysis.



ethyl 2-methylbutanoate

The rate equation for the hydrolysis of esters was determined by a series of experiments. The hydrolysis of the ester, ethyl 2–methylbutanoate, was carried out, using 0.75 mol dm^{-3} hydrochloric acid. The experiment was repeated using 0.75 mol dm^{-3} sulfuric acid. The following graphs were obtained.



(i) Using the graphs above, deduce the order of reaction with respect to $[H^+]$ and [ester]. Hence, write the rate equation of the hydrolysis of the ester, ethyl 2–methylbutananoate. **[3]**

(ii) Calculate the rate constant for the hydrolysis of ethyl 2-methylbutanoate, including its units. **[2]**

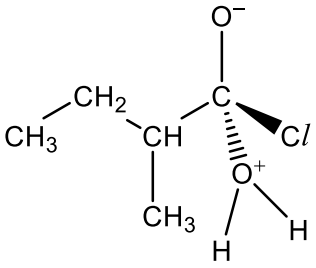
(iii) In the absence of an acid, the hydrolysis of the ester is very slow.
With the aid of a relevant diagram, explain how the rate constant would change if the acid was removed. **[3]**

(e) Ethyl 2-methylbutanoate can also be formed using 2-methylbutanoyl chloride and ethanol.

The reaction takes place under anhydrous conditions as 2-methylbutanoyl chloride undergoes hydrolysis in water to form 2-methylbutanoic acid.

The hydrolysis of 2-methylbutanoyl chloride occurs via a two-stage mechanism:

- The first stage (the addition stage of the reaction) involves a nucleophilic attack on the partial positive carbon atom by one of the lone pairs of electrons on the oxygen atom of a water molecule, giving intermediate **E**.



intermediate **E**

The second stage (the elimination stage) happens in two steps.

1. The carbon-oxygen double bond reforms with a chloride ion as the side product.
2. A hydrogen ion is removed by the chloride ion to give 2-methylbutanoic acid and hydrogen chloride.

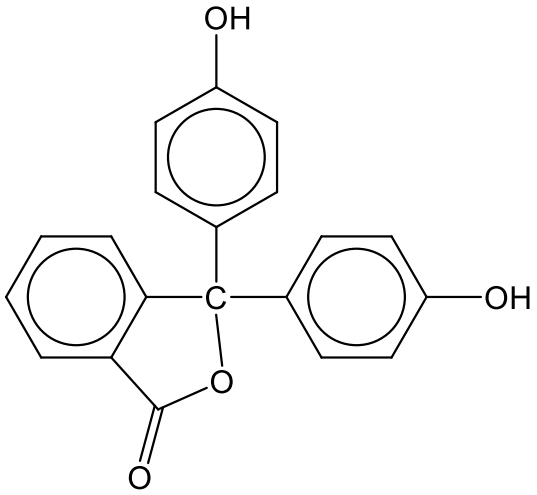
Outline the mechanism for this reaction, given that intermediate **E** is formed after the first stage. Show any relevant lone pairs, dipoles and charges, and indicate the movement of electron pairs with curly arrows. **[3]**

[Total: 23 marks]

Section B

Answer **one** question from this section.

4 Phenolphthalein, a type of triarylmethane dye, is a common indicator used in acid-base titrations.



Phenolphthalein

In its uncharged form, aqueous phenolphthalein is colourless. At pH of 8.2 and above, both phenol groups are deprotonated to form a pink solution.

(a) The pK_b for trimethylamine, $(CH_3)_3N$, at 25 °C is 4.19.

(i) Trimethylamine can behave as a Lewis base. Use the reaction of trimethylamine with aluminium chloride to illustrate this behaviour, writing the equation for the reaction that occurs. **[1]**

(ii) Calculate the pH of an aqueous solution of 0.20 mol dm^{-3} trimethylamine solution. **[1]**

(iii) Calculate the pH of the resulting solution when 10 cm^3 of 0.20 mol dm^{-3} trimethylamine solution and 5 cm^3 of 0.10 mol dm^{-3} HC*l* solution are mixed. **[2]**

(iv) Calculate the pH of the resultant solution when 20 cm^3 of 0.10 mol dm^{-3} HC*l* solution is added to 10 cm^3 of 0.20 mol dm^{-3} trimethylamine solution. **[2]**

(v) Explain why phenolphthalein would not be a suitable indicator for the titration of trimethylamine with HC*l*. **[1]**

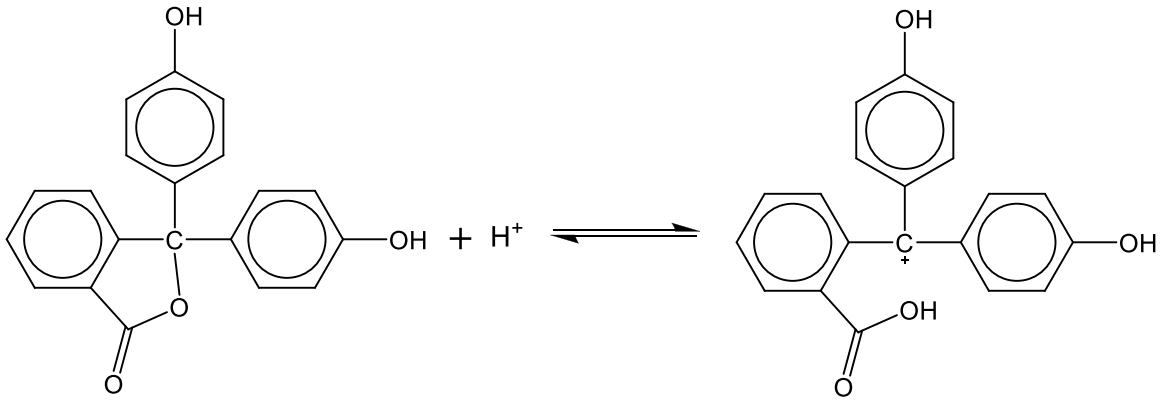
(vi) Methylamine has a pK_b of 3.36. Suggest a reason for the difference in basicity between methylamine and trimethylamine. **[1]**

(b) Draw the structural formula of the product formed when phenolphthalein reacts with each of the following reagents:

(i) excess Br_2 in the presence of A*l*Br_3. **[2]**

(ii) sodium hydroxide with heat. **[2]**

(c) Under extremely acidic conditions (pH < 0), phenolphthalein can be protonated to form an orange solution. This is an endothermic process.



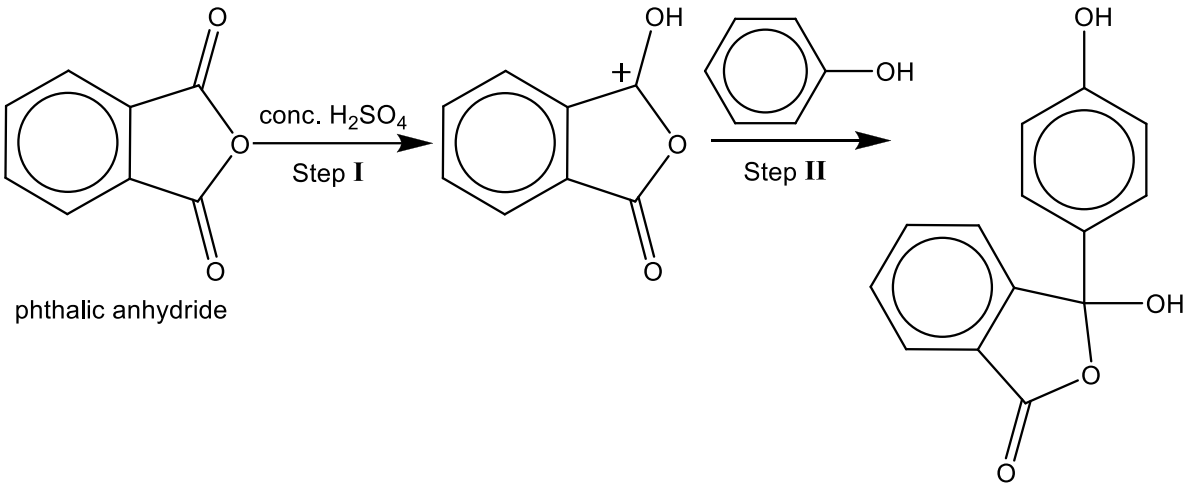
$\Delta H > 0$

Use Le Chatelier's Principle to explain the following observations.

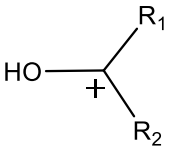
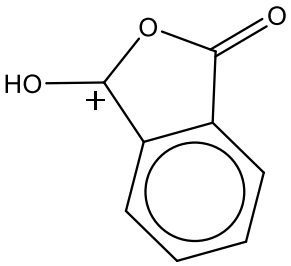
(i) An aqueous solution of phenolphthalein changed from colourless to orange when concentrated sulfuric acid was added to it. **[1]**

(ii) A solution of orange phenolphthalein solution was placed in an ice bath and turned colourless. **[1]**

(d) Part of the process in synthesising phenolphthalein involves the reaction of phthalic anhydride according to the reaction scheme below.

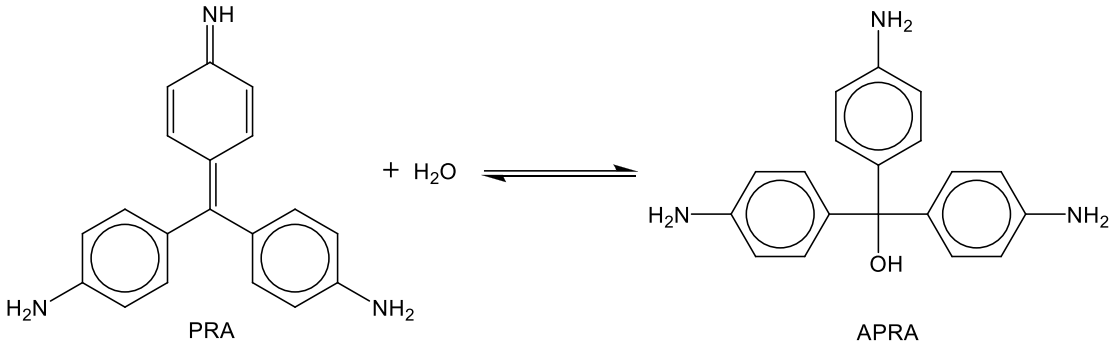


(i) Name and describe the type of mechanism in Step **II**.

You may use  to represent 

[3]

(e) Pararosaniline (PRA), another triarylmethane dye, reacts with water to form acidified pararosaniline (APRA).



0.0040 mol of PRA was dissolved in 25.0 cm^3 of water and the solution allowed to reach equilibrium. After equilibrium was reached, the concentration of APRA was found to be 0.10 mol dm^{-3}.

Write an expression for K_c for the equilibrium above, and use the data given to calculate its value. You can assume that $[H_2O]$ = 55.5 mol dm^{-3} throughout. **[3]**

[Total: 20 marks]

5 Manganese is a highly abundant transition metal in the Earth's crust.

(a) The atomic radii of transition elements is relatively invariant. Explain. **[2]**

(b) Manganese sulfate, $MnSO_4$, is often added to soils to promote plant growth as manganese is an important trace element crucial to photosynthesis and chloroplast formation.

Data concerning $MnSO_4$ at 298 K, are given in the table below.

Enthalpy change of formation $MnSO_4$ / kJ mol^{-1}	−1365
Enthalpy change of hydration of Mn^{2+} / kJ mol^{-1}	−1851
Enthalpy change of hydration of SO_4^{2-}/ kJ mol^{-1}	−1004
Lattice energy of $MnSO_4$ / kJ mol^{-1}	−2747

(i) Define the term *standard enthalpy change of solution*. **[1]**

(ii) Calculate the enthalpy change of solution of $MnSO_4$ at 298 K. **[1]**

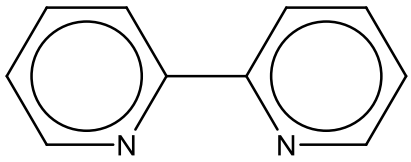
(iii) Using your answer in **(b)(ii)**, calculate the amount of heat evolved when 0.005 mol of $MnSO_4$ is dissolved in 60.0 cm^3 of water at 298 K. Hence, determine the final temperature of the solution.
(You may assume that the specific heat capacity of water is 4.18 J g^{-1} K^{-1}) **[2]**

(c) To promote plant growth, 0.0530 mol dm^{-3} $MnSO_4$ solution is added to the soil. In addition, the pH of the soil must be carefully controlled. The pH of the soil cannot exceed 6.5, because it would cause the precipitation of solid manganese (II) hydroxide, which would prevent the plants from absorbing the necessary amount of manganese.

(i) Using the above information, calculate the K_{sp} of manganese (II) hydroxide. **[2]**

(ii) While the pH of the soil cannot exceed 6.5 in order to promote manganese intake in plants, it cannot fall too low either. Suggest a reason. **[1]**

(d) Manganese can also form complexes. One such complex is $[Mn(C_{10}H_8N_2)_3]^{2+}$, where $C_{10}H_8N_2$ is the bipyridine molecule. Bipyridine acts as a bidentate ligand and has the structure shown below.



Bipyridine

(i) Describe and explain the features of the bipyridine molecule that enable it to act as a ***bidentate*** ligand. Hence, state the type of bond formed between the ligand and the central manganese ion. **[2]**

(ii) State the shape of the $[Mn(C_{10}H_8N_2)_3]^{2+}$ complex and draw its structure. **[2]**

(e) Compound **A** has the molecular formula $C_{10}H_{13}Cl$. It reacts with NaOH under aqueous conditions and heat to form **B**, $C_{10}H_{14}O$. **A** does not react with aqueous Br_2.

B does not react with hot acidified potassium dichromate. **B** reacts with hot acidified potassium manganate to form **C**, $C_{10}H_{12}O_3$.

In the presence of concentrated sulfuric acid, **C** reacts to form a sweet smelling compound **D**, $C_{10}H_8O_2$.

Deduce the structures of **A** – **D**, and explain the chemistry of the reactions described. **[7]**

[Total: 20 marks]

END OF PAPER