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ST ANDREW'S JUNIOR COLLEGE



JC2 Preliminary Examination

ANSWERS

**Chemistry
Higher 1
17th September 2015**

**8872/2
Paper 2
1400 - 1600
2 hours**

Additional Materials: Writing paper, Data Booklet, OAS

READ THESE INSTRUCTIONS FIRST

Write your name and civics group on all the work you hand in.
Write in dark blue or black pen.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Section A:

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

Section B:

Answer **two** questions from this section on separate answer paper.

You are reminded of the need for good English and clear presentation in your answers. The number of marks is given in brackets [] at the end of each question or part question.

For Examiners use only:

This document consists of **19** printed pages including this page.

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Section A

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

- 1 Jet airliners use kerosene as fuel. The formula of kerosene can be taken as $C_{14}H_{30}$. It can be converted into more useful small molecules by the process of cracking.

(a) (i) To which homologous series does kerosene belong?

[1]

Alkane

(ii) Write a balanced equation to show the cracking of kerosene into heptane, propene and ethene only.

[1]



(iii) Suggest a use of ethene during the cracking process.

[1]

Any one of the following:

- form poly(ethene) used as plastic
- form bromoethane to add to the petrol to remove lead
- form ethanol which used as a solvent
- form ethane-1,2-diol to act as anti freeze.

(iv) With the aid of an equation, define standard enthalpy change of combustion of kerosene.

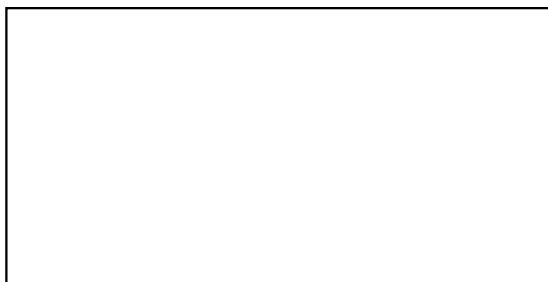
[1]



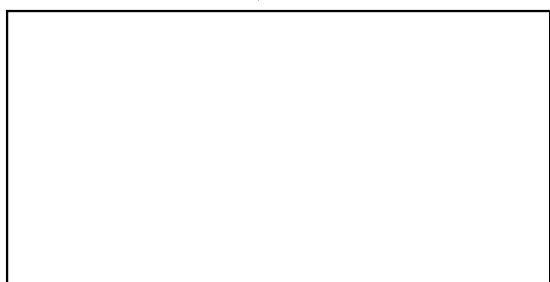
(b) Fill in the boxes with the appropriate structures and state the reagents and conditions of steps **I** and **II**.

Ethene

Step I



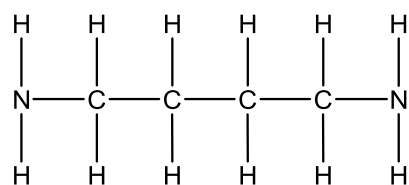
SOCl_2 in pyridine

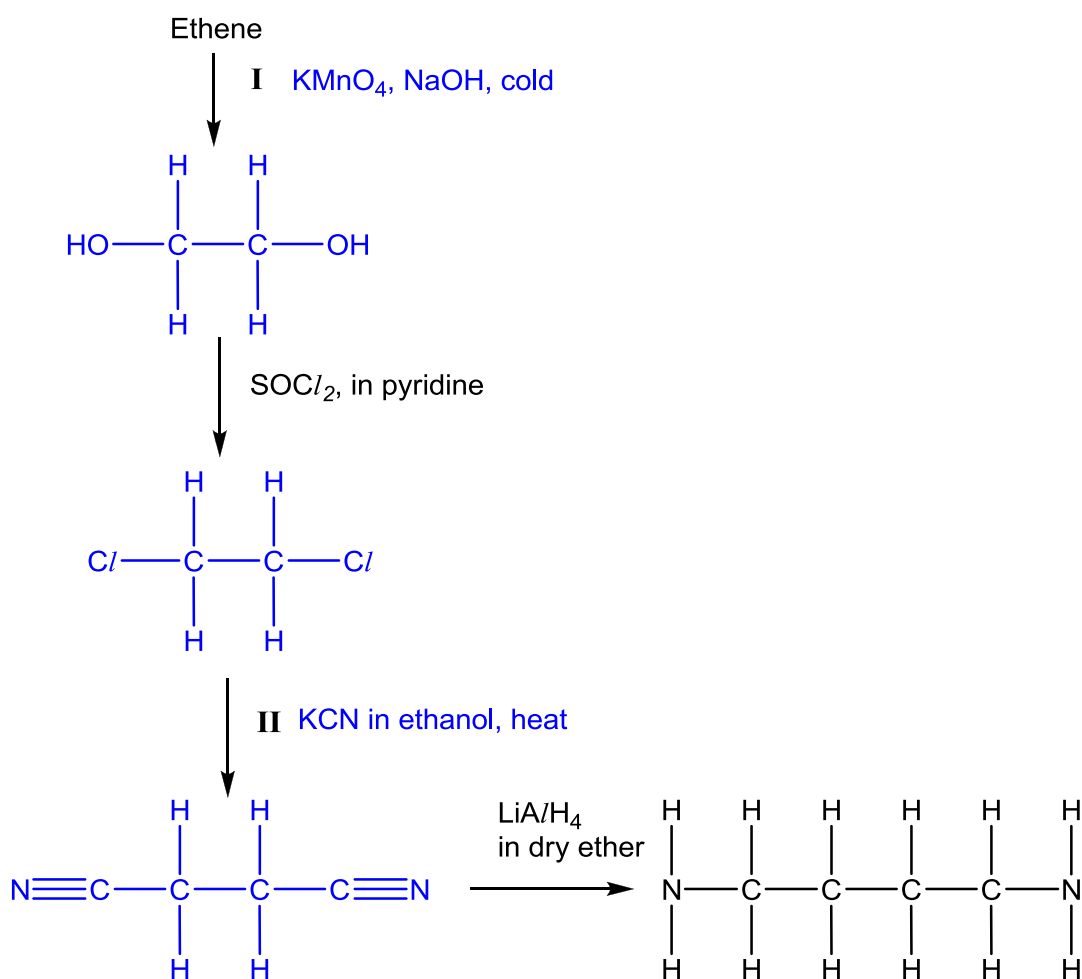


Step II



LiAlH_4
in dry ether





[5]

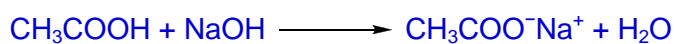
- (c) The propene obtained from cracking of kerosene is bubbled into acidified potassium manganate(VII) solution to form ethanoic acid.

20 cm³ of the ethanoic acid produced is titrated with 3.0 mol dm⁻³ aqueous NaOH using a suitable indicator. The average volume of NaOH used is 12.50 cm³.

Another 20 cm³ of the same ethanoic acid is placed into a plastic cup of negligible heat capacity. A 10.0 cm³ sample of 3.0 mol dm⁻³ aqueous NaOH, at the same initial temperature, is added into the plastic cup. The temperature of the mixture rises by 12.5 K.

- (i) Determine the concentration of the ethanoic acid.

[1]



$$C_a V_a = C_b V_b$$

$$C_a(20) = 3.0(12.50)$$

$$C_a = 1.875 \text{ mol dm}^{-3}$$

- (ii) If the specific heat capacity per unit volume of the mixture is $4.2 \text{ J K}^{-1} \text{ cm}^{-3}$, what is the enthalpy change of neutralization of ethanoic acid?

[2]

$$\text{Heat release} = mc\Delta T$$

$$= 30 \times 4.2 \times 12.5$$

$$= 1575 \text{ J}$$

$$\text{Amount of ethanoic acid} = 1.875 \times 20/1000 = 0.0375 \text{ mol}$$

$$\text{Amount of NaOH} = 3.0 \times 10/1000 = 0.03 \text{ mol}$$

$$\Delta H_n = -1575/0.03 = -52,500 \text{ J mol}^{-1} = -52.5 \text{ kJ mol}^{-1}$$

- (iii) If HCl replaces ethanoic acid in the above experiment, would the temperature rise be higher or lower? Explain your answer.

[2]

The temperature rise would be higher.

HCl is a strong acid, it could completely dissociate into H^+ ion, so no heat is required to dissociate the H^+ ion from the acid hence the temperature rise would be higher.

[Total: 14 marks]

- 2 Chlorine dioxide, ClO_2 , is used for bleaching paper pulp and for water treatment. Over 95% of the chlorine dioxide produced in the world today is made from acidified sodium chlorate, NaClO_3 , with a suitable reagent such as hydrogen peroxide, H_2O_2 .

The half-equation for the reduction of ClO_3^- ions to ClO_2 is shown below.



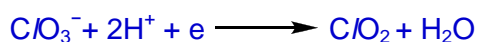
- (a) (i) Using the Data Booklet, write the half equation for H_2O_2 in this reaction.

[1]

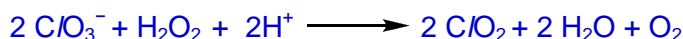


- (ii) Hence, write an equation for the overall reaction.

[1]



Overall equation:



- (iii) Use oxidation numbers to show which species in your equation is oxidised and

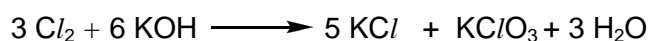
which is reduced.

[1]

C/ in C/O_3^- has been reduced from +5 ON to +4 in C/O_2

O in H_2O_2 has been oxidised from -1 to 0 in O_2

- (b) Metal chlorates can be produced by adding chlorine to hot metal hydroxides as shown below.



- (i) State the type of the reaction above.

[1]

Disproportionation reaction

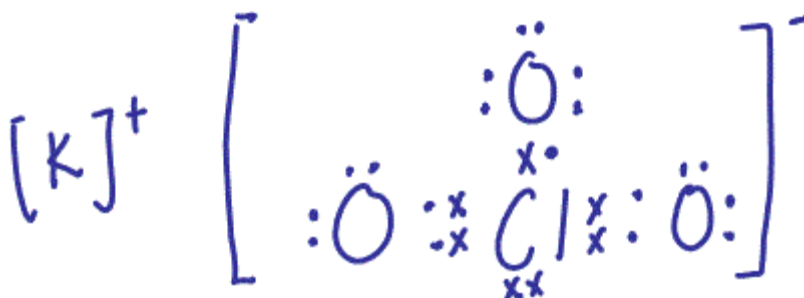
- (ii) Write the electronic configuration of K^+ .

[1]



- (iii) Draw a dot and cross diagram to illustrate the bonding in KC/O_3 , showing the outermost shell electrons only.

[1]



- (c) (i) Using VSEPR Theory, predict and explain the shape and bond angle of C/O_2 .

[2]

C/O_2 is bent, it has 2 bond pairs, 1 lone pair and 1 electron around the central C/ atom, lone-pair-lone-pair repulsion is greater than lone pair- lone electron repulsion, hence, the bond angle would be larger than 104.5° (H_2O), but less than 107° (NH_3 -3bp + 1 lp).

Accept value between $105-106^\circ$

- (ii) Chlorine dioxide is highly soluble even in cold water. Explain your answer with reference to structure and bonding.

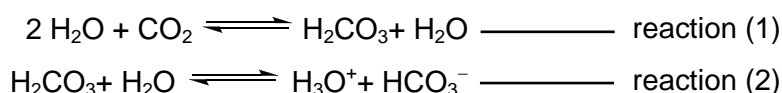
[2]

CO_2 is a polar simple covalent molecule, the hydrogen bonding between CO_2 and water release sufficient energy to overcome the permanent dipole-permanent dipole interactions between the CO_2 molecules and the hydrogen bonding between water molecules; hence it is soluble in cold water.

[Total: 10 marks]

- 3 The body's chemical buffer system consists of three individual buffers: the carbonate/carbonic acid buffer, the phosphate buffer and the buffering of plasma proteins. The first buffer system is usually considered the most important since it is coupled to the respiratory system.

In this buffer system, carbon dioxide combines with water to form carbonic acid (H_2CO_3), which in turn rapidly dissociates to form hydrogen and bicarbonate (HCO_3^-) ions according to the reactions below:



As a buffer, it maintains a relatively constant blood plasma pH and counteracts any change that would alter it. Thus blood pH is regulated to stay within the narrow range of 7.35 to 7.45, making it slightly alkaline. If the pH of the body gets too low (below 7.4), a very serious condition known as acidosis results.

Since carbonic acid is not stable in aqueous solutions, some of it decomposes to form carbon dioxide and water. The respiratory system is responsible for removing the carbon dioxide.

It is the production of carbon dioxide from this reaction that couples the carbonic acid/bicarbonate buffer to the respiratory system.

- (a) (i) The pH of 0.10 mol dm^{-3} carbonic acid was found to be 3.54. Suggest if carbonic acid is a weak or strong acid. Explain your answer.

[1]

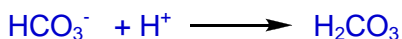
Carbonic acid is a weak acid as $[\text{H}^+]$ is not equal to [carbonic acid].

OR

Carbonic acid did not fully dissociate to give H^+ ions in aqueous solution.

- (ii) With the aid of an equation, explain how the carbonate/ carbonic acid buffer system helps to maintain a relatively constant pH when H^+ ions are added to the blood plasma.

[1]



- (iii) Explain, with reference to the equilibrium reactions, why a reduction in respiratory activity to remove CO_2 will result in acidosis.

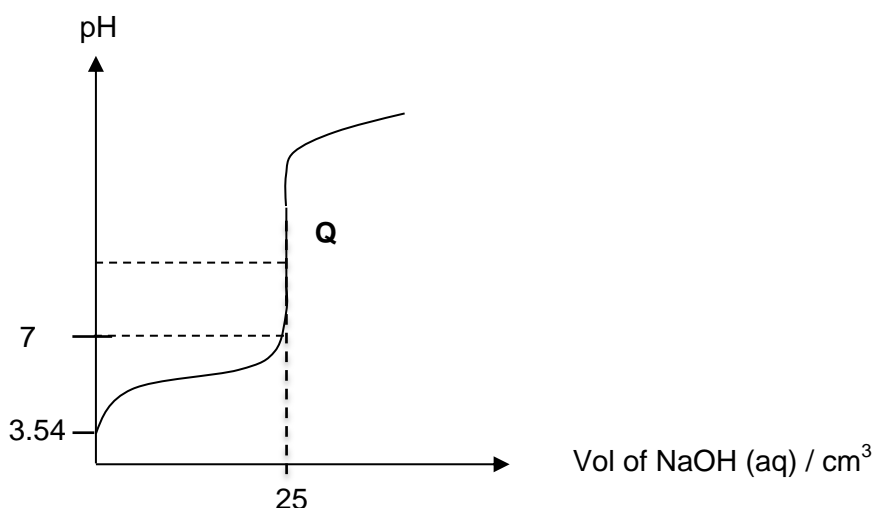
[2]

When CO_2 is not removed, the position of equilibrium in reaction 1 will shift to the right to remove excess CO_2 , producing more carbonic acid.

Therefore the position of equilibrium in reaction 2 will shift to the right to remove excess H_2CO_3 , hence producing more H^+ . This results in a decrease in pH which results in acidosis.

- (b) The acid strength of carbonic acid is determined by titration with aqueous NaOH. 25 cm^3 of 0.10 mol dm^{-3} carbonic acid was pipetted into a conical flask and titrated with 0.10 mol dm^{-3} NaOH in the burette. The titration curve of pH against volume of aqueous NaOH added is shown below.

(You may wish to consider carbonic acid as a monobasic acid.)



- (i) Write the acid dissociation constant, K_a , expression for the following equilibrium.



[1]

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$$

- (b) (ii) Hence, calculate the acid dissociation constant, K_a , for the equilibrium in **b(i)**.

[2]

$$[\text{H}^+] = 10^{-3.54}$$

$$[\text{H}^+] = 2.884 \times 10^{-4} \text{ mol dm}^{-3}$$

	$\text{H}_2\text{CO}_3 (\text{aq})$	$\text{H}_3\text{O}^+(\text{aq})$	$\text{HCO}_3^-(\text{aq})$
Initial conc./mol dm ⁻³	0.10	0	0
Change conc./mol dm ⁻³	$- 2.884 \times 10^{-4}$	$+2.884 \times 10^{-4}$	$+2.884 \times 10^{-4}$
Equilibrium conc./ mol dm ⁻³	0.09971	2.884×10^{-4}	2.884×10^{-4}

$$K_a = \frac{(2.884 \times 10^{-4})^2}{0.09971} = 8.34 \times 10^{-7} \text{ mol dm}^{-3}$$

- (ii) At point **Q**, the amount of NaOH added just neutralises the acid present to form a salt. State the nature of the salt formed and hence illustrate its behaviour with the aid of an equation.

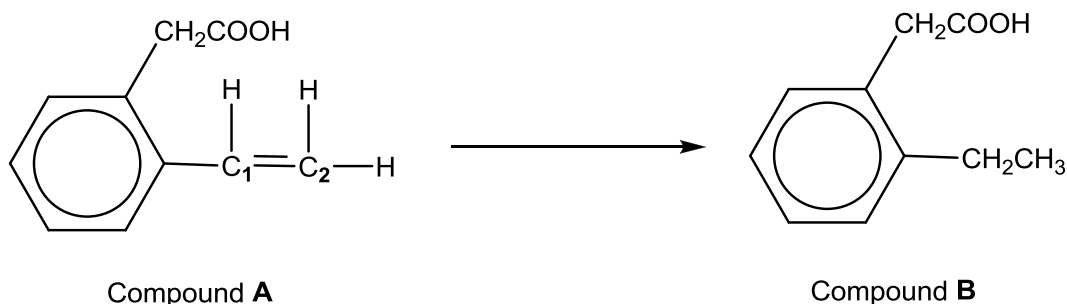
[2]

Basic salt



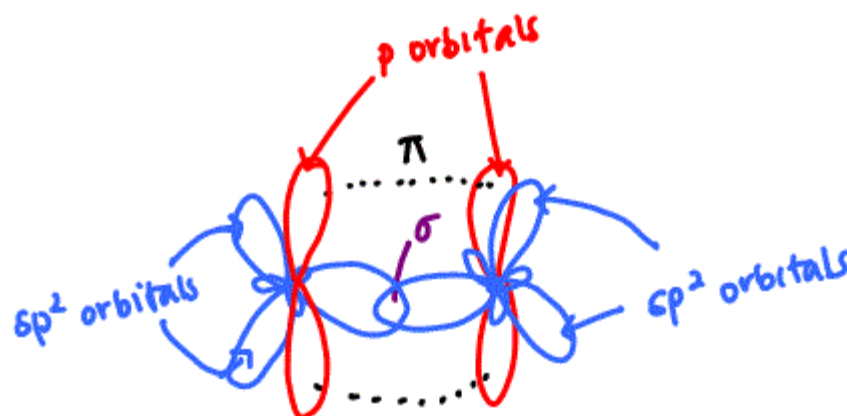
[Total: 9 marks]

- 4 Compound **A** is converted to compound **B** as shown in the synthetic route below.



- (a) Draw a labelled diagram to illustrate the sigma and pi bonds formed between the orbitals of C_1 and C_2 in compound **A**.

[2]



- (b) Suggest the reagents and conditions for the conversion of compound **A** to **B**.

[1]

Hydrogen gas, Nickel catalyst, heat

- (c) Suggest a simple chemical test to distinguish between compound **A** and **B**.

[1]

Add $\text{Br}_2(l)$ in CCl_4 to both A and B separately in the dark.

Compound A decolourises reddish-brown $\text{Br}_2(l)$ while brown $\text{Br}_2(l)$ remains for compound B.

OR

Add $\text{Br}_2(aq)$ to both A and B separately.

Compound A decolourises orange $\text{Br}_2(aq)$ while orange $\text{Br}_2(aq)$ remains for compound B.

OR

Add cold KMnO_4 and H_2SO_4 separately to both A and B.

Compound A decolourises purple KMnO_4 . Purple KMnO_4 remains for compound B.

OR

Add cold KMnO_4 and NaOH

Compound A decolourises purple KMnO_4 and forms brown MnO_2 ppt. Purple KMnO_4 remains for compound B.

- (d) Upon oxidation, both compounds **A** and **B** yield compound **C** with molecular formula $\text{C}_8\text{H}_6\text{O}_4$.

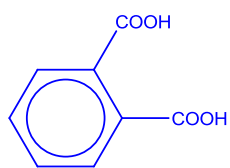
State the reagents and conditions needed for the oxidation and draw the structure of compound **C**.

Hence, write a balanced equation for the oxidation of compound **B** to compound **C**.

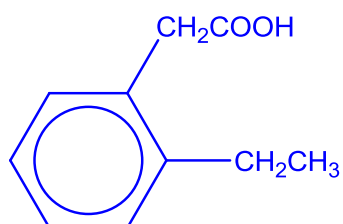
You may use $[\text{O}]$ to represent an oxidising agent.

[3]

Reagents and conditions: KMnO_4 (aq), H_2SO_4 (aq), heat

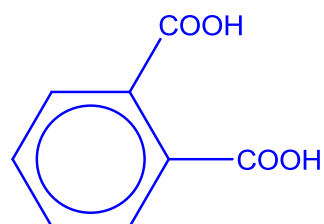


Compound **C**



Compound **B**

+ 9 [O] \longrightarrow



Compound **C**

+ 2 CO_2 + 3 H_2O

[Total: 7 marks]

Section B

Answer **two** questions from this section on separate answer paper.

- 5 Samples of a bromoalkane **A** with the molecular formula $C_5H_{11}Br$ were reacted with aqueous sodium hydroxide at a constant temperature. Several experiments were carried out to investigate the kinetics of the reaction of **A** with aqueous sodium hydroxide. The initial rate of reaction was determined in each case and the following results were obtained.

Expt	Initial $[A]/\text{mol dm}^{-3}$	Initial $[OH^-]/\text{mol dm}^{-3}$	Initial Rate / $\text{mol dm}^{-3} \text{min}^{-1}$
1	0.10	0.10	5.56×10^{-4}
2	0.20	0.05	5.56×10^{-4}
3	0.30	0.10	1.67×10^{-3}

- (a) (i) Deduce the order of reaction with respect to **A** and OH^- respectively, and hence write the rate equation.

[3]

Compare expt 1 and 3, $[OH^-]$ remains constant, $[A] \times 3$, rate $\times 3 \Rightarrow \text{rate} \propto [A]$

Order w.r.t $[A]$ is 1

Let order w.r.t $[OH^-] = x$

$$\frac{5.56 \times 10^{-4}}{5.56 \times 10^{-4}} = \frac{k(0.10)(0.10^x)}{k(0.20)(0.05^x)}$$

$$x = 1$$

Order w.r.t $[OH^-]$ is 1

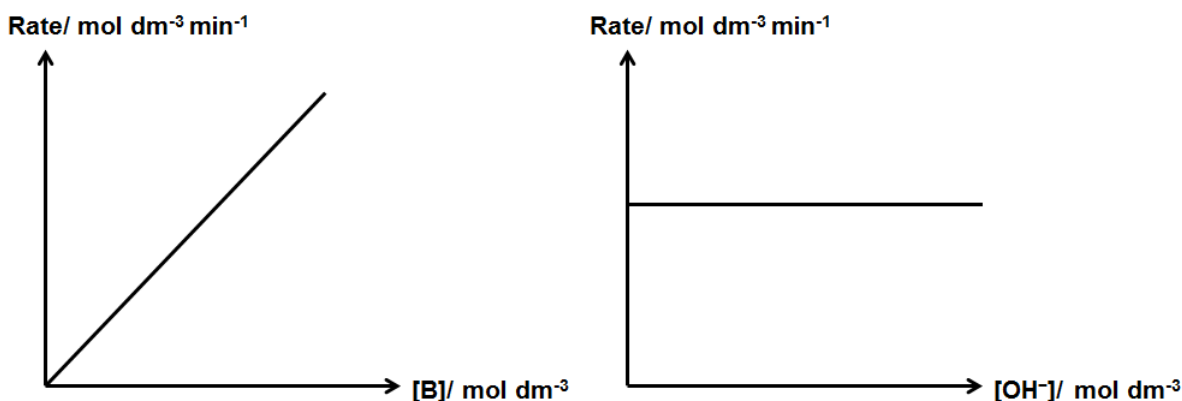
Rate = $k[A][OH^-]$

- (ii) Calculate the value of the rate constant and state its units.

$$k = (5.56 \times 10^{-4}) / (0.10)(0.10) = 0.0556 \text{ mol}^{-1} \text{dm}^3 \text{min}^{-1}$$

[2]

- (b) Another bromoalkane **B**, which is a structural isomer of **A**, was reacted with sodium hydroxide solution and the kinetics of the reaction was investigated. The following graphs were obtained.

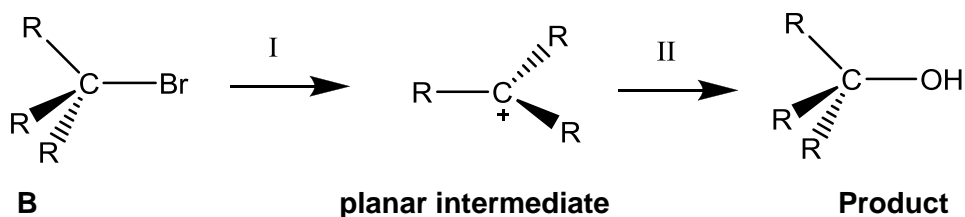


Using the graphs above, write the rate equation for the reaction of compound **B** with aqueous sodium hydroxide.

[1]

$$\text{Rate} = k[\text{B}]$$

- (c) When compound **B** reacts with aqueous sodium hydroxide, the shape of the organic intermediate differs from that of the reactant and product, as shown below.
(where R is an alkyl group)



- (i) By considering the hybridisation state of carbon, deduce whether the C – R bond is longer in **B** or in the intermediate. Explain.

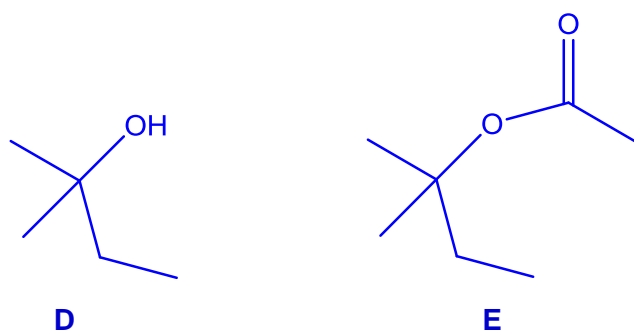
[3]

The C-R bond in **B** is longer.

The C in **B** is sp^3 hybridised while that in the intermediate is sp^2 hybridised. The sp^3 hybridised orbital has more p-character and is more elongated. Hence, there is lesser extent of effective overlap between the sp^3 and sp^3 orbitals as compared to the sp^3 and sp^2 orbitals.

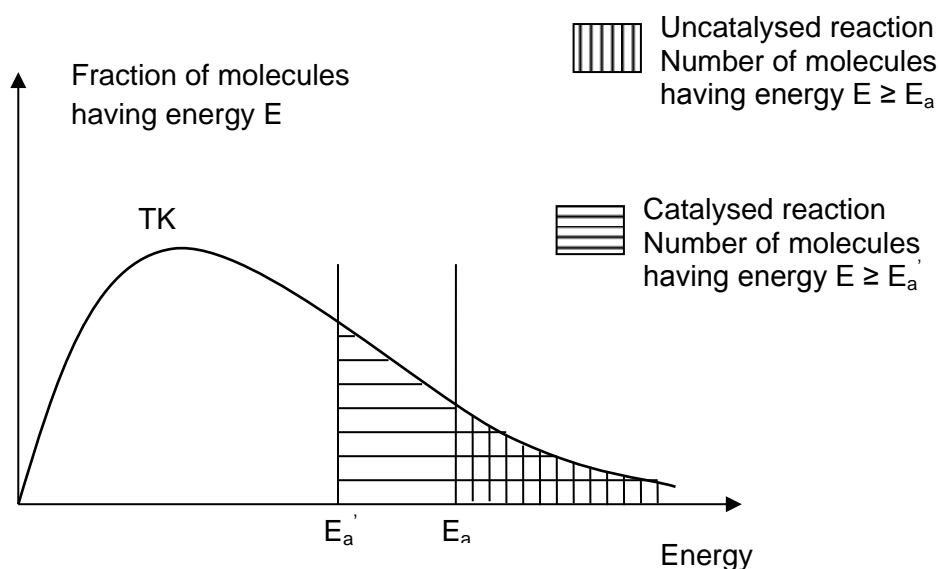
- (d) Compound **B**, $C_5H_{11}Br$, reacted with hot aqueous sodium hydroxide to form an alcohol **D**. Alcohol **D** was not able to react with hot acidified sodium dichromate (VI) but reacted with ethanoic acid in the presence of hot concentrated H_2SO_4 to produce a sweet smelling liquid **E**.
- (i) Suggest the structures of **D** and **E**.

[2]



- (ii) Explain, with the aid of the Maxwell-Boltzmann Curve, the role of concentrated H_2SO_4 in the reaction of **D** with ethanoic acid.

[3]



Effect of concentrated H_2SO_4 :

- Concentrated H_2SO_4 acts as a catalyst to lower the activation energy of the reaction.
- There is an increase in the fraction of particles with energy greater than or equal to the lowered activation energy, E_a' .
- Frequency of effective collisions taking place in the reaction increases.
- Rate of reaction increases.

- (e) **X**, **Y** and **Z** are elements in the third period of the Periodic Table.

There are two chlorides of **X** which fumes in air.

When 2 mol of dilute HCl is added to 1 mol of the oxide of **Y**, the resulting solution is weakly acidic.

The oxide of **Z** is insoluble in water. When one mole of the chloride of **Z** dissolves in water, the resultant solution reacts with 4 moles of aqueous NaOH for complete neutralisation..

- (i) Identify the elements **X**, **Y** and **Z**

[3]

X – Phosphorus

Y – Magnesium

Z – Silicon

- (ii) Write an equation for the reaction between the chloride of **Z** with water.

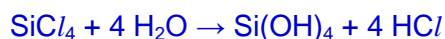
[1]



Or



Or



- (iii) Suggest why the oxide of **Z** is insoluble in aqueous sodium hydroxide.

[2]

The energy released from induced dipole-induced dipole interactions between the molecules and water is not exothermic enough to overcome the extensive network of covalent bonds between **Z** and O atoms and hydrogen bonding between water molecules

[Total: 20 marks]

- 6 (a) Butene (C_4H_8) and butane gas (C_4H_{10}) are commonly used as fuels. The heat energy released when 1 g of a material is combusted is commonly known as its fuel value (in kJ g^{-1}). The standard enthalpy change of combustion of butene is -2715 kJmol^{-1} .

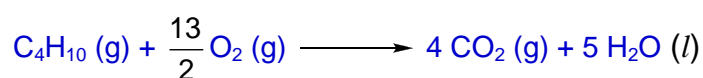
- (i) Use the following information to calculate the enthalpy change of combustion of butane, C_4H_{10} .

Standard enthalpy change of formation of carbon dioxide = -393 kJmol^{-1}

Standard enthalpy change of formation of water = -286 kJmol^{-1}

Standard enthalpy change of formation of butane = -126 kJmol^{-1}

[2]



$$\begin{aligned} \Delta H_r &= 4 (-393) + 5 (-286) - (-126) \\ &= -2876 \text{ kJmol}^{-1} \end{aligned}$$

- (ii) Calculate the fuel value of butane and butene and hence propose a relationship between the hydrogen content and fuel value in hydrocarbons.

[3]

$$\text{Fuel value for butene} = 2715/[4(12)+8] = 48.5 \text{ kJ g}^{-1}$$

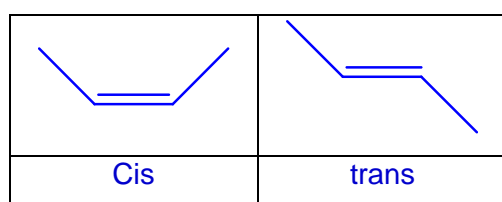
$$\text{Fuel value for butane} = 2876/[4(12)+10] = 49.6 \text{ kJ g}^{-1}$$

The more hydrogen, the greater the fuel value.

- (b) One form of butene exists as a pair of geometrical isomers.

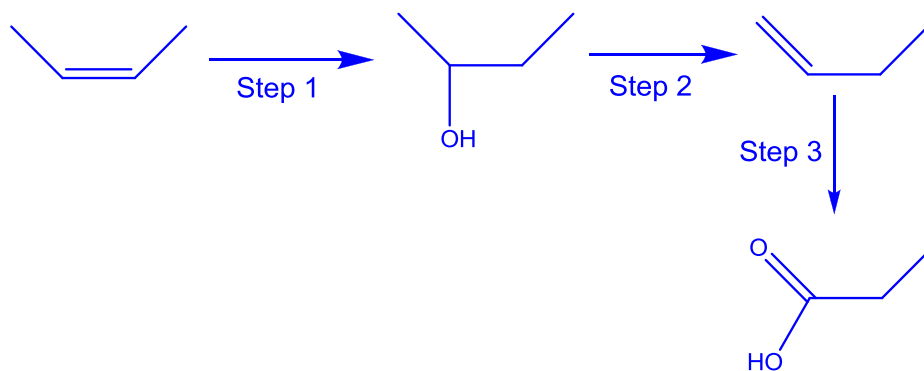
- (i) Draw the pair of geometrical isomers.

[2]



- (ii) Propose a three step synthetic route for the formation of propanoic acid from 2-butene, showing the structures of all intermediate organic compounds and the reagents and conditions of each intermediate step.

[4]



Reagents and conditions:

Step 1: conc. H_2SO_4 , 0°C , followed by boiling with H_2O

Step 2: conc. H_2SO_4 , 170°C

Step 3: $\text{KMnO}_4(\text{aq})$, $\text{H}_2\text{SO}_4(\text{aq})$, heat

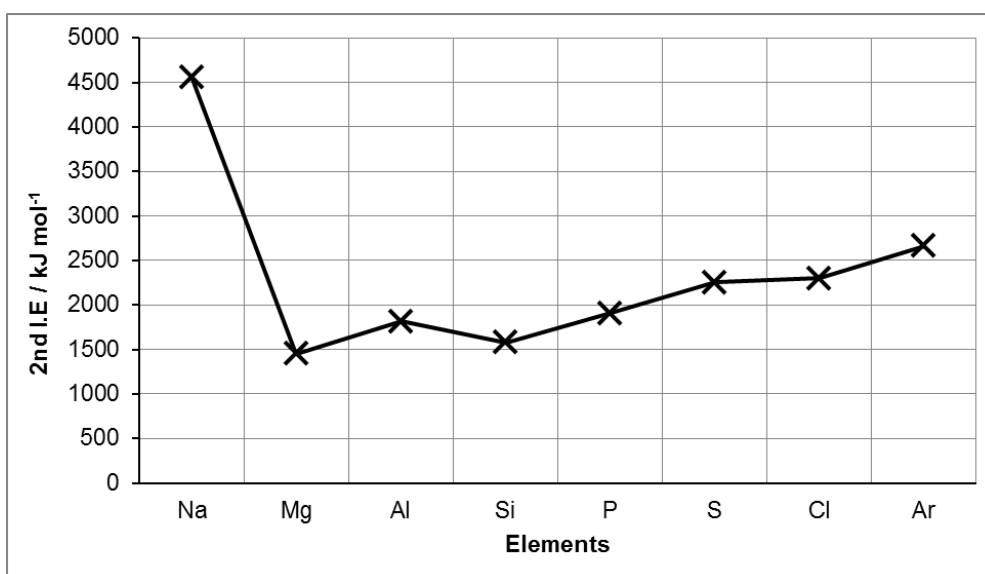
- (iii) Explain why propanoic acid is more soluble in water than 2-butene.

[2]

Propanoic acid can form hydrogen bonds with water molecules which release enough energy to overcome the hydrogen bonds between propanoic acid molecules and also that between water molecules.

2-Butene can only form induced dipole-induced dipole interactions with water molecules which does not release enough energy to overcome the induced dipole-induced dipole interactions between 2-butene molecules and hydrogen bonds between water molecules.

- 6 (c) The graph below shows the trend of second ionisation energies of Period 3 elements.



- (i) Write an equation to represent the second ionisation of sodium.

[1]



- (ii) Explain why sodium has the highest second ionisation energy.

Na has the highest second IE as the second electron is removed from the inner quantum shell which experience much more effective nuclear charge.

[1]

- (iii) Explain the trend of second ionisation energies from magnesium to argon.

[2]

Going across from Mg to Ar, nuclear charge increases as proton increases. Screening effect increases negligibly as additional electron lies in the same outer shell. Increase in nuclear charge outweighs increase in screening effect, effective nuclear charge increases. Electrons are more attracted and require more energy for removal. Hence, second IE increases generally from Mg to Ar.

- (iv) Explain the irregularities observed in the second ionisation energies of silicon and chlorine.

[3]

There is a slight dip in IE from Al^+ to Si^+ as the second electron removed from Si is from the p orbital while that from Al is from the s orbital.

OR



The p electron experiences greater screening effect as it is further away from nucleus hence require lesser energy.

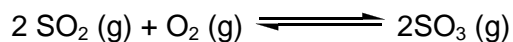


OR

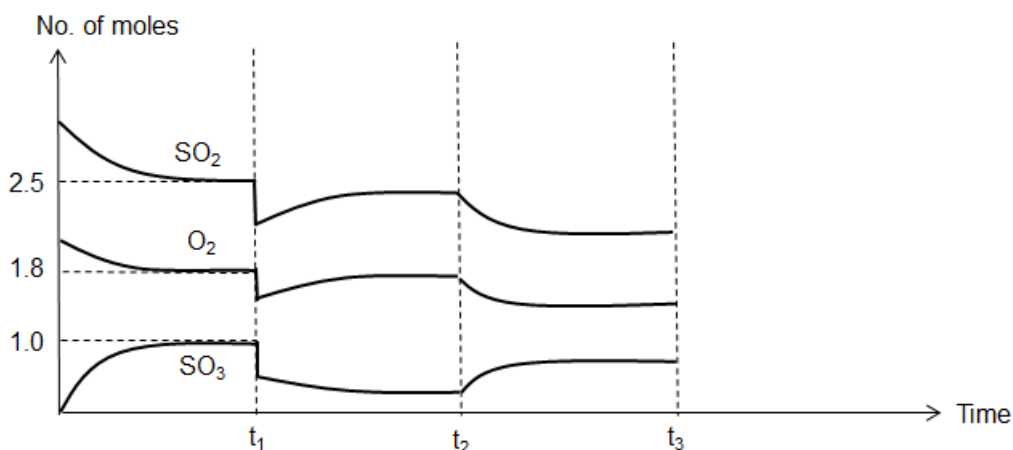
From S^+ to Cl^+ , the anomaly arises as the second electron removed from Cl^+ is a paired electron which experiences inter-electronic repulsion and hence needs less energy to remove.

[Total: 20 marks]

- 7 (a) The equilibrium system shown below is part of the industrial process to synthesize sulfuric acid.



A mixture containing 3 moles of sulfur dioxide gas and 2 moles of oxygen are placed in a 2 dm³ closed vessel at 500 °C. The graph shows how the number of moles of each gas varies with time.



- (i) Describe the reaction of sulfur with oxygen with an aid of an equation.

[2]

Sulfur burns with a blue flame to give SO₂.



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

[1]

$$K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]}$$

Units: mol⁻¹dm³

- (iii) Hence, calculate K_c for this equilibrium system at t₁.

[1]

$$\begin{aligned} K_c &= \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]} \\ &= \frac{\left(\frac{1}{2}\right)^2}{\left(\frac{2.5}{2}\right)^2 \left(\frac{1.8}{2}\right)} = 0.178 \text{ mol}^{-1} \text{dm}^3 \end{aligned}$$

- (iv) Describe and explain what had happened to the equilibrium system at t₁.

[2]

There was a decrease in pressure at t₁, causing the equilibrium system to

increase the pressure by shifting equilibrium to the left to favour the side with more moles of gases.

- (v) At t_2 , the reaction chamber was cooled. Suggest and explain if the reaction is endothermic or exothermic.

By Le Chatelier's Principle, a drop in temperature will cause the system to increase the temperature by favouring the exothermic reaction. Since $[\text{SO}_2]$ and $[\text{O}_2]$ decreases, the equilibrium shifted to the right, hence, the forward reaction must be exothermic.

[2]

- (vi) With reference to a(v), explain how K_c is expected to change with increasing temperature.

Since the forward reaction is an exothermic reaction, when temperature increases, rate of backward reaction increase more than rate of forward reaction. Since $K_c = \frac{k_f}{k_b}$, K_c decreases.

[2]

- (b) Compound **G** has molecular formula, $\text{C}_4\text{H}_8\text{O}$. Reaction of **G** with hot acidified potassium manganate (VII) produces compound **H**, $\text{C}_3\text{H}_4\text{O}_4$, and effervescence is observed. One mole of **H** requires two moles of NaOH for complete neutralisation. One mole of **G** reacted with 1 mole of Cl_2 (g) in the dark to form compound **I**, $\text{C}_4\text{H}_8\text{OCl}_2$. Both **G** and **I** turned hot sodium dichromate (VI) green. Suggest a possible structure for each of the compounds, **G**, **H** and **I**. Explain the chemistry of the reactions described.

[6]

Observations	Deductions
<ul style="list-style-type: none"> G reacts with hot acidified manganate (VII) to give H and effervescence is observed. 	<ul style="list-style-type: none"> G undergoes vigorous oxidation G contains terminal alkene and G contains a primary alcohol group.
<ul style="list-style-type: none"> H requires two moles of NaOH for neutralisation 	<ul style="list-style-type: none"> H contains COOH group H contains 2 acidic groups
<ul style="list-style-type: none"> G reacted with 1 mole of Cl_2 (g) in the dark to form I 	<ul style="list-style-type: none"> G undergoes addition G contains C=C bond G contains 1 C=C bond

<ul style="list-style-type: none"> Both G and I turned hot sodium dichromate (VI) green. 	<ul style="list-style-type: none"> G and I undergo oxidation G and I contains primary alcohol
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G	H	I

- (c) Draw the structural isomers for the carbonyl compounds with formula C_3H_6O . Describe how you can distinguish between the 2 isomers using a simple chemical test.

[4]

Propanone	Propanal

Test 1: Fehling's solution, warm

Observations: brick red ppt observed for propanal but no ppt for propanone

Test 2: Tollen's reagent, warm

Observations: silver mirror observed for propanal but no silver mirror for propanone

Test 3: $KMnO_4(aq)$, $H_2SO_4(aq)$, heat

Observations: purple $KMnO_4$ decolourised for propanal but purple $KMnO_4$ remained for propanone

Test 4: $K_2Cr_2O_7(aq)$, $H_2SO_4(aq)$, heat

Observations: Orange $K_2Cr_2O_7$ turned green for propanal but Orange $K_2Cr_2O_7$ remained for propanone

Test 5: $I_2(aq)$, $NaOH(aq)$, warm

Observations: yellow ppt observed for propanone but no ppt for propanal

[Total: 20 marks]

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