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.

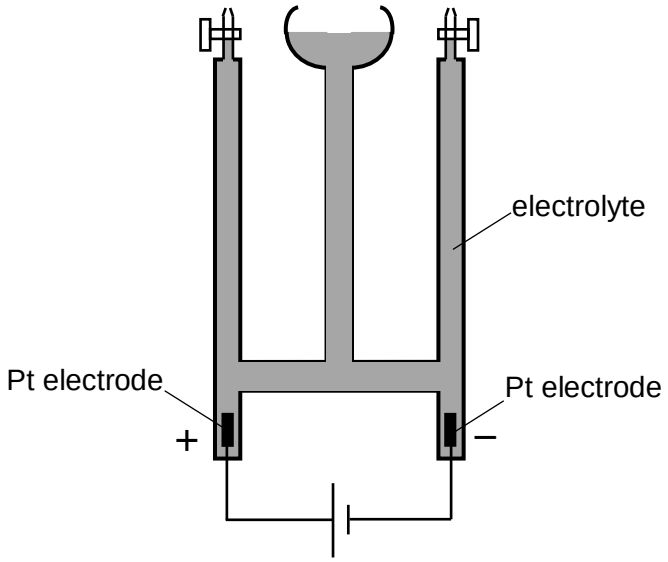
This document consists of **14** printed pages.

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]**

Anode (+): $2Cl^- \longrightarrow Cl_2 + 2e$

Greenish-yellow gas was evolved at the anode.

Cathode (-): $Fe^{3+} + e \longrightarrow Fe^{2+}$

The yellow solution turned green

(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 $E^{\ominus}$ data. **[2]**

Anode (+): $2H_2O \longrightarrow O_2 + 4H^+ + 4e$ (equation not required)

Colourless gas is evolved

the **$E°(O_2/H_2O)$ is +1.23V** which is **more negative** (less positive) / **preferentially oxidised** compared to $E°(Cl_2/ Cl^-)$ = +1.36V.

(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]**

Br_2

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

Cathode: $2H_2O + 2e \longrightarrow H_2 + 2OH^-$

Comments:

- Many students chose the SHE equation. This is not correct as H+ was not mentioned to be present.

(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]**

$3Br_2 + 6OH^- \longrightarrow 5Br^- + BrO_3^- + 3H_2O$

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

Add Br_2 (aq).

For KC*l*, orange Br_2 is not decolourised.

For KI, orange solution of Br_2 turns brown.

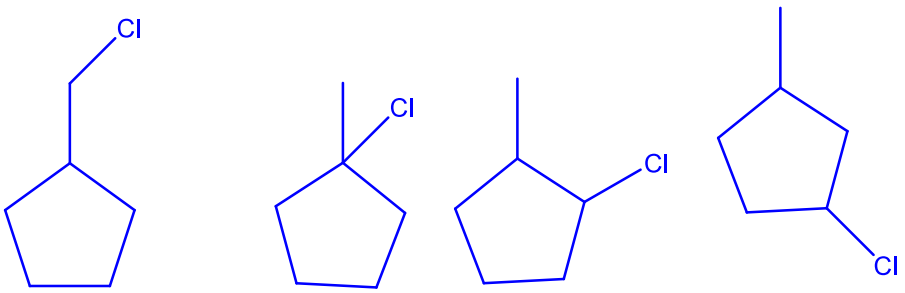
$2I^- + Br_2 \rightarrow I_2 + 2Br^-$

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

Down the group, **size of halogen increases**, leading to **less effective orbital overlap** between H and X.

Bond energy of H – X decreases / **H-X bond is longer and weaker** and is easily broken. Thus, **thermal stability of hydrogen halides decreases** down the group.

(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]**



3 : 1 : 4 : 4

(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]**

$SiCl_4$ has energetically available vacant orbitals to accept lone pair of electrons from H_2O and undergo complete hydrolysis.

$SiCl_4(l) + 2H_2O(l) \rightarrow SiO_2(s) + 4HCl(aq)$

SiO_2 is an acidic oxide and reacts with basic/ionic NaOH.

$SiO_2(s) + 2NaOH\ (conc.) \rightarrow Na_2SiO_3(aq) + H_2O(l)$

SiO_2 is a giant covalent structure with strong covalent bonds, requiring a lot of energy to overcome/break, and hence does not reacts with / not soluble in water.

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

Bond energy is the enthalpy change to break one mole of Cl-Cl bonds in gaseous state.

OR

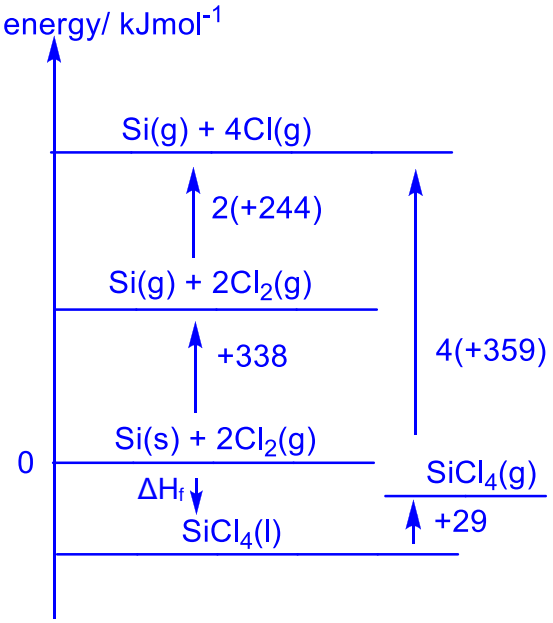
$Cl_2(g) \rightarrow 2Cl(g)$

(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}



ΔH_f = +338 + 2(244) – 4(359) – (29) = -639 kJmol^{-1}

[Total: 21 marks]

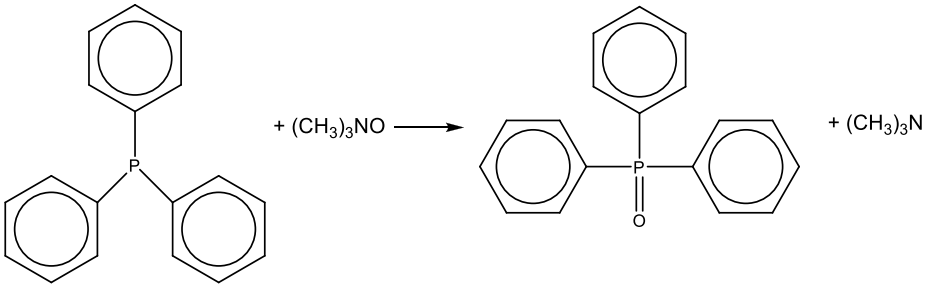
2 (a) Phosphorus-containing compounds can react in various ways: as an acid, as a base, as an electrophile, as a nucleophile, as an oxidising agent and as a reducing agent.

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]**

Acid . donate proton (or H^+) to the water molecule.

(ii)



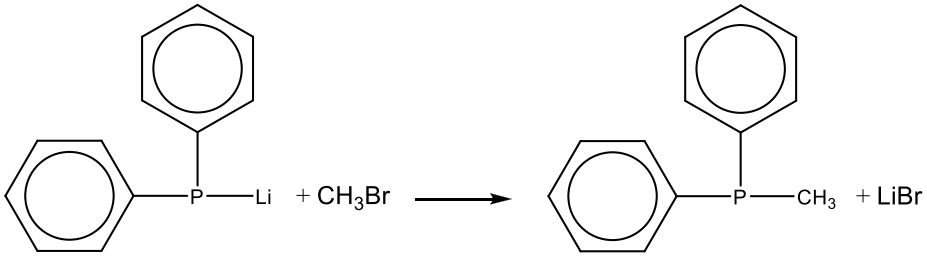
[1]

Reducing agent.

It was oxidised due to the addition of O or Oxidation state of P decreased from +3 to +5 OR

$(CH_3)_3NO$ was reduced since there was a loss of O or Oxidation state of N decreased from -1 to –3

(iii)



[1]

Nucleophile.

The lone pair of electrons on the P attacks the electron deficient C of CH_3Br via nucleophilic substitution.

(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]**

The carbonyl carbon of acyl chloride is bonded to 2 electronegative O and Cl making it highly electron deficient, while the carbon of the alkyl chloride is only bonded to Cl. Hence, acyl chloride is more susceptible to the attack of nucleophiles (water).

(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]**

Aqueous 2-chloropropanoyl chloride is more acidic than aqueous propanoic acid. 2-chloropropanoyl chloride hydrolyses fully in water to form a carboxylic acid and HCl which is a strong acid which dissociates fully in water. Propanoic acid dissociates partially in water.

OR

$CH_3CHClCOCl + H_2O \longrightarrow CH_3CHClCOOH + H^+ + Cl^-$

$CH_3CH_2COOH + H_2O \rightleftharpoons CH_3CH_2COO^- + H_3O^+$

(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

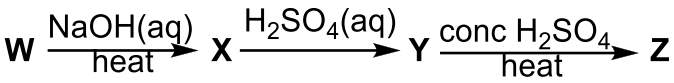


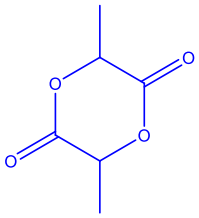
Fig. 2.1

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

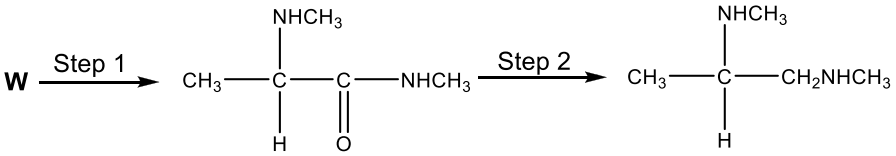
X: $CH_3CH(OH)CO_2^-Na^+$

Y: $CH_3CH(OH)CO_2H$

Z:



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



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

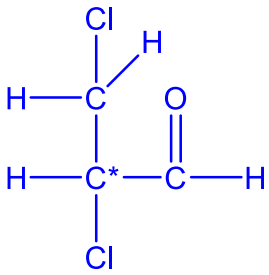
Step 1: (excess) CH_3NH_2, heat

Step 2: $LiAlH_4$, dry ether

(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 range can be used to distinguish 2-chloropropanoyl chloride from propanoic acid. **[1]**

2-chloropropanoyl chloride will have an absorption at 700–800cm^{-1} but propanoic acid would not have.

OR

Propanoic acid will have an absorption at 1210–1440cm^{-1} but 2-chloropropanoyl chloride would not have.

OR

Propanoic acid will have an absorption at 3580–3650cm^{-1} but 2-chloropropanoyl chloride would not have.

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

$\Delta G = \Delta H - T\Delta S$

ΔH is positive and ΔS will be positive as more gaseous molecules formed [1]. Hence, a high temperature is required such that $|T\Delta S| > |\Delta H|$ so $\Delta G < 0$ [1]

[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]**

Enantiomerism

Any of the following 2 explanations

- the mentioning of two non–superimposable mirror images
- explanation in terms of diagram illustrating non–superimposable enantiomer

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

Either

Different enantiomers interact differently with the chiral molecules in the human body

OR

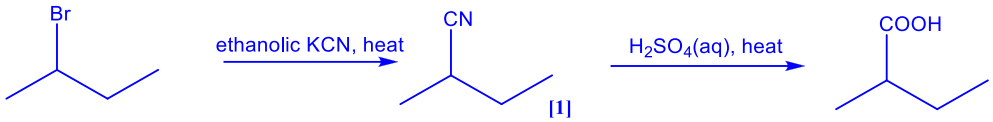
Different enantiomers have different biological properties

(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]**

Step 1: alcoholic KCN, heat

Step 2: aqueous H_2SO_4, heat

Intermediate: $CH_3CH(CN)CH_2CH_3$



Allow for any strong acid solutions (e.g. dil HC*l*)

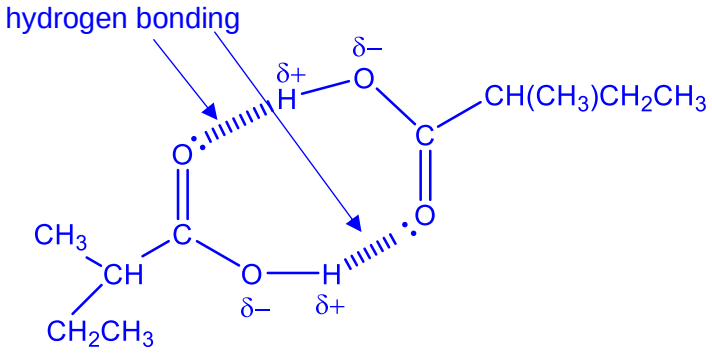
(c) Safety regulations set by many countries state that a factory would be fined, if stinky smelling compounds reached unsafe levels. The factory would have to stop production and undergo cleansing.

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]**

2–methylbutanoic acid is a polar covalent molecule with hydrogen bonding between its molecules.



(ii) 2–methylbutanoic acid has a relatively low boiling point of 176 °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 °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]**

$\ln P = \frac{59100}{8.31}\left(\frac{1}{273 + 176} - \frac{1}{273 + 30.2}\right)$

$P = 4.92 \times 10^{-4}$ atm

(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]

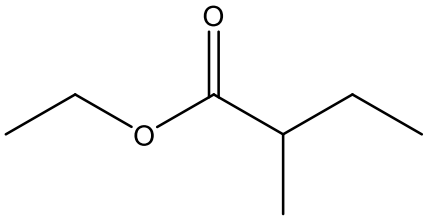
Mole fraction of the odorous 2–methylbutanoic acid

$= \frac{1}{2}\left(\frac{4.92 \times 10^{-4}}{1}\right) \times 10^{6}$

= 246 ppm **[1]**

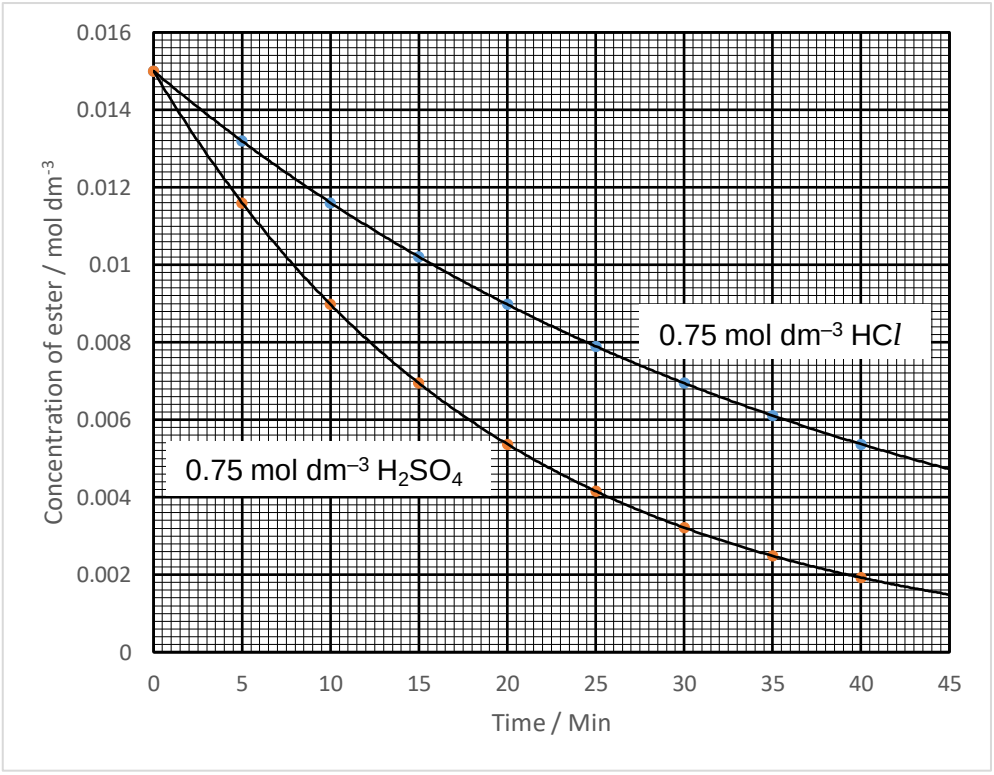
No, the factory would not be fined.

(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.



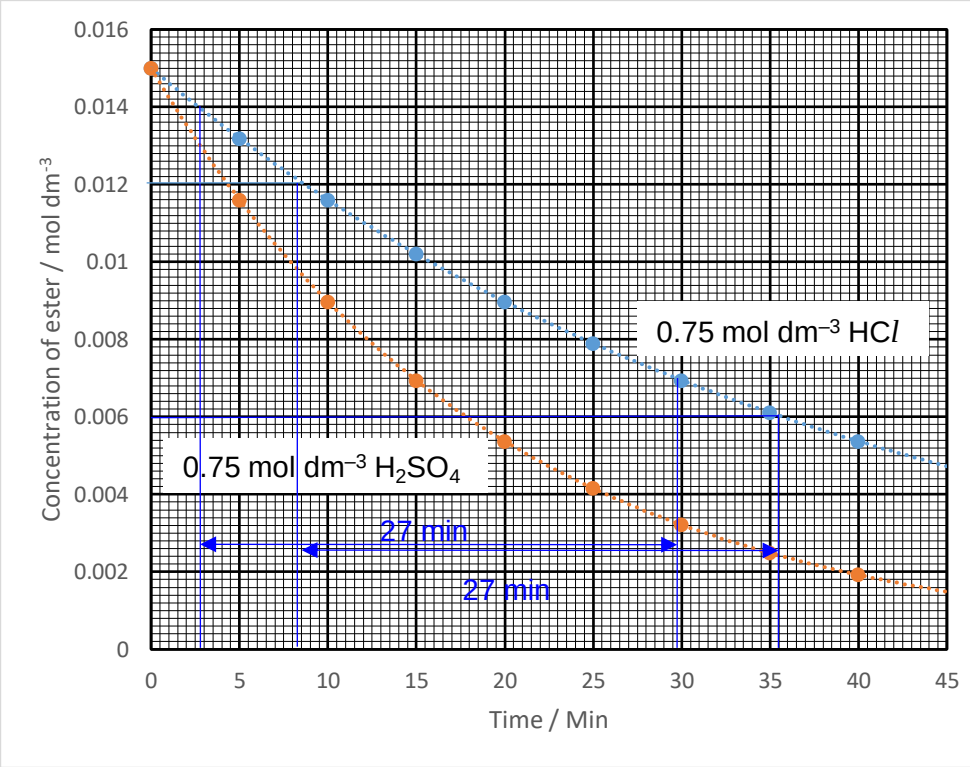
ethyl 2-methylbutanoate

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.

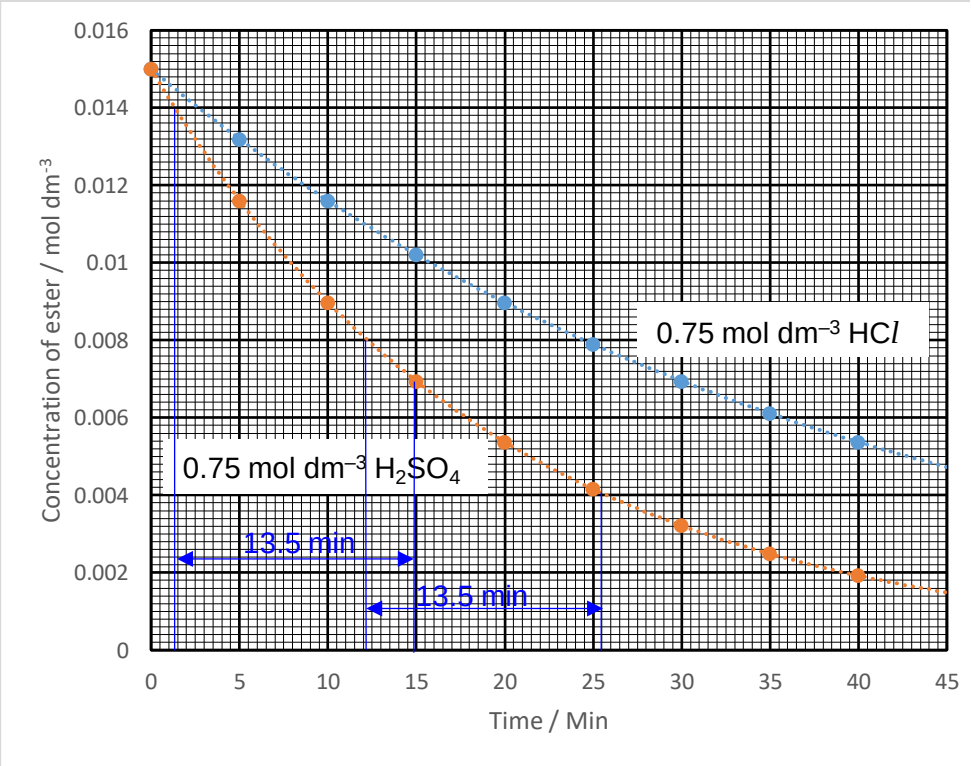


(i) Using the graphs above, deduce the order of reaction with respect to [H^+] and [ester]. Hence, write the rate equation of the hydrolysis of the ester, ethyl 2–methylbutananoate. **[3]**

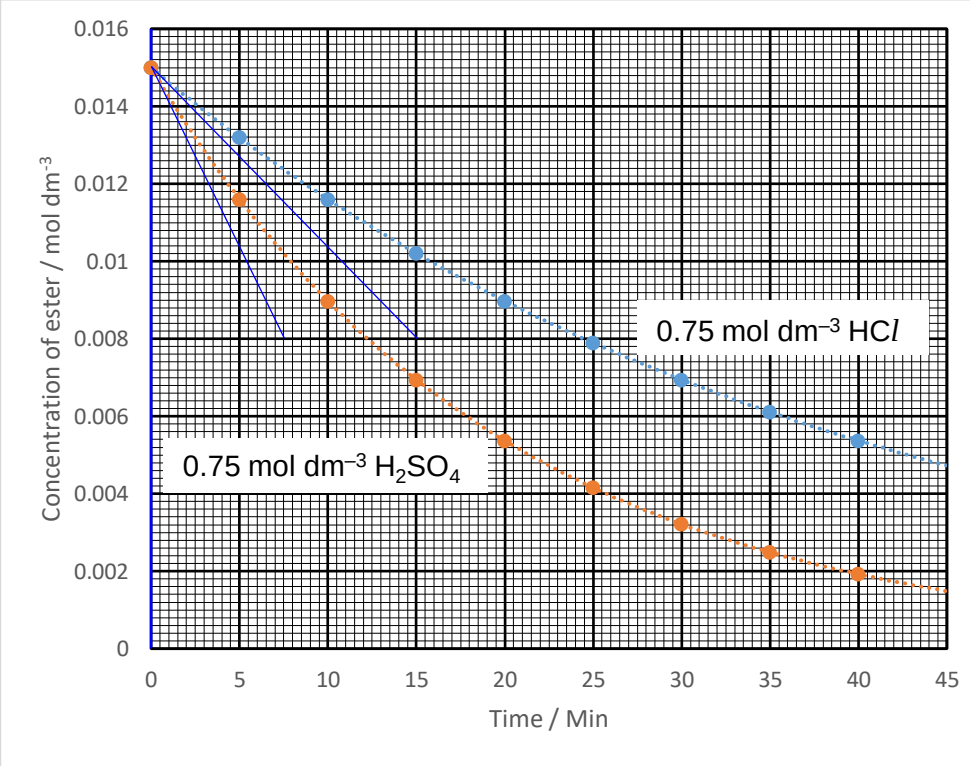
Half-life drawings for HC*l* curve.



Half-life drawings for H_2SO_4 curve.



Gradients of the lines



Change in concentration of ester = 0.007 mol dm^{-3}

Time taken for HC*l* curve = 15 min

Time taken for H_2SO_4 curve = 7.5 min

Rate for HC*l* curve = 4.67×10^{-4} mol dm^{-3} min^{-1}

Rate for H_2SO_4 curve = 9.33×10^{-4} mol dm^{-3} min^{-1}

Half life of line using HC*l* is 27 minutes, and half life of line using H_2SO_4 is 13.5 minutes. Order of reaction with respect to [ester] is 1.

Half life of the 2 lines decrease to half when $[H^+]$ was doubled, order of reaction with respect to $[H^+]$ is 1.

rate = $k[H^+][ester]$

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

$k = \frac{\ln 2}{t_{1/2}[H^+]}$

$= \frac{\ln 2}{27(0.75)}$ (values used here must be correct, part (i) $t_{1/2}$)

$= 0.0342$ [1] $mol^{-1}\ dm^3\ min^{-1}$ (may also use $t_{1/2}$ for H_2SO_4)

If student calculates k' = 0.0257 min^{-1}

Can use initial rates from one experiment – ecf from gradient in (i)

Rate $= k[H^+][Ester]$

$4.67 \times 10^{-4} = k(0.75)(0.015)$ – using HCl values

$k = 0.0415\ mol^{-1}\ dm^3\ min^{-1}$

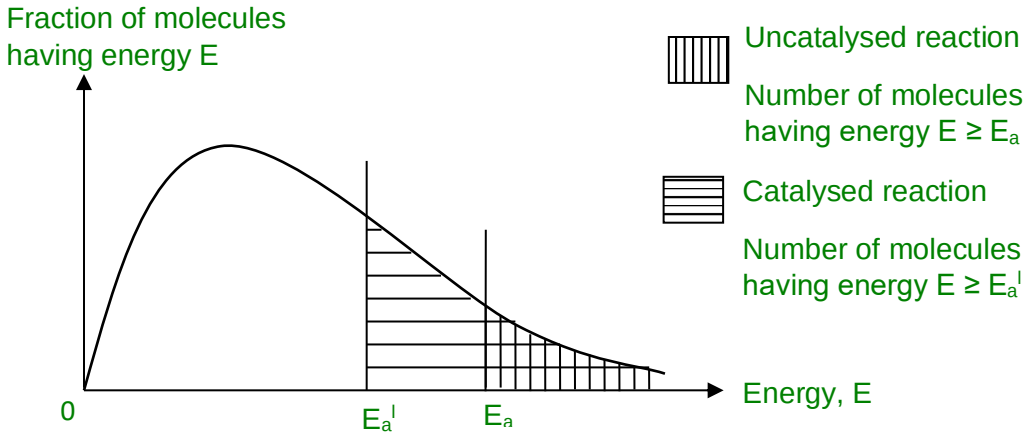
OR

$9.33 \times 10^{-4} = k(1.5)(0.015)$ – using H_2SO_4 values

$k = 0.0415\ mol^{-1}\ dm^3\ min^{-1}$

(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]**



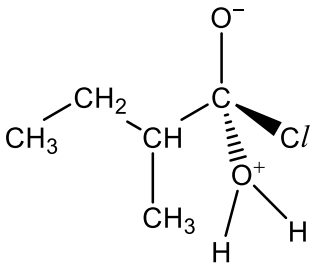
With the absence of the catalyst, the activation energy was larger than the catalysed reaction pathway. The proportion of particles with energy equal to or greater than the activation energy is smaller.[1] The frequency of effective collisions decreases and hence the rate constant decreases[1].

(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**.



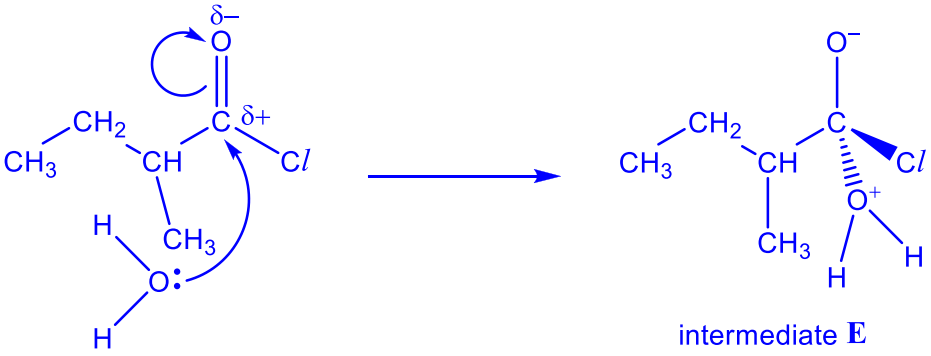
intermediate **E**

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.

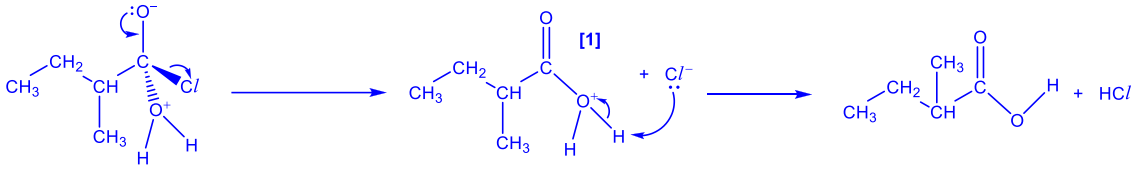
Outline the mechanism for this reaction, given that intermediate **E** is formed after the first stage. Show any relevant lone pairs, dipoles and charges, and indicate the movement of electron pairs with curly arrows. **[3]**

First stage



intermediate **E**

Second stage

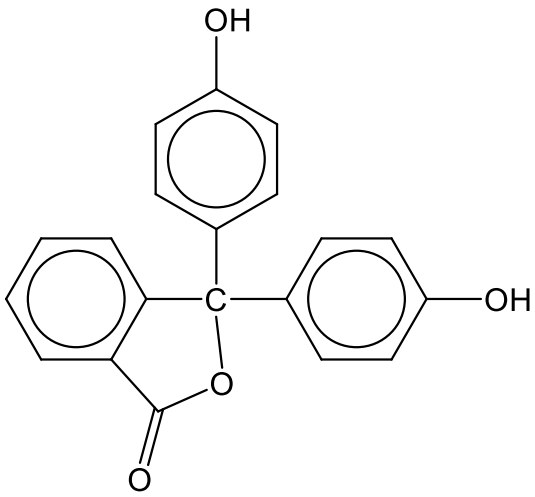


[Total: 23 marks]

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]**

$(CH_3)_3N + AlCl_3 \rightarrow (CH_3)_3N–AlCl_3$

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

$K_b = 10^{-4.19} = 6.46 \times 10^{-5}$ mol dm^{-3}

$[OH^-] = \sqrt{6.46 \times 10^{-5} \times 0.2} = 3.59 \times 10^{-3}$ mol dm^{-3}

pOH = 2.44, pH = 11.56

(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]**

Amount of trimethylamine remaining = $2 \times 10^{-3} – 5 \times 10^{-4} = 1.5 \times 10^{-3}$ mol

Amount of salt formed = 5×10^{-4} mol

$pOH = pK_b + \lg [salt]/[base] = 4.19 + \lg \left(\left[\frac{5 \times 10^{-4}}{\frac{15}{1000}}\right] / \left[\frac{1.5 \times 10^{-3}}{\frac{15}{1000}}\right]\right) = 3.71$

pH = 10.29

(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]**

Amt of salt formed = 2×10^{-3} mol

[salt] = $2 \times 10^{-3} / (10+20) = 0.0667$ mol dm^{-3}

[conj. Acid] = [salt] = 0.0667 mol dm^{-3}

K_a of conj acid = $K_w/K_b = 1.55 \times 10^{-10}$ mol dm^{-3}

$[H^+] = \sqrt{1.55 \times 10^{-10} \times 0.0667} = 3.21 \times 10^{-6}$

pH = 5.49

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

The working range of phenolphthalein does not coincide with the equivalence point pH / region of rapid pH change in the titration curve / vertical section of the titration curve.

OR

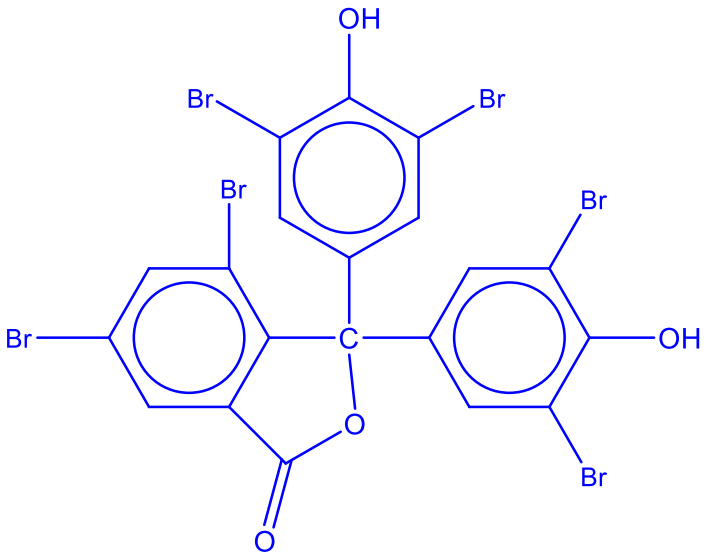
Phenolphthalein will turn colourless at pH 8.2 before the equivalence point is reached.

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

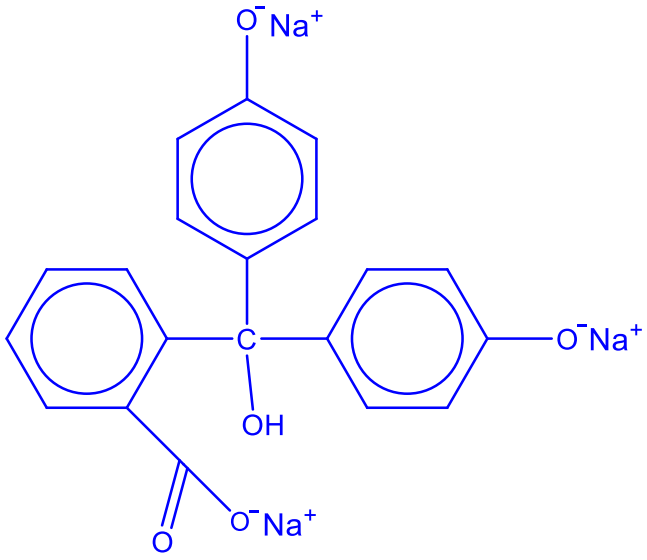
Trimethylamine is less basic than methylamine due to the steric effects of the 3 bulky methyl groups, hence it cannot accept protons easily.

(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]**

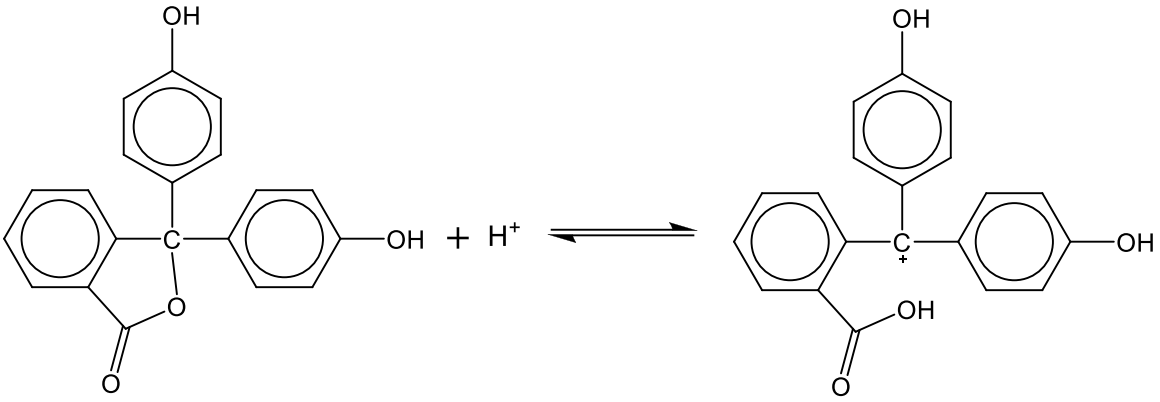


(ii) sodium hydroxide with heat. **[2]**



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

+



Colourless Orange

$\Delta H > 0$

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

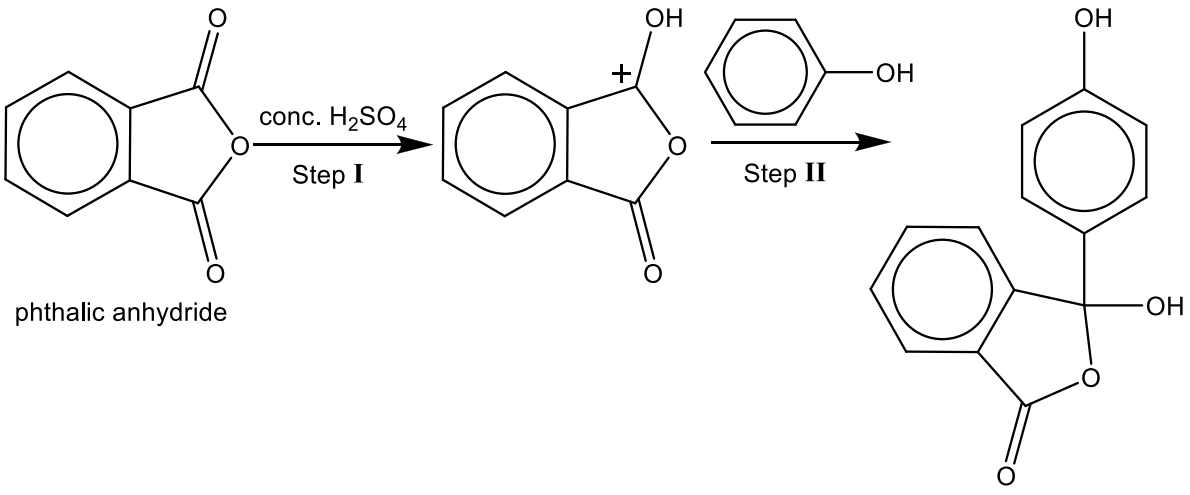
(i) An aqueous solution of phenolphthalein changed from colourless to orange when concentrated sulfuric acid was added to it. **[1]**

The addition of concentrated sulfuric acid increases the concentration of H^+. By LCP, the position of equilibrium will shift right to reduce the concentration of H^+ ions, thus forming more orange phenolphthalein.

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

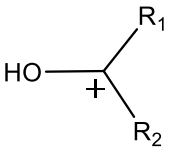
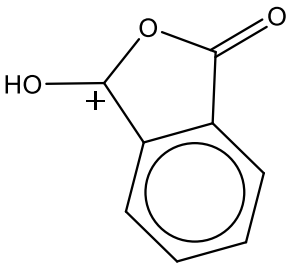
When a solution of phenolphthalein was cooled, the position of equilibrium will shift left to produce heat by favouring the exothermic backwards reaction. Hence more colourless phenolphthalein is formed and the solution turns colourless.

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

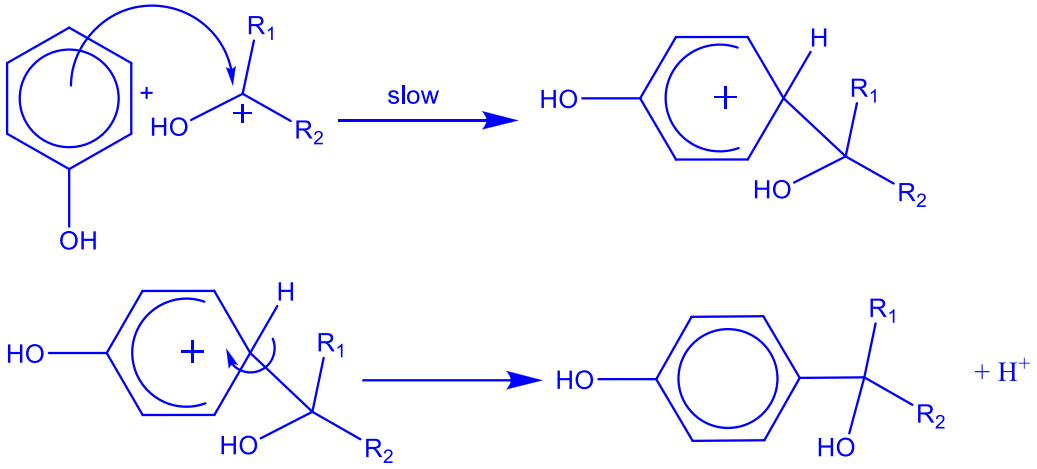


phthalic anhydride

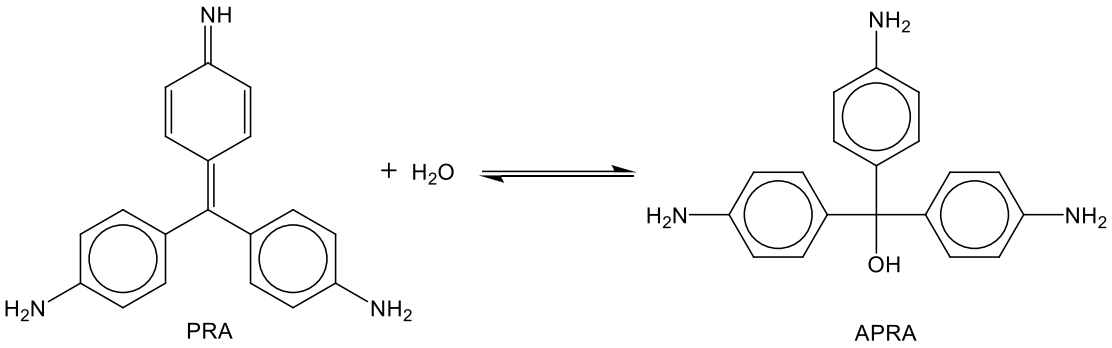
(i) Name and describe the type of mechanism in Step **II**.

You may use  to represent  **[3]**

Electrophilic substitution



(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]**

$K_c = [APRA] / \{[PRA][H_2O]\}$

$[PRA]_{initial} = 0.004 / 25 \times 1000 = 0.16$ mol dm^{-3}

	PRA	+	H_2O <->	APRA
Initial / mol dm^{-3}	0.16		55.5	0
Change / mol dm^{-3}	-0.10		0	+0.10
Final / mol dm^{-3}	0.06		55.5	0.10

K_c = 0.10 / (0.06 x 55.5) = 0.0300 mol^{-1} dm^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]**

Electrons are added to **inner** 3d subshell. The inner 3d electrons **effectively shield** the outer 4s electrons from the nucleus, **cancelling the effect** of the increasing nuclear charge due to increasing proton number across the period.

Thus, the **increase** in effective nuclear charge becomes **insignificant**.

Hence atomic radii remains relatively invariant.

(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]**

The enthalpy change when **one mole of a substance is completely dissolved in a large excess of water** to form an infinitely dilute solution at **298 K and 1 bar**.

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

$\Delta H_{soln}^{\ominus} = \Delta H_{hyd}^{\ominus} - L.E. = (-1851 - 1004) - (-2747) = -108$ kJ mol^{-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]**

Heat evolved = 0.005 x 108 = 0.54 kJ

Q = mcΔT

$\Delta T = Q/mc = (0.54 \times 10^3)/(60 \times 4.18) = 2.15$ °C / K

T = 298 + 2.15 = 300 K (3s.f.)

(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]**

pOH = 14 – 6.5 = 7.5

$[OH^-] = 3.16 \times 10^{-8}$ mol dm^{-3}

$Mn(OH)_2(s) \rightarrow Mn^{2+}(aq) + 2OH^-(aq)$

$K_{sp} = [Mn^{2+}][OH^-]^2 = (0.0530) \times (3.16 \times 10^{-8})^2 = 5.29 \times 10^{-17}$ mol^3 dm^{-9}

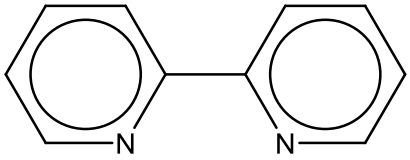
(ii) While the pH of the soil cannot exceed 6.5 in order to promote manganese intake in plants, it cannot fall too low either. Suggest a reason. **[1]**

The soil would be too acidic and may damage the roots of plants.

OR

Too much manganese would be absorbed and it is biologically toxic when in excess amounts.

(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.



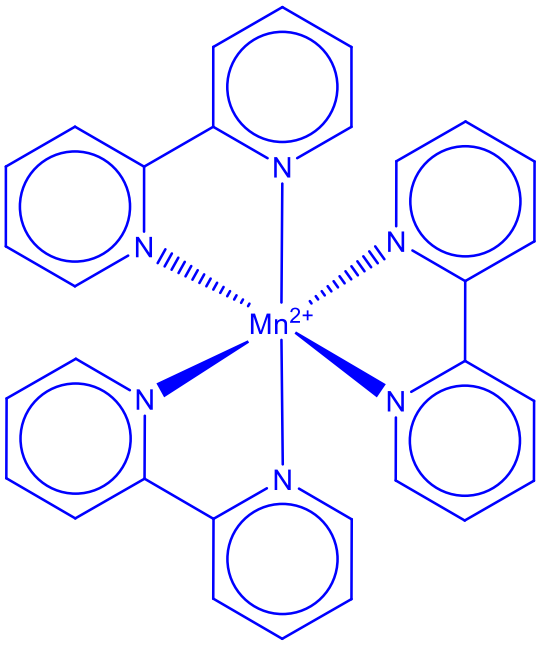
Bipyridine

(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]**

There are two nitrogen atoms, each with a lone pair of electrons, which can be donated to vacant low-lying orbitals of the manganese ion to form 2 dative bonds.

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

Shape: Octahedral



(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**, $C_{10}H_8O_2$.

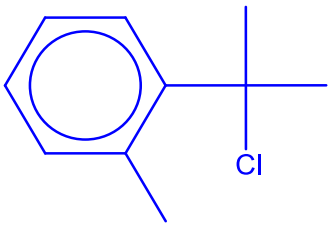
Deduce the structures of **A** – **D**, and explain the chemistry of the reactions described. **[7]**

Observations	**Deductions**
Reacts with NaOH under aqueous conditions to form B, $C_{10}H_{14}O$.	Cl is substituted by OH Nucleophilic substitution. Alcohol formed. A is alky chloride
A does not react with aqueous Br_2.	No alkene present.
B does not react with acidified potassium dichromate.	OH group cannot be oxidised, alcohol is a tertiary alcohol

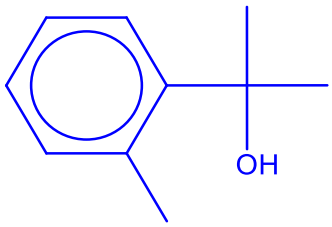
B reacts with hot acidified potassium manganate to form **C**, $C_{10}H_{12}O_3$.	Since –OH group is tertiary alcohol and cannot be oxidised, it does not react with $KMnO_4$. Hence, must be some other form of oxidation. Cannot be alkene due to earlier test. Since 2 H was lost and 2 O was added, then most likely to be side chain oxidation of CH_3 on benzene to form -COOH. Benzene ring present.
In the presence of concentrated sulfuric acid, **C** reacts to form a sweet smelling compound **D**, $C_{10}H_8O_2$.	Condensation reaction. D is an ester. Internal condensation occurred between the OH group and the COOH group. This implies the two groups must be next to each other on the benzene ring.

Structures

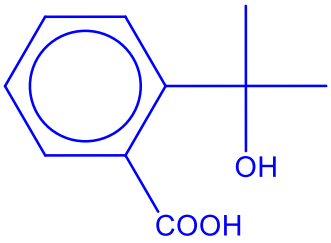
A



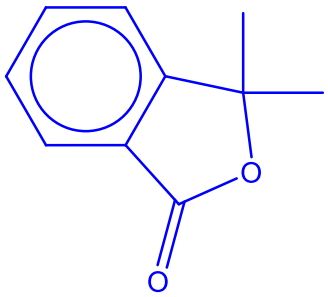
B



C



D



[Total: 20 marks]

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