

Name:		Index Number:		Class:	
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DUNMAN HIGH SCHOOL

Preliminary Examination 2018

Year 6

H2 CHEMISTRY

Paper 1 Multiple Choice

9729/01

24 September 2018

1 hour

Additional Materials: Data Booklet
 Optical Mark Sheet

INSTRUCTIONS TO CANDIDATES

- Write your **name**, **index number** and **class** on this question paper and the OTAS Mark Sheet.
- There are **thirty** 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 separate Optical Mark Sheet.
- Each correct answer will score one mark. A mark will not be deducted for wrong answer.
- Any rough working should be done in this booklet.
- The use of an approved scientific calculator is expected, where appropriate.
- On the OTAS Mark Sheet, please shade the code as "Class/Index number".

For illustration only:

A student from class 6C38, with index number 02, should shade "3802".

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	A	A <input type="checkbox"/>	B <input type="checkbox"/>	C <input type="checkbox"/>	D <input type="checkbox"/>	E <input type="checkbox"/>	F <input type="checkbox"/>	G <input type="checkbox"/>	H <input type="checkbox"/>	I <input type="checkbox"/>	

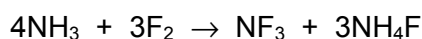
This question paper consists of **15** printed pages and **1** blank page.

1 Which option contains one mole of the stated particles?

[D = ${}^2_1\text{H}$]

- A carbonate ions in 60 g of sodium carbonate
- B neutrons in 1.8 g of heavy water, D_2O
- C electrons in 0.1 mol of OH^- ions
- D oxygen atoms in 11.35 dm^3 of O_3 , under s.t.p.

2 NF_3 can be obtained from the reaction between ammonia and fluorine gas.



Which statement about the reaction is correct?

- A NH_3 undergoes disproportionation.
- B The oxidation number of nitrogen in NF_3 is +3.
- C NH_3 is a stronger oxidising agent than F_2 .
- D One mole of F_2 loses two moles of electrons.

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

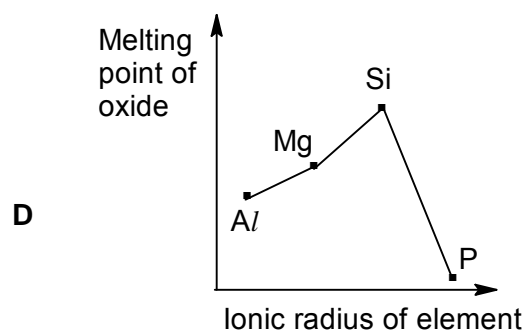
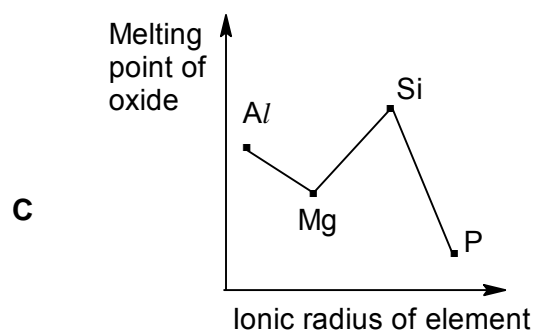
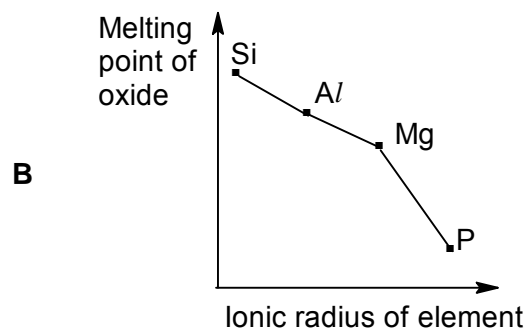
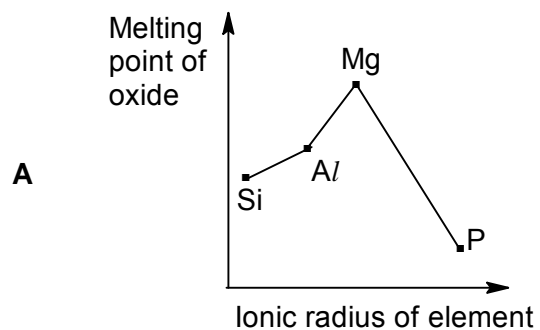
Which statement regarding ${}^{26}\text{Mg}^{2+}$ and ${}^{27}\text{Al}^{3+}$ ions is true?

- 1 ${}^{26}\text{Mg}^{2+}$ has more protons than ${}^{27}\text{Al}^{3+}$.
- 2 Both ions have more neutrons than protons in their nuclei.
- 3 Both ions have outer electronic configuration $2s^22p^6$.
- 4 Both ions have the same number of neutrons.

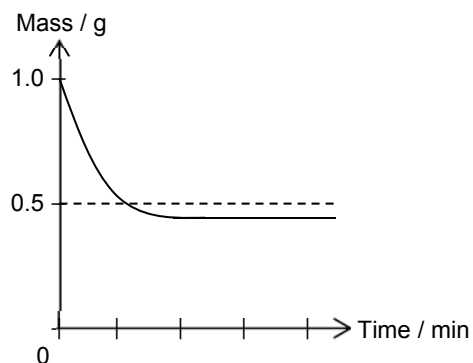
- A 1 and 2 only
- B 1 and 3 only
- C 3 and 4 only
- D 2, 3 and 4 only

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

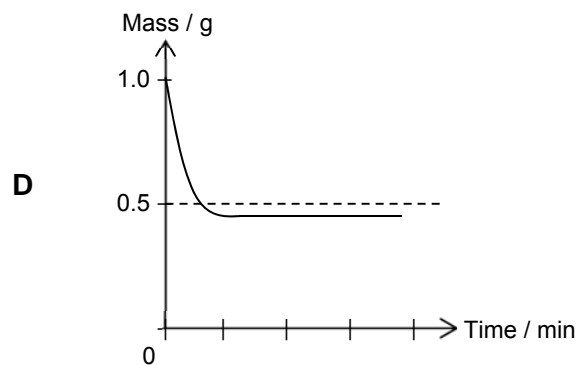
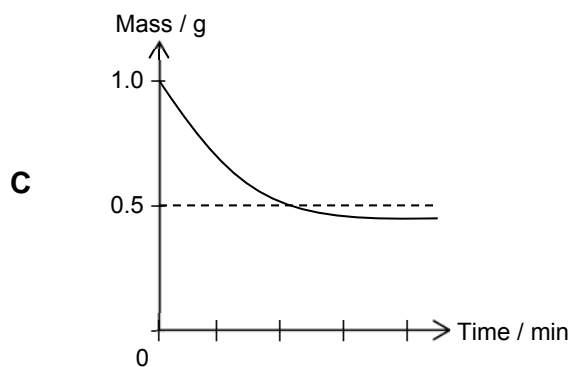
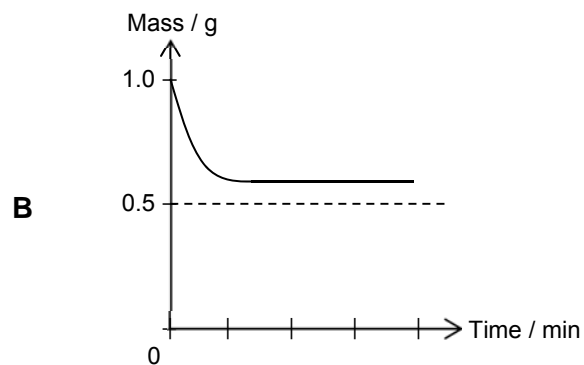
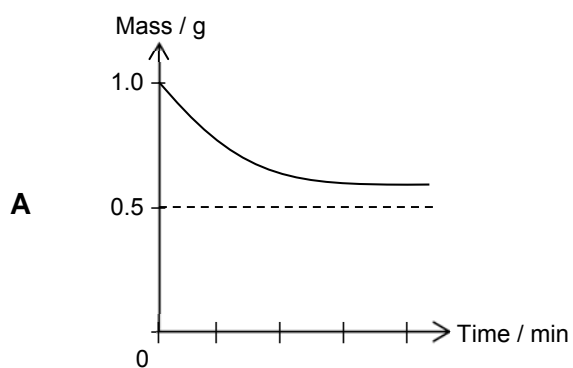
Which graph shows the correct trend when the melting point of the oxide of each of the elements Mg, Al, Si and P is plotted against its ionic radius?



- 7 The graph represents the change in mass that occurs when 1.0 g of powdered magnesium carbonate, MgCO_3 , is heated at a temperature, T .



Which graph would be obtained by heating 1.0 g of powdered calcium carbonate, CaCO_3 , at the same temperature, T ?



- 8 X_2 , Y_2 and Z_2 are Cl_2 , Br_2 and I_2 but are not necessarily in the given order.

The table below recorded observations when these halogens are separately added to aqueous solutions containing the halide ions followed by the addition of an organic solvent, CCl_4 .

Experiment	Reactants	Observation after shaking with CCl_4
1	$X_2(aq) + Y^-(aq)$	Violet organic layer seen.
2	$Y_2(aq) + X^-(aq)$	(Observations not recorded)
3	$Z_2(aq) + X^-(aq)$	Orange-red organic layer seen.
4	$Z_2(aq) + Y^-(aq)$	Violet organic layer seen.

Which statement could be deduced from the above experiments, given $X_2(aq)$ is an orange solution?

- A The colour of the organic layer in Experiments 2 and 4 is the same.
- B Identity of Z_2 is Br_2 .
- C There is no redox reaction occurring in Experiment 3.
- D X_2 is a stronger oxidising agent than Z_2 .
- 9 For which process is the enthalpy change always negative?
- A Dissolving an ionic solid in water.
- B Reaction between an acid and a base.
- C Forming gaseous atoms from a diatomic molecule.
- D Synthesising a compound from its elements.
- 10 A rock sample was found to contain isotopes **T** and **U** which are radioactive. Initially, the ratio of the number of atoms of **T** to **U** in the rock sample is 1 : 16. The decay of isotopes **T** and **U** was found to follow first order kinetics. The half-life of **T** is 12 days while that of **U** is 3 days.

How long, in days, will it take for a rock sample to contain a molar ratio of **T** to **U** of 4 : 1?

- A 6
- B 12
- C 18
- D 24

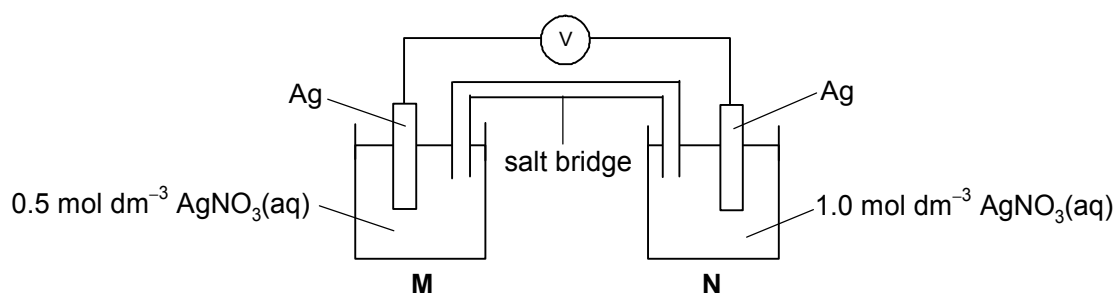
- 13 The solubility products of calcium fluoride and calcium carbonate are $4.0 \times 10^{-11} \text{ mol}^3 \text{ dm}^{-9}$ and $8.7 \times 10^{-9} \text{ mol}^2 \text{ dm}^{-6}$ at 25°C respectively.

Which statement is correct?

- 1 When calcium nitrate is added into a 1 dm^3 solution containing 0.01 mol of fluoride and 0.01 mol of carbonate ions in order to separate fluoride and carbonate ions, calcium fluoride is collected as the filtrate upon filtration.
- 2 Calcium fluoride has a lower molar solubility than calcium carbonate.
- 3 Addition of sodium fluoride to a saturated solution containing calcium fluoride does not change the solubility product of calcium fluoride.

- A 1, 2 and 3 only B 2 and 3 only
C 1 and 3 only D 3 only

- 14 A concentration cell set up is shown below. The net effect of a concentration cell is the same as mixing the two solutions of different concentrations until concentration equilibrium is established.



Which statement is true?

- A The E_{cell} value decreases when small amount of $\text{NH}_3(\text{aq})$ is added to the half-cell **M**.
- B The E_{cell} value increases when small amount of $\text{KCl}(\text{s})$ is added to the half-cell **N**.
- C The electrons flow from half-cell **N** to **M**.
- D **M** is the oxidation half-cell.

- 15 A current of 5 amperes was passed for 5 seconds through a molten salt containing X^{3+} ions. The mass of X deposited was 5 g. If M is the relative molecular mass of X and e is the electronic charge, then an expression of Avogadro Constant is given by

- A $\frac{5M}{3e}$ B $\frac{125}{3Me}$
C $\frac{3e}{5M}$ D $\frac{3Me}{125}$

- 16 The table shows the electronic configuration of three d-block elements in the Periodic Table.

Element	Electronic configuration
X	[Ar]3d ⁷ 4s ²
Y	[Ar]3d ⁸ 4s ²
Z	[Ar]3d ¹⁰ 4s ¹

Which statement is correct?

- The electronic configuration of central metal ion for [Y(CN)₆]⁴⁻ is [Ar]3d⁷.
- Upon reduction from ZCl₂(aq) to [ZCl₂]⁻(aq), a colourless solution will be formed.
- The E^\ominus value of X³⁺/X²⁺ is likely to be less positive than that of Z³⁺/Z²⁺.
- X is likely to form an oxoanion of formula XO₄²⁻.

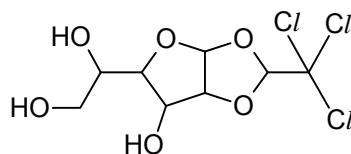
A 1, 2 and 4 only

B 2 and 3 only

C 1 and 4 only

D 3 and 4 only

- 17 Chloralose is a drug that is commonly used in neuroscience and veterinary medicine as an anesthetic.



chloralose

How many stereoisomers does chloralose have?

A 16

B 32

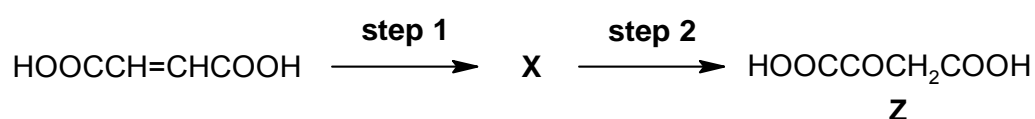
C 64

D 128

- 18 2,2-dimethylpropane reacts with chlorine gas in the presence of ultraviolet light to give a mixture of products.

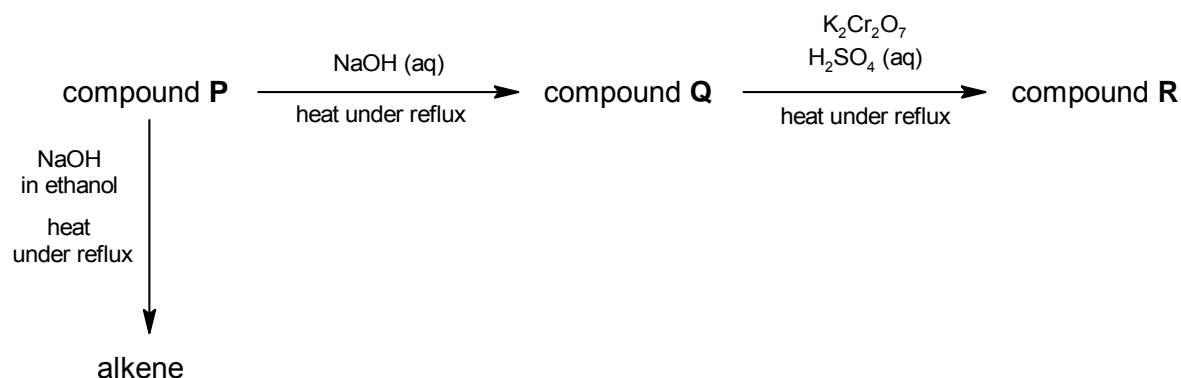
Which statement regarding this reaction is correct?

- A Only one mono-substituted product is formed.
 B Only the propagation step involves C–Cl bond formation.
 C Both propagation and termination steps produce hydrogen chloride.
 D Only the initiation step of the mechanism involves homolytic fission.
- 19 Compound Z can be obtained by a two-step process involving intermediate X.



What is the identity of intermediate X?

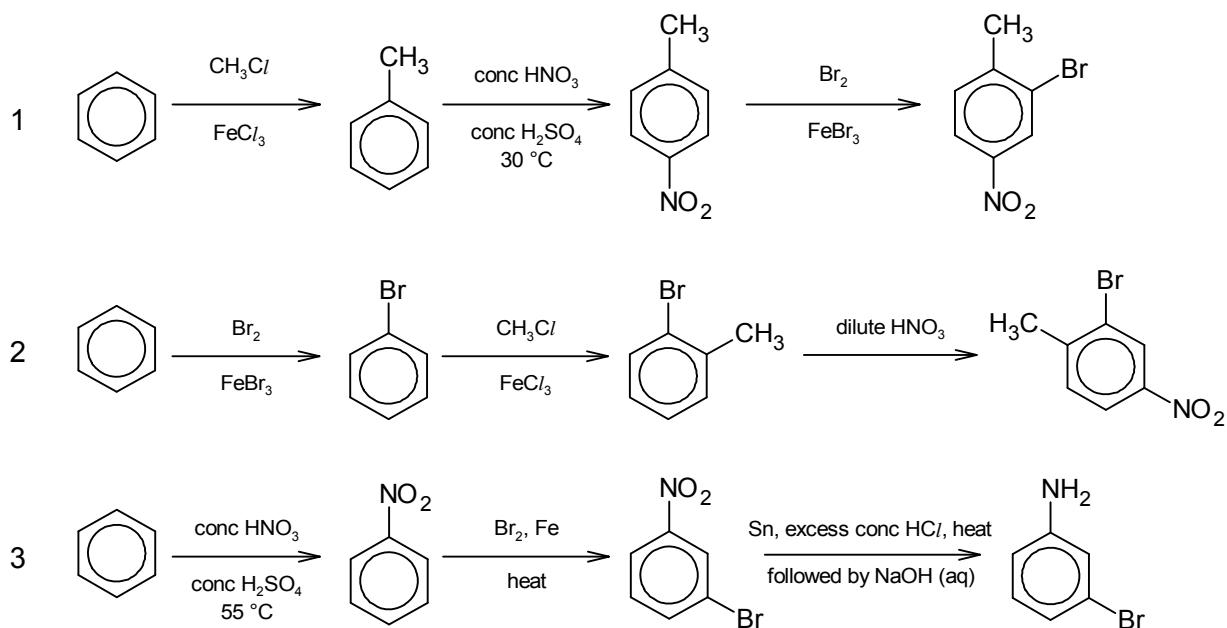
- A $\text{HOOCCH}_2\text{CH}_2\text{COOH}$ B $\text{HOOCCHBrCH}_2\text{COOH}$
 C $\text{HOOCCH}(\text{OH})\text{CH}_2\text{COOH}$ D $\text{HOOCCH}(\text{OH})\text{CH}_2\text{OH}$
- 20 The flow chart below shows a series of reactions.



Which class of compound are P, Q and R?

	P	Q	R
A	halogenoalkane	primary alcohol	carboxylic acid
B	halogenoalkane	primary alcohol	aldehyde
C	primary alcohol	aldehyde	carboxylic acid
D	primary alcohol	halogenoalkane	aldehyde

21 Which of the following synthetic routes is correct?



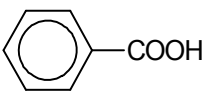
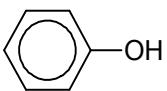
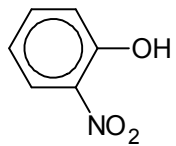
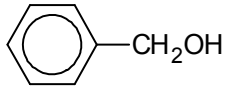
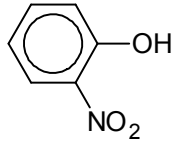
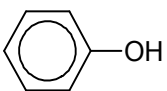
A 1 only

B 1 and 2 only

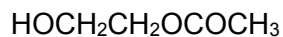
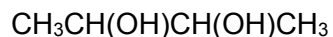
C 2 and 3 only

D 1 and 3 only

22 Which row shows the given molecules arranged in order of increasing pK_a values?

	smallest pK_a value	→	largest pK_a value
A			
B			
C	CF ₃ CH ₂ OH		CH ₃ OH
D			

23 Which reagent is able to distinguish between the two compounds below?

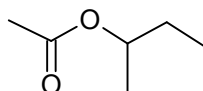


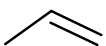
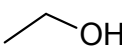
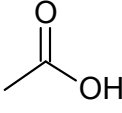
- A Hot alkaline $\text{I}_2(\text{aq})$ B Hot acidified $\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$
 C 2,4-DNPH D Neutral aqueous FeCl_3

24 Which products are formed when butanal reacts with Fehling's solution?

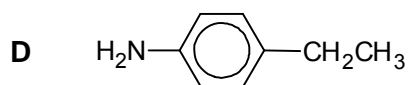
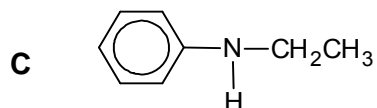
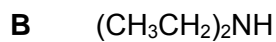
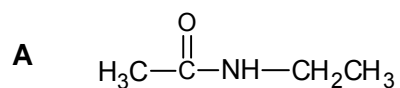
- A Cu_2O and $\text{CH}_3\text{CH}_2\text{COO}^-$
 B Cu_2O and $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$
 C Cu_2O and $\text{CH}_3\text{CH}_2\text{CH}_2\text{COO}^-$
 D CuO and $\text{CH}_3\text{CH}_2\text{CH}_2\text{COO}^-$

25 Which synthetic route will give the following ester as the product?

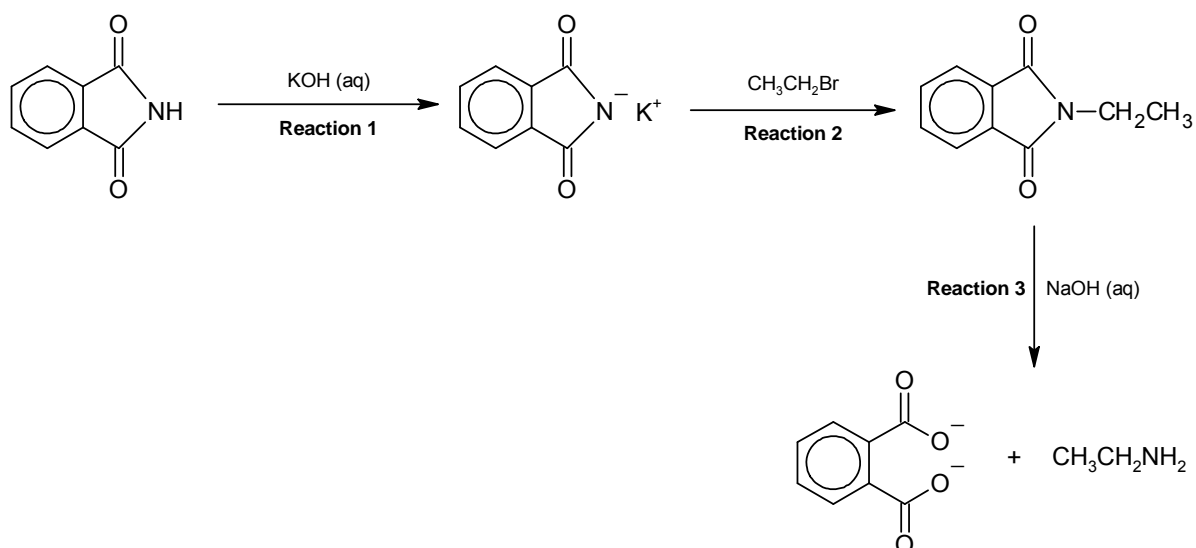


- A  $\xrightarrow{\text{hot acidified KMnO}_4}$ $\xrightarrow{\text{PCl}_5}$ $\xrightarrow{\text{propan-2-ol}}$
- B  $\xrightarrow[\text{heat under reflux}]{\text{KMnO}_4, \text{H}_2\text{SO}_4(\text{aq})}$ $\xrightarrow{\text{SOCl}_2}$ $\xrightarrow{\text{butan-1-ol}}$
- C  $\xrightarrow[\text{in dry ether}]{\text{LiAlH}_4}$ $\xrightarrow{\text{PCl}_5}$ $\xrightarrow{\text{butan-2-ol}}$
- D CH_3Br $\xrightarrow[\text{heat under reflux}]{\text{KCN in ethanol}}$ $\xrightarrow[\text{heat under reflux}]{\text{H}_2\text{SO}_4(\text{aq})}$ $\xrightarrow[\text{heat under reflux}]{\text{butan-2-ol, conc H}_2\text{SO}_4}$

26 Which compound has the lowest pK_b value?



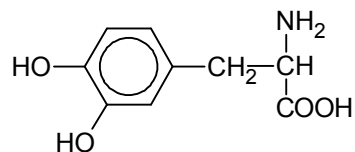
27 The diagram below shows a sequence of reactions.



How can the three reactions be classified?

	Reaction 1	Reaction 2	Reaction 3
A	hydrolysis	substitution	acid-base
B	hydrolysis	addition	acid-base
C	acid-base	substitution	hydrolysis
D	acid-base	addition	hydrolysis

- 28 The molecule shown is used in the treatment of Parkinson's disease.

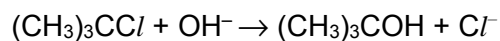


Which statement about the molecule is correct?

- 1 It is likely to be soluble in water due to zwitterion formation.
- 2 Two Br atoms will be incorporated when aqueous bromine is added.
- 3 One mole of molecule reacts with three moles of sodium carbonate to form a salt.

- | | | | |
|----------|--------------|----------|-----------------|
| A | 1 only | B | 1 and 2 only |
| C | 1 and 3 only | D | 1, 2 and 3 only |

- 29 Nucleophilic substitution of 2-chloro-2-methylpropane follows an S_N1 mechanism.



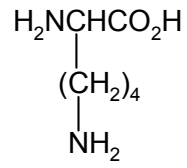
S_N1 reactions take place more rapidly in polar solvents.

Which solvent should be used?

- 1 water
- 2 hexane
- 3 ethanol
- 4 tetrachloromethane

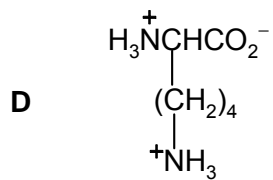
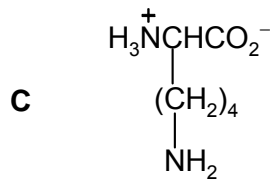
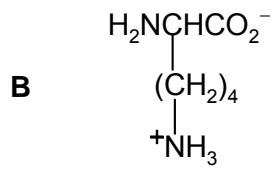
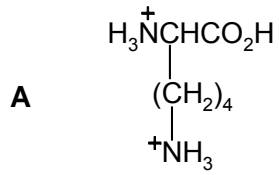
- | | | | |
|----------|-----------------|----------|-----------------|
| A | 1 and 2 only | B | 1 and 3 only |
| C | 1, 2 and 4 only | D | 1, 3 and 4 only |

30 Lysine is an amino acid.



lysine

Which structure is predominant when lysine is in aqueous solution at pH 5?



2018 DHS YEAR 6 H2 CHEMISTRY (9729) Preliminary Examination
Paper 1 MCQ – Answers

1	2	3	4	5	6	7	8	9	10
C	B	D	C	D	A	A	A	B	D

11	12	13	14	15	16	17	18	19	20
C	A	D	D	A	B	C	A	C	A

21	22	23	24	25	26	27	28	29	30
D	B	A	C	D	B	C	A	B	D

Name:		Index Number:		Class:	
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DUNMAN HIGH SCHOOL
Preliminary Examination 2018
Year 6

H2 CHEMISTRY

Paper 2 Structured Questions

9729/02

13 September 2018

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

INSTRUCTIONS TO CANDIDATES

- 1 Write your **name**, **index number** and **class** on this cover page.
- 2 Write in dark blue or black pen.
- 3 You may use an HB pencil for any diagrams or graphs.
- 4 Do not use staples, paper clips, glue or correction fluid.
- 5 Answer **all** questions in the spaces provided on the Question Paper.

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

You are advised to show all workings in calculations.

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

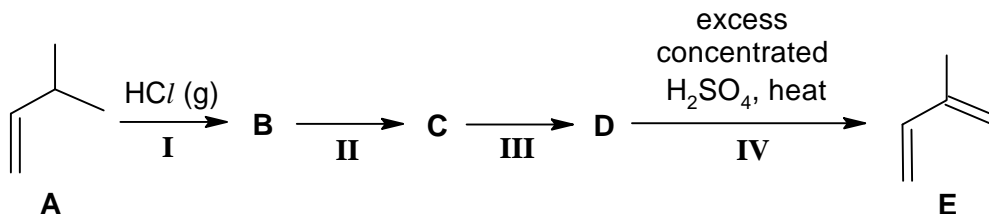
For Examiner's Use	
Question No.	Marks
1	13
2	12
3	25
4	10
5	15
Total	75

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

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

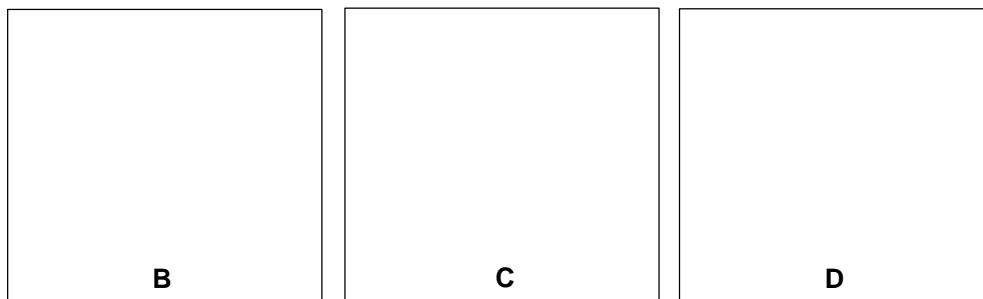
- 1 Isoprene, **E**, is an organic compound that could be used to synthesise limonene, which is commonly used in fragrances.

(a) **E** can be synthesised from 3-methylbut-1-ene, **A**, in a 4-step process as follows.



- (i) **B** is a major product of step I.

Draw the structures of compounds **B**, **C** and **D**.



[3]

- (ii) Suggest the reagents and conditions for steps **II** and **III**.

step **II** :[1]

step **III** :[1]

- (iii) Predict, with reasoning, whether the mixture of products formed in step **I** is optically active.

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.....

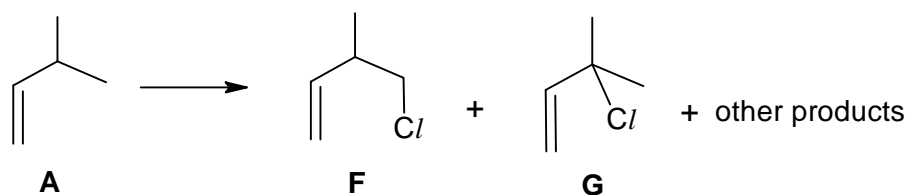
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.....[2]

- (b) The following reaction shows an alternative route to form intermediates for the synthesis of isoprene, **E**.



- (i) State the reagents and conditions used to form **F** and **G** from **A**.

.....[1]

- (ii) Predict the ratio in which **F** and **G** will be formed.

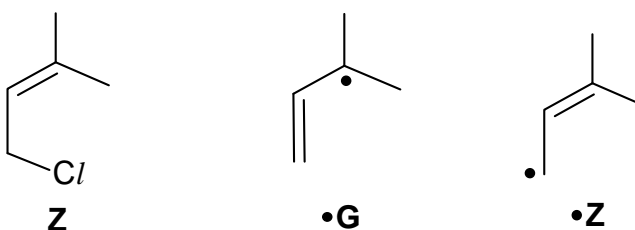
.....[1]

- (iii) **Z** was one of the other products formed in the reaction in (b). It was suggested that the radical, $\bullet\mathbf{G}$, is involved in the formation of **Z**.

The mechanism of $\bullet\mathbf{G}$ converting to **Z** is thought to involve 2 steps.

1. Delocalisation of unpaired electron forming $\bullet\mathbf{Z}$.
2. $\bullet\mathbf{Z}$ reacts with Cl_2 to form **Z** and a radical.

The structures of **Z**, $\bullet\mathbf{G}$ and $\bullet\mathbf{Z}$ are as follows.



Use the information above to draw out the mechanism for the conversion of $\bullet\mathbf{G}$ to **Z**. You are advised to use skeletal or structural formula for all species, so that it is clear which bonds are broken and which are formed. Indicate any unpaired electrons by a dot (\bullet). Use curly half-arrows to indicate the movement of unpaired electrons.

[2]

(iv) Describe a chemical test that could distinguish between **A** and **F**. State reagents, conditions and observations clearly in your test.

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

[Total: 13]

- 2 (a) Fig 2.1 shows a bar chart of the third ionisation energy (3^{rd} IE) of nine consecutive elements (J to R) in Periods 2 and 3 of the Periodic Table.

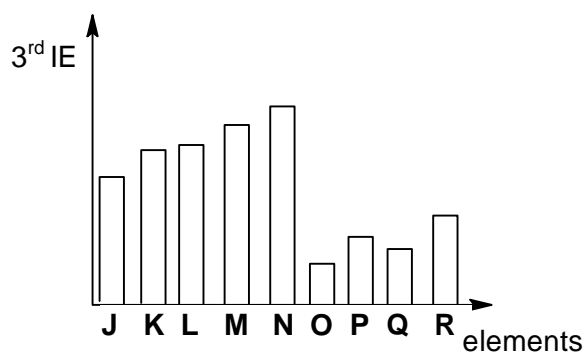


Fig 2.1

- (i) Write an equation for the third ionisation energy of element J.

.....[1]

- (ii) Identify element N.

.....[1]

- (iii) Using your answers in (a)(i), (a)(ii) and the electronic configurations of the species involved, explain the following features of Fig 2.1.

1. The significantly higher 3^{rd} IE of N compared to O.

.....

[2]

2. The lower 3^{rd} IE of Q than P.

.....

[2]

(c) The Periodic Table shows helium placed at the top of Group 18.

(i) Suggest why the element helium could be placed at the top of Group 2.

.....[1]

(ii) Suggest why the element helium is not placed at the top of Group 2, by comparing **one** physical property. Explain your answer.

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

[Total: 12]

3 The ions of transition elements form *complexes* by reacting with *ligands*.

(a) (i) State what is meant by the terms:

- *Complex*

.....

[1]

- *Ligand*

.....

[1]

(ii) Two of the complexes formed by copper are $\text{Cu}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2(\text{OH})_2$ and CuCl_4^{2-} . Draw three-dimensional diagrams of their structures in the boxes below and name their shapes.

$\text{Cu}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2(\text{OH})_2$	CuCl_4^{2-}
Shape:	Shape:

[3]

(iii) State the oxidation number of Cu in $\text{Cu}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2(\text{OH})_2$.

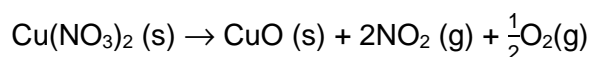
.....[1]

- (c) Copper(I) oxide and copper(II) oxide can both be used in the ceramic industry to give blue, green or red tints to glasses, glazes and enamels.

The table lists the ΔH_f^\ominus values for some compounds.

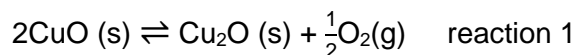
Compound	$\Delta H_f^\ominus / \text{kJ mol}^{-1}$
$\text{Cu}_2\text{O (s)}$	-168.6
CuO (s)	-157.3
$\text{Cu(NO}_3)_2 \text{(s)}$	-302.9
$\text{NO}_2 \text{(g)}$	+33.2

- (i) Copper(II) oxide can be produced in a pure form by heating copper(II) nitrate. Use suitable ΔH_f^\ominus values from the table to calculate the ΔH_r^\ominus for this reaction.



[1]

- (ii) Copper(I) oxide can be produced from copper(II) oxide.



Suggest whether a low or high temperature would favour the production of copper(I) oxide. Explain your reasoning with appropriate calculation.

.....

[2]

- (iii) For reaction 1, $\Delta S^\ominus = +93.6 \text{ J K}^{-1} \text{ mol}^{-1}$. Use this value and your answer in (c)(ii) to calculate ΔG^\ominus .

[1]

- (iv) Write the expression of the equilibrium constant, K_c , for reaction 1. State the units.

[2]

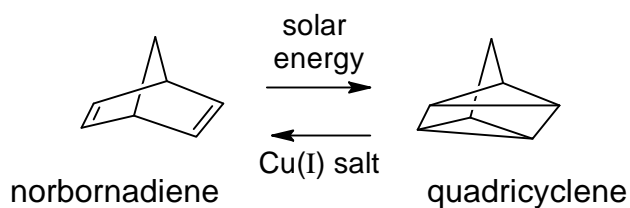
- (v) For any reaction, ΔG^\ominus and the equilibrium constant, K_c , are related according to the equation,

$$\Delta G^\ominus = -2.303RT \log K_c$$

Use this equation to calculate a value of K_c for reaction 1.

[1]

- (d) In 1977, Kutal *et al.* conducted a detailed investigation into the photoassisted (solar energy) isomerisation of norbornadiene to quadricyclene.



In the presence of copper(I) salts as a catalyst, the isomerisation was reversible with the release of approximately 1.08 kJ of energy per gram of quadricyclene.

- (i) State the type of isomerism that has occurred when norbornadiene is converted to quadricyclene.

.....[1]

- (ii) Based on the above given information, suggest a possible practical use of this norbornadiene–quadricyclene interconversion system. Explain how this system can work to fulfil that practical use.

.....

.....

.....

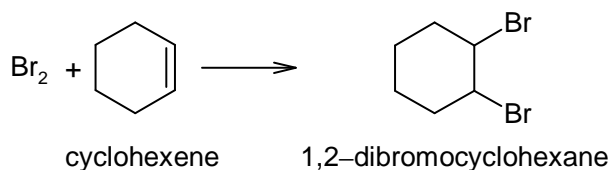
.....

.....

.....[2]

[Total: 25]

- 4 (a) Cyclohexene can react with Br₂ to form 1,2-dibromocyclohexane as shown below.



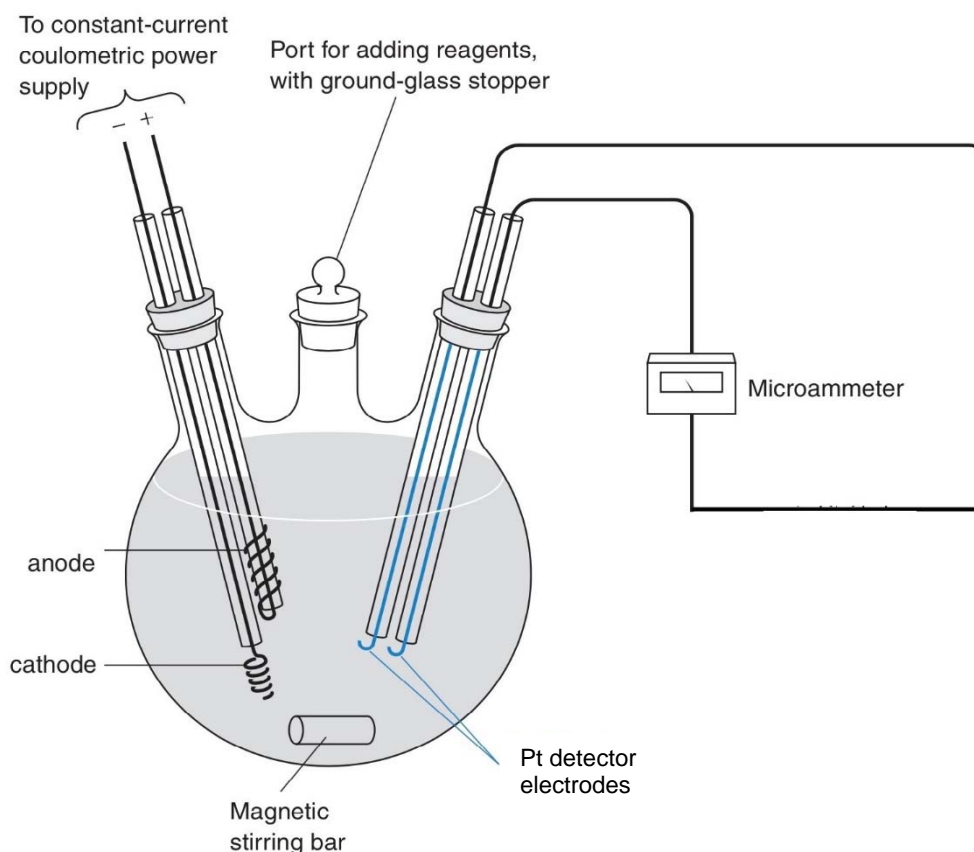
An experiment was carried out where the cyclohexene was titrated with the Br₂ generated by the oxidation of Br⁻ in the electrolytic cell:



The experiment was carried out at a constant current as shown in the figure below.

The initial solution contains an unknown quantity of cyclohexene and a large amount of Br⁻ dissolved in a suitable inert solvent that does not participate in the reaction.

The figure below consists of electrolytic and galvanic cells shown on the left-hand and right-hand sides respectively.

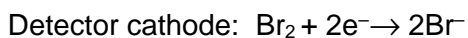
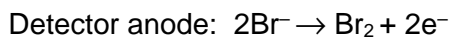


Br₂ generated from electrolysis, reacts with the cyclohexene. At the end-point, all the cyclohexene has reacted and the concentration of Br₂ suddenly rises, signalling the end of the reaction.

- (i) State whether Br₂ is generated at the cathode or anode of the electrolytic cell.

.....[1]

- (ii) The rise in the concentration of Br_2 is detected by measuring the current between the two Pt detector electrodes in the galvanic cell using the microammeter. The detector current flows by virtue of the reactions:



Suggest why there is no current detected before equivalence point is reached.

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

In an experiment, 2 cm^3 of $0.600 \times 10^{-3} \text{ g cm}^{-3}$ cyclohexene is to be titrated.

- (iii) Calculate the amount, in moles, of the cyclohexene used.

[1]

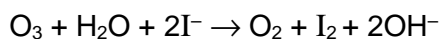
- (iv) The experiment was carried out with a constant current of $5 \times 10^{-3} \text{ A}$ for the electrolytic cell. Determine the time taken for complete titration.

[2]

- (b) Br atoms introduced artificially by industrial activities raise concerns of ozone destruction.

One method that is used to determine the concentration of ozone in the ozone layer is to pass air through alkaline potassium iodide and to measure the amount of iodine liberated.

The following reaction takes place.



The iodine liberated is measured using a platinum electrode immersed in alkaline potassium iodide solution against a standard silver/silver chloride reference electrode. The e.m.f. of the system, in volts, is given by the equation.

$$E = 0.32 + 0.029 \log_{10} [\text{I}_2], \text{ where } [\text{I}_2] \text{ is expressed in mol dm}^{-3}.$$

To determine ozone in the atmosphere, a light-weight balloon containing the electrochemical cell was released into the atmosphere. The data collected was then transmitted to the ground station for further processing.

A sample of air was passed through 10 cm³ of alkaline potassium iodide. The pressure of this sample of air was found to be 0.24 atm measured at room temperature. The potential of the platinum electrode immersed into this solution against the standard silver/silver chloride electrode was 0.21 V.

- (i) Calculate the concentration of iodine liberated.

[1]

- (ii) Hence, calculate the volume of ozone present in this sample of air.

[2]

- (c) Halogens form binary compounds with hydrogen known as hydrogen halides. State and explain how the thermal stability of hydrogen halides varies down the Group.

.....

.....

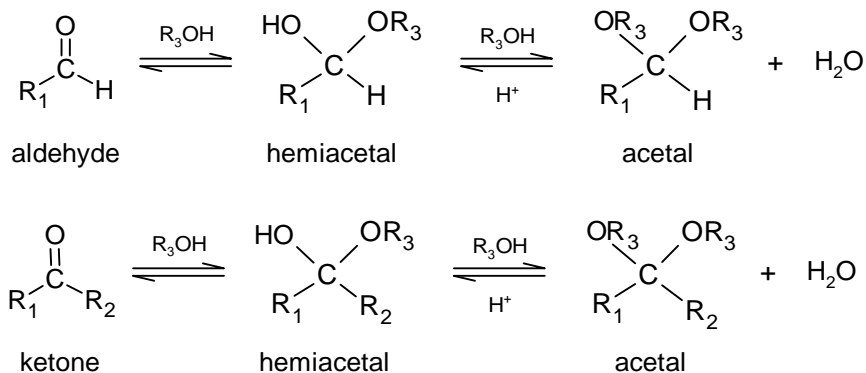
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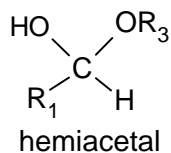
.....[2]

[Total: 10]

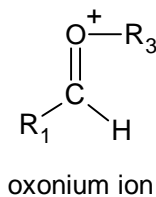
- 5 (a) Nucleophilic addition of an alcohol to aldehydes and ketones yield hemiacetals. The reaction is slow and reversible under neutral conditions. Upon further reaction with alcohols in the presence of acids as catalyst, hemiacetals can form acetals.



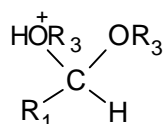
The acid-catalysed acetal formation from the hemiacetal shown below, involves 4 steps.



1. Protonation of the hydroxyl group of the hemiacetal.
2. Loss of water leads to an unstable and highly reactive oxonium ion.



3. Nucleophilic attack of alcohol, R_3OH , on the oxonium ion to give



4. Loss of a proton to give the acetal.

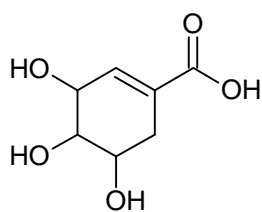
- (i) Draw the mechanism as described above, showing clearly the flow of electrons.

[4]

- (ii) State the purpose of removing water from the reaction mixture.

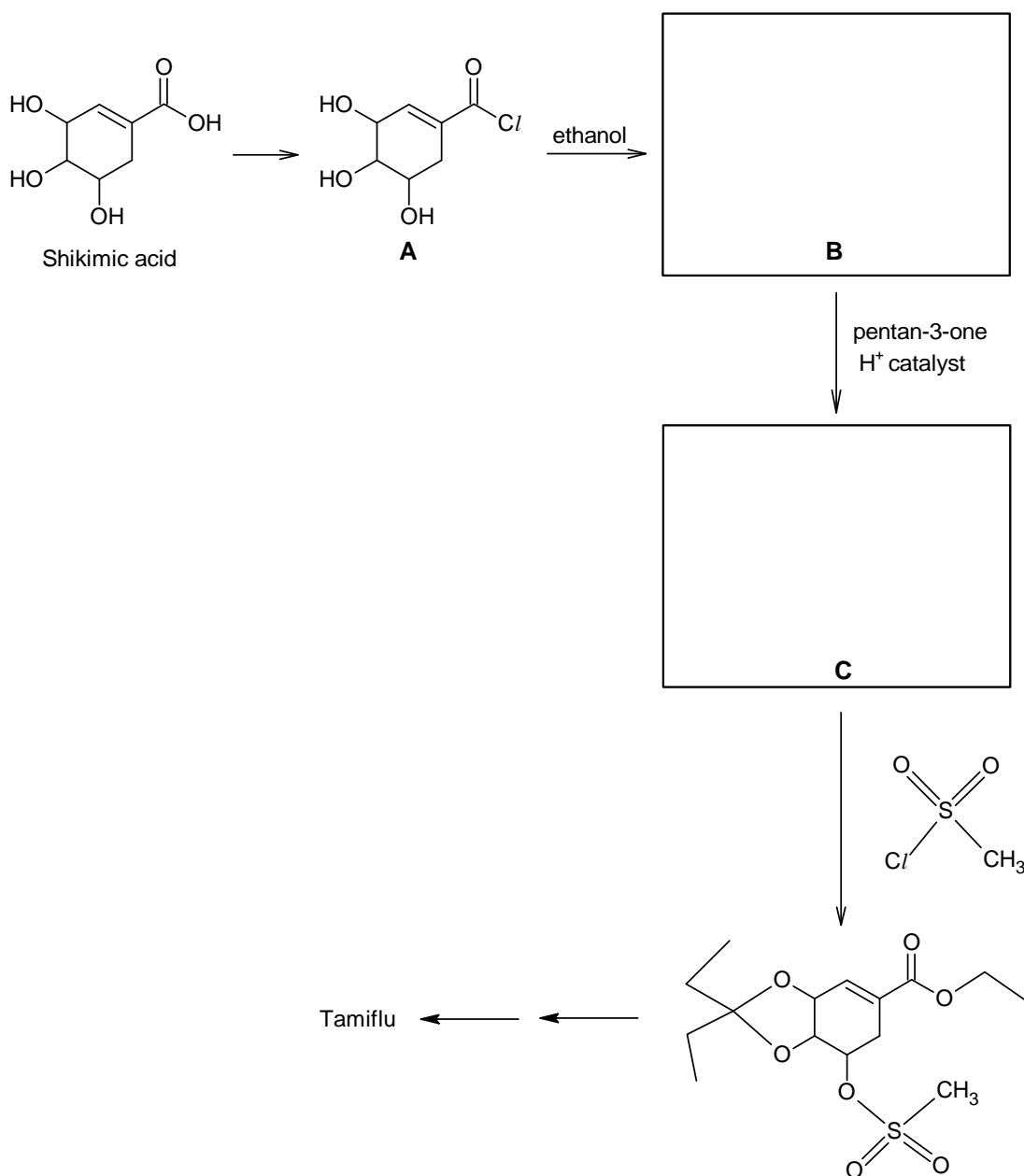
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.....
.....[1]

- (b) Tamiflu is the anti-influenza drug currently being used to treat 'Bird-flu'. It can be synthesised from Shikimic acid, which occurs naturally in star anise.



Shikimic acid

Part of the synthetic route is shown below. Formation of acetals between selected $-OH$ groups of Shikimic acid and ketones helps to control which of the $-OH$ groups reacts to synthesise **C** from **B**.



- (i) Draw the structures of **B** and **C** in the boxes provided above.

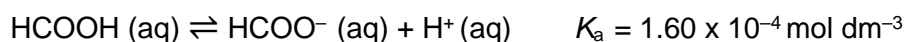
[2]

- (ii) Explain why **B** was formed from **A** instead of Shikimic acid directly.

.....

[1]

- (c) Like Shikimic acid, methanoic acid occurs naturally in ants. It is a weak acid and dissociates according to the equation shown.



- (i) Explain what is meant by the term $\text{p}K_{\text{a}}$ as applied to methanoic acid.

.....

[2]

A flask contains 0.0100 mol of methanoic acid dissolved in 250 cm³ of water.

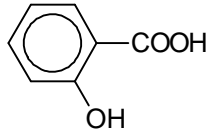
- (ii) Calculate the pH of this solution.

[2]

- (iii) Hence, calculate the degree of dissociation, α , of methanoic acid in this solution.

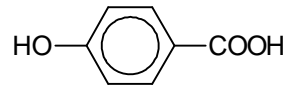
[1]

(d) Salicylic acid occurs naturally in plants.



salicylic acid

$$pK_{a1} = 2.97$$



isomer of
salicylic acid

$$pK_{a1} = 4.54$$

Explain why salicylic acid is more acidic than its isomer.

.....

.....

.....

.....

.....

.....

.....[2]

[Total: 15]

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**DUNMAN HIGH SCHOOL**
Preliminary Examination 2018
Year 6**H2 CHEMISTRY**

Paper 2 Structured Questions

9729/02

13 September 2018**2 hours**

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

INSTRUCTIONS TO CANDIDATES

- 1 Write your **name**, **index number** and **class** on this cover page.
- 2 Write in dark blue or black pen.
- 3 You may use an HB pencil for any diagrams or graphs.
- 4 Do not use staples, paper clips, glue or correction fluid.
- 5 Answer **all** questions in the spaces provided on the Question Paper.

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

You are advised to show all workings in calculations.

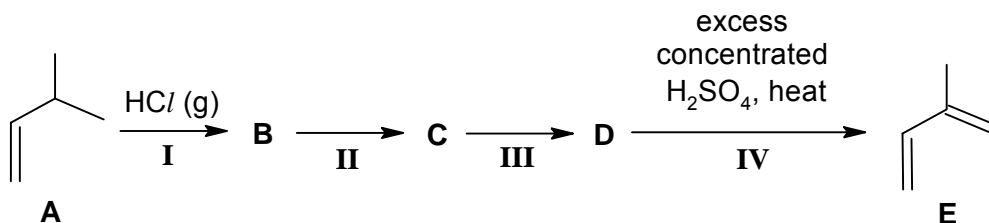
You are reminded of the need for good English and clear presentation in your answers.

For Examiner's Use	
Question No.	Marks
1	13
2	12
3	25
4	10
5	15
Total	75

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

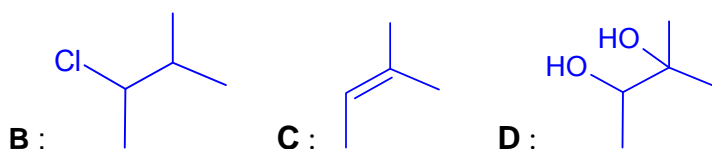
- 1 Isoprene, **E**, is an organic compound that could be used to synthesise limonene, which is commonly used in fragrances.

(a) **E** can be synthesised from 3-methylbut-1-ene, **A**, in a 4-step process as follows.



- (i) **B** is a major product of step I.

Draw the structures of compounds **B**, **C** and **D**.



[3]

- (ii) Suggest the reagents and conditions for steps **II** and **III**.

step **II** : alcoholic NaOH heat under reflux

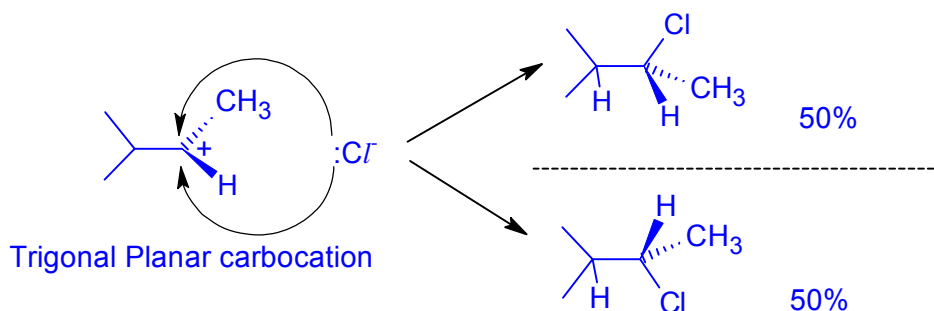
step **III** : cold alkaline KMnO_4

[2]

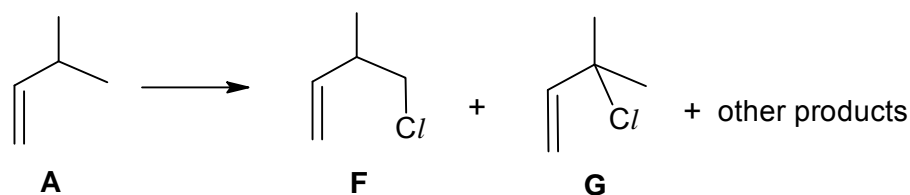
- (iii) Predict, with reasoning, whether the mixture of products formed in step I is optically active.

[2]

The reaction mixture in **B** is **not optically active**. During electrophilic addition, a **trigonal planar carbocation** is formed. Cl^- has a **50% chance** each of **attacking the carbocation from the top or bottom of the plane**. Hence, resulting in a **racemic mixture** formed.



- (b) The following reaction shows an alternative route to form intermediates for the synthesis of isoprene, **E**.



- (i) State the reagents and conditions used to form **F** and **G** from **A**.

[1]

Limited Cl_2 , uv

- (ii) Predict the ratio in which **F** and **G** will be formed.

[1]

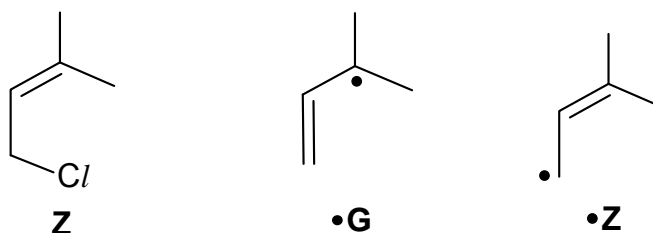
F : **G**
6 : 1

- (iii) **Z** was one of the other products formed in the reaction in (b). It was suggested that the radical, $\bullet\text{G}$, is involved in the formation of **Z**.

The mechanism of $\bullet\text{G}$ converting to **Z** is thought to involve 2 steps.

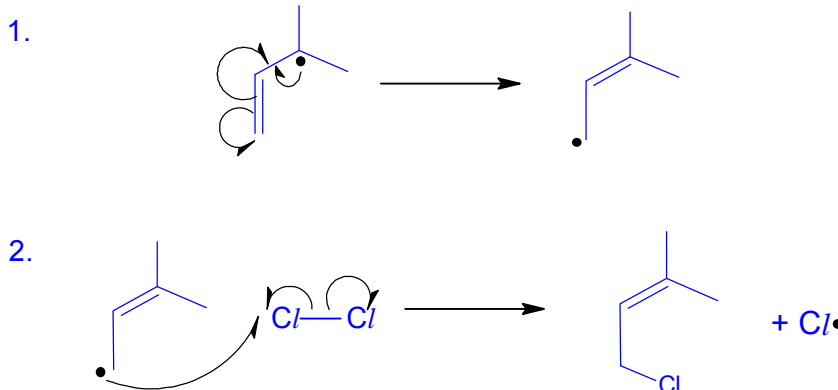
- Delocalisation of unpaired electron forming $\bullet\text{Z}$.
- $\bullet\text{Z}$ reacts with Cl_2 to form **Z** and a radical.

The structures of **Z**, $\bullet\text{G}$ and $\bullet\text{Z}$ are as follows.



Use the information above to draw out the mechanism for the conversion of $\bullet\text{G}$ to **Z**. You are advised to use skeletal or structural formula for all species, so that it is clear which bonds are broken and which are formed. Indicate any unpaired electrons by a dot (\bullet). Use curly half-arrows to indicate the movement of unpaired electrons.

[2]



- (iv) Describe a chemical test that could distinguish between **A** and **F**. State reagents, conditions and observations clearly in your test.

Add 1 cm³ of **A** and **F** each into separate test tubes. Add **NaOH (aq)** into both test tubes and **heat**, **followed by** adding excess **HNO₃ (aq)** then add **AgNO₃ (aq)**.

F : **White ppt** of AgCl seen

A : **no white ppt** seen

[Total: 13]

- 2 (a) Fig 2.1 shows a bar chart of the third ionisation energy (3rd IE) of nine consecutive elements (**J** to **R**) in Periods 2 and 3 of the Periodic Table.

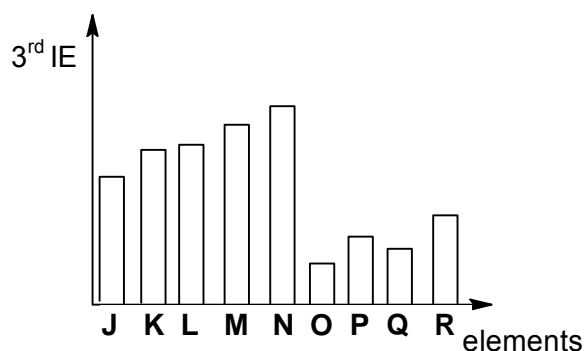


Fig 2.1

- (i) Write an equation for the third ionisation energy of element **J**. [1]
- $$J^{2+}(g) \rightarrow J^{3+}(g) + e^{-}$$
- (ii) Identify element **N**. [1]
- Mg**
- (iii) Using your answers in (a)(i), (a)(ii) and the electronic configurations of the species involved, explain the following features of Fig 2.1.

1. The significantly higher 3rd IE of **N** compared to **O**.

Electronic configuration: **N²⁺ (1s²2s²2p⁶);** **O²⁺ ([Ne]3s¹)**

The 3rd ionisation energy of **N** involves the removal of a **2p** electron

The 3rd ionisation energy of **O** involves the removal of a **3s** electron

A **significantly larger amount of energy** is required to remove the **2p** electron in **N²⁺** which is much more strongly held by the nucleus as it is found in an **inner quantum shell** compared to **3s** electron in **O²⁺**.

Hence 3rd ionisation energy of **N** is significantly higher than that of **O**.

2. The lower 3rd IE of Q than P.

[4]

Electronic configuration: $P^{2+} ([Ne]3s^2)$; $Q^{2+} ([Ne]3s^23p^1)$

The 3rd ionisation energy of P involves the removal of a **3s** electron

The 3rd ionisation energy of Q involves the removal of a **3p** electron

Smaller amount of energy is required to remove the **3p** electron in Q^{2+} which is of **higher energy** than **3s** electron in P^{2+} . (The 3p electron also experiences increased screening effect provided by the filled 3s subshell.)

Hence 3rd ionisation energy of Q is lower than that of P

(b) Fig 2.2 shows another bar chart of the logarithm of all the ionisation energies, $\log(IE)$, of an element S against the number of electrons removed.

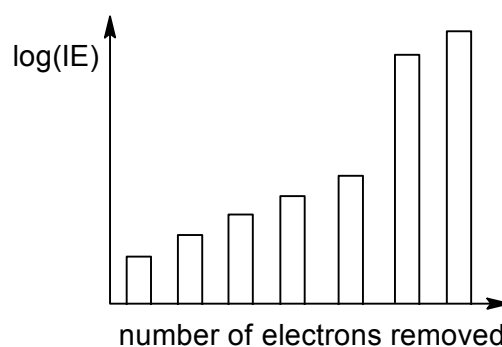


Fig 2.2

(i) Explain the general trend shown in Fig 2.2.

[2]

In an atom of S,

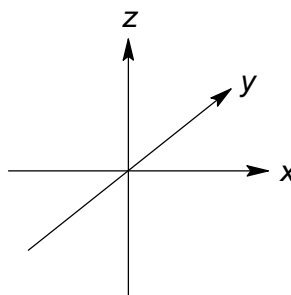
Number of protons unchanged \Rightarrow **nuclear charge unchanged**

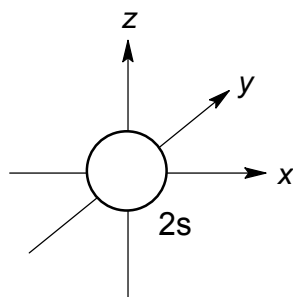
As electrons are removed from the atom, the **increasingly positively charged ion** holds the remaining electrons **more strongly** hence **more energy** is required to remove the remaining electrons resulting in higher I.E

Thus, successive I.E shows an increasing trend.

(ii) On the axes provided, draw and label the orbital which the fifth electron is removed from.

[1]





(c) The Periodic Table shows helium placed at the top of Group 18.

(i) Suggest why the element helium could be placed at the top of Group 2. [1]

Helium has 2 valence electrons like all other Group 2 elements.

(ii) Suggest why the element helium is not placed at the top of Group 2, by comparing **one** physical property. Explain your answer. [2]

Helium atoms are held by weak instantaneous dipole induced dipole interactions while within group 2 elements exist strong electrostatic forces of attraction between cations and a sea of delocalised electrons.

Hence, helium has low melting/boiling point and it exist as a gas while group 2 elements has high melting/boiling point and exist as a solid at room temperature. Include energy

OR

Hence, helium is a non-conductor of electricity due to (absence of mobile/delocalised electrons) while group 2 elements are good conductor of electricity due to (presence of delocalised electrons).

[Total: 12]

3 The ions of transition elements form *complexes* by reacting with *ligands*.

(a) (i) State what is meant by the terms:

Complex

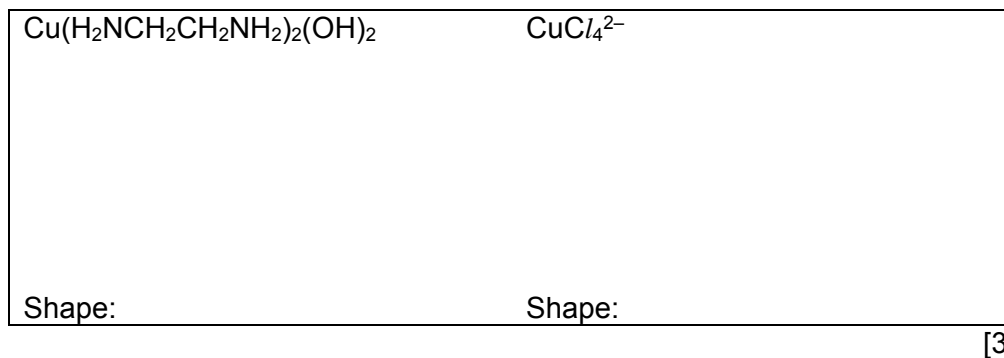
Ligand

[2]

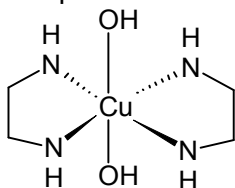
A complex is formed when a **metal ion or atom** forms dative covalent or **coordinate bonds** with **surrounding ion or molecules**.

A ligand is a neutral molecule or an anion containing at least one atom with a **lone pair of electrons that can be donated** into **low lying vacant orbital of metal atom/ion to form a coordinate bond**.

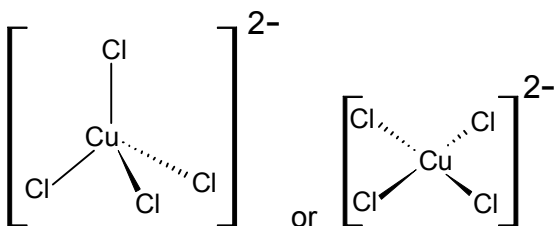
- (ii) Two of the complexes formed by copper are $\text{Cu}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2(\text{OH})_2$ and CuCl_4^{2-} . Draw three-dimensional diagrams of their structures in the boxes below and name their shapes.



Shape: octahedral



Shape: tetrahedral or square planar

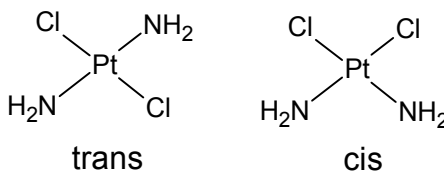


- (iii) State the oxidation number of Cu in $\text{Cu}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2(\text{OH})_2$.

+2

[1]

- (iv) Platinum forms square-planar complexes, in which all four ligands lie on the same plane as the Pt atom. There are two isomeric complexes with the formula $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$. Suggest the structures of the two isomers.



By comparison with a similar type of isomerism in organic chemistry, suggest the type of isomerism shown here and label the isomers above.

Type of isomerism: Cis-trans isomerism

[4]

- (b) Copper forms two series of compounds, one containing copper(II) ions and the other containing copper(I) ions.

- (i) Complete the electronic configuration of these species.

Cu [Ar].....

Cu(I) [Ar].....

Cu [Ar] 3d¹⁰ 4s¹

Cu(I) [Ar] 3d¹⁰

[2]

- (ii) Explain why the following statements are true.

Copper metal is a better electrical conductor than calcium metal.

Copper(II) salts are generally coloured.

[3]

Copper metal are better electrical conductor because both **4s and 3d valence electrons are available for delocalisation**. This increases the number of mobile charge carriers which in turn increases the conductivity of copper metal.

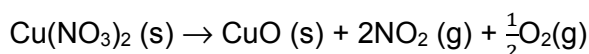
In the presence of ligands, the **degenerate d orbitals are split into two groups of orbital with different energies**. When white light shines on the complex, a d electron **undergoes d-d transition and is promoted to a higher energy partially filled or empty d orbital**. During the transition, the **d electron absorbs a quantum/photon of light of certain wavelength** from the visible region of the electromagnetic spectrum. The **colour observed is the colour of transmitted light** which is a mixture of remaining wavelengths that have not been absorbed. This colour is the complementary colour of the absorbed light.

- (c) Copper(I) oxide and copper(II) oxide can both be used in the ceramic industry to give blue, green or red tints to glasses, glazes and enamels.

The table lists the ΔH_f^\ominus values for some compounds.

Compound	$\Delta H_f^\ominus / \text{kJ mol}^{-1}$
Cu ₂ O (s)	-168.6
CuO (s)	-157.3
Cu(NO ₃) ₂ (s)	-302.9
NO ₂ (g)	+33.2

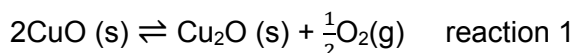
- (i) Copper(II) oxide can be produced in a pure form by heating copper(II) nitrate. Use suitable ΔH_f^\ominus values from the table to calculate the ΔH_r^\ominus for this reaction.



[1]

$$\begin{aligned} \Delta H_r^\ominus &= -157.3 + 2(33.2) + 0 - (-302.9) \\ &= +212 \text{ kJ mol}^{-1} \end{aligned}$$

- (ii) Copper(I) oxide can be produced from copper(II) oxide.



Suggest whether a low or high temperature would favour the production of copper(I) oxide. Explain your reasoning with appropriate calculation. [2]

$$\begin{aligned} \Delta H^\ominus_{\text{r}} &= -168.6 - 2(-157.3) \\ &= +146 \text{ kJ mol}^{-1} \end{aligned}$$

Since the production of copper(I) oxide from copper(II) oxide is an **endothermic process**, it will be favoured by **high temperature** as predicted by **Le Chatelier's Principle**. The equilibrium will **shift to the right** to counter the high temperature.

- (iii) For reaction 1, $\Delta S^\ominus = +93.6 \text{ J K}^{-1} \text{ mol}^{-1}$. Use this value and your answer in (c)(ii) to calculate ΔG^\ominus . [1]

$$\begin{aligned} \Delta G^\ominus &= 146 - (298)(0.0936) \\ &= +118.1 \text{ kJ mol}^{-1} \\ &= +118 \text{ kJ mol}^{-1} \end{aligned}$$

- (iv) Write the expression of the equilibrium constant, K_c , for reaction 1. State the units. [2]

$$\begin{aligned} K_c &= [\text{O}_2]^{1/2} \\ \text{Units: } &\text{mol}^{1/2} \text{ dm}^{-3/2} \end{aligned}$$

- (v) For any reaction, ΔG^\ominus and the equilibrium constant, K_c , are related according to the equation,

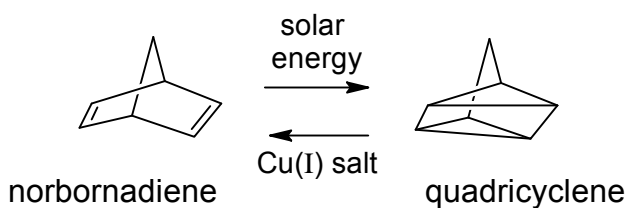
$$\Delta G^\ominus = -2.303RT \log K_c$$

Use this equation to calculate a value of K_c for reaction 1. [1]

$$\log K_c = \frac{-118.1 \times 10^3}{(2.303)(8.31)(298)} = -20.71$$

$$K_c = 1.95 \times 10^{-21}$$

- (d) In 1977, Kutal *et al.* conducted a detailed investigation into the photoassisted (solar energy) isomerisation of norbornadiene to quadricyclene.



In the presence of copper(I) salts as a catalyst, the isomerisation was reversible with the release of approximately 1.08 kJ of energy per gram of quadricyclene.

- (i) State the type of isomerism that has occurred when norbornadiene is converted to quadricyclene. [1]

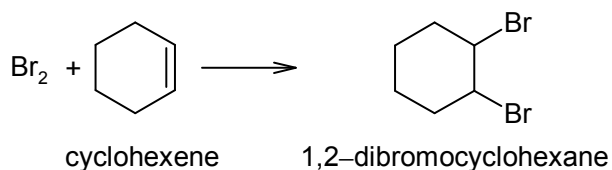
Functional group isomerism

- (ii) Based on the above given information, suggest a possible practical use of this norbornadiene–quadricyclene interconversion system. Explain how this system can work to fulfil that practical use. [2]

This system can potentially work as a solar energy storage system. Norbornadiene is first irradiated with solar energy and converted to quadricyclene. Energy can be released when quadricyclene is reacted with copper(I) salts. This means that solar energy can be stored in the covalent bonds of quadricyclene.

[Total: 25]

- 4 (a) Cyclohexene can react with Br_2 to form 1,2-dibromocyclohexane as shown below.



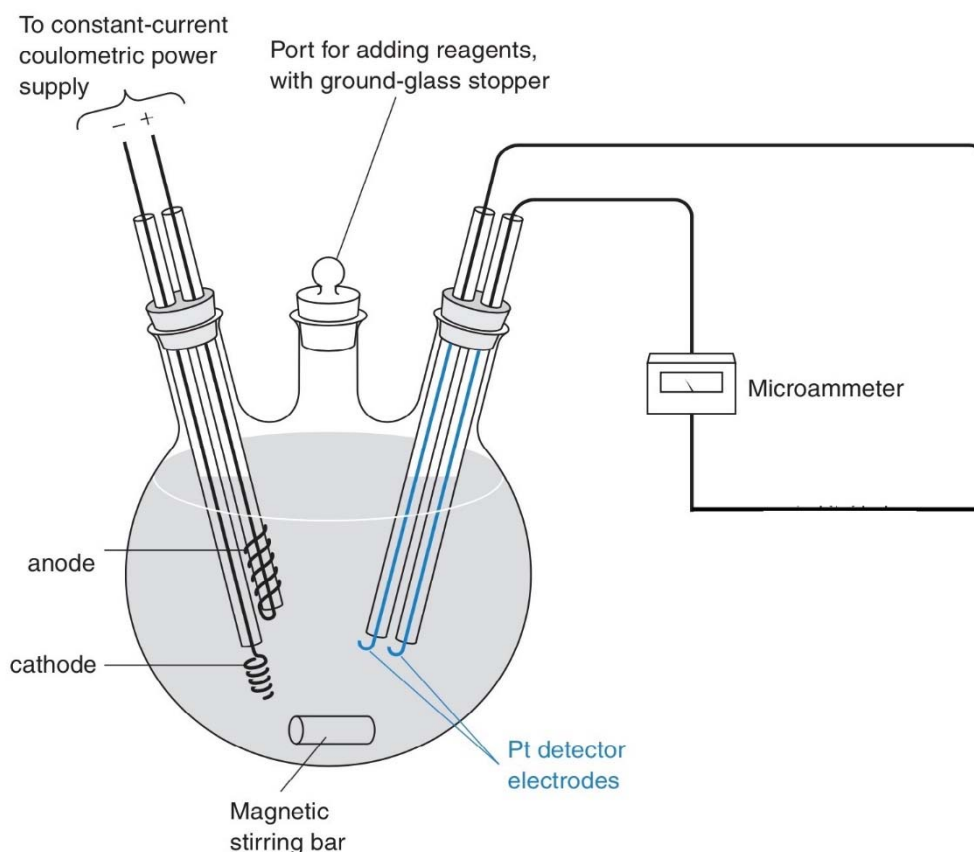
An experiment was carried out where the cyclohexene was titrated with the Br_2 generated by the oxidation of Br^- in the electrolytic cell:



The experiment was carried out at a constant current as shown in the figure below.

The initial solution contains an unknown quantity of cyclohexene and a large amount of Br^- dissolved in a suitable inert solvent that does not participate in the reaction.

The figure below consists of electrolytic and galvanic cells shown on the left-hand and right-hand sides respectively.



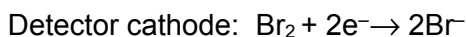
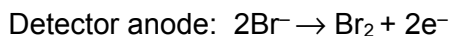
Br_2 generated from electrolysis, reacts with the cyclohexene. At the end-point, all the cyclohexene has reacted and the concentration of Br_2 suddenly rises, signalling the end of the reaction.

- (i) State whether Br_2 is generated at the cathode or anode of the electrolytic cell.

[1]

Anode

- (ii) The rise in the concentration of Br_2 is detected by measuring the current between the two Pt detector electrodes in the galvanic cell using the microammeter. The detector current flows by virtue of the reactions:



Suggest why there is no current detected before equivalence point is reached. [1]

Both Br_2 and Br^- must be present for the detector half-reactions to occur.

Prior to the equivalence point, there is Br^- but no Br_2 is present for reduction at the detector cathode as any Br_2 formed would have reacted with cyclohexene.

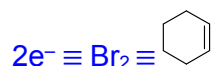
In an experiment, 2 cm^3 of $0.600 \times 10^{-3} \text{ g cm}^{-3}$ cyclohexene is to be titrated.

- (iii) Calculate the amount, in moles, of the cyclohexene used. [1]

$$\begin{aligned} \text{mass of cyclohexene} &= 2 \times 0.600 \times 10^{-3} \\ &= 1.20 \times 10^{-3} \text{ g} \end{aligned}$$

$$\begin{aligned} \text{number of moles of cyclohexene} &= \frac{1.20 \times 10^{-3}}{82.0} \\ &= \underline{1.46 \times 10^{-5} \text{ mol}} \end{aligned}$$

- (iv) The experiment was carried out with a constant current of $5 \times 10^{-3} \text{ A}$ for the electrolytic cell. Determine the time taken for complete titration. [2]



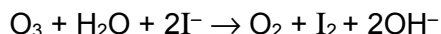
$$\begin{aligned} \text{number of moles of e}^- &= 1.4634 \times 10^{-5} \times 2 \\ &= 2.9268 \times 10^{-5} \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{time taken} &= \frac{nF}{I} \\ &= \frac{2.9268 \times 10^{-5} \times 96500}{5 \times 10^{-3}} \\ &= \underline{595 \text{ s}} \end{aligned}$$

- (b) Br atoms introduced artificially by industrial activities raise concerns of ozone destruction.

One method that is used to determine the concentration of ozone in the ozone layer is to pass air through alkaline potassium iodide and to measure the amount of iodine liberated.

The following reaction takes place.



The iodine liberated is measured using a platinum electrode immersed in alkaline potassium iodide solution against a standard silver/silver chloride reference electrode. The e.m.f. of the system, in volts, is given by the equation.

$$E = 0.32 + 0.029 \log_{10} [\text{I}_2], \text{ where } [\text{I}_2] \text{ is expressed in mol dm}^{-3}.$$

To determine ozone in the atmosphere, a light-weight balloon containing the electrochemical cell was released into the atmosphere. The data collected was then transmitted to the ground station for further processing.

A sample of air was passed through 10 cm³ of alkaline potassium iodide. The pressure of this sample of air was found to be 0.24 atm measured at room temperature. The potential of the platinum electrode immersed into this solution against the standard silver/silver chloride electrode was 0.21 V.

- (i) Calculate the concentration of iodine liberated.

[1]

$$0.21 = 0.32 + 0.029 \log_{10} [\text{I}_2]$$

$$[\text{I}_2] = \underline{1.61 \times 10^{-4} \text{ mol dm}^{-3}}$$

- (ii) Hence, calculate the volume of ozone present in this sample of air.

[2]

$$\begin{aligned} \text{number of moles of O}_3 &= 1.6103 \times 10^{-4} \times \frac{10}{1000} \\ &= 1.6103 \times 10^{-6} \text{ mol} \end{aligned}$$

$$\begin{aligned} pV &= nRT \\ V &= \frac{nRT}{p} \\ &= \frac{(1.6103 \times 10^{-6})(8.31)(293)}{0.24 \times 101325} \\ &= \underline{1.61 \times 10^{-7} \text{ m}^3} \end{aligned}$$

- (c) Halogens form binary compounds with hydrogen known as hydrogen halides. State and explain how the thermal stability of hydrogen halides varies down the Group.

[2]

Thermal stability of hydrogen halides decreases down the group.

Down the group,

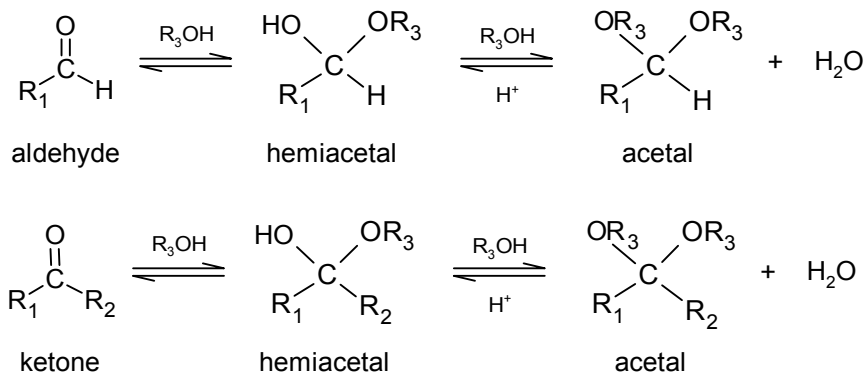
bond energy decreases [BE (H-F) > BE (H-Cl) > BE (H-Br) > BE (H-I)],

covalent bond strength also decreases [H-F > H-Cl > H-Br > H-I].

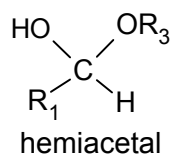
Hence, thermal stability decreases [H-F > H-Cl > H-Br > H-I].

[Total: 10]

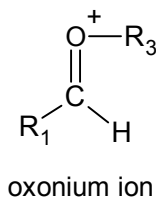
- 5 (a) Nucleophilic addition of an alcohol to aldehydes and ketones yield hemiacetals. The reaction is slow and reversible under neutral conditions. Upon further reaction with alcohols in the presence of acids as catalyst, hemiacetals can form acetals.



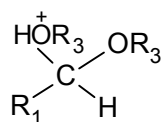
The acid-catalysed acetal formation from the hemiacetal shown below, involves 4 steps.



1. Protonation of the hydroxyl group of the hemiacetal.
2. Loss of water leads to an unstable and highly reactive oxonium ion.



3. Nucleophilic attack of alcohol, R_3OH , on the oxonium ion to give

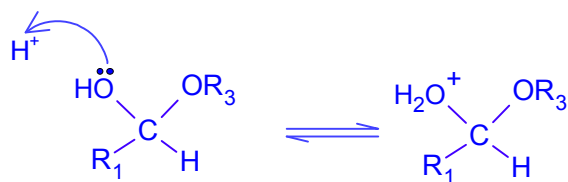


4. Loss of a proton to give the acetal.

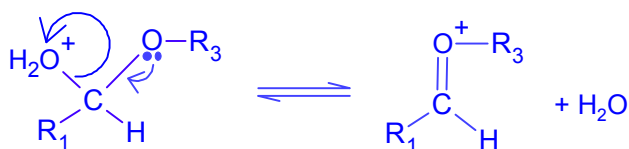
- (i) Draw the mechanism as described above, showing clearly the flow of electrons.

[4]

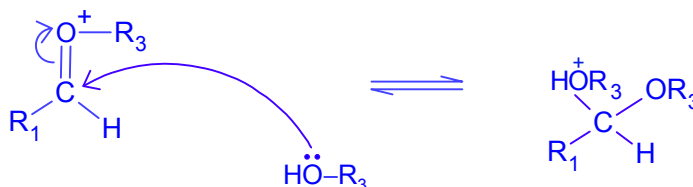
Step 1:



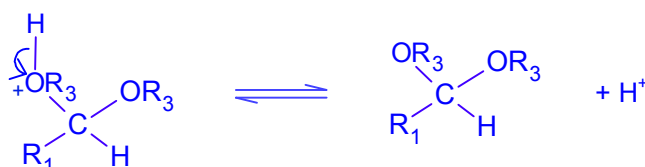
Step 2:



Step 3:



Step 4:



(ii) State the purpose of removing water from the reaction mixture.

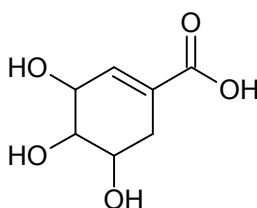
[1]

By Le Chatelier's Principle, removal of water shifts the position of equilibrium to the right, hence increasing the yield.

OR

Water is a competing nucleophile to the alcohol, hence other side products may be formed.

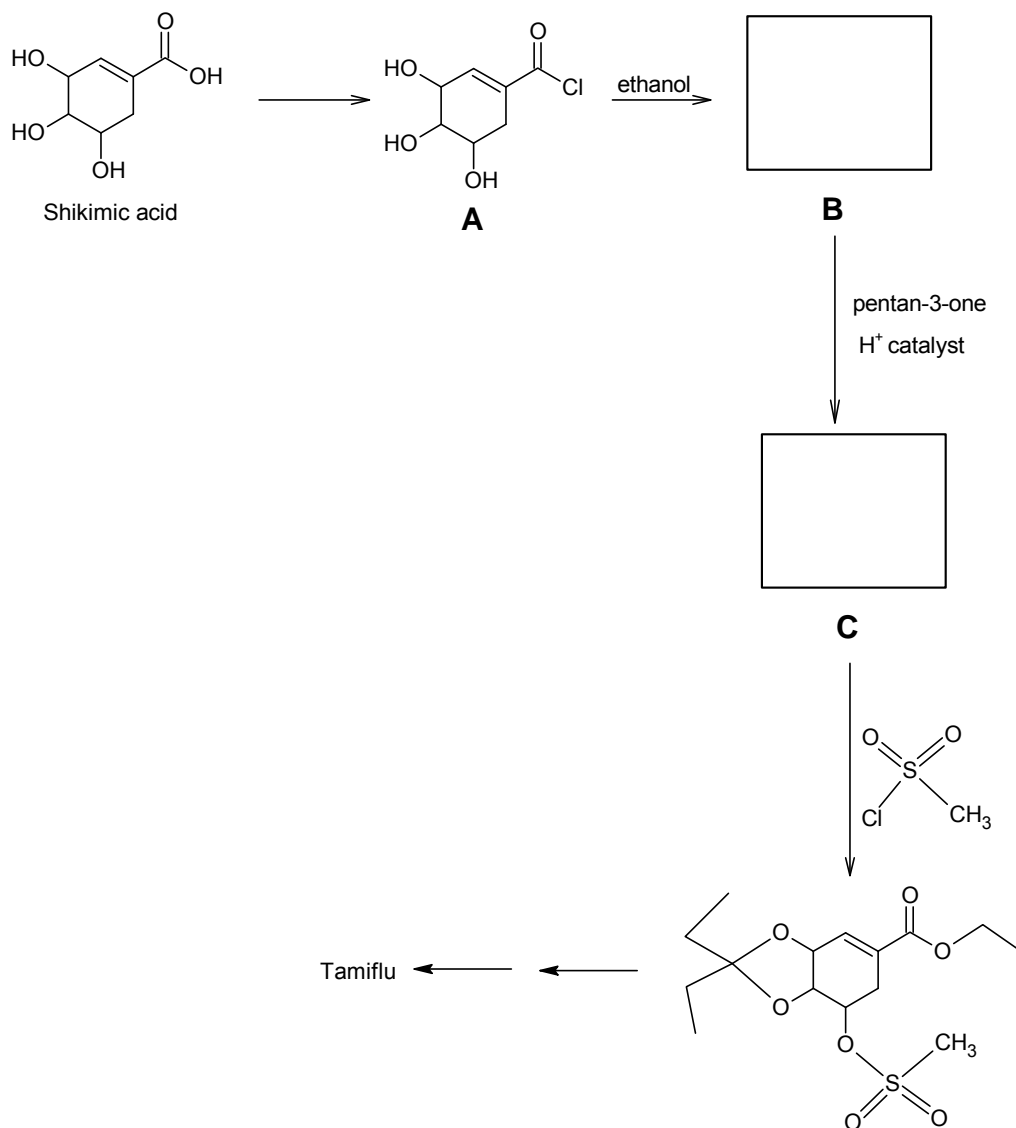
(b) Tamiflu is the anti-influenza drug currently being used to treat 'Bird-flu'. It can be synthesised from Shikimic acid, which occurs naturally in star anise.



Shikimic acid

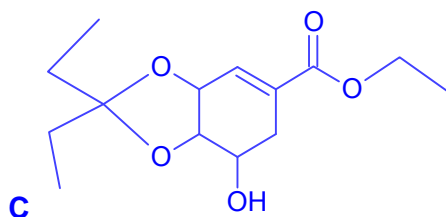
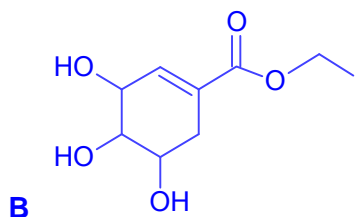
Part of the synthetic route is shown below. Formation of acetals between selected -OH groups of Shikimic acid and ketones helps to control which of the -OH groups reacts to synthesise **C** from **B**.

16



(i) Draw the structures of **B** and **C** in the boxes provided above.

[2]

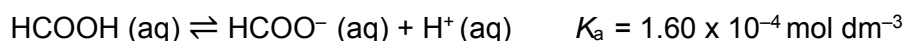


- (ii) Explain why **B** was formed from **A** instead of Shikimic acid directly. [1]

A (acid chloride) is more reactive than Shikimic acid.

Using **A** will give a better yield as the reaction is irreversible compared to reversible reaction when Shikimic acid is used. The reaction also requires milder conditions (doing-away with heating and use of catalyst).

- (c) Like Shikimic acid, methanoic acid occurs naturally in ants. It is a weak acid and dissociates according to the equation shown.



- (i) Explain what is meant by the term pK_a as applied to methanoic acid. [2]

$$pK_a = -\lg K_a$$

$$K_a = \frac{[\text{HCOO}^-][\text{H}^+]}{[\text{HCOOH}]}$$

A flask contains 0.0100 mol of methanoic acid dissolved in 250 cm³ of water.

- (ii) Calculate the pH of this solution. [2]

$$\begin{aligned} [\text{HCOOH}] &= \frac{0.0100}{0.250} \\ &= 0.0400 \text{ mol dm}^{-3} \end{aligned}$$

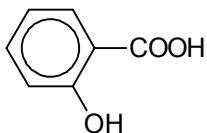
$$\begin{aligned} [\text{H}^+] &= \sqrt{(0.0400)(1.60 \times 10^{-4})} \\ &= 2.5298 \times 10^{-3} \text{ mol dm}^{-3} \end{aligned}$$

$$\begin{aligned} \text{pH} &= -\lg (2.5298 \times 10^{-3}) \\ &= \underline{\underline{2.60}} \end{aligned}$$

- (iii) Hence, calculate the degree of dissociation, α , of methanoic acid in this solution. [1]

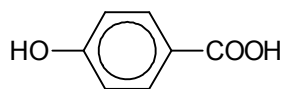
$$\begin{aligned} \alpha &= \frac{[\text{H}^+]}{[\text{HCOOH}]} \\ &= \frac{[2.5298 \times 10^{-3}]}{[0.0400]} \\ &= \underline{\underline{0.0632}} \end{aligned}$$

(d) Salicylic acid occurs naturally in plants.



salicylic acid

$$pK_{a1} = 2.97$$



isomer of
salicylic acid

$$pK_{a1} = 4.54$$

Explain why salicylic acid is more acidic than its isomer.

[2]

The conjugate base formed from the dissociation of salicylic acid is stabilised by hydrogen bonds between the $-OH$ and $-COO^-$ groups.

The conjugate base formed from the dissociation of the isomer **cannot form such a bond as the $-OH$ and $-COO^-$ groups are too far apart.**

Hence the conjugate base formed from the dissociation of salicylic acid is **stabilised to a greater extent** compared to that of the isomer. The position of the dissociation equilibrium lies more to the right and salicylic acid is a stronger acid than the isomer.

[Total: 15]

Name:		Index Number:		Class:	
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DUNMAN HIGH SCHOOL
Preliminary Examination 2018
Year 6

H2 CHEMISTRY

9729/03

Paper 3 Free Response

18 September 2018

2 hours

Candidates answer on separate paper.

Additional Materials: Data Booklet
Writing Paper
Cover Sheet
Graph Paper

INSTRUCTIONS TO CANDIDATES

- 1 Write your **name**, **index number** and **class** on this cover page and on the Cover Sheet provided.
- 2 Write your answers on the separate writing papers provided.
- 3 Write in dark blue or black pen.
- 4 You may use an HB pencil for any diagrams or graphs.
- 5 **Start each question on a fresh sheet of paper.**
**[Marks will be deducted if you fail to do so.]*
- 6 At the end of the examination, fasten all your work securely together with the Cover Sheet on top.
- 7 Do not use staples, paper clips, glue or correction fluid.

Section A

- 8 Answer **all** questions

Section B

- 9 Answer **one** question.

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

You are advised to show all workings in calculations.

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

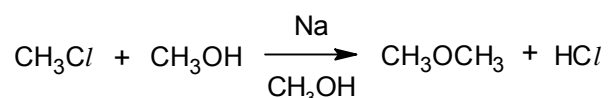
This question paper consists of **16** printed pages and **0** blank page.

Section A

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

- 1 The Williamson ether synthesis is an organic reaction, forming an ether from a halogenoalkane and alcohol in the presence of sodium. This reaction was developed by Alexander Williamson in 1850 and still remains the simplest and most popular method of preparing ethers till today.

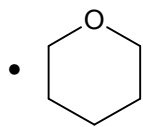
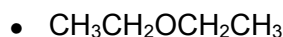
The following equation shows the formation of dimethyl ether, a common aerosol propellant.



- (a) (i) State the purpose of sodium used in the Williamson ether synthesis. [1]

- (ii) Hence, name the mechanism of the reaction. [1]

- (iii) Suggest suitable reagent(s) to synthesise each of the following ethers.



[2]

- (b) Dimethyl ether is known as a symmetrical ether whereas *tert*-butyl ethyl ether, $\text{CH}_3\text{CH}_2\text{OC}(\text{CH}_3)_3$ is an example of an unsymmetrical ether. To prepare *tert*-butyl ethyl ether via the Williamson ether synthesis, there are two possible combinations of reagents, as shown in the table below.

Combination	Reagents
A	$\text{CH}_3\text{CH}_2\text{Br}$ and $(\text{CH}_3)_3\text{COH}$
B	$(\text{CH}_3)_3\text{CBr}$ and $\text{CH}_3\text{CH}_2\text{OH}$

- Identify the combination of reagents that might favour the mechanism identified in (a)(ii) and justify your choice, with reasoning. [2]

- (c) Since the middle of 1990s, dimethyl ether (DME) has been identified as a reliable diesel alternative for cars. The table below compares the physical and chemical properties of DME and diesel fuel.

Property	Unit	DME	Diesel Fuel
Carbon content	mass %	52.2	86
Hydrogen content	mass %	1 – 3	14
Oxygen content	mass %	34.8	0
Liquid density	kg m ⁻³	667	831
*Auto-ignition temperature	K	508	523
^Stoichiometric air/fuel mass ratio	-	9.6	14.6
Normal boiling point	K	248.1	450 – 643
Enthalpy of vaporisation	kJ kg ⁻¹	467.1	300
Energy released at burning	MJ kg ⁻¹	27.6	42.5

*Auto-ignition temperature is the temperature at which a fuel will ignite spontaneously without an external ignition source.

^Stoichiometric air/fuel mass ratio is the mass ratio of air to fuel that completely burns the fuel with no excess air.

With reference to the table, suggest one advantage and one disadvantage of using DME as compared to the conventional diesel fuel.

[2]

- (d) Scientists have recently discovered a new way of synthesising DME by reacting carbon dioxide directly with hydrogen in the presence of Cu-Zn/Al₂O₃ catalyst.

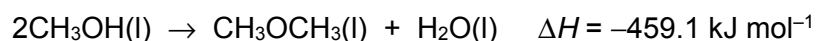
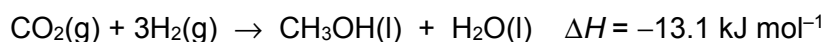
(i) Write the balanced equation for the synthesis of DME from carbon dioxide and hydrogen.

[1]

(ii) State the type of catalysis that Cu-Zn/Al₂O₃ performs and explain briefly how it promotes the synthesis of DME.

[3]

(iii) DME can also be synthesised from carbon dioxide via a two-step reaction in the laboratory.



Using the thermochemical equations given and any relevant data in part (c), draw an energy cycle to determine the enthalpy change of reaction for the synthesis of DME from carbon dioxide and hydrogen at room temperature and pressure.

[5]

- (e) Both dimethyl ether and dimethyl amine have similar hybridisation around the heteroatoms, O and N, respectively.
- (i) State the type of hybridisation of the O and N atoms in dimethyl ether and dimethyl amine respectively. [1]
- (ii) Dimethyl ether has a solubility of 7.1 g per litre of water but dimethyl amine has a solubility of 3.54 kg per litre of water instead. Using suitable equation(s), explain briefly the difference in the solubilities between the two compounds. [3]
- (iii) A 0.1 mol dm^{-3} solution of dimethyl amine containing an unknown concentration of dimethylamine hydrochloride has a pH of 10.57. Given that the numerical value of K_b of dimethyl amine is 7.4×10^{-4} , determine the concentration of dimethylamine hydrochloride in the solution. [3]
- (iv) Explain why trimethyl amine has a higher pK_b than dimethyl amine. [1]

[Total: 25]

2 (a) Carbon undergoes combustion in oxygen to form two common oxides, CO and CO₂. These oxides are also formed when solid magnesium oxalate, MgC₂O₄, is heated strongly.

(i) Explain why magnesium oxalate decomposes at a lower temperature than barium oxalate, BaC₂O₄. [2]

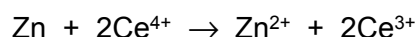
(ii) ZnC₂O₄ undergoes a similar reaction when heated strongly, even though zinc is not a Group 2 element.

Write an equation, with state symbols, to represent the thermal decomposition of solid zinc oxalate. [1]

(iii) Draw the dot-and-cross diagram of C₂O₄²⁻.

State the shape and bond angle around the carbon atoms of the ion. [3]

(b) Zinc can also be used in the manufacturing of rechargeable batteries. Zinc–cerium battery is a type of rechargeable battery using a two–electrolyte system. The overall equation for the discharging process is given below.



(i) Given that the typical cell voltage for the cell is 2.2 V, calculate the standard electrode potential of the Ce⁴⁺/Ce³⁺ half–cell, using relevant data from the *Data Booklet*. [1]

(ii) Using relevant data from the *Data Booklet*, deduce if the Ce⁴⁺/Ce³⁺ half–cell can be replaced with Br₂/Br⁻ half–cell. [1]

- (c) Nickel–metal hydride (Ni–MH) batteries are the most common rechargeable batteries used for devices that require large amounts of energy. Most Ni–MH batteries use an alloy containing mainly lanthanum and nickel.

In one such battery, one of the electrodes is LaNi_5H_6 and the other is $\text{NiO}(\text{OH})$. The electrolyte is aqueous KOH . During the discharging process, an electrochemical reaction takes place to produce $\text{LaNi}_5(\text{s})$ and $\text{Ni}(\text{OH})_2(\text{s})$, and releases electrical energy.

- (i) Construct a half–equation for the reaction that take place at each electrode during discharging.

[2]

- (ii) During recharging, an electrical potential is applied across the electrodes to reverse the electrochemical reaction.

Using your answer in (c)(i), write the overall equation for the reaction that occurs during recharging.

[1]

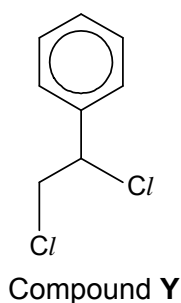
- (iii) Overcharging the Ni–MH battery may result in the electrolyte being discharged at the electrodes to form gaseous products. A safety vent is thus incorporated in the battery to release the excess pressure.

With reference to the *Data Booklet*, suggest a relevant half–equation, with state symbols, for the reaction occurring at one of the electrodes of the Ni–MH battery.

[1]

[Total: 12]

- 3 (a) Compounds **X** and **Y** are dichloroalkanes and constitutional isomers of each other. The structure of **Y** is as shown below.



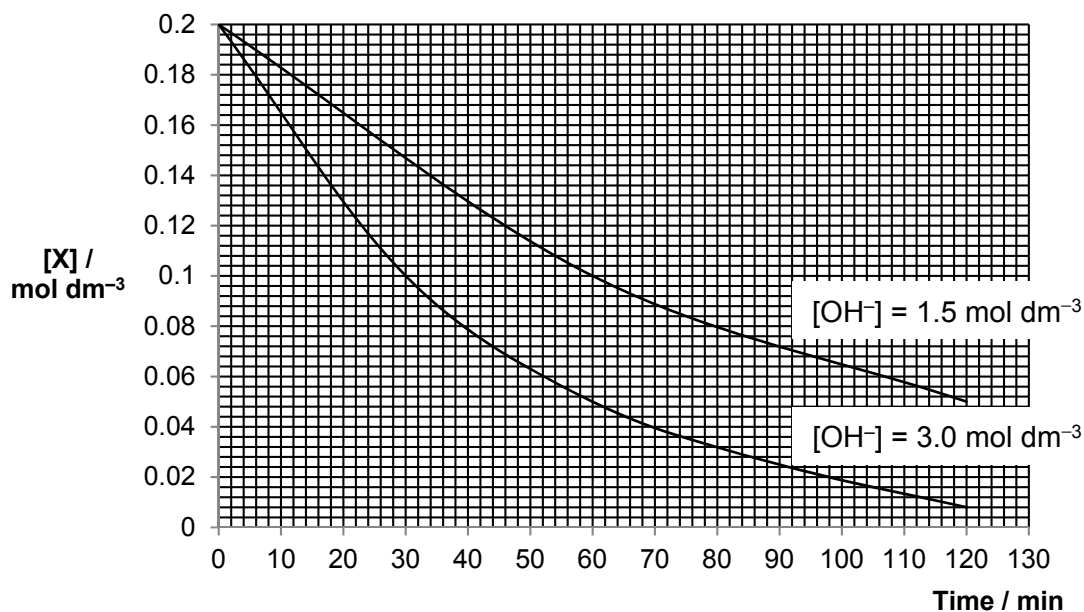
Some additional information is provided about **X**:

- It is not chiral.
- It also contains a benzene ring.
- The two chlorine atoms are not bonded to the same carbon atom.

A series of chemical experiments were also conducted on Compound **X** to further confirm its identity.

Experiment I:

The reaction kinetics of **X** with aqueous sodium hydroxide was determined by monitoring the change in concentration of **X** with time.



Experiment II:

0.25 mol of **X** and **Y** were treated separately with boiling aqueous sodium hydroxide. The products from each compound were then acidified with nitric acid and then treated with silver nitrate solution. The results obtained are shown below.

	Observation upon adding AgNO ₃	Mass of precipitate / g
X	formation of white precipitate	35.85
Y	formation of white precipitate	71.70

- (i) Deduce the rate equation based on the information given in Experiment I. [3]
- (ii) Using your answer in (a)(i) and the information given in Experiment II, deduce, with reasoning, a possible structure of X. [2]
- (iii) Draw the mechanism for the reaction of X with aqueous sodium hydroxide. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons. [3]
- (b) Depending on the mechanism, the solvent affects the stability of nucleophile and/or reaction intermediates in the nucleophilic substitution of halogenoalkanes (RX). The table below shows the rates of reaction when different halogenoalkanes and solvents are used.

Solvent	Type	Relative rates of reaction with OH ⁻	
		1° RX in S _N 2	3° RX in S _N 1
CH ₃ OH	Protic	1	4
H ₂ O	Protic	7	150 000
CH ₃ COOH	Protic	1	1
CH ₃ COCH ₃	Aprotic	5000	–

- (i) Suggest, using **only** structure and bonding, the difference between *protic* and *aprotic* solvents, in terms of solvent-solvent interactions. [1]
- (ii) Suggest an explanation for the effect of solvent on the relative rate of S_N2 reactions. [2]
- (iii) Explain, with an aid of a diagram, how water increases the rate of S_N1 reaction. [2]
- (iv) Would the rate of S_N1 reaction be faster or slower if hexane was used in place of ethanoic acid? [1]

- (c) Silver forms a series of halides of general formula AgX. The chloride, bromide and iodide of silver are sparingly soluble in water at room temperature.

Data about the solubilities in water and the solubility products of the chloride, bromide and iodide of silver at 298 K are given below.

Salt	Solubility / mol dm ⁻³	Solubility product / mol ² dm ⁻⁶
AgCl	1.4 x 10 ⁻⁵	2.0 x 10 ⁻¹⁰
AgBr	7.1 x 10 ⁻⁷	5.0 x 10 ⁻¹³
AgI	8.9 x 10 ⁻⁹	to be calculated

- (i) Write an expression for the solubility product, K_{sp} of silver iodide. [1]

- (ii) From the data above, calculate a value for K_{sp} of silver iodide. [1]

- (iii) Using your answer in (c)(ii), calculate the solubility of AgI in 0.0125 mol dm⁻³ AgNO₃. [2]

- (iv) When silver nitrate is added to solution containing chloride ions, a white precipitate is observed. The white precipitate dissolves when aqueous ammonia was added. Upon adding of aqueous sodium bromide to the resultant mixture, a cream precipitate is obtained.

With the aid of suitable equations, explain the chemistry of the reactions occurring.

[3]

- (v) When a precipitate is formed, ΔG_{ppt}^{\ominus} is given by the following equation.

$$\Delta G_{ppt}^{\ominus} = 2.303 RT \log_{10} K_{sp}$$

For silver fluoride, its K_{sp} value is 1.006 at 298 K.

Use the equation given above to deduce if silver fluoride is soluble in water at 298 K. Explain your answer.

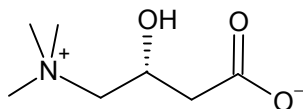
[2]

[Total: 23]

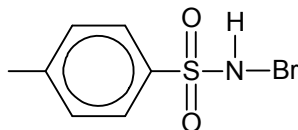
Section B

Answer **one** question from this section.

- 4 Levocarnitine is a quaternary ammonium compound involved in metabolism in most mammals.



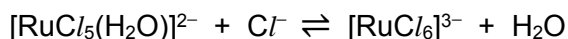
levocarnitine



bromamine-T

- (a) A kinetic study on the reaction between levocarnitine and bromamine-T, in the presence of RuCl_3 , was carried out in aqueous hydrochloric acid.

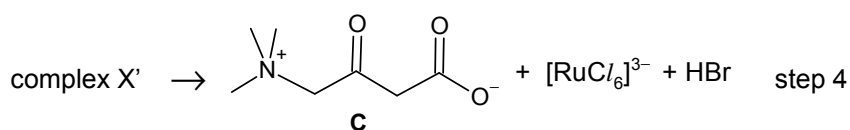
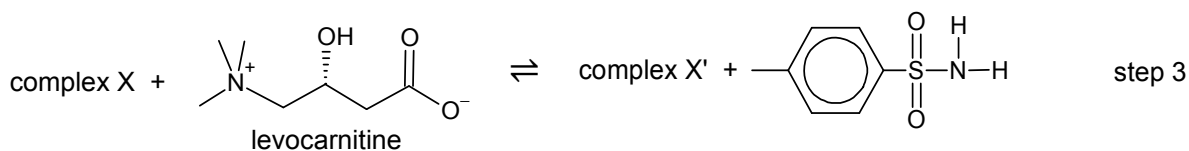
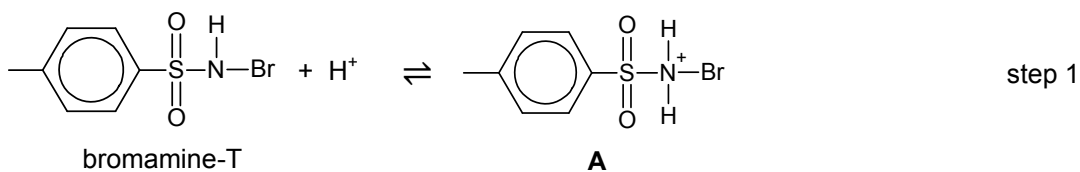
The following equilibrium exists for RuCl_3 in aqueous hydrochloric acid.



Explain why $[\text{RuCl}_6]^{3-}$ is likely to be the reactive species instead of $[\text{RuCl}_5(\text{H}_2\text{O})]^{2-}$ in this study.

[1]

- (b) The mechanism for the reaction between levocarnitine and bromamine-T was proposed as follows.



(i) Use the Lewis theory of acids and bases to identify and explain the role of bromamine-T in step 1. [1]

(ii) The species in the equations shown have various roles. They can be reactants, products, catalysts or intermediates.

Suggest, with a reason in each case, the roles of the species **A**, **B** and **C**. [3]

(iii) State the type of reaction that levocarnitine had undergone with bromamine-T. Explain your answer in terms of changes in oxidation number. [2]

(c) A series of experiments were carried out at different temperatures under pseudo-first order conditions with respect to bromamine-T.

The value of the observed rate constant, k' , for the catalysed reaction was determined at each temperature and the results are summarised in the table below.

k' / 10^4 s^{-1}	temperature, T / K
1.82	293
3.00	303
4.62	313
7.30	323

The activation energy, E_a , and the pre-exponential factor, A , which is a constant, for the reaction can be determined from the equation.

$$k' = Ae^{\frac{-E_a}{RT}}$$

R is the molar gas constant.

T is the reaction temperature in Kelvin.

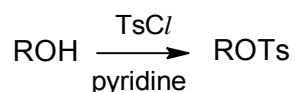
k' is the observed rate constant at a chosen temperature.

(i) Calculate the values of $\ln k'$ and $\frac{1}{T}$ for each of the experiments above. [2]

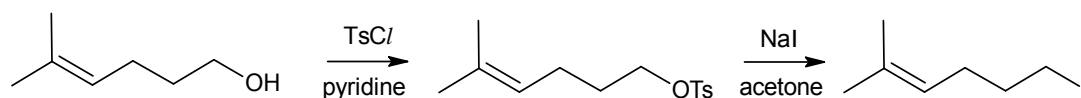
(ii) Hence plot a graph of $\ln k'$ against $\frac{1}{T}$ and determine E_a from the gradient of the best-fit line which is $\frac{-E_a}{R}$. [4]

(iii) How would you expect the activation energy and rate of the reaction to be different if the reaction was uncatalysed? Explain your answer with the aid of a Boltzmann distribution curve. [3]

- (d) Tosyl chlorides (TsCl) are often used to convert alcohols (ROH) into alkyl tosylates (ROTs) as shown below.

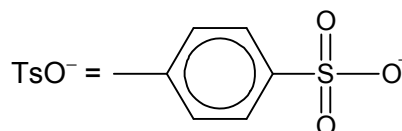


This conversion allows alcohols to undergo nucleophilic substitution reactions by converting the poor leaving group (OH) into a good leaving group (OTs). An example of this application is given below.



- (i) The tosylate group is a better leaving group than the alcohol group due to the greater stability of the TsO^- ion formed compared to OH^- .

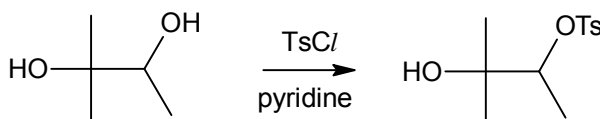
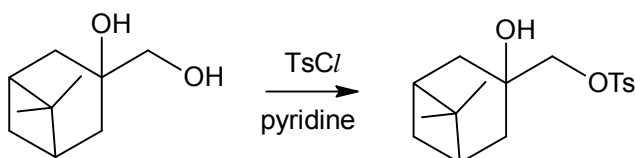
Suggest an explanation for the stability of the TsO^- ion.



[1]

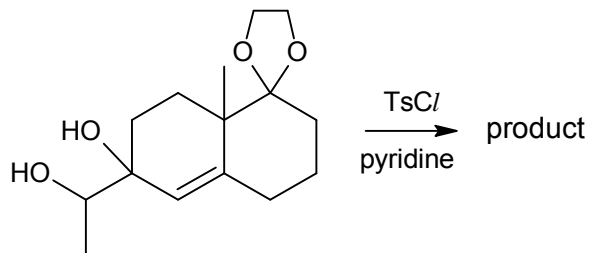
- (ii) The conversion of alcohols into alkyl tosylates using tosyl chlorides is selective in nature.


Consider the following examples involving diols and suggest a factor that affects the selectivity of the conversion. Explain your answer.



[2]

(iii) Predict the product of the following conversion.



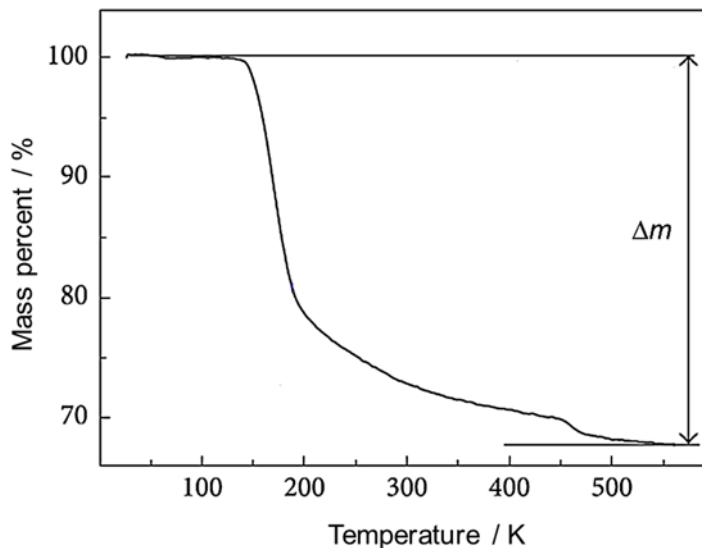
The  ring remains unaltered in the reaction.

[1]

[Total: 20]

- 5 (a) Thermogravimetric analysis (TGA) is a technique where the mass of a sample in a controlled atmosphere is recorded as a function of temperature as the temperature of the sample is increased.

A sample of lithium pentaborate pentahydrate ($\text{LiB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}$) was subject to TGA and the graph obtained is shown below.



Suggest an explanation, supported with relevant calculations, for the loss in mass (Δm) of $\text{LiB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}$ observed in the graph.

$$[M_r(\text{LiB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}) = 278.9]$$

[2]

- (b) The sample of $\text{LiB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}$ used in (a) was synthesised as a system of Li_2O , B_2O_3 and H_2O in the laboratory.

- (i) Deduce the molar ratio of $\text{Li}_2\text{O} : \text{B}_2\text{O}_3 : \text{H}_2\text{O}$ in a pure sample of $\text{LiB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}$.

[1]

- (ii) Aqueous sodium hydroxide can be used to react with B_2O_3 to determine its actual amount in the sample.

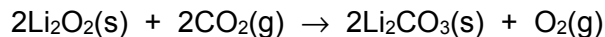
Given that B_2O_3 and Al_2O_3 have similar reactions with aqueous sodium hydroxide under appropriate conditions, write a balanced equation for the reaction between B_2O_3 and aqueous sodium hydroxide.

[1]

(c) Li_2O can be produced from the thermal decomposition of lithium peroxide, Li_2O_2 .

(i) State and explain how the lattice energies of Li_2O and Li_2O_2 would differ. [2]

(ii) Lithium peroxide reacts with carbon dioxide according to the equation shown below.



State the change in oxidation number of oxygen as Li_2O_2 is converted into the products.

[2]

(iii) Calculate the highest temperature reached when the 2.50 g of lithium carbonate was dissolved in 30 cm^3 of water at room temperature. The standard enthalpy change of solution of lithium carbonate is $-18.2 \text{ kJ mol}^{-1}$.

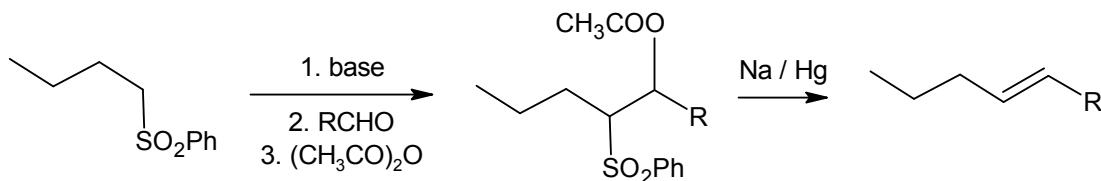
[2]

(iv) Calculate the pH of the resulting solution formed in (c)(iii) given that the K_b of carbonate ion is $1.995 \times 10^{-4} \text{ mol dm}^{-3}$.

[3]

- (d) Phenylsulfonyl (PhSO_2) and acetate (CH_3COO) groups on adjacent carbons in a starting material can be lost to form an alkene via Julia olefination.

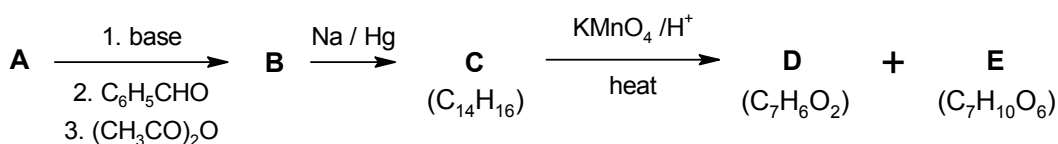
An example of Julia olefination is as follows.



- (i) Suggest the type of reaction occurring in the final step of Julia olefination.

[1]

Consider the reaction scheme below involving Julia olefination.



- (ii) Compound **D** effervesces with sodium carbonate. Suggest the structure of **D**.
- (iii) Compound **E** is non-cyclic and has six carbons in the longest continuous carbon chain. It also does **not** contain any chiral carbon.

One mole of **E** reacts with three moles of thionyl chloride (SOCl_2) to liberate acidic gas.

Identify the functional group present in **E** and suggest its structure.

[2]

- (iv) Hence suggest the structures of compounds **A** to **C**.

[3]

[Total: 20]



DUNMAN HIGH SCHOOL
Preliminary Examination 2018
Year 6

H2 CHEMISTRY

Paper 3 Free Response

9729/03

18 September 2018

2 hours

Candidates answer on separate paper.

Additional Materials: Data Booklet
Writing Paper
Cover Sheet
Graph Paper

INSTRUCTIONS TO CANDIDATES

- 1 Write your **name**, **index number** and **class** on this cover page and on the Cover Sheet provided.
- 2 Write your answers on the separate writing papers provided.
- 3 Write in dark blue or black pen.
- 4 You may use an HB pencil for any diagrams or graphs.
- 5 **Start each question on a fresh sheet of paper.**
**[Marks will be deducted if you fail to do so.]*
- 6 At the end of the examination, fasten all your work securely together with the Cover Sheet on top.
- 7 Do not use staples, paper clips, glue or correction fluid.

Section A

- 8 Answer **all** questions

Section B

- 9 Answer **one** question.

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

You are advised to show all workings in calculations.

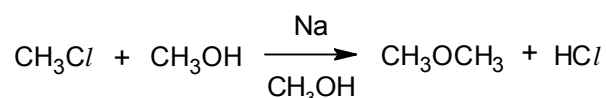
You are reminded of the need for good English and clear presentation in your answers.

Section A

Answer **all** questions.

- 1 The Williamson ether synthesis is an organic reaction, forming an ether from a halogenoalkane and alcohol in the presence of sodium. This reaction was developed by Alexander Williamson in 1850 and still remains the simplest and most popular method of preparing ethers till today.

The following equation shows the formation of dimethyl ether, a common aerosol propellant.



- (a) (i) State the purpose of sodium used in the Williamson ether synthesis. [1]

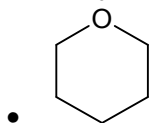
Sodium reacts with CH_3OH to form a **stronger nucleophile, CH_3O^-**

- (ii) Hence, name the mechanism of the reaction. [1]

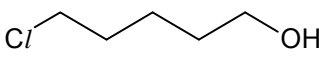
$\text{S}_{\text{N}}2$ / bimolecular nucleophilic substitution

- (iii) Suggest suitable reagent(s) to synthesise each of the following ethers.

- $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$



- $\text{CH}_3\text{CH}_2\text{OH}$ (in the presence of Na) and $\text{CH}_3\text{CH}_2\text{Cl}$

-  (in the presence of Na)

- (b) Dimethyl ether is known as a symmetrical ether whereas *tert*-butyl ethyl ether, $\text{CH}_3\text{CH}_2\text{OC}(\text{CH}_3)_3$ is an example of an unsymmetrical ether. To prepare *tert*-butyl ethyl ether via the Williamson ether synthesis, there are two possible combinations of reagents, as shown in the table below.

Combination	Reagents
A	$\text{CH}_3\text{CH}_2\text{Br}$ and $(\text{CH}_3)_3\text{COH}$
B	$(\text{CH}_3)_3\text{CBr}$ and $\text{CH}_3\text{CH}_2\text{OH}$

Identify the combination of reagents that might favour the mechanism identified in (a)(ii) and justify your choice, with reasoning.

[2]

Combination **A**

$\text{CH}_3\text{CH}_2\text{Br}$ is a **primary alkyl halide**, and hence it will be **less sterically hindered** for the nucleophile / alkoxide ion to **attack from the back** of the halogen as compared to $(\text{CH}_3)_3\text{CBr}$, a tertiary alkyl halide.

- (c) Since the middle of 1990s, dimethyl ether (DME) has been identified as a reliable diesel alternative for cars. The table below compares the physical and chemical properties of DME and diesel fuel.

Property	Unit	DME	Diesel Fuel
Carbon content	mass %	52.2	86
Hydrogen content	mass %	1 – 3	14
Oxygen content	mass %	34.8	0
Liquid density	kg m ⁻³	667	831
*Auto-ignition temperature	K	508	523
^Stoichiometric air/fuel mass ratio	-	9.6	14.6
Normal boiling point	K	248.1	450 – 643
Enthalpy of vaporisation	kJ kg ⁻¹	467.1	300
Energy released at burning	MJ kg ⁻¹	27.6	42.5

*Auto-ignition temperature is the temperature at which a fuel will ignite spontaneously without an external ignition source.

^Stoichiometric air/fuel mass ratio is the mass ratio of air to fuel that completely burns the fuel with no excess air.

With reference to the table, suggest one advantage and one disadvantage of using DME as compared to the conventional diesel fuel.

[2]

Advantage: DME has **lower carbon content** than diesel fuel, and thus contribute to **lower carbon dioxide emission** when the same mass is burnt.

Disadvantage: DME releases **less energy at burning** than diesel fuel, and thus is a **less efficient fuel** for the same mass used.

- (d) Scientists have recently discovered a new way of synthesising DME by reacting carbon dioxide directly with hydrogen in the presence of Cu-Zn/Al₂O₃ catalyst.

- (i) Write the balanced equation for the synthesis of DME from carbon dioxide and hydrogen.

[1]



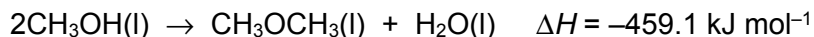
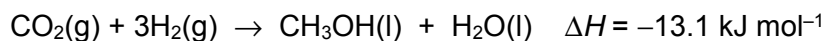
- (ii) State the type of catalysis that Cu-Zn/Al₂O₃ performs and explain briefly how it promotes the synthesis of DME.

[3]

Heterogeneous catalysis

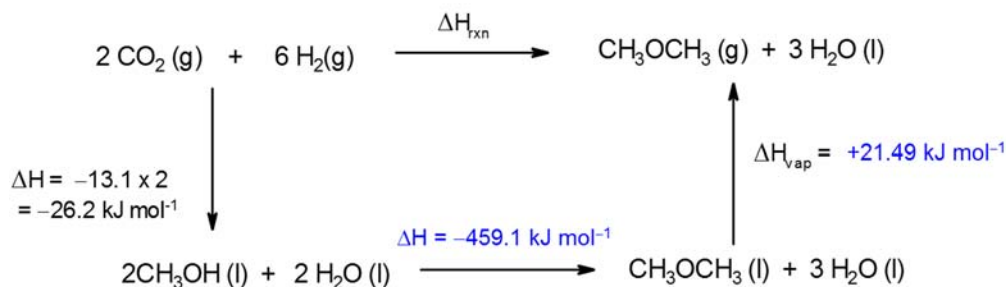
Both H₂ and CO₂ reactants are gases. The solid catalyst provides a surface for the **gaseous molecules to be adsorbed** to the surface, **thus increasing the concentration of the reactants / bringing the molecules closer together** and **weakening the bonds of the reactants molecules**, resulting in a lower E_a.

- (iii) DME can also be synthesised from carbon dioxide via a two-step reaction in the laboratory.



Using the thermochemical equations given and any relevant data in part (c), draw an energy cycle to determine the enthalpy change of reaction for the synthesis of DME from carbon dioxide and hydrogen at room temperature and pressure.

[5]



$$\Delta H_{\text{vap}} = 467.1/1000 \times 46 = +21.49 \text{ kJ mol}^{-1}$$

By Hess' Law,

$$\begin{aligned} \Delta H_{\text{rxn}} &= -26.2 - 459.1 + 21.49 \\ &= \underline{\underline{-464 \text{ kJ mol}^{-1}}} \end{aligned}$$

- (e) Both dimethyl ether and dimethyl amine have similar hybridisation around the heteroatoms, O and N, respectively.

- (i) State the type of hybridisation of the O and N atoms in dimethyl ether and dimethyl amine respectively.

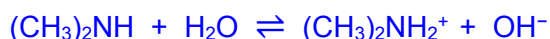
[1]

sp^3

- (ii) Dimethyl ether has a solubility of 7.1 g per litre of water but dimethyl amine has a solubility of 3.54 kg per litre of water instead. Using suitable equation(s), explain briefly the difference in the solubilities between the two compounds.

[3]

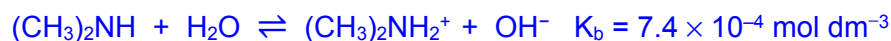
DME can form hydrogen bonds with water molecules whereas dimethyl amine is a weak base and can partially dissociate in water in to form ions which can form ion-dipole interactions with water molecules, hence dimethyl amine has a higher solubility in water.



- (iii) A 0.1 mol dm^{-3} solution of dimethyl amine containing an unknown concentration of dimethylamine hydrochloride has a pH of 10.57. Given that the numerical value of K_b of dimethyl amine is 7.4×10^{-4} , determine the concentration of dimethylamine hydrochloride in the solution.

[3]

A buffer system is set up.



$$\text{pH} = 10.57$$

$$\text{pOH} = 14 - 10.57 = 3.43$$

$$[\text{OH}^-] = 10^{-3.43} \text{ mol dm}^{-3}$$

$$K_b = \frac{[(\text{CH}_3)_2\text{NH}_2^+][\text{OH}^-]}{[(\text{CH}_3)_2\text{NH}]}$$

$$7.4 \times 10^{-4} = \frac{[(\text{CH}_3)_2\text{NH}_2^+][10^{-3.43}]}{0.1}$$

$$\begin{aligned} [(\text{CH}_3)_2\text{NH}_2^+] &= \frac{7.4 \times 10^{-4} \times 0.1}{10^{-3.43}} \\ &= 0.199 \text{ mol dm}^{-3} \end{aligned}$$

OR

$$\text{pOH} = \text{p}K_b + \log_{10} \left(\frac{[(\text{CH}_3)_2\text{NH}_2^+]}{[(\text{CH}_3)_2\text{NH}]} \right)$$

$$14 - 10.57 = -\log_{10}(7.4 \times 10^{-4}) + \log_{10} \left(\frac{[(\text{CH}_3)_2\text{NH}_2^+]}{0.1} \right)$$

$$[(\text{CH}_3)_2\text{NH}_2^+] = 0.199 \text{ mol dm}^{-3}$$

- (iv) Explain why trimethyl amine has a higher $\text{p}K_b$ than dimethyl amine.

[1]

The lone pair of electrons on N in trimethyl amine is less available for donation as it is more sterically hindered with one more $-\text{CH}_3$ group than dimethyl amine, hence decreasing its basicity.

[Total: 25]

- 2 (a) Carbon undergoes combustion in oxygen to form two common oxides, CO and CO₂. These oxides are also formed when solid magnesium oxalate, MgC₂O₄, is heated strongly.

- (i) Explain why magnesium oxalate decomposes at a lower temperature than barium oxalate, BaC₂O₄.

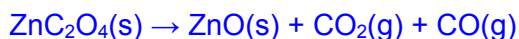
[2]

Mg²⁺ has a **smaller ionic radius and a higher charge density** than Ba²⁺. Therefore, Mg²⁺ has a **greater polarising power** than Ba²⁺. Mg²⁺ **distorts the electron cloud of C₂O₄²⁻ anion / weakens the bonds in the C₂O₄²⁻ anion to a greater extent**. Hence MgC₂O₄ is less thermally stable.

- (ii) ZnC₂O₄ undergoes a similar reaction when heated strongly, even though zinc is not a Group 2 element.

Write an equation, with state symbols, to represent the thermal decomposition of solid zinc oxalate.

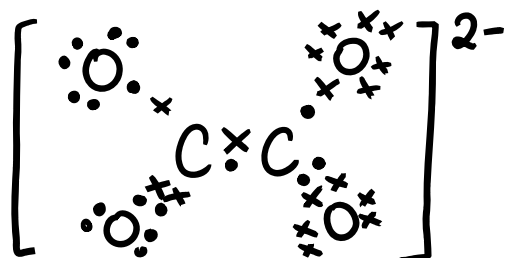
[1]



- (iii) Draw the dot-and-cross diagram of C₂O₄²⁻.

State the shape and bond angle around the carbon atoms of the ion.

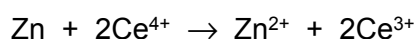
[3]



Shape: Trigonal Planar about each C atom

Bond Angle: 120°

- (b) Zinc can also be used in the manufacturing of rechargeable batteries. Zinc–cerium battery is a type of rechargeable battery using a two–electrolyte system. The overall equation for the discharging process is given below.



- (i) Given that the typical cell voltage for the cell is 2.2 V, calculate the standard electrode potential of the Ce⁴⁺/Ce³⁺ half–cell, using relevant data from the *Data Booklet*.

[1]

From the Data Booklet,

$$E^\ominus(\text{Zn}^{2+}/\text{Zn}) = -0.76 \text{ V}$$

$$E^\ominus_{\text{cell}} = E^\ominus_{\text{cathode}} - E^\ominus_{\text{anode}}$$

$$2.2 = E^\ominus(\text{Ce}^{4+}/\text{Ce}^{3+}) - (-0.76)$$

$$E^\ominus(\text{Ce}^{4+}/\text{Ce}^{3+}) = +1.44 \text{ V}$$

- (ii) Using relevant data from the *Data Booklet*, deduce if the $\text{Ce}^{4+}/\text{Ce}^{3+}$ half-cell can be replaced with Br_2/Br^- half-cell.

[1]

From the *Data Booklet*,

$$E^\ominus(\text{Br}_2/\text{Br}^-) = +1.07 \text{ V}$$

$$\begin{aligned} E^\ominus_{\text{cell}} &= +1.07 - (-0.76) \\ &= +1.83 \text{ V} > 0 \text{ (feasible)} \end{aligned}$$

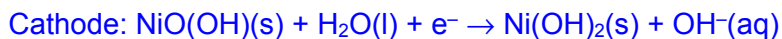
Since it is feasible for the battery to discharge electricity, the $\text{Ce}^{4+}/\text{Ce}^{3+}$ half-cell can be replaced with Br_2/Br^- half-cell.

- (c) Nickel–metal hydride (Ni–MH) batteries are the most common rechargeable batteries used for devices that require large amounts of energy. Most Ni–MH batteries use an alloy containing mainly lanthanum and nickel.

In one such battery, one of the electrodes is LaNi_5H_6 and the other is $\text{NiO}(\text{OH})$. The electrolyte is aqueous KOH . During the discharging process, an electrochemical reaction takes place to produce $\text{LaNi}_5(\text{s})$ and $\text{Ni}(\text{OH})_2(\text{s})$, and releases electrical energy.

- (i) Construct a half-equation for the reaction that take place at each electrode during discharging.

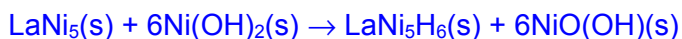
[2]



- (ii) During recharging, an electrical potential is applied across the electrodes to reverse the electrochemical reaction.

Using your answer in (c)(i), write the overall equation for the reaction that occurs during recharging.

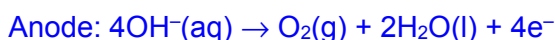
[1]



- (iii) Overcharging the Ni–MH battery may result in the electrolyte being discharged at the electrodes to form gaseous products. A safety vent is thus incorporated in the battery to release the excess pressure.

With reference to the *Data Booklet*, suggest a relevant half-equation, with state symbols, for the reaction occurring at one of the electrodes of the Ni–MH battery.

[1]

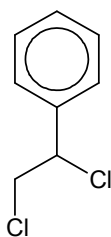


OR



[Total: 12]

- 3 (a) Compounds **X** and **Y** are dichloroalkanes and constitutional isomers of each other. The structure of **Y** is as shown below.



Compound **Y**

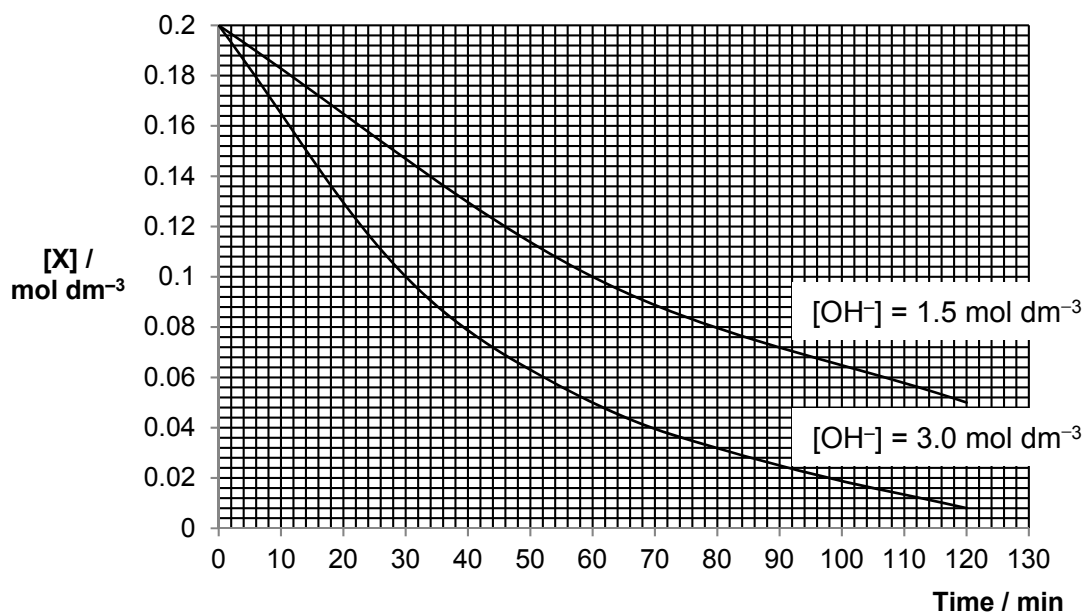
Some additional information is provided about **X**:

- It is not chiral.
- It also contains a benzene ring.
- The two chlorine atoms are not bonded to the same carbon atom.

A series of chemical experiments were also conducted on Compound **X** to further confirm its identity.

Experiment I:

The reaction kinetics of **X** with aqueous sodium hydroxide was determined by monitoring the change in concentration of **X** with time.



Experiment II:

0.25 mol of **X** and **Y** were treated separately with boiling aqueous sodium hydroxide. The products from each compound were then acidified with nitric acid and then treated with silver nitrate solution. The results obtained are shown below.

	Observation upon adding AgNO ₃	Mass of precipitate / g
X	formation of white precipitate	35.85
Y	formation of white precipitate	71.70

- (i) Deduce the rate equation based on the information given in Experiment I. [3]

Using $[\text{OH}^-] = 3.0 \text{ mol dm}^{-3}$ graph,
 $t_{1/2}$ is constant at 30 min, order of reaction with respect to X is 1.

OR

Using $[\text{OH}^-] = 1.5 \text{ mol dm}^{-3}$ graph,
 $t_{1/2}$ is constant at 60 min, order of reaction with respect to X is 1.

Using initial rate method,

Initial rate for graph where $[\text{OH}^-] = 1.5 \text{ mol dm}^{-3}$
 $= 0.2/110 = 0.001818 \text{ mol dm}^{-3} \text{ min}^{-1}$

Initial rate for graph where $[\text{OH}^-] = 3.0 \text{ mol dm}^{-3}$
 $= 0.2/52 = 0.003846 \text{ mol dm}^{-3} \text{ min}^{-1}$

As $[\text{OH}^-]$ increases 2 times, initial rate also increases 2 times
Hence, order of reaction with respect to OH^- is 1.

Rate = k [X] [OH⁻]

- (ii) Using your answer in (a)(i) and the information given in Experiment II, deduce, with reasoning, a possible structure of X. [2]

From (a)(i), X undergoes $\text{S}_{\text{N}}2$ mechanism
 \Rightarrow X is a primary chloroalkane.

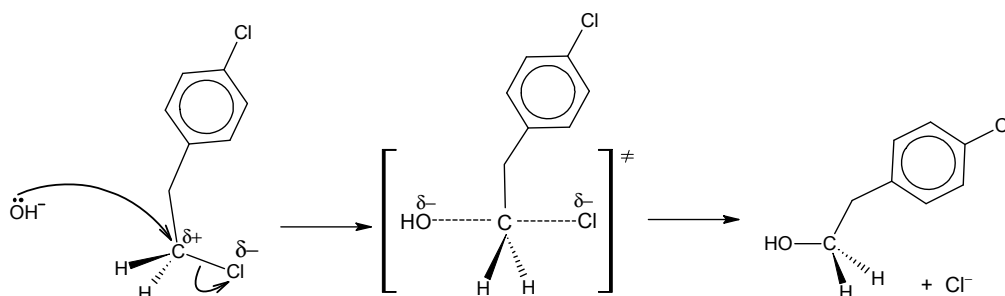
From expt II, 0.25 mol of X forms 0.25 mol of AgCl

\Rightarrow There is only one Cl atom in the alkyl side chain OR there is only one Cl atom bonded to the benzene ring



- (iii) Draw the mechanism for the reaction of **X** with aqueous sodium hydroxide. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons.

[3]



- (b) Depending on the mechanism, the solvent affects the stability of nucleophile and/or reaction intermediates in the nucleophilic substitution of halogenoalkanes (RX). The table below shows the rates of reaction when different halogenoalkanes and solvents are used.

Solvent	Type	Relative rates of reaction with OH ⁻	
		1° RX in S _N 2	3° RX in S _N 1
CH ₃ OH	Protic	1	4
H ₂ O	Protic	7	150 000
CH ₃ COOH	Protic	1	1
CH ₃ COCH ₃	Aprotic	5000	–

- (i) Suggest, using **only** structure and bonding, the difference between *protic* and *aprotic* solvents, in terms of solvent-solvent interactions.

[1]

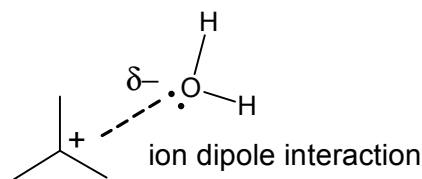
Protic solvent refers to molecules with **H atoms that can be used to form hydrogen bonds**. Aprotic solvents can only form **permanent dipole-permanent dipole interactions between molecules/ have no H atoms that can form hydrogen bonds**.

- (ii) Suggest an explanation for the effect of solvent on the relative rate of S_N2 reactions.

[2]

For S_N2 reactions, protic solvents like water can form **hydrogen bond with OH⁻** and hence, slowing down the rate of reaction. Aprotic solvents like CH₃COCH₃, do not form hydrogen bond and hence **the lone pair of electron on OH⁻ is more available to attack the electron deficient C on 1° RX**.

- (iii) Explain, with an aid of a diagram, how water increases the rate of S_N1 reaction. [2]



The ion dipole interaction stabilised the carbocation.

- (iv) Would the rate of S_N1 reaction be faster or slower if hexane was used in place of ethanoic acid? [1]

Slower.

- (c) Silver forms a series of halides of general formula AgX . The chloride, bromide and iodide of silver are sparingly soluble in water at room temperature.

Data about the solubilities in water and the solubility products of the chloride, bromide and iodide of silver at 298 K are given below.

Salt	Solubility / mol dm^{-3}	Solubility product / $\text{mol}^2 \text{dm}^{-6}$
$AgCl$	1.4×10^{-5}	2.0×10^{-10}
$AgBr$	7.1×10^{-7}	5.0×10^{-13}
AgI	8.9×10^{-9}	to be calculated

- (i) Write an expression for the solubility product, K_{sp} of silver iodide. [1]

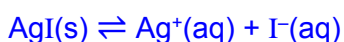
$$K_{sp} = [Ag^+][I^-]$$

- (ii) From the data above, calculate a value for K_{sp} of silver iodide. [1]

$$\begin{aligned} [Ag^+] &= [I^-] \\ K_{sp} &= (8.9 \times 10^{-9})^2 \\ &= \underline{7.92 \times 10^{-17} \text{ mol}^2 \text{dm}^{-6}} \end{aligned}$$

- (iii) Using your answer in (c)(ii), calculate the solubility of AgI in $0.0125 \text{ mol dm}^{-3} AgNO_3$. [2]

Let solubility of AgI in $0.0125 \text{ mol dm}^{-3} AgNO_3$ be $x \text{ mol dm}^{-3}$.



$$K_{sp} = [Ag^+][I^-] = (0.0125 + x)(x) = 7.92 \times 10^{-17}$$

It can be assumed that $x \ll 0.0125$ such that $(0.0125 + x) \approx 0.0125$

$$(0.0125)(x) = 7.92 \times 10^{-17}$$

$$x = 6.34 \times 10^{-15} \text{ mol dm}^{-3}$$

Solubility of AgI in $0.0125 \text{ mol dm}^{-3} \text{ AgNO}_3 = \underline{6.34 \times 10^{-15} \text{ mol dm}^{-3}}$

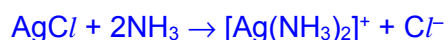
- (iv) When silver nitrate is added to solution containing chloride ions, a white precipitate is observed. The white precipitate dissolves when aqueous ammonia was added. Upon adding of aqueous sodium bromide to the resultant mixture, a cream precipitate is obtained.

With the aid of suitable equations, explain the chemistry of the reactions occurring.

[3]



White ppt is formed due to the formation of insoluble AgCl.



White ppt dissolves due to the formation of a complex ion.



Cream ppt is obtained when NaBr is added to the resultant mixture because K_{sp} of AgBr $<$ K_{sp} of AgCl so ionic product still exceeds K_{sp} of AgBr

- (v) When a precipitate is formed, $\Delta G_{\text{ppt}}^\ominus$ is given by the following equation.

$$\Delta G_{\text{ppt}}^\ominus = 2.303 RT \log_{10} K_{\text{sp}}$$

For silver fluoride, its K_{sp} value is 1.006 at 298 K.

Use the equation given above to deduce if silver fluoride is soluble in water at 298 K. Explain your answer.

[2]

$$\begin{aligned} \Delta G_{\text{ppt}}^\ominus &= 2.303 RT \log_{10} K_{\text{sp}} \\ &= 2.303(8.31)(298)(\log_{10} 1.006) \\ &= \mathbf{+14.8 \text{ J mol}^{-1}} \end{aligned}$$

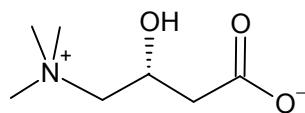
Since $\Delta G_{\text{ppt}}^\ominus > 0$, precipitation will not occur.
Therefore, AgF is soluble in water at 298 K.

[Total: 23]

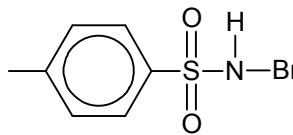
Section B

Answer **one** question from this section.

- 4 Levocarnitine is a quaternary ammonium compound involved in metabolism in most mammals.



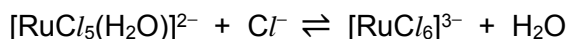
levocarnitine



bromamine-T

- (a) A kinetic study on the reaction between levocarnitine and bromamine-T, in the presence of RuCl_3 , was carried out in aqueous hydrochloric acid.

The following equilibrium exists for RuCl_3 in aqueous hydrochloric acid.

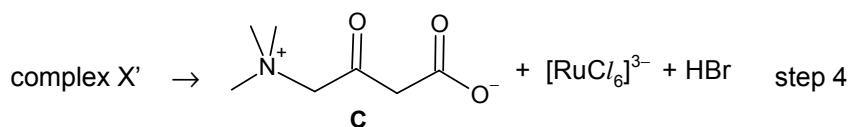
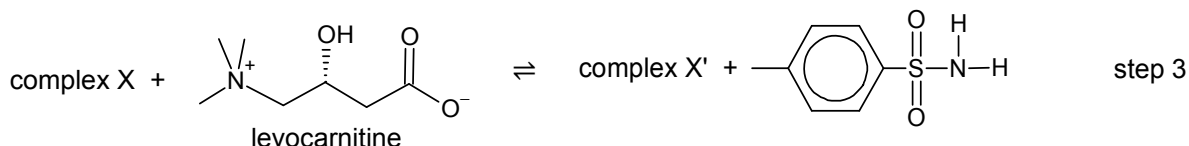
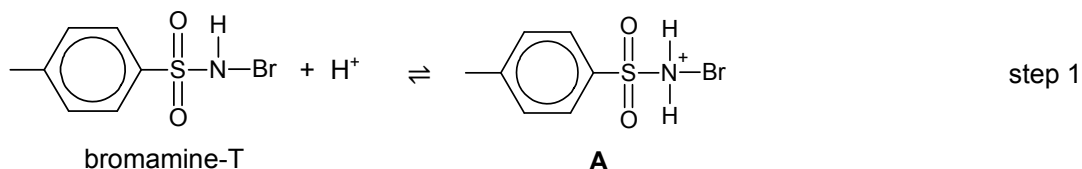


Explain why $[\text{RuCl}_6]^{3-}$ is likely to be the reactive species instead of $[\text{RuCl}_5(\text{H}_2\text{O})]^{2-}$ in this study.

[1]

By Le Chatelier's Principle, the presence of chloride ions from aqueous HCl will shift the position of equilibrium to the right, favouring the formation of $[\text{RuCl}_6]^{3-}$.

- (b) The mechanism for the reaction between levocarnitine and bromamine-T was proposed as follows.



- (i) Use the Lewis theory of acids and bases to identify and explain the role of bromamine-T in step 1.

[1]

Bromamine-T acts as a **Lewis base** in step 1 as it **donates its lone pair of electrons** on N atom to H^+ .

- (ii) The species in the equations shown have various roles. They can be reactants, products, catalysts or intermediates.

Suggest, with a reason in each case, the roles of the species **A**, **B** and **C**.

[3]

A is an **intermediate** as it was **formed in step 1 and then reacted in step 2**.

B is a **catalyst** as it **reacted in step 2 and was regenerated in step 4**.

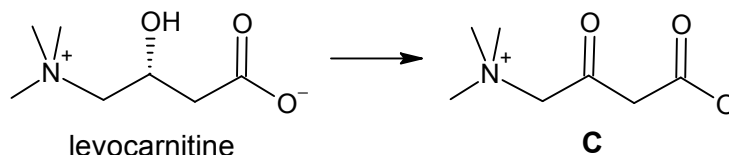
C is a **product** as it was **formed in step 4 and not reacted in other steps**.

- (iii) State the type of reaction that levocarnitine had undergone with bromamine-T. Explain your answer in terms of changes in oxidation number.

[2]

Oxidation

The oxidation number of **carbon** (bonded to -OH group) **increased from 0 in levocarnitine to +2 in species C**.



- (c) A series of experiments were carried out at different temperatures under pseudo-first order conditions with respect to bromamine-T.

The value of the observed rate constant, k' , for the catalysed reaction was determined at each temperature and the results are summarised in the table below.

k' / 10^4 s^{-1}	temperature, T / K
1.82	293
3.00	303
4.62	313
7.30	323

The activation energy, E_a , and the pre-exponential factor, A , which is a constant, for the reaction can be determined from the equation.

$$k' = Ae^{\frac{-E_a}{RT}}$$

R is the molar gas constant.

T is the reaction temperature in Kelvin.

k' is the observed rate constant at a chosen temperature.

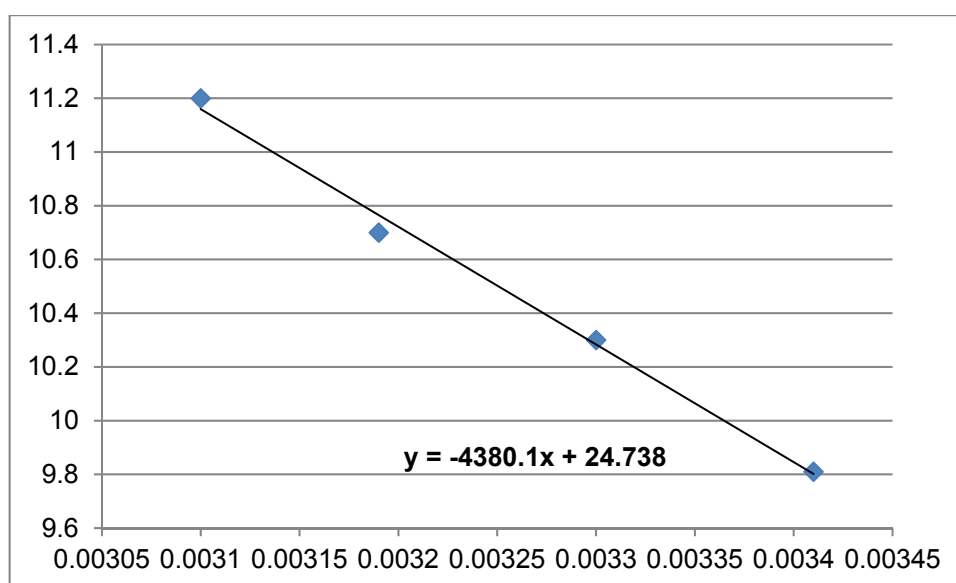
- (i) Calculate the values of $\ln k'$ and $\frac{1}{T}$ for each of the experiments above.

[2]

k' / 10^4 s^{-1}	$\ln k'$	temperature, T / K	$\frac{1}{T}$ / K^{-1}
1.82	9.81	293	0.00341
3.00	10.3	303	0.00330
4.62	10.7	313	0.00319
7.30	11.2	323	0.00310

- (ii) Hence plot a graph of $\ln k'$ against $\frac{1}{T}$ and determine E_a from the gradient of the best-fit line which is $\frac{-E_a}{R}$.

[4]

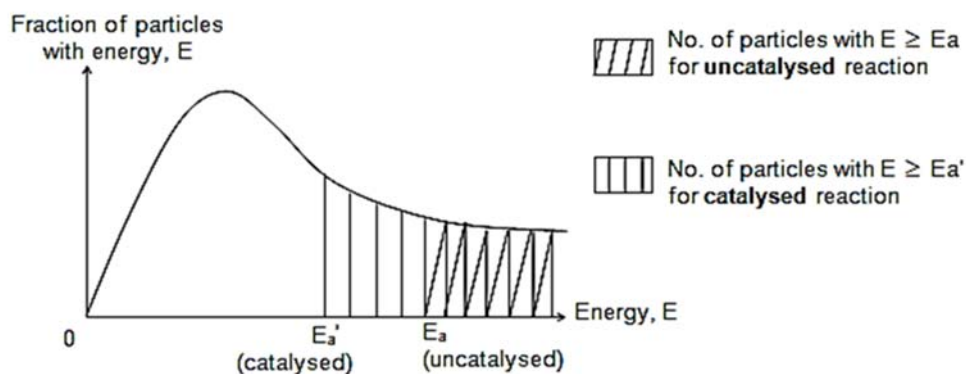


$$\text{Gradient} = \frac{-E_a}{R} = -4380.1 \text{ K}$$

$$\text{Hence } E_a = 36399 \text{ J mol}^{-1} = \underline{\underline{36.4 \text{ kJ mol}^{-1}}}$$

- (iii) How would you expect the activation energy and rate of the reaction to be different if the reaction was uncatalysed? Explain your answer with the aid of a Boltzmann distribution curve.

[3]

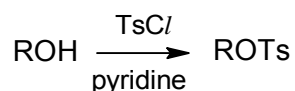


The activation energy will be **higher** and the rate of reaction **slower** if the reaction was uncatalsed.

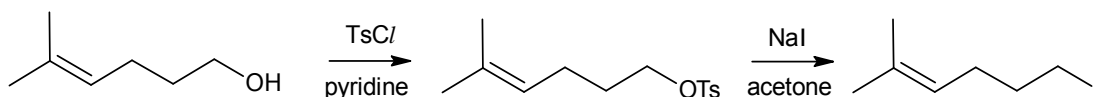
When a catalyst is used,

- reaction takes place via an alternative pathway that requires a lower activation energy
- there are more reactant particles with energy $\geq E_a$ and frequency of effective collisions increases
- rate of reaction increases, since the rate of reaction is proportional to the frequency of effective collisions.

- (d) Tosyl chlorides (TsCl) are often used to convert alcohols (ROH) into alkyl tosylates (ROTs) as shown below.

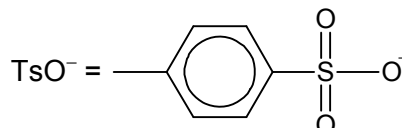


This conversion allows alcohols to undergo nucleophilic substitution reactions by converting the poor leaving group (OH) into a good leaving group (OTs). An example of this application is given below.



- (i) The tosylate group is a better leaving group than the alcohol group due the greater stability of the TsO^- ion formed compared to OH^- .

Suggest an explanation for the stability of the TsO^- ion.

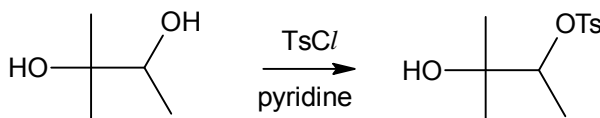
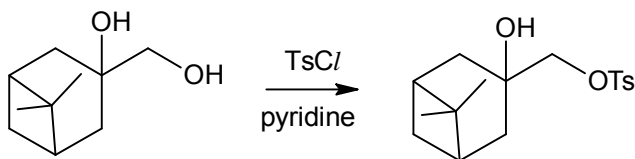


[1]

TsO^- is resonance stabilised as the negative charge on oxygen is delocalised into the adjacent S=O bond.

- (ii) The conversion of alcohols into alkyl tosylates using tosyl chlorides is selective in nature.

Consider the following examples involving diols and suggest a factor that affects the selectivity of the conversion. Explain your answer.

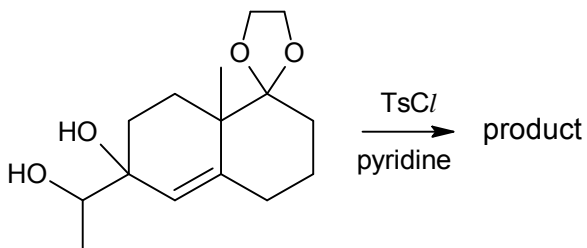



[2]

Degree of substitution of alcohol OR degree of steric hindrance around alcohol group.

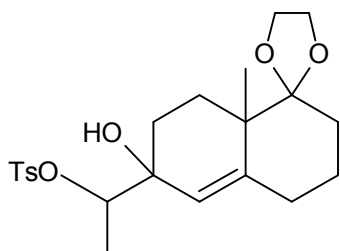
Tosyl group is a bulky group so TsCl/ can approach the less hindered/ less substituted alcohol more easily.

- (iii) Predict the product of the following conversion.



The  ring remains unaltered in the reaction.

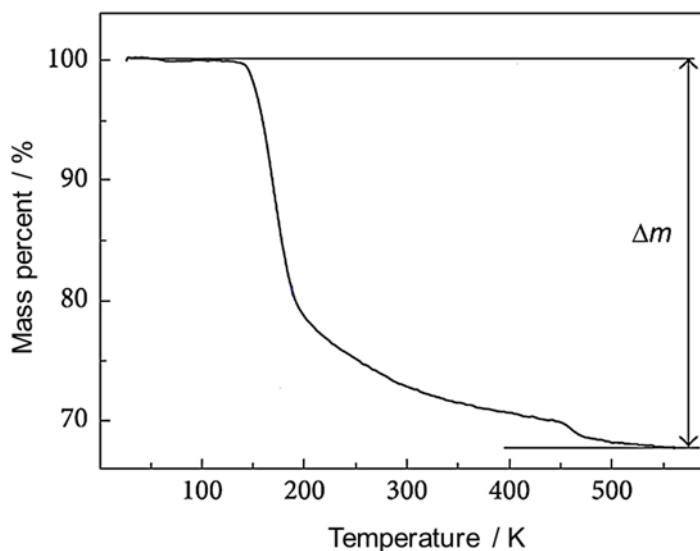
[1]



[Total: 20]

- 5 (a) Thermogravimetric analysis (TGA) is a technique where the mass of a sample in a controlled atmosphere is recorded as a function of temperature as the temperature of the sample is increased.

A sample of lithium pentaborate pentahydrate ($\text{LiB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}$) was subject to TGA and the graph obtained is shown below.



Suggest an explanation, supported with relevant calculations, for the loss in mass (Δm) of $\text{LiB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}$ observed in the graph.

$$[M_r(\text{LiB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}) = 278.9]$$

[2]

The mass loss is likely due to the loss of the five water molecules in $\text{LiB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}$.

$$\% \text{ mass loss} = \frac{5 \times 18}{278.9} \times 100 = \underline{\underline{32.3 \%}}$$

which agrees well with the value obtained from the graph ($\approx 32.5\%$).

- (b) The sample of $\text{LiB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}$ used in (a) was synthesised as a system of Li_2O , B_2O_3 and H_2O in the laboratory.

- (i) Deduce the molar ratio of $\text{Li}_2\text{O} : \text{B}_2\text{O}_3 : \text{H}_2\text{O}$ in a pure sample of $\text{LiB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}$.

[1]

$$\text{Since } \text{LiB}_5\text{O}_8 \cdot 5\text{H}_2\text{O} \equiv \frac{1}{2} \text{Li}_2\text{O} \equiv \frac{5}{2} \text{B}_2\text{O}_3 \equiv 5\text{H}_2\text{O},$$

$$\text{molar ratio of } \text{Li}_2\text{O} : \text{B}_2\text{O}_3 : \text{H}_2\text{O} = \underline{\underline{1 : 5 : 10}}$$

- (ii) Aqueous sodium hydroxide can be used to react with B_2O_3 to determine its actual amount in the sample.

Given that B_2O_3 and Al_2O_3 have similar reactions with aqueous sodium hydroxide under appropriate conditions, write a balanced equation for the reaction between B_2O_3 and aqueous sodium hydroxide.

[1]



(c) Li_2O can be produced from the thermal decomposition of lithium peroxide, Li_2O_2 .

(i) State and explain how the lattice energies of Li_2O and Li_2O_2 would differ.

[2]

$\Delta H_{\text{latt}}^\ominus(\text{Li}_2\text{O})$ will be **more exothermic** than that of $\Delta H_{\text{latt}}^\ominus(\text{Li}_2\text{O}_2)$

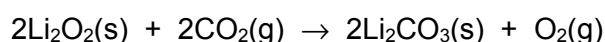
For ionic compounds, $|\Delta H_{\text{latt}}| \propto \frac{q_+q_-}{r_+ + r_-}$

cationic charge (q_+) and radius (r_+) are the **same** for both compounds.

anionic charge (q_-) is the **same** for both compounds.

Anionic radius (r_-): $\text{O}^{2-} < \text{O}_2^{2-}$

(ii) Lithium peroxide reacts with carbon dioxide according to the equation shown below.



State the change in oxidation number of oxygen as Li_2O_2 is converted into the products.

[2]

The oxidation number of O **increases from -1 in Li_2O_2 to 0 in O_2 .**

The oxidation number of O **decreases from -1 in Li_2O_2 to -2 in Li_2CO_3 .**

(iii) Calculate the highest temperature reached when the 2.50 g of lithium carbonate was dissolved in 30 cm^3 of water at room temperature. The standard enthalpy change of solution of lithium carbonate is $-18.2 \text{ kJ mol}^{-1}$.

[2]

Moles of $\text{Li}_2\text{CO}_3 = 2.50 / (6.9 \times 2 + 12 + 16 \times 3) = 0.033875 \text{ mol}$

$q = 18.2 \times 10^3 \times 0.033875 = \mathbf{616.53 \text{ J}}$

$\Delta T = q / mc = 616.53 / (30 \times 4.18) = 4.9165 \text{ }^\circ\text{C/K}$

Highest temperature = $20 + 4.9165 = \mathbf{24.9 \text{ }^\circ\text{C}}$ OR **298 K**

(iv) Calculate the pH of the resulting solution formed in (c)(iii) given that the K_b of carbonate ion is $1.995 \times 10^{-4} \text{ mol dm}^{-3}$.

[3]

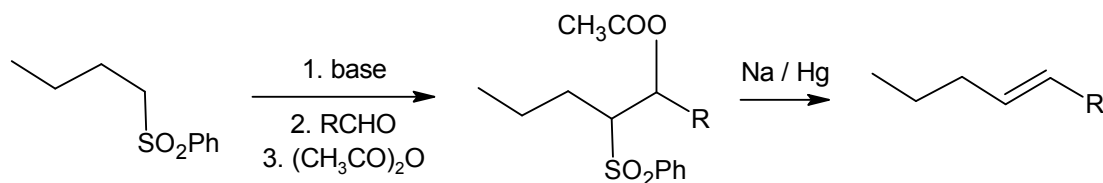
$$[\text{CO}_3^{2-}] = \frac{0.033875}{0.030} = 1.129 \text{ mol dm}^{-3}$$

$$\begin{aligned} [\text{OH}^-] &= \sqrt{(K_b \times [\text{CO}_3^{2-}])} \\ &= \sqrt{(1.995 \times 10^{-4} \times 1.129)} \\ &= 0.01501 \text{ mol dm}^{-3} \end{aligned}$$

$$\text{pH} = 14 - \text{pOH} = 14 + \log_{10}(0.01501) = \mathbf{12.2}$$

- (d) Phenylsulfonyl (PhSO_2) and acetate (CH_3COO) groups on adjacent carbons in a starting material can be lost to form an alkene via Julia olefination.

An example of Julia olefination is as follows.

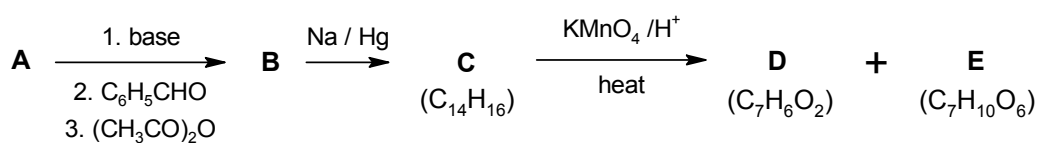


- (i) Suggest the type of reaction occurring in the final step of Julia olefination.

[1]

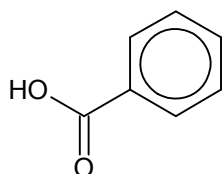
Elimination

Consider the reaction scheme below involving Julia olefination.



- (ii) Compound **D** effervesces with sodium carbonate. Suggest the structure of **D**.

[1]



D
($\text{C}_7\text{H}_6\text{O}_2$)

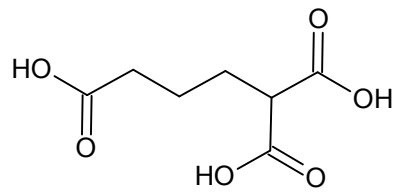
- (iii) Compound **E** is non-cyclic and has six carbons in the longest continuous carbon chain. It also does **not** contain any chiral carbon.

One mole of **E** reacts with three moles of thionyl chloride (SOCl_2) to liberate acidic gas.

Identify the functional group present in **E** and suggest its structure.

[2]

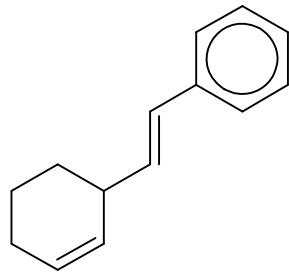
Functional group: carboxylic acid



E
($C_7H_{10}O_6$)

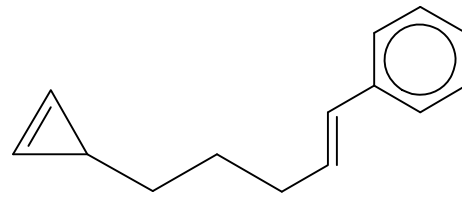
(iv) Hence suggest the structures of compounds **A** to **C**.

[3]

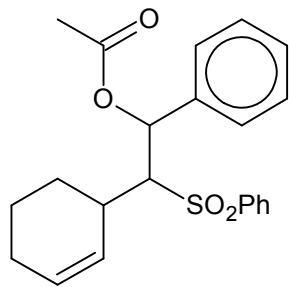


C
($C_{14}H_{16}$)

OR

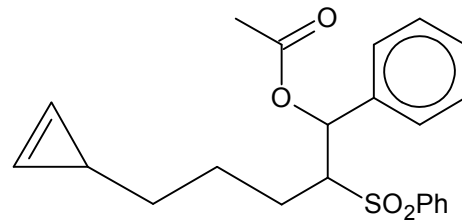


C
($C_{14}H_{16}$)

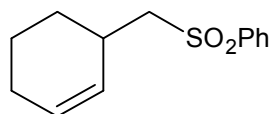


B

OR

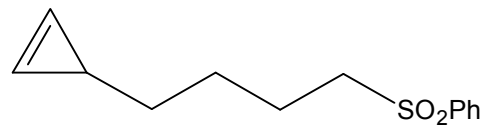


B



A

OR



A

[Total: 20]