TEMASEK
JUNIOR COLLEGE

CHEMISTRY (H2) **9647/03**
Paper 3 Free Response **16th September 2015**
2 hours

Candidates answer on separate paper.

Additional materials: Answer paper
Graph Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, Civics Group, Centre number and Index number in the spaces provided on the cover page and on all the work you hand in.

Write in dark blue or black pen on both sides of the paper.

You may use a HB pencil for any diagrams, graphs or rough working.

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

Answer any **four** questions.

A Data Booklet is provided.

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

You are reminded of the need for good English and clear presentation in your answers.

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 20 printed pages.

1 (a) The halogens and their compounds are useful laboratory reagents and have many applications.

(i) Describe the trend in the colour of the halogens.

• Increasing intensity or darker down the group.
• C*l*$_2$ (g) yellowy-green; Br$_2$ (l) reddish-brown; I$_2$ (s) black

(ii) Explain, in terms of structure and bonding, the trend in the volatility of the halogens.

- **The halogens have <u>simple molecular structure</u> and <u>weak van der Waals</u> forces of attraction between molecules.**
- **Down the group, M_r of X_2 increases, giving a larger electron-cloud, which can be more easily distorted, resulting in stronger van der Waals forces hence requiring more energy to overcome. The volatility decreases from C*l*$_2$ to I$_2$.**

(iii) Halogens are oxidising agents.
By quoting appropriate values from the *Data Booklet*, explain the reactions of the halogens with sodium thiosulfate. Write balanced equations for the reactions.

[6]

½C*l*$_2$ + e	⇌	**C*l*$^-$**	**E = +1.36 V**
½Br$_2$ + e	⇌	**Br$^-$**	**E = +1.07 V**
½I$_2$ + e	⇌	**I$^-$**	**E = +0.54 V**

- *(With quoting of Data)* **<u>Oxidising power of the halogens decreases down the group</u> as can be seen from the less positive E value, hence iodine can only oxidise thiosulfate to tetrathionate.**

[•Bonus mark]

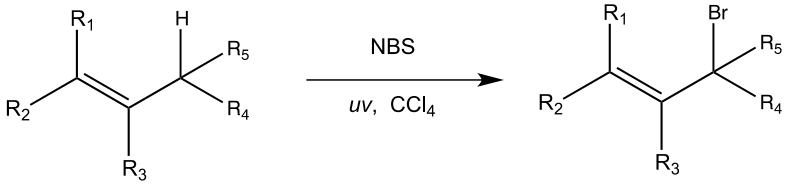
$4C\mathit{l}_2 + S_2O_3^{2-} + 5H_2O \rightarrow 8C\mathit{l}^- + 2SO_4^{2-} + 10H^+$

$4Br_2 + S_2O_3^{2-} + 5H_2O \rightarrow 8Br^- + 2SO_4^{2-} + 10H^+$

- **$I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-$**

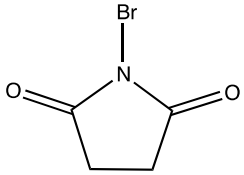
(b) Hydrocarbons react with halogens under different conditions to give a wide range of organic compounds.

The Wohl-Ziegler bromination is shown below.



In this reaction, a bromine atom is incorporated into a molecule at the position next to a carbon-carbon double bond.

The reagent used for the reaction is *N*-bromosuccinimide (NBS).

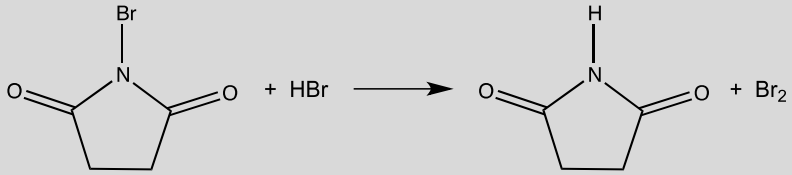


N-bromosuccinimide (NBS)

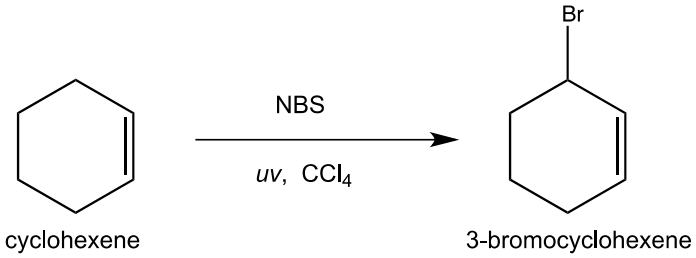
The catalytically active species is bromine, which is present in trace amount in NBS samples. Subsequent amount of bromine is generated in situ when NBS reacts with hydrogen bromide.

(i) NBS reacts with hydrogen bromide in a 1:1 molar ratio to produce bromine and succinimide as the only products. Write a balanced equation for the reaction.

•



In one such reaction, cyclohexene is converted to 3-bromocyclohexene using NBS.



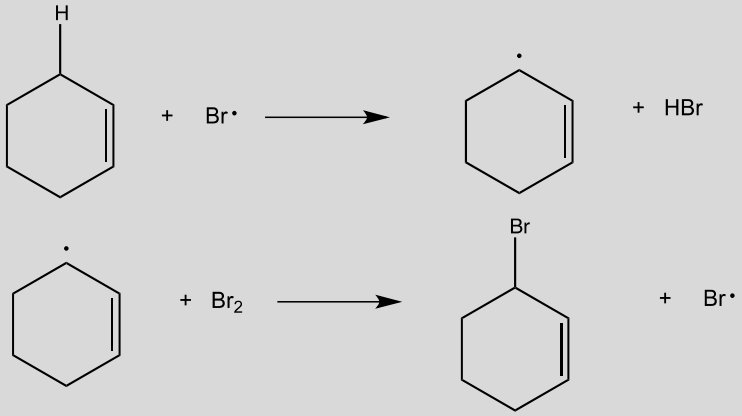
(ii) Describe the mechanism for the formation of 3-bromocyclohexene from cyclohexene and bromine.

- **Free radical substitution**
- •• **Mechanism**

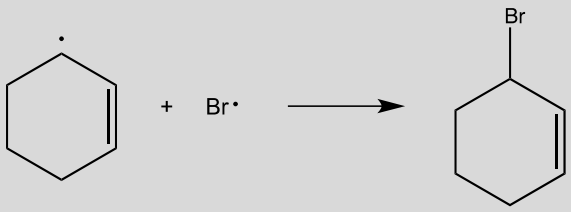
Initiation

$Br_2 \longrightarrow 2Br^{\bullet}$

Propagation



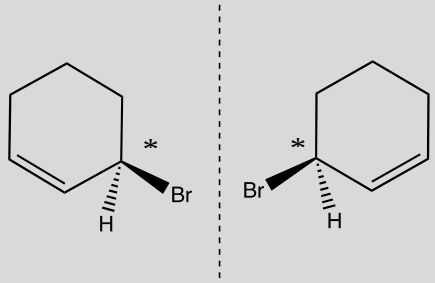
Termination



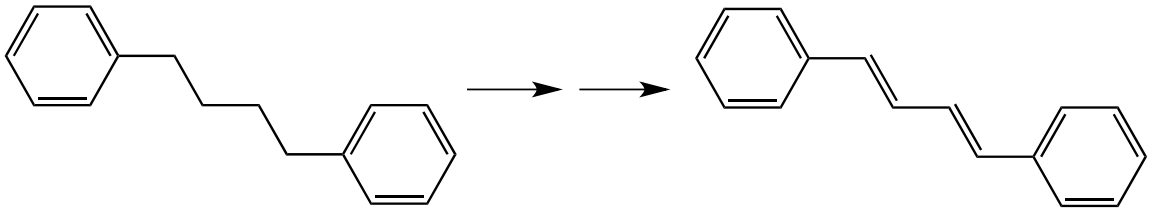
$2Br^{\bullet} \longrightarrow Br_2$

(iii) State the type(s) of stereoisomerism that could be exhibited by 3-bromocyclohexene and draw the isomers.

- **Optical isomerism**
-

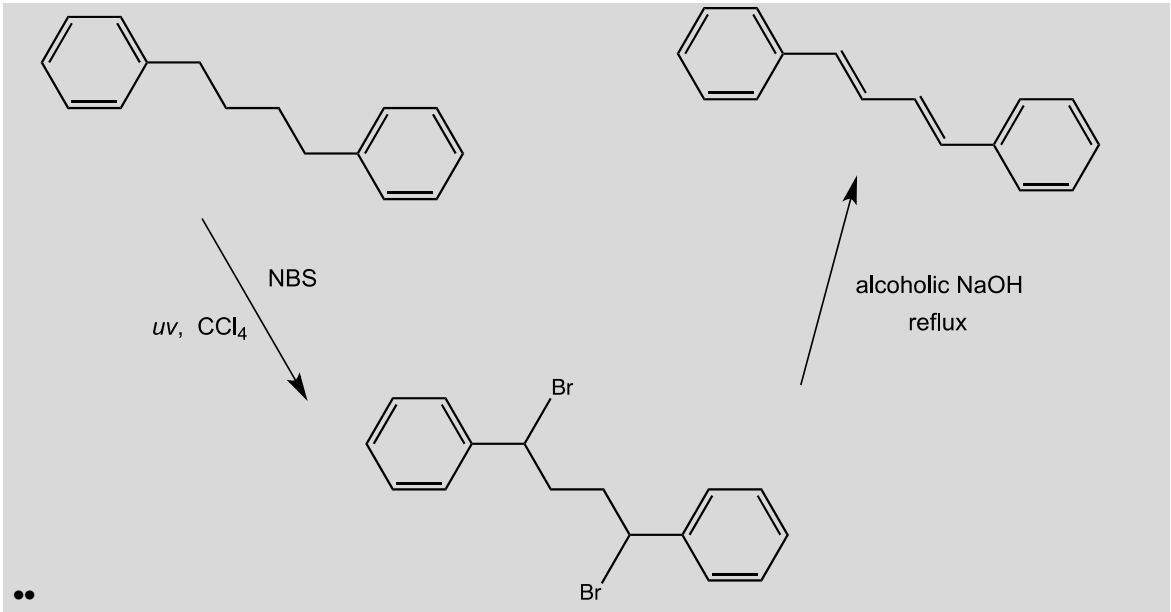


In another reaction, compound **A** can be converted to compound **B** in two steps. One of the steps is the Wohl-Ziegler bromination.



compound **A** compound **B**

(iv) Suggest suitable reagents and conditions and the structural formula for the intermediate formed.

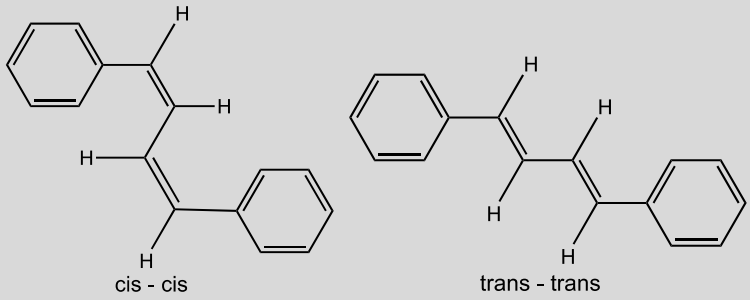


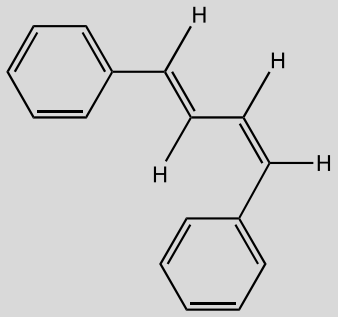
••

(v) State the total number of stereoisomers of compound **B** and draw the isomers.

[10]

•• 3





(c) The mineral fluorspar, which is mainly calcium fluoride, is a major source of fluorine.

The first stage in liberating the fluorine from calcium fluoride is to grind this compound up and react it with concentrated sulfuric acid. The products are hydrogen fluoride and calcium sulfate.

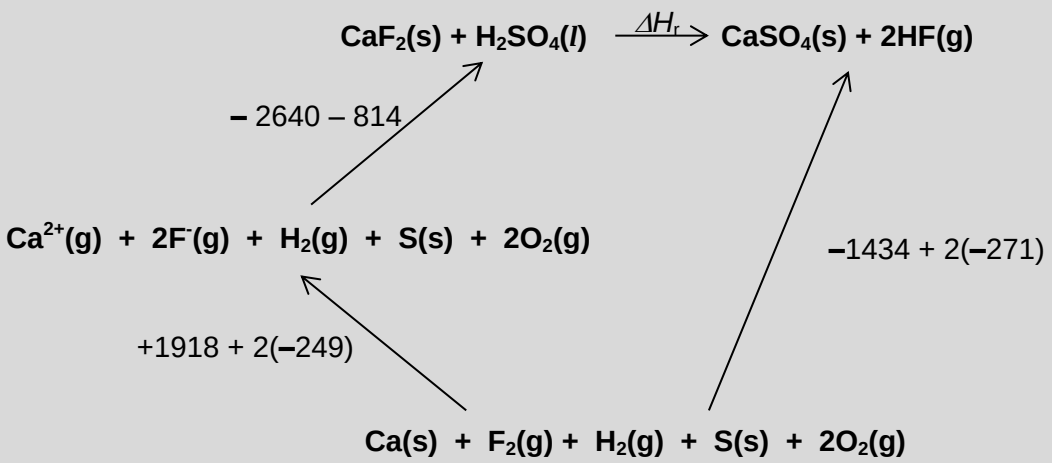
(i) Define the *standard enthalpy change of formation,* $\Delta H_f^{\ominus}$, of a substance.

- **It is the enthalpy change when one mole of the substance is formed from its constituent elements in their standard states at 298 K and 1 atm.**

(ii) Using the following data of ΔH_f and lattice energy, construct an energy cycle to calculate the enthalpy change for the reaction between calcium fluoride and concentrated sulfuric acid.

ΔH_f [HF(g)] = -271 kJ mol^{-1}
ΔH_f [$CaSO_4$(s)] = -1434 kJ mol^{-1}
ΔH_f [Ca^{2+}(g)] = +1918 kJ mol^{-1}
ΔH_f [F^-(g)] = -249 kJ mol^{-1}
L.E. [CaF_2(s)] = -2640 kJ mol^{-1}
ΔH_f [H_2SO_4(*l*)] = -814 kJ mol^{-1}

[4]

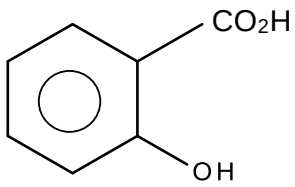


By Hess' Law,
ΔH_r – 2640 + 1918 + 2(–249) + (–814) = –1434 + 2(–271)
ΔH_r = +58 kJ mol^{-1}

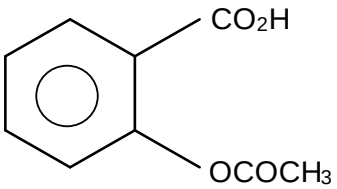
•Balanced equation for the reaction
•working
•Answer

[Total: 20]

2 **(a)** In folk medicine, willow bark teas were used as headache remedies and other tonics. Its analgesic property is due to salicylic acid. Nowadays, salicylic acid is administered in the form of aspirin which is less irritating to the stomach.



Salicylic acid



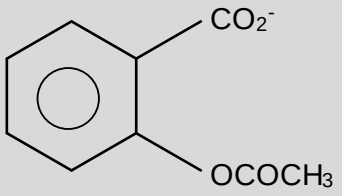
Aspirin

(i) In the preparation of aspirin from salicylic acid, water is added to precipitate aspirin. Explain why aspirin is not soluble in water.

Both aspirin and water have <u>simple molecular structures</u>.
Aspirin has both <u>van der Waals interaction and hydrogen bonding</u> between its molecules. Water has <u>hydrogen bonding</u> between its molecules. The <u>energy released from the hydrogen bonding</u> formed between aspirin and water molecules <u>release insufficient energy to overcome the van der Waals</u> <u>interaction and hydrogen bonding</u> between aspirin molecules and the <u>hydrogen bonding</u> between water molecules. Therefore, aspirin is insoluble in water.
• 1m – explanation
• 1m – bonding and structure

(ii) Aspirin has a pK_a of 3.48 while benzoic acid has a pK_a of 4.2. Explain the difference in their pK_a values.

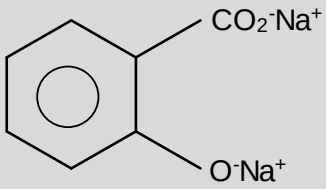
• As Aspirin has a lower pK_a than benzoic acid, aspirin is a <u>stronger acid</u>.
• Aspirin has an <u>electron-withdrawing $-OCOCH_3$ group</u> which further <u>disperses</u>



<u>the negative charge on</u> , making it <u>more stable</u> than benzoate.

(iii) Draw the structure of the 2 organic compounds formed when aspirin is heated with NaOH(aq).

•



• $CH_3CO_2^-Na^+$

(iv)

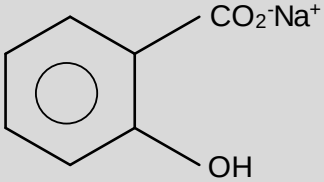
Acid	K_{a1} / mol dm^{-3}	K_{a2} / mol dm^{-3}
Salicylic acid	1.07×10^{-3}	1.82×10^{-14}
Ethanoic acid	1.80×10^{-5}	-
Carbonic acid	4.50×10^{-7}	-

Using the information above, suggest the organic products formed if CO_2 is bubbled through the mixture formed in **(a)(iii)**.

[8]

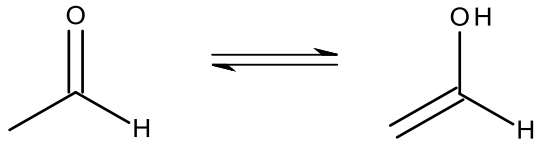
Carbon dioxide dissolves in water to form carbonic acid. As <u>carbonic acid is stronger than the phenolic group in salicylic acid but weaker than carboxylic acid group in salicylic acid and ethanoic acid</u>, the products formed are

•



and • $CH_3CO_2^-Na^+$.

(b) Tautomers are isomers with the same carbon skeleton and differ only in the positions of hydrogen atoms and electrons. Carbonyl compounds such as ethanal exhibits keto-enol tautomerisation as shown below.



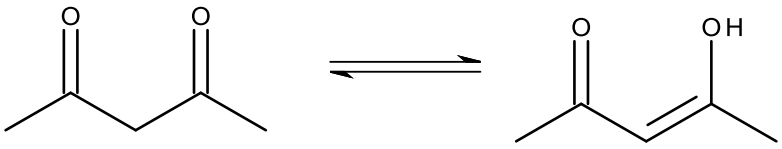
keto enol

Although these 2 isomers exist in equilibrium, the enol form is less stable than the keto form.

(i) Using data from the Data Booklet, calculate the enthalpy change for the conversion of the keto to enol.

Bonds broken: C=O, C-H, C-C
Bonds formed: C=C, C-O, O-H
• ΔH = +740 + 410 + 350 – 610 – 360 – 460
= • + 70 kJ mol^{-1}

(ii) β-diketones such as pentan-2,4-dione also exhibits tautomerisation.

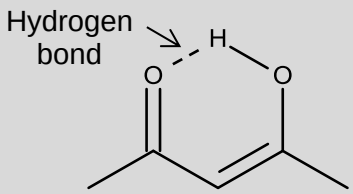


keto enol

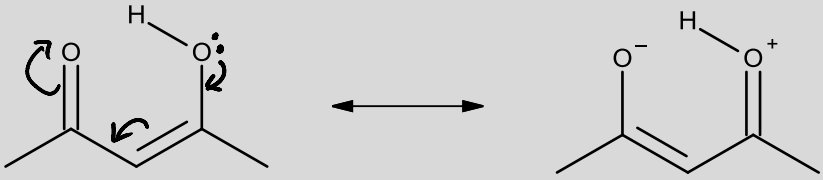
It is found that the enol form is more stable than the keto form. Suggest a reason for this.

[3]

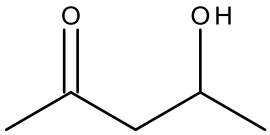
• Intramolecular hydrogen bonding stabilises the enol form.



Alternative answer:
The enol is stabilised by the resonance of the conjugated double bonds (C=C and C=O)

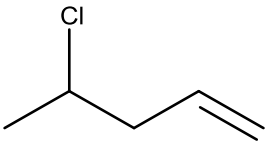


(c) 4-hydroxypentan-2-one gives off a fresh herb smell and has the following structure.



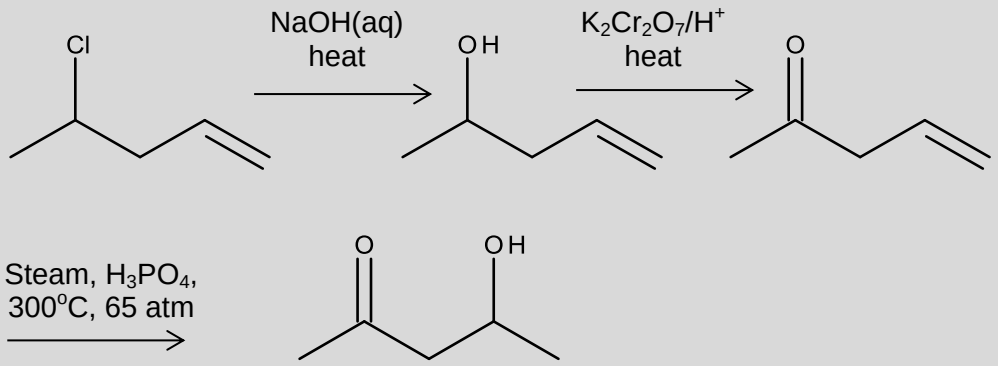
4-hydroxypentan-2-one

(i) 4-hydroxypentan-2-one can be synthesised from 4-chloropent-1-ene in 3 steps.



4-chloropent-1-ene

Suggest the reagents and conditions used in each step and the structural formula for the intermediate formed.



4-hydroxypentan-2-one

5 correct: 3m, 3-4 correct: 2m, 1-2 correct: 1m

Note: Oxidation cannot be the last step and cannot use $KMnO_4$ for oxidation which would otherwise oxidise the alkene. For hydration, also accept cold conc. H_2SO_4, followed by heating with water at 80°C.

Alternative route: hydrate first, oxidise then hydrolysis of RX. In this route, can use $KMnO_4$.

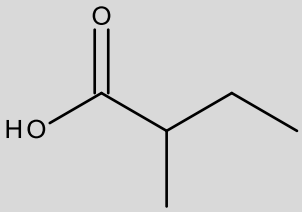
(ii) Compound **R**, $C_6H_{12}O_2$, is neutral and does not decolourise $Br_2(aq)$. When compound **R** is heated with NaOH(aq), one of the products obtained is HCO_2Na.

Upon refluxing compound **R** with acidified $KMnO_4$**,** compound **S** and carbon dioxide gas were formed. Compound **S** is an isomer of 4-hydroxypentan-2-one. It is chiral and gives effervescence with $Na_2CO_3(s)$.

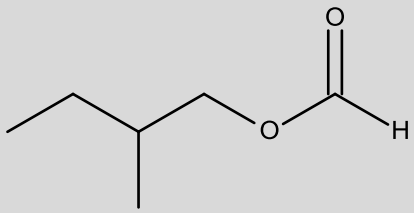
Suggest the structures of compounds **R** and **S**, explaining your answer.

[9]

● R is neutral and undergoes alkaline <u>hydrolysis with NaOH(aq)</u>, it contains an <u>ester group</u>.
● As R does not undergo electrophilic addition with Br_2(aq), <u>C=C is absent</u>.
● After refluxing R with acidified $KMnO_4$, R undergoes <u>hydrolysis and oxidation</u> to form compound S and CO_2 gas, R is an <u>ester.</u>
● S has a <u>chiral carbon with 4 different groups, has no plane of symmetry and non-superimposable mirror images</u>.
● S has a <u>–COOH (carboxylic acid group)</u> as it gives effervescence with Na_2CO_3(s).



● S is



● R is
[1 bonus mark; 7 marking points]

[Total: 20]

3 (a) Acid rain has harmful effects on aquatic animals, plants and infrastructure. It contains sulfuric acid formed from sulfur trioxide. Sulfur trioxide is produced upon atmospheric oxidation of sulfur dioxide from coal burning.

(i) Write an equation for the formation of sulfuric acid from sulfur trioxide.

- **$SO_3 + H_2O \rightarrow H_2SO_4$**

Even before the existence of acid rain, unpolluted rain water was slightly acidic due to dissolved CO_2. The solubility of *pure* carbon dioxide gas in water is 88 cm^3 per 100 cm^3 of water under room conditions.

(ii) Given that air contains 0.033% by volume of carbon dioxide, calculate the concentration in mol dm^{-3} of carbon dioxide dissolved in unpolluted rain water.

If air contains 0.033% by volume of carbon dioxide,

- **Volume of CO_2 dissolved per 100 cm^3 water = $\frac{0.033}{100} \times 88 = 0.0290$ cm^3**
- **No. of moles of CO_2 dissolved per 100 cm^3 water**
  = $\frac{0.0290}{24000} = 1.21 \times 10^{-6}$ mol
- **Concentration of dissolved CO_2 in water = $\frac{1.21 \times 10^{-6}}{\frac{100}{1000}} = 1.21 \times 10^{-5}$ mol dm^{-3}**

Dissolved carbon dioxide forms carbonic acid, H_2CO_3, in water. The acid dissociation constant of carbonic acid is given below.

$$H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \qquad K_{a_1} = 4.5 \times 10^{-7} \text{ mol dm}^{-3}$$

(iii) Using your answers in **(a)(ii)**, calculate the pH of unpolluted rain water (ignore the effect of K_{a_2} on the pH).

Dissolved CO_2 forms carbonic acid, H_2CO_3.
$CO_2 + H_2O \rightarrow H_2CO_3$
$H_2CO_3 \rightleftharpoons HCO_3^- + H^+$

$K_a = \frac{[H^+]^2}{c}$
$[H^+] = \sqrt{4.5 \times 10^{-7} \times 1.21 \times 10^{-5}} = 2.33 \times 10^{-6}$ mol dm^{-3}
- **pH = -lg (2.33×10^{-6}) = 5.63**

Some fishes and shellfish die at pH values of 4.5 to 5.0. Lakes with limestone-rich soil can maintain a relatively stable pH even when acid rain falls due to the HCO_3^-/CO_3^{2-} buffer system.

(iv) With aid of an equation, explain how lakes with limestone-rich soil maintain a relatively stable pH.

- **$CO_3^{2-} + H^+ \rightarrow HCO_3^-$**
- **The base, CO_3^{2-} (from limestone), reacts with H^+ to form HCO_3^-. <u>Negligible changes in pH as H^+ ions are removed</u>.**

An environmental chemist needs a carbonate buffer of pH 10.0 to study the effects of acid rain on limestone-rich soils.

(v) The acid dissociation constant, K_a, of HCO_3^- is 4.7×10^{-11} mol dm^{-3}. Calculate the mass of solid Na_2CO_3 the chemist needs to add to 500 dm^3 of 0.2 moldm^{-3} $NaHCO_3$ to form a buffer of pH 10.0.

[9]

pH = pK_a + lg $\frac{[CO_3^{2-}]}{[HCO_3^-]}$
10 = -lg (4.7×10^{-11}) + lg $\frac{[CO_3^{2-}]}{0.2}$
- **$[CO_3^{2-}] = 0.0940$ mol dm^{-3}**
- **Mass of solid Na_2CO_3 = 500 x 0.094 × 106 = 4.98 kg**

Oxides and halides of Period 3 elements have many applications.

(b) A farmer intends to add a magnesium-containing compound to his farmland to correct magnesium deficiency and raise soil pH.

(i) Suggest whether the farmer should add magnesium oxide or magnesium chloride to his farmland.

- **Magnesium oxide**

(ii) Explain your answer in **(b)(i)** by describing the reactions of the compound suggested with water and acid. Write equations where appropriate and state the pH of the solution formed when the compound is dissolved in water.

[4]

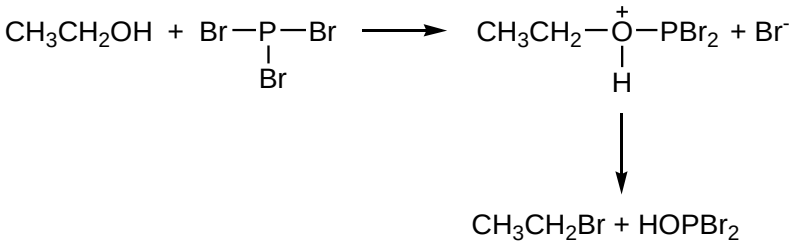
- **MgO reacts with water to a very <u>small extent</u> (or <u>almost insoluble</u> in water) due to its <u>high lattice energy</u>, forming magnesium hydroxide, $Mg(OH)_2$, which is sparingly soluble. <u>pH of solution formed is 9</u>.**

- **$MgO(s) + H_2O(l) \rightleftharpoons Mg(OH)_2(aq)$**

MgO also <u>raises pH by removing/reacting with acid</u> to form salt and water.

- **$MgO(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2O(l)$**

(c) Phosphorus tribromide can be used to synthesise bromoethane from ethanol as shown below.



(i) Name the reaction for the conversion of ethanol to bromoethane.

- **Nucleophilic substitution**

(ii) Suggest how the reactivity of ethanol is increased in the presence of PBr_3.

- **The intermediate $CH_3CH_2-\overset{+}{O}(H)-PBr_2$ formed from PBr_3 is more <u>electron-deficient</u> and susceptible to nucleophilic attack by Br^-.**

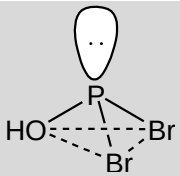
OR

- **$HOPBr_2$ is a <u>better leaving group</u> than OH^-.**

(iii) Suggest why water cannot be used as a solvent for this reaction.

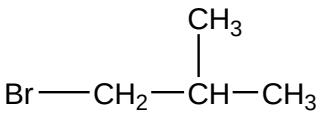
- **PBr_3 undergoes <u>hydrolysis</u> in water to give H_3PO_3 and HBr.**
  $PBr_3(s) + 3H_2O(l) \rightarrow H_3PO_3(aq) + 3HBr(aq)$

(iv) Draw a structure to illustrate the shape about the P atom in a molecule of the product, $HOPBr_2$. Suggest the shape about the P atom.

- 

- **Trigonal pyramidal**

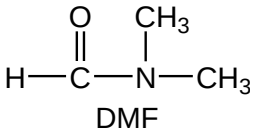
Both bromoethane and 1-bromo-2-methylpropane are primary alkyl halides that undergo S_N2 reaction with CN^- nucleophile.



1-bromo-2-methylpropane

(v) Explain the following observations.

- Bromoethane undergoes S_N2 reaction with CN^- nucleophile at a faster rate than 1-bromo-2-methylpropane.
- Both compounds undergo S_N2 reactions with CN^- at a slower rate when the solvent is ethanol, CH_3CH_2OH, compared to using DMF, as solvent.



DMF

[7]
[Total: 20]

- **The nucleophile experiences <u>less steric hindrance</u> during the S_N2 reaction with bromoethane.**
- **H on –OH group in ethanol forms <u>hydrogen bond</u> with the nucleophile CN^-, making CN^- less reactive.**

4 (a) Hydrogen sulfide is a colourless gas with a characteristic 'rotten egg' smell. It occurs naturally in crude petroleum and reacts with methane according to the following equilibrium.

$$CH_4(g) + 2H_2S(g) \rightleftharpoons CS_2(g) + 4H_2(g) \qquad \Delta H^\ominus = +232 \text{ kJ mol}^{-1}$$

(i) State and explain the effect on the number of moles of methane when the volume of the vessel is reduced at a constant temperature.

- **When the volume of vessel is reduced, the <u>pressure of the system increases</u>. By Le Chatelier's Principle, the system counteracts the change by reducing the total pressure by favouring the <u>backward reaction</u> which generates <u>less number of moles of gases</u>.**
- **Hence, the <u>number of moles of methane increases</u> (answer must come with correct explanation to gain the credit).**

(ii) Write an expression for the equilibrium constant, K_c, stating its units.

- $K_c = \frac{[CS_2][H_2]^4}{[CH_4][H_2S]^2}$
- mol^2dm^{-6}

(iii) In an experiment, 1.00 mol of CH_4, 2.00 mol of H_2S, 1.00 mol of CS_2 and 2.00 mol of H_2 are mixed in a 250 cm^3 vessel at 960 °C. The concentration of methane is found to be 5.56 mol dm^{-3} when the system reaches equilibrium. Calculate the value of K_c at 960 °C.

- **working**

	$CH_4(g)$ +	$2H_2S(g)$	$\rightleftharpoons$	$CS_2(g)$+	$4H_2(g)$
Initial conc/mol dm^{-3}	**4**	**8**		**4**	**8**
Change/ mol dm^{-3}	**+1.56**	**+3.12**		**-1.56**	**-6.24**
Equilibrium/ mol dm^{-3}	**5.56**	**11.12**		**2.44**	**1.76**

- **$K_c = 2.44 \times 1.76^4 / (5.56 \times 11.12^2) = 0.0341\ mol^2dm^{-6}$**

(iv) The equilibrium constant varies with temperature according to the van't Hoff equation:

$$\ln\frac{K_2}{K_1} = -\frac{\Delta H^{\ominus}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

where K_1 is the equilibrium constant at temperature T_1
K_2 is the equilibrium constant at temperature T_2
$\Delta H^{\ominus}$ is the enthalpy change in J mol^{-1}
R is the ideal gas constant and
T is temperature in Kelvin.

Using your answer in **(iii)**, calculate the value of equilibrium constant at 480 °C.

- **working**

$$\ln\frac{K_c}{0.0341} = -\frac{(232 \times 10^3)}{8.31}\left(\frac{1}{753} - \frac{1}{1233}\right)$$

- $K_c = 1.84 \times 10^{-8}$ mol^2dm^{-6}

(v) Hydrogen sulfide can be removed by passing it through nitric acid. 0.15 mol of H_2S was found to react with 0.10 mol of HNO_3 to give a yellow solid and an oxide of nitrogen. Determine the oxidation state of nitrogen in the oxide. Hence, write a balanced equation for the reaction of H_2S and HNO_3.

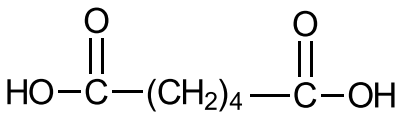
[10]

$3\ H_2S \equiv 3S \equiv 2\ HNO_3 \equiv 6e^-$

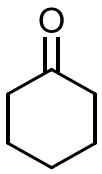
$HNO_3 \equiv 3e^-$

- **Oxidation state of nitrogen decreases from +5 in HNO_3 to <u>+2</u> in the product**
- **$3H_2S + 2HNO_3 \rightarrow 3S + 2NO + 4H_2O$**

(b) Adipic acid is one of the most important dicarboxylic acids and has a wide range of industrial applications. It is used as a monomer in the synthesis of nylon, and in the production of plasticizer and coatings.

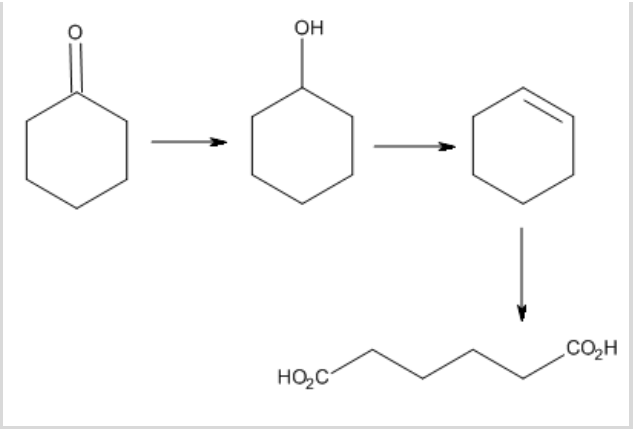


adipic acid



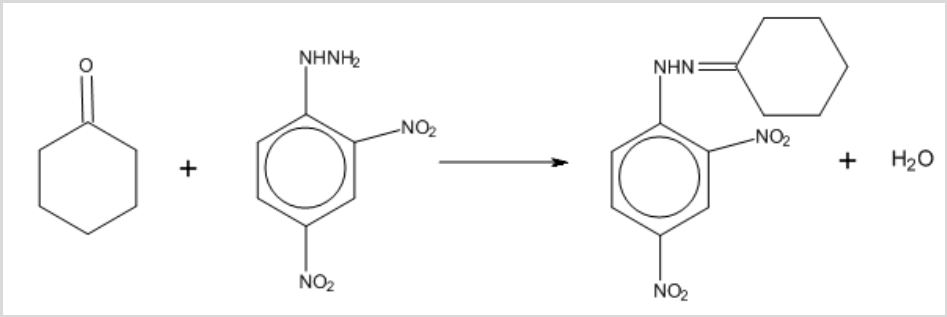
cyclohexanone

(i) Show a three-step synthetic route to obtain adipic acid from cyclohexanone. Suggest reagents and conditions you would use and show the structures of any intermediates formed.



- **LiA*l*H_4 in dry ether, rtp**
  Accept other reducing agents e.g. H_2/Ni, high temp or $NaBH_4$, alcohol, rtp
- **excess concentrated H_2SO_4, 180 °C**
- **acidic $KMnO_4$, reflux**
  [reagent & condition + intermediate = 1 mark]

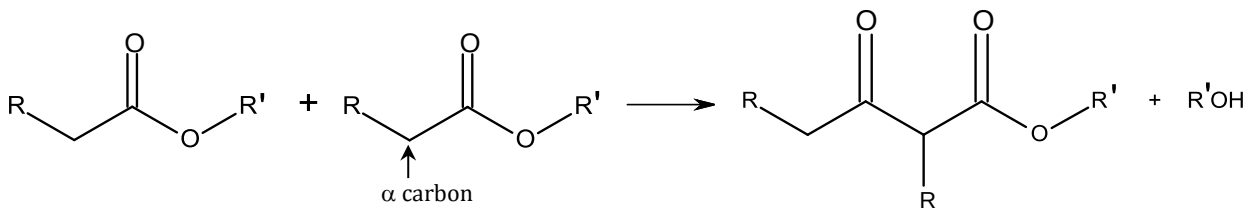
(ii) Suggest a simple chemical test to distinguish between adipic acid and cyclohexanone. State the observations and write a balanced equation for any reaction that occurs.

- **2,4-dinitrophenylhydrazine, rtp**
- **<u>Orange ppt</u> with cyclohexanone, no observable reaction with adipic acid**
- 

OR

- **Na_2CO_3 (aq), rtp**
- **<u>Effervescence</u> of CO_2 with adipic acid, no observable change with cyclohexanone**
- **HO_2C-$(CH_2)_4$-CO_2H + Na_2CO_3 → Na^+ ^-O_2C-$(CH_2)_4$-$CO_2^-Na^+$ + CO_2 + H_2O**

In the 1880s, German chemist Rainer Ludwig Claisen discovered that esters were able to react in the presence of a strong base to give a keto ester. In the first step of the mechanism, a proton is removed from the α carbon of the ester molecule.



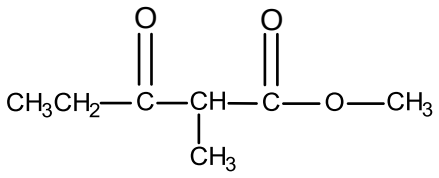
(iii) Suggest a reason why the hydrogen atom on the α carbon is more acidic than the other hydrogen atoms in the same molecule.

- **The anion formed by removal of the α-proton (hydrogen atom on carbon next to the carbonyl carbon) is stabilised by <u>delocalisation of electrons</u>, hence the H^+ is more likely to dissociate from the ester molecule.**

(iv) Name the type of reaction that has taken place between the ester molecules.

- **condensation/ nucleophilic (acyl) substitution/ nucleophilic addition followed by elimination**

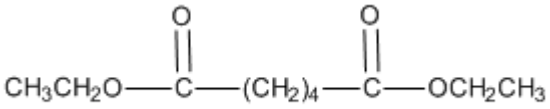
(v) Two molecules of an ester undergoes the above reaction to give methanol and the following organic product.



Suggest the structure of the ester.

- **$CH_3CH_2CO_2CH_3$**

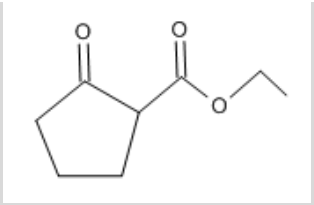
(vi) Adipic acid undergoes esterification to form diethyl adipate.



diethyl adipate

The two ester functional groups of diethyl adipate can react intramolecularly to give a cyclic product and ethanol. Draw the structure of the cyclic product.

[10]

- 

[Total: 20]

5 Aluminium chloride, $AlCl_3$, exhibits properties which differ from chlorides of other Period 3 elements. It sublimes at a relatively low temperature of 180ºC at atmospheric pressure due to the original lattice structure of $AlCl_3$ being converted into Al_2Cl_6 molecules. In the presence of excess water, aluminium chloride forms an acidic solution of pH 3 to 4.

(a) Describe and explain the reactions of aluminium chloride with excess water, writing equations where appropriate.

[2]

- **$AlCl_3$ undergoes <u>hydration</u> in water and dissolves to give an aqueous solution.**
  $AlCl_3 + 6H_2O \longrightarrow [Al(H_2O)_6]^{3+} + 3Cl^-$

- **<u>Hydrolysis</u> also occurs due to the <u>high charge density of Al^{3+} ions</u>. It polarizes the water molecule and <u>weakens the O-H bond</u> of water making it easier for a H^+ ion to leave the water molecule. An acidic solution of pH = 3 – 4 is obtained.**

$[Al(H_2O)_6]^{3+} \rightleftharpoons [Al(H_2O)_5OH]^{2+} + H^+$

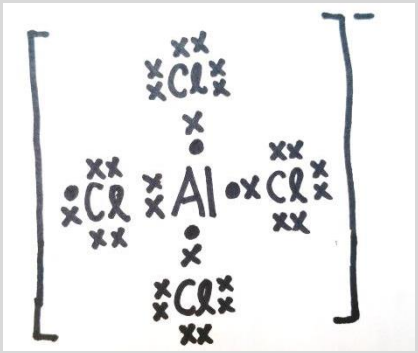
(b) Aluminium chloride reacts with sodium chloride to form sodium chloroaluminate, $NaAlCl_4$. Sodium chloroaluminate is one of the simplest compounds containing chloroaluminate anion and has a melting point of 185 ºC.

(i) Explain why sodium chloroaluminate would be formed from the above reaction, stating the type of bond that is formed during this reaction.

• Aluminium in $AlCl_3$ is electron deficient (or has vacant orbitals) as it only has 6 electrons around it and Cl^- anion has lone pairs of electrons and thus,
•dative bond is formed in the chloroaluminate anion.

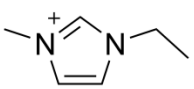
(ii) Draw the dot-and-cross diagram of chloroaluminate anion. Using the valence shell electron pair repulsion theory, state its shape and bond angle.

•1m – dot-and-cross

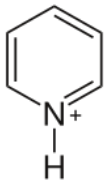


•Shape: Tetrahedral
Bond angle: 109.5º

(iii) A class of compounds called room temperature ionic liquids (RTILs) can be formed from chloroaluminate anion and organic cations such as 1-ethyl-3-methylimidazolium and pyridinium ions.



1-ethyl-3-methylimidazolium



pyridinium ion

Explain the differences in physical states between RTILs and sodium chloroaluminate in terms of bonding.

[6]

RTIL and sodium chloroaluminate are held by ionic bonds. RTIL have a lower melting point and exists as a liquid and sodium chloroaluminate exists as a solid because the •organic cation in RTIL is larger than sodium ion and thus,
•weaker ionic bonds exist between the oppositely-charged ions in RTIL as $|\text{lattice energy}| \propto \left|\frac{q_+q_-}{r_+ + r_-}\right|$.

(c) To determine the rate equation of the following chlorate-chloride reaction, an experiment was conducted using 0.000480 mol dm^{-3} of ClO_3^-, 0.1 mol dm^{-3} of Cl^- and 0.4 mol dm^{-3} of H^+.

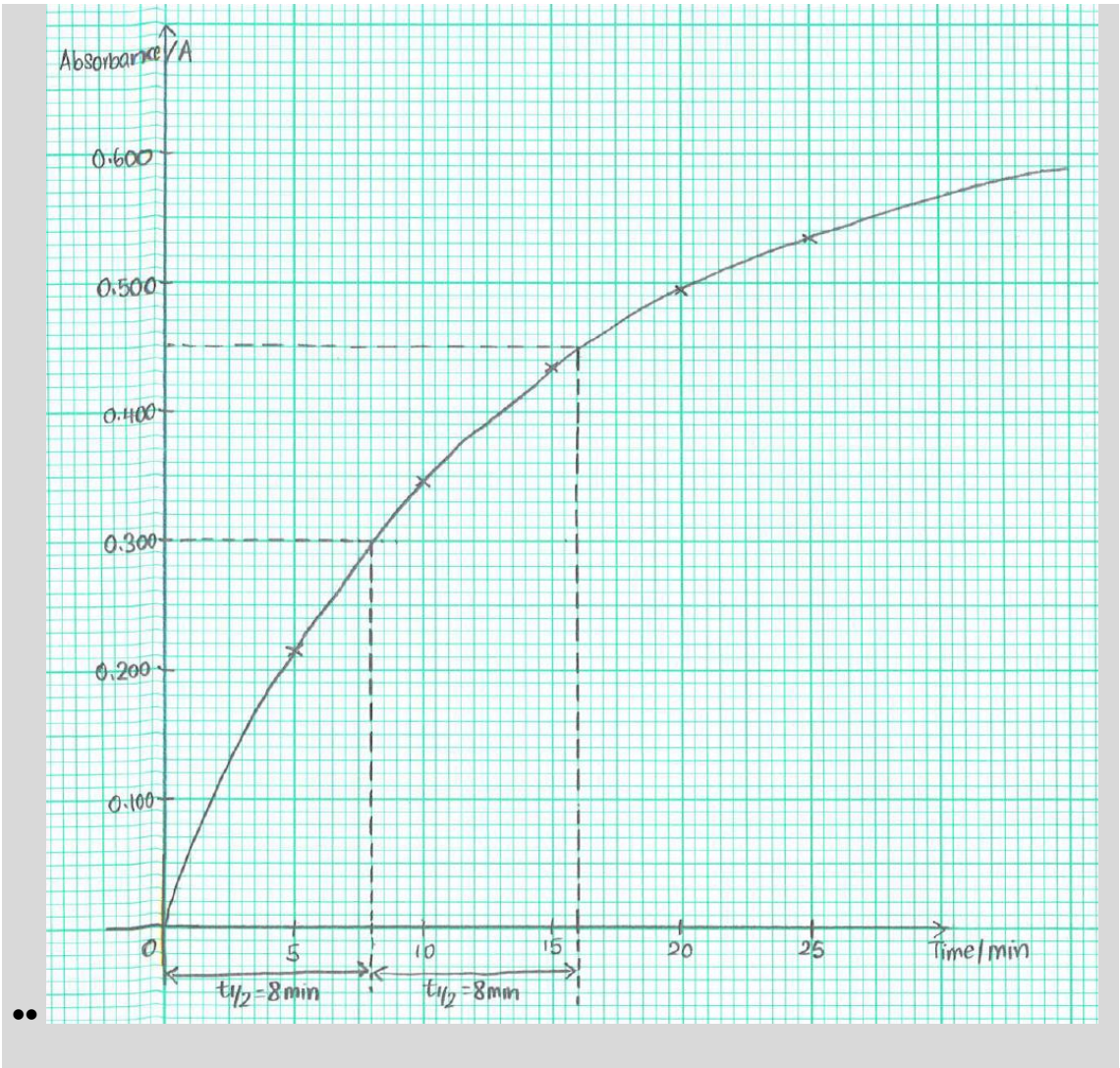
$$2ClO_3^- + 2Cl^- + 4H^+ \rightarrow Cl_2 + 2ClO_2\bullet + 2H_2O$$

At regular 5-minutes intervals, small samples of the reaction mixture were withdrawn, quenched and placed into the UV-vis spectrometer to record its absorbance value. The absorbance value corresponds to the concentration of the product $ClO_2\bullet$.

(i) The results of the above experiment were shown below.

Time/min	0	5	10	15	20	25
Absorbance/A	0.000	0.211	0.348	0.436	0.494	0.531

Plot the graph of absorbance/A against time/min.



(ii) Beer-Lambert's Law states that the absorbance values, A, is directly proportional to the concentration of absorbing species, c, as shown below. The general Beer-Lambert's Law is usually written as,

$$A = \varepsilon cl$$

where ε is the molar extinction coefficient and l is the path length, which is usually 1.0cm.

This equation can be used to calculate the absorbance value when maximum amount of ClO_2• was formed from the above chlorate-chloride reaction.
Prove that the maximum absorbance value in the above experiment is 0.600, given that ε of ClO_2• is 1250 $mol^{-1}dm^3cm^{-1}$. Show your working clearly.

Limiting reagent is ClO_3^-
$ClO_3^- \equiv ClO_2$•

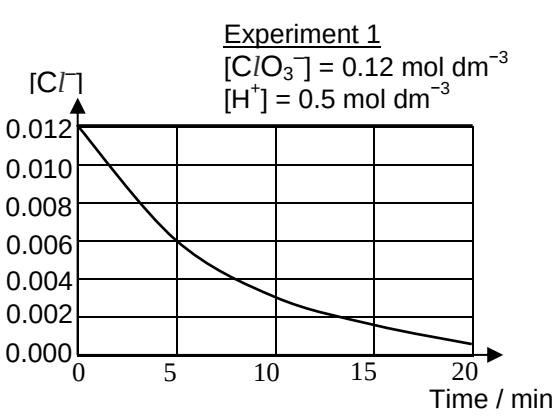
Maximum [ClO_2•] = 0.000480 $moldm^{-3}$
Applying Beer-Lambert's Law, A = εcl
•Maximum absorbance = (1250)(0.000480)(1) = 0.600 *(proven)*

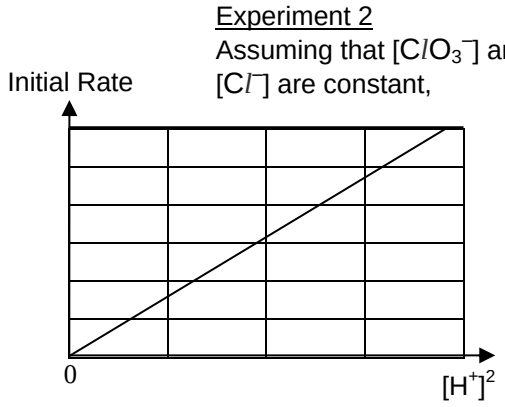
(iii) Using your graph plotted in **(c)(i)** and the information given in **(c)(ii)**, determine the half-life of the experiment and hence the order of reaction with respect to [ClO_3^-].

•1m – dotted lines to read off <u>half-life ($t_{1/2}$)</u> on the graph
•Since <u>half-life ($t_{1/2}$) is constant</u> at <u>8 min</u>, the reaction is <u>1st order with respect to [ClO_3^-].</u>

A research student carried out a series of experiments to further investigate the order of reaction with respect to [Cl^-] and [H^+] in the chlorate-chloride reaction.

The following graphs were plotted.





(iv) Using the above data, deduce the order of the reaction with respect to [Cl^-] and [H^+].

• From experiment 1, the graph of [Cl^-] shows a <u>constant half-life of 5 min</u>.
Rate ∝ $[Cl^-]^1$
1st order with respect to [Cl^-]

• From experiment 2, the graph of initial rate vs. $[H^+]^2$ is a straight line, hence rate of reaction is directly proportional to $[H^+]^2$. Rate ∝ $[H^+]^2$
2nd order with respect to [H^+].

(v) Hence, write a rate equation for the chlorate-chloride reaction.

•Rate = k[C*l*O$_3^-$][C*l*$^-$][H$^+$]^2

(vi) Using the half-life obtained from Experiment 1 in **(c)(iv)**, calculate a value for the rate constant of the rate equation suggested in **(c)(v)**.

Rate = k[C*l*O$_3^-$][C*l*$^-$][H$^+$]^2
Since [C*l*O$_3^-$] and [H$^+$] are in large excess,
Rate = k'[C*l*$^-$] where •k' = k[C*l*O$_3^-$][H$^+$]^2

$$t_{\frac{1}{2}} = \frac{\ln 2}{k'} = \frac{\ln 2}{k[ClO_3][H^+]^2}$$

$$5 = \frac{\ln 2}{k[0.12][0.50]^2}$$

•k = 4.62 mol^{-3} dm^9 min^{-1}

(vii) The following mechanism was proposed by a research student.

Step 1: C*l*O$_3^-$ + C*l*$^-$ + 2H$^+$ → HC*l*O$_2$ + HOC*l* (slow)
Step 2: HC*l*O$_2$ + C*l*O$_3^-$ + H$^+$ → 2C*l*O$_2$• + H$_2$O (fast)
Step 3: HOC*l* + C*l*$^-$ + H$^+$ → C*l*$_2$ + H$_2$O (fast)

From the rate equation in **(c)(v)**, deduce if the proposed mechanism is to be accepted or rejected.

•• Yes, the proposed mechanism could be accepted. Based on the rate equation, it is 1 ion of C*l*O$_3^-$, 1 ion of C*l*$^-$ and 2 ions of H$^+$ reacting in the slow step which agrees with the proposed mechanism and the overall balanced equation from all 3 steps in the mechanism matches the corresponding equation (2C*l*O$_3^-$ + 2 C*l*$^-$ + 4H$^+$ → C*l*$_2$ + 2C*l*O$_2$• + 2H$_2$O)

[12]
[Total: 20]