SERANGOON JUNIOR COLLEGE
General Certificate of Education Advanced Level
Higher 2

Candidate Name	
Class	

CHEMISTRY **9729/01**

JC2 Preliminary Examination 20 September 2018
Paper 1 Multiple Choice 1 hour
Additional Materials: Data Booklet
Optical Mark Sheet (OMS)

READ THESE INSTRUCTIONS FIRST

On the separate multiple choice OMS given, write your name, subject title and class in the spaces provided.
Shade correctly your FIN/NRIC number.

There are **30** questions in 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 using a **soft pencil** on the separate OMS.
Each correct answer will score one mark.
A mark will not be deducted for a wrong answer.

You are advised to fill in the OMS as you go along; no additional time will be given for the transfer of answers once the examination has ended.

Any rough working should be done in this question paper.

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

Answer all questions

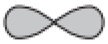
1 One mole of sulfuric acid is used to make an aqueous solution. The solution contains H_2SO_4 molecules, H^+ ions, SO_4^{2-} ions and HSO_4^- ions.

Which statements are correct?

(1) The solution contains 6.02×10^{23} sulfur atoms.
(2) The solution contains an exactly equal number of H^+ ions and HSO_4^- ions.
(3) One mole of SO_4^{2-} ions contains two moles of electrons

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

2 The table refers to the electron distribution in the second shell of an atom with eight protons. Which row is correct for this atom?

	Orbital shape 		Orbital shape 	
	Orbital type	Number of electrons	Orbital type	Number of electrons
A	p	2	s	4
B	p	4	s	2
C	s	2	p	4
D	s	4	p	2

3 50 cm^3 of a 0.10 mol dm^{-3} solution of a metallic salt was found to react exactly with 25.0 cm^3 of 0.10 mol dm^{-3} aqueous sodium sulfite. In this reaction, the sulfite ion is oxidised as follows:

$$SO_3^{2-}(aq) + H_2O(l) \rightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2e$$

What is the new oxidation number of the metal in the salt if its original oxidation number was +3?

A +1

B +2

C +4

D +5

4 A 2 g sample of hydrogen at temperature T and of volume V exerts a pressure *p*.

Deuterium, ${}^{2}_{1}H$ is an isotope of hydrogen.

Which of the following would also exert a pressure of *p* at the same temperature T?

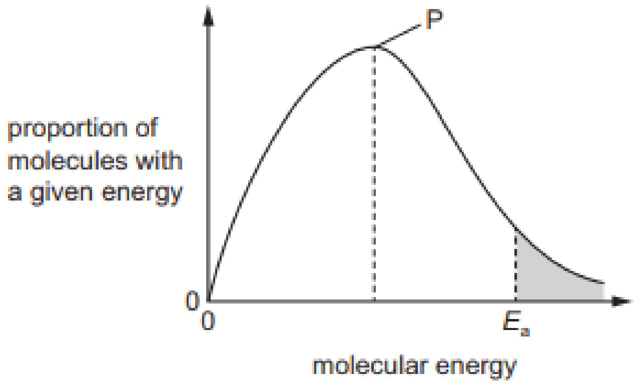
A A mixture of 2 g of hydrogen and 2 g of deuterium of total volume 2V

B A mixture of 1 g of hydrogen and 2 g of deuterium of total volume 2V

C A mixture of 1 g of hydrogen and 2 g of deuterium of total volume V

D A mixture of 1 g of hydrogen and 1 g of deuterium of total volume V

5 The diagram shows the Boltzmann distribution of energies in a gas. The gas can take part in a reaction with an activation energy, E_a.



Which statement is correct?

A If temperature is increased, peak P will be lower and E_a will move to the right.

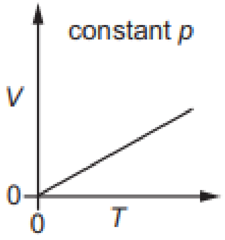
B If temperature is increased, peak P will be higher and E_a will not move

C If temperature is decreased, peak P will be the same and E_a will move to the left.

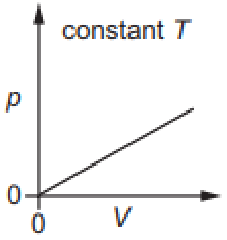
D If temperature is decreased, peak P will be higher and E_a will not move.

6 Which diagram correctly describes the behaviour of a fixed mass of an ideal gas? (T is measured in K.)

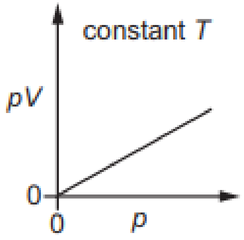
A



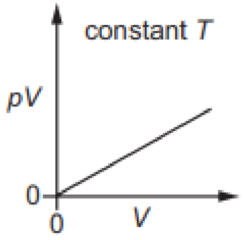
B



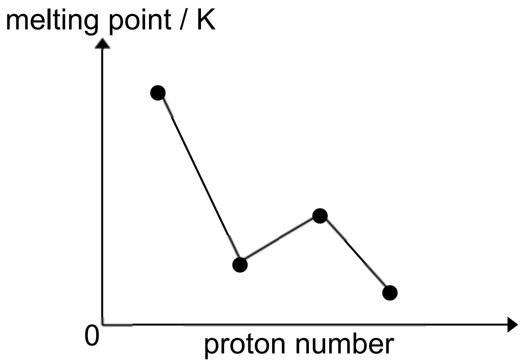
C



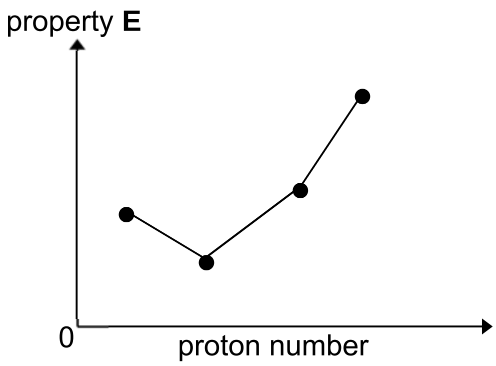
D

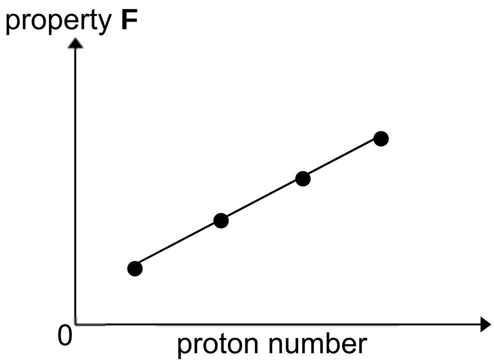


7 The diagram represents the melting points of four consecutive elements in the third period of the Periodic Table.



The sketches below represent another two properties of the elements.





What are properties **E** and **F**?

	property **E**	property **F**
A	third ionisation energy	electronegativity
B	number of valence electrons	boiling point
C	ionic radius	nuclear charge
D	electrical conductivity	atomic radius

8 When 60 cm^3 of 0.1 mol dm^{-3} of sulfuric acid and 40 cm^3 of 0.2 mol dm^{-3} sodium hydroxide were mixed in a styrofoam cup, the temperature rose by 6.5 ^oC.

Calculate the standard enthalpy change of neutralisation. Assume that the specific heat capacity of the solution is 4.2 $Jg^{-1}K^{-1}$.

A + 34.1 kJ mol^{-1}

B + 45.5 kJ mol^{-1}

C - 34.1 kJ mol^{-1}

D - 45.5 kJ mol^{-1}

9 In which reactions does NH_3 behave as a Brønsted-Lowry acid?

(1) $HSO_4^- + NH_3 \rightarrow SO_4^{2-} + NH_4^+$
(2) $Ag^+ + 2NH_3 \rightarrow [Ag(NH_3)_2]$
(3) $2NH_3 \rightarrow NH_2^- + NH_4^+$

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

10 A current of 0.2 ampere passing for 5 hours through a solution of gold ions deposits a mass of 2.45 g of gold on the cathode. Which of these expressions gives the charge on a gold ion?

A $$\frac{2.45 \times 0.2 \times 5 \times 60 \times 60}{197 \times 96500}$$

B $$\frac{0.2 \times 5 \times 60 \times 60 \times 197}{96500 \times 2.45}$$

C $$\frac{2.45 \times 96500}{197 \times 0.2 \times 5 \times 60 \times 60}$$

D $$\frac{197 \times 0.2 \times 5 \times 60 \times 96500}{2.45}$$

11 Pure nitrosyl chloride, NOC*l* gas, was heated at 320°C in a 2.0 dm^3 vessel. At equilibrium, 30% of the NOC*l* gas had dissociated according to the equation below and the total pressure was p atm.

$$2NOCl\ (g) \rightleftharpoons 2NO\ (g) + Cl_2\ (g)$$

What is value of the equilibrium constant, K_p?

A $\frac{17.9}{p}$ **B** $\frac{41.7}{p}$ **C** 0.0120p **D** 0.0130p

12 Calculate the resultant pH of the solution when 10 cm^3 of hydrochloric acid with a concentration of 0.015 mol dm^{-3} was added to a 25 cm^3 sample of ammonia with a concentration of 0.25 mol dm^{-3}.

(K_b of ammonia = 1.778 x 10^{-5} mol dm^{-3})

A 10.9

B 8.25

C 7.64

D 9.25

13 Hydrogen can be made from steam according to the following equation:

$$H_2O(g) + C(s) \rightarrow H_2(g) + CO(g)$$

The Gibbs free energy change of reaction at two different temperature are shown

$\Delta G_1 = +78$ kJ mol^{-1} at 378 K
$\Delta G_2 = -58$ kJ mol^{-1} at 1300 K

Which row of the table gives the correct sign of ΔH and ΔS for this reaction?

	ΔH	ΔS
A	−	−
B	−	+
C	+	−
D	+	+

14 An experiment was carried out to investigate the initial rate of reaction between potassium peroxodisulphate, $K_2S_2O_8$, an oxidising agent, and potassium iodide, KI.

The initial volumes of the $K_2S_2O_8$ and KI solutions in the mixture together with the time taken for the mixture to darken for the various experimental runs are given below.

Volume of $K_2S_2O_8$ / cm^3	Volume KI / cm^3	Volume of water /cm^3	time taken to darken / s
10	20	10	35
5	20	15	70
10	8	22	88
20	40	20	***y***

Select the correct option for the following reaction.

	Order with respect to $K_2S_2O_8$	Order with respect to KI	**y** / s
A	1	1	70.0
B	1	2	17.5
C	1	1	35.0
D	2	1	17.5

15 The enzyme maltase speeds up the reaction between maltose and water.

$$\text{maltose + water} \xrightarrow{\text{maltase}} \text{glucose}$$

Maltase shows **specificity**.

Which statement describes the **specificity** of maltase?

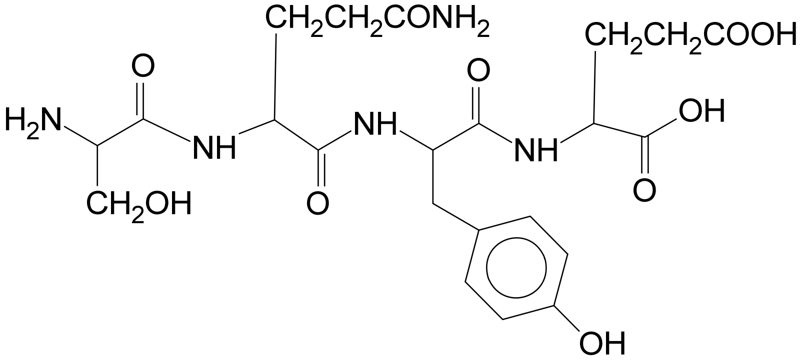
A Maltase is a biological catalyst and it is a type of protein.

B Maltase is most effective between pH 6.1 and pH 6.8.

C Maltase lowers the activation energies of the reactions it catalyses.

D Maltase only speeds up a small number of chemical reactions.

16 The diagram shows the structure of the tetrapeptide, **J**.



Which statements are correct?

(1) When 1 mol of **J** reacts with hot NaOH(aq) until no further reaction occurs, 8 mol of NaOH will react.

(2) When 1 mol of **J** reacts with hot HC*l*(aq) until no further reaction occurs, 5 mol of HC*l* will react.

(3) When 1 mol of **J** reacts with ethanoyl chloride, 3 mol of ethanoyl chloride will react forming ester or amide.

(4) When 1 mol of **J** reacts with Na(s), 4 mol of hydrogen gas will be given out.

A 1 and 2 only

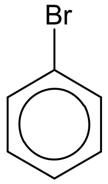
B 2 and 3 only

C 1, 2 and 4 only

D 3 and 4 only

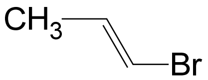
17 Which of these will produce the most silver bromide precipitate when a 1 g sample reacts with excess hot sodium hydroxide, followed by silver nitrate solution?

A



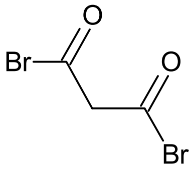
(M_r: 156.9)

B



(M_r: 120.9)

C



(M_r: 229.8)

D CH_3Br (M_r: 94.9)

18 Identify the final product **L** in this sequence of reactions.

$$CH_2CHCOCH_2CHO \xrightarrow[\text{then } H_2O]{NaBH_4 \text{ in } CH_3OH} \mathbf{K} \xrightarrow[\text{heat}]{K_2Cr_2O_7/\ H^+} \mathbf{L}$$

A $CH_2CHCOCH_2COOH$

B $CH_3CH_2COCH_2COOH$

C $CH_2(OH)CH(OH)COCH_2CH_2OH$

D $CH_2(OH)CH(OH)CH(OH)CH_2CH_2OH$

19 An alcohol **M** with molecular formula $C_4H_{10}O$ is oxidised by acidified potassium dichromate(VI) under certain conditions to give **N**.

- **N** does not produce a yellow precipitate with aqueous alkaline iodine
- **N** gives a reddish brown precipitate when reacted with Fehling's solution

How many isomers of alcohol **M** could result in the observations for **N**?

A 1

B 2

C 3

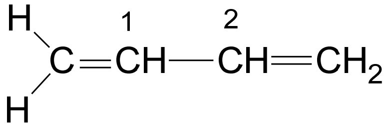
D 4

20 Which of the following compounds has the shortest C1-C2 bond length?

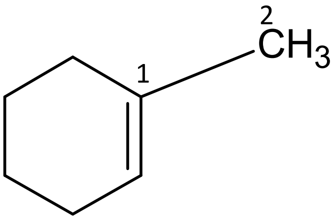
A $\overset{1}{CH_3}-\overset{2}{CH_2}-CH_3$

B $\overset{1}{CH_3}-\overset{2}{CH}=CH_2$

C



D



21 Maleic acid is used in the food industry and for stabilising drugs. It is the cis-isomer of butenedioic acid and has the structural formula $HO_2CCH=CHCO_2H$.

What is the product formed from the reaction of maleic acid with cold, dilute, acidified manganate(VII) ions?

A $HO_2CCH(OH)CH(OH)CO_2H$

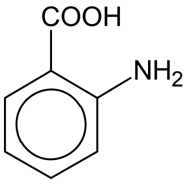
B HO_2CCO_2H

C $HO_2CCH_2CH(OH)CO_2H$

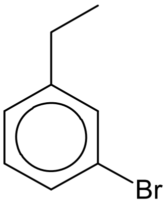
D $HO_2CCOCOCO_2H$

22 Which one of the following compounds **cannot** be synthesised from ethylbenzene?

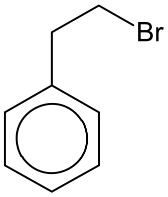
A



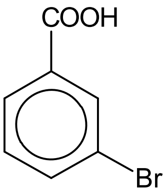
B



C



D

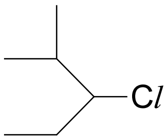


23 Structural isomerism and stereoisomerism should be considered when answering this question.

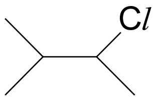
A colourless liquid, $C_5H_{11}Cl$, exists as a mixture of two optical isomers.

When heated with sodium hydroxide in ethanol, a mixture of only **two** alkenes is formed. What could the colourless liquid be?

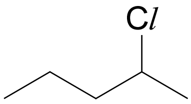
A



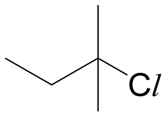
C



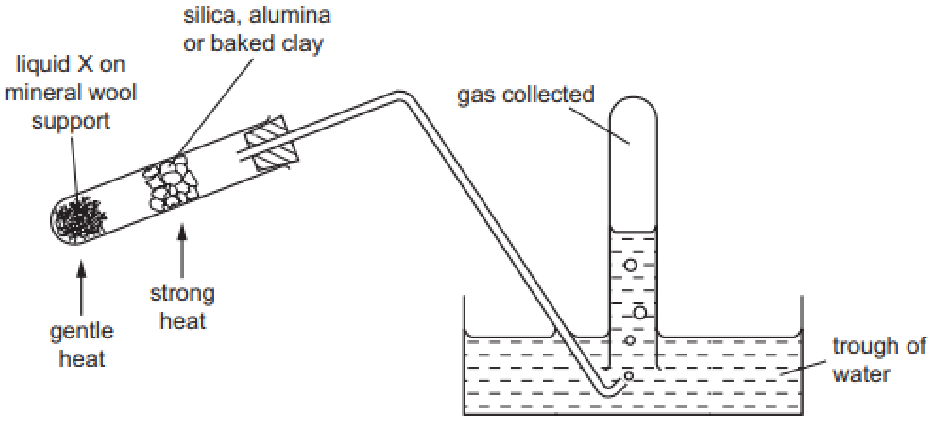
B



D



24 The diagram shows an experimental set-up which can be used in several different experiments.



Which processes could be demonstrated by using the above apparatus?

(1) oxidation of ethanol (liquid X)

(2) dehydration of ethanol (liquid X)

(3) cracking of paraffin (liquid X)

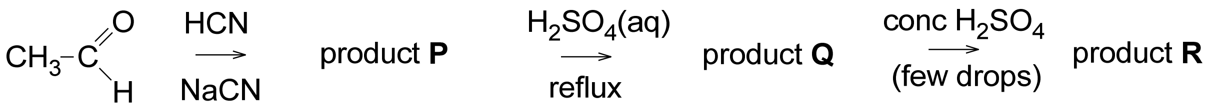
A 1, 2 and 3

B 1 and 2 only

C 2 and 3 only

D 3 only

25 Ethanal, CH_3CHO, is used to make product **R** in a three-stage synthesis.



Two molecules of **Q** react to give one molecule of **R** plus two molecules of water.

R does not react with sodium.

What is the molecular formula and empirical formula of **R**?

	Molecular formula	Empirical formula
A	$C_3H_4O_2$	$C_3H_4O_2$
B	$C_6H_8O_4$	$C_3H_4O_2$
C	$C_3H_5O_2$	$C_3H_5O_2$
D	$C_6H_{10}O_5$	$C_6H_{10}O_5$

26 Chlorofluoroalkanes have been used as the refrigerant in refrigerators but care has to be taken in disposing of old refrigerators.

Which statements about chlorofluoroalkanes are correct?

(1) C–C*l* bonds more readily undergo homolytic fission than C–F bonds.

(2) Care is taken in the disposal of old refrigerators because of possible ozone depletion.

(3) C_2H_4ClF is more volatile than C_2H_6.

A 2 only

B 1 and 2 only

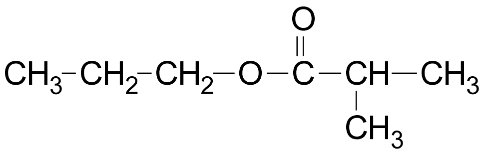
C 2 and 3 only

D 1, 2 and 3

27 Ethyl propanoate is refluxed with aqueous sodium hydroxide. The alcohol produced is then reacted with methyl propanoic acid to make a second ester.

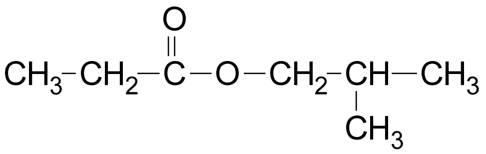
What is the structural formula of this second ester?

A



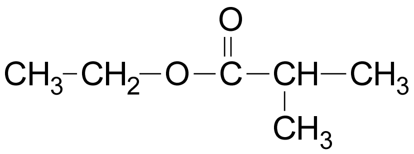
$CH_3-CH_2-CH_2-O-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}-CH_3$

B



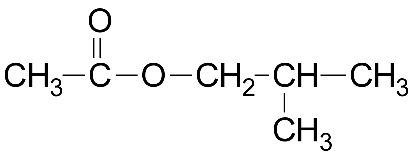
$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-O-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$

C



$CH_3-CH_2-O-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}-CH_3$

D



$CH_3-\overset{\overset{O}{\|}}{C}-O-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$

28 Ethanedioic acid has the formula HO_2CCO_2H.

What is the formula of aluminium ethanedioate?

A AlC_2O_4

B $Al(C_2O_4)_3$

C $Al_2C_2O_4$

D $Al_2(C_2O_4)_3$

29 Which of the following processes lead to an increase in entropy?

(1) Diffusion of air fresher in the lecture theatre.
(2) Combustion of a piece of charcoal to form CO_2 (g) and H_2O (g).
(3) Desalination of sea water by reverse osmosis (solvent passes from a dilute solution to a concentrated solution).

A 1 only

B 1 and 2 only

C 2 and 3 only

D 1, 2 and 3

30 How many structural isomers with the molecular formula $C_5H_{10}O_2$ give infra-red absorptions both at approximately 1300 cm^{-1} and at approximately 1740 cm^{-1}?

A 3

B 5

C 7

D 9

END OF PAPER 1

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General Certificate of Education Advanced Level
Higher 2

Candidate Name

Class

CHEMISTRY

9729/01

JC2 Preliminary Examination
Paper 1 Multiple Choice
Additional Materials: Data Booklet
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20 September 2018
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This document consists of ___ printed pages and __ blank page.

Answer all questions

1 One mole of sulfuric acid is used to make an aqueous solution. The solution contains H_2SO_4 molecules, H^+ ions, SO_4^{2-} ions and HSO_4^- ions.

Which statements are correct?

(1) The solution contains 6.02×10^{23} sulfur atoms.

(2) The solution contains an exactly equal number of H^+ ions and HSO_4^- ions.

(3) One mole of SO_4^{2-} ions contains two moles of electrons

A 1 only

B 1 and 2 only

C 2 and 3 only

D 1 and 3 only

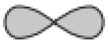
Answer: **A**

For statement 1 is correct: 1 mol of H_2SO_4 has 1 mol of S. The solution contains 6.02×10^{23} S atoms

For statement 2 is wrong: From the question, one mole of H_2SO_4 contains H_2SO_4 molecules, H^+, SO_4^{2-} and HSO_4^-. This means the amt of H^+ and HSO_4^- is not equal as some H_2SO_4 may have dissociate into SO_4^{2-}.

For statement 3 is wrong: One mole of SO_4^{2-} has more than 2 mol of electrons. Do not be tricked by the charge of negative two

2 The table refers to the electron distribution in the second shell of an atom with eight protons. Which row is correct for this atom?

	Orbital shape 		Orbital shape 	
	Orbital type	Number of electrons	Orbital type	Number of electrons
A	p	2	s	4
B	p	4	s	2
C	s	2	p	4
D	s	4	p	2

Answer: **B**

Second shell of an atom with eight protons: oxygen ➔ electronic configuration: $1s^2 2s^2 2p^4$

3 50 cm^3 of a 0.10 mol dm^{-3} solution of a metallic salt was found to react exactly with 25.0 cm^3 of 0.10 mol dm^{-3} aqueous sodium sulfite. In this reaction, the sulfite ion is oxidised as follows:

$$SO_3^{2-}(aq) + H_2O(l) \rightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2e$$

What is the new oxidation number of the metal in the salt if its original oxidation number was +3?

A	+1
B	+2
C	+4
D	+5

Answer: **B**

Amount of sulphite ions = $\frac{25}{1000} \times 0.10$ = 0.0025 mol

Amount of metallic salt = $\frac{50}{1000} \times 0.10$ = 0.005 mol

Let x be the new oxidation no of metal in salt.

[R]: $M^{3+} + (3-x)e \rightarrow M^x$

Since moles of electrons gained = moles of electrons lost in a redox reaction,

$$\frac{3-x}{2} = \frac{0.0025}{0.005}$$

x = <u>+2</u>

4	A 2 g sample of hydrogen at temperature T and of volume V exerts a pressure *p*. Deuterium, ${}^{2}_{1}H$ is an isotope of hydrogen. Which of the following would also exert a pressure of *p* at the same temperature T?	
	A	A mixture of 2 g of hydrogen and 2 g of deuterium of total volume 2V
	B	A mixture of 1 g of hydrogen and 2 g of deuterium of total volume 2V
	C	A mixture of 1 g of hydrogen and 2 g of deuterium of total volume V
	D	A mixture of 1 g of hydrogen and 1 g of deuterium of total volume V

Answer: **C**

P (of sample of 2 g of hydrogen) V = nRT

P (of sample of 2 g of hydrogen) $= \frac{nRT}{V}$

$$= \frac{\frac{2}{2}RT}{V}$$

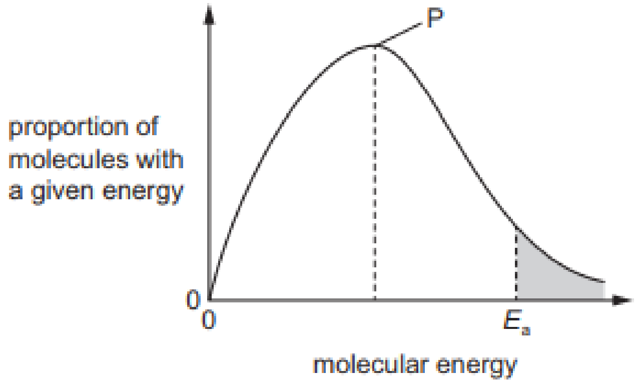
$$= \frac{RT}{V}$$

For option C:

P (of mixture) $= \frac{\frac{1}{2}RT + \frac{2}{4}RT}{V}$

$= \frac{RT}{V}$ (same pressure as the sample of 2 g of hydrogen)

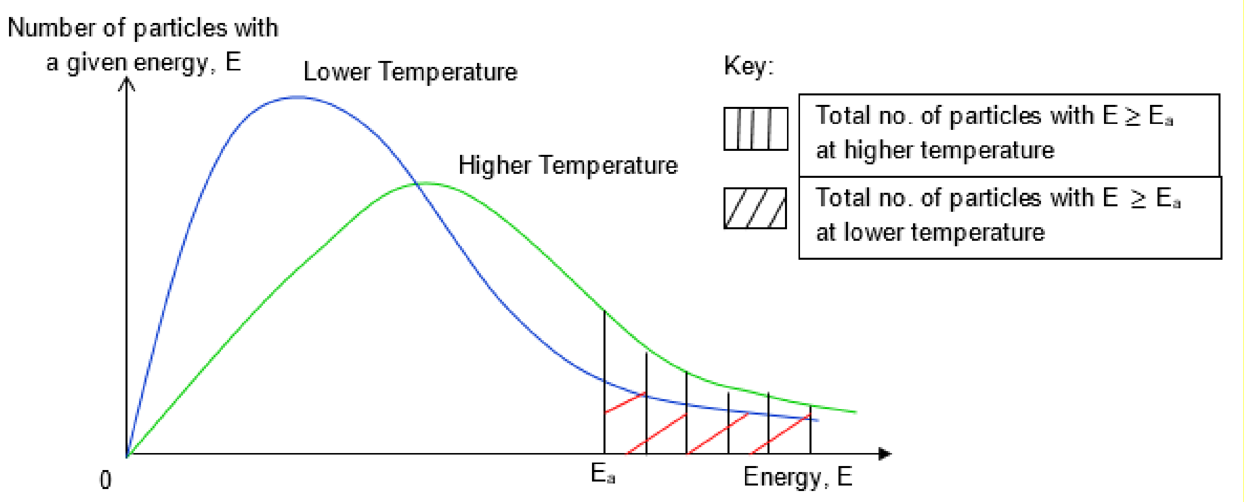
5 The diagram shows the Boltzmann distribution of energies in a gas. The gas can take part in a reaction with an activation energy, E_a.



Which statement is correct?

A	If temperature is increased, peak P will be lower and E_a will move to the right.
B	If temperature is increased, peak P will be higher and E_a will not move
C	If temperature is decreased, peak P will be the same and E_a will move to the left.
D	If temperature is decreased, peak P will be higher and E_a will not move.

Answer: **D**

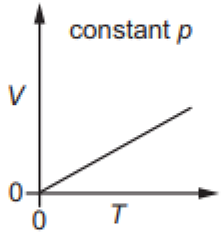


Option A and C are wrong as E_a will not shift when temperature is increased or decreased

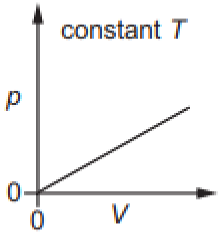
Option B is wrong. When temperature is increased, peak P will shift lower not higher.

6 Which diagram correctly describes the behaviour of a fixed mass of an ideal gas? (T is measured in K.)

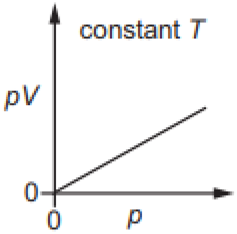
A



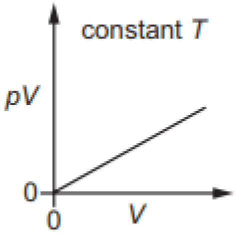
B



C



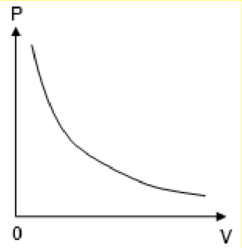
D



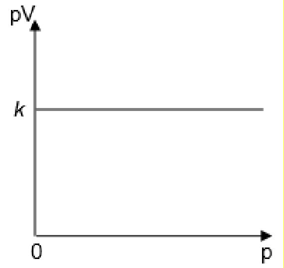
Answer: A

Using pV = nRT

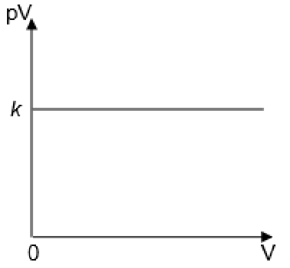
For B the correct graph is as shown



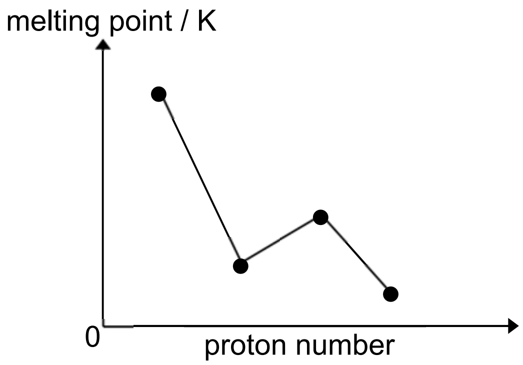
For C the correct graph is as shown



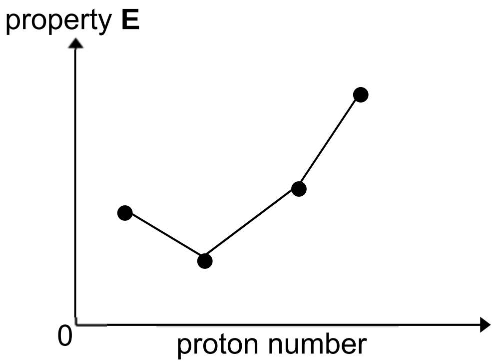
Similarly for D the correct graph is as shown

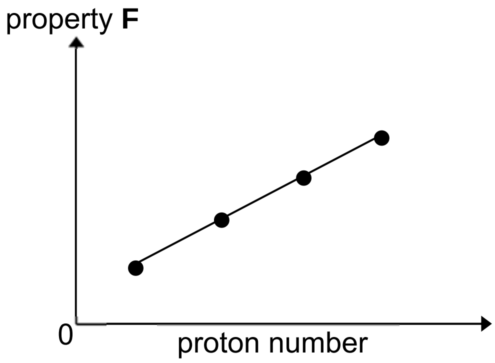


7 The diagram represents the melting points of four consecutive elements in the third period of the Periodic Table.



The sketches below represent another two properties of the elements.





What are properties **E** and **F**?

	property **E**	property **F**
A	third ionisation energy	electronegativity
B	number of valence electrons	boiling point
C	ionic radius	nuclear charge
D	electrical conductivity	atomic radius

Answer: **A**
From the melting point data, student should be able to appreciate the highest m.p should be Si and since they are consecutive elements in third period, the next 3 points will be P, S and P.

Thus, only option A is valid.

8	When 60 cm^3 of 0.1 mol dm^{-3} of sulfuric acid and 40 cm^3 of 0.2 mol dm^{-3} sodium hydroxide were mixed in a styrofoam cup, the temperature rose by 6.5 °C. Calculate the standard enthalpy change of neutralisation. Assume that the specific heat capacity of the solution is 4.2 Jg^{-1}K^{-1}.	
	A	+ 34.1 kJ mol^{-1}
	B	+ 45.5 kJ mol^{-1}
	C	- 34.1 kJ mol^{-1}
	D	- 45.5 kJ mol^{-1}

Answer: C

$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$
Amount of sulfuric acid = $\frac{60}{1000} \times 0.1 = 0.006$ mol
Amount of sodium hydroxide = $\frac{40}{1000} \times 0.2 = 0.008$ mol (limiting reactant)
Amount of sodium hydroxide = amount of water = 0.008 mol

$\Delta H_{\text{neutralisation}} = -\frac{(100)(4.2)(6.5)}{0.008} = -34.1$ kJ mol^{-1}

9	In which reactions does NH_3 behave as a Brønsted-Lowry acid? (1) $HSO_4^- + NH_3 \rightarrow SO_4^{2-} + NH_4^+$ (2) $Ag^+ + 2NH_3 \rightarrow [Ag(NH_3)_2]$ (3) $2NH_3 \rightarrow NH_2^- + NH_4^+$	
	A	1 and 2 only
	B	1 and 3 only
	C	1 only
	D	3 only

Answer: D

For reaction 1, ammonia is functioning as a Brønsted-Lowry base as it received a proton from HSO_4^-

For reaction 2, ammonia is functioning as a Lewis base because it can share its lone pair of electrons with Ag^+.

For reaction 3, ammonia is functioning as both Brønsted-Lowry acid as well as Brønsted-Lowry base.

10	A current of 0.2 ampere passing for 5 hours through a solution of gold ions deposits a mass of 2.45 g of gold on the cathode. Which of these expressions gives the charge on a gold ion?	
	A	$\frac{2.45 \times 0.2 \times 5 \times 60 \times 60}{197 \times 96500}$
	B	$\frac{0.2 \times 5 \times 60 \times 60 \times 197}{96500 \times 2.45}$
	C	$\frac{2.45 \times 96500}{197 \times 0.2 \times 5 \times 60 \times 60}$
	D	$\frac{197 \times 0.2 \times 5 \times 60 \times 96500}{2.45}$

Answer: B

Q = I x t
  = 0.2 x 5 x 60 x 60

$$\text{Amt} = \frac{I \times t}{nF}$$

$$n = \frac{I \times t}{\text{amt} \times F} = \frac{0.2 \times 5 \times 60 \times 60}{\frac{2.45}{197} \times 96500} = \frac{0.2 \times 5 \times 60 \times 60 \times 197}{2.45 \times 96500}$$

11 Pure nitrosyl chloride, NOC*l* gas, was heated at 320°C in a 2.0 dm^3 vessel. At equilibrium, 30% of the NOC*l* gas had dissociated according to the equation below and the total pressure was P atm.

$$2\text{NOC}l\text{ (g)} \rightleftharpoons 2\text{NO (g)} + \text{C}l_2\text{ (g)}$$

What is value of the equilibrium constant, K_p?

A	$\frac{17.9}{p}$	**B**	$\frac{41.7}{p}$	**C**	0.0120p	**D**	0.0130p

Answer: **C**

	$2\text{NOCl (g)} \rightleftharpoons$	$2\text{NO (g)} +$	$\text{Cl}_2\text{ (g)}$
Initial partial pressure/atm	**x**	0	**0**
Change in partial pressure / atm	-0.3x	+0.3x	+0.15x
Equilibrium partial pressure / atm	0.7x	0.3x	0.15x

0.7x + 0.3x + 0.15x = p
x = 0.8696p

$$K_p = \frac{(0.2609p)(0.1304p)^2}{(0.6087p)^2}$$
$= 0.01197$
$= 0.0120p$

12	Calculate the resultant pH of the solution when 10 cm^3 of hydrochloric acid with a concentration of 0.015 mol dm^{-3} was added to a 25 cm^3 sample of ammonia with a concentration of 0.25 mol dm^{-3}. (K_b of ammonia = 1.778 x 10^{-5} mol dm^{-3})	
	A	10.9
	B	8.25
	C	7.64
	D	9.25

Answer: **A**

$HCl + NH_3 \rightarrow NH_4Cl$

Amt HCl given = 10/1000 x 0.015 = 0.00015 mol

Amt NH_3 given = 25/1000 x 0.25 = 0.00625 mol

All the HCl added will be neutralised by the excess NH_3 forming the NH_4^+ thus

[HCl ≡ NH_4^+]

Amt NH_4^+ present = 0.00015 mol

Amt of NH_3 remaining = 0.00625 – 0.00015
= 0.0061 mol

Thus, present of a basic buffer

pOH = pK_b + lg ($[NH_4^+]$ / $[NH_3]$)
= -lg(1.778 x 10^{-5}) + lg
= 3.14

pH = 14 – 3.14 = 10.9

13 Hydrogen can be made from steam according to the following equation:

$$H_2O(g) + C(s) \rightarrow H_2(g) + CO(g)$$

The Gibbs free energy change of reaction at two different temperature are shown

$\Delta G_1 = +78$ kJ mol^{-1} at 378 K
$\Delta G_2 = -58$ kJ mol^{-1} at 1300 K

Which row of the table gives the correct sign of ΔH and ΔS for this reaction?

	ΔH	ΔS
A	−	−
B	−	+
C	+	−
D	+	+

Answer: D

Δn of gas = 2-1 = +1
ΔS is positive.
ΔG = ΔH – TΔS
As temperature increases to 1300 K, ΔG is negative and reaction is spontaneous.

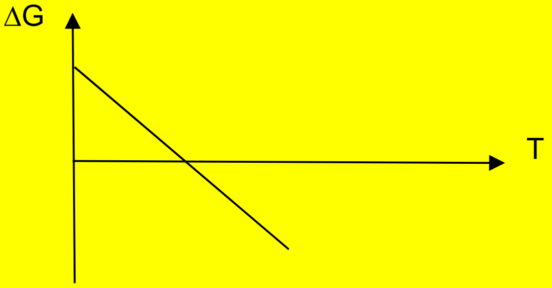
When the temperature is lower at 378 K, ΔG is positive and reaction is non-spontaneous.

Since ΔS is positive, this indicate that ΔH is positive as only low temperature can allow ΔG to become positive.

Alternatively, using ΔG = ΔH – TΔS where

- ΔG (y-axis)
- ΔH (y intercept)
- T (x-axis)
- \- ΔS (gradient)

Since ΔS is positive (which leads to a negative gradient) and ΔG changes from positive to negative with increasing temperature, ΔH is positive.



14 An experiment was carried out to investigate the initial rate of reaction between potassium peroxodisulphate, $K_2S_2O_8$, an oxidising agent, and potassium iodide, KI.

The initial volumes of the $K_2S_2O_8$ and KI solutions in the mixture together with the time taken for the mixture to darken for the various experimental runs are given below.

Volume of $K_2S_2O_8$ / cm^3	Volume KI / cm^3	Volume of water /cm^3	time taken to darken / s
10	20	10	35
5	20	15	70
10	8	22	88
20	40	20	***y***

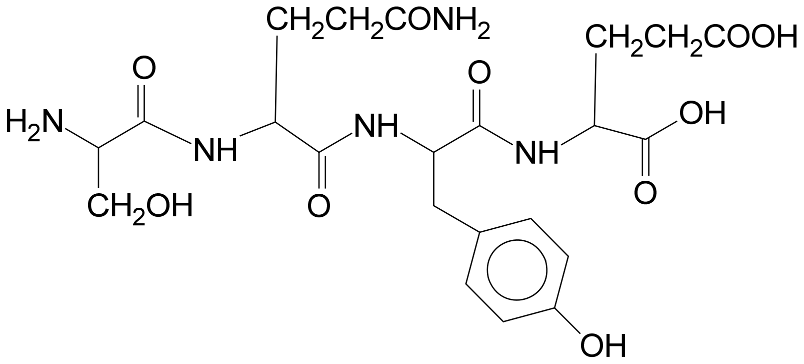
Select the correct option for the following reaction.

	Order with respect to $K_2S_2O_8$	Order with respect to KI	**y** / s	
A	1	1	70.0	
B	1	2	17.5	
C	1	1	35.0	
D	2	1	17.5	

Answer: **C**
From the first two expt, order wrt $K_2S_2O_8$ is one.
From the 1st and 3rd expt, order wrt is KI one.
In the 4th expt, the concentration of $K_2S_2O_8$ and KI are both doubled from experiment one respectively. However, since total volume is doubled too, the concentrations of expt 4 are exaxtly the same as expt one. So the time taken for the solution to darken is the same.

15	The enzyme maltase speeds up the reaction between maltose and water. $$\text{maltose + water} \xrightarrow{\text{maltase}} \text{glucose}$$ Maltase shows **specificity**. Which statement describes the **specificity** of maltase?	
	A	Maltase is a biological catalyst and it is a type of protein.
	B	Maltase is most effective between pH 6.1 and pH 6.8.
	C	Maltase lowers the activation energies of the reactions it catalyses.
	D	Maltase only speeds up a small number of chemical reactions.
Answer: **D** Being a biological catalyst and a type of protein does not define the term **specificity.** Thus option A is out Effectiveness over a pH range does not define the term **specificity**. This make option B wrong. Lowering activation energy does not define the term **specificity**. In fact all catalyst or enzyme lower E_a. Option C is thus wrong.		

16 The diagram shows the structure of the tetrapeptide, **J**.



Which statements are correct?

(1) When 1 mol of **J** reacts with hot NaOH(aq) until no further reaction occurs, 8 mol of NaOH will react.

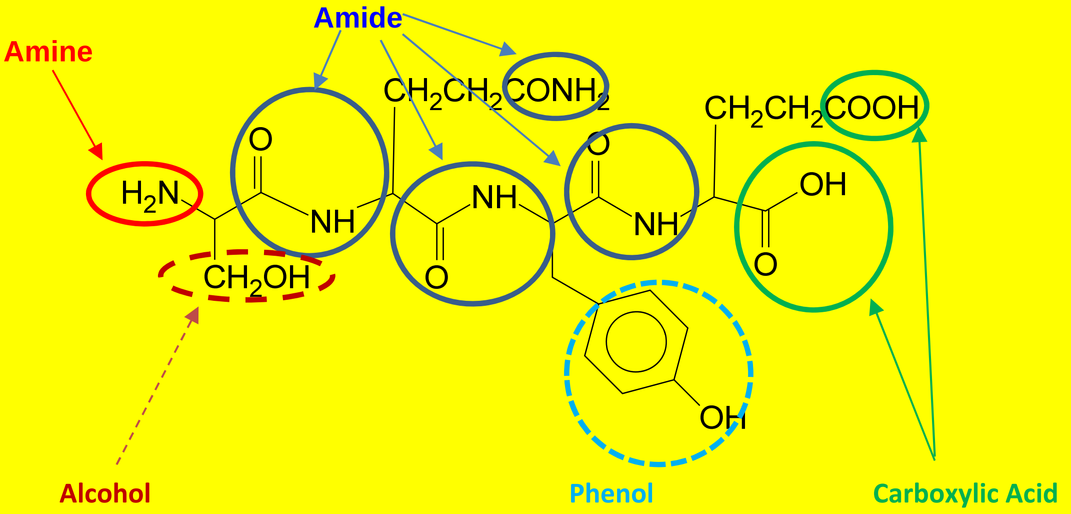
(2) When 1 mol of **J** reacts with hot HC*l*(aq) until no further reaction occurs, 5 mol of HCl will react.

(3) When 1 mol of **J** reacts with ethanoyl chloride, 3 mol of ethanoyl chloride will react forming ester or amide.

(4) When 1 mol of **J** reacts with Na(s), 4 mol of hydrogen gas will be given out.

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

Answer: **B**



Hence, 1 mol of **J** will react with 7 mol of NaOH (aq) (Basic hydrolysis of amides, neutralisation of carboxylic acid and phenols).

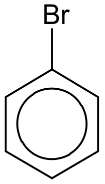
1 mol of **J** will react with 5 mol of HCl (aq) (Acidic hydrolysis of amides, neutralisation of amine).

When 1 mol of **J** reacts with ethanoyl chloride, 3 mol of ethanoyl chloride will react (alcohol, phenol and amine)

When 1 mol of **J** reacts with Na(s), 2 mol of hydrogen gas will be given out. (Phenol, alcohol and carboxylic acid)

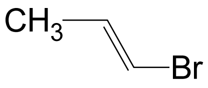
17 Which of these will produce the most silver bromide precipitate when a 1 g sample reacts with excess hot sodium hydroxide, followed by silver nitrate solution?

A



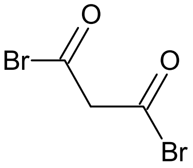
(M_r: 156.9)

B



(M_r: 120.9)

C



(M_r: 229.8)

D CH_3Br (M_r: 94.9)

Answer: **D**

Both A and B are resistant to nucleophilic substitution due to the double bond character between C and Br.

Amt of C in 1g = $\frac{1}{229.8}$ = 0.00435 Hence amt of AgBr formed = 0.0087 mol	Amt of D in 1g = $\frac{1}{94.9}$ = 0.0105 Hence amt of AgBr formed = 0.0105

18 Identify the final product **L** in this sequence of reactions.

$$CH_2CHCOCH_2CHO \xrightarrow[\text{then } H_2O]{NaBH_4 \text{ in } CH_3OH} \textbf{K} \xrightarrow[\text{heat}]{K_2Cr_2O_7/\ H^+} \textbf{L}$$

A $CH_2CHCOCH_2COOH$

B $CH_3CH_2COCH_2COOH$

C $CH_2(OH)CH(OH)COCH_2CH_2OH$

D $CH_2(OH)CH(OH)CH(OH)CH_2CH_2OH$

Answer: **A**

$$\begin{tikzcd} CH_2{=}CHCOCH_2CH{=}O \arrow[r, "\substack{NaBH_4\text{ in }CH_3OH \\ \text{then }H_2O}"] & CH_2{=}CHCH(OH)CH_2CH_2OH \arrow[d, "\substack{K_2Cr_2O_7/\ H^+ \\ \text{heat}}"] \\ & CH_3CH_2COCH_2COOH \end{tikzcd}$$

19 An alcohol **M** with molecular formula $C_4H_{10}O$ is oxidised by acidified potassium dichromate(VI) under certain conditions to give **N**.

- **N** does not produce a yellow precipitate with aqueous alkaline iodine
- **N** gives a reddish brown precipitate when reacted with Fehling's solution

How many isomers of alcohol **M** could result in the observations for **N**?

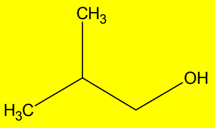
A 1

B 2

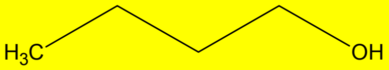
C 3

D 4

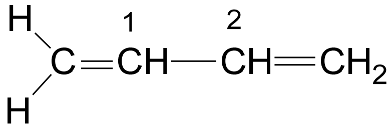
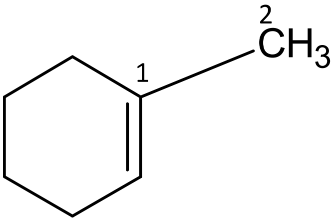
Answer: **B**
Since product **N** gives a reddish brown precipitate when reacted with Fehling's solution, an aldehyde functional group is present. Since aldehydes are formed from controlled oxidation of primary alcohol, the possible structures of primary alcohol from $C_4H_{10}O$ are:



and



Therefore, there are 2 isomers.

20	Which of the following compounds has the shortest C1-C2 bond length?	
	A	$\overset{1}{CH_3}-\overset{2}{CH_2}-CH_3$
	B	$\overset{1}{CH_3}-\overset{2}{CH}=CH_2$
	C	
	D	

Answer: C

Percentage of s character of hybridised orbitals are in order sp > sp^2 > sp^3. The higher the percentage of s character, the shorter the bond formed as the hybridised orbital will be more spherical.

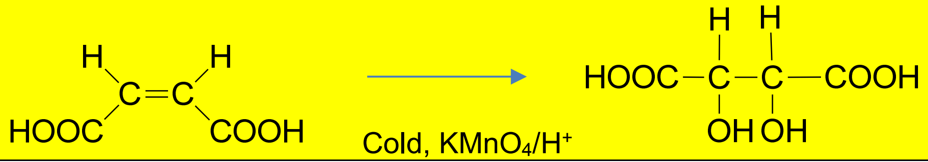
Option A has sp^3-sp^3 overlap.

Option B and D has sp^3-sp^2.

Option C has sp^2-sp^2 overlap.

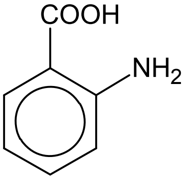
21	Maleic acid is used in the food industry and for stabilising drugs. It is the cis-isomer of butenedioic acid and has the structural formula $HO_2CCH{=}CHCO_2H$. What is the product formed from the reaction of maleic acid with cold, dilute, acidified manganate(VII) ions?	
	A	$HO_2CCH(OH)CH(OH)CO_2H$
	B	HO_2CCO_2H
	C	$HO_2CCH_2CH(OH)CO_2H$
	D	$HO_2CCOCOCO_2H$

Answer: **A**

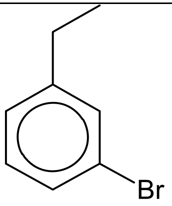


22 Which one of the following compounds **cannot** be synthesised from ethylbenzene?

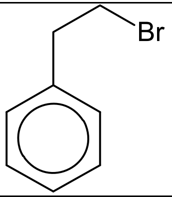
A



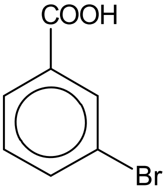
B



C



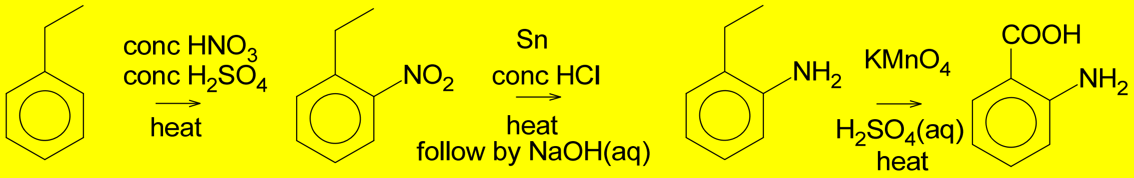
D



Answer: **B**

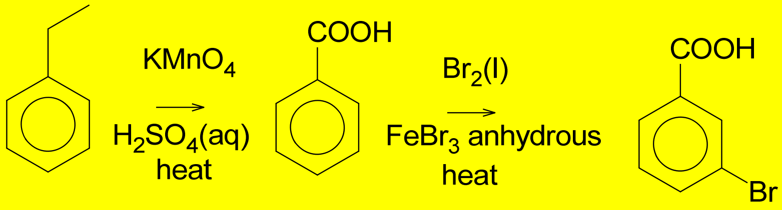
Ethyl group is 2,4 directing. Thus option B is wrong

Option A is correct



Option B is correct. Side chain free radical substitution has occurred.

Option D is correct

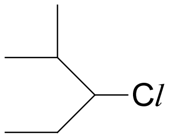


23 Structural isomerism and stereoisomerism should be considered when answering this question.

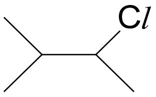
A colourless liquid, $C_5H_{11}Cl$, exists as a mixture of two optical isomers.

When heated with sodium hydroxide in ethanol, a mixture of only **two** alkenes is formed. What could the colourless liquid be?

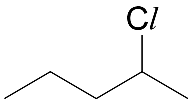
A



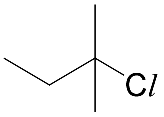
C



B



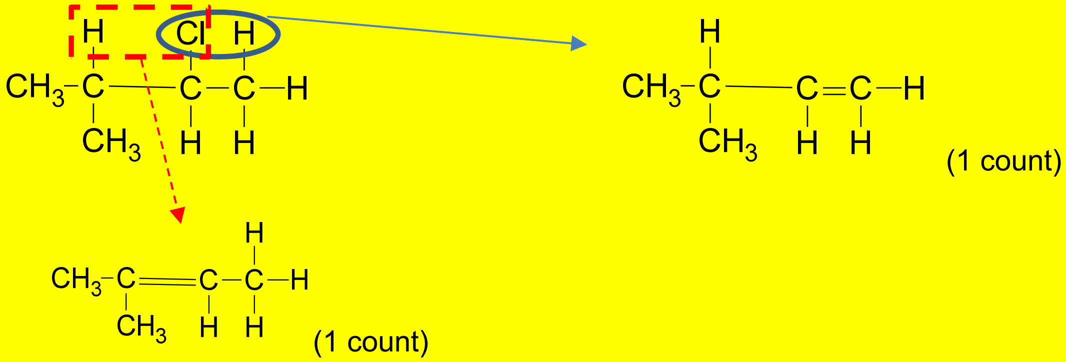
D



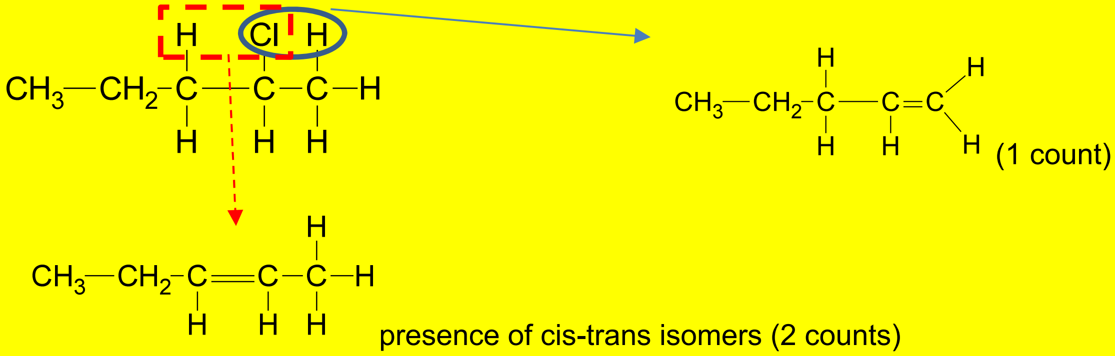
Answer: **C**

Option A is wrong as it has one more carbon and thus does not match the molecular formula. Option D is out as they do not have chiral carbon to allow presence of two optical isomers.

Option C is correct



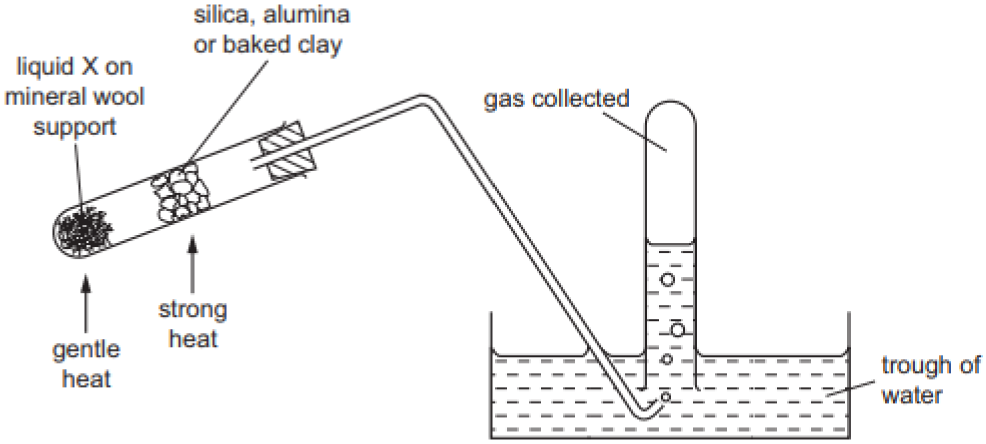
Option B is wrong as during the elimination process (hot sodium hydroxide in ethanol) a mixture of three alkenes were obtained



presence of cis-trans isomers (2 counts)

Thus, Option B structure will result in a mixture of 3 alkenes.

24 The diagram shows an experimental set-up which can be used in several different experiments.



Which processes could be demonstrated by using the above apparatus?

(1) oxidation of ethanol (liquid X)

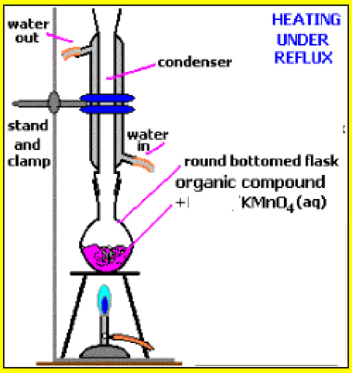
(2) dehydration of ethanol (liquid X)

(3) cracking of paraffin (liquid X)

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

Answer: C

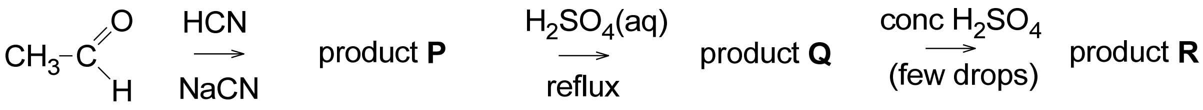
Oxidation of ethanol usually require a reflux set up



From lecture notes:

- Catalytic cracking is used to produce petrol (C_5 to C_{10}) and aromatic hydrocarbons.
- Catalyst: **<u>zeolites</u>** (mixture of Al_2O_3 and SiO_2).
- Temperature: **<u>450 - 550°C</u>** (Notice that lower temperatures are used)

25 Ethanal, CH_3CHO, is used to make product **R** in a three-stage synthesis.



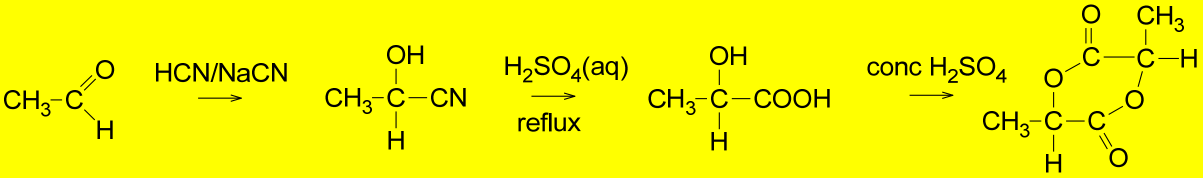
Two molecules of **Q** react to give one molecule of **R** plus two molecules of water.

R does not react with sodium.

What is the molecular formula and empirical formula of **R**?

	Molecular formula	Empirical formula
A	$C_3H_4O_2$	$C_3H_4O_2$
B	$C_6H_8O_4$	$C_3H_4O_2$
C	$C_3H_5O_2$	$C_3H_5O_2$
D	$C_6H_{10}O_5$	$C_6H_{10}O_5$

Answer: **B**



Molecular formula is $C_6H_8O_4$

Empirical formula of product R is $C_3H_4O_2$

26 Chlorofluoroalkanes have been used as the refrigerant in refrigerators but care has to be taken in disposing of old refrigerators.

Which statements about chlorofluoroalkanes are correct?

(1) C–C*l* bonds more readily undergo homolytic fission than C–F bonds.

(2) Care is taken in the disposal of old refrigerators because of possible ozone depletion.

(3) C_2H_4ClF is more volatile than C_2H_6.

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

Answer: B

C-C*l* bonds are weaker than C-F bonds thus C-C*l* bonds require less energy to break when undergoing homolytic fission. Thus statement 1 is correct.

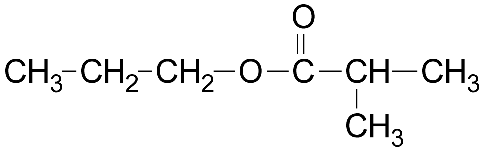
Presence of Chlorofluoroalkanes will result in ozone depletion. Statement 2 is right.

Statement 3 is wrong as C_2H_4ClF is polar and there are presence of stronger intermolecular permanent dipole-permanent dipole interaction as compared to the weaker instantaneous dipole-induced dipole interaction present in the non-polar molecule of C_2H_6.

27 Ethyl propanoate is refluxed with aqueous sodium hydroxide. The alcohol produced is then reacted with methyl propanoic acid to make a second ester.

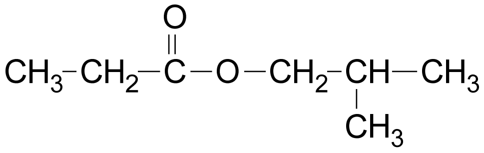
What is the structural formula of this second ester?

A



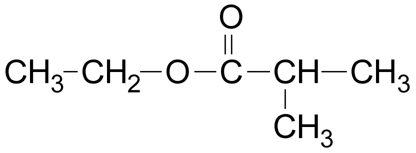
$$CH_3-CH_2-CH_2-O-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_3$$

B



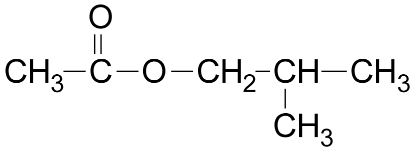
$$CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_3$$

C



$$CH_3-CH_2-O-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_3$$

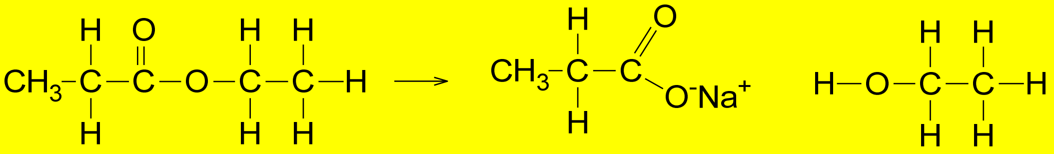
D



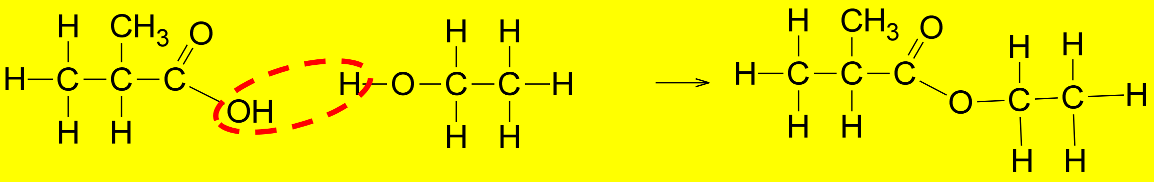
$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_3$$

Answer: **C**

During the basic hydrolysis of ethyl propanoate with NaOH (aq)



Ethanol is produced



28 Ethanedioic acid has the formula HO_2CCO_2H.

What is the formula of aluminium ethanedioate?

A AlC_2O_4

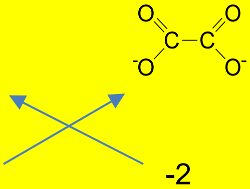
B $Al(C_2O_4)_3$

C $Al_2C_2O_4$

D $Al_2(C_2O_4)_3$

Answer: **D**

Species: Al^{3+}



Charge: +3 -2

Formula $Al_2(C_2O_4)_3$

29 Which of the following processes lead to an increase in entropy?

(1) Diffusion of air fresher in the lecture theatre.

(2) Combustion of a piece of charcoal to form CO_2 (g) and H_2O (g).

(3) Desalination of sea water by reverse osmosis (solvent passes from a dilute solution to a concentrated solution).

A 1 only

B 1 and 2 only

C 2 and 3 only

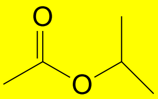
D 1, 2 and 3

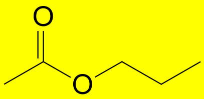
Answer: **B**

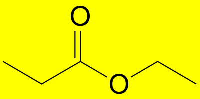
For option 3, there is an increase in orderliness as the solvent passes from a more concentrated solution to a more diluted solution. Hence, entropy will decrease.

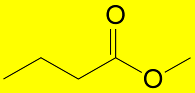
30	How many structural isomers with the molecular formula $C_5H_{10}O_2$ give infra-red absorptions both at approximately 1300 cm^{-1} and at approximately 1740 cm^{-1}?	
	A	3
	B	5
	C	7
	D	9

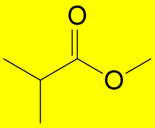
Answer: **B**
Infra-red absorption of 1300 cm^{-1}: carboxylic acid and ester
Infra-red absorption of 1740 cm^{-1}: ketone, aldehyde and ester
Thus, it has to be an ester since both conditions **MUST** be met.











END OF PAPER 1

SERANGOON JUNIOR COLLEGE
General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME

CLASS

CHEMISTRY 9729/02

JC2 Preliminary Examination **12 September 2018**
Paper 2 Structured Questions **2 hours**

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in the brackets [ ] at the end of each question or part questions.

For Examiner's Use	
1	/9
2	/9
3	/22
4	/13
5	/13
6	/9
TOTAL	**/ 75**

This document consists of **19** printed pages and **1** blank page.

1 Elements in Period 3 exhibit a variety of physical and chemical properties.

(a) An element in Period 3 has a high melting point but low electrical conductivity. Identify this element and explain why it has a high melting point using concepts of structure and bonding.

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....
[1]

(b) Two chlorides of Period 3 elements exist as liquids at room temperature. These two chlorides react with water to give white fumes, but only one of them gives a white solid.

(i) Using concepts of structure and bonding, explain why these two chlorides have low boiling points and exist as liquid at room temperature.

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[1]

(ii) Write chemical equations, with state symbols, for each of these chlorides reacting with water.

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[2]

(c) Period 3 elements also form oxides which reacts with water. Na_2O and SO_2 are two such oxides.

(i) Write chemical equations, with state symbols, when each of these oxides react with water.

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[2]

(ii) SO_2 is used as a food preservative. Suggest the property of SO_2 which enables it to function this way.

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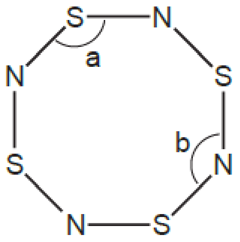
[1]

(d) Sulfur forms the compound S_4N_4 with nitrogen. The structure of S_4N_4 is shown below. Assume all bonds shown are single bonds.



Determine the number of lone pairs of electrons around a sulfur atom and a nitrogen atom in S_4N_4.

(i) Nitrogen atom: …………….. Sulfur atom: ………………..

[1]

(ii) Which bond angle, ***a*** or ***b***, will be smaller? Explain your answer.

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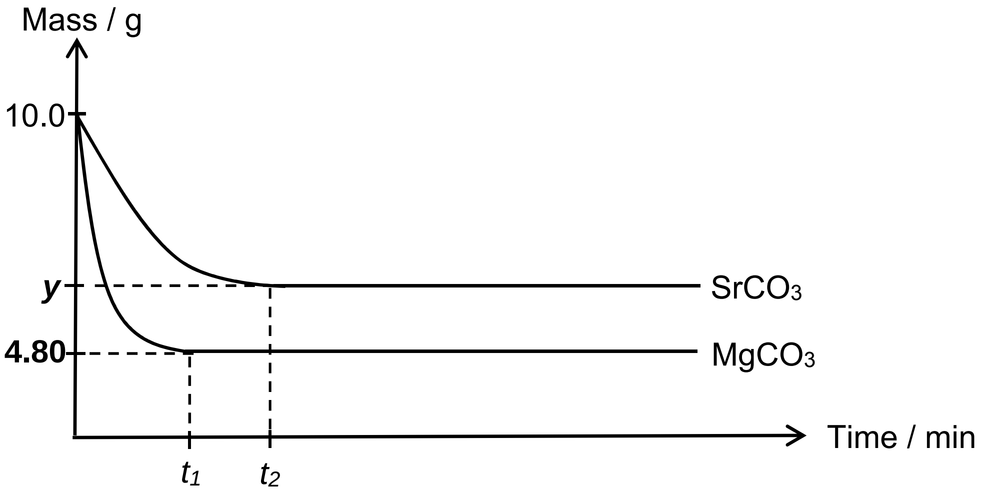
[1]

[Total: 9]

2 The following graph shows the change in mass with time for the decomposition of 10.0 g of magnesium carbonate and 10.0 g of strontium carbonate under the same conditions:



(a) **(i)** Calculate the value of ***y***.

[2]

(ii) Explain why the value of t_2 is larger than t_1.

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[3]

(b) There are three bottles labelled **A**, **B** and **C** in the laboratory. Each bottle contains one of the following reagents: aqueous Cl_2, KI solution and KBr solution.

The following tests were carried out and the results were summarised in the table below.

Experiment	Procedure	Observations
1	mixing reagent in bottle **A** with reagent in bottle **B**	mixture remains colourless
2	mixing reagent in bottle **A** with reagent in bottle **C**	mixture turns brown
3	mixing reagent in bottle **B** with reagent in bottle **C**	mixture turns brown

(i) Which bottle contains aqueous Cl_2?
With the aid of a balanced equation, explain your answer.

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[2]

(ii) If hexane is also provided, how would you use it to identify the contents of the other two bottles? Include the observations in your answer.

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[1]

(c) Using relevant data from the *Data Booklet*, comment on the thermal stability of hydrogen bromide and hydrogen chloride.

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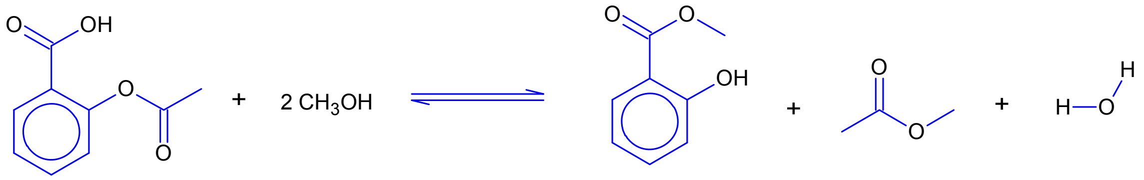
[1]

[Total:9]

3 Methyl salicylate, commonly known as oil of Wintergreen is used as a flavouring agent in candy. When methyl salicylate is applied to the skin, it causes a mild burning sensation which serves as a counter-irritant for sore muscles. It can be synthesise from aspirin. The reaction is as follows.



Methyl salicylate

Reagent	**Density / g cm^{-3}**	**M$_r$**	**Solubility in water**
Acetylsalicylate acid (Aspirin)		180.0	insoluble
Sulfuric acid	1.84	98.0	soluble
Methanol	0.792	32.0	soluble
Methyl salicylate	1.17	152.1	insoluble
Water	1.00	18.0	

Preparation of impure methyl salicylate

1. Weigh approximately 20 g of acetylsalicylate acid into a round-bottom flask. Add 30 cm^3 of methanol and stir until all the acetylsalicylate acid has dissolved.

2. Place 25 cm^3 of concentrated sulfuric acid in the tap funnel and then add the acid dropwise into the reagents in the flask. Keep the contents well shaken and cool occasionally in an ice-water bath.

3. When all of the acid have been added, replace the tap funnel with a reflux condenser and gently boil the mixture for an hour.

4. Remove the condenser and boil off about 50% of the volume.

(a) **(i)** By using the amounts given above, prove that methanol is in excess and suggest why it is done to increase yield.

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[2]

(b) When concentrated sulfuric acid is added to the reaction mixture, cooling is necessary. Suggest the main cause of heat being produced at this stage.

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[1]

(c) The reaction mixture was heated overnight. Why is this process necessary for the preparation of many covalent organic compounds?

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

The crude product formed requires purification as it contains many impurities.

Purification of impure methyl salicylate

5. Transfer the remaining mixture into a separatory funnel. Shake the mixture with 30 cm^3 of ice cool water and separate the aqueous layer from the methyl salicylate. Reject the aqueous layer.

6. Return the methyl salicylate to the funnel. Add 20 cm^3 of dilute sodium hydrogencarbonate in the separating funnel, inverting the flask and opening the tap at intervals to prevent build up of pressure.

7. Transfer the methyl salicylate into a conical flask and add some granular anhydrous calcium sulfate. Swirl the mixture until the liquid is clear.

6. Filter the methyl salicylate into a clean vial. Weigh the purified product.

(d) Volume of methyl salicylate produced is 10 cm^3. Calculate the percentage yield.

[2]

(e) The impure methyl salicylate was shaken with water (step 5) and the two layers are allowed to separate.

(i) By considering the structure and bonding of methyl salicylate, suggest why it is an immiscible with methanol.

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[2]

(ii) Suggest the organic compounds inside both layers. Explain your answer.

Top layer: ……………………….….. Bottom layer: …………………………………

Explanation: ……………………………………………………………………..
[2]

(f) **(i)** It is important to open the tap at intervals to prevent build up of pressure in when dilute aqueous sodium hydrogencarbonate was added (step 6). Explain, with the aid of an equation why this is important.

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[2]

(g) **(i)** Draw the dot-and-cross diagram of calcium sulfate used in step 7.

[2]

(ii) Calcium sulfate is a desiccant to remove any water left in the methyl salicylate product. When the desiccant has dissolved, the anions and cations are each surrounded by a number of water molecules.

Draw simple diagrams to show how a water molecule can be attached to a calcium cation, and to a sulfate anion. Label each of your diagram to show the type of interaction involved.

Ca^{2+} cation	SO_4^{2-} anion

[2]

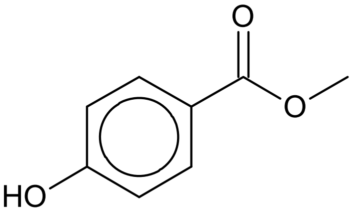
(iii) The lattice energy of calcium sulfate is – 2640 kJ mol^{-1}.

Use the following values of enthalpy change of hydration to construct an energy level diagram and use it to calculate the enthalpy change of solution, $\Delta H_{sol}^{\ominus}$, for calcium sulfate.

	$\Delta H_{hyd}^{\ominus}$ / kJ mol^{-1}
Ca^{2+}	–1577
SO_4^{2-}	–1045

[3]

(h) Methyl 4–hydroxybenzoate is an isomer of methyl salicylate.



methyl 4–hydroxybenzoate

Predict and explain whether methyl 4–hydroxybenzoate or methyl salicylate would have a higher boiling point. [3]

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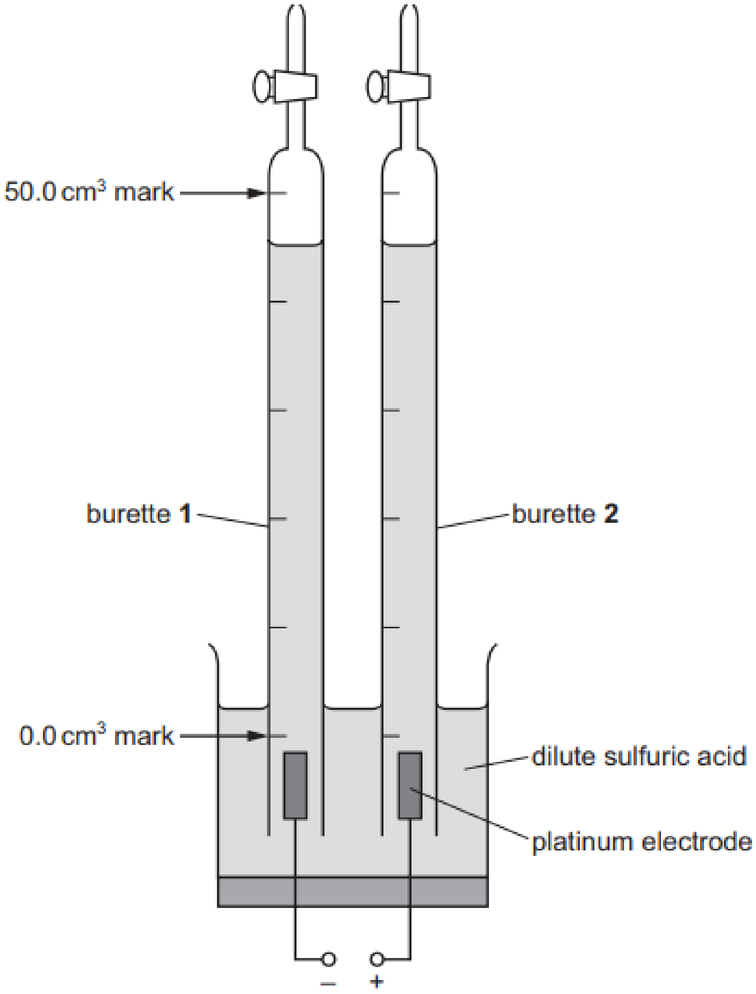
[3]

[Total: 22]

4 Dilute sulfuric acid, H_2SO_4(aq), can be electrolysed using platinum electrode and a direct current. Hydrogen gas is produced at the cathode and oxygen gas is formed at the anode. The two gases are collected separately in burettes filled with dilute sulfuric acid placed over each electrode.



Reaction at electrode in burette **1**: $2H^+(aq) + 2e^- \rightarrow H_2(g)$

Reaction at electrode in burette **2**: $H_2O(l) \rightarrow \frac{1}{2} O_2(g) + 2H^+(aq) + 2e^-$

The production of hydrogen gas over time can be measured, and the data used to determine charge of one mole of electrons, known as the Faraday constant, *F*.

(a) **(i)** Student A performed the experiment and the volume of hydrogen gas produced during the electrolysis process were recorded in the table.

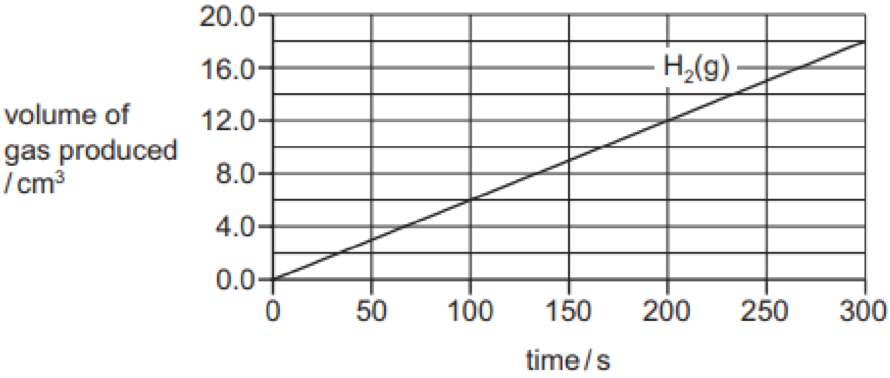
Process the results to calculate the volume of the hydrogen gas produced, in cm^3, and the charge passed, in coulombs, C.

The current was kept constant at 0.80A.

Time/s	Reading on burette **1**/cm^3	Volume of hydrogen gas produced /cm^3	Charge passed /C
0	46.20	0.00	
50	41.20		
100	36.20		
150	31.45		
200	25.80		
250	20.80		

[2]

(ii) Another student B, performed the experiment at room temperature and his graph showing the relationship between volume of $H_2(g)$ produced at the cathode and time was as shown below.



The gradient of the line of best fit gives the volume of hydrogen gas produced per coulomb.

Given that the gradient of the line to be 0.125 $cm^3\ C^{-1}$, calculate the number of moles of hydrogen gas produced per coulomb.

[Molar volume of gas = 24.0 dm^3 at room temperature and pressure]

[1]

(iii) Using your answer from **(a)(ii)** and the half equation for the production of H_2(g), calculate a numerical value for the Faraday constant (the charge of 1 mole of electrons).

[1]

(iv) Using the graph in **(a)(ii)**, draw a line on the graph to show the relationship between volume of O_2(g) produced at the anode and time in this experiment.

[1]

(v) Explain why the volume of O_2(g) measured in the experiment might be **less** than that shown by your drawn line. Assume that no gas is lost from leaks.

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……………………………………………………………………………………………

[1]

(b) A student suggested to replace the platinum electrodes with copper as it would be cheaper in the electrolysis of dilute sulfuric acid.

Quoting relevant data from the *Data Booklet*, suggest what effect, if any, the use of copper electrodes would have on the volume of gas produced at **each** electrode.

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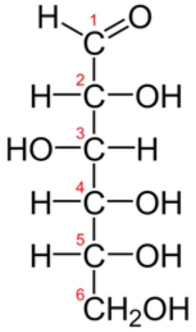
[3]

(c) Fehling's solution is a copper based chemical reagent used to differentiate between water soluble carbohydrate and ketone functional groups. This test was developed by German chemist Hermann von Fehling in 1849.

$RCHO + 2\,Cu(C_4H_4O_6)_2^{2-} + 5OH^- \rightarrow RCOO^- + Cu_2O + 4\,C_4H_4O_6^{2-} + 3H_2O$

Fehling's solution can be used to screen glucose in urine, thus detecting diabetes.



Glucose

(i) Suggest which carbon can be oxidised by Fehling's solution and draw the skeletal formula of the compound **D** which is the oxidised product of glucose after it has been acidified by dilute hydrochloric acid.

Carbon ……………   Compound **D**:

[2]

(ii) Determine the change in oxidation number on the carbon mentioned in **(c)(i)** with respect to glucose and compound **D**.

[1]

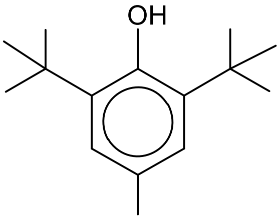
(iii) Hot concentrated sulfuric acid was added to compound **D**. Compound **E** which consists of a 6-atoms ring structure was formed.
Suggest the structure of compound **E**.

[1]

[Total: 13]

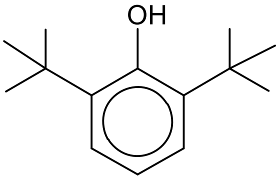
5 This question is about controversial food additives that are Generally Regarded As Safe (GRAS) by the American Food and Drug Administration (FDA), but are suspected to be harmful to humans when consumed.

(a) **(i)** Butylated hydroxytoluene (BHT) is useful for its antioxidant properties, to prevent oxidation in fluids (e.g. fuel, oil) and other foodstuffs where free radicals must be controlled.



Butylated hydroxytoluene (BHT)

Describe the mechanism for the synthesis of BHT using bromomethane and 2,6-di-tert-butylphenol shown below.



2,6-di-tert-butylphenol

[3]

(a) **(ii)** Propose a simple test-tube reaction to differentiate 2,6-di-tert-butylphenol and BHT. You are to clearly state the observation in your answer.

……………………………………………………………………………………………

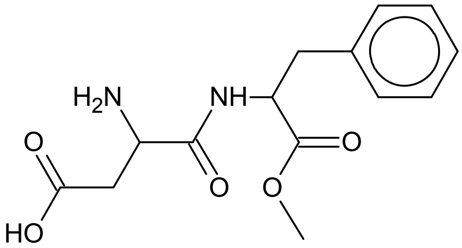
……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

[2]

(b) Aspartame (APM) is an artificial non-carbohydrate sweetener used as a sugar substitute in some foods and beverages, which is especially useful for diabetic patients.



Aspartame (APM)

(i) Label all chiral carbons with an (*) in the diagram above and calculate the total number of possible stereoisomers of APM.

[2]

(ii) Draw all organic products formed when APM is reacted with a hot aqueous alkaline solution.

[3]

(c) Potassium bromate, $KBrO_3$, is typically used as a flour improver. It is a very strong oxidising agent, and allows for the baking of extremely white and fluffy bread, and it has the following half equation.

$$2BrO_3^- + 12H^+ + 10e \rightleftharpoons Br_2 + 6H_2O \quad E^\ominus = +1.50\ V$$

(i) Suggest reagent and conditions for the oxidation of ethene to carbon dioxide.

……………………………………………………………………………………………..

[1]

(ii) Hot acidified bromate is also able to oxidise ethene into carbon dioxide. With reference to the *Data Booklet*, explain.

………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

[1]

(iii) Hence, suggest how the yield of the carbon dioxide produced would be affected due to the use of bromate as an oxidising agent.

………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

[1]

[Total: 13]

6 Compound **G** and **H** have molecular formula of C_4H_8 and C_3H_6 respectively, and do not exhibit cis-trans isomerism.

Both **G** and **H** can decolourise hot potassium manganate(VII) to give compounds **J** and **K** respectively, together with a gas that produces a white precipitate when bubbled through calcium hydroxide.

J produces an orange precipitate when warm with 2,4–dinitrophenylhydrazine, and **K** produces effervescence when sodium hydrogencarbonate is added.
J decolourises alkaline aqueous iodine but not **K**.

(a) Draw the structures of **G**, **H**, **J**, and **K**.

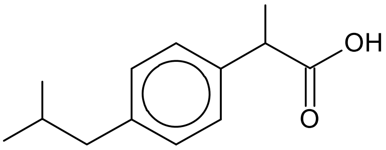
[4]

(b) Construct a balanced chemical equation on how **J** reacts with

- alkaline aqueous iodine,
- 2,4-DNPH.

[2]

(c) Ibuprofen is an oral or intravenous medication that is used for treating pain, fever, and inflammation. It typically begins working within an hour and it has the following structure.

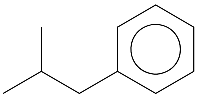


Ibuprofen

Compounds **G** and **H** from **(a)** are both prerequisites for the synthesis of Ibuprofen.

The reaction schema to obtain ibuprofen is described below.

(1) HBr gas is introduced to **G** to form **L**.
(2) **L** is reacted with benzene in the presence of anhydrous $FeBr_3$. Compound **M** is obtained.



Compound **M**

(3) Aqueous Br_2 is added to **H** to form **N**.
(4) **N** and **M** are reacted in the presence of anhydrous $FeBr_3$. Compound **P** with molecular formula $C_{13}H_{20}O$ is produced.
(5) Hot acidified potassium dichromate(VI) is then added to **P** to produce ibuprofen.

Using the structure of ibuprofen and the information provided, draw the structures of **L**, **N** and **P**.

[3]

[Total: 9]

END OF PAPER

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SERANGOON JUNIOR COLLEGE
General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME	
CLASS	

CHEMISTRY 9729/02

JC2 Preliminary Examination **12 September 2018**

Paper 2 Structured Questions (Solutions) **2 hours**

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

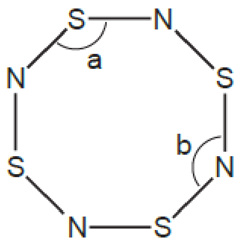
READ THESE INSTRUCTIONS FIRST

Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

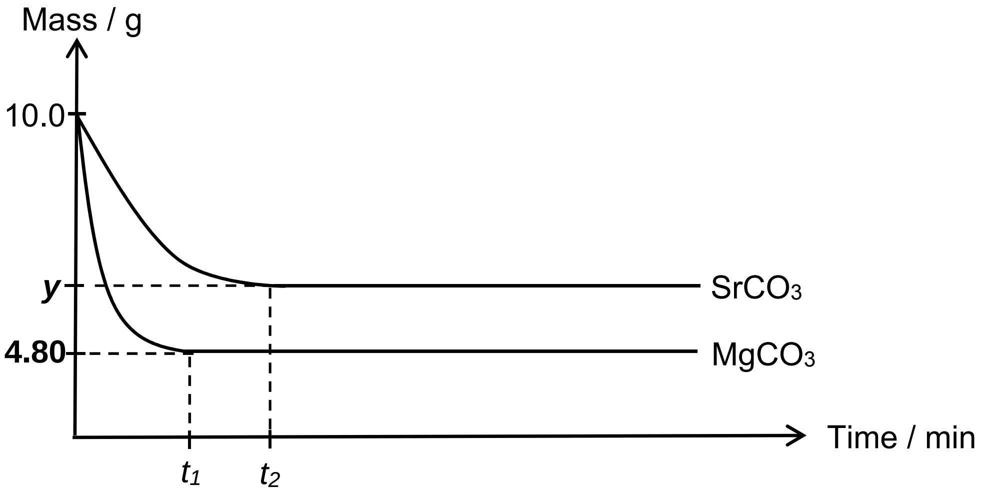
Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in the brackets [ ] at the end of each question or part questions.

For Examiner's Use	
1	/9
2	/9
3	/22
4	/13
5	/13
6	/9
TOTAL	**/ 75**

1	Elements in Period 3 exhibit a variety of physical and chemical properties.		
	(a)	An element in Period 3 has a high melting point but low electrical conductivity. Identify this element and explain why it has a high melting point using concepts of structure and bonding. [1]	
		Silicon has a **giant molecular structure** and **strong covalent bonds between the atoms in the molecule**. Hence it needs a large about of energy to overcome it. [1]	
	(b)	Two chlorides of Period 3 elements exist as liquids at room temperature. These two chlorides react with water to give white fumes, but only one of them gives a white solid.	
		(i)	Using concepts of structure and bonding, explain why these two chlorides have low boiling points and exist as liquid at room temperature. [1]
			Both have **simple molecular structure**. These compounds have low boiling points since **less heat energy** is required to overcome the **weak intermolecular forces of attraction**. [1]
		(ii)	Write chemical equations, with state symbols, for each of these chlorides reacting with water. [2]
			$SiCl_4(l) + 2H_2O(l) \rightarrow SiO_2(s) + 4HCl(g)$ [1] $PCl_3(l) + 3H_2O(l) \rightarrow H_3PO_3(aq) + 3HCl(g)$ [1] Do not accept PCl_5 as it is a solid
	(c)	Period 3 elements also form oxides which reacts with water. Na_2O and SO_2 are two such oxides.	
		(i)	Write chemical equations, with state symbols, when each of these oxides react with water. [2]
			$Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$ [1] $SO_2(g) + H_2O(l) \rightleftharpoons H_2SO_3(aq)$ [1]
		(ii)	SO_2 is used as a food preservative. Suggest the property of SO_2 which enables it to function this way. [1]
			It acts as a reducing agent/ antioxidant. [1] Note: Food may turn bad due to oxidation process. SO_2 will be oxidised in place of the food.
	(d)	Sulfur forms the compound S_4N_4 with nitrogen. The structure of S_4N_4 is shown below. Assume all bonds shown are single bonds. 	

		Determine the number of lone pairs of electrons around a sulfur atom and a nitrogen atom in S_4N_4.	
		(i)	Nitrogen atom Sulfur atom [1]
			Nitrogen atom: **1** lone pair Sulfur atom: **2** lone pairs [1]
		(ii)	Which bond angle, ***a*** or ***b***, will be smaller? Explain your answer. [1]
			Bond angle **a** will be **smaller**. **Lone-pair lone-pair repulsion is greater** than lone-pair single electron repulsion. [1]
			[Total: 9]

2	The following graph shows the change in mass with time for the decomposition of 10.0 g of magnesium carbonate and 10.0 g of strontium carbonate under the same conditions: 		
	(a)	**(i)**	Calculate the value of ***y***. [2]
			$SrCO_3(s) \rightarrow SrO(s) + CO_2(g)$ **y** is the mass of SrO that formed from the decomposition Amount of $SrCO_3$ = $\frac{10}{(87.6+12.0+16.0\times3)} = 0.06775 \, mol$ [1] Amount of SrO formed = 0.06775 mol Mass of SrO, **y** = 0.06775 x (87.6 + 16.0) = 7.02 g [1]

(ii) Explain why the value of t_2 is larger than t_1.

[3]

- **Cationic radius of Sr^{2+} is larger than Mg^{2+}** while cationic charge is the same or **Charge density, and hence polarising power, of the Sr^{2+} is smaller**. **[1]**
- **Polarising effect on the anion by Sr^{2+} is smaller** **[1]** and the anion electron cloud is distorted to a smaller extent.
- More energy is required to overcome the C–O bond in $SrCO_3$.
- **Rate is slower and a longer time (t_2) is needed to decompose $SrCO_3$**.[1]

(b) There are three bottles labelled **A**, **B** and **C** in the laboratory. Each bottle contains one of the following reagents: aqueous Cl_2, KI solution and KBr solution.

The following tests were carried out and the results were summarised in the table below.

Experiment	**Procedure**	**Observations**
1	mixing reagent in bottle **A** with reagent in bottle **B**	mixture remains colourless
2	mixing reagent in bottle **A** with reagent in bottle **C**	mixture turns brown
3	mixing reagent in bottle **B** with reagent in bottle **C**	mixture turns brown

(i) Which bottle contains aqueous Cl_2? With the aid of a balanced equation, explain your answer.

[2]

Bottle **C** **[1]**

$Cl_2 + 2X^- \longrightarrow 2Cl^- + X_2$ where X = Br or I **[1]**

Down the group, reduction potential becomes **less positive**.

The halogens have **lower tendency to be reduced**.

Stronger oxidising agent higher in the Group oxidises (and hence displaces) the **halide ions in aqueous solution further down the Group** **[1]**

(ii) If hexane is also provided, how would you use it to identify the contents of the other two bottles? Include the observations in your answer.

[1]

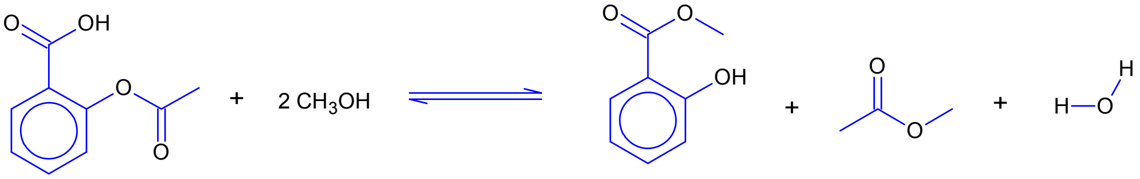
Knowing that bottle **A** and **B** is either KBr or KI, **add hexane to the two brown mixtures obtained, separately.**

If the organic layer is **purple, bottle contains KI**.

If the organic layer is **red–brown, bottle contains KBr.** **[1]**

	(c)	Using relevant data from the *Data Booklet*, comment on the thermal stability of hydrogen bromide and hydrogen chloride. [1]
		Bond energy of H-Br (366 kJ mol^{-1}) is lesser than bond energy of H-C*l* (431 kJ mol^{-1}) Less energy is required to overcome the weaker covalent bond in H-Br thus HBr will decompose at a lower temperature. **[1]**
		[Total:9]

3 Methyl salicylate, commonly known as oil of Wintergreen is used as a flavouring agent in candy. When methyl salicylate is applied to the skin, it causes a mild burning sensation which serves as a counter-irritant for sore muscles. It can be synthesise from aspirin. The reaction is as follows.



Methyl salicylate

Reagent	**Density / g cm^{-3}**	**M$_r$**	**Solubility in water**
Acetylsalicylate acid (Aspirin)	[redacted]	180.0	insoluble
Sulfuric acid	1.84	98.0	soluble
Methanol	0.792	32.0	soluble
Methyl salicylate	1.17	152.1	insoluble
Water	1.00	18.0	[redacted]

Preparation of impure methyl salicylate

1. Weigh approximately 20 g of acetylsalicylate acid into a round-bottom flask. Add 30 cm^3 of methanol and stir until all the acetylsalicylate acid has dissolved.

2. Place 25 cm^3 of concentrated sulfuric acid in the tap funnel and then add the acid dropwise into the reagents in the flask. Keep the contents well shaken and cool occasionally in an ice-water bath.

3. When all of the acid have been added, replace the tap funnel with a reflux condenser and gently boil the mixture for an hour.

4. Remove the condenser and boil off about 50% of the volume.

(a) **(i)** By using the amounts given above, prove that methanol is in excess and suggest why it is done to increase yield.

[2]

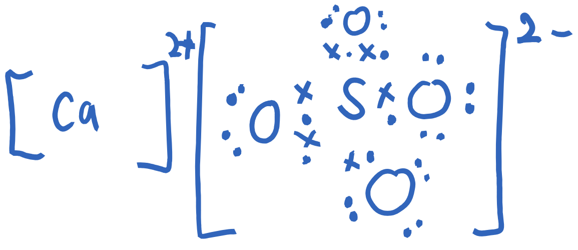
$n_{methanol}$ = (30 x 0.792) / 32 = <u>0.742 mol</u>
$n_{aspirin}$ = 20/180 = <u>0.1111mol</u>
$n_{methanol}$ = ½ aspirin
Hence methanol is in excess. [1]

		By LCP, increase the methanol concentration would cause the position of equilibrium to lie towards the forward reaction (right), [1] increasing the amount of methyl salicylate produced.
(b)		When concentrated sullfuric acid is added to the reaction mixture, cooling is necessary. Suggest the main cause of heat being produced at this stage. [1]
		Dilution of concentrated sulfuric acid produces heat. [1]
(c)		The reaction mixture was heated overnight. Why is this process necessary for the preparation of many covalent organic compounds? [1]
		Breaking strong covalent bonds [1] requires a large amount of energy to overcome.
		The crude product formed requires purification as it contains many impurities. Purification of impure methyl salicylate 5. Transfer the remaining mixture into a separatory funnel. Shake the mixture with 30 cm^3 of ice cool water and separate the aqueous layer from the methyl salicylate. Reject the aqueous layer. 6. Return the methyl salicylate to the funnel. Add 20 cm^3 of dilute sodium hydrogencarbonate in the separating funnel, inverting the flask and opening the tap at intervals to prevent build up of pressure. 7. Transfer the methyl salicylate into a conical flask and add some granular anhydrous calcium sulfate. Swirl the mixture until the liquid is clear. 6. Filter the methyl salicylate into a clean vial. Weigh the purified
(d)		Volume of methyl salicylate produced is 10 cm^3. Calculate the percentage yield.
		Aspirin is the limiting reaction $n_{\text{methyl salicylate}} = n_{\text{aspirin}} = 20/180 = 0.1111\text{mol}$ [1] Theortical yield (in Vol) = $0.1111 \times 152.1 \div 1.17 = 14.44\ cm^3$ % yield = 10/14.44 = 69.2 % [1]
(e)	The impure methyl salicylate was shaken with water (step 5) and the two layers are allowed to separate.	

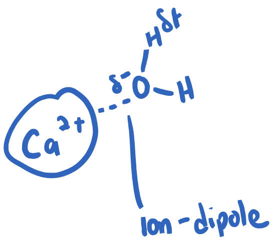
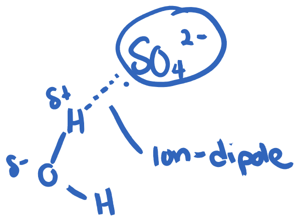
	(i)	By considering the structure and bonding of methyl salicylate, suggest why it is an immiscible with methanol. [2]
		The extensive intermolecular id-id interactions due to the hydrophobic benzene ring [1] is not strong enough to displace the stronger intermolecular hydrogen bonds. [1]
	(ii)	Suggest the organic compounds inside both layers. Explain your answer. [2]
		Top layer: methanol Bottom layer: methyl salicylate [1] for both Explanation: methyl salicylate is more dense than methanol [1] for reason

<table>
<tr><td>(f)</td><td>(i)</td><td>It is important to open the tap at intervals to prevent build up of pressure in when dilute aqueous sodium hydrogencarbonate was added (step 6). Explain, with the aid of an equation why this is important. [2]</td></tr>
<tr><td></td><td></td><td>$H_2SO_4 + 2NaHCO_3 \rightarrow 2CO_2 + 2H_2O + Na_2SO_4$ [1]

(x) but mark reason separately –
$H_2SO_4 + NaHCO_3 \rightarrow CO_2 + H_2O + NaHSO_4$
H_2SO_4 + methyl salicylate → CO_2

Gaseous CO_2 is produced which will increase the pressure in the separatory funnel. [1]</td></tr>
<tr><td>(g)</td><td>(i)</td><td>Draw the dot-and-cross diagram of calcium sulfate used in step 7. [2]</td></tr>
<tr><td></td><td></td><td>

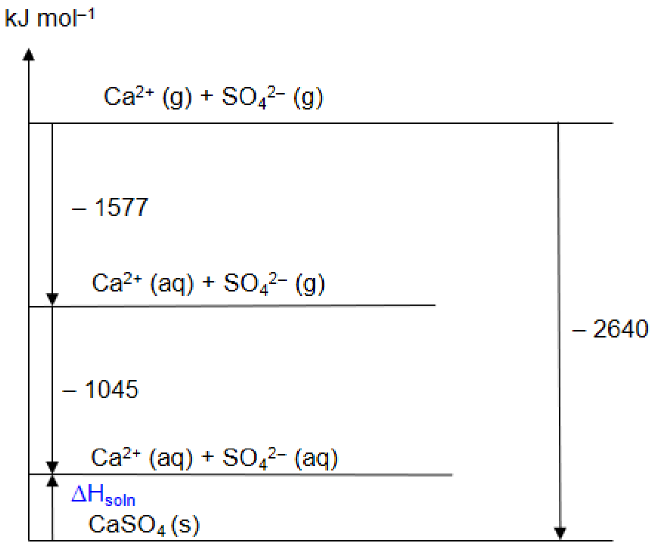
[1] [1]</td></tr>
<tr><td></td><td>(ii)</td><td>Calcium sulfate is a desiccant to remove any water left in the methyl salicylate product. When the desiccant has dissolved, the anions and cations are each surrounded by a number of water molecules.

Draw simple diagrams to show how a water molecule can be attached to a calcium cation, and to a sulfate anion. Label each of your diagram to show the type of interaction involved. [2]</td></tr>
<tr><td></td><td></td><td><table>
<tr><td>
</td><td>
</td></tr>
<tr><td>Ca^{2+} cation</td><td>SO_4^{2-} anion</td></tr>
<tr><td>[1]</td><td>[1]</td></tr>
</table></td></tr>
</table>

(iii) The lattice energy of calcium sulfate is — 2640 kJ mol^{-1}.
Use the following values of enthalpy change of hydration to construct an energy cycle and use it to calculate the enthalpy change of solution, $\Delta H_{sol}^{\ominus}$, for calcium sulfate.

	$\Delta H_{hyd}^{\ominus}$ / kJ mol^{-1}
Ca^{2+}	–1577
SO_4^{2-}	–1045

[3]

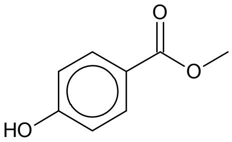


[2] energy level

$\Delta H_{sol}^{\ominus} = \Delta H_{hyd}^{\ominus}(Ca^{2+}) + \Delta H_{hyd}^{\ominus}(SO_4^{2-}) - \Delta H_{latt}^{\ominus}$

$= -1577 + (-1045) - (-2640) =$ **$+ 18.0$ kJ mol^{-1}** [1]

(h) Methyl 4–hydroxybenzoate is an isomer of methyl salicylate.



methyl 4–hydroxybenzoate

Predict and explain whether methyl 4–hydroxybenzoate or methyl salicylate would have a higher boiling point. [3]

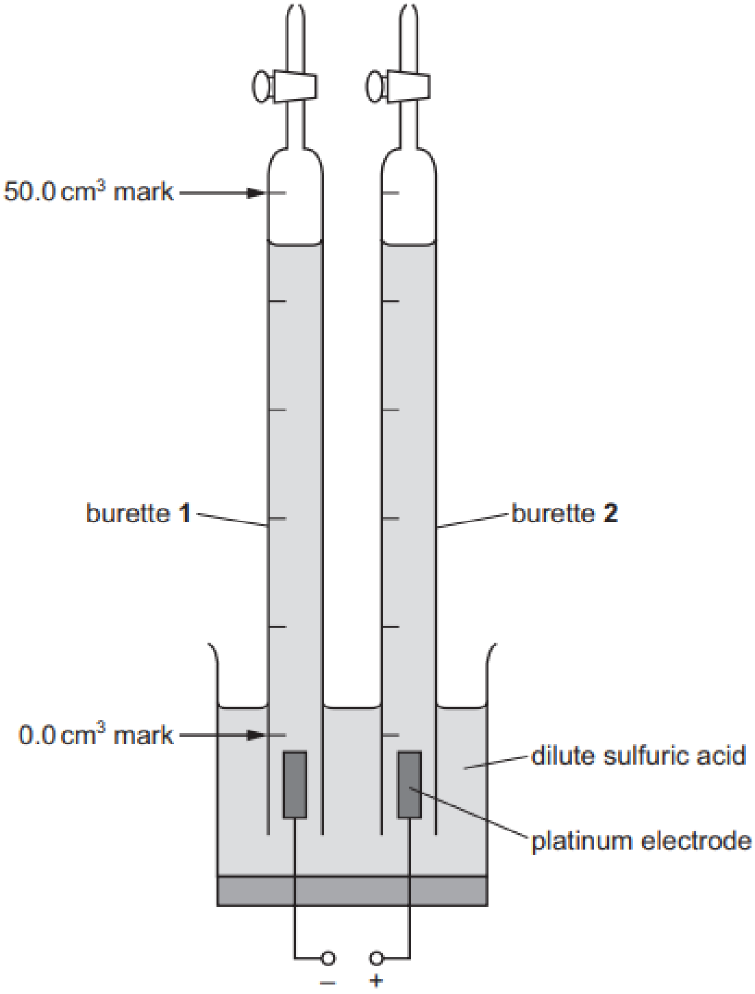
Both have simple molecular structure.
Methyl 4–hydroxybenzoate would have a **higher boiling point** [1] than methyl salicylate.

The **close proximity** of the two substituents on methyl salicylate allows for **intramolecular hydrogen bonding**[1] as compared to methyl 4–hydroxybenzoate which is far apart.

There will be **less energy** required to overcome the **less extensive intermolecular hydrogen bonds** [1] to overcome in methyl salicylate and thus it has a lower boiling point.

[Total: 22]

4 Dilute sulfuric acid, $H_2SO_4(aq)$, can be electrolysed using platinum electrode and a direct current. Hydrogen gas is produced at the cathode and oxygen gas is formed at the anode. The two gases are collected separately in burettes filled with dilute sulfuric acid placed over each electrode.



Reaction at electrode in burette **1**: $2H^+(aq) + 2e^- \rightarrow H_2(g)$
Reaction at electrode in burette **2**: $H_2O(l) \rightarrow \frac{1}{2} O_2(g) + 2H^+(aq) + 2e^-$

The production of hydrogen gas over time can be measured, and the data used to determine charge of one mole of electrons, known as the Faraday constant, *F*.

(a) **(i)** Student A performed the experiment and the volume of hydrogen gas produced during the electrolysis process were recorded in the table.

Process the results to calculate the volume of the hydrogen gas produced, in cm^3, and the charge passed, in coulombs, C.

The current was kept constant at 0.80A.

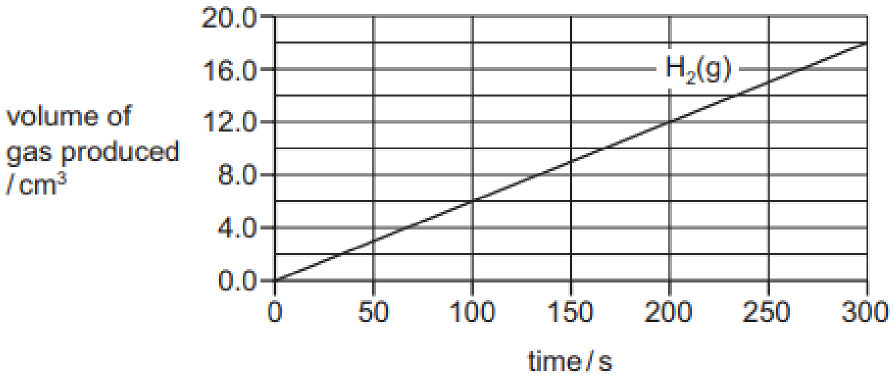
Time/s	Reading on burette **1**/cm^3	Volume of hydrogen gas produced /cm^3	Charge passed /C
0	46.20	0.00	0
50	41.20	5.00	40
100	36.20	10.00	80
150	31.45	14.75	120
200	25.80	20.40	160
250	20.80	25.40	200

[2]

[1]: Volume of H_2 correct and to 2 d.p

[1] charge correct

(ii) Another student B, performed the experiment at room temperature and his graph showing the relationship between volume of $H_2(g)$ produced at the cathode and time was as shown below.



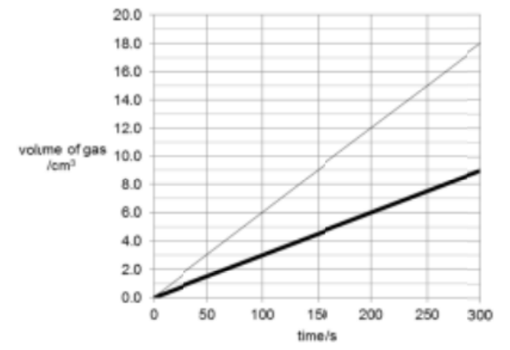
The gradient of the line of best fit gives the volume of hydrogen gas produced per coulomb.

Given that the gradient of the line to be 0.125 cm^3 C^{-1}, calculate the number of moles of hydrogen gas produced per coulomb.

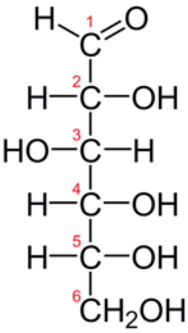
[Molar volume of gas = 24.0 dm^3 at room temperature and pressure]

[1]

$\frac{0.125}{24000} = 5.208\times10^{-6}$ mol C^{-1} [1]

		(iii)	Using your answer from **(a)(ii)** and the half equation for the production of $H_2(g)$, calculate a numerical value for the Faraday constant (the charge of 1 mole of electrons). [1]
			$1 \div \left(2 \times \frac{0.125}{24000}\right)$ = 96000 C mol^{-1} [1]
		(iv)	Using the graph in **(a)(ii)**, draw a line on the graph to show the relationship between volume of $O_2(g)$ produced at the anode and time in this experiment. [1]
			 Straight line from origin to (300, 9.0) [1]
		(v)	Explain why the volume of $O_2(g)$ measured in the experiment might be **less** than that shown by your drawn line. Assume that no gas is lost from leaks. [1]
			Oxygen is slightly soluble in water. [1] Or Oxygen gas is assumed to be ideal based on the fact of 24 dm^3 mentioned in the question.
	(b)		A student suggested to replace the platinum electrodes with copper as it would be cheaper in the electrolysis of dilute sulfuric acid. Quoting relevant data from the *Data Booklet*, suggest what effect, if any, the use of copper electrodes would have on the volume of gas produced at **each** electrode. [3]
			Cu^{2+}/Cu +0.34 V $O_2/2H_2O$ +1.23 V H^+/H_2 0.00 V Cathode: No effect at cathode. [1] Anode: Copper anode will dissolve as it is a reactive electrode as Cu^{2+}/Cu has a more negative E^θ value [1 with data quoted] Less gas produced at anode when copper electrode is used. [1]

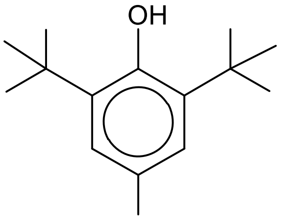
		Reason: *not marking for this question but essential for understanding*. At the anode: Cu^{2+}/Cu has more negative E^{θ}, hence Cu will be oxidised instead of H_2O Anodic reaction when Cu electrode is used: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e$ Anodic reaction when Pt electrode is used: $H_2O(l) \rightarrow \frac{1}{2} O_2(g) + 2H^+(aq) + 2e$ At the cathode: Cathodic reaction for Pt and Cu electrode will be the same $2H^+(aq) + 2e \rightarrow H_2(g)$.

	(c)	Fehling's solution is a copper based chemical reagent used to differentiate between water soluble carbohydrate and ketone functional groups. This test was developed by German chemist Hermann von Fehling in 1849. $RCHO + 2\ Cu(C_4H_4O_6)_2^{2-} + 5OH^- \rightarrow RCOO^- + Cu_2O + 4\ C_4H_4O_6^{2-} + 3H_2O$ Fehling's solution can be used to screen glucose in urine, thus detecting diabetes.  Glucose	
		(i)	Suggest which carbon can be oxidised by Fehling's solution and draw the skeletal formula of the compound **D** which is the oxidised product of glucose after it has been acidified by dilute hydrochloric acid. [2]
			Carbon 1 [1] Compound **D**: [1]
		(ii)	Determine the change in oxidation number on the carbon mentioned in **(c)(i)** with respect to glucose and compound **D**. [1]

			Oxidation number of carbon 1 on glucose: +1 Oxidation number of carbon 1 on compound D +3 The oxidation number changes from +1 to +3 [1] Or The oxidation number increase by 2 Or +2
		(iii)	Hot concentrated sulfuric acid was added to compound **D**. Compound **E** which consists of a 6-atoms ring structure was formed. Suggest the structure of compound **E**. [1]
			 [1]
			[Total: 13]

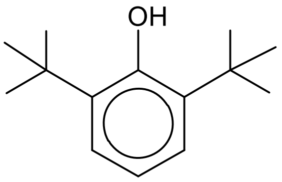
5 This question is about controversial food additives that are Generally Regarded As Safe (GRAS) by the American Food and Drug Administration (FDA), but are suspected to be harmful to humans when consumed.

(a) (i) Butylated hydroxytoluene (BHT) is useful for its antioxidant properties, to prevent oxidation in fluids (e.g. fuel, oil) and other foodstuffs where free radicals must be controlled.



Butylated hydroxytoluene (BHT)

Describe the mechanism for the synthesis of BHT using bromomethane and 2,6-di-tert-butylphenol shown below.



2,6-di-tert-butylphenol

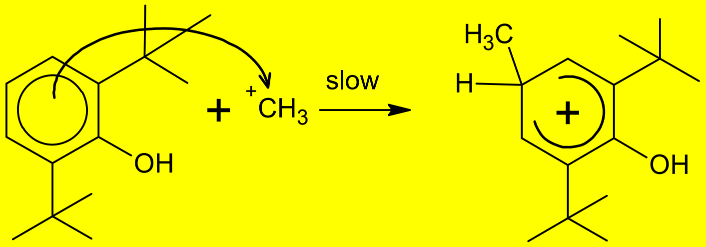
[3]

Electrophilic Substitution

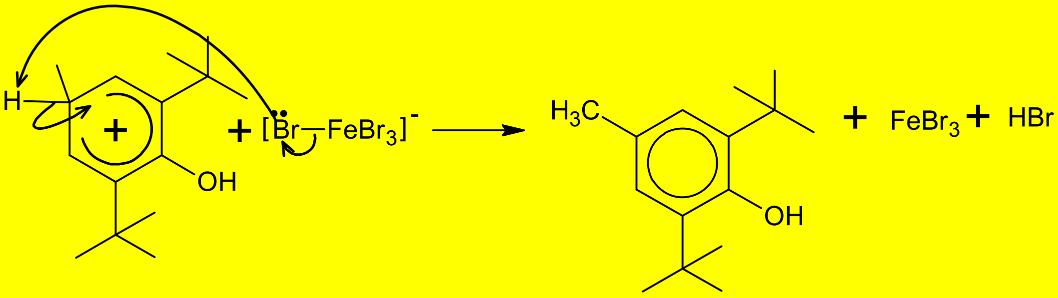
Step 1

$CH_3Br + FeBr_3 \longrightarrow {}^{+}CH_3 + [Br–FeBr_3]^{–}$ (it's in the lecture note ☺)

Step 2

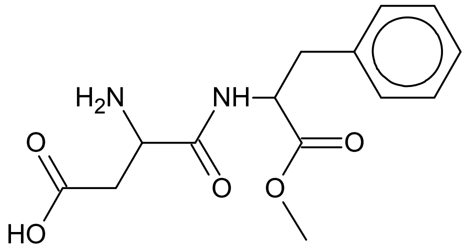
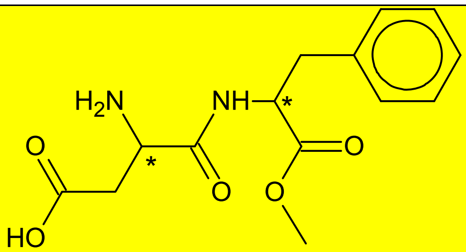
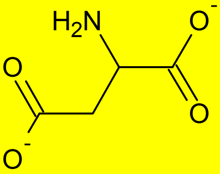
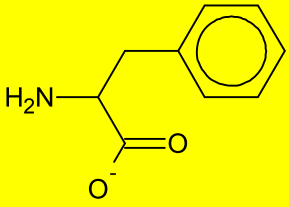


Step 3



If mis-draw the structure penalise one mark

[3m] each mistake minus 1m

	(a)	**(ii)**	Propose a simple test-tube reaction to differentiate 2,6-di-tert-butylphenol and BHT. You are to clearly state the observation in your answer. [2]
			Test: Add Br_2 (aq) [1] Observation: Orange Br_2 decolourises in 2,6-di-tert-butylphenol but not in BHT. [1]
	(b)	Aspartame (APM) is an artificial non-carbohydrate sweetener used as a sugar substitute in some foods and beverages, which is especially useful for diabetic patients.  Aspartame (APM)	
		(i)	Label all chiral carbons with an (*) in the diagram above and calculate the total number of possible stereoisomers of APM. [2]
			 [1] 2^2 = 4 isomers [1]
		(ii)	Draw all organic products formed when APM is reacted with a hot aqueous alkaline solution. [3]
			  $H_3C{-}OH$ [1] for each correct structure

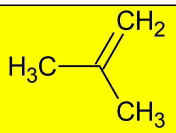
	(c)	Potassium bromate, $KBrO_3$, is typically used as a flour improver. It is a very strong oxidising agent, and allows for the baking of extremely white and fluffy bread, and it has the following half equation. $2BrO_3^- + 12H^+ + 10e \rightleftharpoons Br_2 + 6H_2O \quad E^\ominus = +1.50\ V$	
		(i)	Suggest reagent and conditions for the oxidation of ethene to carbon dioxide.
			$KMnO_4$, H_2SO_4 (aq), Heat [1]
		(ii)	Hot acidified bromate is also able to oxidise ethene into carbon dioxide. With reference to the *Data Booklet*, explain. [1]
			$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{2+} + 4H_2O \quad E = +1.52\ V$ Since the **reduction potential of bromate is similar to that of manganate(VII)**, bromate would be a strong enough oxidising agent to oxidise ethene to carbon dioxide. [1]
		(iii)	Hence, suggest how the yield of the carbon dioxide produced would be affected due to the use of bromate as an oxidising agent. [1]
			The yield of CO_2 produced would be lower than expected as Br_2 would be produced which would then react with some ethene reactant present. [1]
			[Total: 13]

6 Compound **G** and **H** have molecular formula of C_4H_8 and C_3H_6 respectively, and do not exhibit cis-trans isomerism.

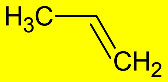
Both **G** and **H** can decolourise hot potassium manganate(VII) to give compounds **J** and **K** respectively, together with a gas that produces a white precipitate when bubbled through calcium hydroxide.

J produces an orange precipitate when warm with 2,4–dinitrophenylhydrazine, and **K** produces effervescence when sodium hydrogencarbonate is added.
J decolourises alkaline aqueous iodine but not **K**.

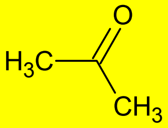
(a) Draw the structures of **G**, **H**, **J**, and **K**. [4]



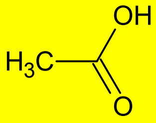
G



H



J



K

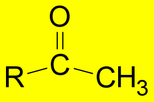
[1] for each correct structure

Statements for your information (not required by question)

✓ Both **G** and **H** has molecular formula with general formula C_nH_{2n}
- G and H are **alkenes**

✓Both **G** and **H** decolourises hot $KMnO_4$ to form **J** and **K** and CO_2
- **oxidation**
- G and H are **terminal alkenes**

✓ **J** produces orange ppt with 2,4–DNPH
- **condensation**
- **J** is a **ketone**

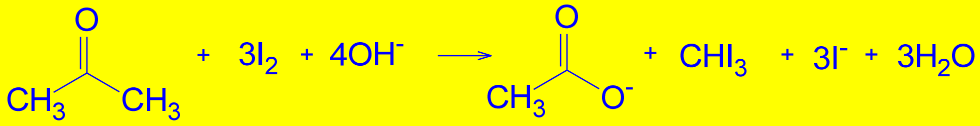
✓ **J** decolourises alkaline I_2
- **Oxidation**
- **J** has  $R-\overset{\overset{\large O}{||}}{C}-CH_3$

✓ **K** produces gas with $NaHCO_3$
- **neutralisation**
- **K** is a **carboxylic acid**

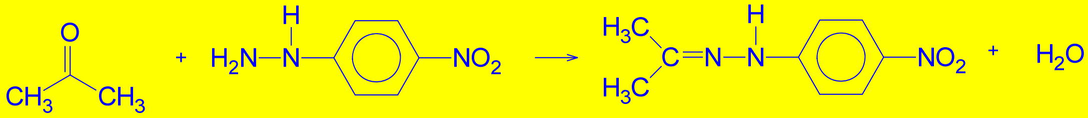
(b) Construct a balanced chemical equation on how **J** reacts with

- alkaline aqueous iodine,
- 2,4-DNPH.

[2]

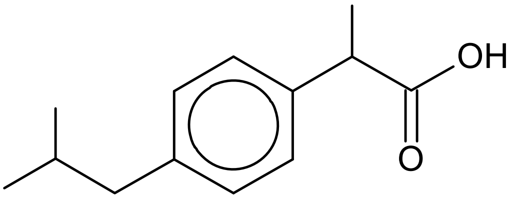


[1]



[1]

(c) Ibuprofen is an oral or intravenous medication that is used for treating pain, fever, and inflammation. It typically begins working within an hour and it has the following structure.



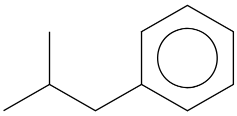
Ibuprofen

Compounds **G** and **H** from **(a)** are both prerequisites for the synthesis of Ibuprofen.

The reaction schema to obtain ibuprofen is described below.

(1) HBr gas is introduced to **G** to form **L**.

(2) **L** is reacted with benzene in the presence of anhydrous $FeBr_3$. Compound **M** is obtained.



Compound **M**

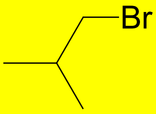
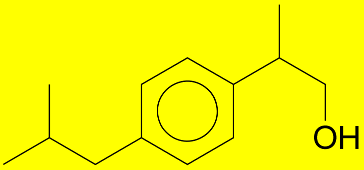
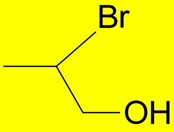
(3) Aqueous Br_2 is added to **H** to form **N**.

(4) **N** and **M** are reacted in the presence of anhydrous $FeBr_3$. Compound **P** with molecular formula $C_{13}H_{20}O$ is produced.

(5) Hot acidified potassium dichromate(VI) is then added to **P** to produce ibuprofen.

Using the structure of ibuprofen and the information provided, draw the structures of **L**, **N** and **P**.

[3]

		L:  [1] **p**:  [1] (only allow 1°) **N:**  [1]
		[Total: 9]

END OF PAPER

SERANGOON JUNIOR COLLEGE
General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME	
CLASS	

CHEMISTRY 9729/03

JC2 Preliminary Examination 19 September 2018
Paper 3 Free Response 2 hours

Candidates answer on separate paper.
Additional materials : Writing Papers
Data Booklet
2 Cover Pages (one for Section **A** and one for Section **B**)

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Section A
Answer **all** questions.

Section B
Answer **one** question.

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

At the end of the examination, fasten all your work securely together.
The number of marks is given in the brackets [ ] at the end of each question or part question.

This document consists of **12** printed pages and **0** blank page.

Section A

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

1 Hydrogen sulfide, H_2S, is a colourless gas with the characteristic foul odour of rotten eggs. It is very poisonous, corrosive and flammable. It occurs naturally in volcanic gases and natural gas and is often produced from the microbial breakdown of organic matter.

(a) H_2S burns readily in oxygen to form water and an acidic gas which briskly decolourises acidified potassium manganate(VII).

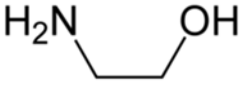
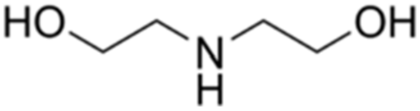
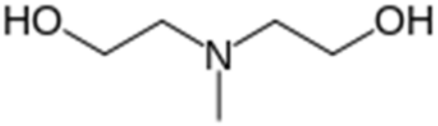
During the combustion process, sulfur atomises and a brightly coloured flame similar to that of its element is observed.

Construct a balanced chemical equation to represent the combustion reaction and predict the colour of the flame.

[2]

(b) The toxicity of H_2S is comparable with that of what carbon monoxide does to the human body, preventing cellular respiration. It is therefore critical to remove H_2S from raw natural gas. This process, commercially known as "*sweetening*", utilises amine treating technologies.

Common "*sweetening*" agents are as shown below.

Name	**Chemical Structure**	***pK$_b$***
Monoethanolamine (MEA)		4.55
Diethanolamine (DEA)		5.12
Methyldiethanolamine (MDEA)		5.48

(i) Describe how H_2S impedes cellular respiratory in the human body. [2]

(ii) Amine compounds are *weak Bronsted-Lowry bases*. What do you understand by the term "*weak Bronsted-Lowry bases*"? [1]

(iii) Explain the trend of the pK_b values of MEA, DEA and MDEA. [2]

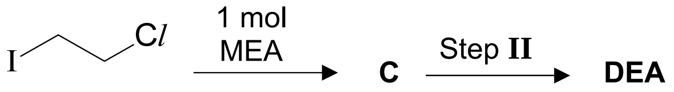
(iv) MEA consists of both amine and alcohol functional groups. It can be exploited in successive reactions involving halogeno organic compounds. A series of experiments are carried out to find out the different reactivity of dihalogeno compounds.

Complete the following of the organic syntheses, drawing the structures of the intermediates, products and stating the reagents and conditions where appropriate.

Reaction (A):

$$\mathrm{C}l\mathrm{CH_2COC}l \xrightarrow{\text{MEA}} \mathbf{A} \xrightarrow{\text{Na (s)}} \textbf{Cyclic compound B} \; (\mathrm{C_4H_7NO_2})$$

Reaction (B):



[4]

(c) Zinc oxide is also used to scavenge hydrogen sulfide in natural gas, where the by-product, zinc sulfide, may be easily filtered off.

$$ZnO + H_2S \rightarrow ZnS + H_2O$$

The solubility of ZnS in pure water is 1.23×10^{-10} g dm^{-3} at 25 ^{o}C.

(i) Write an expression for the solubility product, K_{sp} of ZnS and calculate its value. State its units clearly.

[2]

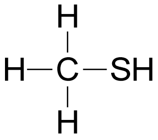
(ii) How would the solubility of ZnS in aqueous $Zn(NO_3)_2$ compared to that in pure water? Use *Le Chatelier's Principle* to justify your answer.

[2]

(iii) Equal volumes of 0.005 mol dm^{-3} Zn^{2+} solution and 0.002 mol dm^{-3} Na_2S solution were mixed. Predict if any precipitate could be filtered off this mixture.

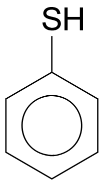
[1]

(d) Thiols are a class of organosulfur compounds known to have strong unpleasant odours. For instance, methanethiol, CH_3SH, is one of the main odourants of human faeces, body odour and bad breath. Other examples of common thiol structures are shown below.

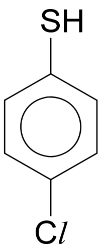


$$H-\overset{H}{\underset{H}{C}}-SH$$

methanethiol



thiophenol



chlorothiophenol

As thiols are the sulfur analogue of alcohols, their relative acidities are often compared. One notable difference is the ability of thiols to react with aqueous alkalis.

$$RSH + NaOH \rightarrow RS^{-}Na^{+} + H_2O$$

The table below shows the pK_a values of alcohols and thiols.

Name of compound	**pK_a**
Butanol, $CH_3CH_2CH_2CH_2OH$	15
Phenol, C_6H_5OH	10
Buthanetiol, $CH_3CH_2CH_2CH_2SH$	10
Thiophenol, C_6H_5SH	6
Chlorothiophenol, C_6H_5ClS	***y***

(i) With reference to the information above, suggest an explanation for the different pK_a value of butanol as compared to buthanetiol.

[1]

(ii) Predict the value ***y*** and explain your answer.

[2]

(iii) Calculate the pH of the solution when 15 cm^3 of 0.10 mol dm^{-3} NaOH is added to 25 cm^3 of 0.10 mol dm^{-3} $CH_3CH_2CH_2CH_2SH$.

[2]

[Total: 21]

2 **(a)** **(i)** Draw a fully labelled diagram to show how the standard electrode of Ni^{2+}(aq) /Ni(s) is being measured in a laboratory. Clearly label the direction of electrons flow and polarity of the electrodes in your diagram. [3]

(ii) Adding a measured quantity of KCN to a solution of $NiCl_2$ produces the complex $[Ni(CN)_2Cl_2]^x$. Suggest how the value of the electrode potential of the Ni^{2+}(aq) /Ni(s) half-cell will varies upon the addition of KCN and deduce the overall charge, *x*, on this complex. [3]

(b) Determine the E^{θ}_{cell} and the ΔG^{θ} when the Ni^{2+}(aq)/Ni(s) half-cell is connected with the Fe^{3+}(aq)/Fe^{2+}(aq) half-cell. [2]

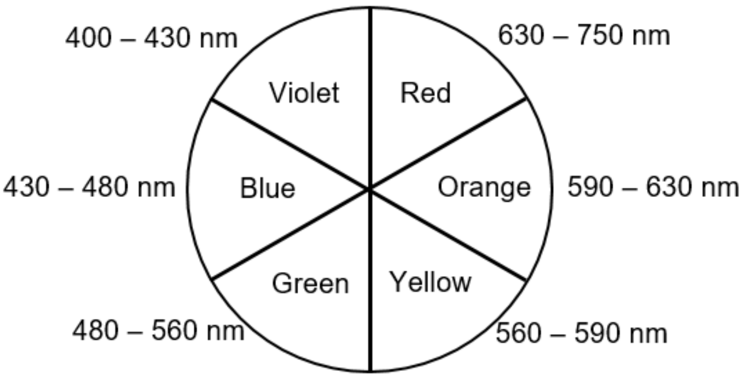
(c) An aqueous solution of KCN is gradually added to a solution of $NiSO_4$ until the KCN is in excess. The following series of reactions takes place.

$$NiSO_4 \xrightarrow{\text{KCN}} \underset{\text{green precipitate}}{\mathbf{D}} \xrightarrow{\text{more KCN}} \underset{\text{yellow solution}}{\mathbf{E}} \xrightarrow{\text{KCN in excess}} \underset{\text{red solution}}{\mathbf{F}}$$

- The oxidation state of nickel does **not** change during the reactions.
- None of **D**, **E** or **F** contains sulfur.
- **D** contains no potassium.
- The K: Ni ratio in **E** is 2:1.
- The K: Ni ratio in **F** is 3:1

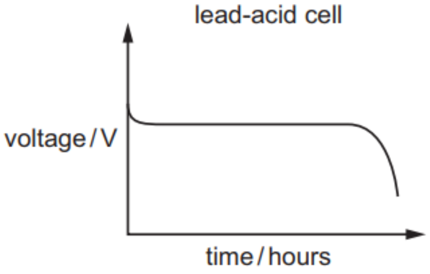
(i) Use the information to suggest the formulae of **D** and **F**. [2]

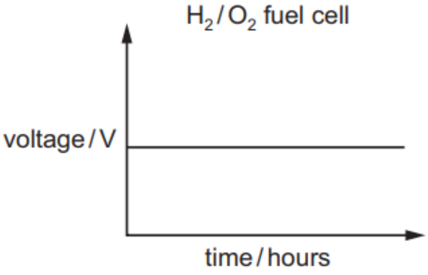
(ii) Using the colour wheel provided, suggest if **E** or **F** has a larger energy gap when the d-orbital split into two different energy levels.



[1]

(d) The diagrams show how the voltage across two different cells changes with time when each cell is used to provide an electric current.





Suggest a reason why.

(i) The voltage of the lead-acid cell changes after several hours. [1]

(ii) The voltage of the fuel cell remains constant. [1]

(e) Describe, using the orientation of the d-orbitals, the splitting of degenerate d-orbitals into two energy levels in octahedral complexes such as $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$. [4]

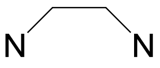
(f) 1,2-diaminoethane, *en*, is a bidentate ligand.

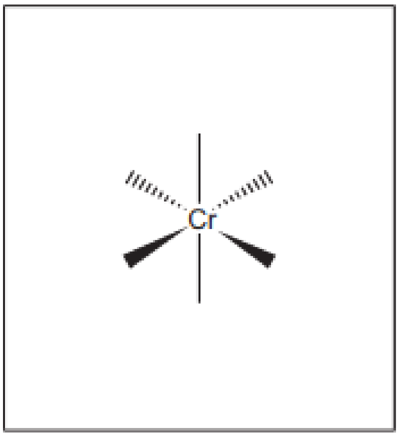
(i) What is meant by the terms *bidentate* and *ligand*? [2]

(ii) There are isomeric complex ions with the formula $[Cr(en)_2Cl_2]^+$.

When all the four nitrogen atoms of the *en* ligands are on the same plane, it is consider a trans configuration. When two of the nitrogen on the *en* ligands are on different plane, it is consider a cis configuration.

Using the three-dimensional diagram below, draw and label the cis-trans isomers on the writing paper you are provided.

(You may use  to represent *en.*)



[2]

[Total: 21]

3 **(a)** Solutions of iron(II) compounds are commonly prepared in the laboratory.

(i) By selecting two appropriate half equations from the *Data Booklet*, explain why iron(II) solutions are normally stored in the presence of acids instead of bases. [3]

(ii) With the aid of suitable equations and standard electrode potential values from the *Data Booklet*, explain why an acidic solution of iron(II) can catalyse the decomposition of hydrogen peroxide.

Decomposition of hydrogen peroxide:

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

State and explain the type of catalysis involved. [3]

(iii) Using an appropriate sketch of the Boltzmann distribution; explain why the addition of acidic solution of iron(II) can catalyse the decomposition of hydrogen peroxide. [3]

(b) Strontium hydroxide is a strong base and has several industrial applications such as plastic stabiliser and paint drier.

The standard enthalpy change of neutralisation was determined experimentally by mixing known volumes of aqueous hydrochloric acid and aqueous strontium hydroxide in a calorimeter. The following results were obtained:

- Initial temperature = 25.0 ^{o}C
- Final temperature = 35.4 ^{o}C
- Volume of 2 mol dm^{-3} hydrochloric acid = 50.0 cm^{3}
- Volume of 0.77 mol dm^{-3} of strontium hydroxide = 50.0 cm^{3}
- Heat capacity of calorimeter = 9.43 J K^{-1}

(i) Define *standard enthalpy change of neutralisation*. [1]

(ii) Use the data above to calculate the standard enthalpy change of neutralisation in kJ mol^{-1}. [3]

(iii) The enthalpy change of neutralisation between aqueous strontium hydroxide and aqueous ethanoic acid was found to be different from the value calculated in **b(ii)**.

State and explain how the magnitude of this value differ from **b(ii)**. [2]

(c) Aqueous strontium hydroxide is formed when solid strontium metal reacts with water

$$Sr(s) + 2H_2O(l) \rightarrow Sr^{2+}(aq) + 2OH^-(aq) + H_2(g)$$

By using the following enthalpy changes and your answer in **b(ii)**, draw an energy cycle to calculate the enthalpy change for the above reaction involving strontium and water.

	kJ mol^{-1}
Enthalpy change for $Sr(s) \rightarrow Sr^{2+}(g) + 2e^-$	+1772
Enthalpy change of hydration of strontium ions	−1337
Enthalpy change for $2H^+(aq) + 2e^- \rightarrow H_2(g)$	−850

[3]

Total [18]

Section B

Answer **one** question in this section.

4 **(a)** Four samples of Period 3 chlorides, **G**, **H**, **J** and **K** are examined.

- These chlorides reacted completely in water, leaving no precipitates. These solutions were tested with universal indicator paper. **G**, **J** and **K** were found to be acidic, while **H** was found to be neutral.
- The melting points of **H** and **J** are approximately 10 times higher than the melting points of **G** and **K**.
- Solid anhydrous **G** is required in the reaction of phenylmethanol with chlorine to form C_7H_7OCl.
- Solid anhydrous **K** reacts with phenylmethanol to form C_7H_7Cl at room temperature.

(i) Identify the chlorides **G**, **H**, **J** and **K**. [2]

(ii) Explain why **H** forms a neutral solution. [2]

(iii) Draw the structure of the resulting compound, C_7H_7OCl. [1]

(iv) Draw the structure of the resulting compound, C_7H_7Cl. [1]

(v) Suggest why chloride **K** has to be anhydrous for the reaction between chloride **K** and phenymethanol to occur. Write a chemical equation to support your answer. [2]

(vi) Using structure and bonding, explain why chloride **J** has a melting point approximately 10 times higher than chloride **G** and **K**. [1]

(b) The reaction of silicon tetrachloride with moist ethoxyethane, produces either oxochlorides, Si_2OCl_6 or $Si_3O_2Cl_8$.

When 0.10g of one of the oxochloride completely reacted with water, all of its chlorine was converted into chloride ions, and produced 0.303 g of silver chloride precipitate when an excess of aqueous silver nitrate was added.

Deduce the identity of the oxochloride. [2]

(c) Fluorine bomb calorimetry has been used to investigate inorganic substances such as silicon compounds that cannot be completely burned in conventional calorimetric reagents such as oxygen under high pressure.

The enthalpy change of reaction of the following silicon containing compounds were investigated during a fluorine bomb calorimeter.

$Si_3N_4 + 6F_2 \rightarrow 3SiF_4 + 2N_2$ $\Delta H = -828.9 \text{ kJ mol}^{-1}$

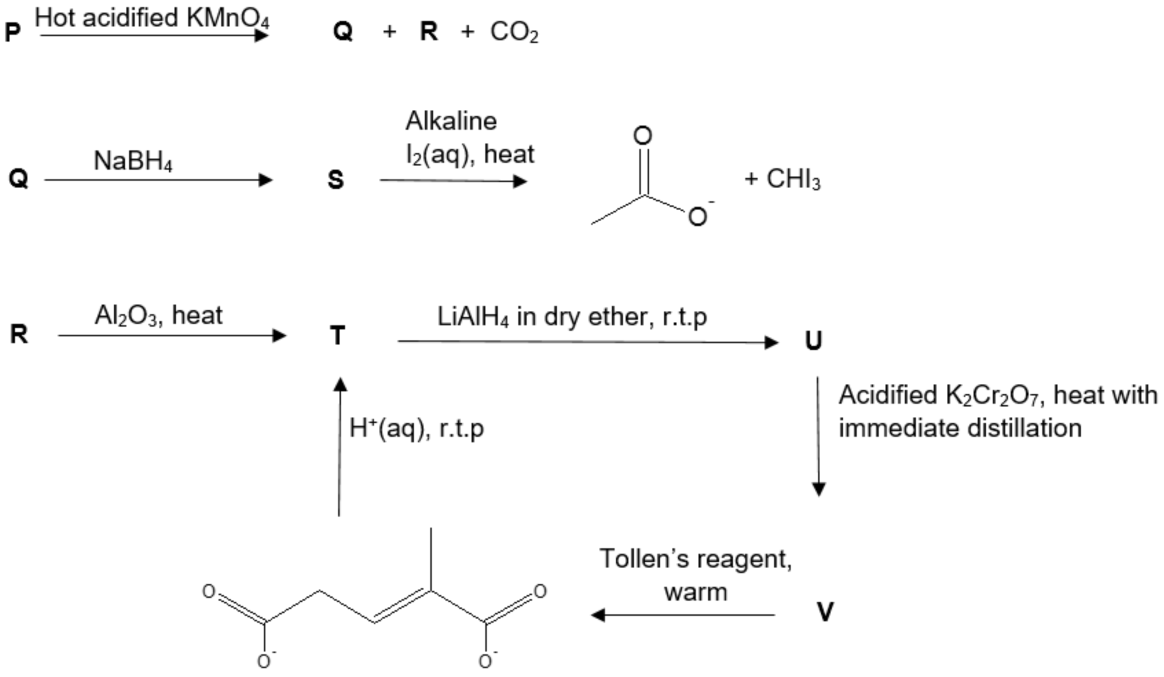
$SiH_4 + 4F_2 \rightarrow SiF_4 + 4HF$ $\Delta H = -2631 \text{ kJ mol}^{-1}$

The following enthalpy change of formation is also given below.

Compound	ΔH_f /kJ mol^{-1}
HF(g)	-272.6
Si_3N_4(s)	-3686.1

Calculate the standard enthalpy change of formation of SiF_4.
Hence, calculate the standard enthalpy change of formation of SiH_4. [2]

(d) Linalool, **P**, is a compound which gives the sweet scent of lavender. Its structure can be deduced from the following series of reactions.



(i) Draw the structures of **S** and **Q**. [2]

(ii) Draw the structures of **R**, **T**, **U** and **V**. [4]

(iii) Hence, deduce the structure of linalool, **P**. [1]

[Total: 20]

5 This question is about the reactions of halogen containing organic compounds.

(a) The Finkelstein reaction, named after the German chemist, Hans Finkelstein, involves the replacement of the halogen atom in a halogenoalkane by an iodide ion from a solution of sodium iodide dissolved in propanone. This reaction goes almost to completion and a precipitate of sodium halide is formed as shown below.

$$RX + NaI \rightleftharpoons RI + NaX$$

A series of experiment can be carried out to determine the order of reaction with respect to a halogenoalkane, C_4H_9Br, and iodide ion. Different concentrations of C_4H_9Br and sodium iodide were used and the following initial rates were obtained.

Experiment Number	$[C_4H_9Br]$ / mol dm^{-3}	[NaI] / mol dm^{-3}	Rate / mol dm^{-3} s^{-1}
1	0.04	0.60	5.68×10^{-5}
2	0.02	0.30	1.42×10^{-5}
3	0.60	0.60	8.52×10^{-4}

(i) Use these data to deduce the order of reaction with respect to each reactant, showing how you arrive at your answers. Hence, write a rate equation for the reaction. [3]

(ii) Based on your answer in **(a)(i)**, deduce a suitable structure for the halogenoalkane, C_4H_9Br which contains a chiral carbon. [2]

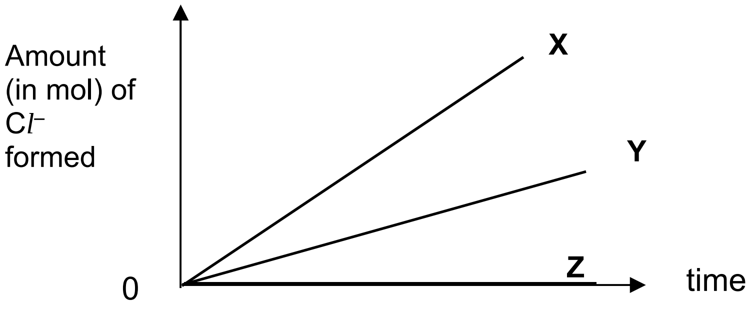
(iii) Using your answer in **(a)(i)** and **(a)(ii)**, describe a mechanism that is consistent with your rate equation. Show relevant lone pairs and dipoles, and use curly arrows to indicate the movement of electron pairs. [2]

(iv) Sodium chloride is precipitated during the Finkelstein reaction due to its limited solubility in propanone.

Explain why the Finkelstein reaction goes almost to completion despite the C-I bond being weaker than the C-C*l* bond. [1]

(b) Halogen-containing organic compounds can be hydrolysed under suitable conditions to produce the corresponding halide ions.

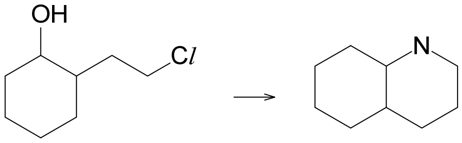
A student investigated the amount of Cl^- produced by hydrolysing ethanoyl chloride, chloroethane and chlorobenzene and the results are shown below.



Deduce **X**, **Y** and **Z**.

[3]

(c) In no more than 4 steps, outline how the following transformation can be achieved. State the reagents and conditions for each step, as well as the structures of any intermediates formed.



[4]

(d) When ester **A** ($C_6H_{11}O_2Cl$) is heated with alkaline $KMnO_4$, two products are formed. Acidification of the two products give **B** and **C**.

C gives a yellow precipitate when warmed with aqueous alkaline iodine. When sodium borohydride is added to **C**, compound **D** is formed. **D** reacts with hot concentrated sulfuric acid to form **E** ($C_4H_6O_2$) that exhibits cis-trans isomerism.

B, **C, D** and **E** all produce effervescence when reacted with aqueous Na_2CO_3.

Draw the structures of **A**, **B**, **C**, **D** and **E**.

[5]

[Total: 20]

END

SERANGOON JUNIOR COLLEGE
General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME ☐

CLASS ☐

CHEMISTRY 9729/03

JC2 Preliminary Examination **19 September 2018**

Paper 3 Free Response **2 hours**

Candidates answer on separate paper.

Additional materials : Answer Paper
Data Booklet
2 Cover Pages

READ THESE INSTRUCTIONS FIRST

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

Section A
Answer **all** questions.

Section B
Answer **one** question.

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

At the end of the examination, fasten all your work securely together.
The number of marks is given in the brackets [ ] at the end of each question or part question.

This document consists of **11** printed pages and **1** blank page.

Section A

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

1 Hydrogen sulfide, H_2S, is a colourless gas with the characteristic foul odour of rotten eggs. It is very poisonous, corrosive and flammable. It occurs naturally in volcanic gases and natural gas and is often produced from the microbial breakdown of organic matter.

(a) H_2S burns readily in oxygen to form water and an acidic gas which briskly decolourises acidified potassium manganate(VII).

During the combustion process, sulfur atomises and a brightly coloured flame similar to that of its element is observed.

Construct a balanced chemical equation to represent the combustion reaction and predict the colour of the flame.

[2]

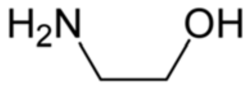
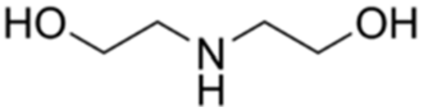
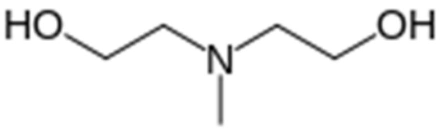
$H_2S + \frac{3}{2}O_2 \rightarrow SO_2 + H_2O$ **[1]** Blue flame **[1]**

FYI:

- SO_2 to SO_3 cannot work as activation energy to form SO_3 is high
- Sulfur element burns in oxygen producing blue flame – Periodicity Notes

(b) The toxicity of H_2S is comparable with that of what carbon monoxide does to the human body, preventing cellular respiration. It is therefore critical to remove H_2S from raw natural gas. This process, commercially known as "*sweetening*", utilises amine treating technologies.

Common "*sweetening*" agents are as shown below:

Name	**Chemical Structure**	***pK$_b$***
Monoethanolamine (MEA)		4.55
Diethanolamine (DEA)		5.12
Methyldiethanolamine (MDEA)		5.48

(i) Describe how H_2S impedes cellular respiratory in the human body.

[2]

H_2S is a strong ligand and **bonds irreversibly** **[1]**via a stronger dative bond with the **iron atom of haemoglobin**, **thus preventing haemoglobin from carrying oxygen** **[1]** to be transported around the body.

(ii) Amine compounds are *weak Bronsted-Lowry bases*. What do you understand by the term "*weak Bronsted-Lowry bases*"? [1]

They **ionise partially** in aqueous solution by **accepting a proton.** **[1]**

(iii) Explain the trend of the pK_b values of MEA, DEA and MDEA. [2]

Since pK_b increases from MEA to DEA to MDEA, it shows that basicity: MEA > DEA > MDEA.

MDEA is the **least basic** as it has **most / 3 alkyl groups / R-groups surrounding the N atom**, **[1]** compared to DEA which has 2 and MEA which has only 1 alkyl group.

Thus, there is **most steric hindrance about the N atom in MDEA**, making it **least available to accept a proton** **[1]** via dative bonding, followed by DEA and MEA.

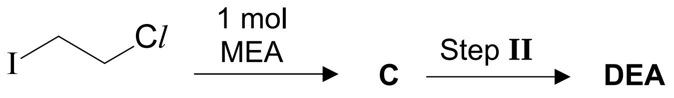
(iv) MEA consists of both amine and alcohol functional groups. It can be exploited in successive reactions involving halogeno organic compounds. A series of experiments are carried out to find out the different reactivity of dihalogeno compounds.

Complete the following of the organic syntheses, drawing the structures of the intermediates, products and stating the reagents and conditions where appropriate.

Reaction (A):

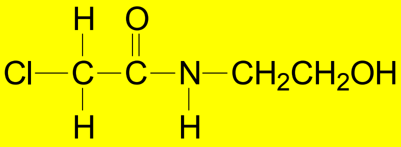
$$ClCH_2COCl \xrightarrow{\text{MEA}} \textbf{A} \xrightarrow{\text{Na (s)}} \textbf{Cyclic compound B}\ (C_4H_7NO_2)$$

Reaction (B):



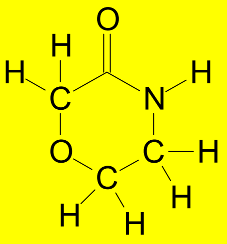
[4]

Reaction (A):

A:


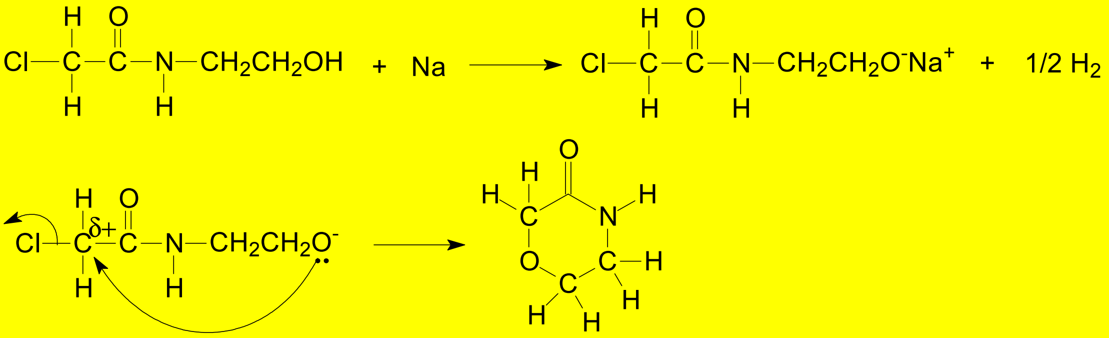
$ClCH_2CONHCH_2CH_2OH$

[1]

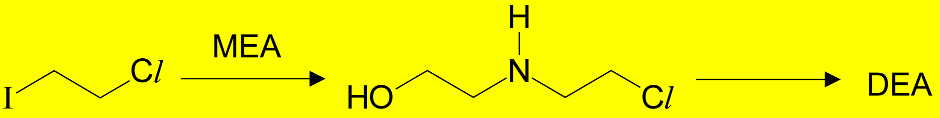
B:


[1]

Explanation for step 2:



Reaction (B):



C **[1]**

Step II: <u>NaOH (aq), heat</u> [1]

FYI:

- C-I bond is weaker than C-Cl bond, hence will undergo NS more readily, when 1 mol MEA is added

(c) Zinc oxide is also used to scavenge hydrogen sulfide in natural gas, where the by-product, zinc sulfide, may be easily filtered off.

$$ZnO + H_2S \rightarrow ZnS + H_2O$$

The solubility of ZnS in pure water is 1.23×10^{-10} g dm^{-3} at 25 °C.

(i) Write an expression for the solubility product, K_{sp} of ZnS and calculate its value. State its units clearly.

[2]

$K_{sp} = [Zn^{2+}][S^{2-}]$ **[1]**

[ZnS] in mol dm^{-3} = $(1.23 \times 10^{-10}) / (65.4+32.1) = 1.26 \times 10^{-12}$ mol dm^{-3}

$K_{sp} = (1.26 \times 10^{-12})^2 =$ **<u>1.6×10^{-24} mol^2 dm^{-6}</u>** **[1] for both**

(ii) How would the solubility of ZnS in aqueous $Zn(NO_3)_2$ compared to that in pure water? Use *Le Chatelier's Principle* to justify your answer.

[2]

$Zn(NO_3)_2 \rightarrow Zn^{2+} + 2NO_3^-$

$ZnS(s) \rightleftharpoons Zn^{2+}(aq) + S^{2-}(aq)$ --- (1)

In presence of aqueous $Zn(NO_3)_2$, **<u>$[Zn^{2+}]$ increases</u>**,

By Le Chatelier's Principle, the above **<u>equilibrium position of (1) shifts left to decrease $[Zn^{2+}]$.</u>** **[1]**

Solubility of ZnS is **<u>reduced</u>** due to **<u>common ion effect.</u>** **[1]**

(iii) Equal volumes of 0.005 mol dm^{-3} Zn^{2+} solution and 0.002 mol dm^{-3} Na_2S solution were mixed. Predict if any precipitate could be filtered off this mixture.

[1]

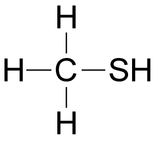
Ionic product = $[Zn^{2+}][S^{2-}] = (\frac{0.005}{2})(\frac{0.002}{2})$

$= 2.5 \times 10^{-6}$ mol^2 dm^{-6}

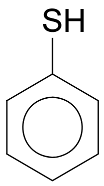
Since **IP > K_{sp}, ZnS ppt will be formed** and the ppt could be filtered off.

[1] with correct calculation of IP and explanation

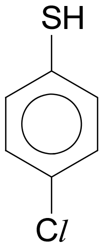
(d) Thiols are a class of organosulfur compounds known to have strong unpleasant odours. For instance, methanethiol, CH_3SH, is one of the main odourants of human faeces, body odour and bad breath. Other examples of common thiol structures are shown below.



methanethiol



thiophenol



chlorothiophenol

As thiols are the sulfur analogue of alcohols, their relative acidities are often compared. One notable difference is the ability of thiols to react with aqueous alkalis.

$$RSH + NaOH \rightarrow RS^-Na^+ + H_2O$$

The table below shows the pK_a values of alcohols and thiols.

Name of compound	**pK_a**
Butanol, $CH_3CH_2CH_2CH_2OH$	15
Phenol, C_6H_5OH	10
Buthanetiol, $CH_3CH_2CH_2CH_2SH$	10
Thiophenol, C_6H_5SH	6
Chlorothiophenol, C_6H_5ClS	***y***

(i) With reference to the information above, suggest an explanation for the different pK_a value of butanol as compared to buthanetiol.

[1]

pK_a values of thiols is **generally lower** than that of alcohols, showing that thiols are **more acidic** than alcohols.

S-H bond in buthanetiol is **weaker than O-H bond** [1] in butanol due to larger atomic radius of S, resulting in less effective overlap of S-H covalent bond. Hence, the dissociation of H^+ for RSH will occur more readily, making thiols more acidic.

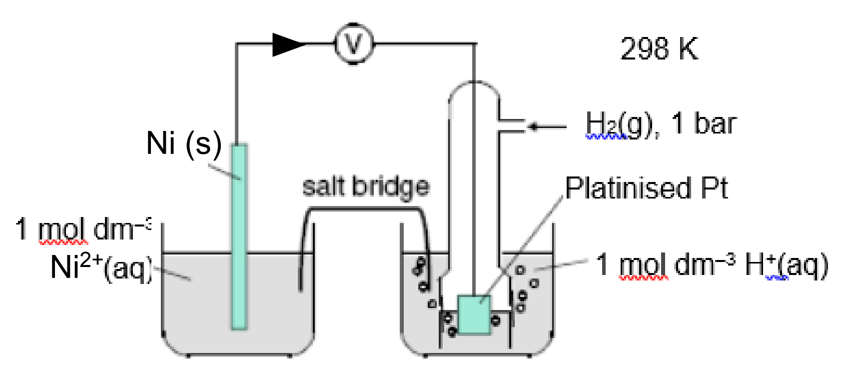
OR

			Thiols consists of a **larger S radius** than O which **allows the negative charge on its conjugate base RS$^-$ to be dispersed more**, stabilising it to a greater extent, making it more acidic than alcohols.
		(ii)	Predict the value ***y*** and explain your answer. [2]
			Value: 2 (accept value 2 to 5) **[1]** **Chlorothiophenol is more acidic** than thiophenol as the **electronegative Cl atom present disperses the negative charge on its conjugate base, stabilising it more / to a greater extent** than thiophenol Hence it has a lower pKa value. **[1]** *(need not take reference to thiophenol, as long as reasoning is logical)*
		(iii)	Calculate the pH of the solution when 15 cm^3 of 0.10 mol dm^{-3} NaOH is added to 25 cm^3 of 0.10 mol dm^{-3} $CH_3CH_2CH_2CH_2SH$. [2]
			$CH_3CH_2CH_2CH_2SH + NaOH \rightarrow CH_3CH_2CH_2CH_2S^-Na^+ + H_2O$ Amt of NaOH = $\frac{15}{1000}$ x 0.10 = 0.0015 mol Amt of RSH = $\frac{25}{1000}$ x 0.10 = 0.0025 mol Since RSH (weak acid) is in excess, a buffer solution is formed. Amt of excess RSH = 0.0025 – 0.0015 = 0.0010 mol **[1] for mol calculations** $pH = pK_a + \lg \frac{[salt]}{[acid]} = 10 + \lg \frac{\frac{0.0015}{40}}{\frac{0.0010}{40}}$ = **10.2** **[1]**
			[Total: 21]

2 **(a)** **(i)** Draw a fully labelled diagram to show how the standard electrode of $Ni^{2+}(aq)$ /Ni(s) is being measured in a laboratory. Clearly label the direction of electrons flow and polarity of the electrodes in your diagram.

[3]

Direction of electron flow [1]



Oxidation (anode) Reduction (cathode)
Negative polarity Positive polarity [1] for both

[1] for correct placement of Fe^{2+}, Fe electrode, Pt electrode, H^+ and H_2 (g); for correct indication of 1 mol dm^{-3} for **Fe^{2+} and H^+, 298 K and 1 bar**

Immediate zero cases:

1. No salt bridge
2. No water line
3. No voltmeter
4. Battery is drawn in the diagram

(ii) Adding a measured quantity of KCN to a solution of $NiCl_2$ produces the complex $[Ni(CN)_2Cl_2]^x$. Suggest how the value of the electrode potential of the $Ni^{2+}(aq)$ /Ni(s) half-cell will vary upon the addition of KCN and deduce the overall charge, *x*, on this complex.

[3]

$Ni^{2+}(aq) + 2e \rightleftharpoons Ni(s)$

When KCN is added to $Ni^{2+}(aq)$/Ni (s) half cell, **Ni^{2+} form a complex with CN^- ions and $[Ni^{2+}]$ decreases**. By Le Chatelier's Principle, the **equilibrium position shifts to the left to increase the $[Fe^{2+}]$**. [1]

Oxidation is more likely to occur and electrode potential of **Ni^{2+}/Ni becomes more negative /less positive** [1]

To solve for x:

$+2+2(-1)+2(-1) = x$

$x = -2$ [1]

(b) Determine the E^{θ}_{cell} and the ΔG^{θ} when the $Ni^{2+}(aq)$/Ni(s) half-cell is connected with the $Fe^{3+}(aq)/Fe^{2+}(aq)$ half-cell.

[2]

$E^{\theta}_{cell} = +0.77 - (-0.25)$
$= 1.02$ V [1]

$\Delta G^{\theta} = -nFE^{\theta}_{cell}$
$= -(2)(96500)(1.02)$
$= -196860$ J mol^{-1} [1]

(c) An aqueous solution of KCN is gradually added to a solution of $NiSO_4$ until the KCN is in excess. The following series of reactions takes place.

$$NiSO_4 \xrightarrow{\text{KCN}} \underset{\text{green precipitate}}{\mathbf{D}} \xrightarrow{\text{more KCN}} \underset{\text{yellow solution}}{\mathbf{E}} \xrightarrow{\text{KCN in excess}} \underset{\text{red solution}}{\mathbf{F}}$$

- The oxidation state of nickel does **not** change during the reactions.
- None of **D**, **E** or **F** contains sulfur.
- **D** contains no potassium.
- The K: Ni ratio in **E** is 2:1.
- The K: Ni ratio in **F** is 3:1

(i) Use the information to suggest the formulae of **D** and **F**. [2]

D is $Ni(CN)_2$ [1] **E** is $K_2Ni(CN)_4$ **F** is $K_3Ni(CN)_5$ [1]

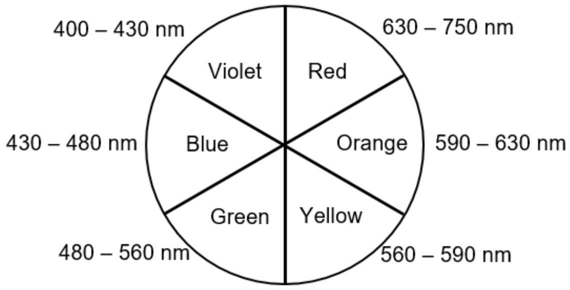
Do not accept $Ni(CN)_4^{2-}$ for D and $Ni(CN)_5^{3-}$ for E as question require the input of formulae.

Thinking process:
For green ppt of **D** to form it must be Ni^{2+} interacting with CN^- resulting in $Ni(CN)_2$. In addition, **D** must not contain potassium which further justify the formula.

As more KCN is added, complex formation will occur as we introduce more CN^- ligand. Given K to Ni ration is 2:1, it means that the complex anion containing Ni need to have a charge of 2– since its required 2 K^+ counter ion. Thus, **E** must have $[Ni(CN)_4]^{2-}$ as the complex anion and as such the **formula** of **E** is $K_2Ni(CN)_4$

When even more KCN is added, complex formation will continue to occur as we more CN^- ligands are being introduced. Given K to Ni ration is now 3:1, it means that the complex anion containing Ni need to have a charge of 3– since its required 3 K^+ counter ion. Thus, **F** must have $[Ni(CN)_4]^{3-}$ as the complex anion and as such the **formula** of **F** is $K_3Ni(CN)_4$

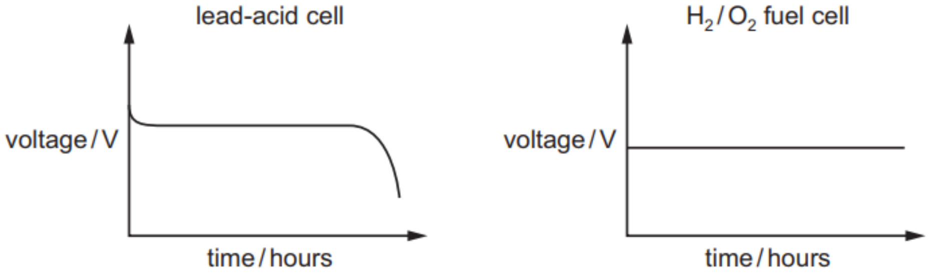
(ii) Using the colour wheel provided, suggest if solution **E** or **F** has a larger energy gap when the d-orbital split into two different energy levels.

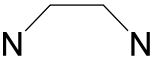
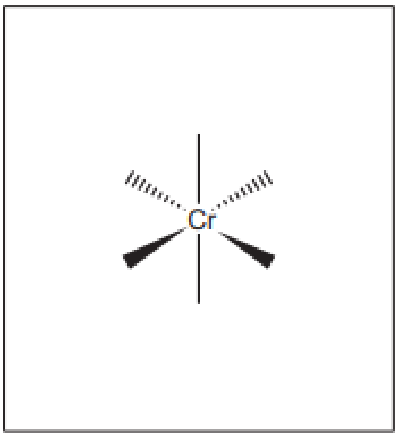
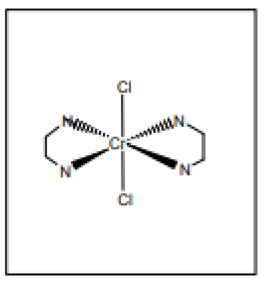
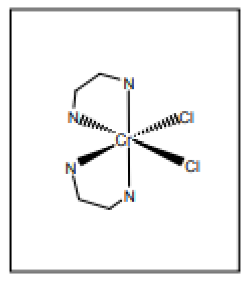
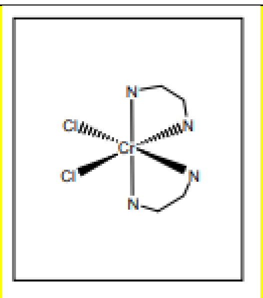


[1]

E is red solution thus it is **transmitting light of higher wavelength which means it is absorbing lower wavelength of light with higher energy**.

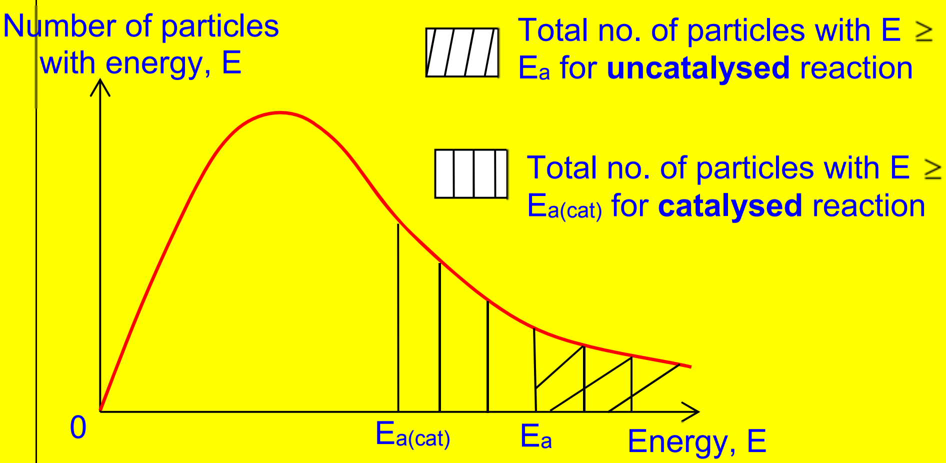
This means the **energy gap in E is larger**. [1] with valid reasoning

	(d)	The diagrams show how the voltage across two different cells changes with time when each cell is used to provide an electric current.  Suggest a reason why.	
		(i)	The voltage of the lead-acid cell changes after several hours [1]
			Reagents (PbO_2 /H_2SO_4) are being used up. [1] Or Concentration of the reagents decreases.
		(ii)	The voltage of the fuel cell remains constant [1]
			As fuel is being continuously supplied, the fuel has not run out. [1]
	(e)	Describe, using the orientation of the d-orbitals, the splitting of degenerate d-orbitals into two energy levels in octahedral complexes such as $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$. [4]	
		In an **octahedral** complex, the ligands are modelled as six point negative charges that surround the positively charged transition metal ion. Each ligand forms a dative bond with the transition metal ion via a lone pair of electrons along the **x, y and z axes**. [1] When the ligands approach the transition metal ion along the x, y, and z axes, there is **inter-electronic repulsion between the lone pair of electrons from the donor atom of the ligand and the electrons in the d orbitals of the transition metal ion**. This causes the energies of these d electrons to increase to different extents. [1] When ligands approach the x, y and z axes, the **electrons in the $d_{x^2-y^2}$ and d_{z^2} orbitals will experience greater repulsion** than those in the d_{xy}, d_{yz} and d_{xz} orbitals. [1] Hence, the five d orbitals will be split into **2 energy levels - the $d_{x^2-y^2}$ and d_{z^2} orbitals at a higher energy level than the d_{xy}, d_{yz} and d_{xz}** orbitals as shown in the diagram below. [1]	

	(f)	1,2-diaminoethane, *en*, is a bidentate ligand.	
		(i)	What is meant by the terms *bidentate* and *ligand*? [2]
			Bidentate: a species that forms **two dative bonds** or donate two lone pairs of electrons. [1] Ligand: a species that uses a **lone pair** of electrons to form a **dative** bond to a **metal atom/metal ion.** [1]
		(ii)	There are isomeric complex ions with the formula $[Cr(\mathit{en})_2Cl_2]^+$. When all the four nitrogen atoms of the *en* ligands are on the same plane, it is consider a trans configuration. When two of the nitrogen on the *en* ligands are on different plane, it is consider a cis configuration. Using the three-dimensional diagrams below, draw and label the cis-trans isomers on the writing paper you are provided. (You may use  to represent *en.*)  [2]
			 [1]  OR  [1]
			[Total: 21]

3	**(a)**	Solutions of iron(II) compounds are commonly prepared in the laboratory.	
		(i)	By selecting two appropriate half equations from the *Data Booklet*, explain why iron(II) solutions are normally stored in the presence of acids instead of bases. [3]
			In acidic medium: $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $E^\theta = +0.77$ V In basic medium: $Fe(OH)_3 + e^- \rightleftharpoons Fe(OH)_2 + OH^-$ $E^\theta = -0.56$ V In acidic medium, **the E^θ value is more positive**. **[1]** Hence **position of equilibrium lies more to the right** and **[1]** Fe (II) is **more stable in acidic medium**. Or Fe^{2+} in **acidic medium is a weaker reducing agent** compared to $Fe(OH)_2$ in basic medium. **[1]**
		(ii)	With the aid of suitable equations and standard electrode potential values from the *Data Booklet*, explain why an acidic solution of iron(II) can catalyse the decomposition of hydrogen peroxide. Decomposition of hydrogen peroxide: $2H_2O_2 \rightarrow 2H_2O + O_2$ State and explain the type of catalysis involved. [3]
			$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$ $E^\theta = +1.77$ V $O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2$ $E^\theta = +0.68$ V $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $E^\theta = +0.77$ V Step 1: **$2Fe^{2+} + H_2O_2 + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O$** **$E^\theta_{cell} = 1.77 - 0.77 = +1.00$ V >0** **Since $E^\theta_{cell} > 0$, reaction is feasible.** Step 2: **$2Fe^{3+} + H_2O_2 \rightarrow 2Fe^{2+} + O_2 + 2H^+$** **$E^\theta_{cell} = 0.77 - 0.68 = +0.09$ V >0** **Since $E^\theta_{cell} > 0$, reaction is feasible.** **[2]** Fe^{2+} is a **homogenous catalyst** since it is in the **same physical state** as the reactants and it take part in the reaction but is regenerated. **[1]**

(iii) Using an appropriate sketch of the Boltzmann distribution; explain why the addition of acidic solution of iron(II) can catalyse the decomposition of hydrogen peroxide. [3]



When a catalyst is present,

- **<u>activation energy is lowered</u>**
- **<u>more reactant particles with energy ≥ $E_{a(cat)}$</u>**
- **<u>more effective collisions</u>**
- **<u>rate of reaction is proportional to the frequency of effective collisions</u>**
- rate of reaction increases

[3]

(b) Strontium hydroxide is a strong base and has several industrial applications such as plastic stabiliser and paint drier.

The standard enthalpy change of neutralisation was determined experimentally by mixing known volumes of aqueous hydrochloric acid and aqueous strontium hydroxide in a calorimeter. The following results were obtained:

- Initial temperature = 25.0 °C
- Final temperature = 35.4 °C
- Volume of 2 mol dm^{-3} hydrochloric acid = 50.0 cm^3
- Volume of 0.77 mol dm^{-3} of strontium hydroxide = 50.0 cm^3
- Heat capacity of calorimeter = 9.43 J K^{-1}

(i) Define *standard enthalpy change of neutralisation*. [1]

Standard enthalpy change of neutralisation is the **<u>energy evolved</u>** when an **<u>acid and a base</u>** react to form **<u>one mole of water</u>** under **<u>standard conditions</u>**. **[1]**

(ii) Use the data above to calculate the standard enthalpy change of neutralisation in kJ mol^{-1}. [3]

$Q = m_{water} \times c_{water} \times \Delta T + C_{calorimeter} \times \Delta T$
$= (50+50) \times 4.18 \times (35.4 - 25.0) + 9.43 \times (35.4 - 25.0)$
$= 4445.3$ J **[1]**

$2HCl + Sr(OH)_2 \rightarrow SrCl_2 + 2H_2O$
$2HCl \equiv Sr(OH)_2 \equiv 2H_2O$

Amount of HCl = $\frac{50}{100} \times 2 = 0.1 mol$

Amount of $Sr(OH)_2$ = $\frac{50}{100} \times 0.77 = 0.0385 mol$

$Sr(OH)_2$ is the limiting reagent
Amount of H_2O formed = 0.0385 x 2 =0.077 mol **[1]**

$\Delta H_n = -\frac{Q}{n_{H_2O}} = -\frac{4445.3}{0.077} = -57731 J mol^{-1} = -57.7 kJ mol^{-1}$ **[1]**

(iii) The enthalpy change of neutralisation between aqueous strontium hydroxide and aqueous ethanoic acid was found to be different from the value calculated in **b(ii)**.

State and explain how the magnitude of this value differ from **b(ii)**.

[2]

The magnitude is **lower** than the value in **b(ii)**. **[1]**

CH_3COOH is a **weak acid which dissociate slightly** in aqueous solution. Some of the **energy evolved from the neutralisation process is used to further dissociate** the weak acid. **[1]**

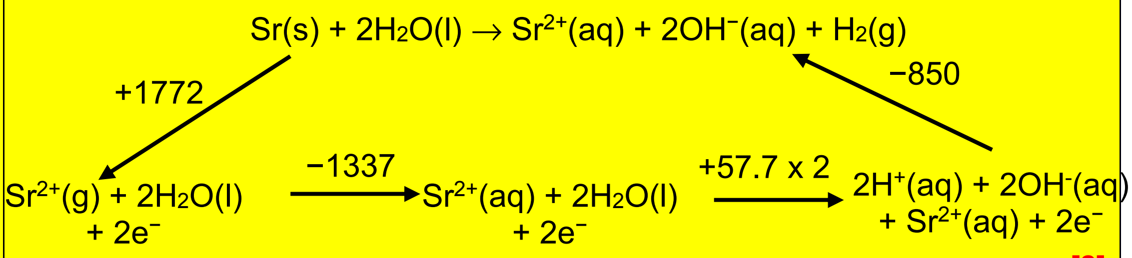
(c) Aqueous strontium hydroxide is formed when solid strontium metal reacts with water

$$Sr(s) + 2H_2O(l) \rightarrow Sr^{2+}(aq) + 2OH^-(aq) + H_2(g)$$

By using the following enthalpy changes and your answer in **b(ii)**, draw an energy cycle to calculate the enthalpy change for the above reaction involving strontium and water.

	kJ mol⁻¹
Enthalpy change for $Sr(s) \rightarrow Sr^{2+}(g) + 2e^-$	+1772
Enthalpy change of hydration of strontium ions	−1337
Enthalpy change for $2H^+(aq) + 2e^- \rightarrow H_2(g)$	−850

[3]



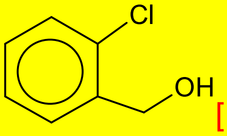
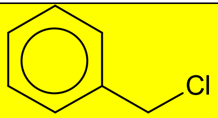
[2]

ΔH_{rxn} = +1772 – 1337 + 57.7 x 2 – 850 = −299.6 kJ mol^{-1} **[1]**

Total= [18]

Section B

Answer **one** question in this section.

4	**(a)**	Four samples of Period 3 chlorides, **G**, **H**, **J** and **K** are examined. • These chlorides reacted completely in water, leaving no precipitates. These solutions were tested with universal indicator paper. **G**, **J** and **K** were found to be acidic, while **H** was found to be neutral. • The melting points of **H** and **J** are approximately 10 times higher than the melting points of **G** and **K**. • Solid anhydrous **G** is required in the reaction of phenylmethanol with chlorine to form C_7H_7OCl. • Solid anhydrous **K** reacts with phenylmethanol to form C_7H_7Cl at room temperature.	
		(i)	Identify the chlorides **G**, **H**, **J** and **K**. [2]
			G – $AlCl_3$ H - $NaCl$ J – $MgCl_2$ K – PCl_5
		(ii)	Explain why **H** forms a neutral solution. [2]
			It dissolves in water to form Na^+ and Cl^-. As Na^+ has a low charge density [1], it is unable to polarise/hydrolyse water molecules and hence remains a neutral solution. [1]
		(iii)	Draw the structure of the resulting compound, C_7H_7OCl. [1]
			 [1] positon of Cl at 2,3,4 are acceptable
		(iv)	Draw the structure of the resulting compound, C_7H_7Cl. [1]
			 [1]
		(v)	Suggest why chloride **K** has to be anhydrous for the reaction between chloride **K** and phenymethanol to occur. Write a chemical equation to support your answer. [2]
			$PCl_5(s) + 4H_2O(l) \rightarrow H_3PO_4(aq) + 5HCl\ (aq)$ [1] PCl_5 undergoes hydrolysis with water to form H_3PO_4. [1]

(vi) Using structure and bonding, explain why chloride **J** has a melting point approximately 10 times higher than chloride **G** and **K**.

[1]

$MgCl_2$ is a giant ionic lattice structure which requires a **larger amount of energy** to overcome the **strong ionic bond** [electrostatic forces of attraction between the oppositely charged ions (Mg^{2+} and Cl^-)].

$AlCl_3$ and PCl_5 are simple molecular structures which require **lesser energy** to overcome the **weak intermolecular forces of attraction between the molecules**. [1]

(b) The reaction of silicon tetrachloride with moist ethoxyethane, produces either oxochlorides, Si_2OCl_6 or $Si_3O_2Cl_8$.

When 0.10g of one of the oxochloride completely reacted with water, all of its chlorine was converted into chloride ions, and produced 0.303 g of silver chloride precipitate when an excess of aqueous silver nitrate was added.
Deduce the identity of the oxochloride.

[2]

Amount of AgC*l* = amount of Cl^- present = $\frac{0.303}{107.9+35.5} = 0.002113$mol

Amount of Cl^- in Si_2OCl_6 = $6 \times \frac{0.1}{2(28.1)+16.0+6(35.5)}$ =0.002104 mol

Amount of C*l*- in $Si_3O_2Cl_8$ = $8 \times \frac{0.1}{3(28.1)+2(16.0)+8(35.5)} = 0.002$ mol

Since **amt of Cl^- in Si_2OCl_6 ≈amt of C*l*- in the AgC*l***, [1]
the oxochloride is **Si_2OCl_6** [1]

(c) Fluorine bomb calorimetry has been used to investigate inorganic substances such as silicon compounds that cannot be completely burned in conventional calorimetric reagents such as oxygen under high pressure.
The enthalpy change of reaction of the following silicon containing compounds were investigated during a fluorine bomb calorimeter.

$Si_3N_4 + 6F_2 \rightarrow 3SiF_4 + 2N_2$ $\Delta H = -828.9\ kJ\ mol^{-1}$
$SiH_4 + 4F_2 \rightarrow SiF_4 + 4HF$ $\Delta H = -2631\ kJ\ mol^{-1}$

The following enthalpy change of formation is also given below:

Compound	ΔH_f /kJ mol^{-1}
HF(g)	-272.6
Si_3N_4(s)	-3686.1

Calculate the standard enthalpy change of formation of SiF_4.
Hence, calculate the standard enthalpy change of formation of SiH_4.

[2]

$3\Delta H_f(SiF_4) = -3686.1 - 828.9 = -4515\ kJmol^{-1}$

$\Delta H_f(SiF_4) = -1505\ kJ\ mol^{-1}$ [1]

$$\begin{tikzcd} SiH_4 + 4F_2(g) \arrow[rr, "-2631"] & & SiF_4 + 4HF \\ & Si(s) + 2H_2(g) + 2F_2(g) \arrow[ul, "\Delta H_f(SiH_4)"] \arrow[ur, "-1505"] \arrow[ur, "4(-272.6)"'] & \end{tikzcd}$$

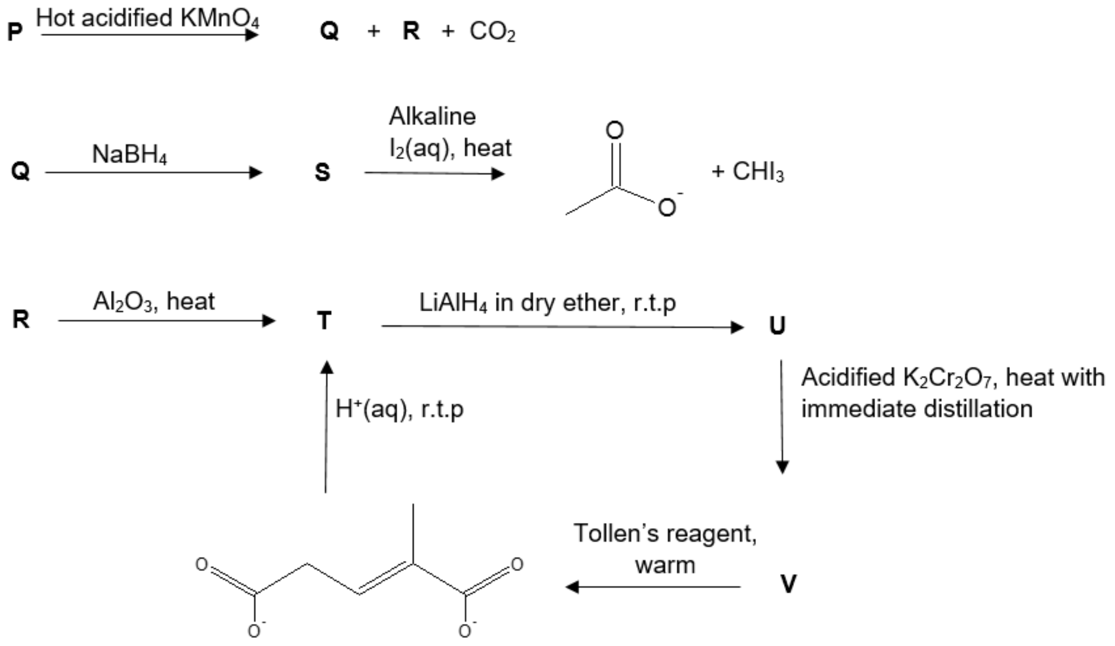
(energy cycle not required)

$-2631 = -\Delta H_f(SiH_4) - 1505 + 4(-272.6)$

$\Delta H_f(SiH_4) = 2631 - 1505 + 4(-272.6)$

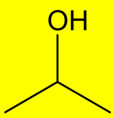
$=$ **$+35.6\ kJ\ mol^{-1}$** [1]

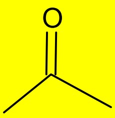
(d) Linalool, **P**, is a compound which gives the sweet scent of lavender. Its structure can be deduced from the following series of reactions.

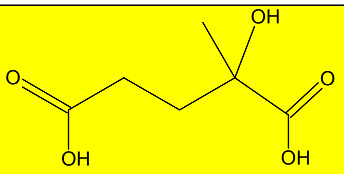
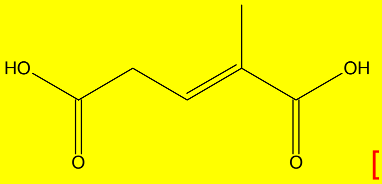
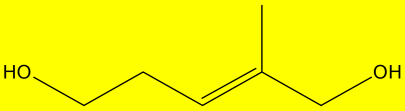
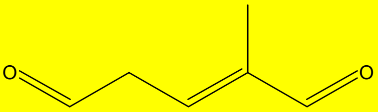
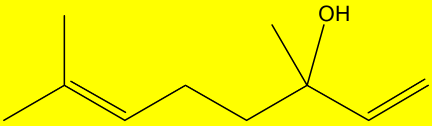


(i) Draw the structures of **S** and **Q**.

[2]

S: 

Q: 

		(ii)	Draw the structures of **R**, **T**, **U** and **V**. [4]
			R:  [1] **T:**  [1] **U:**  [1] **V:**  [1]
		(iii)	Hence, deduce the structure of linalool, **P**.
			P:  [1]
			[Total: 20]

5 This question is about the reactions of halogen containing organic compounds.

(a) The Finkelstein reaction, named after the German chemist, Hans Finkelstein, involves the replacement of the halogen atom in a halogenoalkane by an iodide ion from a solution of sodium iodide dissolved in propanone. This reaction goes almost to completion and a precipitate of sodium halide is formed as shown below.

$$RX + NaI \rightleftharpoons RI + NaX$$

A series of experiment can be carried out to determine the order of reaction with respect to a halogenoalkane, C_4H_9Br, and iodide ion. Different concentrations of C_4H_9Br and sodium iodide were used and the following initial rates were obtained.

Experiment Number	$[C_4H_9Br]$ / mol dm^{-3}	[NaI] / mol dm^{-3}	Rate / mol dm^{-3} s^{-1}
1	0.04	0.60	5.68×10^{-5}
2	0.02	0.30	1.42×10^{-5}
3	0.60	0.60	8.52×10^{-4}

(i) Use these data to deduce the order of reaction with respect to each reactant, showing how you arrive at your answers. Hence, write a rate equation for the reaction.

[3]

Let rate = $k\,[C_4H_9Br]^x[I^-]^y$

Comparing experiments 1 and 3,

$$\frac{rate\,1}{rate\,3} = \frac{k(0.04)^x(0.6)^y}{k(0.6)^x(0.6)^y}$$

$$\frac{5.68 \times 10^{-5}}{8.52 \times 10^{-4}} = \left(\frac{0.04}{0.6}\right)^x$$

$$x = 1$$

∴ Order of reaction w.r.t. C_4H_9Br = **1** **[1]**

Comparing experiments 1 and 2,

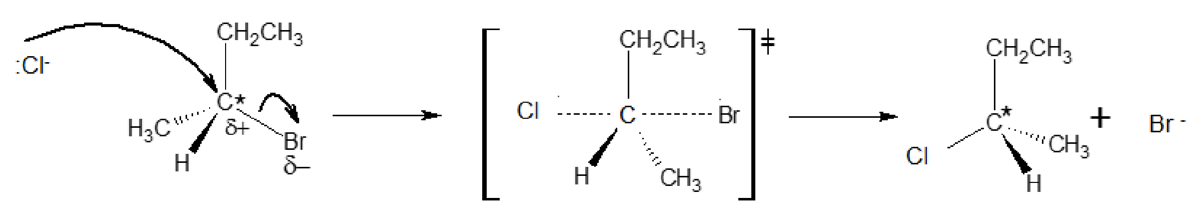
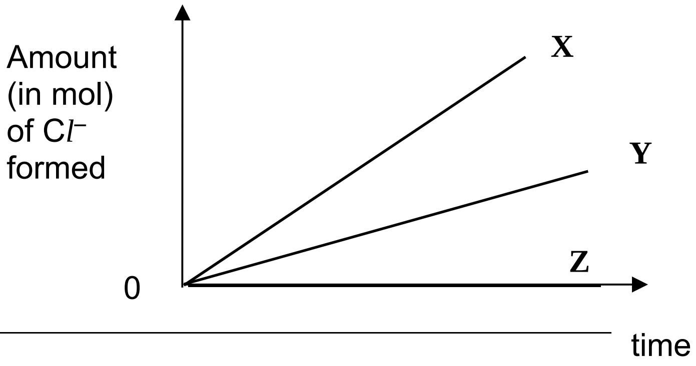
$$\frac{rate\,1}{rate\,2} = \frac{k(0.04)^1(0.6)^y}{k(0.02)^1(0.3)^y}$$

$$\frac{5.68 \times 10^{-5}}{1.42\ x\ 10^{-5}} = \left(\frac{0.04}{0.02}\right)\left(\frac{0.6}{0.3}\right)^y$$

$$y = 1$$

∴ Order of reaction w.r.t. iodide = **1** **[1]**

rate = $k\,[C_4H_9Br][I^-]$ [1]

		(ii)	Based on your answer in **(a)(i)**, deduce a suitable structure for the halogenoalkane, C_4H_9Br which contains a chiral carbon.
			[2]
			$CH_3CH_2CH(Br)CH_3$. **[1]** From the rate equation, the **slow step consists of 1 C_4H_9Br molecule and 1 I^- reacting with each other.** This is consistent with a **S_N2** mechanism. However, since C_4H_9Br contains a chiral carbon, the compound must be a **secondary** halogenoalkane. **[1]**
		(iii)	Using your answer in **(a)(i)** and **(a)(ii)**, describe a mechanism that is consistent with your rate equation. Show relevant lone pairs and dipoles, and use curly arrows to indicate the movement of electron pairs.
			[2]
Nucleophilic substitution, S_N2  			
		(iv)	Sodium chloride is precipitated during the Finkelstein reaction due to its limited solubility in propanone. Explain why the Finkelstein reaction goes almost to completion despite the C-I bond being weaker than the C-C*l* bond.
			[1]
			$RCl_{(propanone)} + NaI_{(propanone)} \rightleftharpoons RI_{(propanone)} + NaCl\,(s)$ As NaC*l* is precipitated out of propanone solution, **[C*l*⁻] decreases** continuously. By Le Chatelier's principle, the e**quilibrium position shifts to the right to increase [Cl⁻].** Hence the reaction goes almost to completion. **[1]**
	(b)	Halogen-containing organic compounds can be hydrolysed under suitable conditions to produce the corresponding halide ions, X^-. A student investigated the amount of Cl^- produced by hydrolysing ethanoyl chloride, chloroethane and chlorobenzene and the results are shown below.  	

Deduce **X**, **Y** and **Z**.

[3]

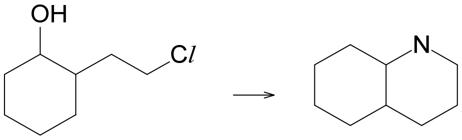
X is **ethanoyl chloride**. **Y** is **chloroethane** and **Z** is **chlorobenzene**. **[1]**

Ethanoyl chloride hydrolyses at the fastest rate. This is because the **carbonyl C atom has 2 very electronegative atoms (O and C*l*) bonded to it**
This makes the **carbonyl C atom highly electron deficient**, **hence nucleophilic substitution occurs very readily**. **[1]**

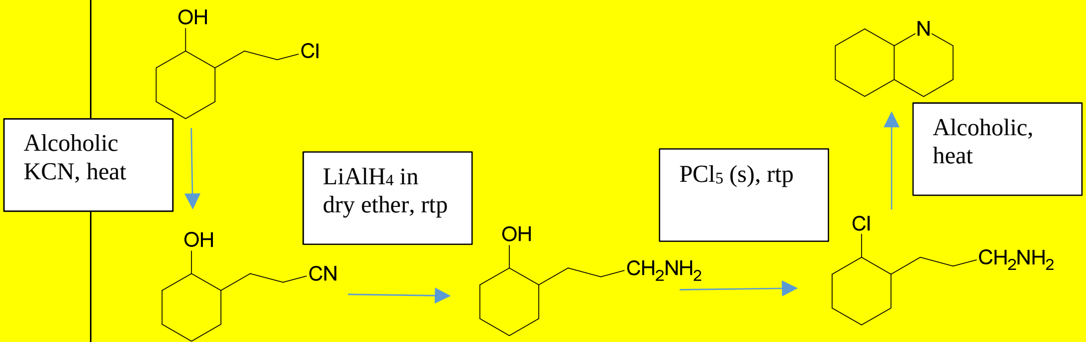
Chlorobenzene hydrolyses the slowest because the **lone pair of electrons** of the halogen atom can **delocalise into the π electron cloud of the benzene ring**.

This results in **partial double bond** character in C-Cl bond and the **strengthening** of the C-Cl bond. **[1]**

(c) In no more than 4 steps, outline how the following transformation can be achieved. State the reagents and conditions for each step, as well as the structures of any intermediates formed.



[4]



[1] each intermediate + R+C

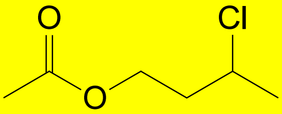
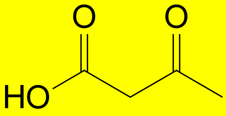
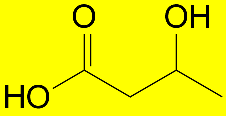
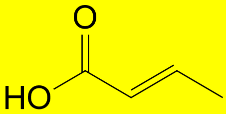
(d) When ester **A** ($C_6H_{11}O_2Cl$) is heated with alkaline $KMnO_4$, two products are formed. Acidification of the two products give **B** and **C**.

C gives a yellow precipitate when warmed with aqueous alkaline iodine. When sodium borohydride is added to **C**, compound **D** is formed. **D** reacts with hot concentrated sulfuric acid to form **E** ($C_4H_6O_2$) that exhibits cis-trans isomerism.

B, **C, D** and **E** all produce effervescence when reacted with aqueous Na_2CO_3.

Draw the structures of **A**, **B**, **C**, **D** and **E**.

[5]

			A:  [1] **B:** CH_3COOH [1] **C:**  [1] **D:**  [1] **E:**  [1]
			[Total: 20]

END