

NATIONAL JUNIOR COLLEGE
SH2 PRELIMINARY EXAMINATION
Higher 1

CANDIDATE
NAME

SUBJECT
CLASS

REGISTRATION
NUMBER

CHEMISTRY

Paper 2 Structured Questions

8872/02

Friday 28 Aug 2015

Answer Section A on the Question Paper.

Additional Materials: Data Booklet

2 hours

READ THE INSTRUCTIONS FIRST

Write your subject class, registration number and name on all the work you hand in.

Write in dark blue or black pen on both sides of the paper. You may use a soft pencil for any diagrams, graphs or rough working.

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

Section A

Answers **all** questions.

Section B

Answer **two** questions on separate answer paper.

The number of marks is given in brackets [] at the end of each question or part question.

For Examiner's Use

A1	
A2	
A3	
A4	
B5	
B6	
B7	
Total	

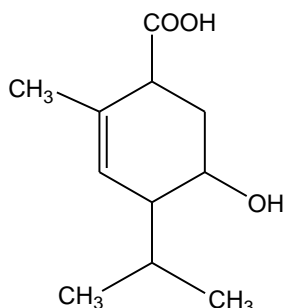
This document consists of **13** printed pages and **0** blank page.

Section A

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

For Examiner's use

- 1** Menthol is an important compound extracted from the peppermint plant. It has important uses in flavouring. The structure of a derivative of menthol is shown below.



- (a)** Name **two** other functional groups, other than the carboxylic acid, that are present in the above structure.

2° alcohol, alkene

[1]

- (b)** State the type of reaction that occurs, if any, and draw the structure of the organic products, when the above compound is added to the following reagents.

	Reagent and conditions	Structure of organic product(s), if any
(i)	Acidified KMnO_4 , heat	
	Type of reaction: oxidation	
(ii)	H_2 , Pt	
	Type of reaction: reduction	
(iii)	$\text{CH}_3\text{CO}_2\text{H}$, conc. H_2SO_4 , reflux	
	Type of reaction: condensation	

[6]

[Total: 7]

2

- (a) Sodium, magnesium and phosphorus are all elements in Period 3 of the Periodic Table. What will you see when these elements are burned separately in excess oxygen? Give an equation, with state symbols, for each reaction. [4]

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Sodium burns with a bright yellow flame.



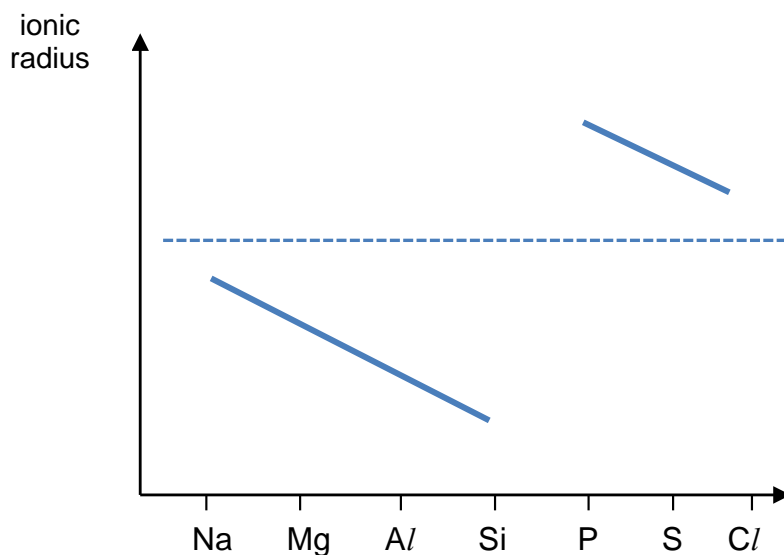
Magnesium burns with a brilliant white flame.



Phosphorus burns with a white flame.

[1 mark each colour, any wrong equation minus ½ mark]

- (b) On the axes below, sketch a graph to illustrate the variation of ionic radius of the elements sodium to chlorine.



Explain the shape of your sketch.

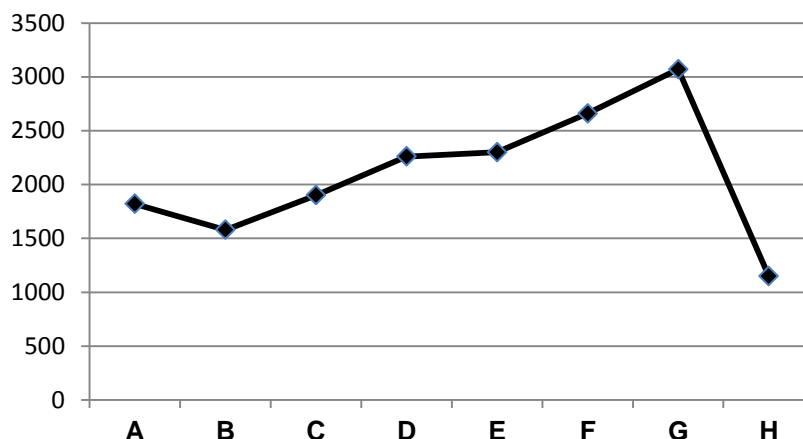
Across each isoelectronic series, Na^+ to Si^{4+} , and P^{3-} to Cl^- , there is increase in nuclear charge. In each series, there is increase in effective nuclear charge since there is increasing no of protons attracting similar no of electrons. Hence size of ionic radii decrease across each series. The anions are bigger than cations as there is increased shielding effect due to an additional shell of shielding electrons.

[3]

- (c) The graph below shows the second ionisation energies of eight consecutive elements **A** to **H** in Period 3 and 4 of the Periodic Table.

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2^{nd} IE/ kJ mol^{-1}



- (i) Deduce which group does element **F** belongs to? Explain your answer.

Group no: 0

Explanation: Element **G** has the highest 2^{nd} IE since the second most loosely held electron is removed from an inner quantum shell ($n=3$) which is closer to the nucleus and experiences greater nuclear attraction than that for element **H** whose second most loosely held electron is removed from the outer quantum shell ($n=4$). Therefore element **G** belongs to grp I and hence element **F** belongs to grp O.

[3]

- (ii) Give the formula of the compound formed between elements **A** and **E**.

AE_3

[Total: 11]

3 The table below gives some information of various organic compounds.

Compound	Formula	M_r	$K_a / \text{mol dm}^{-3}$	Boiling point / $^{\circ}\text{C}$
Propanoic acid	$\text{CH}_3\text{CH}_2\text{COOH}$	74	1.3×10^{-5}	141
2-chloropropanoic acid	$\text{CH}_3\text{CHClCOOH}$	108.5	1.5×10^{-3}	172
Methanoic acid	HCOOH	46	1.8×10^{-4}	101
Propanol	$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	60	1.0×10^{-18}	97
Methyl ethanoate	$\text{CH}_3\text{OCOCH}_3$	74	-	57

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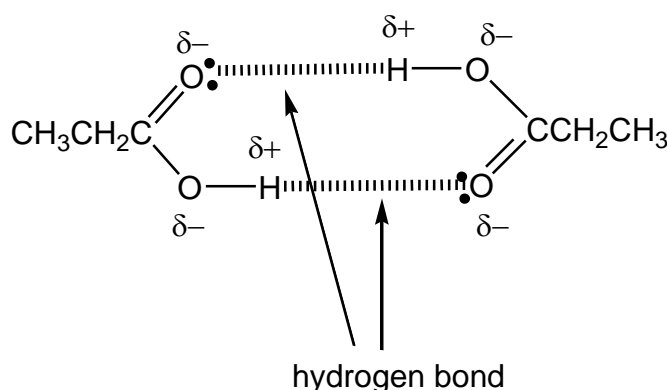
- (a) Explain the difference in the acid strength of propanoic acid, 2-chloropropanoic acid and methanoic acid.

2-chloropropanoic acid is a stronger acid than propanoic acid since the electronegative Cl can further disperse the negative charge on the conjugate base, making it more stable than the conjugate base of propanoic acid, favouring its dissociation to give more H^+ , i.e. stronger acid.

Propanoic acid is a weaker acid than methanoic acid since the ethyl group is electron donating, intensifying the negative charge on the conjugate base, destabilising it, making its dissociation less favourable, i.e. weaker acid.

[4]

- (b) Given that propanoic acid dimerises in non-polar solvents, draw the structure of this dimer. [2]



- (c) Explain the observed trend for the boiling points of propanol, propanoic acid and methyl ethanoate.

Propanoic acid forms stronger hydrogen bonds than propanol due to the additional $\text{C}=\text{O}$ group in $-\text{COOH}$ that withdraws electron density towards itself, making the H in propanoic acid more protonic. Hence, more energy is required to break the stronger hydrogen bonds between propanoic acid, resulting in the highest boiling point. Methyl ethanoate has permanent-dipole dipole interactions between its molecules which are weaker than hydrogen bonds, lesser energy required to break them, hence lowest boiling point. [3]

[Total: 9]

- 4 Our main source of energy is the combustion of fossil fuels, namely coal, oil and natural gas. They give out large amounts of energy when burned, but there are disadvantages to their use.

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use

Natural gas is a combustible mixture of hydrocarbon gases, mainly methane, ethane, propane and butane. Contaminants such as nitrogen and hydrogen sulfide are also present in small amounts. The chart below outlines the typical makeup of natural gas before it is refined.

Typical Composition of Natural Gas (by volume)

Methane	CH ₄	70-90%
Ethane	C ₂ H ₆	0-20%
Propane	C ₃ H ₈	
Butane	C ₄ H ₁₀	
Carbon Dioxide	CO ₂	0-8%
Oxygen	O ₂	0-0.2%
Nitrogen	N ₂	0-5%
Hydrogen sulfide	H ₂ S	0-5%
Rare gases	Ar, He, Ne, Xe	trace

Natural gas is usually considered sour if the hydrogen sulfide content exceeds 5.7 milligrams of H₂S per cubic meter of natural gas. The process for removing hydrogen sulfide from sour gas is commonly referred to as 'sweetening' the gas.

In the process of sweetening sour natural gas, the sour gas is run through a tower, which contains an amine solution. The amine solution will absorb hydrogen sulfide from natural gas as it passes through. The effluent gas is virtually free of hydrogen sulfide, and thus loses its sour gas status.

- (a) State one disadvantage of the use of fossil fuels as our main source of energy.

Their supply is finite/ It is non-renewable/ Emit greenhouse gases that trap heat.

[1]

- (b) Determine the maximum percentage by volume of H₂S that can be present in a sample of natural gas in order not for it to be considered sour. Assume room conditions in your calculations. [2]

$$\text{Amount of H}_2\text{S} = (5.7 \times 10^{-3}) / 34.1 = 1.67 \times 10^{-4} \text{ mol}$$

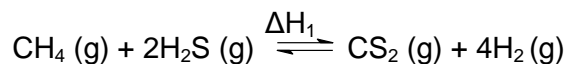
$$\text{Volume of H}_2\text{S} = 1.67 \times 10^{-4} \times 24 \times 0.001 = 4.012 \times 10^{-6} \text{ m}^3$$

$$\% \text{ by volume} = (4.012 \times 10^{-6}) / 1 \times 100\% = 4.01 \times 10^{-4}\%$$

- (c) During the sweetening of sour natural gas, H_2S acts as a *Bronsted-Lowry* acid. Using RNH_2 to represent the amine, write a balanced equation to show how H_2S reacts with RNH_2 .



- (d) (i) Other than using amine solution to remove H_2S from natural gas, another method that could be adopted is by reacting H_2S with methane, as represented by the equation below:



Using the data given below, calculate ΔH_1 .

$$\Delta H_f(\text{CH}_4) = -74.9 \text{ kJ mol}^{-1}$$

$$\Delta H_f(\text{H}_2\text{S}) = -20.6 \text{ kJ mol}^{-1}$$

$$\Delta H_f(\text{CS}_2) = +116.7 \text{ kJ mol}^{-1}$$

$$\Delta H_1 = 116.7 - (2)(-20.6) - (-74.9) = +232.8 \text{ kJ mol}^{-1} = +233 \text{ kJ mol}^{-1}$$

- (ii) ΔH_1 can also be calculated using bond energies values. Using appropriate values from the *Data Booklet* as well as the values given below, calculate an alternative value for ΔH_1

$$\text{Bond energy of C=S} = 573 \text{ kJ mol}^{-1}$$

$$\text{Bond energy of H-S} = 368 \text{ kJ mol}^{-1}$$

$$\Delta H_1 = \text{Energy taken in during bond breaking} + \text{energy given out during bond formation}$$

$$= 4(410) + 4(368) + 2(-573) + 4(-436)$$

$$= +222 \text{ kJ mol}^{-1}$$

- (iii) Hence, suggest a reason for the discrepancy between the values in (i) and (ii).

Bond energy values in *Data Booklet* are only average values of the particular bond.

[5]

- (e) Besides methane, many other organic compounds are also used as an energy source, one of which is the use of methanol in spirit lamps.
The standard enthalpy change of combustion of methanol is -715 kJ mol^{-1} .

- (i) Write a thermochemical equation to represent the *standard enthalpy change of combustion* of methanol. [1]



- (ii) A student carried out an experiment to find out the minimum mass of methanol required to bring 100 g of water to boil from room temperature, i.e. 25°C . Assume that the process is 80% efficient and that the specific heat capacity of water is $4.18 \text{ J g}^{-1} \text{ K}^{-1}$.
Calculate the minimum mass of methanol required.

[3]

$$Q = mc\Delta T = 100 \times 4.18 \times 75 = 31350 \text{ J}$$

$$\text{Actual } Q = 31350 / 80 \times 100 = 39187.5 \text{ J}$$

$$\Delta H = -\frac{Q}{n}$$

$$715000 = -\frac{39187.5}{n}$$

$$n = 0.0548 \text{ mol}$$

$$\text{Mass of methanol} = 0.0548 \times 32 = 1.754 \text{ g} = 1.75 \text{ g (3 sf)}$$

[Total: 13]

Section B

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

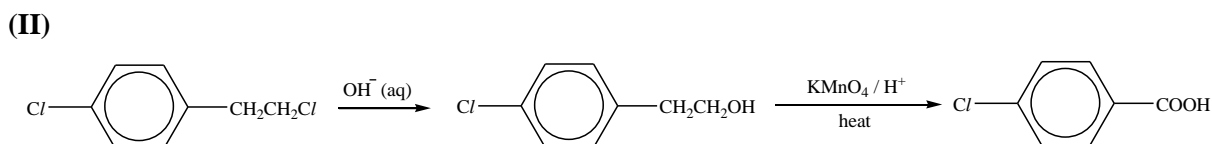
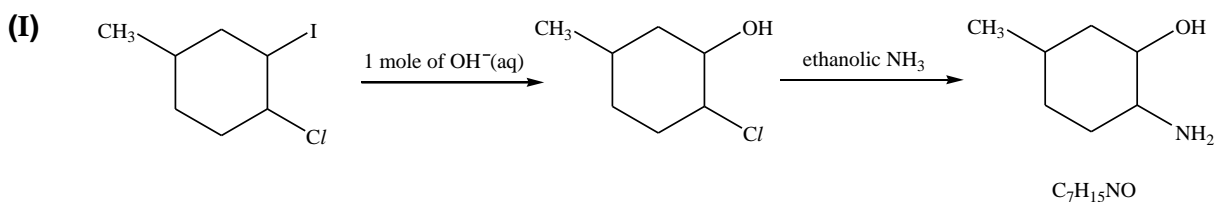
- 5 (a) Describe and explain the relative reactivities of chloropropane and iodopropane with respect to hydrolysis.

C_3H_7Cl undergo hydrolysis at a lower rate than C_3H_7I . This is due to the stronger C–Cl bond (bond energy = 340 kJ mol^{-1}) being harder to break as compared to the weaker C–I bond (bond energy = 240 kJ mol^{-1}).

[2]

- (b) The different reactivities of organic halogeno compounds can be exploited in successive reactions of dihalogeno compounds.

Predict the outcomes of the following transformations, drawing the structures of the intermediates **C** and **E** and the products **D** and **F**.



[4]

- (c) Samples of 2-chloropropane were dissolved in dilute aqueous ethanol and reacted with hot sodium hydroxide solution. Two separate experiments with different concentrations of 2-chloropropane, were carried out to study the kinetics of the reaction.

The following results were obtained.

	Experiment 1 [2-chloropropane] = 0.05 mol dm^{-3}	Experiment 2 [2-chloropropane] = 0.10 mol dm^{-3}
Time / min	[NaOH] / mol dm^{-3}	[NaOH] / mol dm^{-3}
0	0.0050	0.0050
15	0.0045	0.0040
30	0.0040	0.0032
45	0.0036	0.0026
60	0.0032	0.0021
75	0.0029	0.0017
90	0.0026	0.0014

- (i) The results of **Experiment 1** has been plotted on the **INSERT** provided. On the same **INSERT**, plot a graph for **Experiment 2**.
- (ii) Use your graph in (i) to deduce the order of reaction with respect to 2-chloropropane and sodium hydroxide solution. Show your working clearly.

[4]

From graph for Expt 2, since $t_{1/2}$ is constant at 48 min, the reaction is first order wrt NaOH.

$$\text{For Expt 1, gradient} = \text{rate} = \frac{0.005 - 0.0042}{0 - 22} = -3.64 \times 10^{-5}$$

$$\text{For Expt 2, gradient} = \text{rate} = \frac{0.005 - 0.0042}{0 - 12} = -6.67 \times 10^{-5}$$

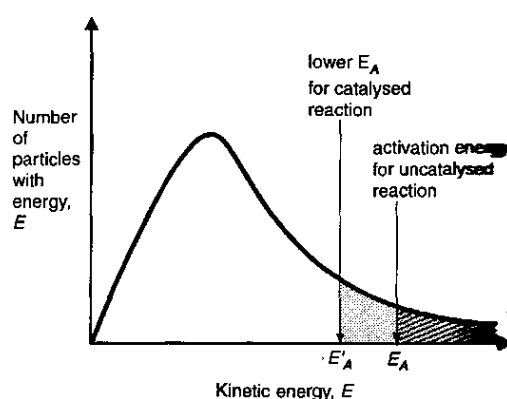
When [2-chloropropane] doubles from 0.05 mol dm^{-3} to 0.10 mol dm^{-3} , rate doubles from -3.64×10^{-5} to -6.67×10^{-5} . Hence, reaction is first order wrt 2-chloropropane.

- (iii) Use your answer in (ii) to write a rate equation for the reaction. [1]
Rate = $k[2\text{-chloropropane}][\text{NaOH}]$

- (iv) The numerical value of the rate of reaction was measured as 0.048 when $[\text{NaOH}] = 0.20 \text{ mol dm}^{-3}$, $[2\text{-chloropropane}] = 0.10 \text{ mol dm}^{-3}$. Determine the rate constant for this reaction and state its units. [3]

$$k = \frac{0.048}{[0.10][0.20]} = 2.40 \text{ mol}^{-1}\text{dm}^3 \text{ min}^{-1}$$

- (v) Sketch a Maxwell-Boltzmann curve for the reactants and use it to explain the effect of a catalyst on the rate of reaction in **Experiment 2**. [3]



When catalyst is used, the **activation energy, E_a , is lowered** and there **are more molecules with kinetic energy $> E_a$** . Therefore, **the frequency of effective collision increases** and the rate of reaction increases.

- (vi) In the reaction described in (c), suggest why 2-chloropropane is dissolved in dilute aqueous ethanol before it is reacted with hot sodium hydroxide solution.

To increase miscibility and hence enable reaction between 2-chloropropane and sodium hydroxide to occur. (2-chloropropane is miscible with ethanol through pdd; sodium hydroxide is miscible with ethanol through H-bonding.)

[14]

[Total:20]

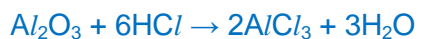
- 6 (a) The acid-base behaviour of aluminium oxide, Al_2O_3 , shows similarities to that of magnesium oxide, MgO on the one hand, and phosphorus(V) oxide, P_4O_{10} ,

on the other.

Describe what these similarities are, and explain why aluminium oxide occupies this in-between position.

Write equations for all the reactions you choose to illustrate your answer.

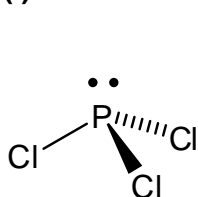
MgO is a basic oxide and can react with acids while P₄O₁₀ is an acidic oxide and can react with bases. In Al₂O₃, Al³⁺ has high charge/radius ratio, high polarising power to distort the electron cloud of O²⁻, resulting in covalent character, hence it is ionic with some covalency and exhibits amphoteric properties, i.e. can react with both acids and bases.



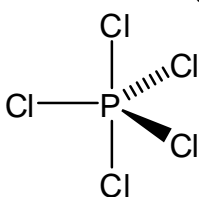
[4]

(b) Phosphorus is able to form more than one chloride, PCl₃ and PCl₅.

(i) Draw the lewis structures of PCl₃ and PCl₅, and state their shapes.



Trigonal pyramidal



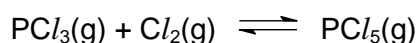
Trigonal bipyramidal

(ii) Predict the solubility of PCl₅ in CCl₄.

[4]

Soluble due to favourable temporary dipole-induced dipole interactions formed.

PCl₅ can be produced by reacting PCl₃ with chlorine gas.



(c)

The process is carried out in a V dm³ reaction vessel. 1.80 mol of PCl₃ and 1.50 mol of Cl₂ are allowed to reach equilibrium at 180 °C.

0.60 mol of PCl₅ is found to be present in the equilibrium mixture.

(i) Given that the value of equilibrium constant, K_c for the reaction is 0.311, determine V. [2]

	$\text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{PCl}_5(\text{g})$	
Initial /mol	1.80	1.50
Change / mol	-0.60	-0.60
Eqm /mol	1.20	0.90

$$K_c = \frac{[\text{PCl}_5]}{[\text{Cl}_2][\text{PCl}_3]}$$

$$0.311 = \frac{\left(\frac{0.60}{V}\right)}{\left(\frac{1.20}{V}\right)\left(\frac{0.90}{V}\right)} \quad \text{Hence, } V = 0.560 \text{ dm}^3$$

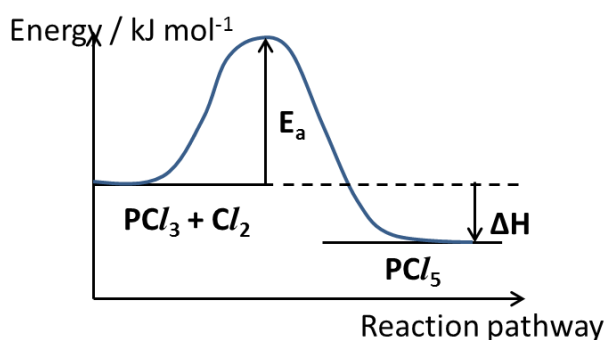
(ii) The percentage yield of PCl_5 at different temperatures is shown below.

Temperature	Percentage yield
200°C	70%
300°C	65%
400°C	50%

With reference to the data above, deduce whether the production of PCl_5 is an endothermic or exothermic reaction. Explain your answer. [2]

When temperature increases, percentage yield decreases. When temperature increases, the backward reaction is favoured to partially offset the excess heat energy. The backward reaction is endothermic hence production of PCl_5 is an exothermic reaction.

(iii) By making use of your answer in (ii), draw a well-labelled reaction profile diagram for the forward reaction.



(iv) State and explain how the position of equilibrium and the equilibrium constant would change when the reaction is carried out in a bigger reaction vessel.

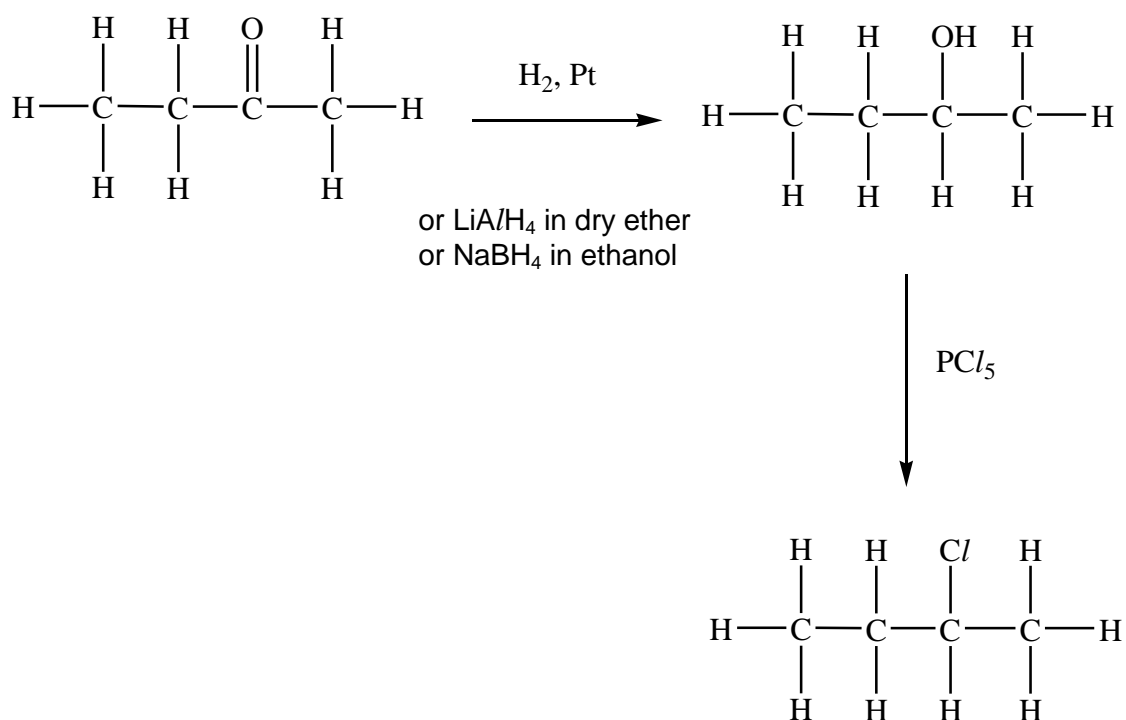
[9]

Pressure is decreased when a bigger reaction vessel is used. Position of equilibrium shifts left to partially offset the decrease in pressure. There is no change to the equilibrium constant since temperature remains unchanged.

(d)

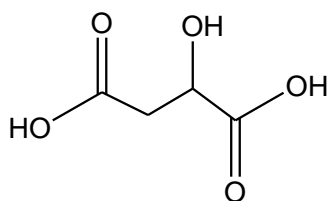
One of the uses of PCl_5 includes the chlorinating of organic compounds. Propose a synthetic pathway (making use of PCl_5 in one of your steps) for the conversion of butanone to 2-chlorobutane.

[3]



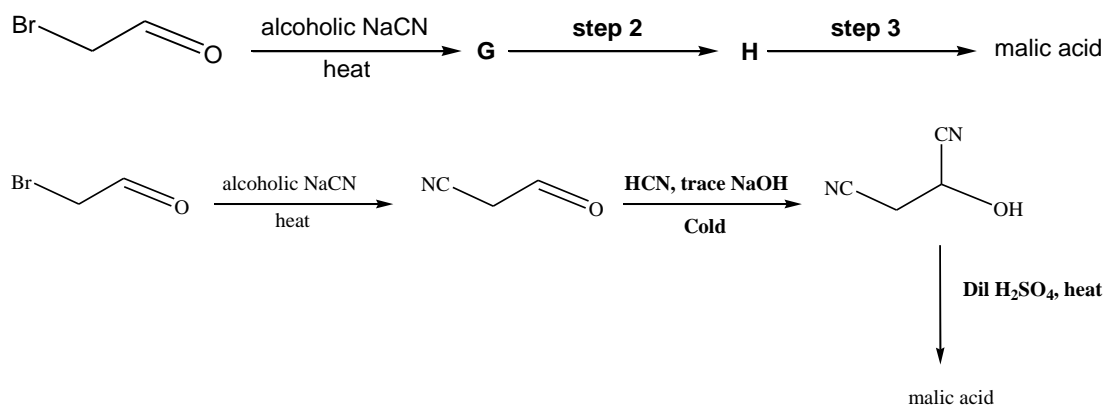
[Total: 20]

- 7 Malic acid can be found in green apples and grapes. It is often added to beverages and confectionery to confer a sour taste.



Malic acid

- (a) Suggest the reagents and conditions you would use in a three-step synthesis of malic acid from bromoethanal, identifying the intermediates **G** and **H**.



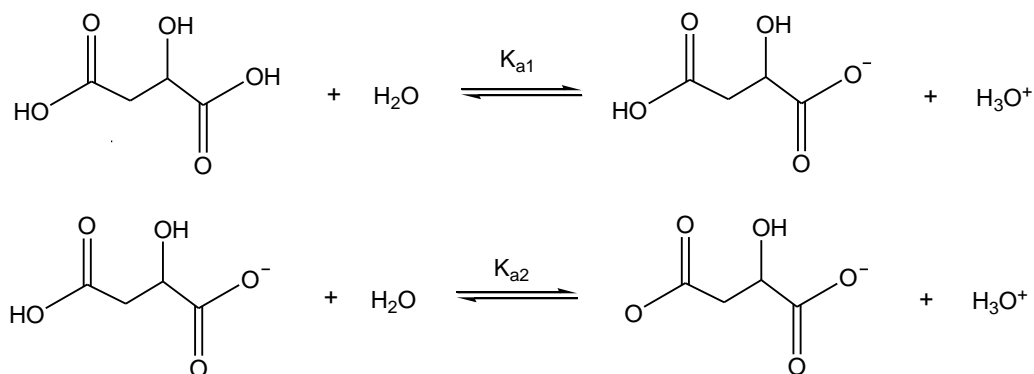
[4]

- (b) Malic acid is classified as a *Bronsted-Lowry* acid. It is a dibasic acid.

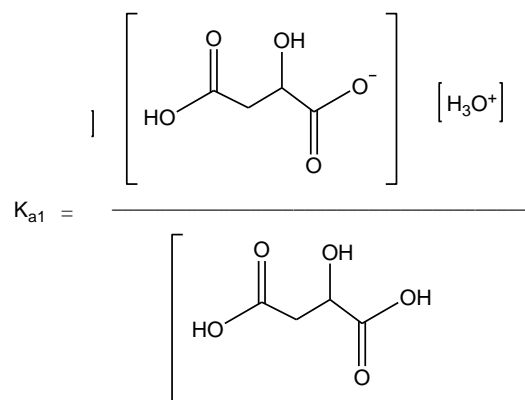
- (i) Explain what is meant by a *dibasic* acid.

A dibasic acid is one that donates 2 H^+ in aqueous solutions per mole of acid.

- (ii) Malic acid dissociates in water according to the equations shown below:



(I) Write the K_{a1} expression.



(II) Given that the K_{a1} value of malic acid is 10^{-3} , calculate the pH of a 0.10 mol dm^{-3} solution of malic acid. Hence, deduce if malic acid is a strong or a weak acid. [2]

Let HA represent malic acid.

$$K_a = \frac{[H^+]^2}{[HA]}$$

$$10^{-3} = \frac{[H^+]^2}{[0.10]}$$

$$[H^+] = 0.01 \text{ mol dm}^{-3}$$

$$\text{pH} = -\lg(0.01) = 2$$

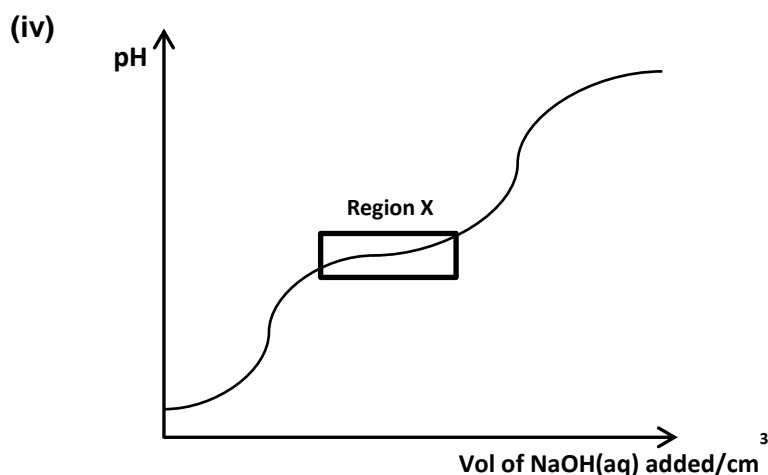
Since $[H^+]$ is lesser than $[HA]$, malic acid has only dissociated partially, hence, it is a weak acid.

(iii) 25.0 cm^3 of a 0.10 mol dm^{-3} solution of malic acid was titrated with 0.20 mol dm^{-3} of aqueous sodium hydroxide. Calculate the total volume of aqueous sodium hydroxide required for complete neutralisation. [2]

$$\text{Amount of } H^+ = 2 \times 25/1000 \times 0.10 = 5 \times 10^{-3} \text{ mol}$$

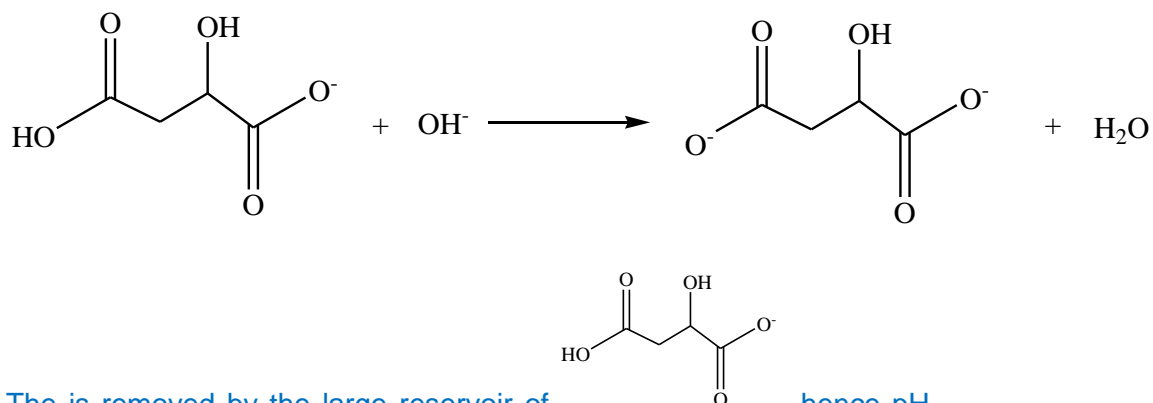
$$\text{Amount of } OH^- \text{ required} = 5 \times 10^{-3} \text{ mol}$$

$$\begin{aligned} \text{Volume of NaOH required} &= 1000/0.2 \times 5 \times 10^{-3} \\ &= 25.0 \text{ cm}^3 \end{aligned}$$



The above pH curve was obtained in the titration procedure as described in (iii). With the aid of an equation, explain why the pH of the mixture remained fairly constant at region X when a small amount of NaOH(aq) is added. [1]

When a small amount of OH^- is added,



The is removed by the large reservoir of , hence pH remains fairly constant.

- (v) Phenolphthalein was used as the indicator in the titration procedure as described in (iii). Explain why is phenolphthalein a suitable indicator and suggest the colour that will be observed at the end of the titration. [2]
 The pH at equivalence is > 7 , which lies within the working range of phenolphthalein.
 Pink.

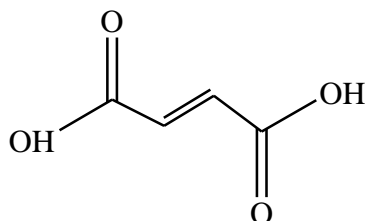
[9]

- (c) Malic acid can be dehydrated to give a mixture of two geometric isomers of alkenedioic acids with the molecular formula $C_4H_4O_4$.

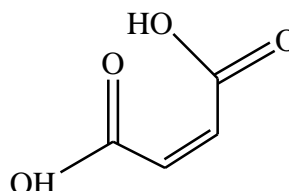
- (i) Suggest reagents and conditions for the dehydration of malic acid. [2]

Excess conc H_2SO_4 , $170^\circ C$.

- (ii) Draw the structural formulae of the two geometric isomers, and explain why geometric isomerism arises. [3]



Trans-isomer



Cis-isomer

There is restricted rotation about the double bond. There are 2 different groups bonded to each of the doubly bonded carbon.

- (iii) Explain why the *trans*-isomer has a higher boiling point than the *cis*-isomer. [2]

Cis-isomer has intramolecular hydrogen bond due to the close proximity of the $-OH$ and $-C=O$ groups. Hence, it has less extensive intermolecular hydrogen bonding than trans-isomer. More energy is required to break the more extensive intermolecular hydrogen bonding in trans-isomer, hence higher boiling point.

[7]

[Total:20]