| Class | Adm No |
|---|---|
|  |  |

Candidate Name: ____________________

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# 2016 Preliminary Examination II
## Pre-University 3

**H2 CHEMISTRY** **9647/01**

Paper 1 Multiple Choice **21st Sept 2016**

**1 hour**

Additional materials: Multiple Choice Answer Sheet
Data Booklet

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**READ THESE INSTRUCTIONS FIRST**

**Do not turn over this question paper until you are told to do so**
Write in soft pencil.
Do not use staples, paper clips, glue or correction fluid.
Write your name, class and admission number in the spaces provided at the top of this page and on the Multiple Choice Answer Sheet provided.

There are **forty** questions on this paper. Answer **ALL** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.
Choose the **one** you consider correct and record your choice in **soft pencil** on the Multiple Choice Answer Sheet provided.

**Read the instructions on the Multiple Choice Answer Sheet very carefully.**

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
Any rough working should be done in this question paper.
The use of an approved scientific calculator is expected, where appropriate.

| FOR EXAMINER'S USE | |
|---|---|
| TOTAL (40 marks) |  |

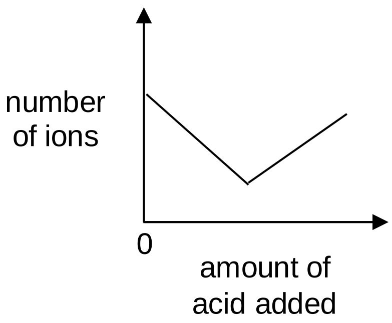
## Section A

For each question there are four possible answers, **A**, **B**, **C**, and **D**. Choose the **one** you consider to be correct.

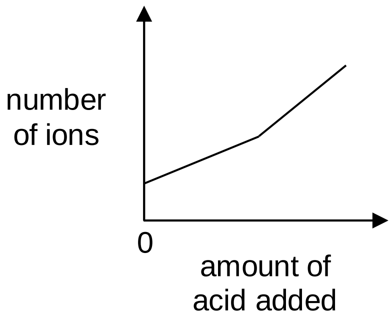
**1** Gaseous hydrochloric acid was bubbled through a solution of sodium carbonate until the solution turned blue litmus paper red.

How will the total number of ions present in solution in the reaction mixture vary?

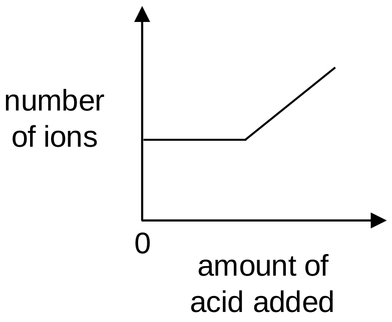
**A**



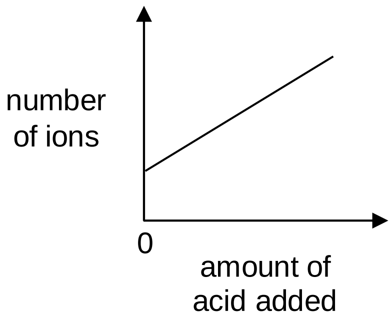
**B**



**C**



**D**

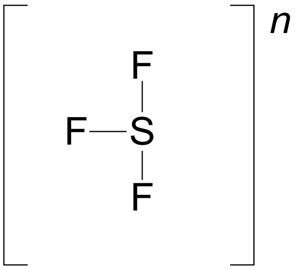


**2** In winter, ice forms only on the surface of lakes and rivers, allowing aquatic life to survive below the surface.

Which of the following statements about ice does **not** explain this phenomenon?

**A** Ice has an open structure.
**B** The water molecules in ice are in an orderly tetrahedral arrangement.
**C** Water molecules can form intermolecular hydrogen bonding in ice.
**D** Water molecules have a much lower energy in ice than in water.

**3** An ion $SF_3^{n}$ is T-shaped as shown below.



What is the value of *n*?

**A** –2 **B** –1 **C** +1 **D** +2

**4** What is the new pressure of a sample of gas, initially at 1 atm, when it is heated from 25 °C to 75 °C at constant volume?

**A** 0.3 atm **B** 0.9 atm **C** 1.2 atm **D** 3.0 atm

**5** Diboron tetrachloride, $B_2Cl_4$, is a colourless liquid at room temperature. The combination of gaseous atoms of boron and chlorine to form $B_2Cl_4(g)$ is represented by the equation below.

$$2B(g) + 4Cl(g) \rightarrow B_2Cl_4(g) \qquad \Delta H = -2127 \text{ kJ mol}^{-1}$$

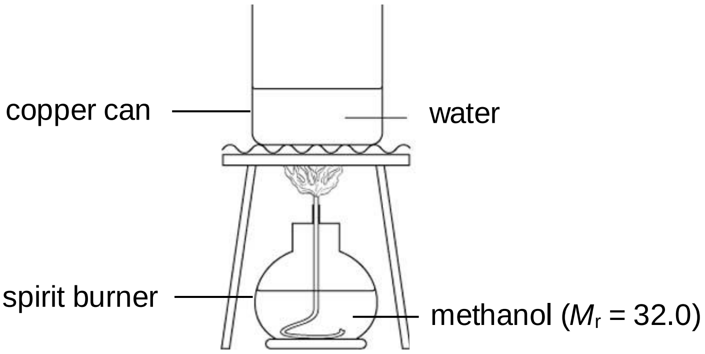
The bond energy of a B–B bond is +303 kJ $mol^{-1}$.

What is the bond dissociation energy of a B–C*l* bond?

**A** –608 kJ $mol^{-1}$ **B** –456 kJ $mol^{-1}$ **C** +456 kJ $mol^{-1}$ **D** +608 kJ $mol^{-1}$

**6** *Use of the Data Booklet is relevant to this question.*

A student carried out an experiment to determine the heat capacity of a copper can using the setup below.



The following data was recorded by the student:

| | |
|---|---|
| Initial temperature of water / °C | 25 °C |
| Final temperature of water / °C | 42 °C |
| Mass of spirit burner before burning / g | 220.00 g |
| Mass of spirit burner after burning / g | 219.50 g |
| Volume of water / $cm^3$ | 150 $cm^3$ |

Given that the enthalpy change of combustion of methanol is –715 kJ $mol^{-1}$, determine the heat capacity of the copper can.

**A** 30.2 J $K^{-1}$ **B** 43.8 J $K^{-1}$ **C** 626 J $K^{-1}$ **D** 655 J $K^{-1}$

**7** The following reaction is thermodynamically feasible **only** at a high temperature.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

What are the signs of $\Delta H$ and $\Delta S$ for the reaction?

| | $\Delta H$ | $\Delta S$ |
|---|---|---|
| **A** | – | – |
| **B** | + | – |
| **C** | – | + |
| **D** | + | + |

**8** The mechanism involved in the formation of compound **Z** is as follows:

Step I: **W** + **X** $\rightleftharpoons$ **Y** (fast)

Step II: **W** + **Y** $\rightarrow$ **Z** (slow)

What is the rate equation for this reaction?

**A** Rate = k[**W**][**X**]

**B** Rate = k[**W**][**Y**]

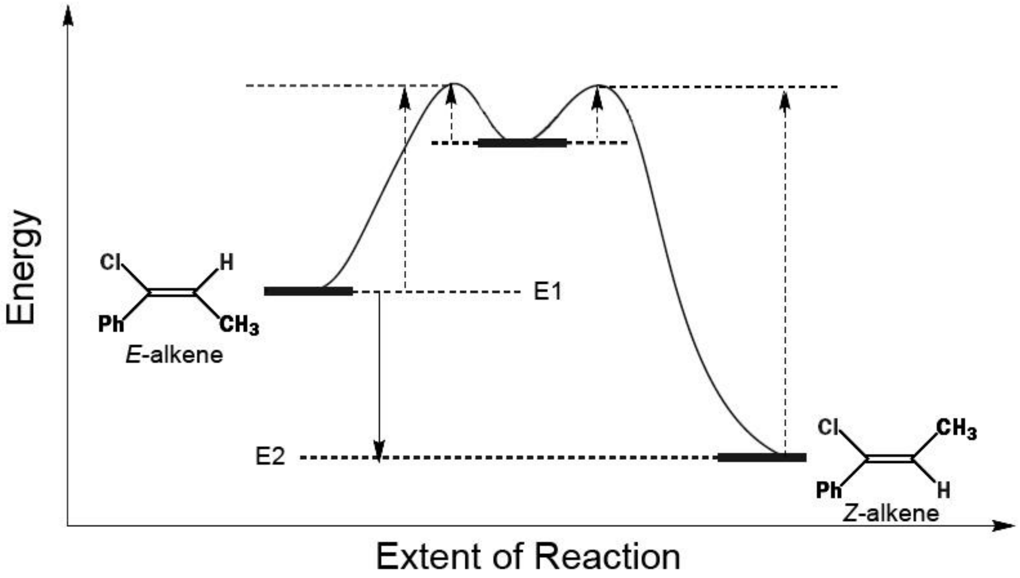
**C** Rate = k[**W**][**Y**]$^2$

**D** Rate = k[**W**]$^2$[**X**]

**9** Alkenes in an acidic medium can isomerise in the presence of $Al_2O_3$ catalyst.

*E*–alkene $\rightleftharpoons$ *Z*–alkene

The energy profile diagram of the reaction is shown below.



Which of the following statements is correct?

**A** (E1 – E2) corresponds to the enthalpy change of the forward reaction.

**B** Leaving pure *E*–alkene to isomerise for a long duration yields mainly *Z*–alkene.

**C** The isomerisation produces more *Z*–alkene at high temperatures and produces more *E*–alkene at low temperatures.

**D** There are 2 intermediates in the isomerisation process.

**10** At 313 K, iodine monochloride exists in equilibrium with iodine and chlorine.

$$I_2(g) + Cl_2(g) \rightleftharpoons 2ICl(g)$$

When a mixture of iodine and chlorine in the mole ratio of 1:1 is heated at 313 K and a constant pressure of 1 atm, the mole fraction of iodine monochloride present at equilibrium is 0.23.

What is the equilibrium constant, $K_p$?

**A** 0.299 **B** 0.357 **C** 0.597 **D** 1.55

**11** The concentration of $Sr^{2+}$ ions in a 0.5 dm$^3$ solution is $2.0 \times 10^{-2}$ mol dm$^{-3}$. $Na_2CO_3$ solid was added to the solution in excess until the concentration of $CO_3^{2-}$ ions remained at $2.5 \times 10^{-6}$ mol dm$^{-3}$.

Given that the $K_{sp}$ of $SrCO_3$ is $1.6 \times 10^{-9}$, what mass of $SrCO_3$ was precipitated?

**A** 0.0472 g

**B** 0.0944 g

**C** 1.43 g

**D** 2.86 g

**12** Halogens **T**$_2$, **U**$_2$ and **V**$_2$ were added to separate aqueous solutions containing **T**$^-$, **U**$^-$ and **V**$^-$ ions and observations recorded in the table below.

| | **T**$^-$(aq) | **U**$^-$(aq) | **V**$^-$(aq) |
|---|---|---|---|
| **T**$_2$ | no reaction | **U**$_2$ formed | **V**$_2$ formed |
| **U**$_2$ | no reaction | no reaction | no reaction |
| **V**$_2$ | no reaction | **U**$_2$ formed | no reaction |

In which sequence is reducing power of the halides arranged in increasing order?

**A** **T**$^-$ < **V**$^-$ < **U**$^-$

**B** **U**$^-$ < **T**$^-$ < **V**$^-$

**C** **U**$^-$ < **V**$^-$ < **T**$^-$

**D** **V**$^-$ < **U**$^-$ < **T**$^-$

**13** It is known that lithium and magnesium have similar chemical properties.

Which property of the following lithium compounds is likely to be wrong?

**A** $Li_2CO_3$ undergoes thermal decomposition to produce carbon dioxide as the only gas.
**B** $LiNO_3$ produces oxygen as the only gas upon heating.
**C** $Li_2O$ dissolves in water to form a solution of pH greater than 7.
**D** $LiSO_4$ is soluble in water.

**14** The following Group II elements form sulfates with the following crystalline forms:

$MgSO_4.7H_2O$ $CaSO_4.2H_2O$ $SrSO_4$ $BaSO_4$

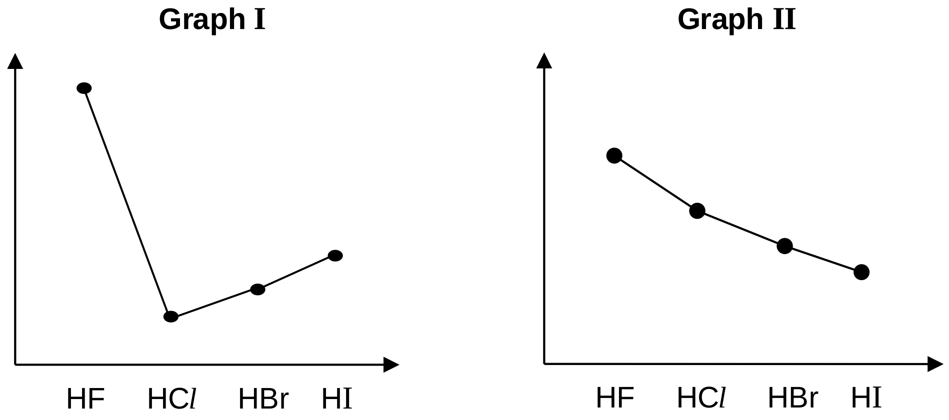
Which of the following explains the observed trend in number of moles of water of crystallisation?

**A** Atomic radius of the elements increases down the group.
**B** Ionic character of sulfates increases down the group.
**C** Ionisation energy of the elements decreases down the group.
**D** Radius of the cations increases down the group.

**15** What are the products formed when chlorine gas is bubbled into cold aqueous sodium hydroxide?

**A** $NaCl$ and $NaClO$
**B** $NaCl$ and $NaClO_3$
**C** $NaClO$ only
**D** $NaClO_3$ only

**16** The graphs below show the variation of two properties of the halogen hydrides.



Which properties are illustrated in **Graphs I** and **II**?

| | **Graph I** | **Graph II** |
|---|---|---|
| **A** | Boiling point | Thermal stability |
| **B** | pH of solution | Thermal stability |
| **C** | Thermal stability | Melting point |
| **D** | Thermal stability | pH of solution |

**17** When halogenomethanes are warmed in aqueous NaOH followed by acidified $AgNO_3$, the rate of formation of precipitate is observed to be in the order:

$$CH_3F < CH_3Cl < CH_3Br < CH_3I$$

Which of the following best explains this observation?

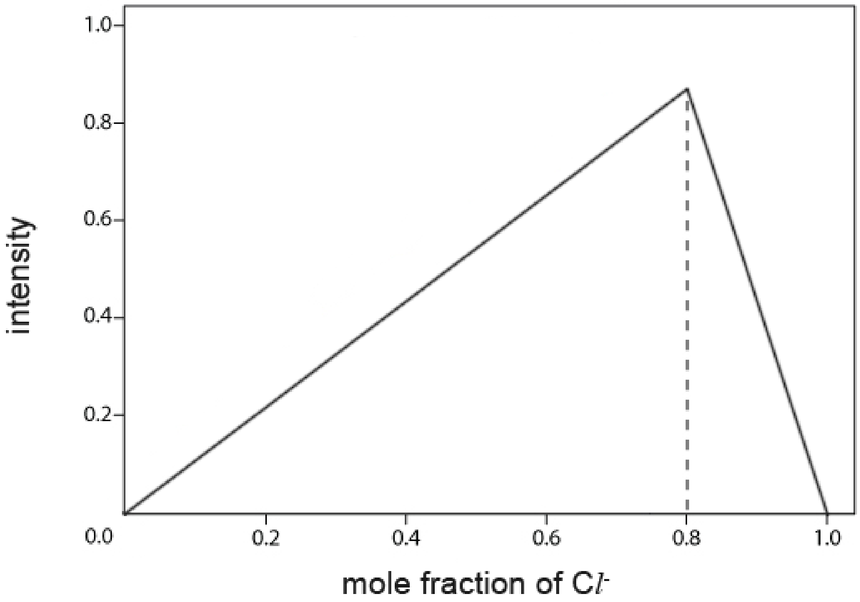
**A** Anionic radius increases from F to I.

**B** Bond energy decreases from C–F to C–I.

**C** Bond polarity decreases from C–F to C–I.

**D** Charge density decreases from $F^-$ to $I^-$.

**18** The $Co^{2+}$ ion forms a blue complex with $Cl^-$ ions. Various samples containing different amounts of $Co^{2+}$ and $Cl^-$ were prepared, and their colour intensities measured using a colorimeter. The following graph was obtained.



Which statement about the complex ion formed is correct?

**A** The complex ion absorbs blue light.

**B** The co-ordination number of the $Co^{2+}$ ion is 4.

**C** The geometry of the complex ion is octahedral about $Co^{2+}$.

**D** The overall charge of the complex ion is 2+.

**19** A compound with the molecular formula $C_5H_{10}$ reacts with hot acidified $KMnO_4$ to form products that give a white precipitate with limewater and a yellow precipitate with aqueous alkaline iodine.

What is the identity of the compound?

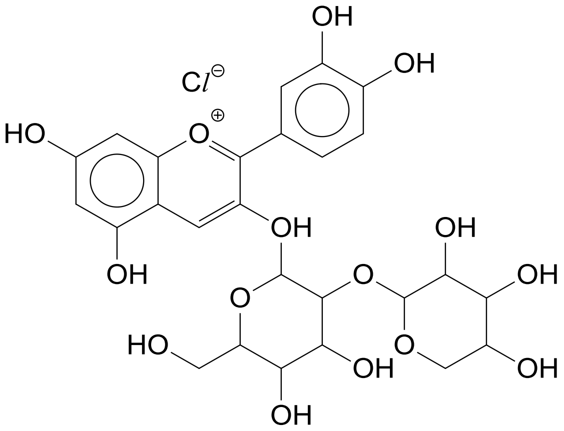
**A** $CH_3CH_2CH_2CH{=}CH_2$

**B** $CH_3CH_2CH{=}CHCH_3$

**C** $CH_3CH(CH_3)CH{=}CH_2$

**D** $CH_3CH_2C(CH_3){=}CH_2$

**20** The deep purple colour of elderberries originates from cyanidin 3-sambubioside.



cyanidin 3-sambubioside

How many optical isomers does cyanidin 3-sambubioside have?

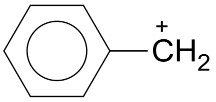
**A** $2^6$

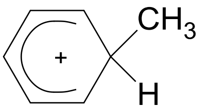
**B** $2^8$

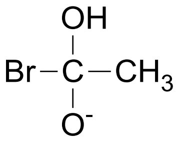
**C** $2^9$

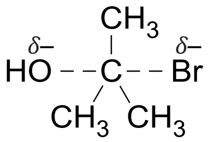
**D** $2^{11}$

**21** Which species could be an intermediate in an $S_N1$ substitution?

**A** 

**B** 

**C** 
$Br-\overset{\displaystyle OH}{\underset{\displaystyle O^-}{C}}-CH_3$

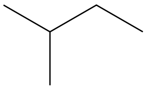
**D** 

**22** When heated with bromine, hydrocarbon **Q** undergoes free radical substitution. In the propagation step, free radical **R•** is formed.

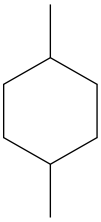
$$\mathbf{Q} + Br\bullet \rightarrow \mathbf{R}\bullet + HBr$$

If there are exactly three possible structures of **R•**, which of the following is a possible structure of **Q**?

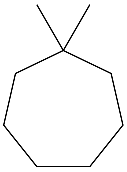
**A**



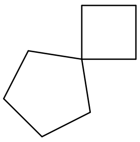
**B**



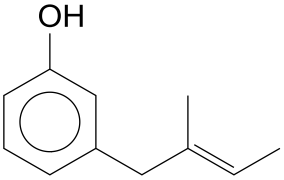
**C**



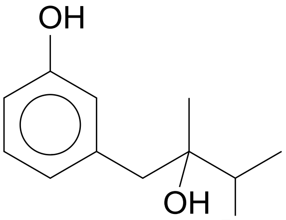
**D**



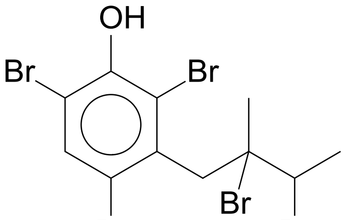
**23** What is the major organic product formed when excess aqueous bromine is added to the following compound?



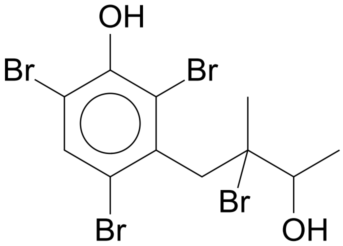
**A**



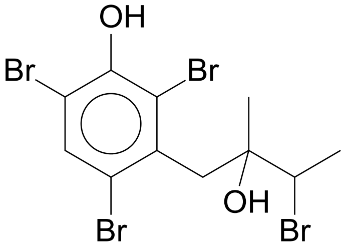
**B**



**C**

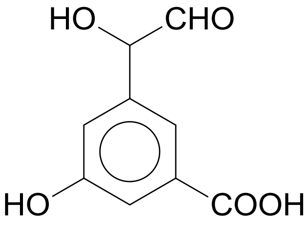


**D**



**[Turn over**

**24** Which graph shows the amounts of gases evolved when 1 mol of compound **M** is subjected to reagents **I** and **II** separately?

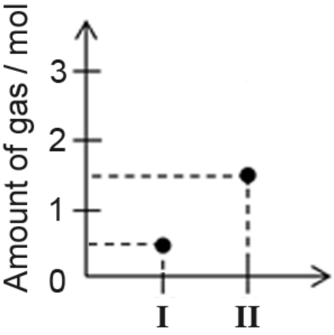


**M**

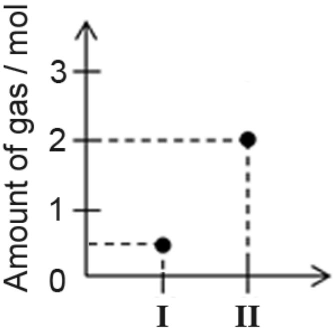
**I**: $Na_2CO_3$(s) in excess

**II**: Na(s) in excess

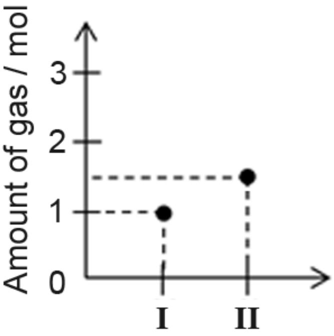
**A**



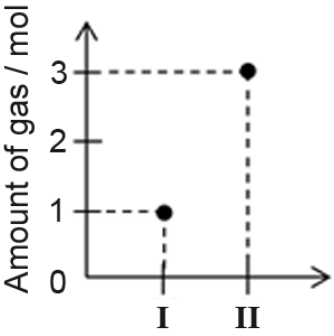
**B**



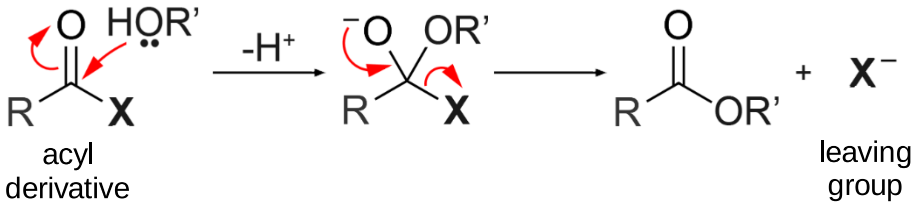
**C**



**D**



**25** The mechanism of esterification with acyl derivatives in base is as follows, where R'OH is the alcohol and $\mathbf{X}^-$ is the leaving group.

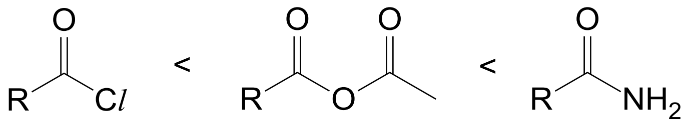


The rate of esterification is known to increase with better leaving group ability, which is related to basicity. The less basic the leaving group, the better its ability to leave.

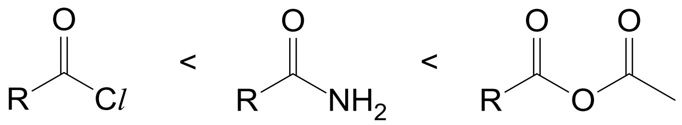
Which of the following is the reactivity of acyl derivatives arranged in increasing order?

**Acyl derivative**

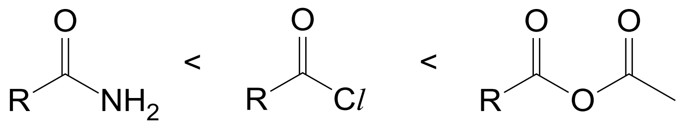
**A**



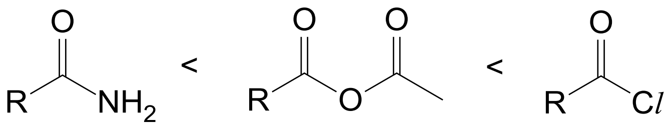
**B**



**C**

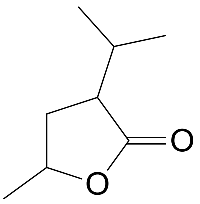


**D**

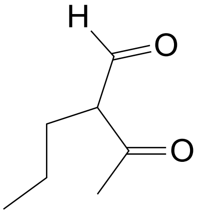


[Turn over

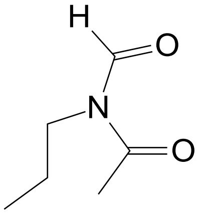
**26** Compounds **K**, **L** and **M** have the following structures.



**K**



**L**

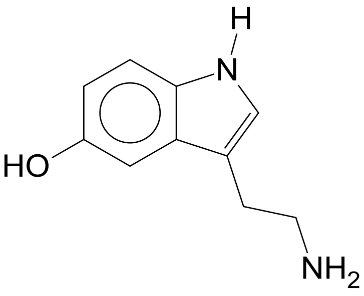


**M**

Which pair of statements about the properties of **K**, **L** and **M** are correct?

| | **gives a red precipitate with Fehling's solution** | **gives a yellow precipitate with hot alkaline aqueous iodine** |
|---|---|---|
| **A** | **K**, **L** and **M** | **L** only |
| **B** | **L** and **M** only | **L** and **M** only |
| **C** | **L** only | **L** only |
| **D** | **L** only | **K** and **L** only |

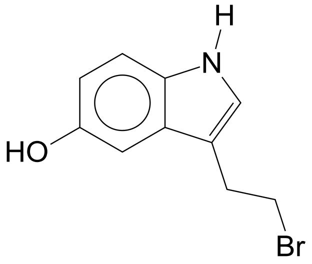
**27** Serotonin is a neurotransmitter found in the central nervous system of humans.



serotonin

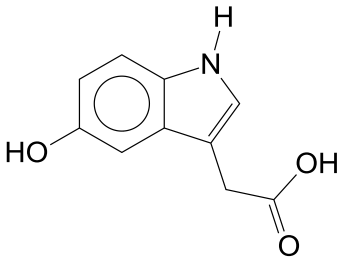
Which of the following could be used to synthesise serotonin?

**A**



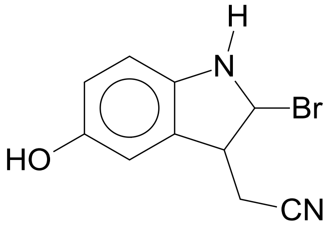
$\xrightarrow[\text{reflux}]{\text{KCN in ethanol}}$ intermediate $\xrightarrow[\text{heat}]{H^{+}(aq)}$ serotonin

**B**



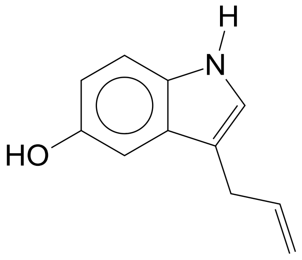
$\xrightarrow{\text{LiA}l\text{H}_4 \text{ in dry ether}}$ intermediate $\xrightarrow[\text{reflux}]{\text{NH}_3}$ serotonin

**C**



$\xrightarrow{\text{LiA}l\text{H}_4 \text{ in dry ether}}$ intermediate $\xrightarrow[\text{reflux}]{\text{ethanolic NaOH}}$ serotonin

**D**

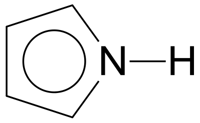


$\xrightarrow{\text{HBr(g)}}$ intermediate $\xrightarrow[\text{reflux}]{\text{NH}_3}$ serotonin

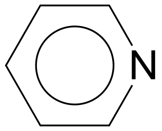
**[Turn over**

**28** Huckel’s rule dictates that when there are 6 delocalised π-electrons, the compound has additional stability and is considered to be aromatic. Benzene is one such aromatic compound.

Pyrrole and pyridine are two nitrogen containing aromatic compounds with 6 delocalised π-electrons.



pyrrole

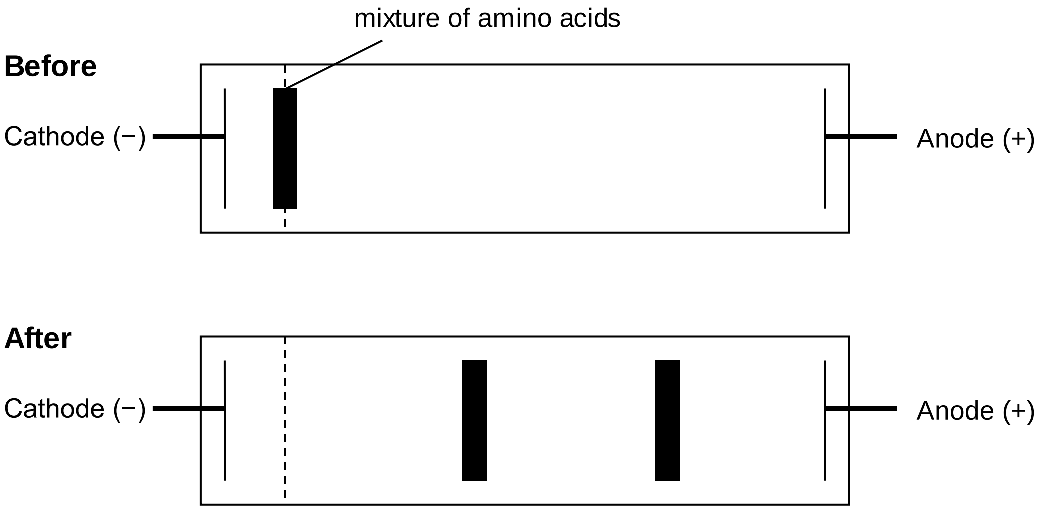


pyridine

How many electrons do the nitrogen atoms in pyrrole and pyridine contribute to their delocalised π-electron cloud respectively?

| | **pyrrole** | **pyridine** |
|---|---|---|
| **A** | 1 | 1 |
| **B** | 1 | 2 |
| **C** | 2 | 1 |
| **D** | 2 | 2 |

**29** A mixture of two amino acids, leucine and aspartic acid, were run on a gel electrophoresis plate. The following results were obtained:

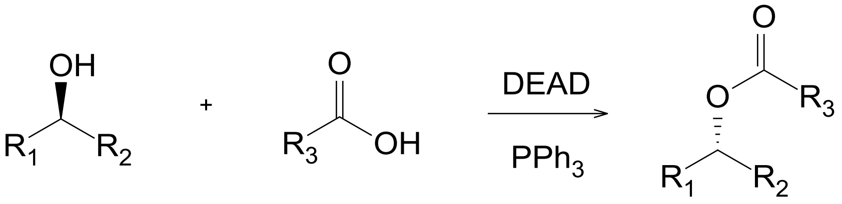


| **Amino acid** | **Side chain** | **p$K_a$** | | |
|---|---|---|---|---|
| | | **–COOH** | **$-NH_3^+$** | **Side chain** |
| Leucine | $-CH_2CH(CH_3)_2$ | 2.3 | 9.7 | – |
| Aspartic acid | $-CH_2COOH$ | 2.0 | 9.9 | 3.9 |

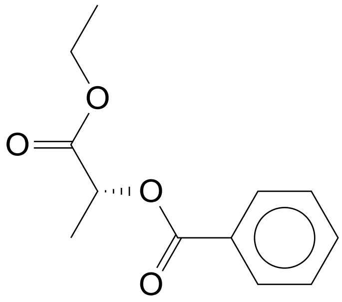
What pH was the gel likely to be buffered at?

**A** 1.5 **B** 3.9 **C** 9.8 **D** 10.5

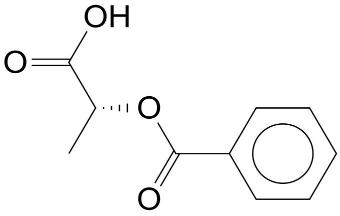
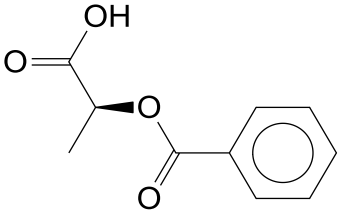
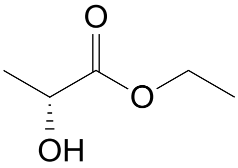
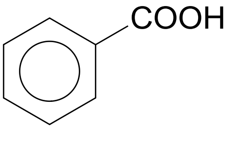
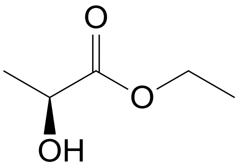
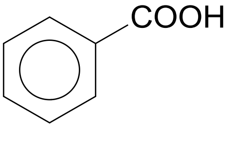
**30** The Mitsunobu reaction is a procedure that allows for the conversion of primary and secondary alcohols into esters with the addition of a carboxylic acid and a DEAD catalyst. The reaction is highly useful as the stereochemistry at the chiral carbon is completely inverted.



Which pair of alcohol and carboxylic acid could give compound **E**?



Compound **E**

| | **alcohol** | **carboxylic acid** |
|---|---|---|
| **A** | $CH_3CH_2OH$ |  |
| **B** | $CH_3CH_2OH$ |  |
| **C** |  |  |
| **D** |  |  |

## Section B

For each of the questions in this section, one or more of the three numbered statements **1** to **3** may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct).

The responses **A** to **D** should be selected on the basis of

| **A** | **B** | **C** | **D** |
|---|---|---|---|
| **1**, **2** and **3** are correct | **1** and **2** only are correct | **2** and **3** only are correct | **1** only is correct |

No other combination of statements is used as a correct response.

**31** Which properties of beryllium chloride are related to its electron-deficient Be atom?

**1** its tendency to polymerise
**2** its covalent character
**3** its acidity in aqueous solution

**32** The following diagram illustrates the energy changes of a set of reactions.

$$\begin{tikzcd}
\frac{1}{2}\mathbf{X}_2\text{(standard state)} \arrow[r, "\Delta H = -581\text{ kJ mol}^{-1}"] \arrow[d] & \mathbf{X}^-\text{(aq)} \arrow[d, "\Delta H = +351\text{ kJ mol}^{-1}"] \\
\mathbf{X}\text{(g)} \arrow[r, "\Delta H = -342\text{ kJ mol}^{-1}"'] & \mathbf{X}^-\text{(g)}
\end{tikzcd}$$

Which of the following can be deduced from the diagram?

**1** The first electron affinity of **X** is –581 kJ $mol^{-1}$.
**2** The enthalpy change from $\mathbf{X}$(g) → $\mathbf{X}^-$(aq) is exothermic.
**3** The enthalpy change for the reaction ½$\mathbf{X}_2$(standard state) → $\mathbf{X}$(g) is +112 kJ $mol^{-1}$.

**[Turn over**

The responses **A** to **D** should be selected on the basis of

| **A** | **B** | **C** | **D** |
|---|---|---|---|
| **1**, **2** and **3** are correct | **1** and **2** only are correct | **2** and **3** only are correct | **1** only is correct |

No other combination of statements is used as a correct response.

**33** *Use of Data Booklet is relevant to this question.*

A voltaic cell is set up using a $Zn^{2+}(aq)/Zn(s)$ half-cell and a $Cu^{2+}(aq)/Cu(s)$ half-cell. What are the features of the above set up?

**1** Electrons flow in the external circuit from zinc to copper.
**2** Reduction takes place at the copper terminal and the copper electrode increases in mass over time.
**3** The zinc electrode is the negative electrode.

**34** Three elements **H**, **I** and **J** belong to the same period of the Periodic Table.

The oxide of **H** reacts with both strong acids and bases. The oxide of **I** gives a solution of pH > 7 in water and the oxide of **J** gives a solution pH < 7 in water.

Which statements about elements **H**, **I** and **J** are always correct?

**1** Element **H** has the highest electrical conductivity.
**2** The ionic radius decreases in the order **I**, **H**, **J**.
**3** The electronegativity of the elements decreases in the order **I**, **H**, **J**.

**35** Samples of strontium and barium are burnt in air.

Which of the following flame colours are observed?

**1** pale green
**2** orange-red
**3** lilac

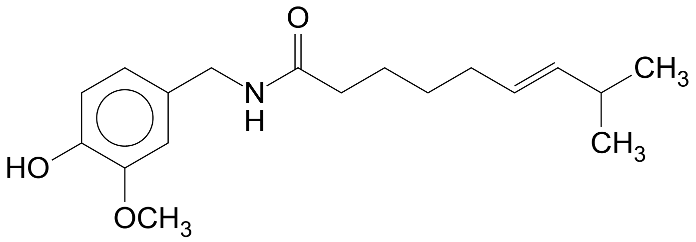
**36** Which of the following titanium compounds are likely to exist?

**1** $Ti_2O_5$

**2** $TiBr_4$

**3** $K_2Ti_2O_3$

**37** Capsaicin is the chemical found in chillies that gives rise to the sensation of spiciness.



Capsaicin

Which of the following statements about capsaicin are correct?

**1** Capsaicin decolourises cold alkaline potassium manganate(VII).

**2** Capsaicin gives a positive $FeCl_3$ test.

**3** Capsaicin gives an orange precipitate with 2,4-dinitrophenylhydrazine.

**38** Bromobenzene is unreactive to nucleophiles while 3-bromopropene is very reactive in comparison.

What could be reasons for the lack of reactivity of bromobenzene with nucleophiles?

**1** The $\pi$ electrons repel incoming attacking nucleophiles.

**2** The C–Br bond in bromobenzene is stronger than the C–Br bond in 3-bromopropene.

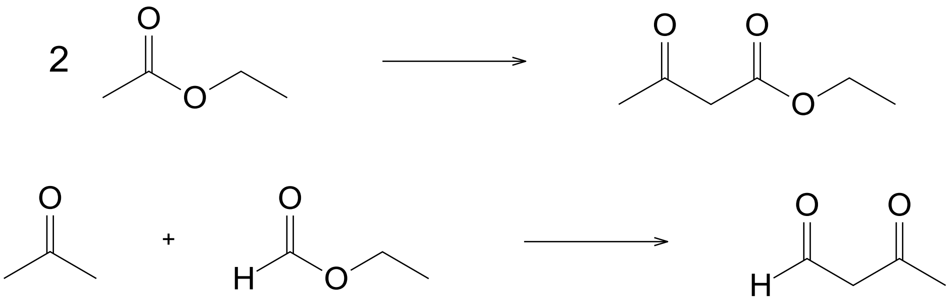
**3** The C–Br bond is unable to rotate freely.

The responses **A** to **D** should be selected on the basis of

| A | B | C | D |
|---|---|---|---|
| **1**, **2** and **3**<br>are<br>correct | **1** and **2**<br>only are<br>correct | **2** and **3**<br>only are<br>correct | **1** only<br>is<br>correct |

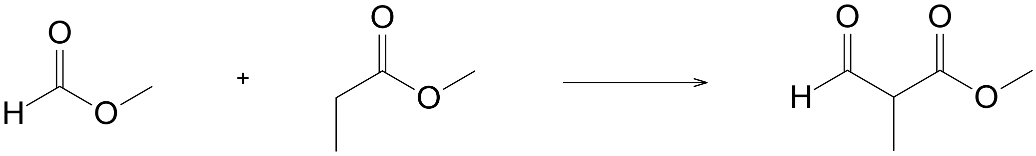
No other combination of statements is used as a correct response.

**39** The Claisen Condensation is a reaction that occurs between two esters, or between one ester and another carbonyl compound.

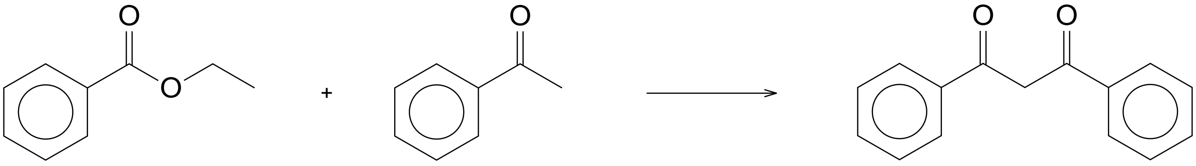


Which of the following are examples of the Claisen Condensation reaction?

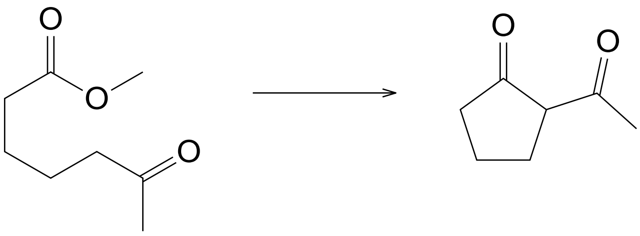
**1**



**2**



**3**



**40** Hair contains chains of the protein keratin, which comprises amino acids forming interactions with other keratin chains. Hair can be treated in many ways to achieve a desired hair style.

Which of the following treatments will produce the desired styles?

**1** Heating hair with steam can help to elongate it.
**2** The curling of hair requires both reducing and oxidising agents.
**3** Usage of ammonia causes hair to soften and uncurl.

**END OF PAPER**

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**2016 PU3 H2 CHEM PRELIM 2 EXAM**

**ANSWER SHEET (H2)**

| *Question Number* | *Key* | *Question Number* | *Key* |
|---|---|---|---|
| 1 | **B** | 21 | **A** |
| 2 | **D** | 22 | **B** |
| 3 | **B** | 23 | **D** |
| 4 | **C** | 24 | **A** |
| 5 | **C** | 25 | **D** |
| 6 | **A** | 26 | **D** |
| 7 | **D** | 27 | **C** |
| 8 | **D** | 28 | **C** |
| 9 | **B** | 29 | **D** |
| 10 | **B** | 30 | **D** |
| 11 | **C** | 31 | **D** |
| 12 | **A** | 32 | **C** |
| 13 | **B** | 33 | **A** |
| 14 | **D** | 34 | **D** |
| 15 | **A** | 35 | **D** |
| 16 | **A** | 36 | **C** |
| 17 | **B** | 37 | **B** |
| 18 | **B** | 38 | **B** |
| 19 | **D** | 39 | **A** |
| 20 | **C** | 40 | **A** |

| | Class | Adm No |
|---|---|---|
| Candidate Name: ______________________________ | | |

# 2016 Preliminary Examination II
## Pre-University 3

**H2 CHEMISTRY** **9647/02**

Paper 2 Structured **15th Sept 2016**

**2 hours**

Candidates answer on the Question Paper.

Additional materials: Data Booklet

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**READ THESE INSTRUCTIONS FIRST**

**Do not turn over this question paper until you are told to do so**

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

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

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

Answer **all** the questions.

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.

| Question | **1** | **2** | **3** | **4** | **5** | **6** | **Total** |
|---|---|---|---|---|---|---|---|
| Marks | **12** | **12** | **7** | **16** | **11** | **14** | **72** |

This question paper consists of **21** printed pages and **1** blank page.

**Answer ALL questions on the spaces provided.**

**1 Planning**

A student found a bottle of solid transition metal complex, **X**, in the laboratory. The label on the bottle showed that the molecular formula of **X** is $Cr(H_2O)_6Br_3$ and that the cation of complex **X** is octahedral in shape. The label also showed that **X** is soluble in water.

**(a)** State the oxidation state of Cr in complex **X** and hence the full electronic configuration of the Cr ion in **X**.

…………………………………………………………………………………………..........[2]

The student researched online and found out that **X** could have any of the four structural formulae below:

$[Cr(H_2O)_6]Br_3$
$[CrBr(H_2O)_5]Br_2 \bullet H_2O$
$[CrBr_2(H_2O)_4]Br \bullet 2H_2O$
$[CrBr_3(H_2O)_3] \bullet 3H_2O$

The student wanted to determine the structural formula of **X** using precipitation and gravimetric analysis. Gravimetric analysis involves the measurement of mass of the precipitate collected after a suspension is filtered.

In order to perform the experiment, a 100 $cm^3$ standard solution of 0.100 mol $dm^{-3}$ of $Cr(H_2O)_6Br_3$ needs to be prepared.

**(b)** Write a plan to prepare the standard solution. In your plan, provide details of calculation of mass of solid **X** used. You may assume you are provided with:

- solid **X**
- distilled water
- apparatus normally found in a school laboratory.

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For examiner's use

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……………………………………………………………………………………………[3]

With the standard solution of **X** prepared, the student wanted to carry out an experiment to determine the structural formula of **X**.

**(c)** You are to design an experiment to help the student determine the structural formula of **X** using the method of precipitation of silver bromide followed by gravimetric analysis.

You may assume that you are provided with:

- standard solution prepared in **(b)**
- aqueous silver nitrate of concentration 2.0 mol $dm^{-3}$
- apparatus normally found in a school laboratory.

Your plan should include:

- the quantity of the reagents used
- the procedure for the precipitation and gravimetric analysis
- an outline of how the experimental data would be used to determine the structural formula of **X**.

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**[Turn over**

For
examiner's
use

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……………………………………………………………………………………………[5]

**(d)** In an experiment using a different sample of $Cr(H_2O)_6Br_3$, it was found that the mole ratio of $Cr(H_2O)_6Br_3$ to AgBr formed is 1: 1. Given that the shape of the cation of this sample is also octahedral and that it can exhibit geometric isomerism, draw the structures of the two isomers of the cation.

For examiner's use

[2]

[Total: 12]

**[Turn over**

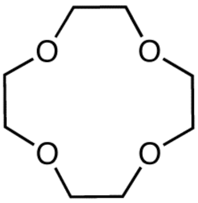
**2** **(a)** This question is about the chemistry of crown ethers.

Crown ethers are cyclic chemical compounds that consist of a ring containing several ether groups. The most common crown ethers are oligomers of ethylene oxide, the repeating unit being ethyleneoxy, i.e. -$CH_2CH_2O$-. The term “crown” refers to the resemblance between the structure of a crown ether bound to a cation, and a crown sitting on a person’s head.

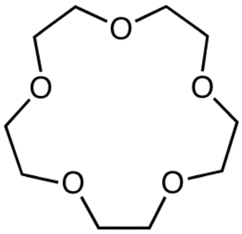
The first number in a crown ether’s name refers to the number of atoms in the ring, and the second number refers to the number of oxygen atoms in the crown ether.

Crown ethers strongly bind to certain cations, forming complexes. The oxygen atoms are well situated to coordinate with a cation located at the interior of the ring, whereas the exterior of the ring is hydrophobic.

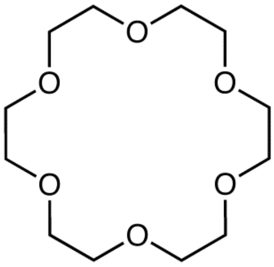
Structures of common crown ethers are shown below.



12-crown-4



15-crown-5



**Q**

**(i)** Name the crown ether **Q**.

……………………………………………………………………………………………..[1]

**(ii)** Predict and explain whether crown ethers are soluble in water.

……………………………………………………………………………………………....

……………………………………………………………………………………………..[2]

Crown ethers are *size-selective*, as they form the most stable complexes with metal ions that fit best into the ring. The metal cation sits in the centre of the ring and interacts with lone pairs from all of the oxygen atoms.

**Q** forms stable complexes with $K^+$ metal ion.

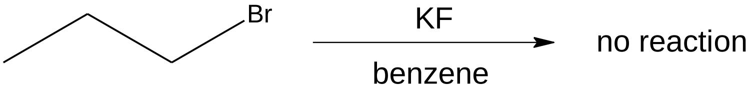
**(iii)** Illustrate how $K^+$ metal ion binds to **Q** with an aid of a diagram. State the type of bonding between the crown ether and the metal ion.

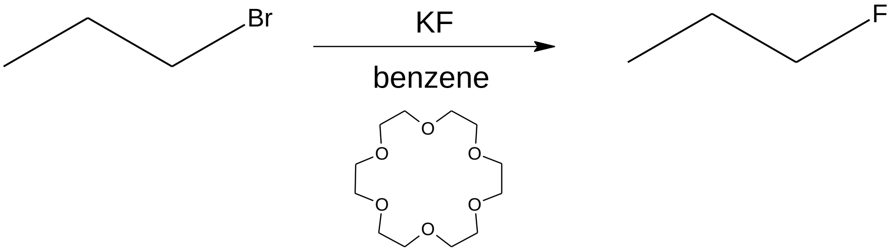
[2]

**(iv)** Suggest the identity of a Group I cation which would be most suitable to bind with 15-crown-5.

……………………………………………………………………………………….[1]

**(v)** When propyl bromine is treated with KF in benzene, no reaction takes place. But when the crown ether **Q** is added to the reaction mixture, the desired propyl fluoride is produced.



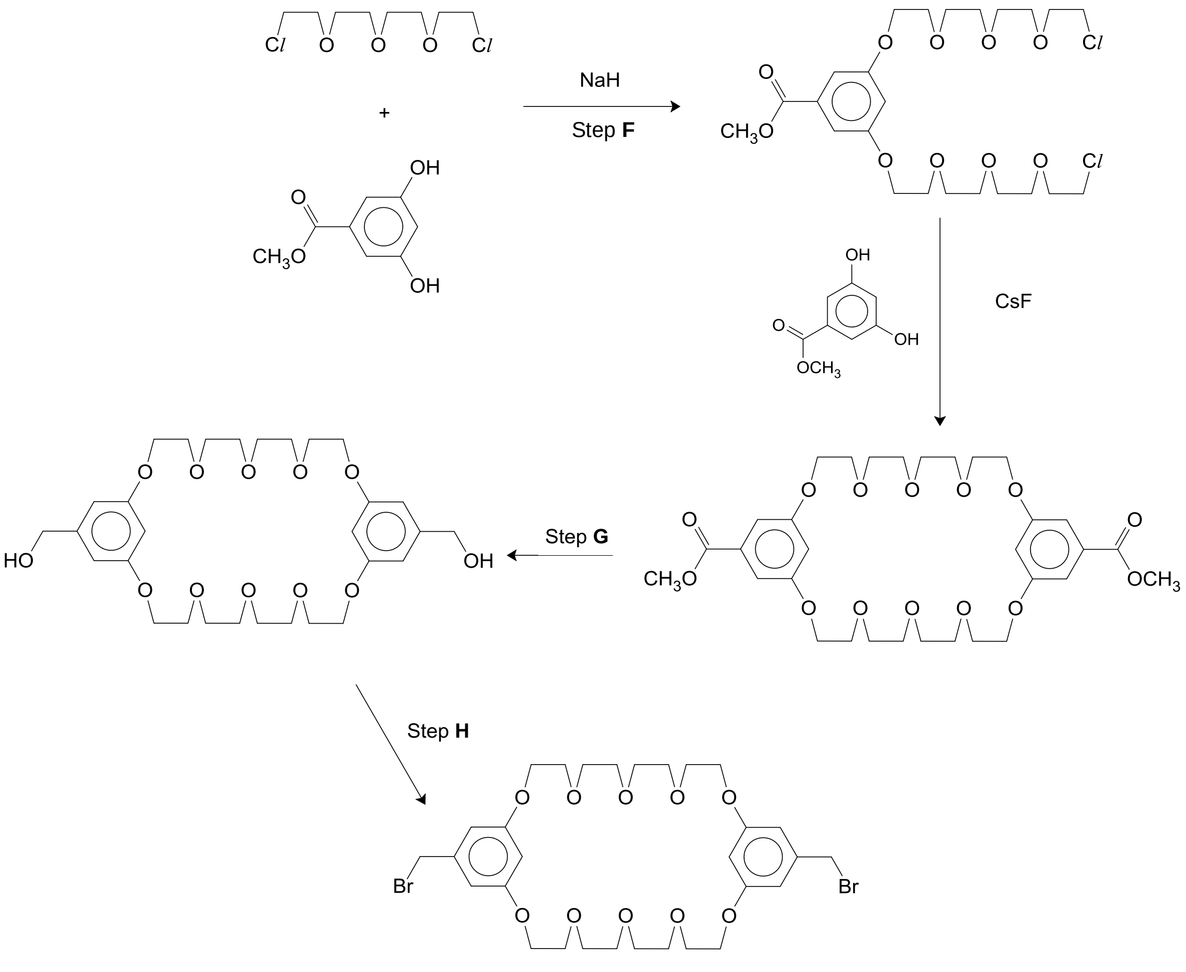


Explain why this is so.

..........................................................................................................................

..........................................................................................................................[2]

**(b)** Crown ethers are generally synthesised involving the Williamson ether syntheses between excess dichloride derivatives of the appropriate ethylene glycols and the appropriate bishydroxy benzenes. The synthesis scheme for the synthesis of difunctionalised 32-crown-10 derivative is shown below.



32-crown-10 derivative

**(i)** Suggest the roles of NaH and CsF in the reaction scheme.

..........................................................................................................[1]

**(ii)** State the type of reaction occurring in step **F**.

..........................................................................................................[1]

**(iii)** State the reagents and conditions required for steps **G** and **H**.

For examiner's use

Step **G**:……………………………………………………………………………….

Step **H**:……………………………………………………………………………..
[2]

[Total: 12]

**3** In the Periodic Table, there is said to be a 'diagonal relationship' between elements of the second and third periods of the Periodic Table exemplified by lithium and magnesium.

An element **R** is related to aluminium by such a relationship and **R** also has the highest first ionisation energy of its group.

**(a)** **(i)** Identify **R** and explain the similarity in polarising powers of the cations of **R** and $Al^{3+}$.

.....................................................................................................................

.....................................................................................................................[2]

**(ii)** Predict and explain the pH of the solution formed when the chloride of **R** dissolves in water.

.....................................................................................................................

.....................................................................................................................[2]

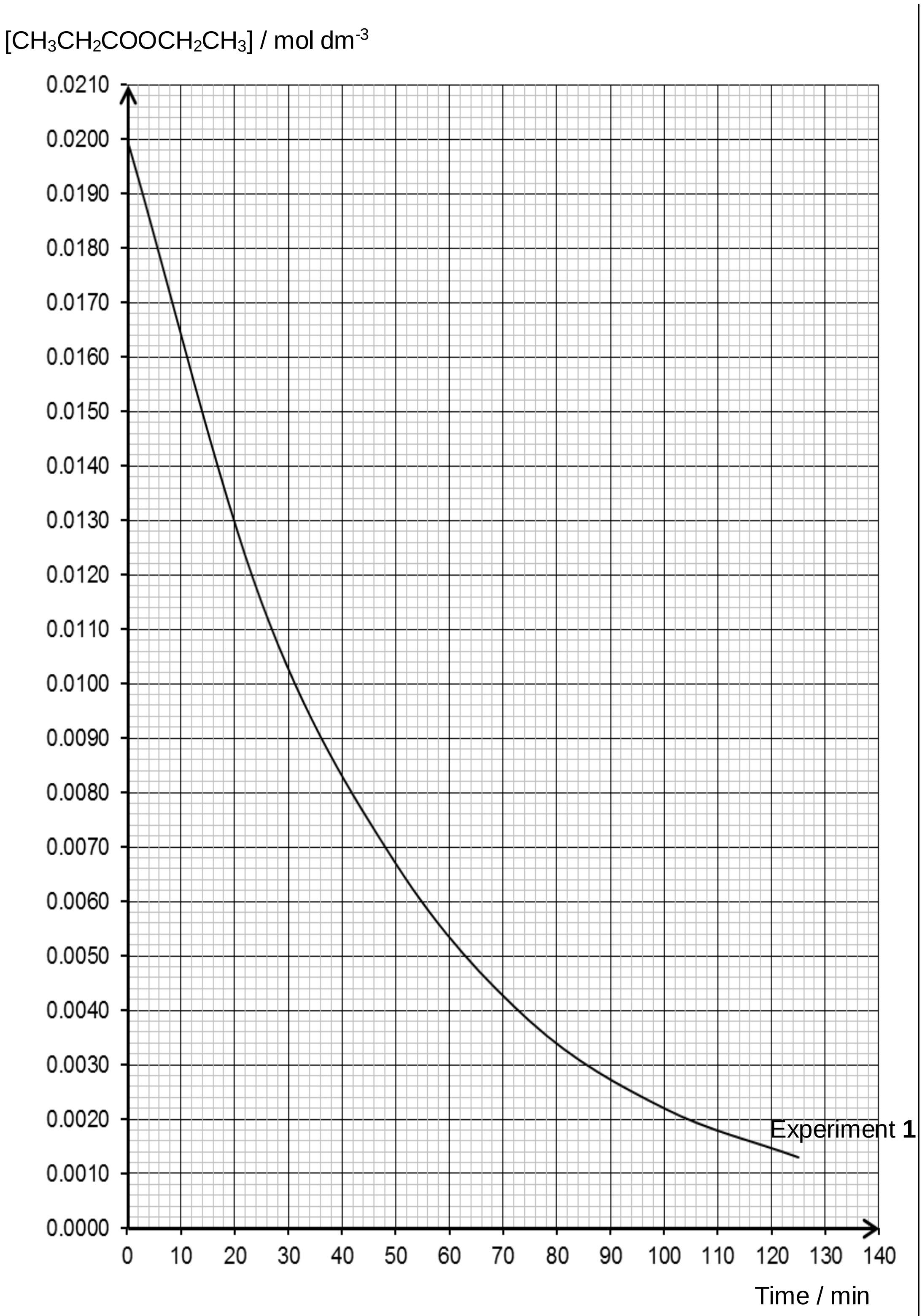
**(b)** Another class of chlorides, acid chlorides, can react with alcohols to form esters which are sweet-smelling. Esters have been used as flavourings in food and perfumes. For example, ethyl propanoate is an ester with pineapple-like smell.

The kinetics of the hydrolysis of ethyl propanoate in alkaline medium at ***T*** K was studied.

Two separate experiments were carried out with varying concentrations of aqueous sodium hydroxide solution. For each experiment, the concentration of ethyl propanoate was determined at regular time intervals.
The graph below shows the results of Experiment **1** with [NaOH] = 2.0 mol $dm^{-3}$.

For examiner's use

**[Turn over**


[$CH_3CH_2COOCH_2CH_3$] / mol dm$^{-3}$
0.0210
0.0200
0.0190
0.0180
0.0170
0.0160
0.0150
0.0140
0.0130
0.0120
0.0110
0.0100
0.0090
0.0080
0.0070
0.0060
0.0050
0.0040
0.0030
0.0020
0.0010
0.0000
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
Time / min
Experiment **1**

The results of Experiment **2** with [NaOH] = 1.0 mol dm$^{-3}$ are shown below.

| **Time / min** | **Experiment 2 with [NaOH] = 1.0 mol dm$^{-3}$ [$CH_3CH_2COOCH_2CH_3$] / mol dm$^{-3}$** |
|---|---|
| 0 | 0.0200 |
| 25 | 0.0152 |
| 50 | 0.0115 |
| 75 | 0.0088 |
| 100 | 0.0067 |
| 125 | 0.0051 |

**(i)** Plot the results of Experiment **2** on the same graph above. Label your graph clearly. [1]

**(ii)** Use the two graphs to determine the order of reaction with respect to [$CH_3CH_2CO_2CH_2CH_3$] and [NaOH], showing your working clearly.

[2]

[Total: 7]

**[Turn over**

For examiner's use

**4** 2-propanol is a colourless, flammable liquid with a strong odour. It is widely used as a solvent in many industrial applications.

**(a)** 2-propanol can be used as a fuel in the fuel cell. At the anode of the cell, 2-propanol is oxidised to carbon dioxide. The electrons pass around the external circuit to the cathode. The protons formed from the oxidation move through the conducting polymer electrolyte to the cathode, where they react with oxygen to produce water.

**(i)** Construct ion-electron equations for the reactions at the anode and cathode respectively.

Anode:…………………………………………………...…………………………......

Cathode:……………………………………………………………………………..[2]

**(ii)** Hence construct the equation for the overall reaction.

…………………………………………………………………………………….....[1]

**(iii)** The cell is capable of producing an e.m.f. of 1.56 V. By using suitable data from the *Data Booklet*, suggest a value for the $E^\ominus$ of the $CO_2/CH_3CH(OH)CH_3$ electrode reaction.

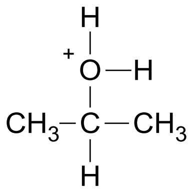
[2]

**(iv)** Suggest a possible advantage of using the 2-propanol fuel cell compared to a hydrogen fuel cell.

……………………………………………………………………………………........

…………………………………………………………………………………….....[1]

**(b)** 2-propanol reacts with hot excess concentrated sulfuric acid to form propene. The reaction follows a 3-step mechanism as described below:

| | |
|---|---|
| **Step 1** | The oxygen atom on 2-propanol is protonated by $H_2SO_4$ forming intermediate **A** and $HSO_4^-$ in an exothermic reaction.<br><br>$CH_3-CH(\overset{+}{O}H_2)-CH_3$<br>Intermediate **A** |
| **Step 2** | The C-O bond in intermediate **A** breaks, forming a carbocation **B** and water. This step is endothermic and is the rate determining step. |
| **Step 3** | The carbocation is then deprotonated in an exothermic reaction, forming propene. $H_2SO_4$ is regenerated. |

**(i)** State the type of reaction undergone when 2-propanol reacts with hot excess concentrated sulfuric acid.

……………………………………………………………………………………………[1]

**(ii)** Use the information given in the table above to draw out the full mechanism for the reaction between 2-propanol and concentrated sulfuric acid, indicating the movement of electrons using curly arrows and showing clearly the lone pair of electrons involved in the mechanism. You are advised to use structural formulae for all species, so that it is clear which bonds are broken and which are formed.

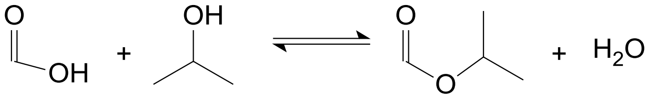
[3]

**[Turn over**

**(iii)** Using the information given in the table in **(b)**, sketch a fully labelled energy profile diagram of the reaction between 2-propanol and concentrated sulfuric acid.

[2]

**(c)** 2-propanol reacts with methanoic acid in the presence of concentrated sulfuric acid, producing an ester, isopropyl formate, and water. The equilibrium below is set up during the reaction:



isopropyl formate

If 0.500 mol of methanoic acid and 0.300 mol of 2-propanol were mixed with a small amount of concentrated sulfuric acid and allowed to reach equilibrium, the equilibrium mass of isopropyl formate was found to be 16.64 g.

**(i)** Write an expression for the equilibrium constant, $K_c$, for the reaction.

[1]

**(ii)** Calculate a value for $K_c$.

[2]

**(iii)** A molecular sieve is a crystalline substance with pores of molecular dimensions which permits the passage of very small molecules such as water. The use of molecular sieves in the reaction above increases the yield of isopropyl formate. Suggest a reason for the increase in yield.

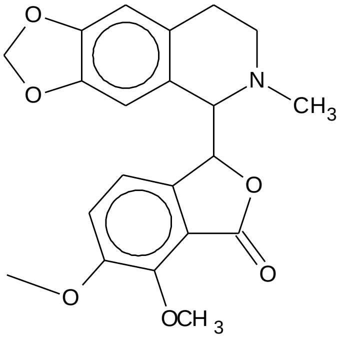
…………………………………………………………………………………………......

………………………………………………………………………………………….....[1]

[Total: 16]

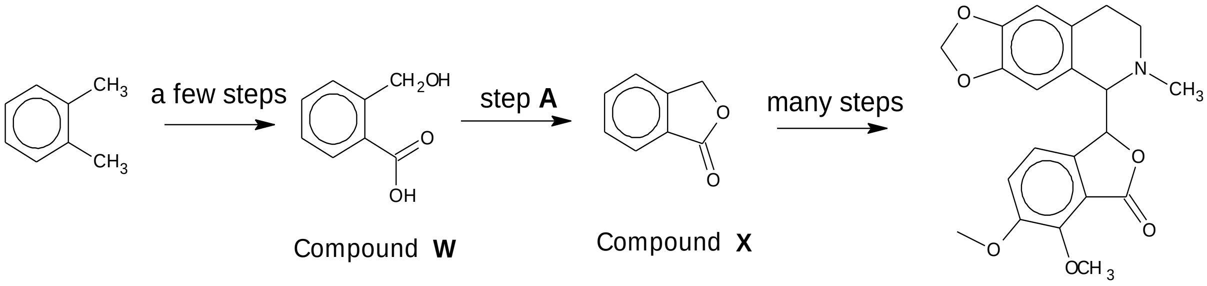
**[Turn over**

**5** Hydrastine is a nitrogen containing drug used in the treatment of memory-related disorders such as Alzheimer's disease and schizophrenia and has the structure shown below.



Hydrastine

A chemist planned a synthetic route to synthesise Hydrastine from 1,2-dimethylbenzene through the intermediates, compounds **W** and **X**, as shown below.



Compound **W**

Compound **X**

Hydrastine

**(a)** Hydrastine can be hydrolysed in either

**I** acidic or

**II** basic conditions.

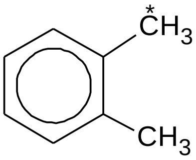
Draw the structures of the products obtained for **each** case. Assume that the ether group (C-O-C) is inert. [2]

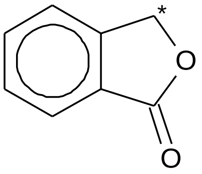
| I | II |
|---|---|
| | |

**(b)** Devise a reaction scheme to help him synthesise compound **X** via compound **W** from 1,2-dimethylbenzene. Show clearly the reagents and conditions required for each step.

[4]

**(c)** State the oxidation numbers of the carbon atoms, labelled with an *, in 1,2-dimethylbenzene and compound **X**.





Oxidation number of $C^*$ in 1,2-dimethylbenzene:…………………………………………...

Oxidation number of $C^*$ in compound **X**: ………..……………………...……………..…[2]

**(iv)** Compare the relative acidity of the alcohol and the carboxylic acid groups present in compound **W**.

………………………………………………………………………………………….........

…………………………………………………………………………………………......

…………………………………………………………………………………………......[3]

[Total: 11]

[Turn over

**6** **(a)** Boiling raw eggs in hot spring water at pH = 9.2 produces black eggs (kuro tamago) through a chemical reaction with geothermal heat and volcanic gas as iron properties ahere to the porous shells. The black colour of iron sulfide is a result of a reaction with hydrogen sulfide, and it produces boiled eggs with black shells.

Iron sulfide is precipitated according to the following reaction.

*reaction 1:* $Fe^{2+}(aq) + S^{2-}(aq) \rightleftharpoons FeS(s) \quad \Delta H^{\ominus}_{ppt}$

Hydrogen sulfide gas from volcanic systems is released into the hot spring water and behaves as a dibasic (diprotic) weak acid.

$$H_2S(g) + aq \rightleftharpoons 2H^+(aq) + S^{2-}(aq)$$

In a saturated solution of hydrogen sulfide,

$[H^+]^2[S^{2-}] = 1.0 \times 10^{-23}$ mol$^3$ dm$^{-9}$

**(i)** Calculate the maximum concentration of sulfide ions present in hot spring water.

[2]

**(ii)** Hence, calculate the minimum concentration of $Fe^{2+}$ that must be present in hot spring water in order for precipitation to occur.

($K_{sp}$ of FeS = $4.9 \times 10^{-18}$ mol$^2$ dm$^{-6}$)

[1]

**(iii)** Use the following data, together with relevant data from the *Data Booklet*, to calculate $\Delta H^{\ominus}_{\text{ppt}}$ for reaction 1 with the aid of an energy cycle.

| | |
|---|---|
| standard enthalpy change of formation of FeS(s) | $-102$ kJ mol$^{-1}$ |
| standard enthalpy change of atomisation of Fe(s) | $+415$ kJ mol$^{-1}$ |
| standard enthalpy change of atomisation of S(s) | $+279$ kJ mol$^{-1}$ |
| sum of first two electron affinities of S(g) | $+337$ kJ mol$^{-1}$ |
| enthalpy change of hydration of $Fe^{2+}$(g) | $-1981$ kJ mol$^{-1}$ |
| enthalpy change of hydration of $S^{2-}$(g) | $-1372$ kJ mol$^{-1}$ |

[4]

**(b)** When a precipitate is formed, $\Delta G^{\ominus}_{\text{ppt}}$, in J mol$^{-1}$, is given by the following expression.

$$\Delta G^{\ominus}_{\text{ppt}} = 2.303RT \log K_{\text{sp}}$$

**(i)** Use the data given in **(a)(ii)** to calculate $\Delta G^{\ominus}_{\text{ppt}}$, in kJ mol$^{-1}$, for FeS.

[1]

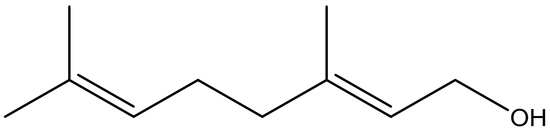
**[Turn over**

For examiner's use

**(ii)** Use your answer in **(a)(iii) and (b)(i)** to calculate $\Delta S^{\ominus}_{\text{ppt}}$ , in J mol$^{-1}$ K$^{-1}$, for the formation of the precipitate FeS(s) at 298 K.

[1]

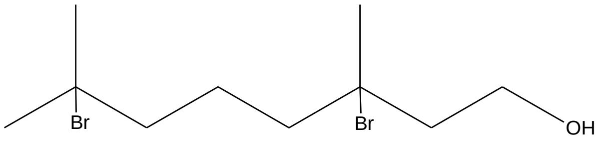
**(c)** Geraniol ($C_{10}H_{18}O$) appears as a clear to pale-yellow oil that is insoluble in water but soluble in most common organic solvents. It has a rose-like scent and is commonly used in perfumes.



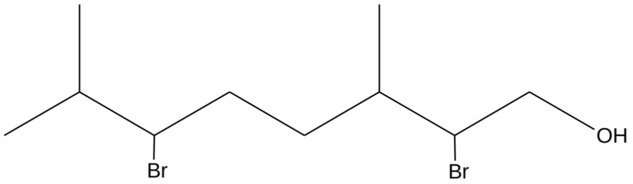
Geraniol

Geraniol reacts with HBr(g) to form the two possible products:

**I** :



**II**:



**(i)** State which of the products would be the major product. Explain your answer.

…………………………………………………………………………………………...

…………………………………………………………………………………………......

……………………………………………………………………………………….[3]

**(ii)** Draw a diagram to illustrate the bonding in C=C bond in geraniol in terms of orbital overlap.

[2]

[Total: 14]

**END OF PAPER**

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| | Class | Adm No |
|---|---|---|
| Candidate Name: ______________________________ | | |

# 2016 Preliminary Examination II
## Pre-University 3

**H2 CHEMISTRY** **9647/02**

Paper 2 Structured Questions **15 Sept 2016**

**2 hours**

Candidates answer on the Question Paper.

Additional materials: Data Booklet

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**READ THESE INSTRUCTIONS FIRST**

**Do not turn over this question paper until you are told to do so**

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

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

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

Answer **all** the questions.

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.

| Question | **1** | **2** | **3** | **4** | **5** | **6** | **Total** |
|---|---|---|---|---|---|---|---|
| Marks | **12** | **12** | **7** | **16** | **11** | **14** | **72** |

This question paper consists of **17** printed pages and **1** blank page.

**Answer ALL questions on the spaces provided.**

**1** **Planning**

A student found a bottle of solid transition metal complex, **X**, in the laboratory. The label on the bottle showed that the molecular formula of **X** is $Cr(H_2O)_6Br_3$ and that the cation of complex **X** is octahedral in shape. The label also showed that **X** is soluble in water.

**(a)** State the oxidation state of Cr in complex **X** and hence the full electronic configuration of the Cr ion in **X**. [2]

+3

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3$

The student researched online and found out that **X** could have any of the four structural formulae below:

$[Cr(H_2O)_6]Br_3$

$[CrBr(H_2O)_5]Br_2 \bullet H_2O$

$[CrBr_2(H_2O)_4]Br \bullet 2H_2O$

$[CrBr_3(H_2O)_3] \bullet 3H_2O$

The student wanted to determine the structural formula of **X** using precipitation and gravimetric analysis. Gravimetric analysis involves the measurement of mass of the precipitate collected after a suspension is filtered.

In order to perform the experiment, a 100 $cm^3$ standard solution of 0.100 mol $dm^{-3}$ of $Cr(H_2O)_6Br_3$ needs to be prepared.

**(b)** Write a plan to prepare the standard solution. In your plan, provide details of calculation of mass of solid **X** used. You may assume you are provided with:

- solid **X**
- distilled water
- apparatus normally found in a school laboratory. [3]

Mass of **X** needed = (100/1000) × 0.100 × 399.7 = 3.997g

- Using a mass balance, weigh accurately 3.997g of solid **X** in a weighing bottle.
- Transfer the solid into a 250$cm^3$ beaker, rinsing the weighing bottle with distilled water and pouring the washing into the beaker. Dissolve the solid with distilled water.

- Transfer the solution into a 100cm$^3$ volumetric flask, making sure all washing goes into the volumetric flask.
- Add distilled water into the volumetric flask and top up to the mark.
- Stopper the volumetric flask and shake well to form a homogeneous solution.

With the standard solution of **X** prepared, the student wanted to carry out an experiment to determine the structural formula of **X**.

**(c)** You are to design an experiment to help the student determine the structural formula of **X** using the method of precipitation of silver bromide followed by gravimetric analysis.

You may assume that you are provided with:

- standard solution prepared in **(b)**
- aqueous silver nitrate of concentration 2.0 mol dm$^{-3}$
- apparatus normally found in a school laboratory.

Your plan should include:

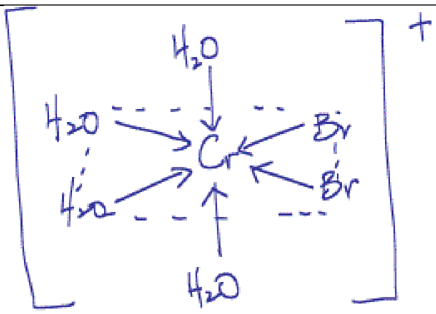
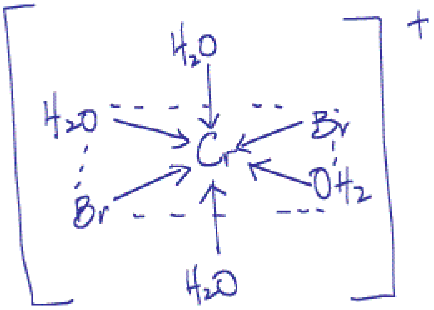
- the quantity of the reagents used
- the procedure for the precipitation and gravimetric analysis
- an outline of how the experimental data would be used to determine the structural formula of **X**. [5]

- Using a pipette, transfer 10.0 cm$^3$ of the standard solution of **X** into a beaker.
- Add aqueous silver nitrate until in excess and stir with a glass rod. Stop adding when the cream precipitate formed does not increase in mass (or at least 3 times the amount of **X** in 10 cm$^3$).
- Using a filter funnel, filter the mixture to obtain the residue.
- Transfer the residue to a pre-weighed dry evaporating dish and heat the residue to dryness by placing the evaporating dish on top of a Bunsen burner with tripod.
- Cool and reweigh the evaporating dish to obtain mass of the residue.
- Repeat the heating, cooling and weighing until a constant mass is obtained.
- Amount of **X** used = (10/1000) × 0.100 = 0.00100 mol

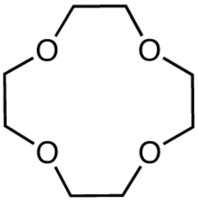
  Amount of residue formed = mass of residue / 187.9 = y

| **Mol ratio of X to AgBr** | **Structural formula** |
|---|---|
| 1 : 0 | $[CrBr_3(H_2O)_3] \bullet 3H_2O$ |
| 1 : 1 | $[CrBr_2(H_2O)_4]Br \bullet 2H_2O$ |
| 1 : 2 | $[CrBr(H_2O)_5]Br_2 \bullet H_2O$ |
| 1 : 3 | $[Cr(H_2O)_6]Br_3$ |

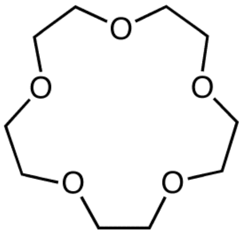
**[Turn over**

| | | |
|---|---|---|
| | | |
| | **(d)** | In an experiment using a different sample of $Cr(H_2O)_6Br_3$, it was found that the mole ratio of $Cr(H_2O)_6Br_3$ to AgBr formed is 1: 1. Given that the shape of the cation of this sample is also octahedral and that it can exhibit geometric isomerism, draw the structures of the two isomers of the cation. [2] |
| | | <br> <br><br> |
| | [Total: 12] | |

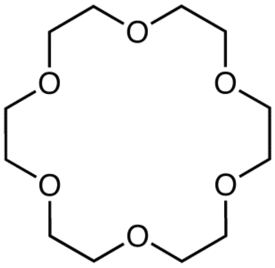
| | | |
|---|---|---|
| **2** | **(a)** | This question is about the chemistry of crown ethers.<br>Crown ethers are cyclic chemical compounds that consist of a ring containing several ether groups. The most common crown ethers are oligomers of ethylene oxide, the repeating unit being ethyleneoxy, i.e. $–CH_2CH_2O-$. The term “crown” refers to the resemblance between the structure of a crown ether bound to a cation, and a crown sitting on a person’s head.<br>The first number in a crown ether’s name refers to the number of atoms in the ring, and the second number refers to the number of oxygen atoms in the crown ether.<br>Crown ethers strongly bind to certain cations, forming complexes. The oxygen atoms are well situated to coordinate with a cation located at the interior of the ring, whereas the exterior of the ring is hydrophobic.<br>Structures of common crown ethers are shown below. |



12-crown-4



15-crown-5



***Q***

**(i)** Name the crown ether ***Q***. [1]

18-crown-6

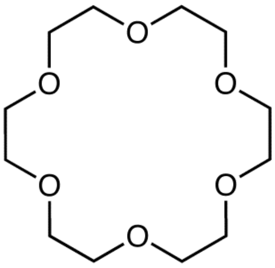
**(ii)** Predict and explain whether crown ethers are soluble in water. [2]

Crown ethers are generally insoluble in water because the hydrogen bonds formed between crown ethers and water are not exothermic enough to break the temporary dipole-induced dipole interactions between crown ether molecules and hydrogen bonds between water molecules.

Crown ethers are *size-selective*, as they form the most stable complexes with metal ions that fit best into the ring. The metal cation sits in the centre of the ring and interacts with lone pairs from all of the oxygen atoms.

***Q*** forms stable complexes with $K^+$ metal ion.

**(iii)** Illustrate how $K^+$ metal ion binds to ***Q*** with an aid of a diagram. State the type of bonding between the crown ether and the metal ion. [2]

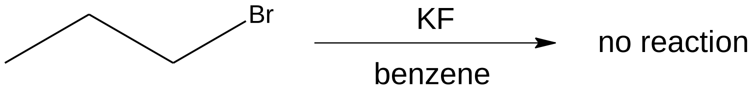


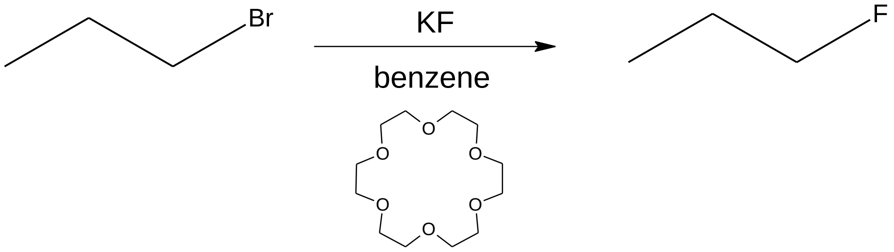
Coordinate / Dative bonding

**(iv)** Suggest the identity of a Group I cation which would be most suitable to bind with 15-crown-5. [1]

$Na^+$

**(v)** When propyl bromine is treated with KF in benzene, no reaction takes place. But when the crown ether ***Q*** is added to the reaction mixture, the desired propyl fluoride is produced.



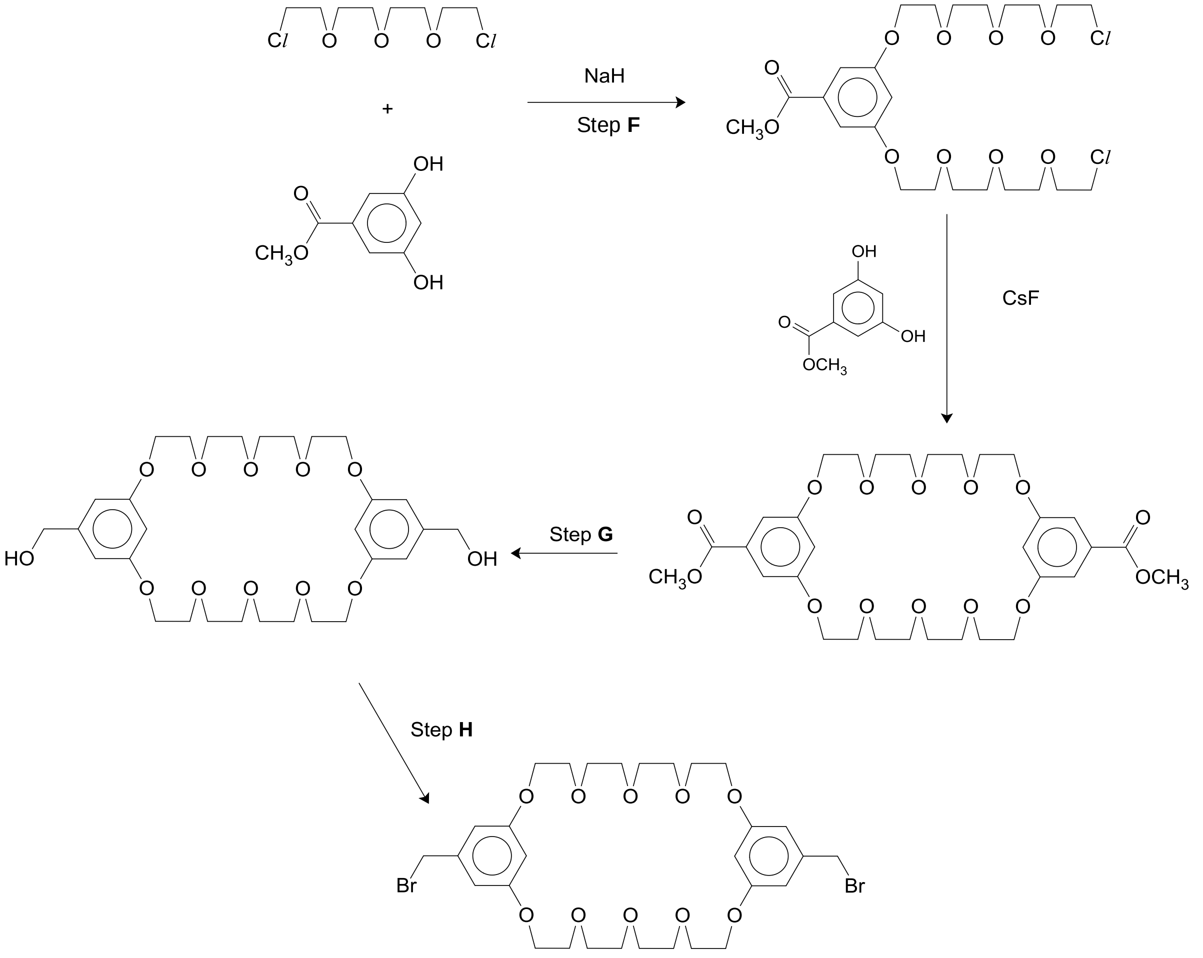


Explain why this is so. [2]

KF is insoluble in benzene, so $F^-$ is unavailable to attack the propyl bromine.

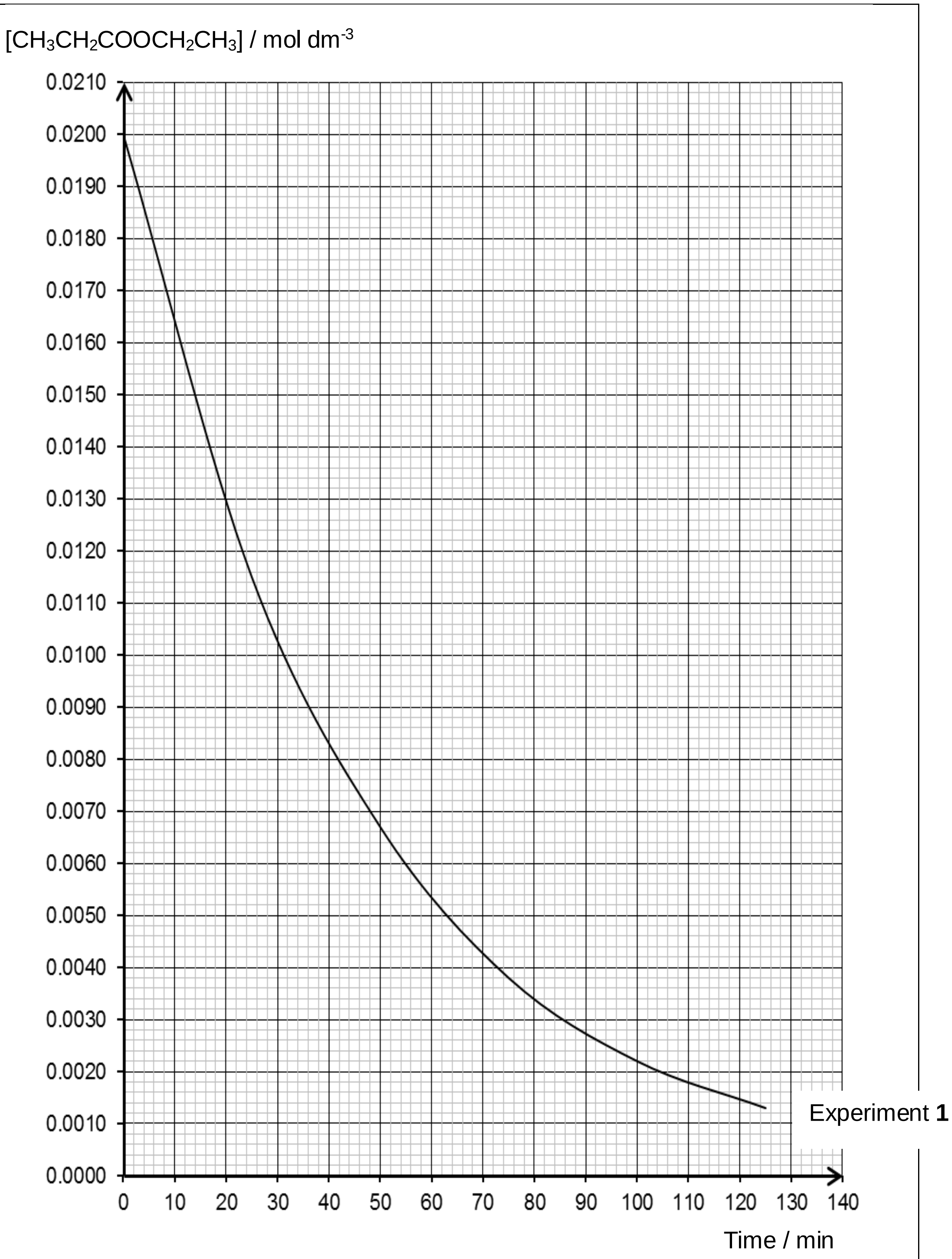
When 18-crown-6 is added, the crown ether surrounds the $K^+$ ion, allowing the $F^-$ ion to be formed for nucleophilic substitution, so the reaction can proceed

**(b)** Crown ethers are generally synthesised involving the Willaimsen ether syntheses between excess dichloride derivatives of the appropriate ethylene glycols and the appropriate bishydroxy benzenes. The synthesis scheme for the synthesis of difunctionalised 32-crown-10 derivative is shown below.

| | | | | |
|---|---|---|---|---|
| | |  | | |
| | | **(i)** | Suggest the roles of NaH and CsF in the reaction scheme. | [1] |
| | | | They act as bases, abstracting a proton from phenol. | |
| | | **(ii)** | State the type of reaction occurring in step **F**. | [1] |
| | | | Nucleophilic Substitution ($S_N2$) | |
| | | **(iii)** | State the reagents and conditions required for Steps **G** and **H**. | [2] |
| | | | Step G: $LiAlH_4$ dry ether, rtp<br>Step H: $PBr_3$ / $SOBr_2$ , rtp | |
| | | | | [Total: 12] |

**[Turn over**

| | | | |
|---|---|---|---|
| **3** | In the Periodic Table, there is said to be a 'diagonal relationship' between elements of the second and third periods of the Periodic Table exemplified by lithium and magnesium.<br>An element **R** is related to aluminium by such a relationship and **R** also has the highest first ionisation energy of its group. | | |
| | **(a)** | **(i)** | Identify **R** and explain the similarity in polarising powers of the cations of **R** and $Al^{3+}$. [2] |
| | | | R is beryllium.<br>Polarising power Is directly proportional to charge density ( q/r). Although $Al^{3+}$ is of a higher charge than $Be^{2+}$, $Al^{3+}$ is also larger in size. The two ions have similar charge densities and hence, similar polarising powers. |
| | | **(ii)** | Predict and explain the pH of the solution formed when the chloride of **R** dissolves in water. [2] |
| | | | pH = 3 ( accept any value from 1 to 4 )<br>Due to the high charge density of $Be^{2+}$, it undergoes hydrolysis whereby it weakens and breaks the O-H bond in $H_2O$, readily donating a proton. Hence the solution becomes acidic. |
| | | | |
| | **(b)** | Another class of chlorides, acid chlorides, can react with alcohols to form esters which are sweet-smelling. Esters have been used as flavourings in food and perfumes. For example, ethyl propanoate is an ester with pineapple-like smell.<br>The kinetics of the hydrolysis of ethyl propanoate in alkaline medium at ***T*** K was studied.<br>Two separate experiments were carried out with varying concentrations of aqueous sodium hydroxide solution. For each experiment, the concentration of ethyl propanoate was determined at regular time intervals as the reaction proceeded.<br>The graph below shows the results of Experiment **1** with [NaOH] = 2.0 mol $dm^{-3}$. The results of Experiment **2** with [NaOH] = 1.0 mol $dm^{-3}$ are shown below. | |


[$CH_3CH_2COOCH_2CH_3$] / mol dm$^{-3}$
0.0210
0.0200
0.0190
0.0180
0.0170
0.0160
0.0150
0.0140
0.0130
0.0120
0.0110
0.0100
0.0090
0.0080
0.0070
0.0060
0.0050
0.0040
0.0030
0.0020
0.0010
0.0000
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
Time / min
Experiment **1**

**[Turn over**

| **Time / min** | **Experiment 2 with [NaOH] = 1.0 mol dm$^{-3}$ [$CH_3CH_2COOCH_2CH_3$] / mol dm$^{-3}$** |
|---|---|
| 0 | 0.0200 |
| 25 | 0.0152 |
| 50 | 0.0115 |
| 75 | 0.0088 |
| 100 | 0.0067 |
| 125 | 0.0051 |

**(i)** Plot the results of Experiment **2** on the same graph above. Label your graph clearly. [1]

**(ii)** Use the two graphs to determine the order of reaction with respect to $CH_3CH_2CO_2CH_2CH_3$ and NaOH, showing your working clearly. [2]

**To find the order of reaction with respect to the ester.**

Consider the graph for experiment 1.

1st $t_{1/2}$ = 31.0 min (with construction lines shown on the graph)
2nd $t_{1/2}$ = 32.0 min (with construction lines shown on the graph)

Since $t_{1/2}$ is almost constant, order of reaction with respect to ethyl propanoate = 1

**Alternative answer**

Can also use the graph for experiment 2 to find two $t_{1/2}$ values.

1st $t_{1/2}$ = 63.0 min (with construction lines shown on the graph)
2nd $t_{1/2}$ = 63.0 min (with construction lines shown on the graph)

Since $t_{1/2}$ is constant, order of reaction with respect to ethyl propanoate = 1

**To find the order of reaction with respect to NaOH.**

For experiment 1, initial rate = 0.010/24.0 = $4.17 \times 10^{-4}$ mol dm$^{-3}$ min$^{-1}$
For experiment 2, initial rate = 0.010/48.0 = $2.08 \times 10^{-4}$ mol dm$^{-3}$ min$^{-1}$
When [NaOH] is doubled, initial rate is also doubled ($4.17\text{x}10^{-4}/2.08\text{x}10^{-4} = 2$).
Hence order of reaction with respect to NaOH = 1

**Alternative answer**

Consider the graph for experiment 2.
$t_{1/2}$ = 63.0 min
$\Rightarrow$ $t_{1/2}$ for experiment 2 = (2)($t_{1/2}$ for experiment 1)
$\Rightarrow$ reaction rate is halved when [NaOH] is halved.
Hence order of reaction with respect to NaOH = 1

[Total: 7]

**4** 2-propanol is a colourless, flammable liquid with a strong odour. It is widely used as a solvent in many industrial applications.

**(a)** 2-propanol can be used as a fuel in the fuel cell. At the anode of the cell, 2-propanol is oxidised to carbon dioxide. The electrons pass around the external circuit to the cathode. The protons formed from the oxidation move through the conducting polymer electrolyte to the cathode, where they react with oxygen to produce water.

**(i)** Construct ion-electron equations for the reactions at the anode and cathode respectively. [2]

Anode: $CH_3CH(OH)CH_3 + 5H_2O \rightarrow 3CO_2 + 18H^+ + 18e$

Cathode: $O_2 + 4H^+ + 4e \rightarrow 2H_2O$

**(ii)** Hence construct the equation for the overall reaction. [1]

$2CH_3CH(OH)CH_3 + 9O_2 \rightarrow 6CO_2 + 8H_2O$

**(iii)** The cell is capable of producing an e.m.f. of 1.56 V. By using suitable data from the *Data Booklet*, suggest a value for the $E^\ominus$ of the $CO_2/CH_3CH(OH)CH_3$ electrode reaction. [2]

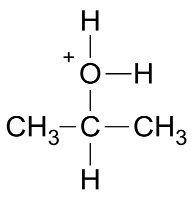
$1.56 = +1.23 - E^\ominus_{anode}$

$E^\ominus_{anode} = -0.33V$

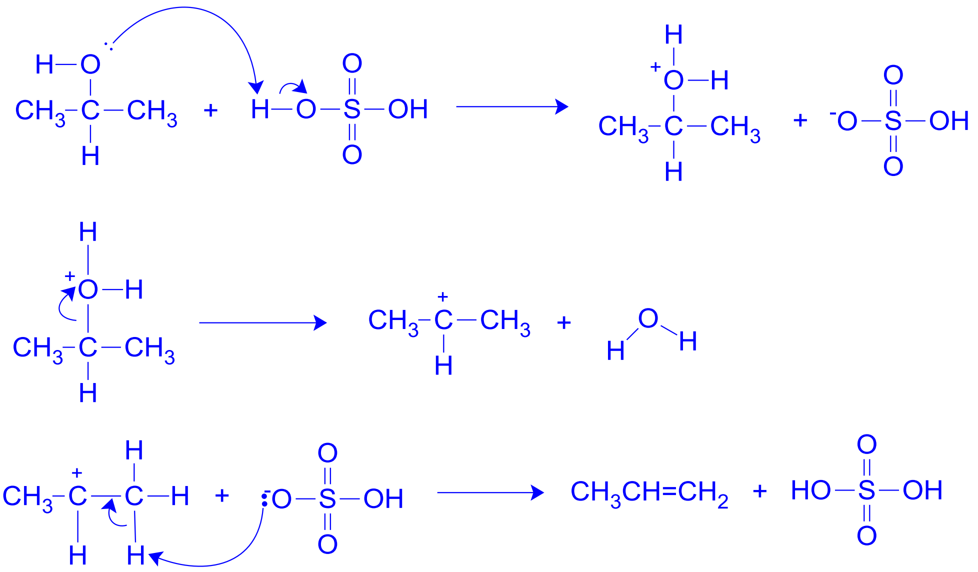
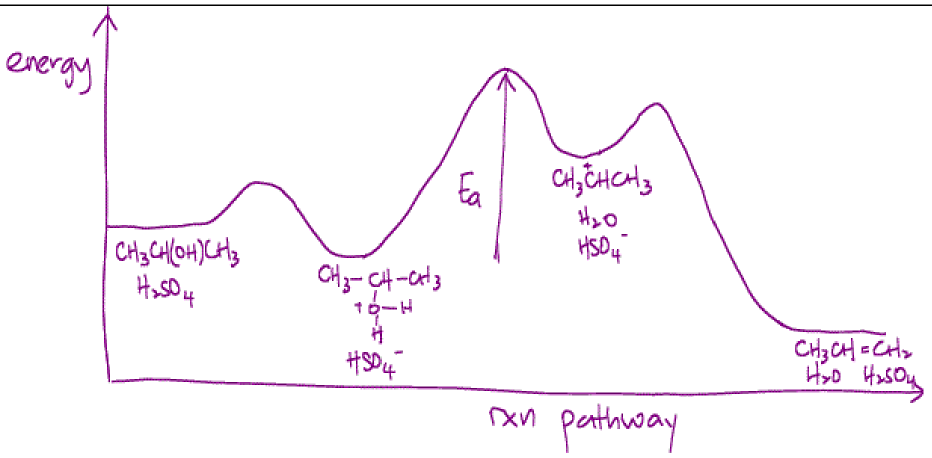
**(iv)** Suggest a possible advantage of using the 2-propanol fuel cell compared to a hydrogen fuel cell. [1]

2-propanol is a liquid but hydrogen is a gas at rtp. 2-propanol is easier to store and transport.

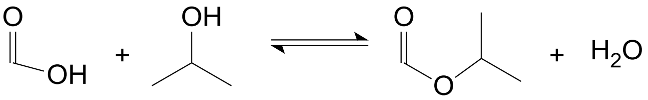
**(b)** 2-propanol reacts with hot excess concentrated sulfuric acid to form propene. The reaction follows a 3-step mechanism as described below:

| | |
|---|---|
| Step 1 | The oxygen atom on 2-propanol is protonated by $H_2SO_4$ forming intermediate **A** and $HSO_4^-$ in an exothermic reaction.<br><br>$CH_3-\underset{H}{\overset{H-\overset{+}{O}-H}{C}}-CH_3$<br>Intermediate **A** |
| Step 2 | The C-O bond in intermediate **A** breaks, forming a carbocation **B** and water. This step is endothermic and is the rate determining step. |

**[Turn over**

| | | | |
|---|---|---|---|
| | | Step 3 | The carbocation is then deprotonated in an exothermic reaction, forming propene. $H_2SO_4$ is regenerated. |
| | | | |
| | | **(i)** | State the type of reaction undergone when 2-propanol reacts with hot excess concentrated sulfuric acid. [1] |
| | | | Elimination |
| | | **(ii)** | Use the information given in the table above to draw out the full mechanism for the reaction between 2-propanol and concentrated sulfuric acid, indicating the movement of electrons using curly arrows and showing clearly the lone pair of electrons involved in the mechanism. You are advised to use structural formulae for all species, so that it is clear which bonds are broken and which are formed. [3] |
| | | |  |
| | | **(iii)** | Using the information given in the table above, sketch a fully labelled energy profile diagram of the reaction between 2-propanol and concentrated sulfuric acid. [2] |
| | | |  |

**(c)** 2-propanol reacts with methanoic acid in the presence of concentrated sulfuric acid, producing an ester, isopropyl formate, and water. The equilibrium below is set up during the reaction:



If 0.500 mol of methanoic acid and 0.300 mol of 2-propanol were mixed with a small amount of concentrated sulfuric acid and allowed to reach equilibrium, the equilibrium mass of isopropyl formate was found to be 16.64 g.

**(i)** Write the expression for $K_C$. [1]

$$K_C = \frac{[\text{isopropyl formate}][H_2O]}{[\text{methanoic acid}][\text{2-propanol}]}$$

**(ii)** Calculate a value for $K_C$. [2]

Amount of isopropyl formate = 16.64 / 88 = 0.189 mol

| | acid | + | alcohol | ⇌ | ester | + | water |
|---|---|---|---|---|---|---|---|
| Initial amount / mol | 0.500 | | 0.300 | | 0 | | 0 |
| Change / mol | -0.189 | | -0.189 | | +0.189 | | +0.189 |
| Eqm amount / mol | 0.311 | | 0.111 | | 0.189 | | 0.189 |

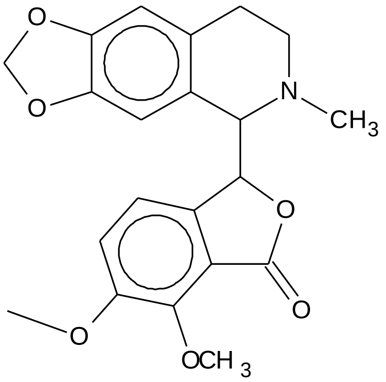
$$K_C = \frac{\left(\frac{0.189}{V}\right)\left(\frac{0.189}{V}\right)}{\left(\frac{0.311}{V}\right)\left(\frac{0.111}{V}\right)} = 1.03$$

**(iii)** A molecular sieve is a crystalline substance with pores of molecular dimensions which permits the passage of very small molecules such as water. The use of molecular sieves in the reaction above increases the yield of isopropyl formate. Suggest a reason for the increase in yield. [1]

The molecular sieve removes water, causing concentration of water to decrease. By LCP, equilibrium will then shift to the right to replenish water, hence increasing the yield.

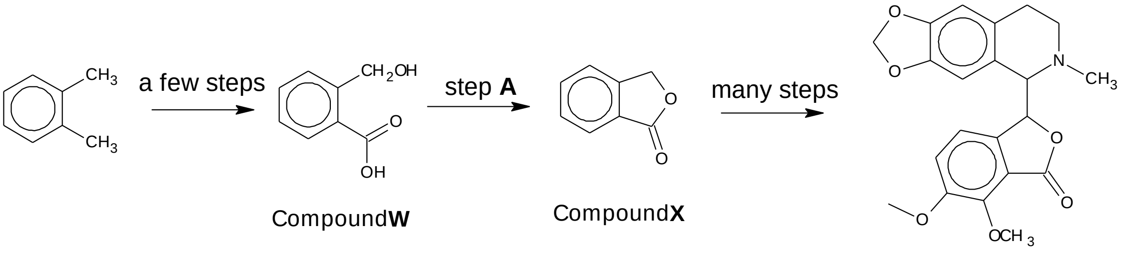
[Total: 16]

**5** **(a)** Hydrastine is a nitrogen containing drug used in the treatment of memory-related disorders such as Alzheimer's disease and schizophrenia and has the structure shown below.



Hydrastine

A chemist planned a synthetic route to synthesise Hydrastine from 1,2-dimethylbenzene through the intermediates, compounds **W** and **X**, as shown below.

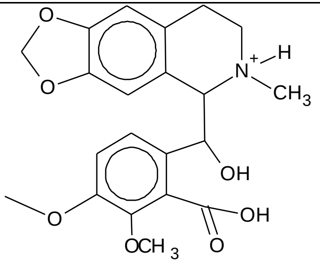


**(i)** Hydrastine can be hydrolysed in either

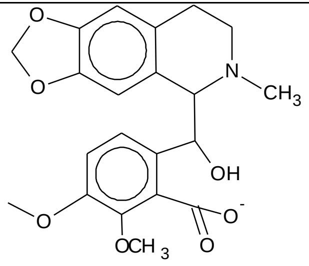
**I** acidic or

**II** basic conditions.

Draw the structures of the products obtained for **each** case. Assume that the ether group (C-O-C) is inert. [2]



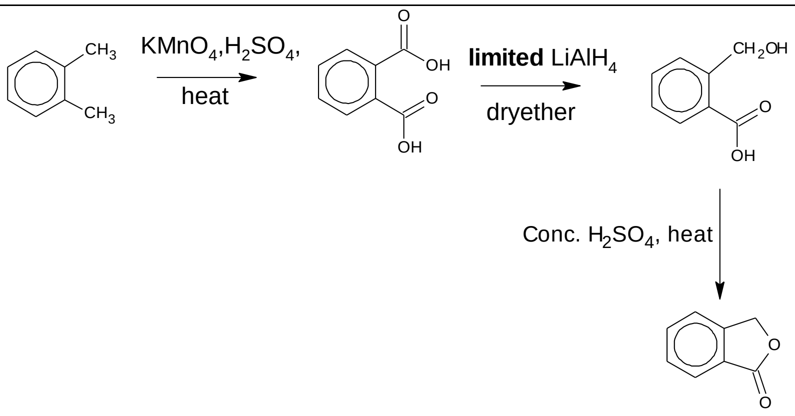
Acidic conditions



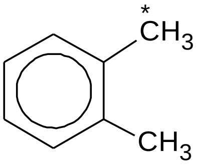
basic conditions

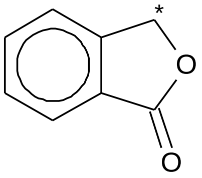
**(ii)** Devise a reaction scheme to help him synthesise compound **X** via compound **W** from 1,2-dimethylbenzene. Show clearly the reagents and conditions required for each step.

[4]



**(iii)** State the oxidation numbers of the carbon atoms, labelled with an *, in 1,2-dimethylbenzene and compound **X**.





[2]

In 1,2-dimethylbenzene, C = -3
In compound X , C = -1

**(iv)** Compare the relative acidity of the alcohol and the carboxylic acid groups present in compound **W**.

The R-CH$_2$OH is less acidic as compared to R-COOH; The electron donating R group intensifies the negative charge on the oxygen atom of the conjugate base, making the conjugate base less stable; The R-COOH is more acidic because the negative charge on the oxygen atom can undergo resonance and disperse the –ve charge among the 3 atoms of the carboxylate group, thus making the conjugate base more stable;

[Total: 11]

**[Turn over**

**6** **(a)** Boiling raw eggs in hot spring water at pH = 9.2 produces black eggs (kuro tamago) through a chemical reaction with geothermal heat and volcanic gas as iron properties ahere to the porous shells. The black colour of iron sulfide is a result of a reaction with hydrogen sulfide, and it produces boiled eggs with black shells.

Iron sulfide is precipitated according to the following reaction.

*reaction 1:* $Fe^{2+}(aq) + S^{2-}(aq) \rightleftharpoons FeS(s) \quad \Delta H^{\ominus}_{ppt}$

Hydrogen sulfide gas from volcanic systems is released into the hot spring water and behaves as a dibasic (diprotic) weak acid.

$H_2S(g) + aq \rightleftharpoons 2H^+(aq) + S^{2-}(aq)$

In a saturated solution of hydrogen sulfide,

$[H^+]^2[S^{2-}] = 1.0 \times 10^{-23}$ mol$^3$ dm$^{-9}$

**(i)** Calculate the maximum concentration of sulfide ions present in hot spring water. [2]

$[H^+] = 10^{-9.2}$

$= 6.31 \times 10^{-10}$ mol dm$^{-3}$

$[S^{2-}] = \dfrac{1.0 \times 10^{-23}}{(6.31 \times 10^{-10})^2} = 2.51 \times 10^{-5}$ mol dm$^{-3}$

**(ii)** Hence, calculate the minimum concentration of $Fe^{2+}$ present in hot spring water in order for precipitation to occur.

($K_{sp}$ of FeS = $4.9 \times 10^{-18}$ mol$^2$ dm$^{-6}$) [1]

$K_{sp} = [Fe^{2+}][S^{2-}]$

$[Fe^{2+}] = \dfrac{4.9 \times 10^{-18}}{2.51 \times 10^{-5}} = 1.95 \times 10^{-13}$ mol dm$^{-3}$

**(iii)** Use the following data, together with relevant data from the *Data Booklet*, to calculate $\Delta H^{\ominus}_{ppt}$ for reaction 1 with the aid of an energy cycle.

| | |
|---|---|
| standard enthalpy change of formation of FeS(s) | –102 kJ $mol^{-1}$ |
| standard enthalpy change of atomisation of Fe(s) | +415 kJ $mol^{-1}$ |
| standard enthalpy change of atomisation of S(s) | +279 kJ $mol^{-1}$ |
| sum of first two electron affinities of S(g) | +337 kJ $mol^{-1}$ |
| enthalpy change of hydration of $Fe^{2+}(g)$ | –1981 kJ $mol^{-1}$ |
| enthalpy change of hydration of $S^{2-}(g)$ | –1372 kJ $mol^{-1}$ |

[4]

$–102 = 415 + 279 + 337 + 762 + 1560 – 1981 – 1372 + \Delta H^{\ominus}_{ppt}$

$\Delta H^{\ominus}_{ppt} = –102 \text{ kJ mol}^{-1}$

**(b)** When a precipitate is formed, $\Delta G^{\ominus}_{ppt}$, in J $mol^{-1}$, is given by the following expression.

$$\Delta G^{\ominus}_{ppt} = 2.303RT \log K_{sp}$$

**(i)** Use the data given in **(a)(ii)** to calculate $\Delta G^{\ominus}_{ppt}$, in kJ $mol^{-1}$, for FeS. [1]

$\Delta G^{\ominus}_{ppt} = 2.303 \times 8.31 \times 298 \times \lg(4.9 \times 10^{-18})$

$= –98.7 \text{ kJ mol}^{-1}$

**(ii)** Use your answer in **(a)(iii) and (b)(i)** to calculate $\Delta S^{\ominus}_{ppt}$ , in J $mol^{-1}$ $K^{-1}$, for the formation of the precipitate FeS(s) at 298 K. [1]

$\Delta G^{\ominus}_{ppt} = \Delta H^{\ominus}_{ppt} - T\Delta S^{\ominus}_{ppt}$

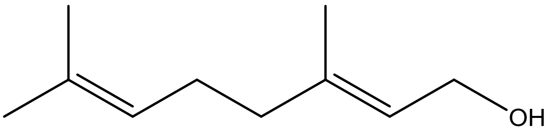
$–98.7 = –102 – 298\ \Delta S^{\ominus}_{ppt}$

$\Delta S^{\ominus}_{ppt} = \dfrac{-102+98.7}{298}$

$= –11.1 \text{ J mol}^{-1} \text{ K}^{-1}$

**[Turn over**

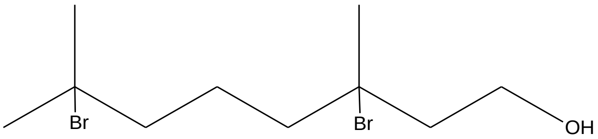
**(c)** Geraniol ($C_{10}H_{18}O$) appears as a clear to pale-yellow oil that is insoluble in water but soluble in most common organic solvents. It has a rose-like scent and is commonly used in perfumes.



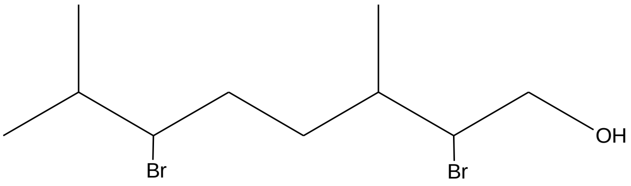
Geraniol

Geraniol reacts with HBr(g) to form the two possible products:

**I :**



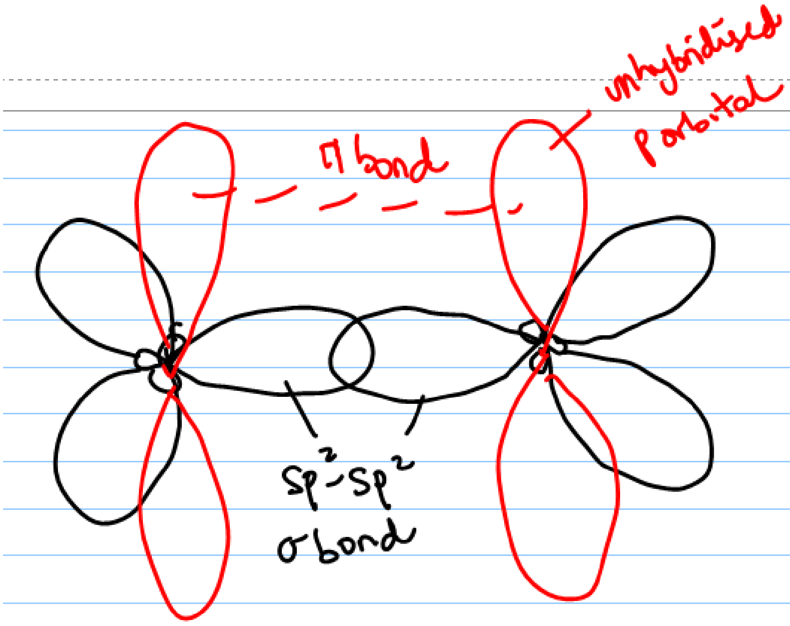
**II:**



**(i)** State which of the products would be the major product. Explain your answer. [3]

I would be the major product. This is due to the fact that by Markovnikov's rule, the tertiary carbocation intermediate formed after the addition of H is more stable than that of II, which forms a secondary carbocation, due to more electron donating alkyl groups attached to the carbocation which stabilises the cation more.

**(ii)** Draw a diagram to illustrate the bonding in any of the C=C bond in geraniol in terms of orbital overlap. [2]

| | | | |
|---|---|---|---|
| | | |  |
| | | | [Total: 14] |
| | | | |

**[Turn over**

| Class | Adm No |
|---|---|
|  |  |

Candidate Name: ____________________

# 2016 Preliminary Examination II

## Pre-University 3

**H2 CHEMISTRY** **9647/03**

Paper 3 Free Response **19th Sept 2016**

**2 hours**

Candidates answer on separate paper.

Additional materials: Cover Page
Answer Paper
Data Booklet

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**READ THESE INSTRUCTIONS FIRST**

**Do not turn over this question paper until you are told to do so**

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

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

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

Answer any **four** questions.

A Data Booklet is provided.

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

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

At the end of the examination, fasten all your work securely together.

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

**1** **(a)** At room temperature, the electrode potential *E* for the system

$$[MnO_4^-(aq) + 8H^+(aq)], [Mn^{2+}(aq) + 4H_2O(l)] / Pt$$

is given by the equation

$$E = E^\theta + \frac{0.059}{5} \log \frac{[MnO_4^-(aq)]\,[H^+(aq)]^8}{[Mn^{2+}(aq)]}$$

where $E^\theta$ = +1.51 V. *E* values at various pH are given below when $[MnO_4^-(aq)]$ = 0.01 mol dm$^{-3}$ and $[Mn^{2+}(aq)]$ = 0.0001 mol dm$^{-3}$.

| **pH** | ***E* / V** |
|---|---|
| 0 | +1.52 |
| 3 | +1.24 |
| 7 | +0.83 |

**(i)** Define what the symbol $E^\theta$ refers to. [1]

**(ii)** Calculate the electrode potential of the cell at pH 1, when the manganate(VII) ion concentration is 0.01 mol dm$^{-3}$ and the manganese(II) ion concentration is 0.001 mol dm$^{-3}$. [2]

**(iii)** Predict at which pH value (0, 3 or 7) the solution is the most oxidising. [1]

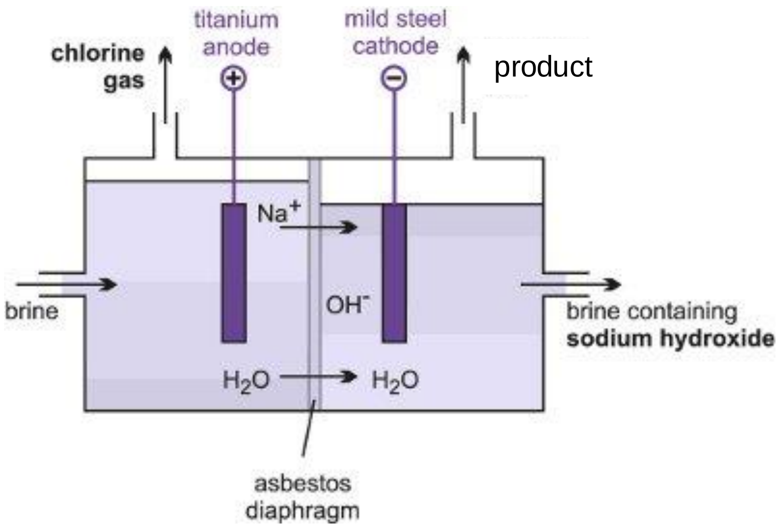
The electrolytic conductivity ,Ϗ, of a solution in a cell is given by the following formula:

$$Ϗ = \frac{(c)\,(l)}{a}$$

where *c* is the conductance of the cell and *a* is the cross-sectional area of the electrodes, separated by a distance *l*.

**(iv)** Often the term $\frac{l}{a}$ is replaced by a cell constant *K*. Calculate the cell constant of a particular cell if it was found that the conductance of the cell containing $Mn^{2+}(aq)$ of concentration 0.100 mol dm$^{-3}$ is 0.022 Ω$^{-1}$ and the electrolytic conductivity,Ϗ, was 0.011 Ω$^{-1}$ cm$^{-1}$. State the units of *K*. [2]

**(b)** A diaphragm cell consisting brine solution, concentrated NaC*l*, is used in the commercial electrolytic production of chlorine and sodium hydroxide.



**(i)** Write the ion-electron equations for the reactions occurring at the cathode and at the anode. [2]

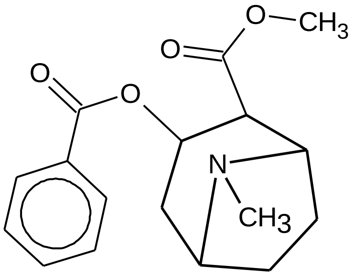
**(ii)** The chlorine gas is collected separately at the anode to prevent a side reaction that will occur with one of the products formed. Write a balanced equation for this side reaction that occurs at room conditions. State the oxidation numbers of chlorine in all the products formed. [2]

**(iii)** In an electrolytic experiment using this diaphragm cell, 1.0 mol of gas is produced at the cathode. Calculate the mass of chlorine gas that is produced in the same experiment. [1]

**(c)** Chlorine contains electrons which occupy the n = 2 principal quantum shell. Draw all the possible shapes of orbitals at the energy level, n = 2. [2]

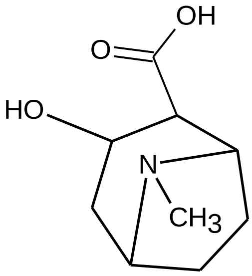
**(d)** Explain why aqueous manganese(II) ions are coloured. [3]

**(e)** Cocaine, $C_{17}H_{21}NO_4$, was first used as a local anaesthetic. It is also a powerful stimulant and its structure is shown below.



Cocaine

Student **X** was asked to suggest a suitable synthetic route to prepare cocaine from methylbenzene and compound **A**.



Compound **A**

Student **X** suggested the following steps:

| | |
|---|---|
| **Step 1** | Methylbenzene is oxidised with hot, acidified $KMnO_4$(aq) to give benzoic acid. |
| **Step 2** | Benzoic acid is converted into benzoyl chloride by reacting the resultant solution from **step 1** with thionyl chloride. |
| **Step 3** | Benzoyl chloride is reacted with compound **A** at room temperature. |
| **Step 4** | The resultant compound from **step 3** is reacted with methanol in the presence of concentrated sulfuric acid. |

**(i)** Give two reasons why the method suggested would not work. [2]

**(ii)** Draw the **aromatic** organic product formed when cocaine undergoes acidic hydrolysis. [1]

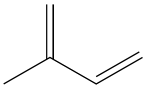
Cocaine is smuggled and inhaled as its protonated hydrochloride salt, known as cocaine hydrochloride. Smoking cocaine is more stimulating than inhaling the salt as it is absorbed quickly by the capillaries in the lung tissues. The salt is hence converted back to cocaine before smoking. This is also done as the salt will decompose before it vapourises.

**(iii)** Suggest a suitable reagent to convert cocaine hydrochloride back into cocaine. [1]

[Total: 20]

**2** Researchers at the Max Planck Institute of Chemistry conducted a study to determine whether the chemicals emitted by human beings via their breath and their skin vary in response to audiovisual stimulus. In one of the experiments carried out during the screening of The Hunger Games 2 in a cinema, the researchers detected that there were spikes of emission of a diene, isoprene, twice; when the heroine's dress caught fire and when the final battle began. Isoprene is associated with muscle contraction, hence the spikes in emission could be due to unconscious muscle twitching as the audience empathised with the heroine.

The structure of isoprene is shown below. In its pure form, it exists as a colourless volatile liquid.



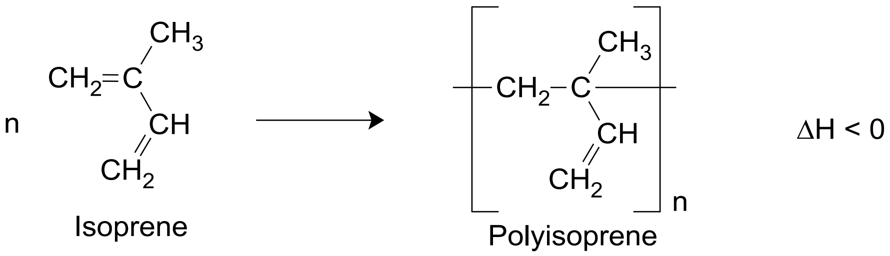
Isoprene

**(a)** Isoprene reacts with gaseous HBr at room temperature.

**(i)** Draw the structure of the major product of the reaction and hence state the IUPAC name of the major product. [2]

**(ii)** Name and illustrate with a diagram the type of stereoisomerism exhibited by the major product of the reaction. [2]

**(b)** Polyisoprene, a polymer of isoprene, is the primary chemical constituent of natural rubber.

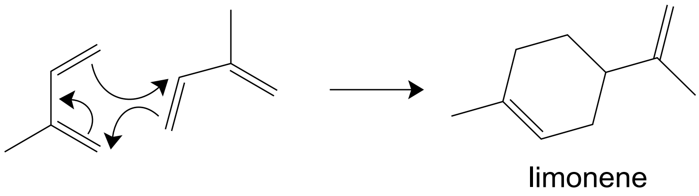


**(i)** Predict, with a reason, the sign of the entropy change of the polymerisation process of isoprene. [1]

**(ii)** With reference to your answer in **(b)(i)**, state and explain if the polymerisation is more spontaneous or less spontaneous at higher temperatures. [2]

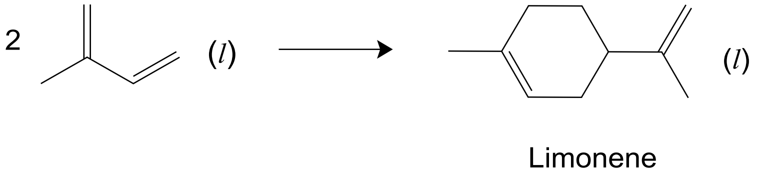
**(iii)** Natural rubber is insoluble in water. With reference to the structure of polyisoprene, explain why. [2]

**(c)** In a Diels-Alder reaction, 2 moles of isoprene react to form 1 mole of limonene. Limonene is a colourless liquid which possesses a strong smell of oranges. The mechanism of the reaction proceeds as follow.



The enthalpy changes of vaporisation of isoprene and limonene are +26.4 kJ mol$^{-1}$ and +39.4 kJ mol$^{-1}$ respectively.

Using the data given and relevant data from the *Data Booklet*, construct an energy cycle to calculate the enthalpy change for the reaction below.



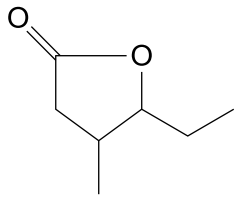
You may use $C_5H_8$ and $C_{10}H_{16}$ in your energy cycle to represent isoprene and limonene respectively. [3]

**(d)** Compound **P** is an isomer of limonene. When **P** is oxidised by hot acidified potassium manganate(VII), **Q**, $C_3H_4O_3$, and **R**, $C_7H_{12}O_3$, are formed.

Both **Q** and **R** give orange precipitate with 2,4-dinitrophenylhydrazine and give effervescence when reacted with solid calcium carbonate. Only **Q** gives a yellow precipitate with warm alkaline iodine.

When **Q** reacts with $NaBH_4$ in methanol, **S** is formed. 1 mole of **S** gives 1 mole of $H_2$(g) upon reaction with excess sodium metal.

**R** reacts with phosphorus pentachloride, giving white fumes and **T**, $C_7H_{11}ClO_2$. When **T** reacts with ethereal $LiAlH_4$, **U**, as shown below is formed.

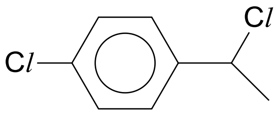


compound **U**

Deduce the structures for compounds **P** – **T**, explaining the chemistry involved. [8]

[Total: 20]

**3** Compound **U** reacts with aqueous hydroxide ions when heated under reflux.



Compound **U**

The product of the reaction between **U** and hot aqueous hydroxide ions does not have optical activity.

**(a)** **(i)** Describe the full mechanism of the reaction. [3]

**(ii)** Explain why the product of the reaction does not exhibit optical activity. [2]

**(b)** When 0.100 mol $dm^{-3}$ of hydroxide ions react with 0.00100 mol $dm^{-3}$ of compound **U** at 90 °C, the half-life of compound **U** is 25 s.

**(i)** Define the term *half-life*. [1]

**(ii)** Using your answer in **(a)(i)**, state the rate equation of the reaction. [1]

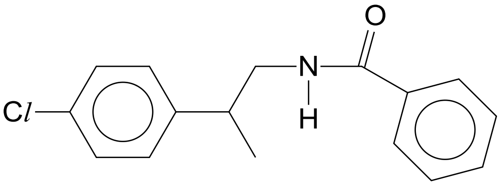
**(iii)** Calculate the rate constant at 90 °C, stating its units. [1]

**(iv)** If the reaction is repeated using 0.100 mol $dm^{-3}$ of hydroxide ions and 0.00200 mol $dm^{-3}$ of **U** at the same temperature, state the half-life of **U** in the new experiment. [1]

**(v)** With the aid of a clearly labelled Boltzmann distribution curve, explain why the rate of the reaction decreases when the temperature of the reaction decreases. [2]

**(c)** 0.450 g of **U** was reacted completely with excess hot aqueous sodium hydroxide. The reaction mixture was cooled and acidified with excess $HNO_3$(aq). Calculate the mass of silver chloride formed when an excess of $AgNO_3$(aq) was added. [2]

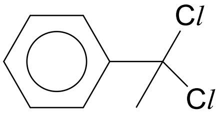
**(d)** Compound **V** can be formed from compound **U** in 3 steps.



compound **V**

Propose a 3-step synthesis of **V** from **U**, indicating clearly all reagents and conditions used. Draw the structures of all intermediates. [5]

**(e)** Compound **W** is an isomer of **U**.



compound **W**

When **W** is boiled with aqueous sodium hydroxide, it immediately loses water to form an organic compound **X** which gives a yellow precipitate with a medicinal smell when reacted with warm iodine in KOH(aq).

Suggest the structure of **X** and write a balanced chemical equation for the reaction of **X** with warm iodine in KOH(aq). [2]

[Total: 20]

**4** **(a)** Boron is a metalloid chemical element in Group III. However due to its smaller size compared to other Group III elements, its charge over mass ratio is closer to that of silicon. Hence it resembles silicon in many reactions.

**(i)** Predict the pH of the solution when $BCl_3$ is added into water. Hence write an equation for the reaction. [2]

**(ii)** Explain why $CCl_4$ does not undergo the same reaction as $BCl_3$ when it is added to water. [1]

**(iii)** The oxide of boron reacts with NaOH the same way $SiO_2$ reacts with NaOH. One of the products of the reaction is $Na_3BO_3$. Propose a chemical equation for the reaction between the oxide of boron and NaOH. [1]

**(b)** The following equilibrium exists when $BCl_3(g)$ is mixed with $NH_3(g)$.

$$BCl_3(g) + NH_3(g) \rightleftharpoons Cl_3BNH_3(s)$$

**(i)** Draw a dot-and-cross diagram of the $Cl_3BNH_3$ molecule showing clearly its co-ordinate (dative covalent) bonds. [1]

**(ii)** Suggest the shape and the bond angle of the $BCl_3$ molecule. [1]

**(iii)** Predict the effect of decreasing the temperature on the above equilibrium. Explain your answer. [3]

**(iv)** At a total initial pressure of 3 atm, a 1 : 2 mixture of $BCl_3$ and $NH_3$ was allowed to reach equilibrium at 60 ˚C. It was found that the equilibrium partial pressure of $BCl_3$ was 0.68 atm.

Determine the value of the equilibrium constant, $K_p$, for this reaction at 60 ˚C, stating its units. [2]

**(c)** Keratin is a fibrous protein that acts as the key structural component of hair. The amino acid content of keratin in hair of human varies slightly with ethnicity.

The hair sample of an Asian was analysed. Eight of the amino acids in a keratin molecule present in the hair are listed below.

| **Amino acid** | **Formula of side chain** (**R** in **R**CH($NH_2$)COOH) | **Number of amino acid residues per molecule of keratin** |
|---|---|---|
| cysteine | $-CH_2SH$ | 1200 |
| glutamic acid | $-CH_2CH_2COOH$ | 1026 |
| serine | $-CH_2OH$ | 990 |
| threonine | $-CH(OH)CH_3$ | 572 |
| leucine | $-CH_2CH(CH_3)_2$ | 520 |
| aspartic acid | $-CH_2COOH$ | 478 |
| glycine | $-H$ | 464 |
| valine | $-CH(CH_3)_2$ | 456 |

**(i)** Use **any three** of the above amino acids to construct the displayed formula of a possible section of the protein chain of keratin. [2]

**(ii)** Describe how a polypeptide chain of keratin is held in the shape of an $\alpha$-helix. [2]

**(iii)** The cysteine residues in the keratin molecule can form *disulfide bridges*. Illustrate this process by means of a balanced equation.

Assuming all the disulfide bridges are intramolecular, what is the maximum number of bridges which could be formed within each keratin molecule? [2]

**(iv)** Apart from the disulfide bridges mentioned in **(c)(iii)**, describe, by means of diagrams, **two** other types of side-chain interaction, using suitable pairs of amino acids from the table above. [2]

**(v)** Glutamic acid has three p$K_a$ values: 2.1, 4.1 and 9.5.
Suggest the structure of the major species present in solutions of glutamic acid at pH 7. [1]

[Total: 20]

**5** Fluorine is a highly toxic pale yellow diatomic gas under standard conditions. As the most electronegative element, it is highly reactive.

Hydrogen fluoride is also a highly toxic gas which forms corrosive hydrofluoric acid upon contact with water.

**(a)** State and explain which gas, fluorine or hydrogen fluoride, displays greater deviation from ideal gas behaviour. [2]

**(b)** Fluorine reacts with hydrogen to form hydrogen fluoride.
Write an equation with state symbols for the reaction and describe how you would expect the reaction of hydrogen with fluorine to differ from that of hydrogen with chlorine. [2]

**(c)** Hydrofluoric acid is a weak acid. It forms a buffer solution with salts containing its conjugate base.
Calculate the mass of solid sodium fluoride required to be added into a 250 $cm^3$ solution of 0.00420 mol $dm^{-3}$ of HF to form a buffer solution of pH 5.6.
[$K_a$ of HF = $7.20 \times 10^{-4}$ mol $dm^{-3}$] [2]

**(d)** Hydrofluoric acid is a poison with greater hazards than strong acids even though it is a weak acid. It can react with calcium in the blood leading to hypocalcemia and potentially causing death through cardiac arrhythmia. This is due to the formation of sparingly soluble calcium fluoride in the body.

**(i)** The solubility of calcium fluoride in water is $2.707 \times 10^{-4}$ mol $dm^{-3}$. Calculate the solubility of calcium fluoride in a solution of 0.00200 mol $dm^{-3}$ of aqueous NaF. [2]

**(ii)** Explain briefly how the presence of NaF affects the solubility of calcium fluoride. [1]

**(e)** HC*l* is a reagent often used in organic reactions.

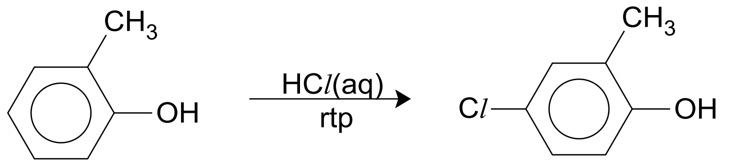
**(i)** For each of the following types of reaction, write a balanced equation for a reaction involving HC*l* as a reagent or as a catalyst. You may use any organic compound as the starting material for each reaction.

**I** Hydrolysis

**II** Neutralisation

**III** Addition [3]

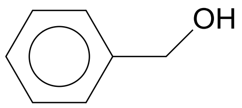
**(ii)** A student proposed the following reaction for the conversion of 2-methylphenol to 4-chloro-2-methylphenol using aqueous hydrochloric acid as the reagent.



2-methylphenol 4-chloro-2-methylphenol

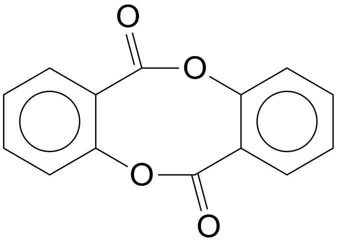
Explain why the reaction he proposed is not likely to work, and suggest how the student can improve the conversion. [3]

**(iii)** Suggest a simple chemical test to distinguish between 2-methylphenol and phenylmethanol. State clearly the reagent and conditions used as well as the observations expected. [2]



phenylmethanol

**(iv)** Compound **Z** can be formed from 2-methylphenol in two steps.



compound **Z**

Propose a two-step synthesis of **Z** from 2-methylphenol, stating the reagents and conditions for each step and showing the structure of the intermediate. **Your synthesis should involve 2-methylphenol as the only organic reactant.** [3]

[Total: 20]

**END OF PAPER**

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Candidate Name: ____________________

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# 2016 Preliminary Examination II

## Pre-University 3

**H2 CHEMISTRY** **9647/03**

Paper 3 Free Response **19th Sept 2016**

**2 hours**

Candidates answer on separate paper.

Additional materials: Cover Page
Answer Paper
Data Booklet

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**READ THESE INSTRUCTIONS FIRST**

**Do not turn over this question paper until you are told to do so**

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

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

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

Answer any **four** questions.

A Data Booklet is provided.

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

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

At the end of the examination, fasten all your work securely together.

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

This question paper consists of 11 printed pages and 1 blank page.

**1** **(a)** At room temperature, the electrode potential $E$ for the system

$$[MnO_4^-(aq) + 8H^+(aq)], [Mn^{2+}(aq) + 4H_2O(l)] / Pt$$

is given by the equation

$$E = E^{\varnothing} + \frac{0.059}{5} \log \frac{[MnO_4^-(aq)]\,[H^+(aq)]^8}{[Mn^{2+}(aq)]}$$

where $E^{\varnothing}$ = +1.51 V. $E$ values at various pH are given below when $[MnO_4^-(aq)]$ = 0.01 mol dm$^{-3}$ and $[Mn^{2+}(aq)]$ = 0.0001 mol dm$^{-3}$

| **pH** | ***E* / V** |
|---|---|
| 0 | +1.52 |
| 3 | +1.24 |
| 7 | +0.83 |

**(i)** Define what the symbol $E^{\varnothing}$ refers to. [1]

It refers to the standard electrode potential under standard conditions of 298K, 1 atm and 1 mol dm$^{-3}$ electrolyte used.

**(ii)** Calculate the electrode potential of the cell at pH 1, when the manganate(VII) ion concentration is 0.01 mol dm$^{-3}$ and the manganese(II) ion concentration is 0.001 mol dm$^{-3}$. [2]

*pH = 1*

$[H^+] = 10^{-1} = 0.100$ mol dm$^{-3}$

$$E = +1.51 + \frac{0.059}{5} \log \frac{(0.01)\,[0.1]^8}{[0.001]} = +1.43 \text{ V}$$

**(iii)** Predict at which pH value, from the table above, the solution is the most oxidising. [1]

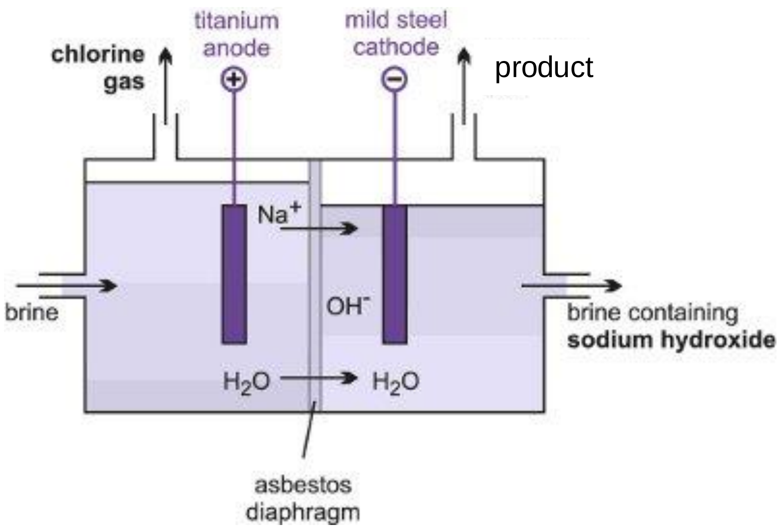
At pH=0

The electrolytic conductivity $\kappa$ of a solution in a cell is given by the following formula:

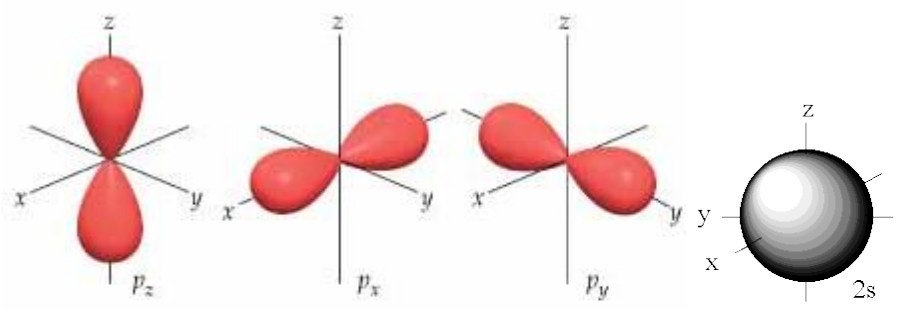
$$\kappa = \frac{(c)\,(l)}{a}$$

where $c$ is the conductance of the cell and $a$ is the cross-sectional area of the electrodes, separated by a distance $l$.

**(iv)** Often the term $\frac{l}{a}$ is replaced by a cell constant $K$. Calculate the cell constant of a particular cell if it was found that the conductance of the cell

| | | | |
|---|---|---|---|
| | | | containing $Mn^{2+}$(aq) of concentration 0.100 mol $dm^{-3}$ is 0.022 $\Omega^{-1}$ and the electrolytic conductivity, $\kappa$, was 0.011 $\Omega^{-1}$ $cm^{-1}$. State the units of $K$. [2] |
| | | | 0.011 = K (0.022)<br>K = 0.500 $cm^{-1}$ |
| | **(b)** | A diaphragm cell consisting brine solution, concentrated NaC*l*, is used in the commercial electrolytic production of chlorine and sodium hydroxide.<br><br> | |
| | | **(i)** | Write the ion-electron equations for the reactions occurring at the cathode and at the anode. [2] |
| | | | Anode: $2Cl^- \rightarrow Cl_2 + 2e^-$<br>Cathode: $2H_2O + 2e^- \rightarrow H_2 + OH^-$ |
| | | | |
| | | **(ii)** | The chlorine gas is collected separately at the anode to prevent a side reaction that will occur with one of the products formed. Write a balanced equation for this side reaction that occurs at room conditions. State the oxidation numbers of chlorine in all the products formed. [2] |
| | | | $Cl_2 + 2OH^- \rightarrow Cl^- + ClO^- + H_2O$<br>Oxidation no. of Cl in $Cl^-$ = -1 Oxidation no of Cl in $ClO^-$ = +1 |
| | | | |
| | | **(iii)** | In an electrolytic experiment using this diaphragm cell, 1.0 mol of gas is produced at the cathode. Calculate the mass of chlorine gas that is produced in the same experiment. [1] |
| | | | 1 mol of $H_2$ produced ≡ 1 mol of $Cl_2$ produced<br>Mass of $Cl_2$ produced = 1 x 71.0 = 71.0 g |

**(c)** Chlorine contains electrons which occupy the n=2 principal quantum shell. Draw all the possible shapes of orbitals at the energy level, n=2. [2]



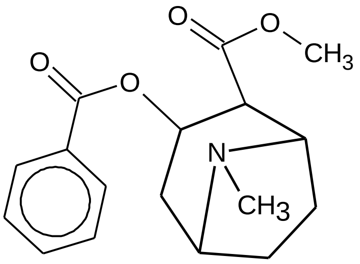
**(d)** Explain why aqueous manganese(II) ions are coloured. [3]

●$Mn^{2+}$ has partially-filled d-orbitals. When the ligands approach the central metal ion, splitting of the d-orbitals occurs.

●The energy gap, ΔE, between the non-degenerate orbitals corresponds to the wavelength of light in the visible region of the electromagnetic spectrum.

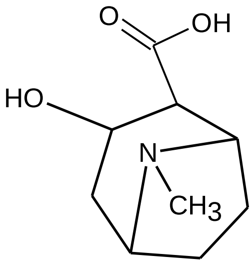
●When an electron from a lower energy d orbital is promoted to a higher energy d orbital (d-d electron transition), radiation corresponding to ΔE is absorbed. The complementary colour will be seen as the colour of the complex.

**(e)** Cocaine, $C_{17}H_{21}NO_4$, was first used as a local anaesthetic. It is also a powerful stimulant and its structure is shown below.



Cocaine

Student **X** was asked to suggest a suitable synthetic route to prepare cocaine from methylbenzene and compound **A**.



Compound **A**

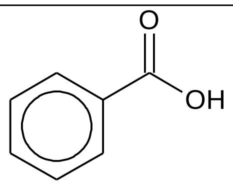
Student **X** suggested the following steps:

| | |
|---|---|
| Step 1 | Methylbenzene is oxidised with hot, acidified $KMnO_4$ to give benzoic acid. |
| Step 2 | Benzoic acid is converted into benzoyl chloride by reacting the resultant solution from step 1 with thionyl chloride. |
| Step 3 | Benzoyl chloride is reacted with compound **A** at room temperature. |
| Step 4 | The resultant compound from step 3 is reacted with methanol in the presence of concentrated sulfuric acid. |

**(i)** Give two reasons why the method suggested would not work. [2]

1. In step 2, thionyl chloride will hydrolyse in the presence of aqueous solution
2. The final product will be the protonated form of cocaine since it is prepared in an acidic medium.
3. Heat is required for step 4.

**(ii)** Draw the **aromatic** organic product formed when cocaine undergoes acidic hydrolysis. [1]



Cocaine is smuggled and inhaled as its protonated hydrochloride salt, known as cocaine hydrochloride. Smoking cocaine is more stimulating than inhaling the salt as it is absorbed quickly by the capillaries in the lung tissues. The salt is hence converted back to cocaine before smoking. This is also done as the salt will decompose before it vapourises.

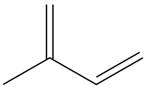
**(iii)** Suggest a suitable reagent to convert cocaine hydrochloride back into cocaine. [1]

Dilute NaOH

[Total: 20]

**2** Researchers at the Max Planck Institute of Chemistry conducted a study to determine whether the chemicals emitted by human beings via their breath and their skin vary in response to audiovisual stimulus. In one of the experiments carried out during the screening of The Hunger Games 2 in a cinema, the researchers detected that there were spikes of emission of a diene, isoprene, twice; when the heroine's dress catches fire and when the final battle begins. Isoprene is associated with muscle contraction, hence the spikes in emission could be due to unconscious muscle twitching as the audience empathises with the heroine.

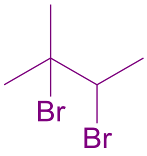
The structure of isoprene is shown below. In its pure form, it exists as a colourless volatile liquid.



Isoprene

**(a)** Isoprene reacts with gaseous HBr at room temperature.

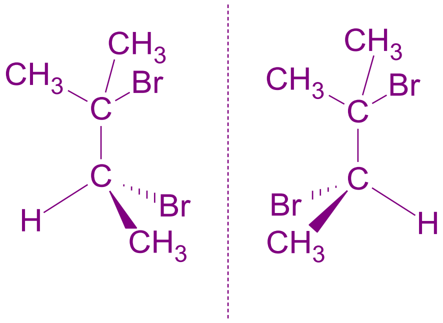
**(i)** Draw the structure of the major product of the reaction and hence state the IUPAC name of the major product. [2]



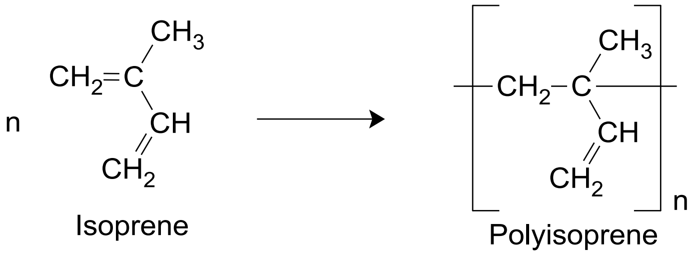
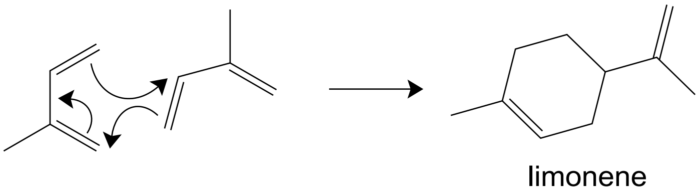
2,3-dibromo-2-methylbutane

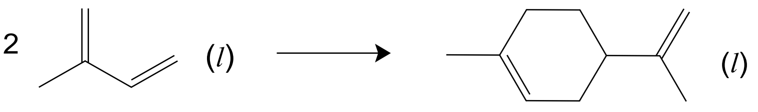
**(ii)** Name and illustrate with a diagram the type of stereoisomerism exhibited by the major product of the reaction. [2]

Optical isomerism



**(b)** Polyisoprene, a polymer of isoprene, is the primary chemical constituent of natural rubber.

| | | | |
|---|---|---|---|
| | |  <br>$\Delta H < 0$ | |
| | | **(i)** | Predict, with a reason, the sign of the entropy change of the polymerisation process of isoprene. [1] |
| | | | Negative, because the system becomes less disorderly as the number of molecules decrease, hence having less way to arrange |
| | | **(ii)** | With reference to your answer in **(b)(i)**, state and explain if the polymerisation is more spontaneous or less spontaneous at higher temperatures. [2] |
| | | | $\Delta G = \Delta H - T\Delta S$<br>$\Delta H$ and $\Delta S$ are both negative. At high temperature, magnitude of $T\Delta S$ is larger than magnitude of $\Delta H$ hence $\Delta G$ is more positive.<br>Less spontaneous |
| | | **(iii)** | Natural rubber is insoluble in water. With reference to the structure of polyisoprene, explain why. [2] |
| | | | Energy evolved from the formation of td-id between polyisoprene and water is not sufficient to overcome the hydrogen bonds between water molecules. |
| | **(c)** | In a Diels-Alder reaction, 2 moles of isoprene react to form 1 mole of limonene. Limonene is a colourless liquid which possesses a strong smell of oranges. The mechanism of the reaction proceeds as follow.<br> <br>The enthalpy changes of vaporisation of isoprene and limonene are +26.4 kJ mol$^{-1}$ and +39.4 kJ mol$^{-1}$ respectively.<br>Using the data given and relevant data from the *Data Booklet*, construct an energy cycle to calculate the enthalpy change for the reaction below. | |



Limonene

You may use $C_5H_8$ and $C_{10}H_{16}$ in your energy cycle to represent isoprene and limonene respectively. [3]

$$\begin{tikzcd}
2C_5H_8(l) \arrow[r, "\Delta H"] \arrow[d, "2\times(+26.4)"] & C_{10}H_{16}(l) \arrow[d, "+39.4"] \\
2C_5H_8(g) \arrow[r, "\Delta H_1"'] & C_{10}H_{16}(g)
\end{tikzcd}$$

;

Using bond energy,

$\Delta H_1 = 2 \times BE(C=C) - 4 \times BE(C\text{-}C) = 2(610) - 4(350) = -180 \text{ kJ mol}^{-1}$

By Hess' Law,

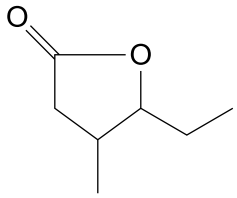
$\Delta H = 2(+26.4) + (-180) - (+39.4) = -166.6 \approx -167 \text{ kJ mol}^{-1}$

**(d)** Compound **P** is an isomer of limonene. When **P** is oxidised by hot acidified potassium manganate(VII), **Q**, $C_3H_4O_3$, and **R**, $C_7H_{12}O_3$, are formed.

Both **Q** and **R** give orange precipitate with 2,4-dinitrophenylhydrazine and give effervescence when reacted with solid calcium carbonate. Only **Q** gives a yellow precipitate with warm alkaline iodine.

When **Q** reacts with $NaBH_4$ in methanol, **S** is formed. 1 mole of **S** gives 1 mole of $H_2(g)$ upon reaction with excess sodium metal.

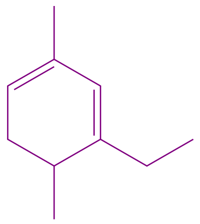
**R** reacts with phosphorus pentachloride, giving white fumes and **T**, $C_7H_{11}ClO_2$. When **T** reacts with ethereal $LiAlH_4$, **U**, as shown below is formed.



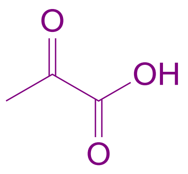
compound **U**

Deduce the structures for compounds **P** – **T**, explaining the chemistry involved. [8]

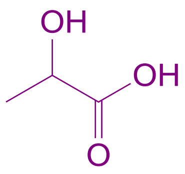
| Information | Deduction |
|---|---|
| Both **Q** and **R** give orange precipitate with 2,4-dinitrophenylhydrazine and give effervescence when reacted with solid calcium carbonate. | **Q** and **R** are ketones.<br>**Q** and **R** has carboxylic acid group. |
| Only **Q** gives a yellow precipitate with warm alkaline iodine. | **Q** has the structure $CH_3CO$- |
| When **Q** reacts with $NaBH_4$ in methanol, **S** is formed. | Reduction of ketone.<br>**S** is secondary alcohol. |
| 1 mole of **S** gives 1 mole of $H_2$(g) upon reaction with excess sodium metal. | Acid-metal reaction<br>**S** has two –OH groups |
| **R** reacts with phosphorus pentachloride, giving white fumes and **T**, $C_7H_{11}ClO_2$. | Substitution reaction<br>**T** has acyl chloride |
| When **T** reacts with ethereal $LiAlH_4$, **U** is formed. | Reduction of ketone to secondary alcohol<br>Followed by nucleophilic substitution to form ester. |



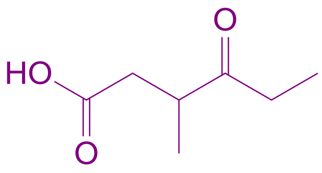
P



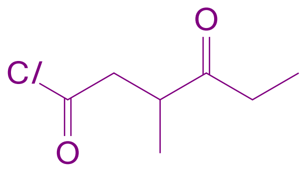
Q



S

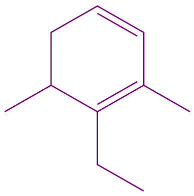


R

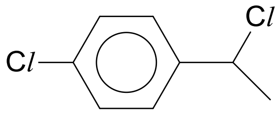
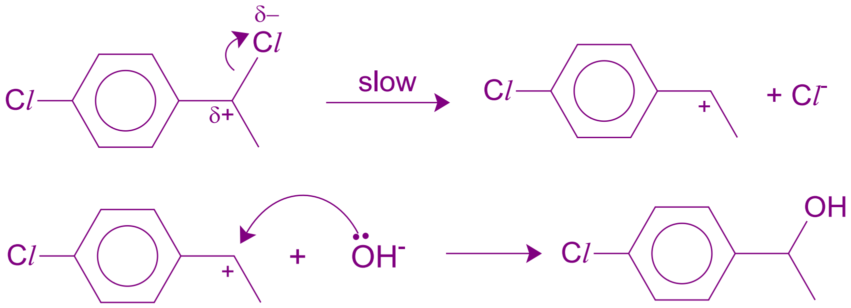
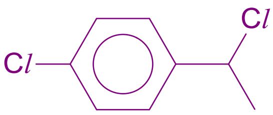


T

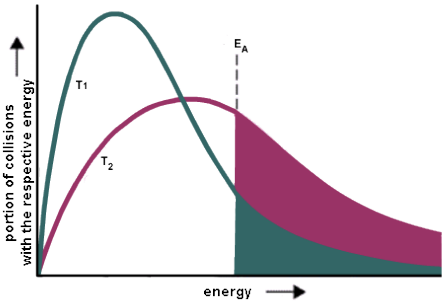
Alternative answer for **P**:



[Total: 20]

| | | | |
|---|---|---|---|
| 3 | Compound **U** reacts with aqueous hydroxide ions when heated under reflux.<br> <br>Compound **U**<br>The product of the reaction between **U** and hot aqueous hydroxide ions does not have optical activity. | | |
| | **(a)** | **(i)** | Describe the full mechanism of the reaction. [3] |
| | | | Nucleophilic substitution<br> |
| | | **(ii)** | Explain why the product of the reaction does not exhibit optical activity. [2] |
| | | | The intermediate formed in the first step is trigonal planar at the C with the positive charge. The nucleophile can attack the carbon from the top or the bottom of the plane.<br>A racemic mixture is formed. |
| | **(b)** | When 0.100 mol $dm^{-3}$ of hydroxide ions react with 0.00100 mol $dm^{-3}$ of compound **U** at 90˚C, the half-life of compound **U** is 25 s. | |
| | | **(i)** | Define the term *half-life*. [1] |
| | | | Half-life is the time taken for the concentration of a reactant to reduce to half its original value. |
| | | **(ii)** | Using your answer in **(a)(i)**, state the rate equation of the reaction. [1] |
| | | | Rate = k[ ] |
| | | **(iii)** | Calculate the rate constant at 90˚C, stating its units. [1] |
| | | | $k=\frac{\ln 2}{\text{half life}}=\frac{\ln 2}{25}=0.0277\ s^{-1}$ |
| | | **(iv)** | If the reaction is repeated using 0.100 mol $dm^{-3}$ of hydroxide ions and 0.002 mol $dm^{-3}$ of **U** at the same temperature, state the half-life of **U** in the new experiment. [1] |
| 3 | | | 25 s |

**(v)** With the aid of a clearly labelled Boltzmann distribution curve, explain why the rate of the reaction decreases when the temperature of the reaction decreases. [2]



$T_1 < T_2$

At lower temperature, kinetic energy of molecules decreases, less molecules have energy greater than or equal to activation energy. Frequency of effective collision decreases.

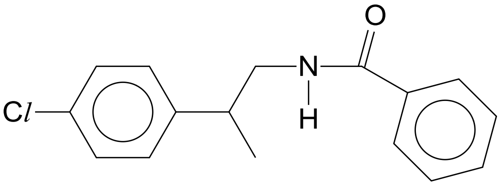
**(c)** 0.450 g of **U** was reacted completely with excess hot aqueous sodium hydroxide. The reaction mixture was cooled and acidified with excess $HNO_3$. Calculate the mass of silver chloride formed when an excess of $AgNO_3$(aq) was added. [2]

Amount of **U** = 0.450 / 175 = 0.002571 mol

Amount of AgCl = 0.002571 mol

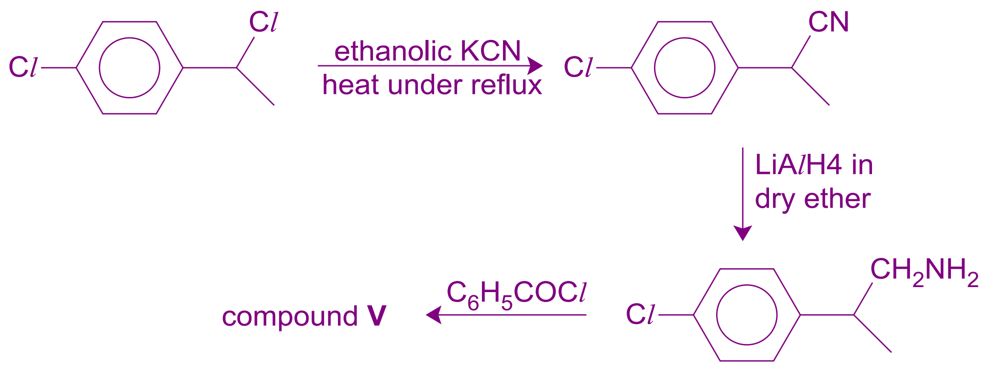
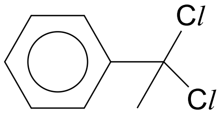
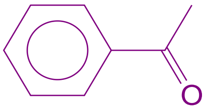
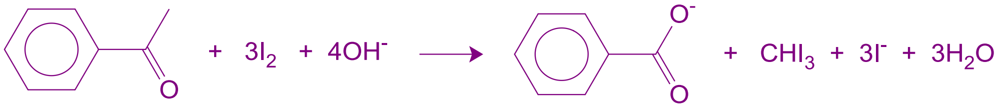
Mass of AgCl = 0.002571 × (108+35.5) = 0.369 g

**(d)** Compound **V** can be formed from compound **U** in 3 steps.



compound **V**

Propose a 3-step synthesis of **V** from **U**, indicating clearly all reagents and conditions used. Draw the structures of all intermediates. [5]

| | | |
|---|---|---|
| | |  |
| | **(e)** | Compound **W** is an isomer of **U**.<br> <br>compound **W**<br>When **W** is boiled with aqueous sodium hydroxide, it immediately loses water to form an organic compound **X** which gives a yellow precipitate with a medicinal smell when reacted with warm iodine in KOH(aq).<br>Suggest the structure of **X** and write a balanced chemical equation for the reaction of **X** with warm iodine in KOH(aq). [2] |
| | |  <br> |
| | | [Total: 20] |

| | | | |
|---|---|---|---|
| 4 | **(a)** | Boron is a metalloid chemical element in Group III. However due to its smaller size compared to other Group III elements, its charge over mass ratio is closer to that of silicon. Hence it resembles silicon in many reactions. | |
| | | **(i)** | Predict the pH of the solution when $BCl_3$ is added into water. Hence write an equation for the reaction. [2] |
| | | | pH 2 (accept between 1 to 2)<br>$BCl_3 + 3H_2O \rightarrow B(OH)_3 + 3HCl$<br>Also accept:<br>$2BCl_3 + 3H_2O \rightarrow B_2O_3 + 6HCl$ |

**(ii)** Explain why $CCl_4$ does not undergo the same reaction as $BCl_3$ when it is added to water. [1]

B in $BCl_3$ has energetically accessible empty orbital to accept lone pair from O of $H_2O$ but C in $CCl_4$ do not.

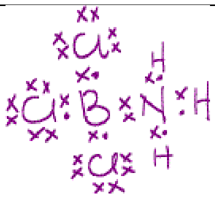
**(iii)** The oxide of boron reacts with NaOH the same way $SiO_2$ reacts with NaOH. One of the products of the reaction is $Na_3BO_3$. Propose a chemical equation for the reaction between the oxide of boron and NaOH. [1]

$B_2O_3 + 6NaOH \rightarrow 2Na_3BO_3 + 3H_2O$

**(b)** The following equilibrium exists when $BCl_3(g)$ is mixed with $NH_3(g)$.

$$BCl_3(g) + NH_3(g) \rightleftharpoons Cl_3BNH_3(s)$$

**(i)** Draw a dot-and-cross diagram of the $Cl_3BNH_3$ molecule including its co-ordinate (dative covalent) bonds. [1]



**(ii)** Suggest the shape and the bond angle of the $BCl_3$ molecule. [1]

trigonal planar 120˚

**(iii)** Predict the effect of decreasing the temperature on the above equilibrium. Explain your answer. [3]

Reaction is exothermic since it involves formation of dative bonds

By LCP, position of equilibrium will shift to the right

This is to increase the temperature of the system by favouring the exothermic reaction.

**(iv)** At a total initial pressure of 3 atm, a 1 : 2 mixture of $BCl_3$ and $NH_3$ was allowed to reach equilibrium at 60 ˚C. It was found that the equilibrium partial pressure of $BCl_3$ was 0.68 atm.

Determine the value of the equilibrium constant, $K_p$, for this reaction at 60 ˚C, stating its units. [2]

| | $BCl_3(g)$ | + | $NH_3(g)$ | $\rightleftharpoons$ | $Cl_3BNH_3(s)$ |
|---|---|---|---|---|---|
| Initial partial pressure | 1 | | 2 | | 0 |
| Change / atm | -0.32 | | -0.32 | | +0.32 |
| Eqm partial pressure | 0.68 | | 1.68 | | 0.32 |

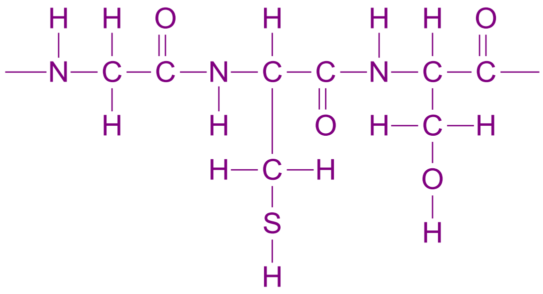
$K_p = \frac{1}{(0.68)(1.68)} = 0.875\ atm^{-2}$

**(c)** Keratin is a fibrous protein that acts as the key structural component of hair. The amino acid content of keratin in hair of human varies slightly with ethnicity.

The hair sample of an Asian was analysed. Eight of the amino acids in a keratin molecule present in the hair are listed below.

| **Amino acid** | **Formula of side chain** (R in $RCH(NH_2)COOH$) | **Number of amino acid residues per molecule of keratin** |
|---|---|---|
| cysteine | $-CH_2SH$ | 1200 |
| glutamic acid | $-CH_2CH_2COOH$ | 1026 |
| serine | $-CH_2OH$ | 990 |
| threonine | $-CH(OH)CH_3$ | 572 |
| leucine | $-CH_2CH(CH_3)_2$ | 520 |
| aspartic acid | $-CH_2COOH$ | 478 |
| glycine | $-H$ | 464 |
| valine | $-CH(CH_3)_2$ | 456 |

**(i)** Use **any three** of the above amino acids to construct the displayed formula of a possible section of the protein chain of keratin. [2]



or any other combination

**(ii)** Describe how a polypeptide chain of keratin is held in the shape of an $\alpha$-helix. [2]

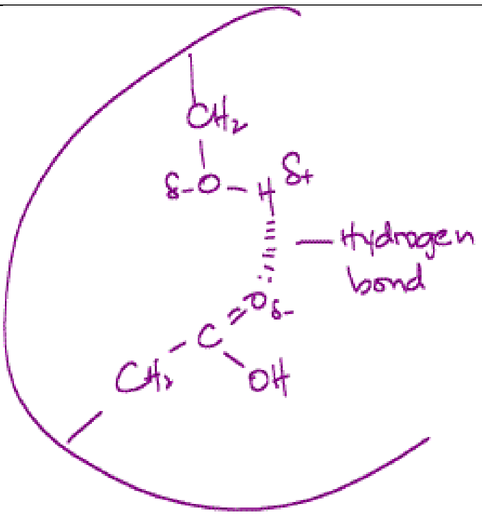
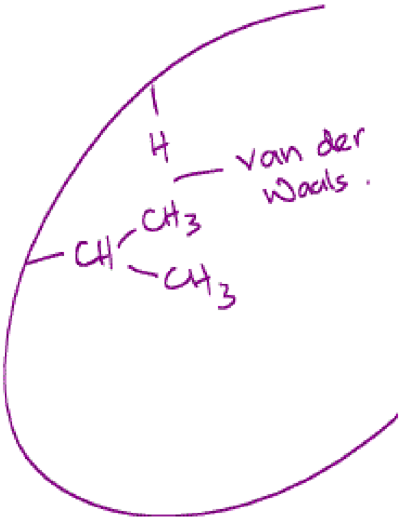
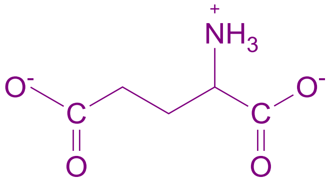
The a-helix is held in place via <u>hydrogen bonds</u> formed <u>between O of -C=O of a peptide and H of –NH of another peptide</u>.

**(iii)** The cysteine residues in the keratin molecule can form *disulfide bridges*. Illustrate this process by means of a balanced equation.

Assuming all the disulfide bridges are intramolecular, what is the maximum number of bridges which could be formed within each keratin molecule? [2]

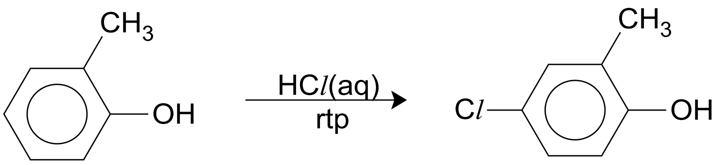
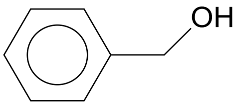
$2\ -CH_2SH \rightarrow -CH_2S\text{-}SCH_2\text{-}\ + 2H$

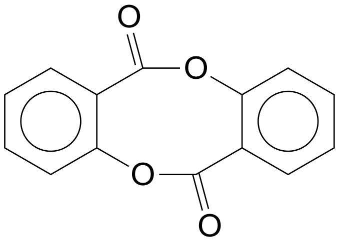
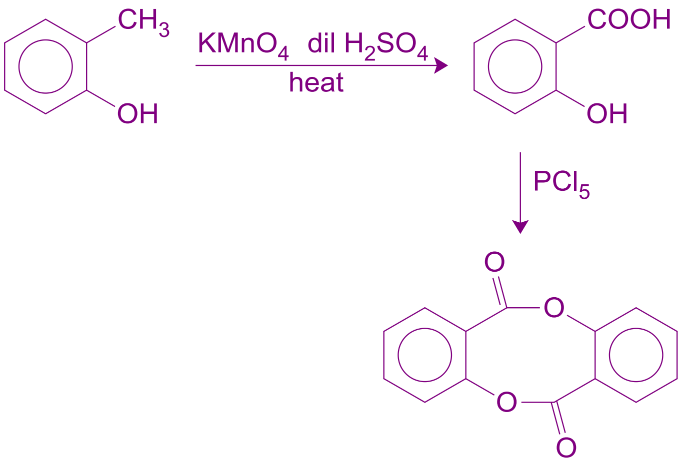
600

| | | | |
|---|---|---|---|
| | | **(iv)** | Apart from the disulfide bridges mentioned in **(c)(iii)**, describe, by means of diagrams, **two** other types of side-chain interaction, using suitable pairs of amino acids from the table above. [2] |
| | | |   |
| | | **(v)** | Glutamic acid has three p$K_a$ values: 2.1, 4.1 and 9.5.<br>Suggest the structure of the major species present in solutions of glutamic acid at pH 7. [1] |
| | | |  |
| | | | [Total: 20] |

| | | |
|---|---|---|
| **5** | Fluorine is a highly toxic pale yellow diatomic gas under standard conditions. As the most electronegative element, it is highly reactive.<br>Hydrogen fluoride is also a highly toxic gas which forms corrosive hydrofluoric acid upon contact with water. | |
| | **(a)** | State and explain which gas, fluorine or hydrogen fluoride, displays greater deviation from ideal gas behaviour. [2] |
| | | Hydrogen fluoride is held by hydrogen bonds and fluorine is held by td-id.<br>Hydrogen fluoride has stronger intermolecular forces of attraction hence has greater deviation from ideal gas behaviour. |
| | **(b)** | Fluorine reacts with hydrogen to form hydrogen fluoride.<br>Write an equation with state symbols for the reaction and describe how you would expect the reaction of hydrogen with fluorine to differ from that of hydrogen with chlorine. [2] |
| | | $H_2(g) + F_2(g) \rightarrow 2HF(g)$ |

| | | | | |
|---|---|---|---|---|
| | | Fluorine reacts explosively and more vigorously with hydrogen compared to chlorine with hydrogen. | | |
| | **(c)** | Hydrofluoric acid is a weak acid. It forms a buffer solution with salts containing its conjugate base.<br>Calculate the mass of solid sodium fluoride required to be added into a 250 $cm^3$ solution of 0.00420 mol $dm^{-3}$ of HF to form a buffer solution of pH 5.6.<br>[$K_a$ of HF = $7.20 \times 10^{-4}$ mol $dm^{-3}$] [2] | | |
| | | $pH = pK_a + \lg([salt]/[acid])$<br>$5.6 = -\lg(7.20 \times 10^{-4}) + \lg([NaF]/0.0042)$<br>$[NaF] = 1.204$ mol $dm^{-3}$<br>mass of NaF = $1.204 \times (250/1000) \times (23.0 + 19.0) = 12.6$ g | | |
| | **(d)** | Hydrofluoric acid is a poison with greater hazards than strong acids even though it is a weak acid. It can react with calcium in the blood leading to hypocalcemia and potentially causing death through cardiac arrhythmia. This is due to the formation of sparingly soluble calcium fluoride in the body. | | |
| | | **(i)** | The solubility of calcium fluoride in water is $2.707 \times 10^{-4}$ mol $dm^{-3}$. Calculate the solubility of calcium fluoride in a solution of 0.00200 mol $dm^{-3}$ of aqueous NaF. [2] | |
| | | | $CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$<br>$K_{sp} = [Ca^{2+}][F^-]^2 = (2.707\times 10^{-4})(2 \times 2.707\times 10^{-4})^2 = 7.93 \times 10^{-11}$ $mol^3$ $dm^{-9}$<br>$7.93 \times 10^{-11} = y \times (2y + 0.002)^2 \approx y \times (0.002)^2$<br>$y = 1.98 \times 10^{-5}$ mol $dm^{-3}$ | |
| | | **(ii)** | Explain briefly how the presence of NaF affects the solubility of calcium fluoride. [1] | |
| | | | $CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$<br>The presence of NaF increases $[F^-]$, hence by LCP shifting the equilibrium to the left. | |
| | **(e)** | HC*l* is a reagent often used in organic reactions. | | |
| | | **(i)** | For each of the following types of reaction, write a balanced equation for a reaction involving HC*l* as a reagent or as a catalyst. You may use any organic compound as the starting material for each reaction. [3] | |
| | | | **I** | Hydrolysis |
| | | | | any correct equation showing hydrolysis of ester, amide or nitrile |
| | | | **II** | Neutralisation |
| | | | | any correct equation showing acid-base reaction of amine or carboxylate salt |

| | | | | |
|---|---|---|---|---|
| | | | **III** | Addition |
| | | | | any correct equation showing addition equation of alkene forming alcohol (must balance equation with water) |
| | | **(ii)** | A student proposed the following reaction for the conversion of 2-methylphenol to 4-chloro-2-methylphenol using aqueous hydrochloric acid as the reagent.<br><br> <br>2-methylphenol<br>4-chloro-2-methylphenol<br>Explain why the reaction he proposed is not likely to work.<br>Hence suggest the correct reagent and conditions for the conversion. [3] | |
| | | | The reaction involves electrophilic substitution of benzene. Hence a electrophile $Cl^+$ is required for the reaction<br>However in HCl, since Cl is more electronegative, $Cl^+$ is not likely to be formed.<br>$Cl_2$ in $CCl_4$ at room temperature | |
| | | **(iii)** | Suggest a simple chemical test to distinguish between 2-methylphenol and phenylmethanol. State clearly the reagent and conditions used as well as the observations expected. [2]<br><br> <br>phenylmethanol | |
| | | | $K_2Cr_2O_7$ in dilute $H_2SO_4$, heat<br>orange solution turns green for phenylmethanol<br>orange solution remains orange for 2-methylphenol<br>OR<br>$Br_2$(aq) ;<br>orange solution decolourises for 2-methylphenol, forming white ppt<br>orange solution remains orange for phenylmethanol, no ppt formed<br>OR<br>neutral $FeCl_3$ ;<br>violet colouration formed for 2-methylphenol<br>no violet colouration for phenylmethanol | |

| | | | |
|---|---|---|---|
| | | **(iv)** | Compound **Z** can be formed from 2-methylphenol in two steps.<br><br>compound **Z**<br>Propose a two-step synthesis of **Z** from 2-methylphenol, stating the reagents and conditions for each step and showing the structure of the intermediate.<br>**Your synthesis should involve 2-methylphenol as the only organic reactant.** [3] |
| | | |  |
| | | | [Total: 20] |