NATIONAL JUNIOR COLLEGE
SH 2 PRELIMINARY EXAMINATION

Higher 1

CANDIDATE NAME			
SUBJECT CLASS		REGISTRATION NUMBER	

CHEMISTRY

8873/02

Paper 2 Structured Questions

Tues 21 Aug 2018
2 hours

Candidates answer **all** questions on the Question Paper.
Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your subject class, registration number and name on all the work you hand in.
Write in dark blue or black pen.
You may use a soft pencil for any diagrams, graphs.
Do not use staples, paper clips, glue or correction fluid/tape.

Section **A**
Answer **all** the questions.

Section **B**
Answer **only one** question.

The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

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.

For Examiner's Use				
1	/5			
2	/10			
3	/7			
4	/12			
5	/16			
6	/8			
7	/5			
8 OR 9	/20			
Penalty units				
Penalty sf				
Paper 2	/83			

Answer <u>ALL</u> questions on the space provided.
This paper consists of **20** printed pages.

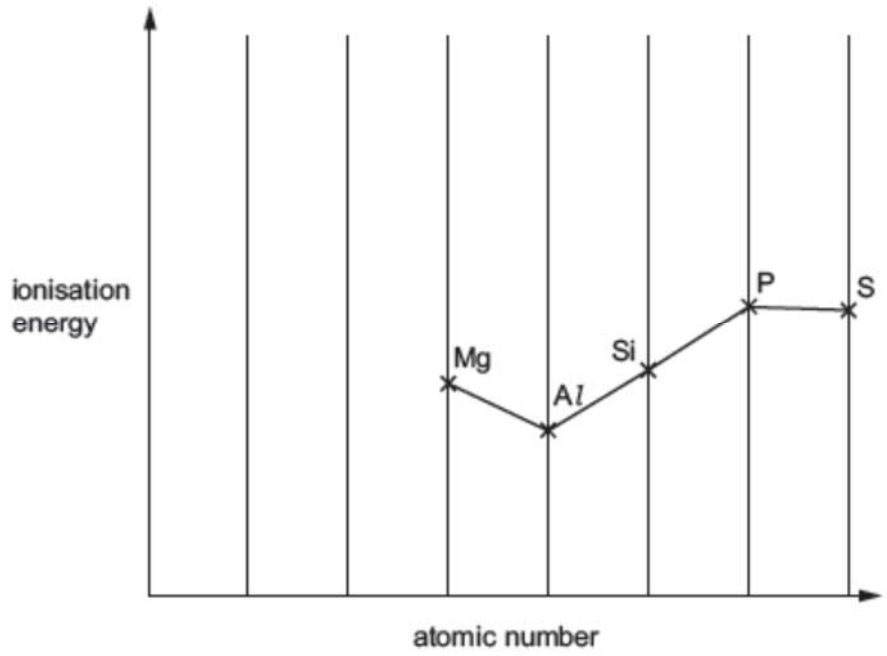
Section A

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

1 The properties of elements and their compounds show similarities, differences and trends depending on the positions of the elements.

(a) The elements in the third period, and their compounds, show trends in their physical and chemical properties.

A sketch graph of the first ionisation energies of five successive elements in the third period is shown.



(i) Sketch on the graph, the position of the ionisation energy of the two elements that come before Mg in this sequence.

[1]

(ii) Explain, with reference to electronic arrangements, the decreases in first ionisation energy between Mg and A*l* and between P and S.

Mg and A*l*: .....

.....

.....

P and S: .....

.....

.....

[2]

(b) The chlorides of the elements in the third period behave in different ways when added to water, depending on their structure and bonding.

L is a chloride of an element in Period 3. A student investigated **L** and the results are as given below.

- **L** is a white crystalline solid with a melting point of 987 K.
- **L** dissolves in water to form a weakly acidic solution.
- Addition of NaOH(aq) to an aqueous solution of **L** produces a white precipitate.

(i) Identify **L.**

L: …… [1]

(ii) Write an equation to illustrate the formation of the weakly acidic solution.

…… [1]

[Total: 5]

2 Nanomaterials research takes a materials science-based approach to nanotechnology, leveraging advances in materials metrology and synthesis which have been developed in support of microfabrication research. Materials with structures at the nanoscale often have unique optical, electronic, or mechanical properties as compared to its corresponding bulk materials.

Graphene is a nanomaterials which is an allotrope of carbon such as graphite and diamond. It has many uncommon properties. Graphene is the strongest material ever tested, efficiently conducts heat and electricity, and is nearly transparent.

Because nanotechnology is a recent development, the health and safety effects of exposures to nanomaterials and nanoparticles, and what levels of exposure may be acceptable, are subjects to ongoing research.

(a) State the difference between a nanoparticle and a nanomaterials in terms of size.

……

……

[1]

(b) Describe the property of nanomaterials. Explain how this property enables it to be used in the following application:

1 Catalysis

.....

.....

.....

2 Climbing ability of geckos

.....

.....

.....[4]

(c) With the aid of a labelled diagram, describe the structure of graphene. Explain how this structure gives graphene the properties of high electrical conductivity and high tensile strength.

.....

.....

.....

.....

.....[3]

(d) Cerium oxide is being used in electronics, biomedical supplies, energy and fuel additives.
Predict how nanoparticles of cerium oxide could present a risk to human health **and** the environment.

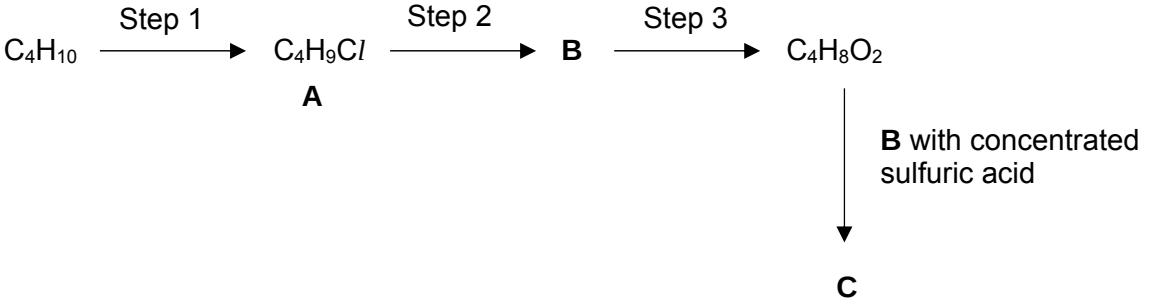
.....

.....

.....

.....[2]
[Total: 10]

3 Student **M** suggested a 2-step process as shown, to synthesise **B** from a suitable butane.



(a) Identify the structures of compounds **B** and **C**. Suggest reagents and conditions for each of the steps.

Structure of **B**	Structure of **C**

Step 1: **……**

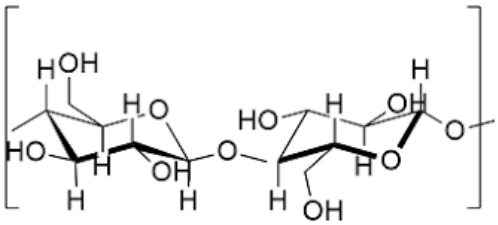
Step 2: **……**

Step 3: **……** [5]

(b) Compound **D,** an isomer of compound **A**, is formed after **step 1.**
Suggest the structure of compound **D**. Hence, state the approximate ratio in which compounds **A** and **D** are formed.

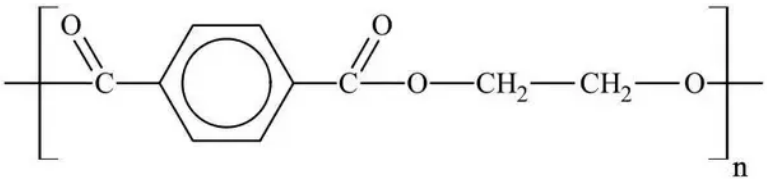
[2]
[Total:7]

4 In the past, football shirts were made from cotton, or even wool. These cotton or wool shirts trapped heat and readily soaked up any sweat produced, making them rather uncomfortable to wear.



Repeating unit of cotton

Nowadays, polyethylene terephthalate (PET) and spandex are used in manufacture of football shirts. Cotton can absorb 7% of its weight in water, whereas polyester only absorbs about 0.4% of its weight. PET also does not crease easily.



Repeating unit of PET

(a) (i) Suggest why cotton can absorb more water than PET.

……

……

[1]

(ii) Explain why PET does not crease easily with respect to its **structure.**

……

……

[1]

(b) (i) Calculate the percentage of mass of carbon in PET.

[2]

(ii) Identify the type of polymerisation in the formation of PET and provide **two** reasons to explain your answer.

Type of polymer .....

Reason 1.....

.....

Reason 2.....

.....

[3]

(iii) Explain why a PET fabric dissolves slowly when placed in aqueous alkali.

……..……

……..……

[1]

(iv) Write an equation for **one repeat unit** of PET reacting with aqueous sodium hydroxide.

[1]

(c) PET is a thermoplastic. With respect to the structure and interactions of polymer chains, explain

(i) the difference between thermoplastics and thermosets.

……..……

……..……

[1]

(ii) why PET can be used as a fabric.

……..……

……..……

……..……

[2]

[Total: 12]

5 On 11 May 2018, Mount Merapi on Central Java, Indonesia erupted, causing the local airport to be closed. The eruption was reported to be caused by accumulation of volcanic gases. The volcanic ash and gases spewed can be dangerous to planes passing through the plume. The most abundant volcanic gas is harmless water vapour. However, significant amounts of carbon dioxide, sulfur dioxide, hydrogen sulfide and hydrogen halides are also emitted.

When carbon dioxide is emitted from volcanoes, it typically becomes diluted to low concentrations very quickly and is not life threatening. However, cold carbon dioxide gas can flow into low-lying areas where it can reach much higher concentrations. Breathing air with more than 3% CO_2 can quickly lead to headaches, dizziness, increased heart rate and difficulty breathing. At about 15%, unconsciousness and death can result quickly.

Table 1: Volcanic gas composition in area **A**

Gas	Volume Percentage
Water vapour, H_2O	87.1
Carbon dioxide, CO_2	unknown
Sulfur dioxide, SO_2	0.5
Hydrogen, H_2	0.7
Carbon monoxide, CO	0.01
Hydrogen sulfide, H_2S	0.23
Hydrogen halides	unknown

Composition of the volcanic gases are typically expressed in terms of volume percentage, which can be calculated as follows

$$\text{volume percentage} = \frac{\text{volume of gas}}{\text{total volume}} \times 100\%$$

(a) (i) Draw the dot-and-cross diagram of H_2S.

[1]

(ii) State and explain whether H_2S or H_2O has a larger bond angle with respect to its central atom.

……

……

……

……

[2]

(iii) Suggest a reason why at low temperature, carbon dioxide would sink rapidly and accumulate to high concentrations.

……

……

……
[2]

(iv) People living in area **A** were evacuated as the level of carbon dioxide was increasing rapidly. Given that 0.3 g of CO_2 was present in 1 dm^3 of gas mixture at r.t.p, determine the volume percentage of carbon dioxide present.

Hence comment on the possible danger if people remained in the area.

Volume percentage of carbon dioxide = ……

……

……
[2]

(b) Hydrogen sulfide can react with methane in the following equation.

$$CH_4(g) + 2\ H_2S(g) \rightleftharpoons CS_2(g) + 4H_2(g)$$

1 mol of CH_4, 2 mol of H_2S, 1 mol of CS_2 and 1 mol of H_2 were allowed to reach equilibrium in a 2 dm^3 container at a constant temperature and pressure.

(i) State the oxidation state of carbon in each carbon-containing compound.

CH_4 : ……... CS_2: …… [1]

(ii) Hence comment on the role of H_2S in the reaction.

……
. [1]

(iii) Given that CS_2 was found to be 1.2 mol at equilibrium, determine the value of K_c, giving its units.

[2]

(iv) Using the *Data Booklet,* calculate the enthalpy change of the above reaction. Assume bond energy of C-S bond is 272 kJ mol^{-1}.

[2]

(v) Hence state and explain the effect of increasing the temperature of the system on

- position of the equilibrium
- rate of the reaction.

……

……

……

……

……

[3]

[Total: 16]

6 1–chloro–1–phenylethane undergoes hydrolysis with hydroxide ions to produce 1–phenylethanol, as shown in the equation below.

$$C_6H_5CHClCH_3 + OH^- \rightarrow C_6H_5CH(OH)CH_3 + Cl^-$$

1-chloro-1-phenylethane — 1-phenylethanol

The rate of this reaction can be studied by measuring the amount of hydroxide ions that remain in the solution at a given time after the reaction has been quenched.

(a) Suggest a suitable quenching agent that can be used to slow down the rate of the reaction effectively.

.....

[1]

(b) The rate of this reaction was measured using different initial concentrations of the two reagents and the results are shown below.

Experiment	$[C_6H_5CHClCH_3]$ / mol dm^{-3}	$[OH^-]$ / mol dm^{-3}	Relative rate
1	0.05	0.10	1.0
2	0.10	0.20	2.0
3	0.15	0.10	3.0

(i) Deduce the order of reaction with respect to each of the reagents. Explain your reasoning.

Order with respect to $C_6H_5CHClCH_3$ = **.....**

Order with respect to OH^- = **.....**

[2]

(ii) Write the rate equation for this reaction, stating the units of the rate constant, *k*.

rate = **.....** mol dm^{-3} s^{-1}

units of *k* = **.....**

[2]

[Total: 5]

7 Lithium is a scavenger for hydrogen, hence able to prevent the reaction between hydrogen and copper during pure copper casting. Reaction with hydrogen makes the copper brittle, causing it to fall apart under very light stress.

Table 2

	Enthalpy / kJ mol^{-1}
Enthalpy change of formation of Li*Al*H$_4$(*l*)	–152.5
Enthalpy change of formation of Li*Al*H$_6$(s)	–454

(a) Heating lithium in a stream of hydrogen gas produces white, crystalline, ionic lithium hydride, LiH.

(i) By quoting relevant data from the *Data Booklet*, suggest and explain how the magnitude of the lattice energy of Li*Cl* would compare to that of LiH.

……

……

……

[2]

(b) When lithium hydride is heated with anhydrous aluminium chloride, lithium aluminium hydride, Li*Al*H$_4$ and lithium chloride are produced.

Balance the equation for the above reaction.

…….. LiH + …… A*lCl*$_3$ → …….. Li*Al*H$_4$ + …….Li*Cl*

[1]

(c) Just above its melting point, Li*Al*H$_4$ decomposes according to the following equation.

$$3\ LiAlH_4\ (l) \rightarrow LiAlH_6(s) + 2Al(s) + 3H_2(g)$$

Using **Table 2**, calculate the standard enthalpy change of this reaction.

[2]
[Total: 5]

Section B

Answer only **one** question from this section, in the spaces provided.

8(a) With the aid of a Boltzman distribution curve, explain how the presence of a catalyst increase the rate of a reaction.

.....

.....

.....

[3]

(b) The melting points of some compounds are given.

Substance	Octan-1-ol	Iodine	Fullerene	Graphite
Formula	$CH_3(CH_2)_9OH$	I_2	C_{60}	C
Melting point/ K	277	286	873	>3000

(i) Explain why the melting points of octan-1-ol and iodine are comparable.

.....

.....

.....

.....

[2]

(ii) Explain why the melting point of graphite is higher than that of fullerene.

.....

.....

.....

[2]

(iii) By quoting relevant data from the *Data Booklet*, account for the trend in the thermal stabilities from HC*l* to HI.

……

……

……

[2]

(iv) Arrange the pH of HC*l* to HI in aqueous solution in ascending order.

Explain the variation you have outlined.

……

……

……

[2]

(c) Compound **X** has the molecular formula $C_4H_8O_2$.

(i) Treatment of **X** with acidified potassium dichromate(VII) produces a green solution.

What could be the functional groups present in **X**?

……

……

[1]

(ii) There is no reaction when **X** is treated with aqueous sodium carbonate, Na_2CO_3.

What could be the functional groups absent in **X**?

……

……

[1]

(iii) When **X** is shaken with aqueous bromine, the orange colour disappears.

What could be the functional groups present in **X**?

……

……

[1]

(iv) The molecule of **X** has the following features.

- The carbon chain is unbranched and the molecule is not cyclic.
- No oxygen atom is attached to any carbon atom which is involved in π bonding.
- No carbon atom has more than one oxygen atom joined to it.

There are four possible isomers of **X** which fit these data.

Draw displayed formulae of **all** possible isomers and state which type of isomerism they show.

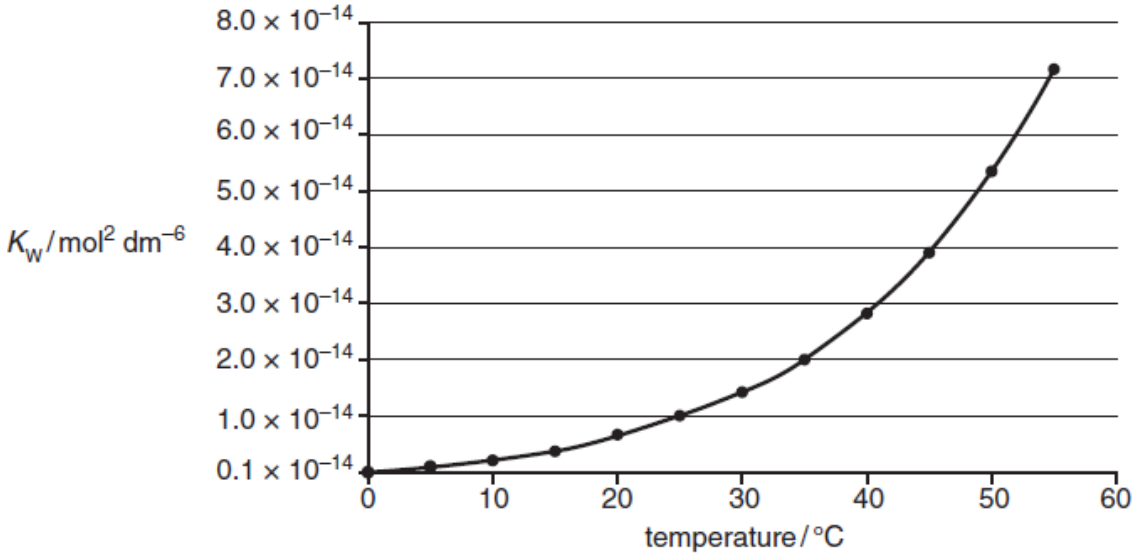
[6]
[Total: 20]

9 (a) The dissociation of water is a reversible reaction.

$$H_2O\,(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

The ionic product of water, K_w, measures the extent of dissociation of water. K_w varies with temperature. It is always important to quote the temperature at which measurements are being taken.

The graph below shows the variation of K_w. between 0 °C and 60 °C.



(i) Write the expression for K_w.

.....

[1]

(ii) Calculate the concentration of hydroxide ions, $[OH^-]$, in an aqueous solution of hydrochloric acid at pH of 4.37 at 25 °C.

[2]

(iii) Using the graph, explain whether the dissociation of water is an exothermic or endothermic process.

……

……

……

……

[2]

(iv) Using the graph, determine the pH of pure water at body temperature, at 37 ^{o}C.

[3]

(v) Given the following data:

Indicator	Colour change (acidic to basic medium)	pH range in which colour change occurs
Bromothylmol blue	yellow to blue	6.0 – 7.6

State the colour observed when a few drops of bromothylmol blue is added to a sample of pure water at body temperature, at 37 ^{o}C.

……

[1]

(vi) Buffer solutions are important in biological systems and in industry to maintain almost constant pH values

In the human body, one important buffer system in blood involves the hydrogencarbonate ion, HCO_3^- and carbonic acid, H_2CO_3, which is formed when carbon dioxide dissolves in water.

Use the following equation to explain how this buffer maintains a constant pH of 7.41 even if a small amount of acid enters the bloodstream.

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

.....

.....

.....

.....

.....

[2]

(b) The hydrocarbons **A**, C_4H_{10}, and **B**, C_4H_8, are both unbranched.
A does **not** decolourise bromine.
B decolourises bromine and shows cis-trans isomerism.

(i) Draw the skeletal formula of **A**.

[1]

(ii) The hydrocarbon **A**, C_4H_{10}, has a branched isomer.
Suggest why unbranched **A** has a higher boiling point than its branched isomer.

.....

.....

.....

.....

[2]

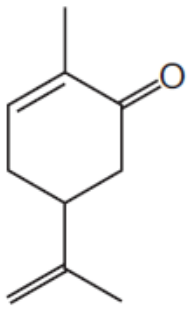
(iii) Draw the structure of the product obtained from the reaction between **B** and bromine. State the type of reaction that occurred.

Type of reaction: …….

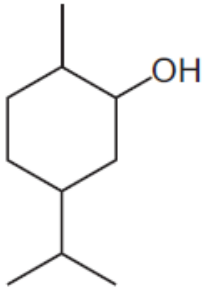
Product:

[2]

(c) Carvone occurs in spearmint and can be converted to compound **M**.



carvone



M

(i) State the reagent and conditions for the conversion of carvone to compound **M**.

name of reagent…..……

conditions…..……..
[1]

(ii) Draw the structure of the product when **M** is treated with excess concentrated sulfuric acid at 170 ^{o}C.

[1]

(d) Write an equation for the reaction that occurs when silicon tetrachloride is added to water. Predict the pH of the resulting solution.

……

……
[2]

[Total: 20]

End of Paper

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Penalty units				
Penalty sf				
Paper 2	/80			

Answer <u>ALL</u> questions on the space provided.
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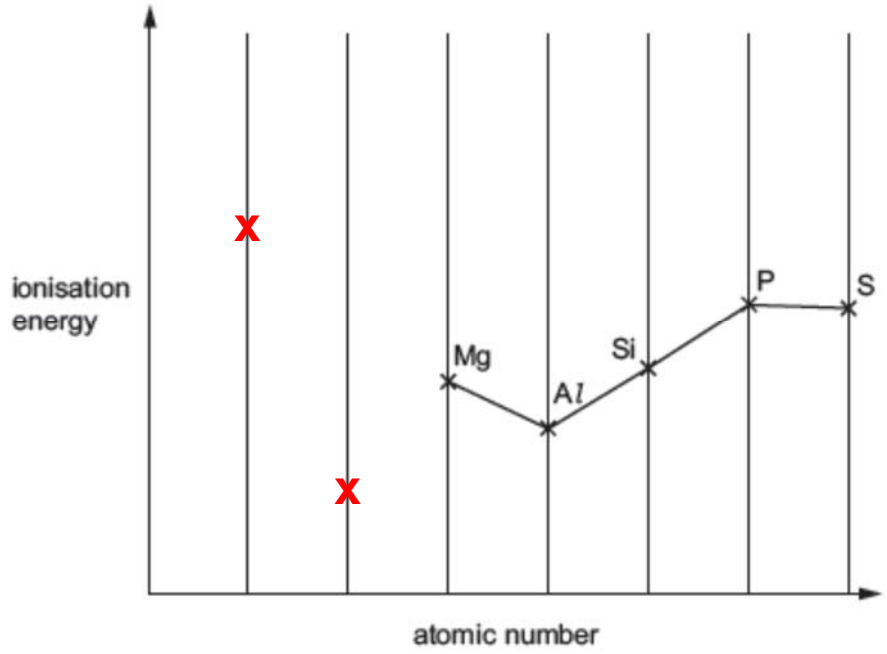
Section A

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

1 The properties of elements and their compounds show similarities, differences and trends depending on the positions of the elements.

(a) The elements in the third period, and their compounds, show trends in their physical and chemical properties.

A sketch graph of the first ionisation energies of five successive elements in the third period is shown.



(i) Sketch on the graph, the position of the ionisation energy of the two elements that come before Mg in this sequence.

[1]

Cross shown on first vertical line from the y-axis (group 0/Ne) is clearly higher than all shown.
Cross shown on second vertical line from the y-axis (group 1/Na) is clearly lower than all shown.

[1]

(ii) Explain, with reference to electronic arrangements, the decreases in first ionisation energy between Mg and A*l* and between P and S.

Mg and A*l*: The most loosely held electron in A*l* is in the **higher energy 3p subshell** while that of Mg is in the **lower energy 3s subshell.**
This **outweighs the effect of the increase in nuclear charge** from Mg to A*l*.
Hence **nuclear attraction for the most loosely held electron in A*l* is weaker**, i.e. A*l* has a lower 1st IE. [1]

P and S: The most loosely held electron in S is one of the **paired electrons in 3p** orbital while that of P is in the **singly filled 3p** orbital.
Inter-electronic repulsion between the paired electrons in the same p orbital **outweighs the effect of an increase in nuclear charge**.
Hence, **nuclear attraction for the most loosely held electrons is weaker in**

S, i.e. S has a lower first IE. [1]

[2]

(b) The chlorides of the elements in the third period behave in different ways when added to water, depending on their structure and bonding.

L is a chloride of an element in Period 3. A student investigated **L** and the results are as given below.

- **L** is a white crystalline solid with a melting point of 987 K.
- **L** dissolves in water to form a weakly acidic solution.
- Addition of NaOH(aq) to an aqueous solution of **L** produces a white precipitate.

(i) Identify **L.**

L: $MgCl_2$ [1]

(ii) Write an equation to illustrate the formation of the weakly acidic solution.

$[Mg(H_2O)_6]^{2+}(aq) + H_2O(l) \rightleftharpoons [Mg(H_2O)_5(OH)]^{+}(aq) + H_3O^{+}(aq)$ [1]
(state symbols not necessary)

[Total: 5]

2 Nanomaterials research takes a materials science-based approach to nanotechnology, leveraging advances in materials metrology and synthesis which have been developed in support of microfabrication research. Materials with structures at the nanoscale often have unique optical, electronic, or mechanical properties as compared to its corresponding bulk materials.

Graphene is a nanomaterials which is an allotrope of carbon such as graphite and diamond. It has many uncommon properties. Graphene is the strongest material ever tested, efficiently conducts heat and electricity, and is nearly transparent.

Because nanotechnology is a recent development, the health and safety effects of exposures to nanomaterials and nanoparticles, and what levels of exposure may be acceptable, are subjects to ongoing research.

(a) State the difference between a nanoparticle and a nanomaterials in terms of size.

Nanomaterials: A material with at least one dimension to be in the nanoscale (1 – 100 nm)

Nanoparticles: A material with all dimensions to be in the nanoscale (1- 100 nm)

[1]

(b) Describe the property of nanomaterials. Explain how this property enables it to be used in the following application:

1 Catalysis

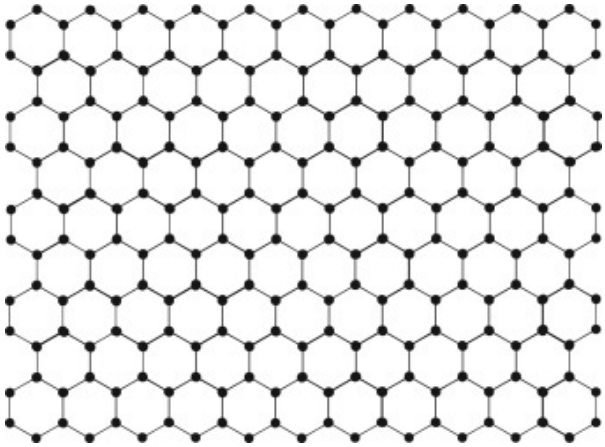
By using nanoparticles of the precious metals instead of larger particles, less metal is needed to produce the same surface area over the ceramic base of the catalyst

2 Climbing ability of geckos

The spatula-shaped setae arranged in lamellae on gecko footpads enable attractive van der Waals' forces between spatulae structures and the surface.

Use of small van der Waals attraction force requires very large surface areas.
[4]

(c) With the aid of a labelled diagram, describe the structure of graphene. Explain how this structure gives graphene the properties of high electrical conductivity and high tensile strength.



One p electrons per C atom delocalised so high electrical conductivity

Each C attached to 3 others by a network of strong covalent bonds so high strength.
[3]

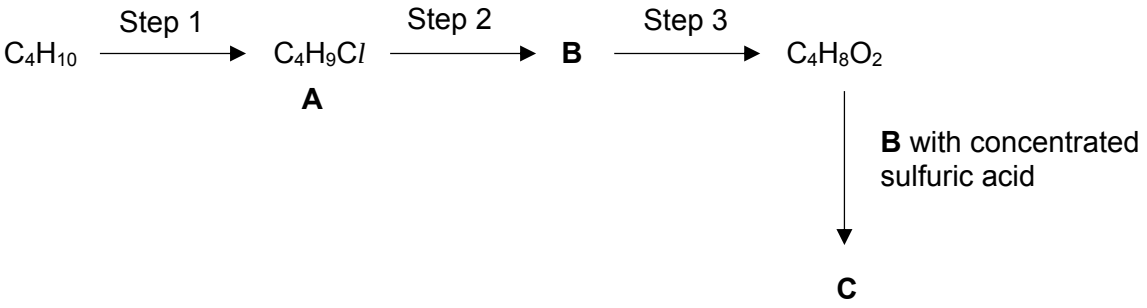
(d) Cerium oxide is being used in electronics, biomedical supplies, energy and fuel additives.
Predict how nanoparticles of cerium oxide could present a risk to human health **and** the environment.

Small enough to go through the pores AND can get into the blood and affects organs

High energy requirements for synthesizing nanoparticles causing high energy demand./Dissemination of toxic, persistent nanosubstances originating environmental harm/ Lower recovery and recycling rates

[2]
[Total: 10]

3 Student **M** suggested a 2-step process as shown, to synthesise **B** from a suitable butane.



(a) Identify the structures of compounds **B** and **C**. Suggest reagents and conditions for each of the steps.

$CH_3CH_2CH_2CH_2OH$ Structure of **B**	$CH_3CH_2CH_2CH_2OCOCH_2CH_2CH_3$ Structure of **C**

Step 1: Cl_2 (g), uv light/ heat

Step 2: KOH(aq), heat or NaOH(aq), heat

Step 3: $KMnO_4$, H_2SO_4(aq), heat or $K_2Cr_2O_7$, H_2SO_4(aq), heat under reflux

[5]

(b) Compound **D,** an isomer of compound **A**, is formed after **step 1.**
Suggest the structure of compound **D**. Hence, state the approximate ratio in which compounds **A** and **D** are formed.

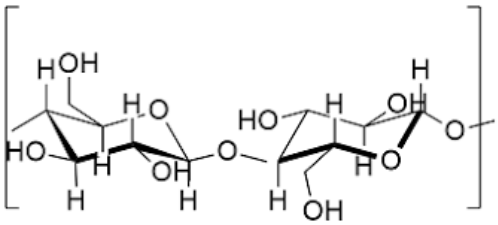
Compound A: $CH_3CH_2CH_2CH_2Cl$, 1-chlorobutane

Compound D: $CH_3CH_2CHClCH_3$, 2-chlorobutane

approximate ratio for **A**: **D**
3: 2

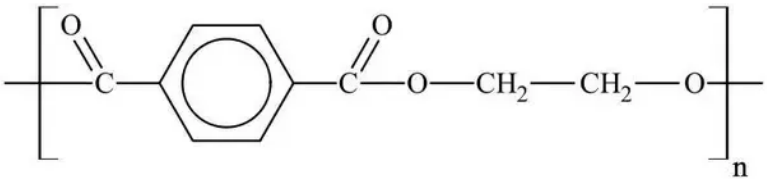
[2]
[Total:7]

4 In the past, football shirts were made from cotton, or even wool. These cotton or wool shirts trapped heat and readily soaked up any sweat produced, making them rather uncomfortable to wear.



Repeating unit of cotton

Nowadays, polyethylene terephthalate (PET) and spandex are used in manufacture of football shirts. Cotton can absorb 7% of its weight in water, whereas polyester only absorbs about 0.4% of its weight. PET also does not crease easily.



Repeating unit of PET

(a) (i) Suggest why cotton can absorb more water than PET.

Cotton has many hydroxyl groups (OH groups), thus able to form more extensive hydrogen bonds with water molecules, trapping water. PET form less extensive hydrogen bonding with water.

[1]

(ii) Explain why PET does not crease easily with respect to its **structure.**

The aromatic benzene ring adds rigidity to PET's structure and prevents polyester from deforming easily. OR

There is restricted rotation of bonds due to the presence of double bonds in the benzene rings or due to the presence of the COO group which is planar, this prevents polyester from deforming easily.

[1]

(b) (i) Calculate the percentage of mass of carbon in PET.

Formula of repeating unit: $C_{10}H_8O_4$
Mr of repeating unit = 10(12) + 8(1) + 4(16) = 192
Percentage of mass of carbon = $\frac{10(12)}{192} \times 100\%$ = 62.5%

[2]

(ii) Identify the type of polymerisation in the formation of PET and provide **two** reasons to explain your answer.

Type of polymerisation : Condensation polymerisation [1]

Reason 1: PET is formed when 2 different types of monomers (with different functional groups) reacted to form a long chain polymer molecule [1]

Reason 2: a small molecule is are eliminated during the reaction [1]

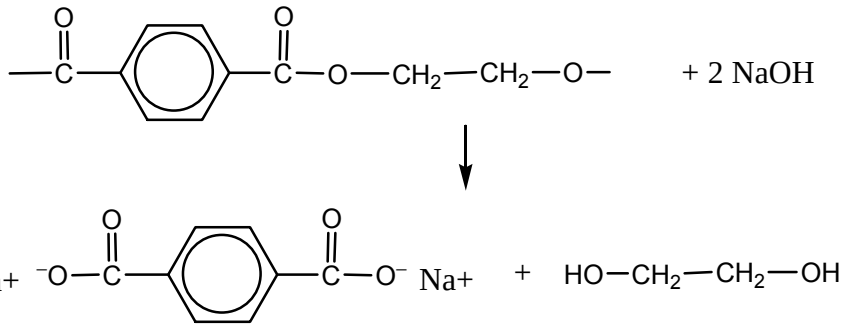
[3]

(iii) Explain why a PET fabric dissolves slowly when placed in aqueous alkali.

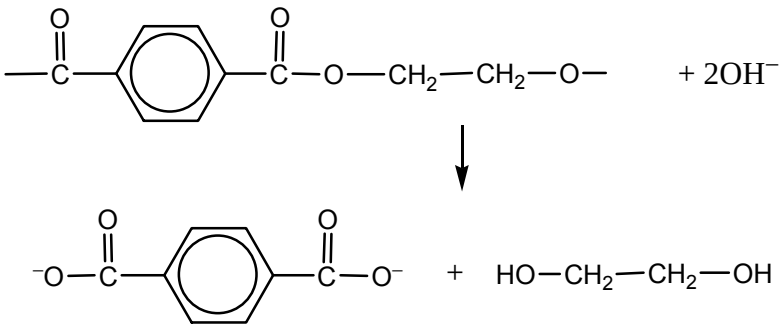
PET undergoes hydrolysis when exposed to alkali, causing the ester linkages to break.

[1]

(iv) Write an equation for **one repeat unit** of PET reacting with aqueous sodium hydroxide.



OR



[1]

(c) PET is a thermoplastic. With respect to the structure and interactions of polymer chains, explain

(i) the difference between thermoplastics and thermosets.

Thermoplastics have no cross links between the chains. Thermoset have cross links between the chains.

[1]

(ii) why PET can be used as a fabric.

In PET, there are **weak permanent dipole-permanent dipole interactions** between the side groups of neighbouring polymer chains, hence allowing the chains to side over each other, giving the flexibility/ fluidity as a fabric.

[2]

[Total: 12]

5 On 11 May 2018, Mount Merapi on Central Java, Indonesia erupted, causing the local airport to be closed. The eruption was reported to be caused by accumulation of volcanic gases. The volcanic ash and gases spewed can be dangerous to planes passing through the plume. The most abundant volcanic gas is harmless water vapour. However, significant amounts of carbon dioxide, sulfur dioxide, hydrogen sulfide and hydrogen halides are also emitted.

When carbon dioxide is emitted from volcanoes, it typically becomes diluted to low concentrations very quickly and is not life threatening. However, cold carbon dioxide gas can flow into low-lying areas where it can reach much higher concentrations. Breathing air with more than 3% CO_2 can quickly lead to headaches, dizziness, increased heart rate and difficulty breathing. At about 15%, unconsciousness and death can result quickly.

Table 1: Volcanic gas composition in area **A**

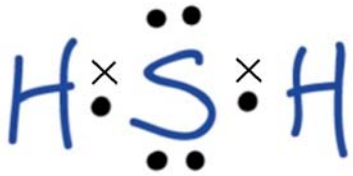
Gas	Volume Percentage
Water vapour, H_2O	87.1
Carbon dioxide, CO_2	unknown
Sulfur dioxide, SO_2	0.5
Hydrogen, H_2	0.7
Carbon monoxide, CO	0.01
Hydrogen sulfide, H_2S	0.23
Hydrogen halides	unknown

Composition of the volcanic gases are typically expressed in terms of volume percentage, which can be calculated as follows

$$\text{volume percentage} = \frac{\text{volume of gas}}{\text{total volume}} \times 100\%$$

(a) **(i)** Draw the dot-and-cross diagram of H_2S.

[1]



(ii) State and explain whether H_2S or H_2O has a larger bond angle with respect to its central atom.

H_2S and H_2O are bent as there are 2 bond pairs and 2 lone pairs around each central atom.

H_2O has a larger bond angle than H_2S as

1) O is more electronegative than S, O pulls electron density of bond pairs more towards itself, leading to greater bond-pair bond-pair repulsion.
   OR
2) O has a smaller lone pair region than S (O is above S in group 16). Lone-pair bond-pair repulsion is smaller, leading to a larger bond angle.

(iii) Suggest a reason why at low temperature, carbon dioxide would sink rapidly and accumulate to high concentrations.

At low temperatures, there is insufficient energy to overcome the strong temporary dipole induced dipole (tdid) interactions between CO_2 molecules. Hence CO_2 would aggregate together/ more CO_2 molecules in a smaller volume and have a higher density thus sink down.

[2]

(iv) People living in area **A** were evacuated as the level of carbon dioxide was increasing rapidly. Given that 0.3 g of CO_2 was present in 1 dm^3 of gas mixture at r.t.p, determine the volume percentage of carbon dioxide present.

Hence comment on the possible danger if people remained in the area.

Amt of CO_2 = $\frac{0.30}{44.0} = 0.006818\ mol$

Vol of CO_2 = $0.006818\ (24.0) = 0.1636\ dm^3$

volume percentage of CO_2= $\frac{0.1636}{1} \times 100\%$ = 16.4%

Ans: 16.4% unconsciousness and death can result quickly

[2]

(b) Hydrogen sulfide can react with methane in the following equation.

$$CH_4(g) + 2\ H_2S(g) \rightleftharpoons CS_2(g) + 4H_2(g)$$

1 mol of CH_4, 2 mol of H_2S, 1 mol of CS_2 and 1 mol of H_2 were allowed to reach equilibrium in a 2 dm^3 container at a constant temperature and pressure.

(i) State the oxidation state of carbon in each carbon-containing compound.

CH_4 : –4 CS_2: +4 [1]

(ii) Hence comment on the role of H_2S in the reaction.

H_2S is an oxidising agent.

. [1]

(iii) Given that CS_2 was found to be 1.2 mol at equilibrium, determine the value of K_c, giving its units.

[2]

	$CH_4(g)$	$+ 2\ H_2S(g)$	$\rightleftharpoons$	$CS_2(g)$	$+ 4\ H_2(g)$
Initial/ mol	1	2		1	1
Eqm/ mol	1-x	2-2x		1 + x	1 + 4 x
	=0.8	= 1.6		=1.2	=1.8
Eqm / mol dm^{-3}	0.8/ 2 = 0.4	1.6/2 = 0.8		1.2/ 2 = 0.6	1.8/ 2 = 0.9

1 + x = 1.2
x = 0.2

Volume is 2 dm^3 container

$$K_c = \frac{(H_2)^4.CS_2}{CH_4.(H_2S)^2}$$

$$K_c = \frac{(0.9)^4(0.6)}{(0.4).(0.8)^2} = 1.537 = 1.54\ mol^{\ 2}\ dm^{-6}$$

(iv) Using the *Data Booklet,* calculate the enthalpy change of the above reaction. Assume bond energy of C-S bond is 272 kJ mol^{-1}.

Bond break / kJ mol^{-1}	Bond form kJ mol^{-1}
4 C–H = 4(410)	2 C–S = 2(272)
4 S–H = 4(347)	4 H–H = 4(436)
3028	2288

ΔH reaction = bond breaking – bond forming
= + 3028 – 2288
= + 740 kJ mol^{-1}

[2]

(v) Hence state and explain the effect of increasing the temperature of the system on

- position of the equilibrium
- rate of the reaction.

Increasing the temperature **shifts eqm to the right** to favour the forward endothermic reaction as to partially absorb some heat.

Rate of reaction increases. Increasing the temperature increases energy of particles. There is a **greater proportion of particles with energy greater than activation energy**, hence frequency of effective collisions increases, leading to increase rate of reaction.

[3]

[Total: 16]

6 1–chloro–1–phenylethane undergoes hydrolysis with hydroxide ions to produce 1–phenylethanol, as shown in the equation below.

$$\underset{\text{1-chloro-1-phenylethane}}{C_6H_5CHClCH_3} + OH^- \rightarrow \underset{\text{1-phenylethanol}}{C_6H_5CH(OH)CH_3} + Cl^-$$

The rate of this reaction can be studied by measuring the amount of hydroxide ions that remain in the solution at a given time after the reaction has been quenched.

(a) Suggest a suitable quenching agent that can be used to slow down the rate of the reaction effectively.

cold water

[1]

.

[1]

(b) The rate of this reaction was measured using different initial concentrations of the two reagents and the results are shown below.

Experiment	$[C_6H_5CHClCH_3]$ / mol dm^{-3}	$[OH^-]$ / mol dm^{-3}	Relative rate
1	0.05	0.10	1.0
2	0.10	0.20	2.0
3	0.15	0.10	3.0

(i) Deduce the order of reaction with respect to each of the reagents. Explain your reasoning.

Comparing experiment 1 & 3, when $[OH^-]$ is constant, $[C_6H_5CHClCH_3]$ is tripled, relative rate is tripled. Hence, reaction is 1st order with respect to $C_6H_5CHClCH_3$. [1]

Comparing experiment 1 & 2, when both $[OH^-]$ and $[C_6H_5CHClCH_3]$ are doubled, relative rate is doubled. Since reaction is 1st order with respect to $C_6H_5CHClCH_3$, the doubling of $[OH^-]$ has no effect on rate, so reaction is zero order with respect to OH^-. [1]

* Accept if student write conc / rate increases by 3 times.

Order with respect to $C_6H_5CHClCH_3$ = **first order**

Order with respect to OH^- = **zero order**

[2]

(ii) Write the rate equation for this reaction, stating the units of the rate constant, k.

rate = $k[C_6H_5CHClCH_3]$ mol dm^{-3} s^{-1}

units of k = s^{-1}

[2]
[Total: 5]

7 Lithium is a scavenger for hydrogen, hence able to prevent the reaction between hydrogen and copper during pure copper casting. Reaction with hydrogen makes the copper brittle, causing it to fall apart under very light stress.

Table 2

	Enthalpy / kJ mol^{-1}
Enthalpy change of formation of $LiAlH_4(l)$	–152.5
Enthalpy change of formation of $LiAlH_6(s)$	–454

(a) Heating lithium in a stream of hydrogen gas produces white, crystalline, ionic lithium hydride, LiH.

(i) By quoting relevant data from the *Data Booklet*, suggest and explain how the magnitude of the lattice energy of LiC*l* would compare to that of LiH.

$$|LE| = \left|\frac{q^+q^-}{r^+ + r^-}\right|$$

Ionic radii of Cl^- = 0.181, ionic radii of H^- = 0.208nm
They have the same product but LiH has a larger interionic distance than LiC*l*, therefore LE magnitude of LiH is smaller.

[2]

(b) When lithium hydride is heated with anhydrous aluminium chloride, lithium aluminium hydride, $LiAlH_4$ and lithium chloride are produced.

Balance the equation for the above reaction.

……4…….. LiH + ……1…… $AlCl_3$ → …1…….. $LiAlH_4$ + ……3….LiC*l*

[1]

(c) Just above its melting point, $LiAlH_4$ decomposes according to the following equation.

$$3\ LiAlH_4\ (l) \rightarrow LiAlH_6(s) + 2Al(s) + 3H_2(g)$$

Using **Table 2**, calculate the standard enthalpy change of this reaction.

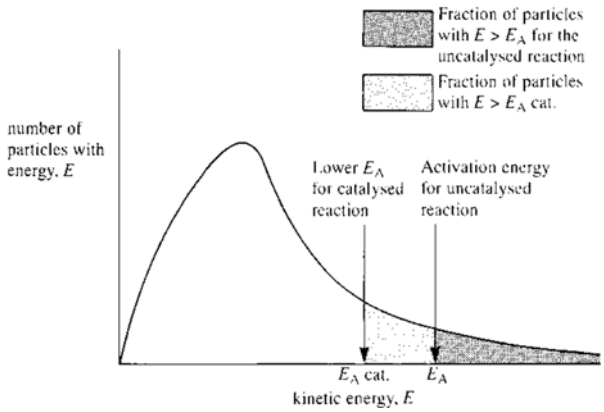
$\Delta H_{reaction}$ **= Σ**$n\Delta Hf$(products) - $\Sigma n\Delta Hf$(reactants)
= –454 – 3(–152.5)
= +3.5 kJmol^{-1}

[2]
[Total: 5]

Section B

Answer only **one** question from this section, in the spaces provided.

8(a) With the aid of a Boltzman distribution curve, explain how the presence of a catalyst increase the rate of a reaction.



A catalyst provides an alternative pathway for the reaction, **lowering the activation energy** required. Hence there is **a greater proportion of particles with energy greater than activation energy** as reflected by the shaded region in the diagram above. Frequency of effective collisions increases, leading to increase rate of reaction.

[3]

(b) The melting points of some compounds are given.

Substance	Octan-1-ol	Iodine	Fullerene	Graphite
Formula	$CH_3(CH_2)_9OH$	I_2	C_{60}	C
Melting point/ K	277	286	873	>3000

(i) Explain why the melting points of octan-1-ol and iodine are comparable.

Both octan-1-ol and iodine have simple covalent structure.
Strength of Td-Id in iodine due to its large electron cloud size is comparable to the stronger hydrogen bonding between octan-1-ol molecules.

[2]

(ii) Explain why the melting point of graphite is higher than that of fullerene.

Graphite has a giant molecular structure with strong covalent bonds between carbon atoms to be overcome during melting.
Fullerene has a simple covalent structure with weaker td-id interactions between fullerene molecules to be overcome during melting.
Hence, more energy is required to melt graphite and a higher temperature is required.
.

[2]

(iii) By quoting relevant data from the *Data Booklet*, account for the trend in the thermal

stabilities from HC*l* to HI.

Bond energy/ kJ mol^{-1} : H–C*l* = 431, H–Br = 366 , H–I = 299

Down the group, less energy is needed to break the weaker H–X bond, resulting in decreasing thermal stability of HX.

[2]

(iv) Arrange the pH of HC*l* to HI in aqueous solution in ascending order.

Explain the variation you have outlined.

pH decreases from HCl to HI as the it is easier to break the H-X bond from H-Cl to H-I to donate a proton.

[2]

(c) Compound **X** has the molecular formula $C_4H_8O_2$.

(i) Treatment of **X** with acidified potassium dichromate(VII) produces a green solution.

What could be the functional groups present in **X**?

Alcohol

[1]

(ii) There is no reaction when **X** is treated with aqueous sodium carbonate, Na_2CO_3.
What could be the functional groups absent in **X**?

Carboxylic acid

[1]

(iii) When **X** is shaken with aqueous bromine, the orange colour disappears.
What could be the functional groups present in **X**?
Alkene

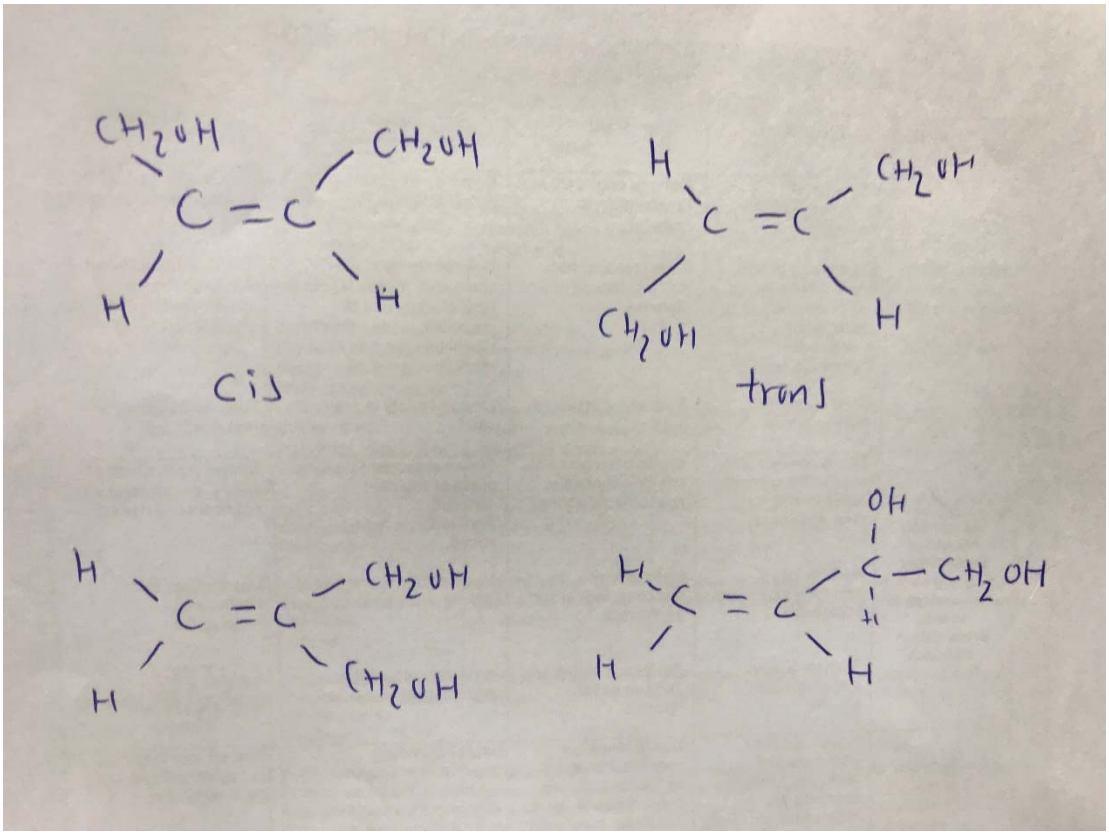
[1]

(iv) The molecule of **X** has the following features.

- The carbon chain is unbranched and the molecule is not cyclic.
- No oxygen atom is attached to any carbon atom which is involved in π bonding.
- No carbon atom has more than one oxygen atom joined to it.

There are four possible isomers of **X** which fit these data.

Draw displayed formulae of **all** possible isomers and state which type of isomerism they show.


CH2OH
CH2OH
C=C
H
H
cis
H
CH2OH
C=C
CH2OH
H
trans
H
CH2OH
C=C
H
CH2OH
OH
H
C
CH2OH
C=C
H
H
H

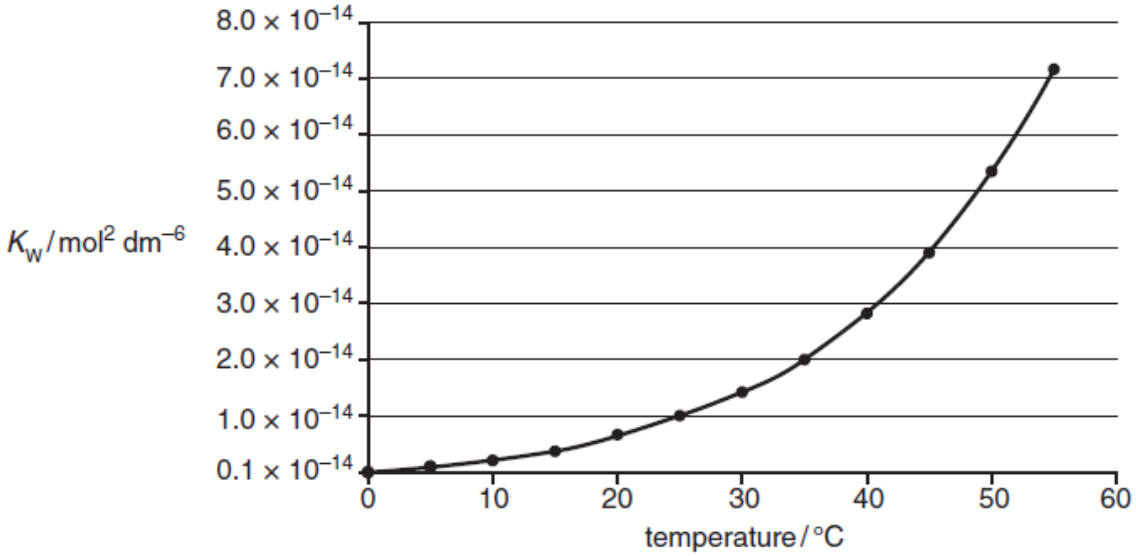
[6]
[Total: 20]

9 (a) The dissociation of water is a reversible reaction.

$$H_2O\ (l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

The ionic product of water, K_w, measures the extent of dissociation of water. K_w varies with temperature. It is always important to quote the temperature at which measurements are being taken.

The graph below shows the variation of K_w. between 0 °C and 60 °C.



(i) Write the expression for K_w.

$K_w = [H^+][OH^-]$

.....

[1]

(ii) Calculate the concentration of hydroxide ions, $[OH^-]$, in an aqueous solution of hydrochloric acid at pH of 4.37 at 25 °C.

Method 1

pH = 4.37

$-\lg [H^+] = 4.37$

$[H^+] = 10^{-4.37} = 4.265 \times 10^{-5}$ mol dm^{-3}

$[OH^-] = 1 \times 10^{-14} \div 4.265 \times 10^{-5} = 2.34 \times 10^{-10}$ mol dm^{-3}

Method 1

pH + pOH = 14

pOH = 14 - 4.37 = 9.63

$[OH^-] = 10^{-9.63} = 2.34 \times 10^{-10}$ mol dm^{-3}

[2]

(iii) Using the graph, explain whether the dissociation of water is an exothermic or endothermic process.

As K_w increases with temperature; the forward reaction is favoured by higher temperature. By Le Chatelier's Principle, as temperature increases, the position of equilibrium shifts to favour the endothermic reaction to partially remove some heat.

Thus dissociation of water (forward reaction) is endothermic.

[2]

(iv) Using the graph, determine the pH of pure water at body temperature, at 37 °C.

At 37 °C, $K_w = 2.5 \times 10^{-14}$ mol dm^{-3}

$[H^+] = \sqrt{K_w} = 1.58 \times 10^{-7}$ mol dm^{-3}

pH = 6.80

[3]

(v) Given the following data:

Indicator	Colour change (acidic to basic medium)	pH range in which colour change occurs
Bromothylmol blue	yellow to blue	6.0 – 7.6

State the colour observed when a few drops of bromothylmol blue is added to a sample of pure water at body temperature, at 37 °C.

Green (due to mixture of yellow and blue)

[1]

(vi) Buffer solutions are important in biological systems and in industry to maintain almost constant pH values

In the human body, one important buffer system in blood involves the hydrogencarbonate ion, HCO_3^- and carbonic acid, H_2CO_3, which is formed when carbon dioxide dissolves in water.

Use the following equation to explain how this buffer maintains a constant pH of 7.41 even if a small amount of acid enters the bloodstream.

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

When a small amount of acid enters bloodstream, HCO_3^- will remove the acid to form H_2CO_3/ eqm (above) shifts to the left.

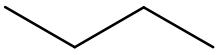
The excess H_2CO_3 produced is then removed by an increase in the rate of respiration and the rapid expulsion of CO_2 from the lungs. Eqm (2) shifts to the left.

$$H_2CO_3 \rightleftharpoons CO_2 + H_2O$$

[2]

(b) The hydrocarbons **A**, C_4H_{10}, and **B**, C_4H_8, are both unbranched.
A does **not** decolourise bromine.
B decolourises bromine and shows cis-trans isomerism.

(i) Draw the skeletal formula of **A**.



[1]

(ii) The hydrocarbon **A**, C_4H_{10}, has a branched isomer.
Suggest why unbranched **A** has a higher boiling point than its branched isomer.

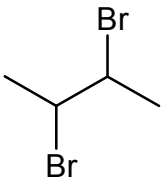
Straight chain A/ unbranched A has greater surface area of contact between molecules compared to branched isomer. Hence temporary dipole-induced dipole (tdid) interactions are more easily induced between molecules of A. More energy is required to stronger tdid interactions in A, hence higher bp.

[2]

(iii) Draw the structure of the product obtained from the reaction between **B** and bromine. State the type of reaction that occurred.

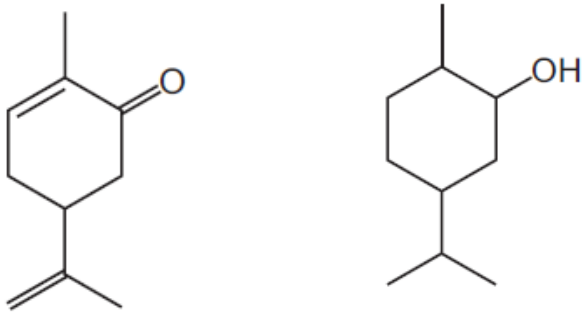
Type of reaction: …**addition** ……

Product:



[2]

(c) Carvone occurs in spearmint and can be converted to compound **M**.



carvone **M**

(i) State the reagent and conditions for the conversion of carvone to compound **M**.

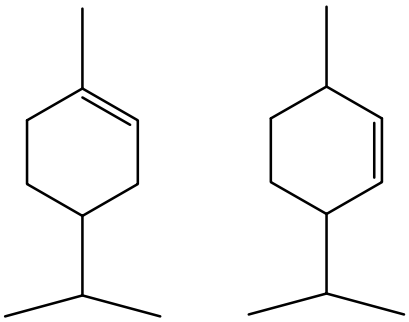
name of reagent: **H_2**

conditions: **Ni, heat / Pt**

[1]

(ii) Draw the structure of the product when **M** is treated with excess concentrated sulfuric acid at 170 °C.

Either structures



[1]

(d) Write an equation for the reaction that occurs when silicon tetrachloride is added to water. Predict the pH of the resulting solution.

$SiCl_4 + 4H_2O \rightarrow SiO_2.2H_2O + 4\ HCl$ or
$SiCl_4 + 4H_2O \rightarrow Si(OH)_4 + 4\ HCl$ or

$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4\ HCl$

pH = 2 or 1

[2]

[Total: 20]

End of Paper