ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY **9729/01**
Higher 2

Paper 1 Multiple Choice

18 September 2019
1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, glue or correction fluid.
Write your name, index number and tutorial class on the Answer Sheet in the spaces provided unless this has been done for you.

There are **thirty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.

Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.

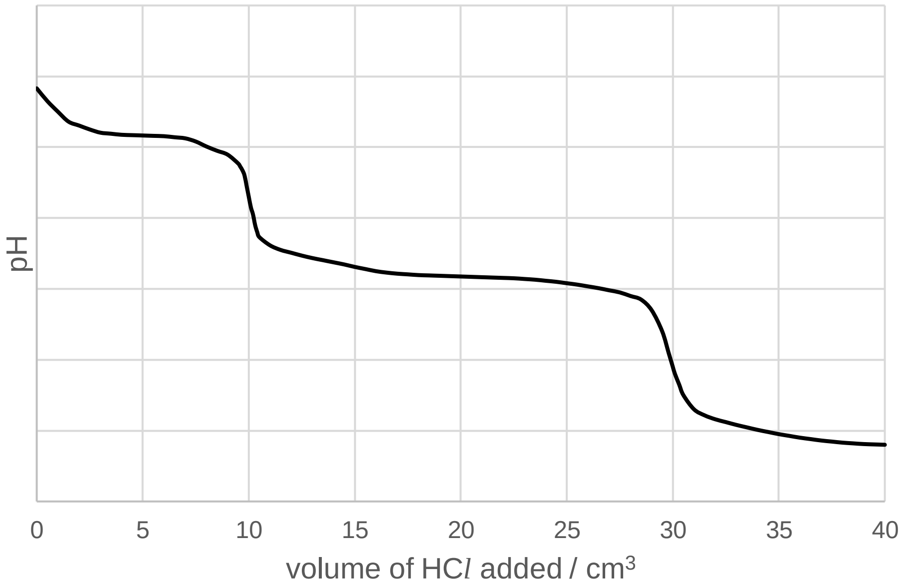
Any rough working should be done in this booklet.

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

This document consists of **18** printed pages.

1 An aqueous mixture of sodium carbonate and sodium hydrogencarbonate was titrated with hydrochloric acid and the pH was recorded.

What is a suitable indicator to use for detecting the first end point and the ratio of sodium carbonate to sodium hydrogencarbonate in the mixture?



	indicator	ratio
A	methyl orange	1:1
B	methyl orange	1:2
C	thymol blue	1:1
D	thymol blue	1:2

2 The most common oxidation state of americium, Am, in aqueous solution is +3.

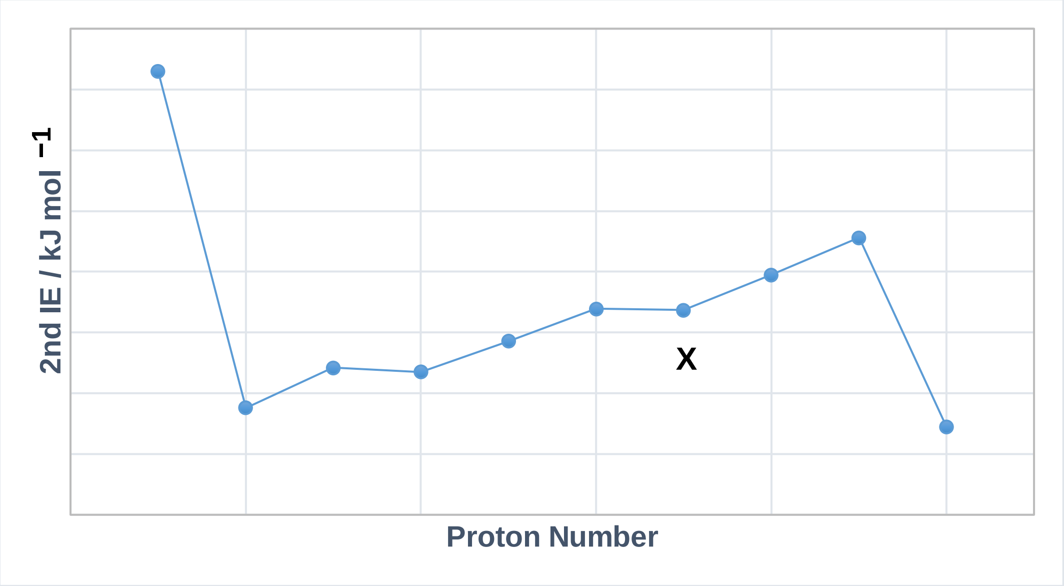
Recently, Cu^{3+} has been shown to quantitatively oxidise Am^{3+}(aq) in dilute HNO_3, while itself is reduced to Cu^{2+}.

In an experiment, 20.0 cm^3 of 0.0120 mol dm^{-3} Am^{3+}(aq) was found to require 24.00 cm^3 of 0.0300 mol dm^{-3} Cu^{3+} for complete oxidation.

What is the formula of the americium-containing species formed?

A AmO^+ **B** AmO^{2+} **C** AmO_2^{2+} **D** $Am_2O_2^{2+}$

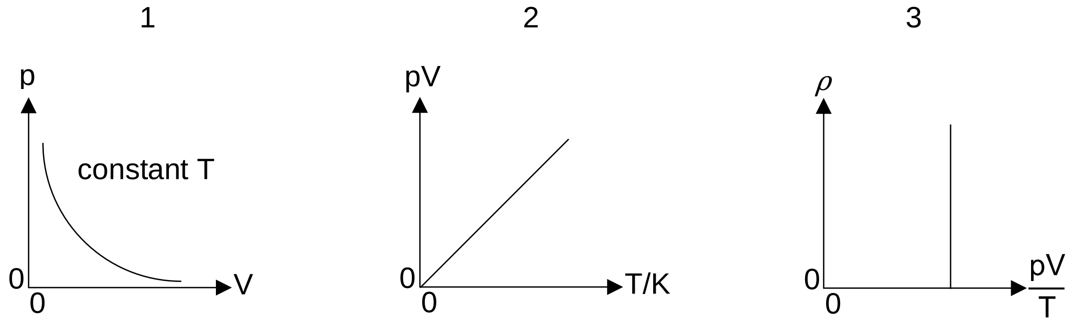
3 The graph shows the second ionisation energies for ten consecutive elements.



Which of the following could be **X**?

A oxygen **B** fluorine **C** neon **D** sodium

4 Which of the following graphs are correct about a fixed amount of an ideal gas?



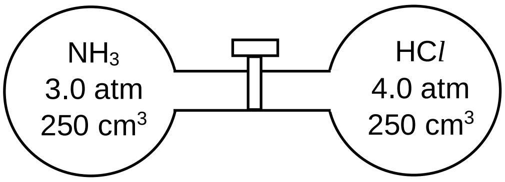
A 1 and 2 only

B 1 and 3 only

C 2 and 3 only

D all of the above

5 Two single-neck round-bottomed flasks were evacuated and insulated from the surroundings. They were filled separately with gaseous ammonia and gaseous hydrogen chloride at room temperature and connected with a gas tap joint.



When the gas tap joint is opened, the two gases are allowed to mix.

What is the final pressure of the resultant gas mixture?

A more than 3.5 atm but less than 7.0 atm

B exactly 3.5 atm

C more than 0.5 atm but less than 1.0 atm

D exactly 0.5 atm

6 When 1.00 g of ethanol was burned under a beaker of water, it was found that 100 cm^3 of water was heated from 15 °C to 65 °C. The process was known to be only 70% efficient.

Use these data and values from the *Data Booklet* to calculate the enthalpy change of combustion of ethanol.

A −209 kJ mol^{-1} **B** −673 kJ mol^{-1}

C −1373 kJ mol^{-1} **D** +1373 kJ mol^{-1}

7 Some standard enthalpy changes are given below.

	$\Delta H^{\ominus}$ / kJ mol^{-1}
$Ca^{2+}(g) + aq \longrightarrow Ca^{2+}(aq)$	–1650
$Cl^{-}(g) + aq \longrightarrow Cl^{-}(aq)$	–364
$Ca^{2+}(g) + 2Cl^{-}(g) \longrightarrow CaCl_2(s)$	–2258

What is the standard enthalpy change of solution of calcium chloride?

A +244 kJ mol^{-1}

B –120 kJ mol^{-1}

C –2378 kJ mol^{-1}

D –4636 kJ mol^{-1}

8 Hydrogen peroxide reacts with acidified iodide ions, liberating iodine.

$$H_2O_2 + 2I^- + 2H^+ \rightarrow I_2 + 2H_2O$$

In the investigation of this reaction, the following results were obtained.

initial concentrations of reactants / mol dm^{-3}			initial rate of formation of iodine / mol dm^{-3} s^{-1}
$[H_2O_2]$	$[I^-]$	$[H^+]$	
0.01	0.01	0.10	2.0×10^{-6}
0.03	0.01	0.10	6.0×10^{-6}
0.03	0.02	0.10	1.2×10^{-5}
0.03	0.02	0.20	1.2×10^{-5}

Which of the following statements are correct?

1 The rate equation can be written as: rate = k $[H_2O_2][I^-]$.

2 The reaction is second order with respect to H^+.

3 The value of the rate constant is 0.2.

A 1 only

B 2 only

C 1 and 2

D 1, 2 and 3

9 Phosphorus(V) chloride, PCl_5, is a white solid which sublimes at 160 °C.

When gaseous phosphorus(V) chloride is heated in a closed container, the following equilibrium is established.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) \qquad \Delta H > 0$$

Rate constant, k_b, applies for the backward reaction and equilibrium constant, K_c, applies for the overall process.

How will the values of k_b and K_c change when the equilibrium is established at a higher temperature than before?

	k_b	K_c
A	increase	increase
B	increase	decrease
C	decrease	increase
D	decrease	decrease

10 When gaseous phosphorus(V) chloride is heated in a closed container, the following equilibrium is established.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) \qquad \Delta H > 0$$

0.0200 moles of phosphorus(V) chloride was vaporised completely in a 2.0 dm^3 container. The amount of chlorine gas detected at equilibrium was found to be 0.00400 moles.

What is the value of K_c at this temperature?

A 1.0×10^{-3}

B 8.0×10^{-4}

C 5.0×10^{-4}

D 4.0×10^{-4}

11 The value of pK_w at 40 °C is 13.54.

What is the pH of an aqueous solution of 0.05 mol dm^{-3} $Ba(OH)_2$ at 40 °C?

A 12.23

B 12.54

C 12.70

D 13.00

12 In which of the following solutions will solid calcium phosphate, $Ca_3(PO_4)_2$, be the least soluble at 25 °C? The numerical value of K_{sp} of $Ca_3(PO_4)_2$ is 2.07×10^{-33}.

A 0.3 mol dm^{-3} $Ca(NO_3)_2$ (aq)

B 0.3 mol dm^{-3} Na_3PO_4 (aq)

C 0.6 mol dm^{-3} HNO_3 (aq)

D water

13 A cell diagram is written as follows:

$$Ti(s)\,|\,Ti^{2+}(aq)\,\|\,H_2SO_4(aq)\,|\,SO_2(g)\,|\,Pt(s)$$

Use relevant data from the *Data Booklet*, and the following electrode potential

$$Ti^{2+}(aq) + 2e^{-} \rightleftharpoons Ti(s) \qquad E^{\ominus} = -1.63V$$

to calculate the standard Gibbs free energy change of the cell in kJ mol^{-1}.

A −37 **B** −157 **C** −282 **D** −347

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

The standard reduction potentials of some vanadium species are tabulated below.

half-reaction	$E^{\ominus}$ / V
$V^{2+}(aq) + 2e^{-} \rightleftharpoons V(s)$	–1.20
$V^{3+}(aq) + e^{-} \rightleftharpoons V^{2+}(aq)$	–0.26
$VO^{2+}(aq) + 2H^{+}(aq) + e^{-} \rightleftharpoons V^{3+}(aq) + H_2O(l)$	+0.34

Which of the following metals, when added in excess, will reduce VO^{2+} to V^{3+}?

1 Sn

2 Zn

3 Pb

A 1 and 3

B 2 and 3

C 1 only

D 2 only

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

Impure copper containing traces of cobalt, iron and silver was purified via electrolysis.

Which cations of the trace metals can be found in solution?

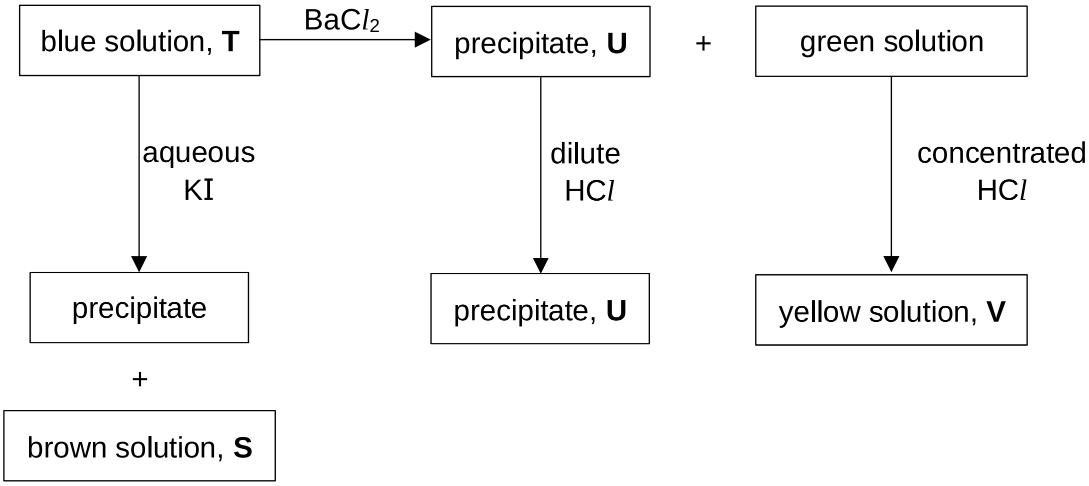
A Ag^+ only

B Ag^+ and Fe^{2+}

C Co^{2+} and Fe^{2+}

D Co^{3+} and Fe^{3+}

16 An aqueous transition metal compound, **T**, was subjected to a series of reactions.



Which statements are correct?

1 The anion in **S** is I^-.

2 The anion in **U** is SO_3^{2-}.

3 The anion in **V** is $CuCl_4^{2-}$

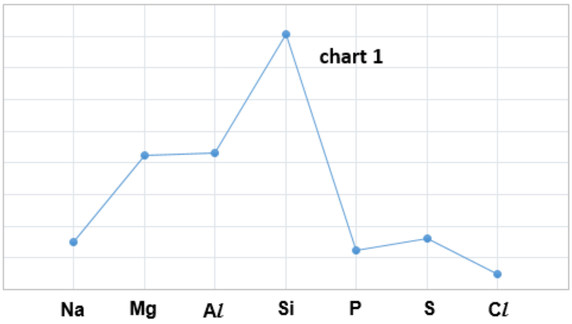
A 1 and 2

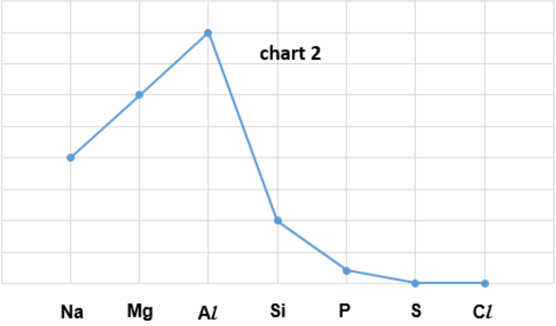
B 2 and 3

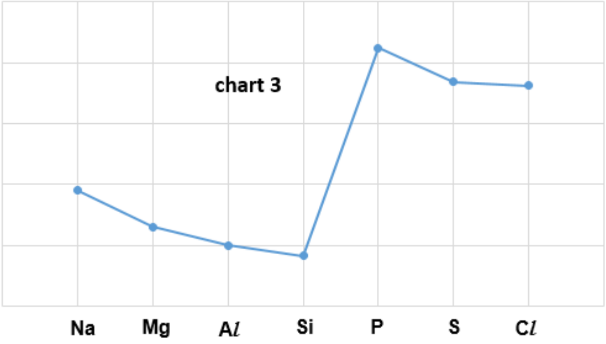
C 1, 2 and 3

D 3 only

17 Three charts below show the variation of three physical properties for the Period 3 elements.







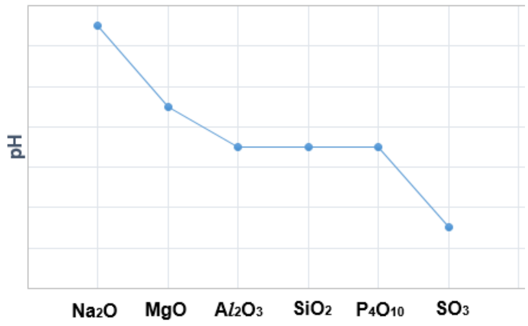
Which of the following is correct?

	chart 1	chart 2	chart 3
A	ionic radius	electrical conductivity	melting point
B	electrical conductivity	melting point	ionic radius
C	melting point	ionic radius	electrical conductivity
D	melting point	electrical conductivity	ionic radius

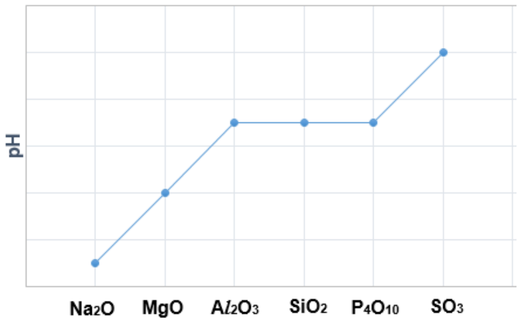
18 The highest oxides of the elements sodium to sulfur are added separately to water.

Which of the following diagrams best represents the pH of the solutions produced?

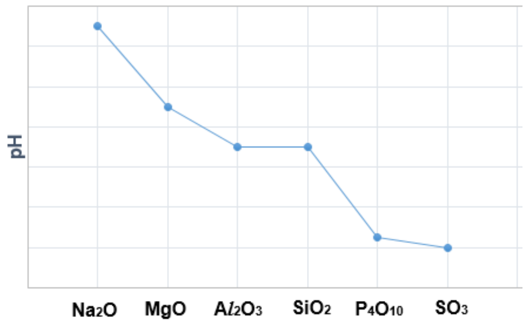
A



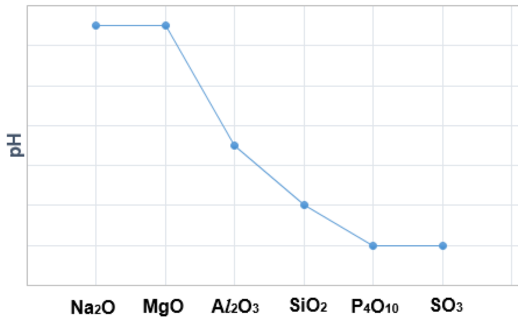
B



C



D



19 Stability constants and colours are given in the following table for this reaction.

$$Fe(H_2O)_6^{3+} + L^- \rightleftharpoons Fe(L)(H_2O)_5^{2+} + H_2O$$

ligand	lg K_{stab}	colour of $Fe(L)(H_2O)_5^{2+}$
SCN^-	2.1	blood red
F^-	5.4	colourless

What would be observed when the following reagents are added to a solution of iron(III) nitrate?

- potassium fluoride
- followed by potassium thiocyanate

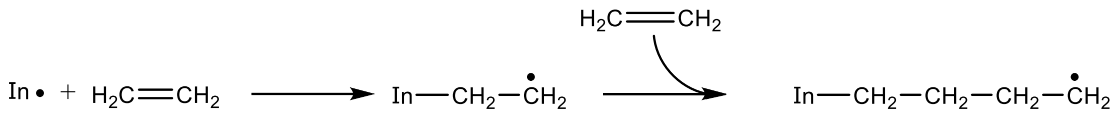
A Solution turns from green to colourless, and then blood red.

B Solution turns from green to colourless, and then remains colourless.

C Solution turns from yellow to colourless, and then to blood red.

D Solution turns from yellow to colourless, and then remains colourless.

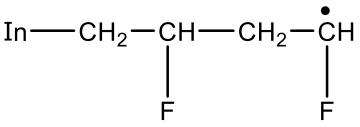
20 Free radical addition is a mechanism used in the synthesis of some addition polymers. Alkene monomers will polymerise in the presence of a radical initiator (In•). For instance, the synthesis of polyethene begins as such.



$$\text{In}\bullet + H_2C{=}CH_2 \longrightarrow \text{In}{-}CH_2{-}\dot{C}H_2 \xrightarrow{H_2C{=}CH_2} \text{In}{-}CH_2{-}CH_2{-}CH_2{-}\dot{C}H_2$$

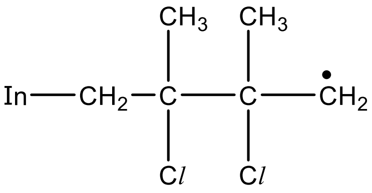
Which of the following chains could **not** have arisen from free radical addition?

A



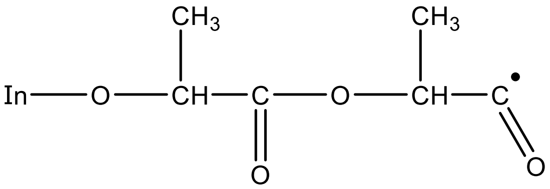
$$\text{In}{-}CH_2{-}\underset{\displaystyle F}{\underset{|}{CH}}{-}CH_2{-}\underset{\displaystyle F}{\underset{|}{\dot{C}H}}$$

B

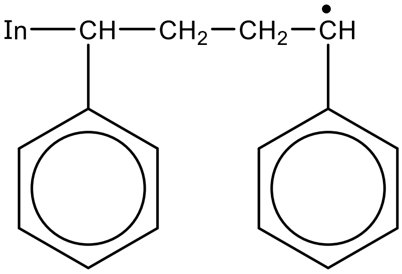


$$\text{In}{-}CH_2{-}\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle Cl}{\underset{|}{C}}}}{-}\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle Cl}{\underset{|}{C}}}}{-}\dot{C}H_2$$

C

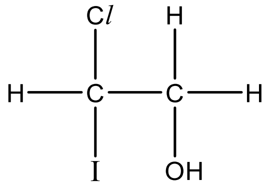
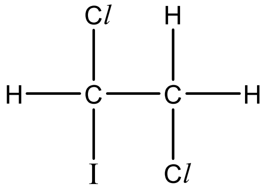
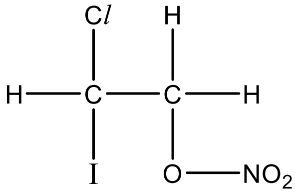
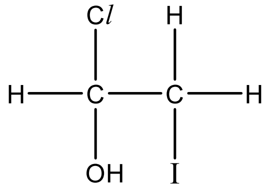
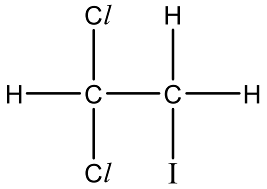
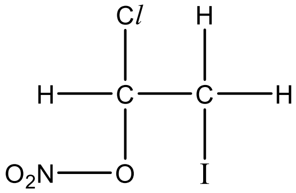
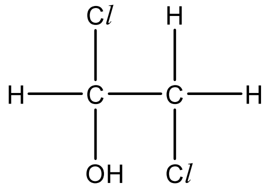
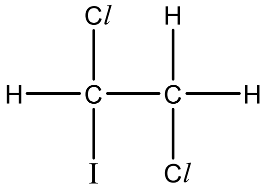
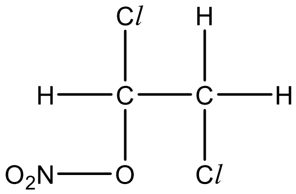
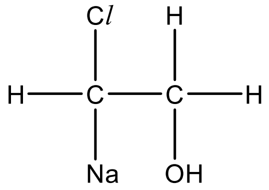
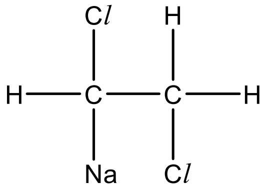
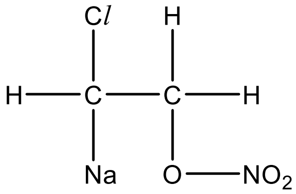


D

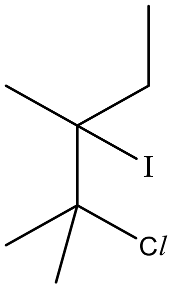


21 Chloroethene is reacted with iodine monochloride in the presence of aqueous sodium nitrate.

Which are the major and minor products?

	major product	minor products
A	 $\mathrm{H-\overset{Cl}{\underset{I}{C}}-\overset{H}{\underset{OH}{C}}-H}$	 $\mathrm{H-\overset{Cl}{\underset{I}{C}}-\overset{H}{\underset{Cl}{C}}-H}$  $\mathrm{H-\overset{Cl}{\underset{I}{C}}-\overset{H}{\underset{O-NO_2}{C}}-H}$
B	 $\mathrm{H-\overset{Cl}{\underset{OH}{C}}-\overset{H}{\underset{I}{C}}-H}$	 $\mathrm{H-\overset{Cl}{\underset{Cl}{C}}-\overset{H}{\underset{I}{C}}-H}$  $\mathrm{H-\overset{Cl}{\underset{O_2N-O}{C}}-\overset{H}{\underset{I}{C}}-H}$
C	 $\mathrm{H-\overset{Cl}{\underset{OH}{C}}-\overset{H}{\underset{Cl}{C}}-H}$	 $\mathrm{H-\overset{Cl}{\underset{I}{C}}-\overset{H}{\underset{Cl}{C}}-H}$  $\mathrm{H-\overset{Cl}{\underset{O_2N-O}{C}}-\overset{H}{\underset{Cl}{C}}-H}$
D	 $\mathrm{H-\overset{Cl}{\underset{Na}{C}}-\overset{H}{\underset{OH}{C}}-H}$	 $\mathrm{H-\overset{Cl}{\underset{Na}{C}}-\overset{H}{\underset{Cl}{C}}-H}$  $\mathrm{H-\overset{Cl}{\underset{Na}{C}}-\overset{H}{\underset{O-NO_2}{C}}-H}$

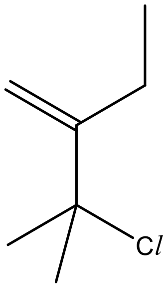
22 The following compound **Y** is reacted with ethanolic sodium hydroxide.



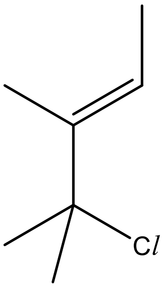
Compound **Y**

Which of the following is the **major** product?

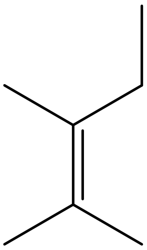
A



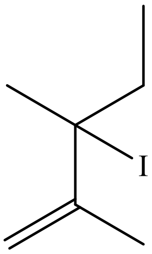
B



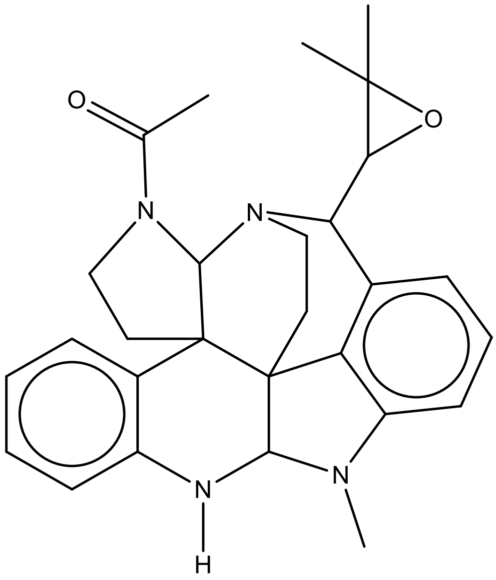
C



D



23 Communesin A is a natural product.



Which of the following statements about communesin A is correct?

A Communesin A gives a yellow precipitate when warmed with alkaline iodine solution.

B There are three tertiary amines in communesin A.

C It is a planar molecule.

D One of the oxygen atoms is sp^3 hybridised; the other is sp^2 hybridised.

24 Compound **B**, $C_6H_{12}O_6$, is an important biomolecule abundant in the brain as it mediates cell signal transduction in response to a variety of hormones and neurotransmitters.

All the atoms (besides the hydrogen atoms) in **B** are sp^3 hybridised.

On adding excess sodium to **B**, hydrogen gas is liberated.

Which of the following statements about compound **B** is true?

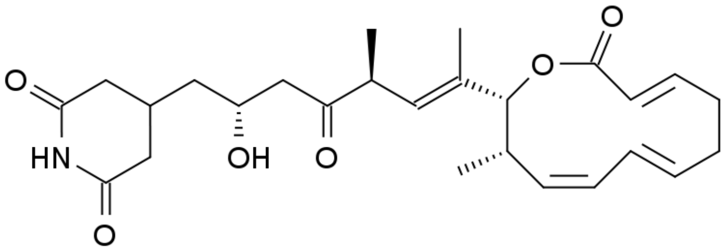
A Compound **B** forms a purple colouration with neutral iron(III) chloride solution.

B Compound **B** forms a yellow precipitate with warmed alkaline iodine solution.

C Compound **B** forms a bright orange precipitate with 2,4-dinitrophenylhydrazine.

D Compound **B** forms a brick-red precipitate with Fehling’s solution.

25 Lactimidomycin is an antibiotic with anti-viral and anti-cancer properties.



Which statements about lactimidomycin are correct?

1 One mole of lactimidomycin reacts completely with four moles of 2,4-dinitrophenylhydrazine.

2 On reacting lactimidomycin with hot acidified $KMnO_4$, there is no gas evolved.

3 On heating lactimidomycin with KOH(aq), there is ammonia gas evolved.

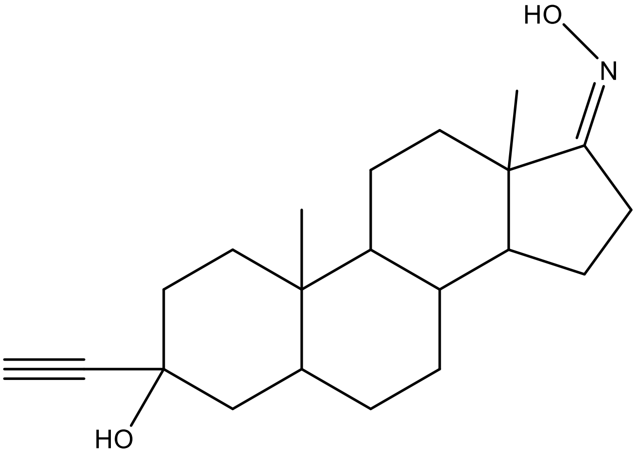
A 1 and 2

B 2 and 3

C 1 only

D 3 only

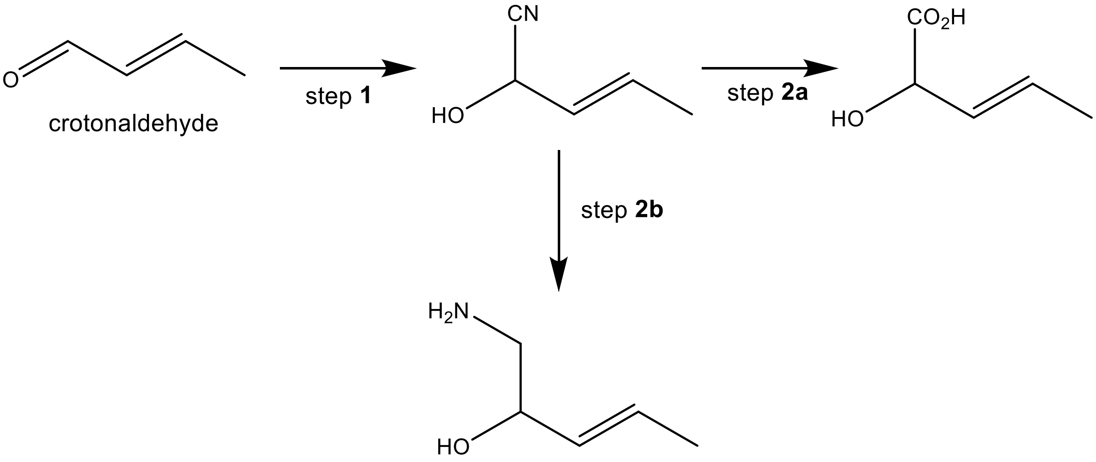
26 Golexanolone is a drug currently being studied for the treatment of hypersomnia.



What is the total number of stereoisomers exhibited by golexanolone?

A 512 **B** 256 **C** 128 **D** 64

27 Crotonaldehyde is an important biomolecule.



Which of the following statements is true about the above synthetic scheme?

A The reaction of crotonaldehyde with hot acidified $KMnO_4$ produces only one organic product.

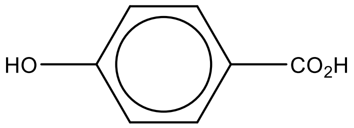
B Step **1** involves heating crotonaldehyde with NaCN in ethanol.

C Step **2a** involves the oxidation of crotonaldehyde because it gained oxygen atoms.

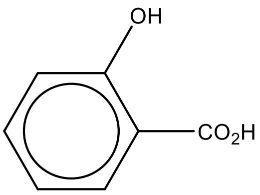
D $NaBH_4$ is the reagent used in step **2b**.

28 4-hydroxybenzoic acid, 2-hydroxybenzoic acid and 3,4-dihydroxybenzaldehyde share the same molecular formula.

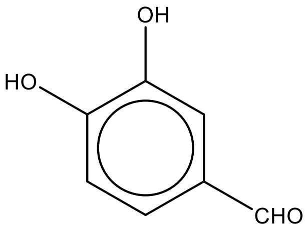
The standard enthalpy changes of formation for 4-hydroxybenzoic acid, 2-hydroxybenzoic acid and 3,4-dihydroxybenzaldehyde are –481 kJ mol^{-1}, –493 kJ mol^{-1} and –392 kJ mol^{-1} respectively.



4-hydroxybenzoic acid



2-hydroxybenzoic acid



3,4-dihydroxybenzaldehyde

Which of the following statements is correct?

1 The thermodynamic stability of these three compounds decrease in the order:
2-hydroxybenzoic acid > 4-hydroxybenzoic acid > 3,4-dihydroxybenzaldehyde

2 3,4-dihydroxybenzaldehyde and 4-hydroxybenzoic acid are positional isomers.

3 The magnitude of the standard enthalpy change of combustion of these three compounds increase in the order:
3,4-dihydroxybenzaldehyde < 4-hydroxybenzoic acid < 2-hydroxybenzoic acid

A 1 only

B 2 only

C 1 and 3

D 2 and 3

29 Chloroethane can be used to make sodium propanoate.

$$\text{chloroethane} \longrightarrow \textbf{Z} \longrightarrow \text{sodium propanoate}$$

The intermediate, **Z**, is treated with boiling aqueous sodium hydroxide to give sodium propanoate.

Which reagent would produce the intermediate, **Z**, from chloroethane?

A potassium cyanide in ethanol

B hydrogen cyanide

C sodium hydroxide in ethanol

D alkaline $KMnO_4$

30 A polypeptide is subjected to hydrolysis by cyanogen bromide and two digestive enzymes.

- The chemical cyanogen bromide cleaves the peptide bond at the carboxylic end of methionine (met) to give a tetrapeptide and a tripeptide.
- The enzyme chemotrypsin hydrolyses a peptide bond at the carboxylic end of tryptophan (trp) to give two dipeptides and a tripeptide.
- The enzyme trypsin, which hydrolyses a peptide bond at the carboxylic end of lysine (lys) to give 2 tripeptides and gly.

What is the sequence of the amino acids in this polypeptide?

A ser-trp-lys-trp-met-lys-gly

B ser-trp-lys-met-trp-lys-gly

C gly-lys-met-trp-lys-trp-ser

D gly-lys-trp-met-lys-trp-ser

ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY **9729/01**
Higher 2

Paper 1 Multiple Choice

18 September 2019
1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, glue or correction fluid.
Write your name, index number and tutorial class on the Answer Sheet in the spaces provided unless this has been done for you.

There are **thirty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.

Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.

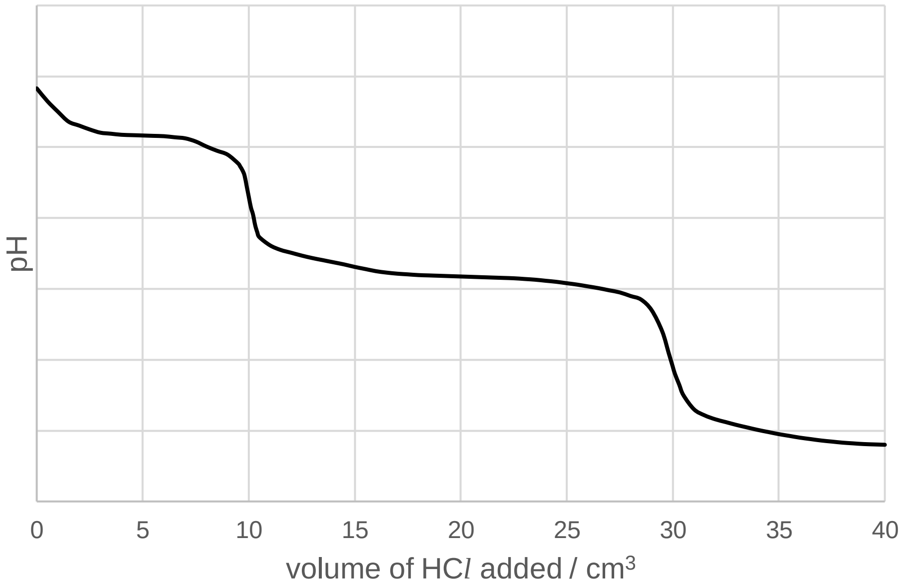
Any rough working should be done in this booklet.

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

This document consists of **18** printed pages.

1 An aqueous mixture of sodium carbonate and sodium hydrogencarbonate was titrated with hydrochloric acid and the pH was recorded.

What is a suitable indicator to use for detecting the first end point and the ratio of sodium carbonate to sodium hydrogencarbonate in the mixture?



	indicator	ratio
A	methyl orange	1:1
B	methyl orange	1:2
[✓ **C**]	thymol blue	1:1
D	thymol blue	1:2

Solution

The working range of methyl orange is between pH 3.1 to 4.4 and thus is not suitable for detecting the first end point between carbonate and H^+ at a pH that is above 7. Thus thymol blue is a more suitable choice.

$CO_3^{2-} + H^+ \longrightarrow HCO_3^-$

$HCO_3^- + H^+ \longrightarrow H_2CO_3$

If 10 cm^3 of H^+ is needed to react with the carbonate ions present in solution, then the same volume of H^+ is needed to react with the hydrogencarbonate produced after the first end point, i.e. 10 cm^3. Thus the other 10 cm^3 portion of H^+ is used to react with the initial hydrogencarbonate present. Hence ratio of carbonate to hydrogencarbonate is 1:1.

Comment: Students who were not careful erroneously chose D because of the convenient 1:2 ratio that they see from the graph.

2 The most common oxidation state of americium, Am, in aqueous solution is +3.

Recently, Cu^{3+} has been shown to quantitatively oxidise $Am^{3+}(aq)$ in dilute HNO_3, while itself is reduced to Cu^{2+}.

In an experiment, 20.0 cm^3 of 0.0120 mol dm^{-3} $Am^{3+}(aq)$ was found to require 24.00 cm^3 of 0.0300 mol dm^{-3} Cu^{3+} for complete oxidation.

What is the formula of the americium-containing species formed?

A AmO^+ **B** AmO^{2+} **C** AmO_2^{2+}✓ **D** $Am_2O_2^{2+}$

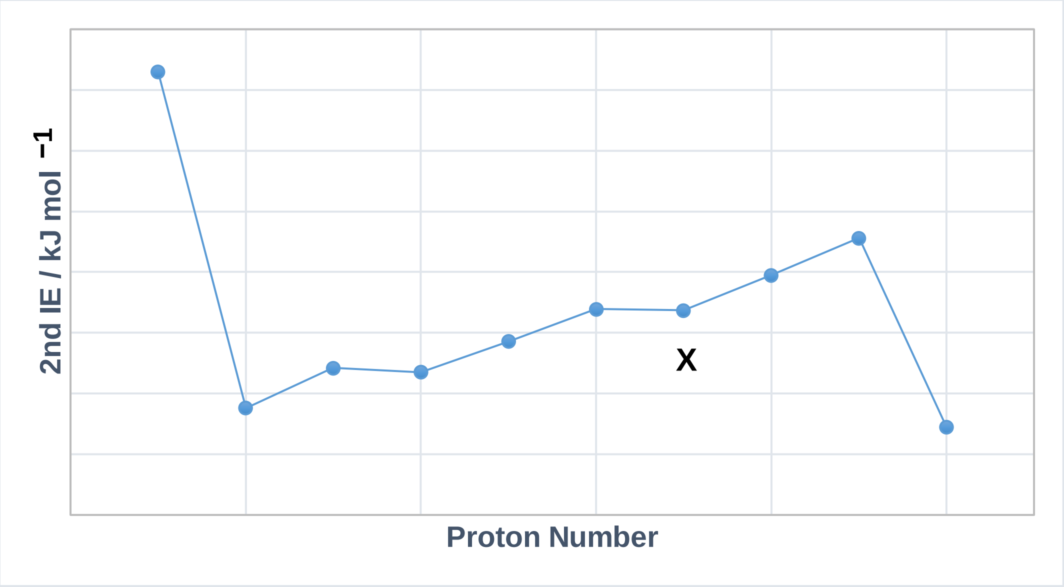
Solution

n(electrons) = n(Cu^{3+}) = 7.20 X 10^{-4}

change in oxidation state of Am = (7.20 X 10^{-4}) / (20.0 X 0.0120 / 1000) = +3

Initial oxidation state of Am = +3 +3 = +6

3 The graph shows the second ionisation energies for ten consecutive elements.



Which of the following could be **X**?

A oxygen **B** fluorine✓ **C** neon **D** sodium

Solution

2nd IE: $X^+(g) \rightarrow X^{2+}(g) + e$

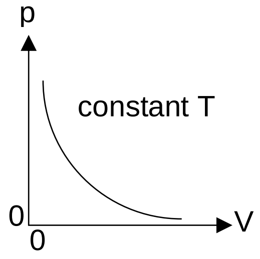
1st Dip is for this case:	**$1s^2\ 2s^2$**	**to**	**$1s^2\ 2s^2\ 2p^1$**	**(2p electron further away)**
2nd Dip is for this case:	**$1s^2\ 2s^2\ 2p^3$**	**to**	**$1s^2\ 2s^2\ 2p^4$**	**(inter-electron repulsion)**

$X^+(g)$ has this electronic configuration: $1s^2\ 2s^2\ 2p^4$

Hence X is $1s^2\ 2s^2\ 2p^5$. X is Fluorine.

4 Which of the following graphs are correct about a fixed amount of an ideal gas?

1



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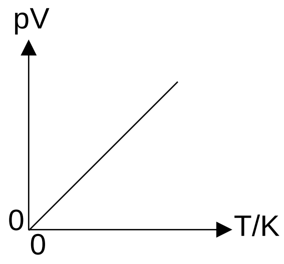
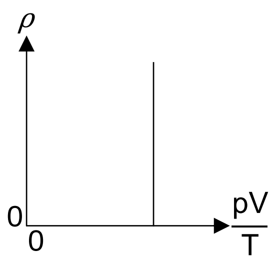


3



A 1 and 2 only

B 1 and 3 only

C 2 and 3 only

✓ **D** all of the above

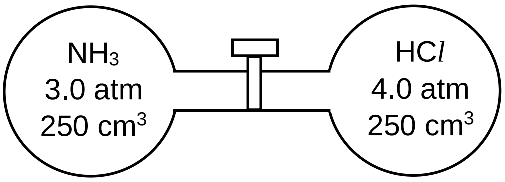
Solution

Using the ideal gas equation, pV = nRT, p=$\frac{nRT}{V}$. Since n, R and T are constant for (1), then p has an inverse relationship with V producing a "y=1/x" graph in (1).

pV has a direct positive relationship T as seen in the ideal gas equation and thus produces a "y=x" graph in (2).

$\frac{pV}{T}$=nR, where nR is a constant. Thus we expect to see a "x = k" graph in (3).

5 Two single-neck round-bottomed flasks were evacuated and insulated from the surroundings. They were filled separately with gaseous ammonia and gaseous hydrogen chloride at room temperature and connected with a gas tap joint.



When the gas tap joint is opened, the two gases are allowed to mix.

What is the final pressure of the resultant gas mixture?

A more than 3.5 atm but less than 7.0 atm

B exactly 3.5 atm

✓ **C** more than 0.5 atm but less than 1.0 atm

D exactly 0.5 atm

Solution

$NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$
All the $NH_3(g)$ will react with $HCl(g)$ to produce $NH_4Cl(s)$ which will deposit on the walls/bottom of the flasks. The solids' volume is negligible compared to the volume of the flasks.

That supposedly leaves us with 0.5 atm of $HCl(g)$ in a combined volume of 500 cm^3. But the reaction is exothermic and heat is given off. Since the flasks are insulated, the system will heat up and we expect the pressure of the system to be higher than 0.5 atm.

Comment: This question was poorly done with approximately half the cohort having chosen B, thinking that it was a simple mixing of the two gases.

6 When 1.00 g of ethanol was burned under a beaker of water, it was found that 100 cm^3 of water was heated from 15 ºC to 65 ºC. The process was known to be only 70% efficient.

Use these data and values from the *Data Booklet* to calculate the enthalpy change of combustion of ethanol.

A −209 kJ mol^{-1}

B −673 kJ mol^{-1}

✓ **C** −1373 kJ mol^{-1}

D +1373 kJ mol^{-1}

Solution

Heat absorbed by water = $mc\Delta T$ = (100)(4.18)(65 – 15) = 20,900 Joule

Heat given out by combustion = Heat absorbed by water ÷ 0.70 = 29,857 Joule

ΔHc(ethanol) = − Heat / Amount of Limiting Reagent
= − 29,857 / (1 ÷ 46.0)
= −1,373,000 J mol^{-1}

7 Some standard enthalpy changes are given below.

	$\Delta H^\ominus$ / kJ mol^{-1}
$Ca^{2+}(g) + aq \longrightarrow Ca^{2+}(aq)$	–1650
$Cl^-(g) + aq \longrightarrow Cl^-(aq)$	–364
$Ca^{2+}(g) + 2Cl^-(g) \longrightarrow CaCl_2(s)$	–2258

What is the standard enthalpy change of solution of calcium chloride?

A +244 kJ mol^{-1}

✓ **B** –120 kJ mol^{-1}

C –2378 kJ mol^{-1}

D –4636 kJ mol^{-1}

Solution

$\Delta H_{soln} = \sum\Delta H_{hyd}(Ca^{2+} + 2Cl^{-}) - LE$

$= -1650 + 2(-364) - (-2258)$

$= -120$ kJ mol^{-1}

Students would have chosen A if they had only taken the ΔH_{hyd} for 1 mole of Cl^{-}.

Students would have chosen C if they misinterpret ΔH_{soln} as the summation of ΔH_{hyd} values.

Option D is just a summation of all three given enthalpy changes, factoring in ΔH_{hyd} for 2 moles of Cl^{-}.

8 Hydrogen peroxide reacts with acidified iodide ions, liberating iodine.

$$H_2O_2 + 2I^{-} + 2H^{+} \rightarrow I_2 + 2H_2O$$

In the investigation of this reaction, the following results were obtained.

initial concentrations of reactants / mol dm^{-3}			initial rate of formation of iodine / mol dm^{-3} s^{-1}
$[H_2O_2]$	$[I^{-}]$	$[H^{+}]$	
0.01	0.01	0.10	2.0×10^{-6}
0.03	0.01	0.10	6.0×10^{-6}
0.03	0.02	0.10	1.2×10^{-5}
0.03	0.02	0.20	1.2×10^{-5}

Which of the following statements are correct?

1 The rate equation can be written as: rate = k $[H_2O_2][I^{-}]$.

2 The reaction is second order with respect to H^{+}.

3 The value of the rate constant is 0.2.

✓ **A** 1 only

B 2 only

C 1 and 2

D 1, 2 and 3

Solution

**Compare Expt 1 and 2, keeping $[I^{-}]$ and $[H^{+}]$ constant, triple $[H_2O_2]$, rate triple.
Order of reaction wrt H_2O_2 is ONE.**

**Compare Expt 2 and 3, keeping $[H_2O_2]$ and $[H^{+}]$ constant, double $[I^{-}]$, rate double.
Order of reaction wrt I^{-} is ONE.**

Compare Expt 3 and 4, keeping $[H_2O_2]$ and $[I^-]$ constant, double $[H^+]$, rate constant. Order of reaction wrt H^+ is ZERO.

Rate = k $[H_2O_2]$ $[I^-]$

Using Expt 1 data, 2.0×10^{-6} = k (0.01) (0.01)
Therefore k = 0.02 $mol^{-1}\ dm^3\ s^{-1}$

9 Phosphorus(V) chloride, PCl_5, is a white solid which sublimes at 160 °C.

When gaseous phosphorus(V) chloride is heated in a closed container, the following equilibrium is established.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) \qquad \Delta H > 0$$

Rate constant, k_b, applies for the backward reaction and equilibrium constant, K_c, applies for the overall process.

How will the values of k_b and K_c change when the equilibrium is established at a higher temperature than before?

		k_b	K_c
✓	**A**	increase	increase
	B	increase	decrease
	C	decrease	increase
	D	decrease	decrease

Solution

Increasing temperature will lead to an increase in rate of reaction because of increased frequency of effective collisions thus k_b will increase.

As the reaction is endothermic, $\Delta H > 0$, increasing temperature will favour the endothermic process to absorb the heat and thus position of equilibrium will shift to the right. POE shifting right increases K_c.

Comments: This question was poorly done, with more than half the cohort having chosen C thinking that with POE going right, k_b will decrease with no regard for the increase in temperature.

10 When gaseous phosphorus(V) chloride is heated in a closed container, the following equilibrium is established.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) \qquad \Delta H > 0$$

0.0200 moles of phosphorus(V) chloride was vaporised completely in a 2.0 dm^3 container. The amount of chlorine gas detected at equilibrium was found to be 0.00400 moles.

What is the value of K_c at this temperature?

A 1.0×10^{-3}

B 8.0×10^{-4}

✓ **C** 5.0×10^{-4}

D 4.0×10^{-4}

Solution

	$PCl_5(g)$	$\rightleftharpoons$	$PCl_3(g)$	+	$Cl_2(g)$
initial / mol dm^{-3}	**0.0200/2.0 = 0.0100**		**0**		**0**
change / mol dm^{-3}	**–0.00200**		**+0.00200**		**+0.00200**
equilibrium / mol dm^{-3}	**0.00800**		**0.00200**		**0.00400/2.0 = 0.00200**

$K_c = \frac{0.00200^2}{0.0080} = 5.0 \times 10^{-4}$

Students would have chosen A if they had taken $\frac{0.00400^2}{0.0160} = 1.0 \times 10^{-3}$

Students would have chosen B if they had taken $\frac{0.00400^2}{0.0200} = 8.0 \times 10^{-4}$

Students would have chosen D if they had taken $\frac{0.00200^2}{0.0100} = 4.0 \times 10^{-4}$

Comment: Most students could get this question correct with the most common error being A.

11 The value of pK_w at 40 °C is 13.54.

What is the pH of an aqueous solution of 0.05 mol dm^{-3} $Ba(OH)_2$ at 40 °C?

A 12.23

✓ **B** 12.54

C 12.70

D 13.00

Solution

[OH^-] = 0.10 mol dm^{-3}

pOH = 1

pH = pK_w – pOH = 13.54 – 1 = 12.54

12 In which of the following solutions will solid calcium phosphate, $Ca_3(PO_4)_2$, be the least soluble at 25 °C? The numerical value of K_{sp} of $Ca_3(PO_4)_2$ is 2.07×10^{-33}.

✓ **A** 0.3 mol dm^{-3} $Ca(NO_3)_2$ (aq)

B 0.3 mol dm^{-3} Na_3PO_4 (aq)

C 0.6 mol dm^{-3} HNO_3 (aq)

D water

Solution

Notice that common ion effect is involved in options A and B – the common ion being Ca^{2+} and PO_4^{3-} respectively. Option D should be ruled out straightaway once it is realized that the question is asking for the least solubility and that common ion effects are involved in options A and B.

Notice that the concentrations of Ca^{2+} and PO_4^{3-} are equal in options A and B. Hence we can look at the power of the ion's concentration in the K_{sp} expression – the larger the power the more the solubility of the salt will be decreased.

Option C actually enhances the solubility.

13 A cell diagram is written as follows:

$$Ti(s) \,|\, Ti^{2+}(aq) \,\|\, H_2SO_4(aq) \,|\, SO_2(g) \,|\, Pt(s)$$

Use relevant data from the *Data Booklet*, and the following electrode potential

$$Ti^{2+}(aq) + 2e^- \rightleftharpoons Ti(s) \qquad E^\ominus = -1.63V$$

to calculate the standard Gibbs free energy change of the cell in kJ mol^{-1}.

A −37 **B** −157 **C** −282 **D** −347 ✓

Solution

From Data Booklet, $SO_4^{2-} + 4H^+ + 2e \rightleftharpoons SO_2 + 2H_2O$ **+0.17 Volt**

$E^\ominus_{cell} = (+0.17) - (-1.63) = +1.80$ **Volt**

$\Delta G = -nF E^\ominus_{cell} = -(2)(96500)(+1.80) = -347$ **kJ** mol^{-1}

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

The standard reduction potentials of some vanadium species are tabulated below.

half-reaction	$E^\ominus$ / V
$V^{2+}(aq) + 2e^- \rightleftharpoons V(s)$	–1.20
$V^{3+}(aq) + e^- \rightleftharpoons V^{2+}(aq)$	–0.26
$VO^{2+}(aq) + 2H^+(aq) + e^- \rightleftharpoons V^{3+}(aq) + H_2O(l)$	+0.34

Which of the following metals, when added in excess, will reduce VO^{2+} to V^{3+}?

1 Sn

2 Zn

3 Pb

✓ **A** 1 and 3

B 2 and 3

C 1 only

D 2 only

Solution

E_{cell} between Sn and VO^{2+} is positive, +0.48 V. But E_{cell} between Sn and V^{3+} is negative, -0.12 V. Hence V^{3+} will be the final vanadium species.

E_{cell} between Zn and VO^{2+} is positive, +1.10 V. E_{cell} between Zn and V^{3+} is also positive, +0.50 V. Hence V^{3+} will NOT be the final vanadium species.

E_{cell} between Pb and VO^{2+} is positive, +0.47 V. But E_{cell} between Pb and V^{3+} is negative, -0.13 V. Hence V^{3+} will be the final vanadium species.

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

Impure copper containing traces of cobalt, iron and silver was purified via electrolysis.

Which cations of the trace metals can be found in solution?

A Ag^+ only

B Ag^+ and Fe^{2+}

✓ **C** Co^{2+} and Fe^{2+}

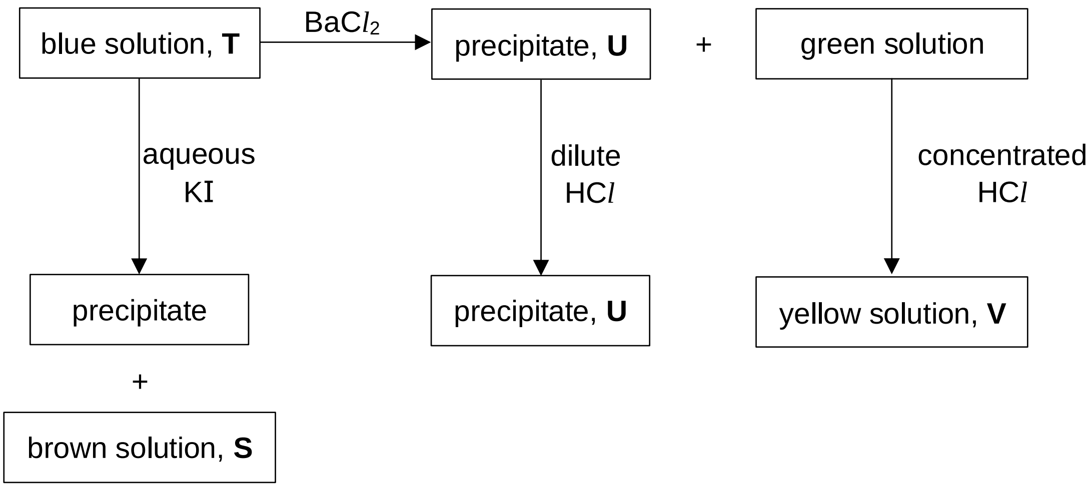
D Co^{3+} and Fe^{3+}

Solution

$Ag^+ + e^- \rightleftharpoons Ag$	+0.80 V
$Co^{2+} + 2e^- \rightleftharpoons Co$	–0.28 V
$Co^{3+} + e^- \rightleftharpoons Co^{2+}$	+1.89 V
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34 V
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	–0.44 V
$Fe^{3+} + 3e^- \rightleftharpoons Fe$	–0.04 V
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.77 V

During the electrolysis of impure copper, Cu is oxidised to Cu^{2+} in solution. As such, Co and Fe will oxidise to Co^{2+}, Fe^{2+} and Fe^{3+}. It's unlikely we'd get any significant oxidation of Ag due to its electrode potential being more positive than Cu. Further oxidation of Co^{2+} to Co^{3+} is unlikely to occur too.

16 An aqueous transition metal compound, **T**, was subjected to a series of reactions.



Which statements are correct?

1 The anion in **S** is I^-.

2 The anion in **U** is SO_3^{2-}.

3 The anion in **V** is $CuCl_4^{2-}$

A 1 and 2

B 2 and 3

C 1, 2 and 3

✓ **D** 3 only

Solution

T is $CuSO_4$.

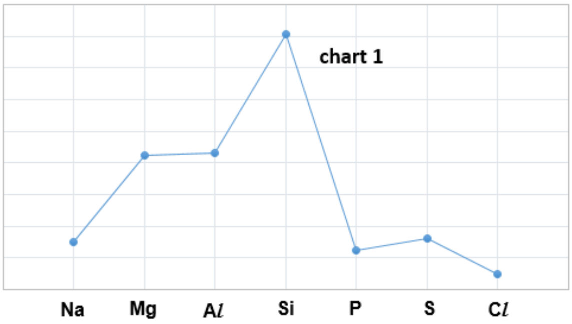
Ppt formed on reaction with KI is CuI and anion in brown solution, S, is I_3^-.
$2Cu^{2+} + 4I^- \longrightarrow 2CuI + I_2$
$I_2 + I^- \rightleftharpoons I_3^-$

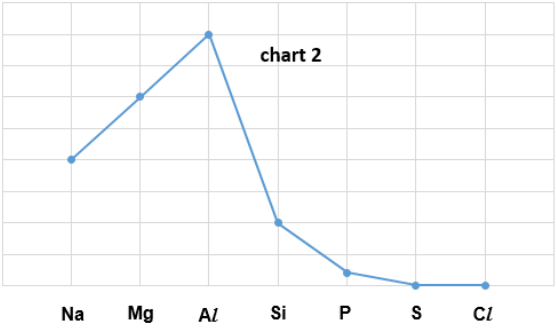
Ppt U is $BaSO_4$ which does not react with HCl.
$Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4(s)$

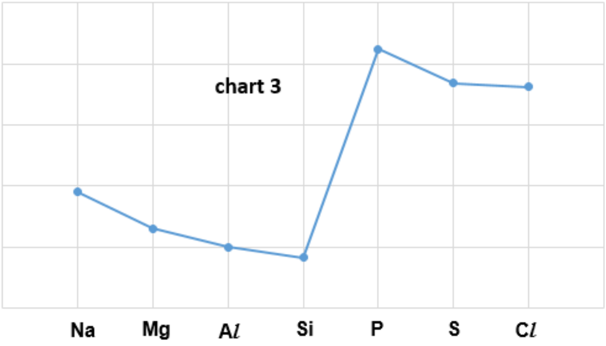
Green solution formed is $CuCl_2$ which reacts further with more Cl^- ligands to form $CuCl_4^-$ anion complex in V.

Comment: Approximately 40% of students chose C and 40% chose the correct option D.

17 Three charts below show the variation of three physical properties for the Period 3 elements.







Which of the following is correct?

	chart 1	chart 2	chart 3
A	ionic radius	electrical conductivity	melting point
B	electrical conductivity	melting point	ionic radius
C	melting point	ionic radius	electrical conductivity
✓ **D**	melting point	electrical conductivity	ionic radius

Solution

Chart 1 (Melting Point):
Silicon has highest mp.
Na, Mg, Al as a group has the second highest mp.
P_4, S_8 and Cl_2 as a group has the lowest mp.

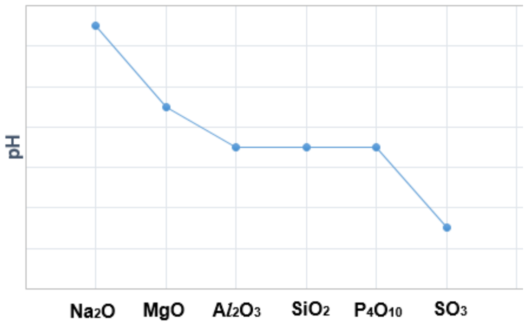
Chart 2 (Electrical Conductivity):
Na, Mg, Al as a group has the highest electrical conductivity.
Silicon is a semi-conductor.
P_4, S_8 and Cl_2 as a group has the lowest electrical conductivity.

Chart 3 (Ionic Radius):
Na^+, Mg^{2+}, Al^{3+} and Si^{4+} as a group has the smallest ionic radii.
P^{3-}, S^{2}− and Cl^- as a group has the lowest electrical conductivity.

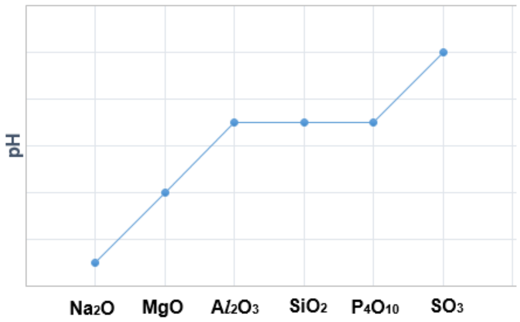
18 The highest oxides of the elements sodium to sulfur are added separately to water.

Which of the following diagrams best represents the pH of the solutions produced?

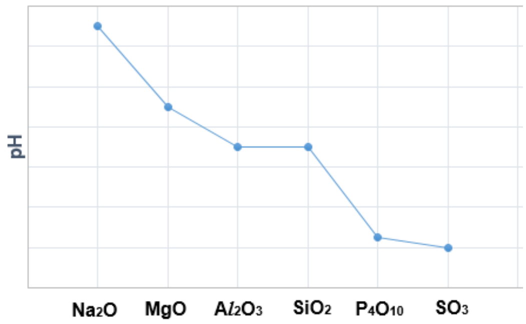
A



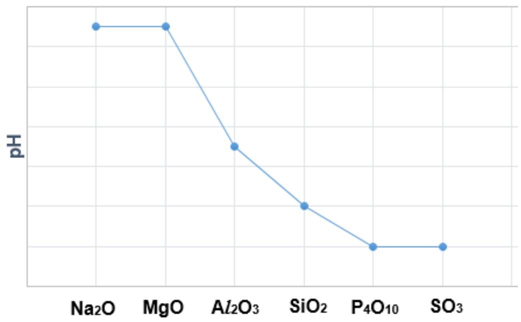
B



✓ **C**



D



Solution

Al_2O_3 and SiO_2 are insoluble in water. Hence water remains at pH = 7.

Na_2O dissolves in water to give alkaline solution of about pH = 13

MgO dissolves slightly in water to give alkaline solution of about pH = 9.

P_4O_{10} and SO_3 dissolve in water to give acidic solution of about pH = 2.

19 Stability constants and colours are given in the following table for this reaction.

$$Fe(H_2O)_6^{3+} + L^- \rightleftharpoons Fe(L)(H_2O)_5^{2+} + H_2O$$

ligand	lg K_{stab}	colour of $Fe(L)(H_2O)_5^{2+}$
SCN^-	2.1	blood red
F^-	5.4	colourless

What would be observed when the following reagents are added to a solution of iron(III) nitrate?

- potassium fluoride
- followed by potassium thiocyanate

A Solution turns from green to colourless, and then blood red.

B Solution turns from green to colourless, and then remains colourless.

C Solution turns from yellow to colourless, and then to blood red.

✓ **D** Solution turns from yellow to colourless, and then remains colourless.

Solution

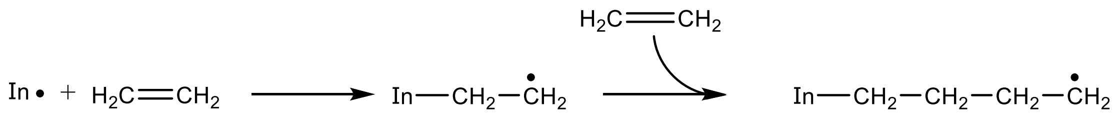
$Fe(H_2O)_6^{3+}$ is yellow; $FeF(H_2O)_5^{2+}$ is colourless.

Since lg K_{stab} = 5.4, F^- is a stronger ligand than H_2O and F^- will replace H_2O ligand to form $FeF(H_2O)_5^{2+}$. Hence yellow solution turns colourless.

$Fe(SCN)(H_2O)_5^{2+}$ is blood red.

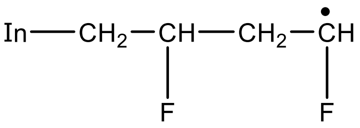
Since Since lg K_{stab} = 2.1 is smaller than lg K_{stab} = 5.4, SCN^- is a weaker ligand than F^-. Hence SCN^- will not replace F^-. Solution remains colourless.

20 Free radical addition is a mechanism used in the synthesis of some addition polymers. Alkene monomers will polymerise in the presence of a radical initiator (In•). For instance, the synthesis of polyethene begins as such.

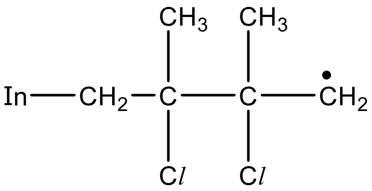


Which of the following chains could **not** have arisen from free radical addition?

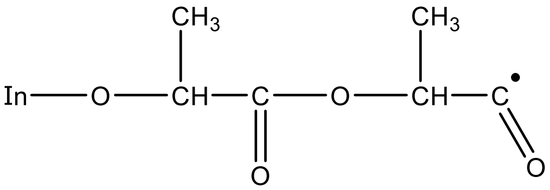
A



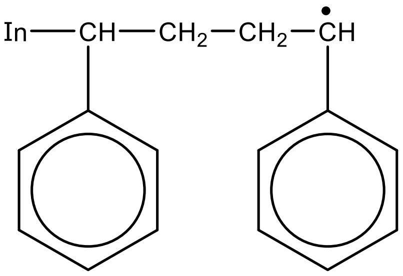
B



✓ **C**



D



Solution

For free radical addition to occur, students must recognise that an alkene is needed as the monomer.

A uses fluoroethene, $H_2C=CHF$

B uses 2-chloropropene, $H_2C=C(CH_3)Cl$

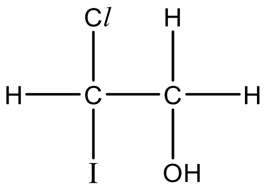
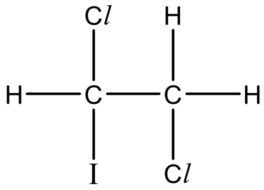
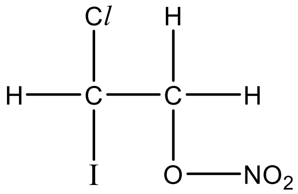
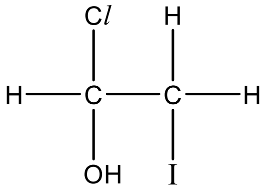
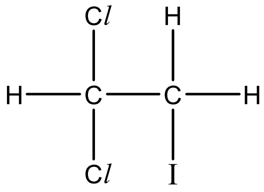
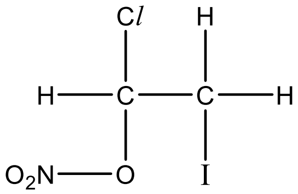
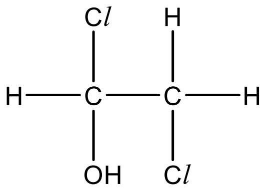
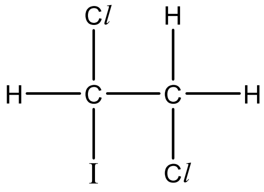
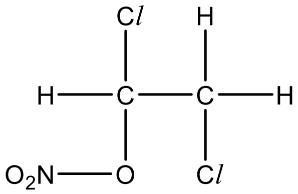
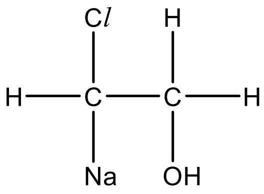
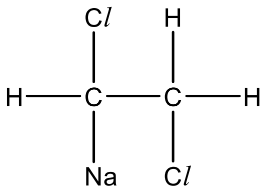
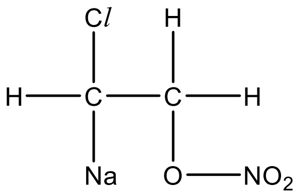
D uses phenylethene, $(C_6H_5)CH=CH_2$

There is no known monomer that can reasonably give rise to the structure in C. More accurately, it should be formed as a condensation polymer of lactic acid, 2-hydroxypropanoic acid.

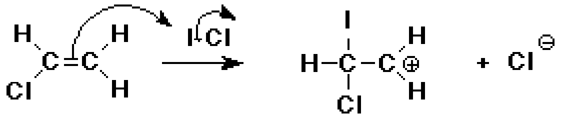
Comment: Fairly well done with approximately 70% of students getting it right.

21 Chloroethene is reacted with iodine monochloride in the presence of aqueous sodium nitrate.

Which are the major and minor products?

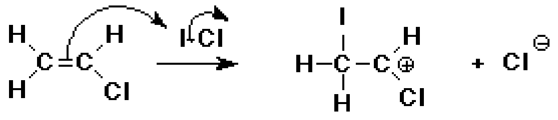
	major product	minor products	
✓ **A**			
B			
C			
D			

Step 1

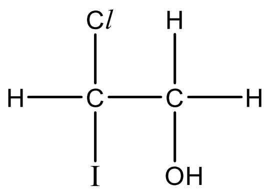


more stable ion

OR

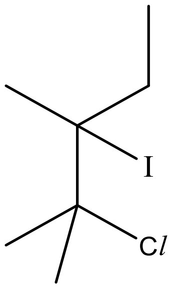


less stable ion



In Step 2, H_2O being the solvent, is present in large amount. H_2O has the highest chance of attacking the more stable ion to give rise to the major product.

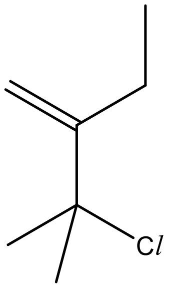
22 The following compound **Y** is reacted with ethanolic sodium hydroxide.



Compound **Y**

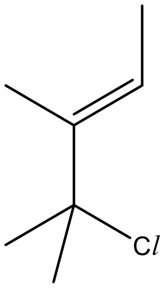
Which of the following is the **major** product?

A

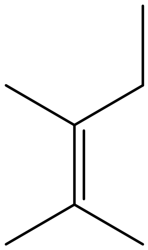


B

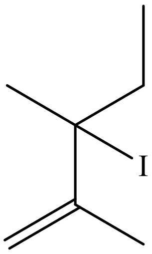
✓



C



D



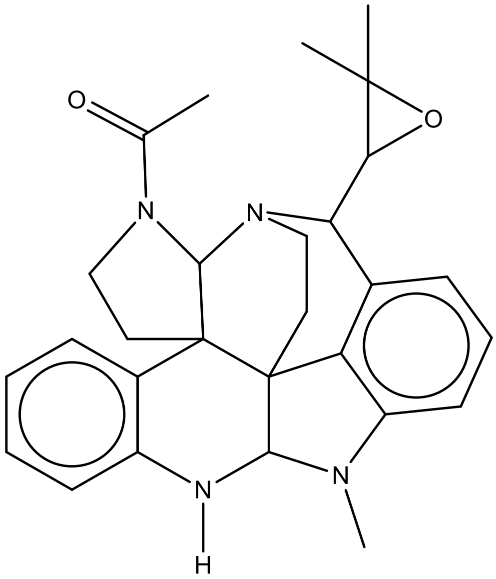
Solution

Elimination takes place when RX is heated with NaOH (in ethanol).

C−I being weaker than C−Cl, will break, forming an alkene.

Zaitsev's Rule says that "more substituted alkene will be the major product". Hence tri-substituted alkene will be the major product, not the di-substituted alkene.

23



Which of the following statements about communesin A is correct?

A Communesin A gives a yellow precipitate when warmed with alkaline iodine solution.

B There are three tertiary amines in communesin A.

C It is a planar molecule.

✓ **D** One of the oxygen atoms is sp^3 hybridised; the other is sp^2 hybridised.

Solution

Option A is deceptive because students will mistake the tertiary amide at the top left hand corner of the molecule as a methyl ketone.

Option B is deceptive because while communesin A indeed contains three amines, only two of them are actually tertiary.

Option C is out because there are many sp^3 hydridised carbon atoms present in the structure of communesin A.

Option D: Do take note that it is possible to talk about the hybridization of terminal (non-central) atoms. The ketone O is sp_2 hybridised and the O involved in the ring is sp^3 hybridised.

24 Compound **B**, $C_6H_{12}O_6$, is an important biomolecule abundant in the brain as it mediates cell signal transduction in response to a variety of hormones and neurotransmitters.

All the atoms (besides the hydrogen atoms) in **B** are sp^3 hybridised.

On adding excess sodium to **B**, hydrogen gas is liberated.

Which of the following statements about compound **B** is true?

A Compound **B** forms a purple colouration with neutral iron(III) chloride solution.

✓ **B** Compound **B** forms a yellow precipitate with warmed alkaline iodine solution.

C Compound **B** forms a bright orange precipitate with 2,4-dinitrophenylhydrazine.

D Compound **B** forms a brick-red precipitate with Fehling's solution.

Solution

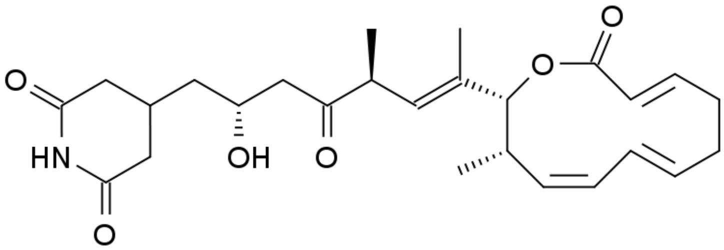
Option A requires a phenol. But no phenol is present in B because "all the atoms (besides the hydrogen atoms) in B are sp^3 hybridised."

Option B requires a methyl ketone or a –CH(CH_3)OH group. It is still possible for B to possess the latter.

Option C requires an aldehyde or ketone. But no such functional groups are present in B because "all the atoms (besides the hydrogen atoms) in B are sp^3 hybridised."

Option D requires an aldehyde. But no aldehyde is present in B because "all the atoms (besides the hydrogen atoms) in B are sp^3 hybridised."

25



Which statements about lactimidomycin are correct?

1 One mole of lactimidomycin reacts completely with four moles of 2,4-dinitrophenylhydrazine.

2 On reacting lactimidomycin with hot acidified $KMnO_4$, there is no gas evolved.

3 On heating lactimidomycin with KOH(aq), there is ammonia gas evolved.

A 1 and 2

B 2 and 3

C 1 only

✓ **D** 3 only

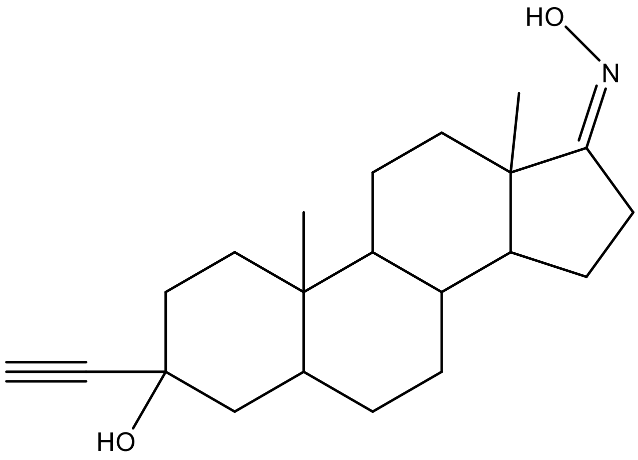
Solution

Statement 1 is deceptive because only one out of the four C=O groups will undergo condensation with 2,4-dinitrophenylhydrazine. Three of these groups are actually ester and amides.

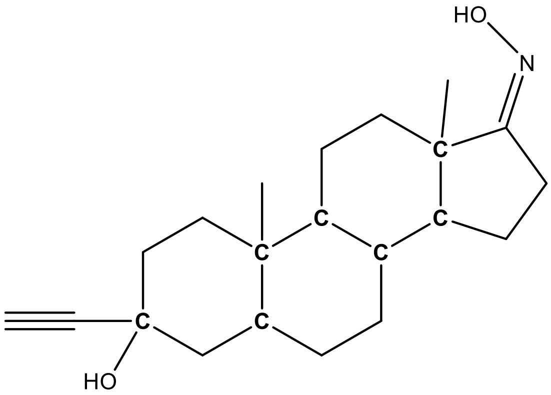
Statement 2 is wrong because carbon dioxide gas will be released; in fact four moles of it per mole of lactimidomycin.

Statement 3 involves alkaline hydrolysis. Indeed ammonia will be released from the "di-amide" (actually it is called imide) on the LHS of the molecule.

26 Golexanolone is a drug currently being studied for the treatment of hypersomnia.



What is the total number of stereoisomers exhibited by golexanolone?

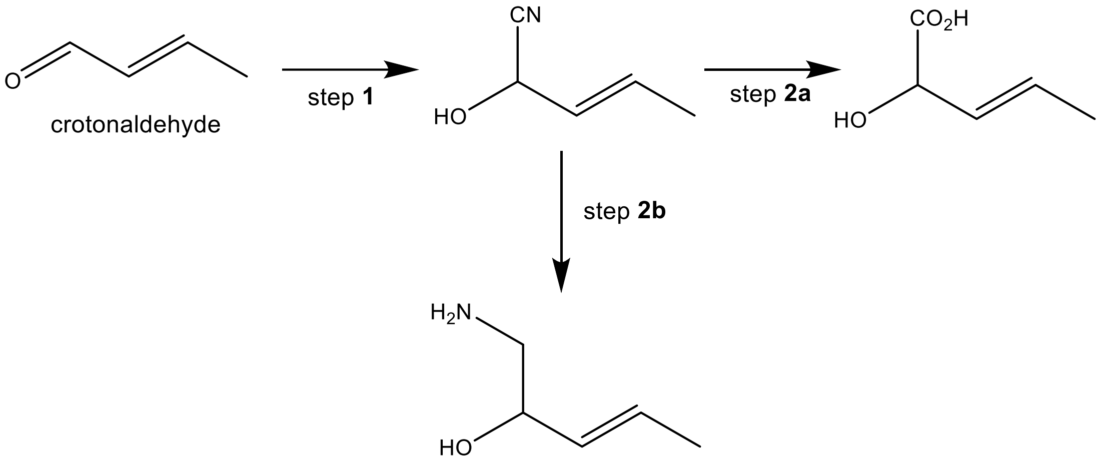


A 512 **B** 256✓ **C** 128 **D** 64

Solution

There are seven chiral carbons – bolded in the above structure. The C=N at the top right hand corner can show cis-trans isomerism. Hence the total number of stereoisomers is 2 raised to the power of 8, which is 256.

27 Crotonaldehyde is an important biomolecule.



Which of the following statements is true about the above synthetic scheme?

✓ **A** The reaction of crotonaldehyde with hot acidified $KMnO_4$ produces only one organic product.

B Step **1** involves heating crotonaldehyde with NaCN in ethanol.

C Step **2a** involves the oxidation of crotonaldehyde because it gained oxygen atoms.

D $NaBH_4$ is the reagent used in step **2b**.

Solution

Option A: Two products are formed – CO_2 (which is NOT organic) and ethanoic acid.

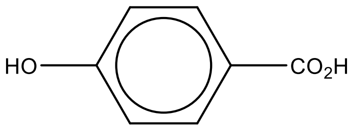
Option B: Step 1 is nucleophilic addition. The reagents and conditions mentioned in this option is for nucleophilic substitution.

Option C: Step 2a is a hydrolysis reaction, not an oxidation reaction.

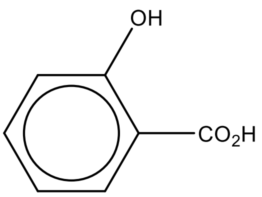
Option D: $LiAlH_4$ can reduce nitriles but $NaBH_4$ is not reducing enough for this purpose.

28 4-hydroxybenzoic acid, 2-hydroxybenzoic acid and 3,4-dihydroxybenzaldehyde share the same molecular formula.

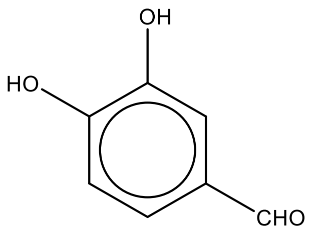
The standard enthalpy changes of formation for 4-hydroxybenzoic acid, 2-hydroxybenzoic acid and 3,4-dihydroxybenzaldehyde are –481 kJ mol^{-1}, –493 kJ mol^{-1} and –392 kJ mol^{-1} respectively.



4-hydroxybenzoic acid



2-hydroxybenzoic acid



3,4-dihydroxybenzaldehyde

Which of the following statements is correct?

1 The thermodynamic stability of these three compounds decrease in the order: 2-hydroxybenzoic acid > 4-hydroxybenzoic acid > 3,4-dihydroxybenzaldehyde

2 3,4-dihydroxybenzaldehyde and 4-hydroxybenzoic acid are positional isomers.

3 The magnitude of the standard enthalpy change of combustion of these three compounds increase in the order: 3,4-dihydroxybenzaldehyde < 4-hydroxybenzoic acid < 2-hydroxybenzoic acid

✓ **A** 1 only

B 2 only

C 1 and 3

D 2 and 3

Solution

Statement 2: They are functional group isomers.

To verify statements 1 and 3, it is best to represent both the enthalpy changes of formation and combustion in the same energy level diagram. With this combined energy level diagram, it is clear that statement 1 is true while statement 3 is false.

29 Chloroethane can be used to make sodium propanoate.

$$\text{chloroethane} \longrightarrow \textbf{Z} \longrightarrow \text{sodium propanoate}$$

The intermediate, **Z**, is treated with boiling aqueous sodium hydroxide to give sodium propanoate.

Which reagent would produce the intermediate, **Z**, from chloroethane?

✓ **A** potassium cyanide in ethanol

B hydrogen cyanide

C sodium hydroxide in ethanol

D alkaline $KMnO_4$

Solution

Recognise that the number of carbon atoms increased by 1 from chloroethane to sodium propanoate – there is a step-up reaction involving cyanide somewhere in the two steps. We seem to need to perform nucleophilic substitution on chloroethane as the first step.

Option B is the reagent for nucleophilic addition on aldehydes and ketones.

Option C is the reagent for elimination; but is there a point in converting chloroethane to ethene in this context?

Option D is the reagent for mild oxidation; but how does chloroethane actually react with it?

30 A polypeptide is subjected to hydrolysis by cyanogen bromide and two digestive enzymes.

- The chemical cyanogen bromide cleaves the peptide bond at the carboxylic end of methionine (met) to give a tetrapeptide and a tripeptide.
- The enzyme chemotrypsin hydrolyses a peptide bond at the carboxylic end of tryptophan (trp) to give two dipeptides and a tripeptide.
- The enzyme trypsin, which hydrolyses a peptide bond at the carboxylic end of lysine (lys) to give 2 tripeptides and gly.

What is the sequence of the amino acids in this polypeptide?

A ser-trp-lys-trp-met-lys-gly

✓ **B** ser-trp-lys-met-trp-lys-gly

C gly-lys-met-trp-lys-trp-ser

D gly-lys-trp-met-lys-trp-ser

Solution

"At the carboxylic end of [some amino acid]" – the RHS end of the mentioned amino acid.

Option A is out because cyanogen bromide cleaves it into a pentapeptide and a dipeptide instead. It is possible that the student think that this is the correct option if he cleaves at the LHS end of methionine.

Option C is out because trypsin does not cleave it to give glycine. In fact, instead of obtaining 2 tripeptides and glycine, we obtain two dipeptides and a tripeptide. Neither does it fit the description under chemotrypsin – there would be a tetrapeptide formed.

Option D is out because chemotrypsin cleaves it into two tripeptides and serine instead. It is possible that the student think that this is the correct option if he cleaves at the LHS end of tryptophan.

1	2	3	4	5	6	7	8	9	10
C	C	B	D	C	C	B	A	A	C
11	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**
B	A	D	A	C	D	D	C	D	C
21	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**29**	**30**
A	B	D	B	D	B	A	A	A	B

Index No.	Name	Form Class	Tutorial Class	Subject Tutor

ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY 9729/02
Higher 2

Paper 2 Structured Questions

26 August 2019
2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, index number, form class, tutorial class and subject tutor's name on all the work you hand in.
Write in dark blue or black pen.
You may use a soft pencil for any diagrams, graphs or rough working.
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 brackets [ ] at the end of each question or part question.

For Examiner's Use	
Question no.	**Marks**
1	**/ 7**
2	**/ 21**
3	**/ 15**
4	**/ 7**
5	**/ 11**
6	**/ 14**
TOTAL	**/ 75**

This document consists of **22** printed pages.

1 **(a)** The element aluminium and its compounds have some properties characteristic of metals, and some of non-metals. Aluminium hydroxide, for example, is known to be *amphoteric*.

(i) Explain the meaning of the word “amphoteric”. [1]

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Aluminium sulfate and calcium oxide are sometimes added to water supplies to co-precipitate suspended solids and bacteria. A small amount of aluminium-containing ions remains in solution and its presence in drinking water may contribute to the mental illness known as Alzheimer’s disease.

(ii) Write a balanced equation for the reaction that occurs when aluminium sulfate and calcium oxide are added to water, given that aluminium hydroxide is one of the products formed. [1]

………………………………………………………………………………

(iii) By considering the nature of calcium oxide, explain why adding too much of it would increase the risk of contracting Alzheimer’s disease.

Write an equation to illustrate how “aluminium-containing ions remains in (drinking water)” as a result of adding too much calcium oxide. [2]

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1 **(b)** Beryllium oxide (BeO) is amphoteric, just like A*l*(OH)$_3$.

(i) Beryllium oxide reacts with sodium hydroxide according to the equation,

$$2NaOH + BeO \longrightarrow Na_2BeO_2 + H_2O$$

Given the position of beryllium in the Periodic Table, explain how this reaction illustrates the amphoteric nature of beryllium oxide. [2]

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(ii) To further illustrate its amphoteric nature, at 500 °C, BeO reacts with Na_2O to form compound **F** as the **sole product**. The molar masses of all three compounds are tabulated below.

compound	**molar mass / g mol^{-1}**
BeO	25
Na_2O	62
F	149

Write a balanced equation of the above reaction. [1]

………………………………………………………………………………………

[Total: 7]

2 **(a)** In the laboratory, there are three bottles labelled **X**, **Y** and **Z**. Each bottle contains one of the following reagents:

KI(aq), Cl_2(aq), and NaBr(aq)

Three tests were carried out using the reagents in the bottles. The results are summarised in the table below:

test	procedure	observations
1	mix reagent in bottle **X** with reagent in bottle **Z**	no change in colour
2	mix reagent in bottle **Y** with reagent in bottle **Z**	mixture turns brown
3	mix reagent in bottle **Y** with reagent in bottle **X**	mixture turns reddish-brown

(i) By comparing relevant standard reduction potential values from the *Data Booklet*, explain how it can be deduced that **Y** is aqueous chlorine. There is **no** need for calculations. [1]

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(ii) Tests 2 and 3 were executed to determine the reagents in bottles **X** and **Z**.

Hexane was added to the resulting reaction mixture after the tests were conducted. The bottles were then shaken and allowed to stand.

State the observations that will indicate whether the bottles contained KI(aq) or NaBr(aq) initially. [2]

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2 **(b)** Sulfur dichloride, SCl_2, is a cherry-red liquid at room temperature and pressure.

SCl_2 is formed from S_8 and Cl_2.

(i) Explain why S_8 exists as a solid while Cl_2 exists as a gas at room temperature. [2]

....

....

....

....

(ii) The formation of SCl_2 from S_8 and Cl_2 takes place in two steps.

The first step involves disulfur dichloride, S_2Cl_2, as an intermediate.

$$S_8 + 4Cl_2 \rightarrow 4S_2Cl_2$$

Write the equation of the second step. [1]

....

Some chemists speculate that the intermediate is not disulfur dichloride but **K**.
K shares the same elemental mass percentages as sulfur dichloride and has a molar mass of 206.2 g mol^{-1}.

(iii) State the molecular formula of **K**. [1]

....

(iv) All the chlorine atoms in **K** are terminal.
There are only two central atoms in **K**.
The bond angles about each central atom are different.

State the shape around each central atom and the respective bond angles. [2]

....

....

2 **(c)** Sulfuryl chloride, SO_2Cl_2, is commonly confused with thionyl chloride, $SOCl_2$.

The properties of these two sulfur oxychlorides are quite different. SO_2Cl_2 is a source of chlorine while $SOCl_2$ is a source of chloride ions for various organic reactions.

When heated, sulfuryl chloride decomposes endothermically as follows:

$$SO_2Cl_2\,(g) \rightleftharpoons SO_2\,(g) + Cl_2\,(g)$$

In an experiment, 1.00 mol of SO_2Cl_2 vapour was heated in a closed 4.00 dm^3 flask at 500 K until equilibrium was established. The flask was then rapidly cooled to liquefy SO_2Cl_2.

After removing gaseous SO_2 and Cl_2, excess water was then carefully added to the liquid SO_2Cl_2, causing the following reaction to occur.

$$SO_2Cl_2\,(l) + 2H_2O\,(l) \rightarrow H_2SO_4\,(aq) + 2HCl\,(aq)$$

The resulting solution was made up to 250 cm^3 in a standard graduated flask.

20.0 cm^3 of this solution was titrated with 1.00 mol dm^{-3} NaOH. 40.00 cm^3 of NaOH was required for complete neutralisation.

(i) Write an expression for K_c for the equilibrium above and state its units. [2]

(ii) Calculate the equilibrium amount of SO_2Cl_2, SO_2, and Cl_2 in the original equilibrium at 500 K. Hence calculate a value for the K_c for the equilibrium. [4]

2 **(c)** **(iii)** A student suggested to carry out the decomposition process at a higher temperature and high pressure to decrease the time required for the process. Discuss the effects of the proposed changes on the rate and the yield. [2]

………………………………………………………………………………………

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2 **(d)** SO_2Cl_2 is widely used as a reagent in chlorination of the hydrocarbons. Such reactions occur under free radical conditions using H_2O_2 as an initiator.

For example, methylbenzene undergoes free radical substitution with SO_2Cl_2 to give benzyl chloride, $C_6H_5CH_2Cl$.

The mechanism of this reaction involves three stages:
I. Initiation
II. Propagation
III. Termination

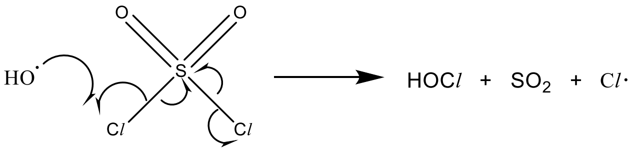
- The **initiation** stage is unique as it involves two successive steps.

(i) In the first step, there is an initial homolytic breaking of the peroxide bond in hydrogen peroxide forming two hydroxyl radicals.

Using curly arrows, show the mechanism for this step.

[1]

The second initiation step involves the reaction between the hydroxyl radical and SO_2Cl_2 to give SO_2, $HOCl$ and a chlorine radical. It has been drawn for you below.



After these two initiation steps,

- The chlorine radical then reacts with methylbenzene in two **propagation** steps to form benzyl chloride and regenerating the hydroxyl radicals.
- The chain reaction **terminates** when two radicals combine to give stable compounds.

2 **(d)** **(ii)** Complete the mechanism by writing the steps for the **propagation** and **termination** stages.

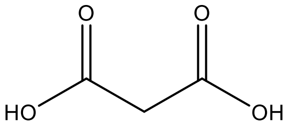
[3]

Propagation

Termination

[Total: 21]

3 Malonic acid is an important precursor to some polyesters.



(a) Malonic acid can be synthesised in more than one way.

(i) Suggest a three-step synthetic route from ethene to malonic acid. [5]

(ii) Malonic acid can be made by reacting two moles of **L** with a mole of carbon suboxide.

[1]

$O{=}C{=}C{=}C{=}O$

carbon suboxide

Identify **L**.

……………………………………………………………………………………

3 **(b)** Malonic acid behaves as a diprotic acid. The values of its K_{a1} and K_{a2} are 1.51×10^{-3} mol dm^{-3} and 2.00×10^{-6} mol dm^{-3} respectively.

In an experiment, 15.0 cm^3 of a 0.100 mol dm^{-3} solution of malonic acid was titrated against 0.100 mol dm^{-3} NaOH.

(i) Calculate the initial pH. [1]

(ii) Calculate the volume of NaOH required for the first equivalence point. [1]

(iii) Write an equation to explain why the second equivalence point is above 7. [1]

……………………………………………………………………………………

(iv) Calculate the second equivalence pH. [2]

A buffer is obtained after the addition of 12.00 cm^3 of NaOH solution.

3 **(b)** **(v)** Write an equation for the reaction that occurs when a drop of HNO_3 is added to this buffer. [1]

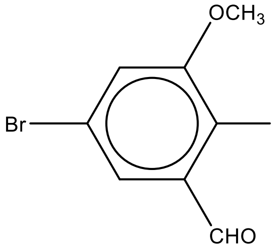
…………………………………………………………………………………

(vi) Calculate the pH of this buffer. [2]

(vii) Another buffer is obtained after the addition of 22.50 cm^3 of NaOH solution. Calculate its pH. [1]

[Total: 15]

4 **V** is a mono-brominated derivative of *ortho*-vanillin. *Ortho*-vanillins are used in the study of mutagenesis and as a synthetic precursor for pharmaceuticals.



V

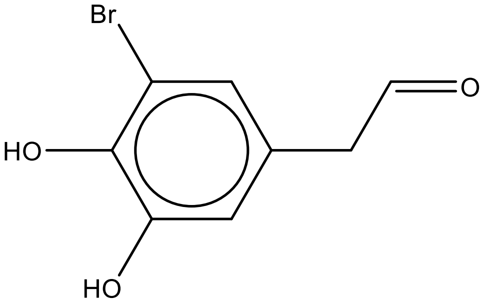
(a) Define the term "constitutional isomerism".

[1]

……………………………………………………………………………………

……………………………………………………………………………………

(b) **U** is a constitutional isomer of **V**.



U

State a simple chemical test to distinguish between **U** and **V**. State the observations.

[2]

……………………………………………………………………………………

……………………………………………………………………………………

The structures you draw from 4(c) to 4(e) must contain one benzene ring.

4 **(c)** Draw the structural formula of a constitutional isomer of **V** which can be distinguished from **V** itself by cold $AgNO_3$ solution. State the observations. [2]

(d) Draw the structural formula of a constitutional isomer of **V** which can be distinguished from **V** itself by warm alkaline iodine. [1]

(e) Draw the structural formula of a constitutional isomer of **V** which can be distinguished from **V** itself via 2,4-dinitrophenylhydrazine but not neutral iron(III) chloride solution nor sodium metal. [1]

[Total: 7]

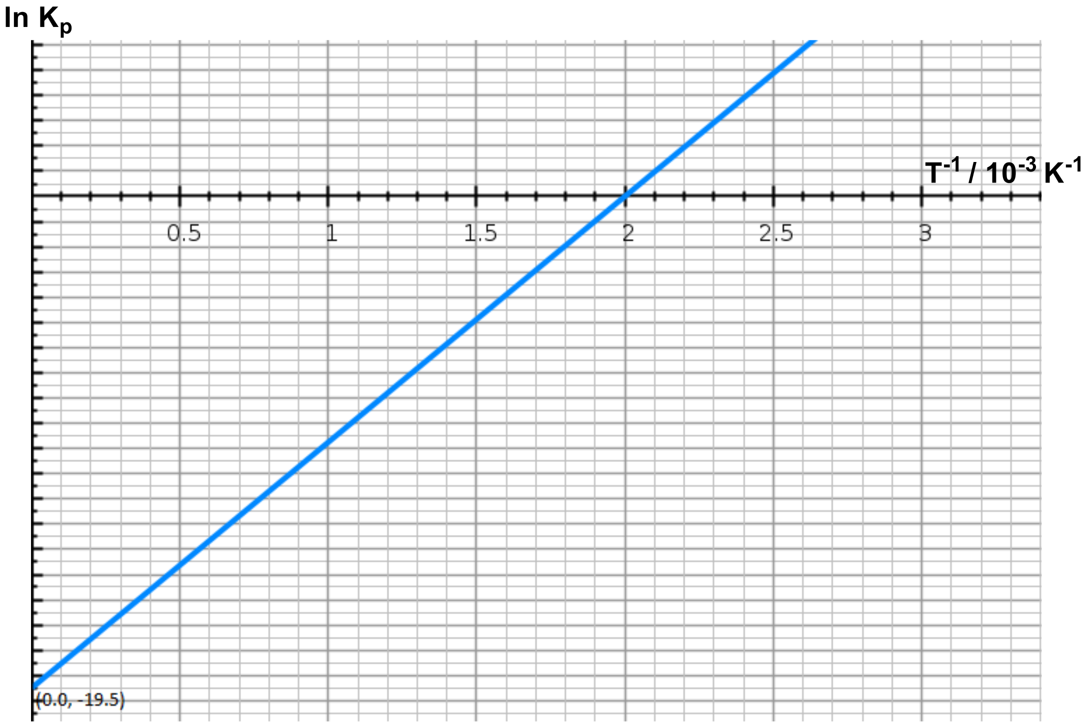
5 Space-suits need to be designed in such a way to supply oxygen to astronauts and to remove the carbon dioxide exhaled by them.

(a) Metal oxides like silver oxide, Ag_2O, are used to get rid of the carbon dioxide.

Ag_2O reacts reversibly with carbon dioxide, as described in the equilibrium equation,

$$Ag_2O\ (s) + CO_2\ (g) \rightleftharpoons Ag_2CO_3\ (s)$$

The van't Hoff plot shows how the equilibrium constant, K_p, of this reaction varies with temperature.



(i) From the above graph, deduce the relationship between K_p and T. [1]

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……………………………………………………………………………………

(ii) Hence, explain whether the reaction between silver oxide and carbon dioxide is exothermic or endothermic. [2]

……………………………………………………………………………………

……………………………………………………………………………………

5 **(a)** **(iii)** Given that the straight line graph for ln K_p versus T^{-1} is described by the equation

$$\ln K_\mathrm{p} = \left(\frac{-\Delta \mathrm{H}^0}{\mathrm{R}}\right)\frac{1}{\mathrm{T}} + \frac{\Delta S^0}{\mathrm{R}}$$

Calculate the standard entropy change of this reaction and explain the significance of its sign with respect to the reaction. [2]

After absorbing carbon dioxide for some time, most if not all of the silver oxide would have been depleted. To **recharge** the system, heat is applied into the system to form Ag_2O again.

(iv) ΔG^0 and K_p are mathematically related by the equation

$$\Delta G^0 = -RT \ln K_p$$

Using the graph, estimate the minimum temperature at which the **recharging** of this system becomes spontaneous. [1]

5 **(b)** Silver carbonate (relative formula mass = 275.8) is a sparingly soluble salt. At 25 ^{o}C, its solubility is 0.032 g dm^{-3} of water.

(i) Show that the value of the K_{sp} of silver carbonate at 25 ^{o}C is 6.25×10^{-12}. [1]

(ii) Calculate the solubility of silver carbonate in 0.100 mol dm^{-3} silver nitrate at 25 ^{o}C. [1]

(iii) 1.00 cm^3 of a 1.20×10^{-5} mol dm^{-3} silver nitrate solution was mixed with 3.00 cm^3 of a 7.45×10^{-5} mol dm^{-3} sodium carbonate solution.

Determine whether there would be precipitation of silver carbonate. [2]

5 **(c)** Silver carbonate can be reacted with ammonia to form silver fulminate, AgCNO, a powerful primary explosive.

$$4\ Ag_2CO_3 + 4\ NH_3 \rightarrow 4\ AgCNO + 6\ H_2O + 4\ Ag + O_2$$

Draw the dot-and-cross diagram of the fulminate ion given that the N is the central atom and the negative charge is on the carbon.

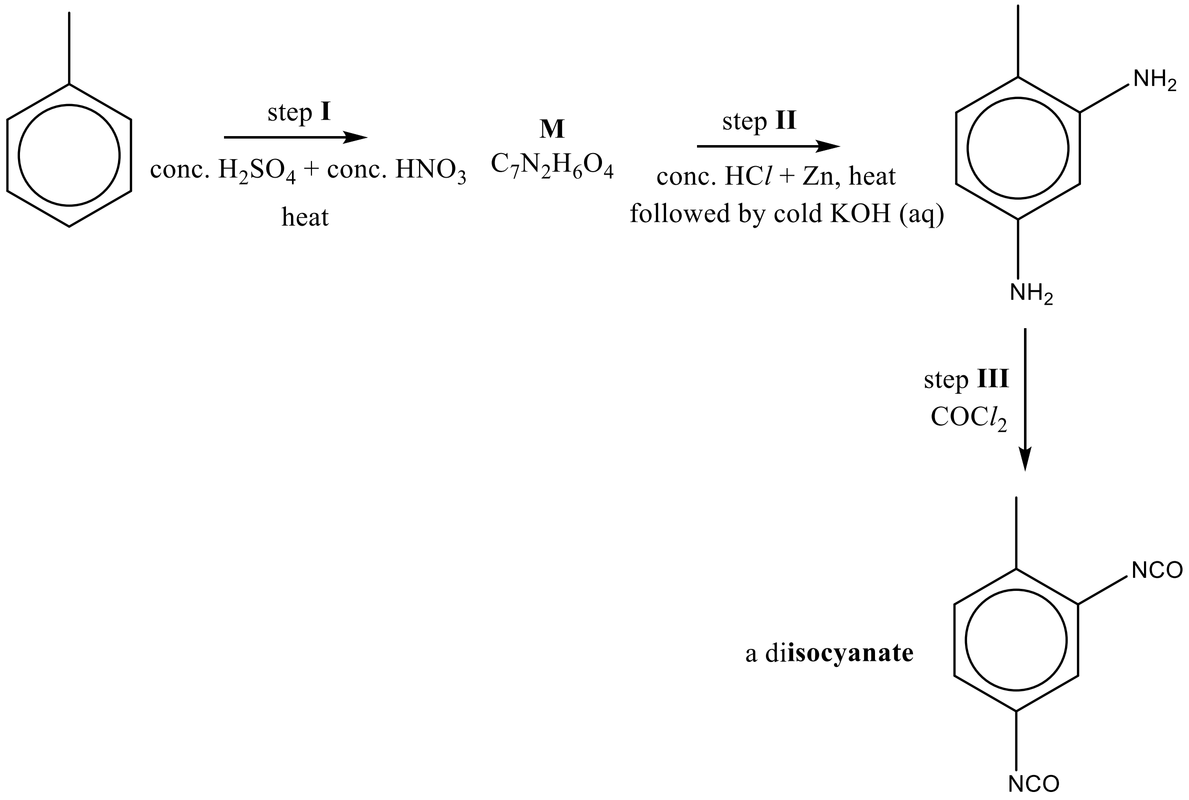
[1]

[Total: 11]

6 The isocyanate functional group is a constitutional isomer of the fulminate, which was mentioned in question **5(c)**. The isocyanate has the carbon atom instead of nitrogen atom as the central atom.

Isocyanates are important industrial chemicals; they react with alcohols to produce polyurethane polymers, which are components of polyurethane foams, thermoplastic elastomers and polyurethane paints.

(a) This part is about the synthesis of a diisocyanate from methylbenzene.



(i) State the type of reaction in step **I**. [1]

……………………………………………………………………………………

(ii) Draw the structure of **M**. [1]

6 **(a)** **(iii)** Draw the structure of the isomer of **M** which is formed as a side-product in step **I**. [1]

(iv) Explain the purpose of KOH in step **II**. [1]

………………………………………………………………………………………

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(v) Write a balanced equation for the overall reaction in step **II**. You are to use [H] to balance the equation. [1]

(vi) State the type of reaction in step **III**. [1]

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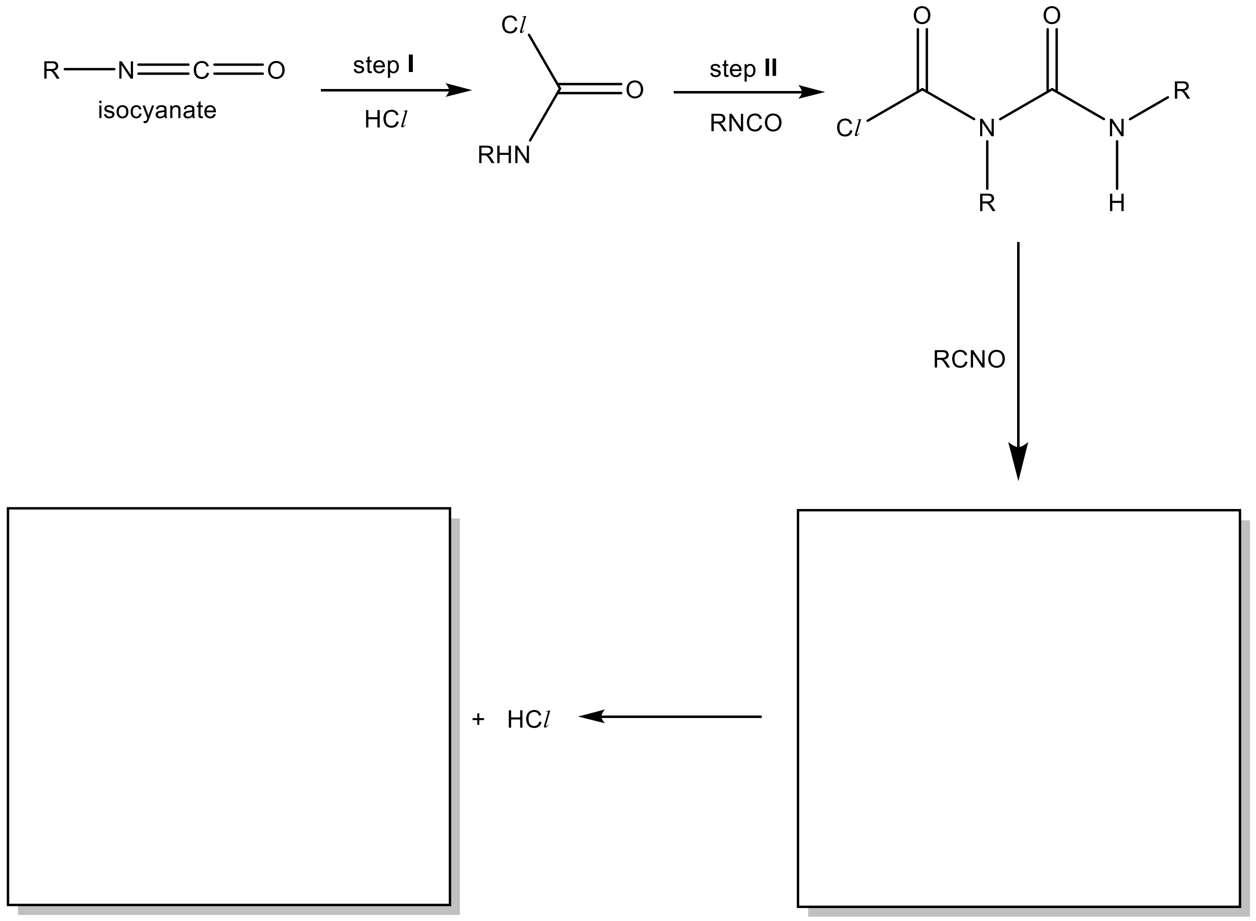
6 **(b)** Examine the synthetic route below.



cyclic trimer **T**
$R_3C_3N_3O_3$

Q
$R_3C_3N_3O_3HCl$

(i) Draw the skeletal formulae of **Q** and the cyclic trimer **T** in the boxes provided. [2]

(ii) Step **I** is an electrophilic addition reaction. Draw the mechanism of step **I**. [3]

6 **(c)** When heated with HC*l* (aq), organic isocyanates (RNCO) are hydrolysed to the amine salt ($RNH_3^+Cl^-$) and carbon dioxide.

$$RNCO + HCl + H_2O \rightarrow RNH_3^+Cl^- + CO_2$$

A 1.13 g sample of an organic isocyanate was treated in this way, and the carbon dioxide produced was absorbed in an excess of aqueous $Ba(OH)_2$, according to the equation shown.

$$Ba(OH)_2\,(aq) + CO_2\,(g) \longrightarrow H_2O\,(l) + BaCO_3\,(s)$$

The mixture was filtered and the residue $BaCO_3$ washed and dried thoroughly. The mass of the residue was 1.97 g.

(i) Show that the molecular mass of the organic isocyanate is 113 g mol^{-1}. [1]

(ii) The R group in RNCO and $RNH_3^+Cl^-$ contains only carbon and hydrogen.

Use the molecular mass mentioned in **(i)** to suggest the molecular formula of the organic isocyanate. [1]

(iii) Given that a pure sample of this organic isocyanate rotates plane-polarised light, draw a possible stereochemical formula of it. [1]

[Total: 14]

~ End of Paper ~

Index No.	Name	Form Class	Tutorial Class	Subject Tutor

ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY 9729/02
Higher 2

Paper 2 Structured Questions **26 August 2019**
2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, index number, form class, tutorial class and subject tutor’s name on all the work you hand in.
Write in dark blue or black pen.
You may use a soft pencil for any diagrams, graphs or rough working.
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 brackets [ ] at the end of each question or part question.

For Examiner's Use	
Question no.	**Marks**
1	**/ 7**
2	**/ 21**
3	**/ 15**
4	**/ 7**
5	**/ 11**
6	**/ 14**
TOTAL	**/ 75**

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

1	**(a)**	The element aluminium and its compounds have some properties characteristic of metals, and some of non-metals. Aluminium hydroxide, for example, is known to be *amphoteric*.	
		(i)	Explain the meaning of the word “amphoteric”. [1]
			The ability to react with both acids and bases.
		Aluminium sulfate and calcium oxide are sometimes added to water supplies to co-precipitate suspended solids and bacteria. A small amount of aluminium-containing ions remains in solution and its presence in drinking water may contribute to the mental illness known as Alzheimer’s disease.	
		(ii)	Write a balanced equation for the reaction that occurs when aluminium sulfate and calcium oxide are added to water, given that aluminium hydroxide is one of the products formed. [1]
			$Al_2(SO_4)_3 + 3CaO + 3H_2O \rightarrow 2Al(OH)_3 + 3CaSO_4$
		(iii)	By considering the nature of calcium oxide, explain why adding too much of it would increase the risk of contracting Alzheimer’s disease. Write an equation to illustrate how “aluminium-containing ions remains in (drinking water)” as a result of adding too much calcium oxide. [2]
			CaO dissolves slightly to form an alkaline solution. OH^- thus formed reacts with $Al(OH)_3$ to form a soluble complex. $Al(OH)_3 + OH^- \rightarrow Al(OH)_4^-$
1	**(b)**	Beryllium oxide (BeO) is amphoteric, just like $Al(OH)_3$.	
		(i)	Beryllium oxide reacts with sodium hydroxide according to the equation, $2NaOH + BeO \longrightarrow Na_2BeO_2 + H_2O$ Given the position of beryllium in the Periodic Table, explain how this reaction illustrates the amphoteric nature of beryllium oxide. [2] BeO: Gp 2 (**metallic**) oxide, expected to form basic oxide and to react with acid. but here it is reacting with an alkali, illustrating its acidic nature.

(ii) To further illustrate its amphoteric nature, at 500 °C, BeO reacts with Na_2O to form compound **F** as the **sole product**. The molar masses of all three compounds are tabulated below.

compound	molar mass / g mol^{-1}
BeO	25
Na_2O	62
F	149

Write a balanced equation of the above reaction. [1]

$BeO + 2Na_2O \rightarrow Na_4BeO_3$

[Total: 7]

2 **(a)** In the laboratory, there are three bottles labelled **X**, **Y** and **Z**. Each bottle contains one of the following reagents:

KI(aq), Cl_2(aq), and NaBr(aq)

Three tests were carried out using the reagents in the bottles. The results are summarised in the table below:

test	procedure	observations
1	mix reagent in bottle **X** with reagent in bottle **Z**	no change in colour
2	mix reagent in bottle **Y** with reagent in bottle **Z**	mixture turns brown
3	mix reagent in bottle **Y** with reagent in bottle **X**	mixture turns reddish-brown

(i) By comparing relevant standard reduction potential values from the Data Booklet, explain how it can be deduced that **Y** is aqueous chlorine. There is **no** need for calculations. [1]

Chlorine has the most positive standard reduction potential (compared to that of bromine and iodine) hence it is able to oxidise both iodide and bromide.

		(ii)	Tests 2 and 3 were executed to determine the reagents in bottles **X** and **Z**. Hexane was added to the resulting reaction mixture after the tests were conducted. The bottles were then shaken and allowed to stand. State the observations that will indicate whether the bottles contained KI(aq) or NaBr(aq) initially. [2] The bottle with orange-red organic layer contains NaBr (aq) initially. The bottle with violet / purple organic layer contains KI (aq) initially.
2	**(b)**	Sulfur dichloride, SCl_2, is a cherry-red liquid at room temperature and pressure. SCl_2 is formed from S_8 and Cl_2.	
		(i)	Explain why S_8 exists as a solid while Cl_2 exists as a gas at room temperature. [2] Both exist as non-polar simple covalent molecules. The size of the electron cloud of sulfur is so much larger hence the idid interactions amongst sulfur molecules are stronger than the idid amongst chlorine molecules. Therefore the melting point of sulfur is significantly higher than that of chlorine.
		(ii)	The formation of SCl_2 from S_8 and Cl_2 takes place in two steps. The first step involves disulfur dichloride, S_2Cl_2, as an intermediate. $S_8 + 4Cl_2 \rightarrow 4S_2Cl_2$ Write the equation of the second step. [1] $S_2Cl_2 + Cl_2 \rightarrow 2SCl_2$
		Some chemists speculate that the intermediate is not disulfur dichloride but **K**. **K** shares the same elemental mass percentages as sulfur dichloride and has a molar mass of 206.2 g mol^{-1}.	
		(iii)	State the molecular formula of **K**. [1] S_2Cl_4
		(iv)	All the chlorine atoms in **K** are terminal. There are only two central atoms in **K**. The bond angles about each central atom are different. State the shape around each central atom and the respective bond angles. [2] See-saw (90^0 and/or 120^o). (88^0 and/or 118^0) and bent (105^0 or 104.5^0)

2 **(c)** Sulfuryl chloride, SO_2Cl_2, is commonly confused with thionyl chloride, $SOCl_2$.

The properties of these two sulfur oxychlorides are quite different. SO_2Cl_2 is a source of chlorine while $SOCl_2$ is a source of chloride ions for various organic reactions.

When heated, sulfuryl chloride decomposes endothermically as follows:

$$SO_2Cl_2\,(g) \rightleftharpoons SO_2\,(g) + Cl_2\,(g)$$

In an experiment, 1.00 mol of SO_2Cl_2 vapour was heated in a closed 4.00 dm^3 flask at 500 K until equilibrium was established. The flask was then rapidly cooled to liquefy SO_2Cl_2.

After removing gaseous SO_2 and Cl_2, excess water was then carefully added to the liquid SO_2Cl_2, causing the following reaction to occur.

$$SO_2Cl_2\,(l) + 2H_2O\,(l) \rightarrow H_2SO_4\,(aq) + 2HCl\,(aq)$$

The resulting solution was made up to 250 cm^3 in a standard graduated flask.

20.0 cm^3 of this solution was titrated with 1.00 mol dm^{-3} NaOH. 40.00 cm^3 of NaOH was required for complete neutralisation.

(i) Write an expression for K_c for the equilibrium above and state its units. [2]

$K_c = [SO_2][Cl_2] / [SO_2Cl_2]$

mol dm^{-3}

(ii) Calculate the equilibrium amount of SO_2Cl_2, SO_2, and Cl_2 in the original equilibrium at 500 K. Hence calculate a value for the K_c for the equilibrium. [4]

$n(H_2SO_4) = \frac{1}{4}\,(40.00/1000)(250/20.0) = 0.125$
$n(SO_2Cl_2)$ at eqm = 0.125
$n(SO_2)$ and $n(Cl_2)$ at eqm are 1.00 – 0.125 = 0.875 each
$K_c = (0.875)^2 / (0.125 \times 4) = 1.53$ mol dm^{-3}

2 **(c)** **(iii)** A student suggested to carry out the decomposition process at a higher temperature and high pressure to decrease the time required for the process. Discuss the effects of the proposed changes on the rate and the yield. [2]

At a higher temperature, both rate and yield would increase.

However, at high pressures, the rate (but not the yield) would increase as the position of equilibrium will be shifted to the LHS

2 **(d)** SO_2Cl_2 is widely used as a reagent in chlorination of the hydrocarbons. Such reactions occur under free radical conditions using H_2O_2 as an initiator.

For example, methylbenzene undergoes free radical substitution with SO_2Cl_2 to give benzyl chloride, $C_6H_5CH_2Cl$.

The mechanism of this reaction involves three stages:

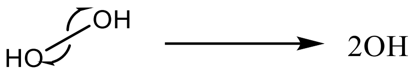
I. Initiation
II. Propagation
III. Termination

- The **initiation** stage is unique as it involves two successive steps.

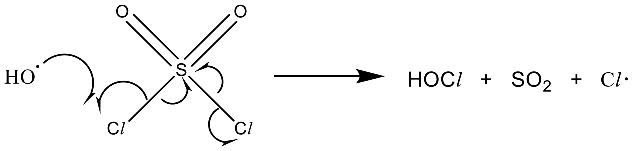
(i) In the first step, there is an initial homolytic breaking of the peroxide bond in hydrogen peroxide forming two hydroxyl radicals.

Using curly arrows, show the mechanism for this step.

[1]



The second initiation step involves the reaction between the hydroxyl radical and SO_2Cl_2 to give SO_2, $HOCl$ and a chlorine radical. It has been drawn for you below.



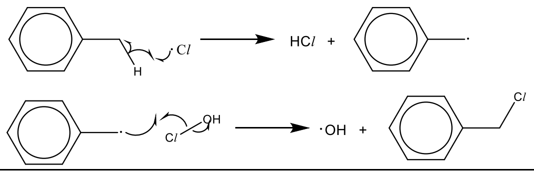
After these two initiation steps,

- The chlorine radical then reacts with methylbenzene in two **propagation** steps to form benzyl chloride and regenerating the hydroxyl radicals.
- The chain reaction **terminates** when two radicals combine to give stable compounds.

(ii) Complete the mechanism by writing the steps for the **propagation** and **termination** stages.

[3]

Propagation



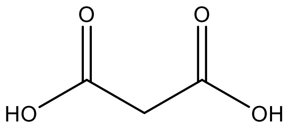
Termination

2OH → H_2O_2

HO + Cl → HOCl

[Total: 21]

3 Malonic acid is an important precursor to some polyesters.



(a) Malonic acid can be synthesised in more than one way.

(i) Suggest a three-step synthetic route from ethene to malonic acid. [5]

1) aqueous bromine
2) KCN (ethanolic) heat
3) acidified $KMnO_4$ (or $K_2Cr_2O_7$), heat with reflux

Intermediates: 2-bromoethanol; 3-hydroxypropanenitrile.

(ii) Malonic acid can be made by reacting two moles of **L** with a mole of carbon suboxide. [1]

$$O=C=C=C=O$$

carbon suboxide

Identify **L**.

H_2O

(b) Malonic acid behaves as a diprotic acid. The values of its K_{a1} and K_{a2} are 1.51×10^{-3} mol dm^{-3} and 2.00×10^{-6} mol dm^{-3} respectively.

In an experiment, 15.0 cm^3 of a 0.100 mol dm^{-3} solution of malonic acid was titrated against 0.100 mol dm^{-3} NaOH.

(i) Calculate the initial pH. [1]

pH = - log (1.51×10^{-2}) = 1.91

(ii) Calculate the volume of NaOH required for the first equivalence point. [1]

15.0 times 0.100 / 0.100 = 15.00 cm^3

(iii) Write an equation to explain why the second equivalence point is above 7. [1]

$$^{-}O_2CCH_2CO_2^{-} + H_2O \rightleftharpoons HO_2CCH_2CO_2^{-} + HO^{-}$$

(iv) Calculate the second equivalence pH. [2]

2nd equivalence volume = 30.0 cm^3
$[^{-}OOCCH_2COO^{-}]$ at 2nd equivalence point = 15/(30+15) X 0.100
= 0.0333 mol dm^{-3}

$K_b = 10^{-14} / K_{a2} = 5.00 \times 10^{-9}$ mol dm^{-3}
pOH = - ½ log ($5.00 \times 10^{-9} \times 0.0333$) = 4.89
pH = 14 – pOH = 9.11

3 **(b)** A buffer is obtained after the addition of 12.00 cm^3 of NaOH solution.

(v) Write an equation for the reaction that occurs when a drop of HNO_3 is added to this buffer. [1]

$$HO_2CCH_2CO_2^- + H^+ \rightarrow HO_2CCH_2CO_2H$$

(vi) Calculate the pH of this buffer. [2]

n(malonic acid) remaining = [(15.0)(0.100)-(12.00)(0.100)] / 1000
= 3.00 X 10^{-4}

n($HO_2CCH_2CO_2^-$) = (12.00)(0.100) / 1000
= 1.20 X 10^{-3}

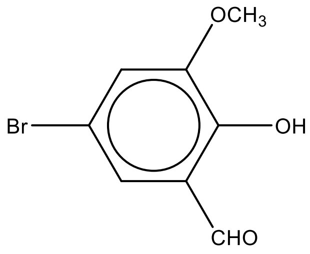
$pH = -\log(1.51 \times 10^{-3}) + \log(12.0/3.00) = 3 + \log(4/1.51) = 3.42$

(vii) Another buffer is obtained after the addition of 22.50 cm^3 of NaOH solution. Calculate its pH. [1]

$pH = pK_{a2} = -\log(2.00 \times 10^{-6}) = 6 - \lg 2.00 = 5.70$

[Total: 15]

4 **V** is a mono-brominated derivative of *ortho*-vanillin. *Ortho*-vanillins are used in the study of mutagenesis and as a synthetic precursor for pharmaceuticals.

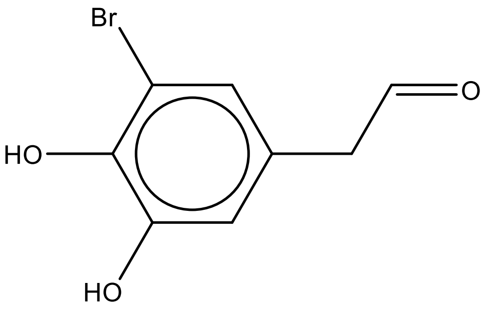


V

(a) Define the term "constitutional isomerism". [1]

Compounds having the same molecular formula but different structural formulae/different structures.

(b) **U** is a constitutional isomer of **V**.



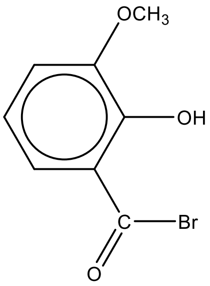
U

State a simple chemical test to distinguish between **U** and **V**. State the observations. [2]

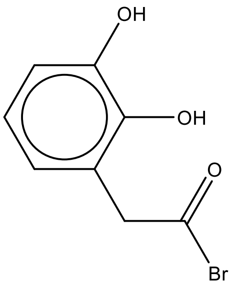
Fehling’s test.
No ppt for V. brick-red/brown/reddish-brown ppt for U.

The structures you draw from 4(c) to 4(e) must contain one benzene ring.

(c) Draw the structural formula of a constitutional isomer of **V** which can be distinguished from **V** itself by cold $AgNO_3$ solution. State the observations. [2]



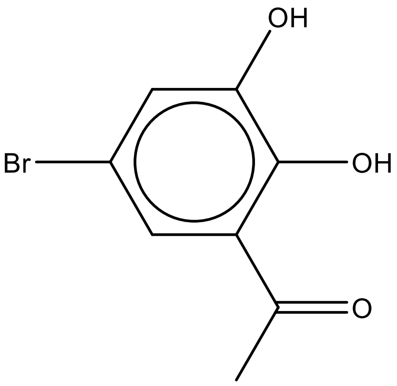
or

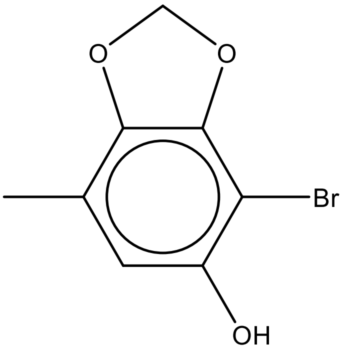


No ppt for X.
Cream/off-white ppt for this constitutional isomer.

The structures you draw from 4(c) to 4(e) must contain one benzene ring.

4 **(d)** Draw the structural formula of a constitutional isomer of **V** which can be distinguished from **V** itself by warm alkaline iodine. [1]



	(e)	Draw the structural formula of a constitutional isomer of **V** which can be distinguished from **V** itself via 2,4-dinitrophenylhydrazine but not neutral iron(III) chloride solution not sodium metal. [1] 
		[Total: 7]

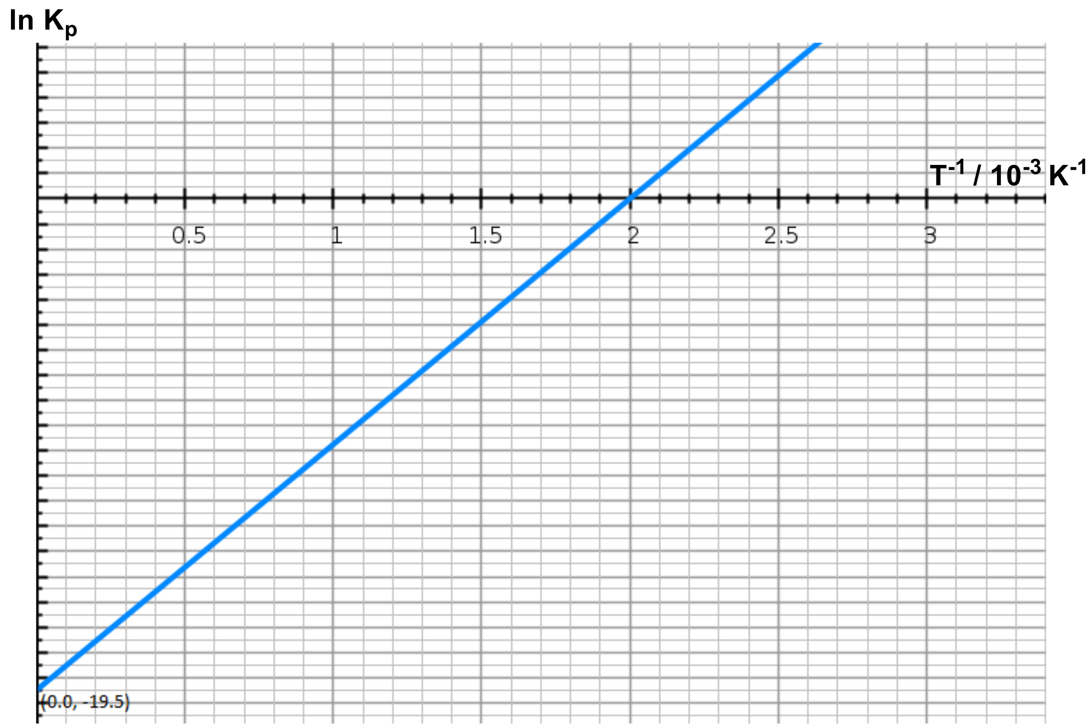
5 Space-suits need to be designed in such a way to supply oxygen to astronauts and to remove the carbon dioxide exhaled by them.

(a) Metal oxides like silver oxide, Ag_2O, are used to get rid of the carbon dioxide.

Ag_2O reacts reversibly with carbon dioxide, as described in the equilibrium equation,

$$Ag_2O\ (s) + CO_2\ (g) \rightleftharpoons Ag_2CO_3\ (s)$$

The van't Hoff plot shows how the equilibrium constant, K_p, of this reaction varies with temperature.



(i) From the above graph, deduce the relationship between K_p and T. [1]

When one increases, the other decreases/inversely related/inverse relationship.

(ii) Hence, explain whether the reaction between silver oxide and carbon dioxide is exothermic or endothermic. [2]

The reaction is exothermic.
Explanation:
as the T increases/decreases, K_p decreases/increases,
implying that PoE shifted left/right,
which further implies that the backward reaction is endothermic/forward reaction is exothermic.

5 (a) (iii) Given that the straight line graph for ln K_p versus T^{-1} is described by the equation

$$\ln K_p = \left(\frac{-\Delta H^0}{R}\right)\frac{1}{T} + \frac{\Delta S^0}{R}$$

Calculate the standard entropy change of this reaction and explain the significance of its sign with respect to the reaction. [2]

y-intercept = -19.5

$\Delta S = (-19.5) \times 8.31 = -162 \text{ J mol}^{-1} \text{ K}^{-1}$

The sign is negative because there is a decrease in the amount of gas. [

After absorbing carbon dioxide for some time, most if not all of the silver oxide would have been depleted. To **recharge** the system, heat is applied into the system to form Ag_2O again.

(iv) ΔG^0 and K_p are mathematically related by the equation

$$\Delta G^0 = -RT \ln K_p$$

Using the graph, estimate the minimum temperature at which the **recharging** of this system becomes spontaneous. [1]

x-intercept = $2 \times 10^{-3} \text{ K}^{-1}$

minimum temperature = $1 / (2 \times 10^{-3} \text{ K}^{-1}) = 500 \text{ K}$

5 (b) Silver carbonate (relative formula mass = 275.8) is a sparingly soluble salt. At 25 °C, its solubility is 0.032 g dm^{-3} of water.

(i) Show that the value of the K_{sp} of silver carbonate at 25 °C is 6.25×10^{-12}. [1]

$4(0.032 / 275.8)^3 = 6.25 \times 10^{-12} \text{ mol}^3 \text{ dm}^{-9}$

(ii) Calculate the solubility of silver carbonate in 0.100 mol dm^{-3} silver nitrate at 25 °C. [1]

$6.25 \times 10^{-12} = (0.100 + 2x)^2 x$

$x = 6.25 \times 10^{-10} \text{ mol dm}^{-3}$

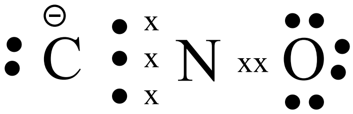
(iii) 1.00 cm^3 of a 1.20×10^{-5} mol dm^{-3} silver nitrate solution was mixed with 3.00 cm^3 of a 7.45×10^{-5} mol dm^{-3} sodium carbonate solution.

Determine whether there would be precipitation of silver carbonate. [2]

Ionic Product = $(0.25 \times 1.20 \times 10^{-5})^2(0.75 \times 7.45 \times 10^{-5})$

$= 5.03 \times 10^{-16} \text{ mol}^3 \text{ dm}^{-9}$

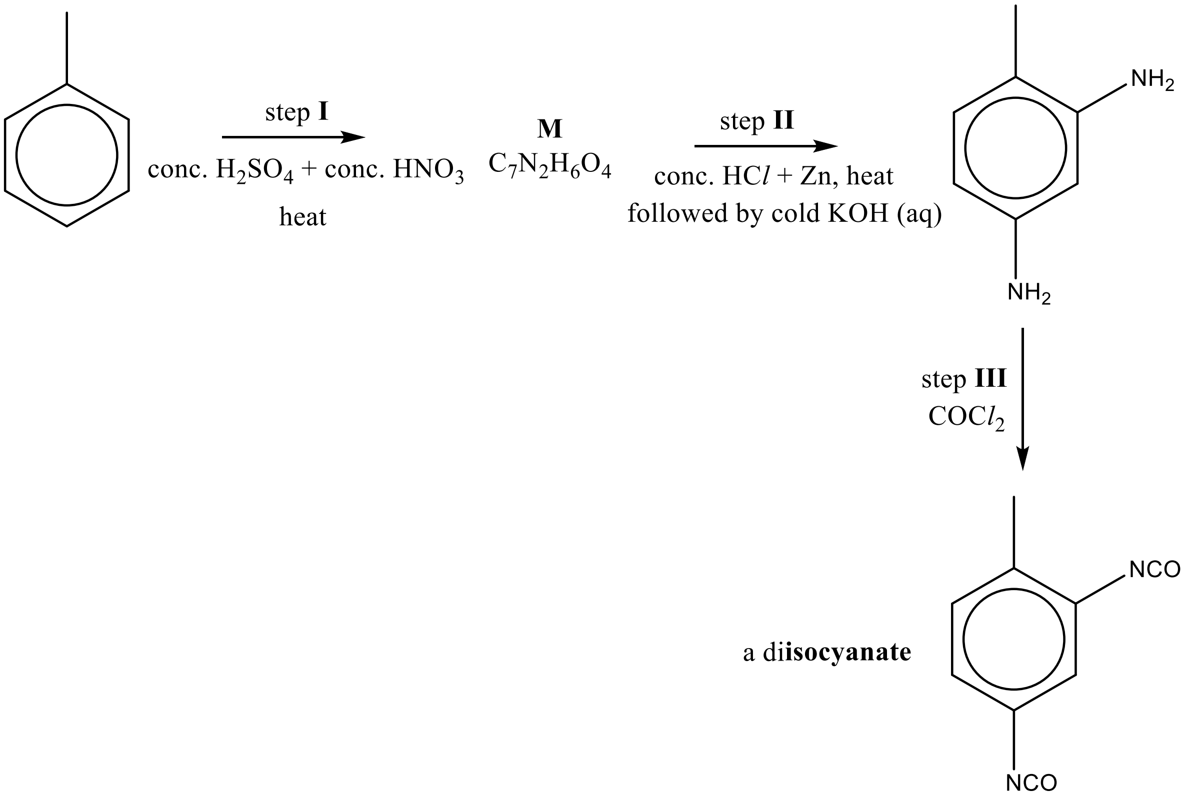
As IP < K_{sp}, there will not be precipitate of silver carbonate.

5	**(c)**	Silver carbonate can be reacted with ammonia to form silver fulminate, AgCNO, a powerful primary explosive. $4\ Ag_2CO_3 + 4\ NH_3 \rightarrow 4\ AgCNO + 6\ H_2O + 4\ Ag + O_2$
		Draw the dot-and-cross diagram of the fulminate ion given that the N is the central atom and the negative charge is on the carbon. [1] 
		[Total: 11]

6 The isocyanate functional group is a constitutional isomer of the fulminate, which was mentioned in question **5(c)**. The isocyanate has the carbon atom instead of nitrogen atom as the central atom.

Isocyanates are important industrial chemicals; they react with alcohols to produce polyurethane polymers, which are components of polyurethane foams, thermoplastic elastomers and polyurethane paints.

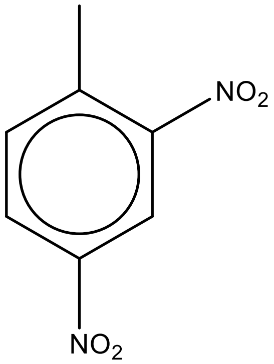
(a) This part is about the synthesis of a diisocyanate from methylbenzene.

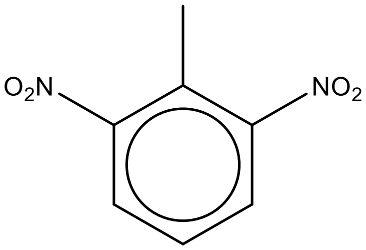
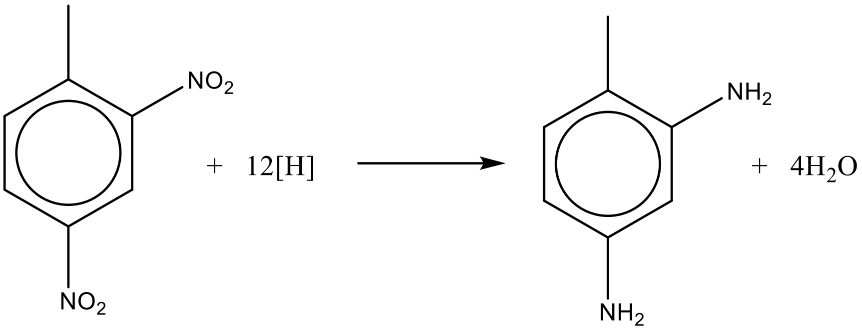


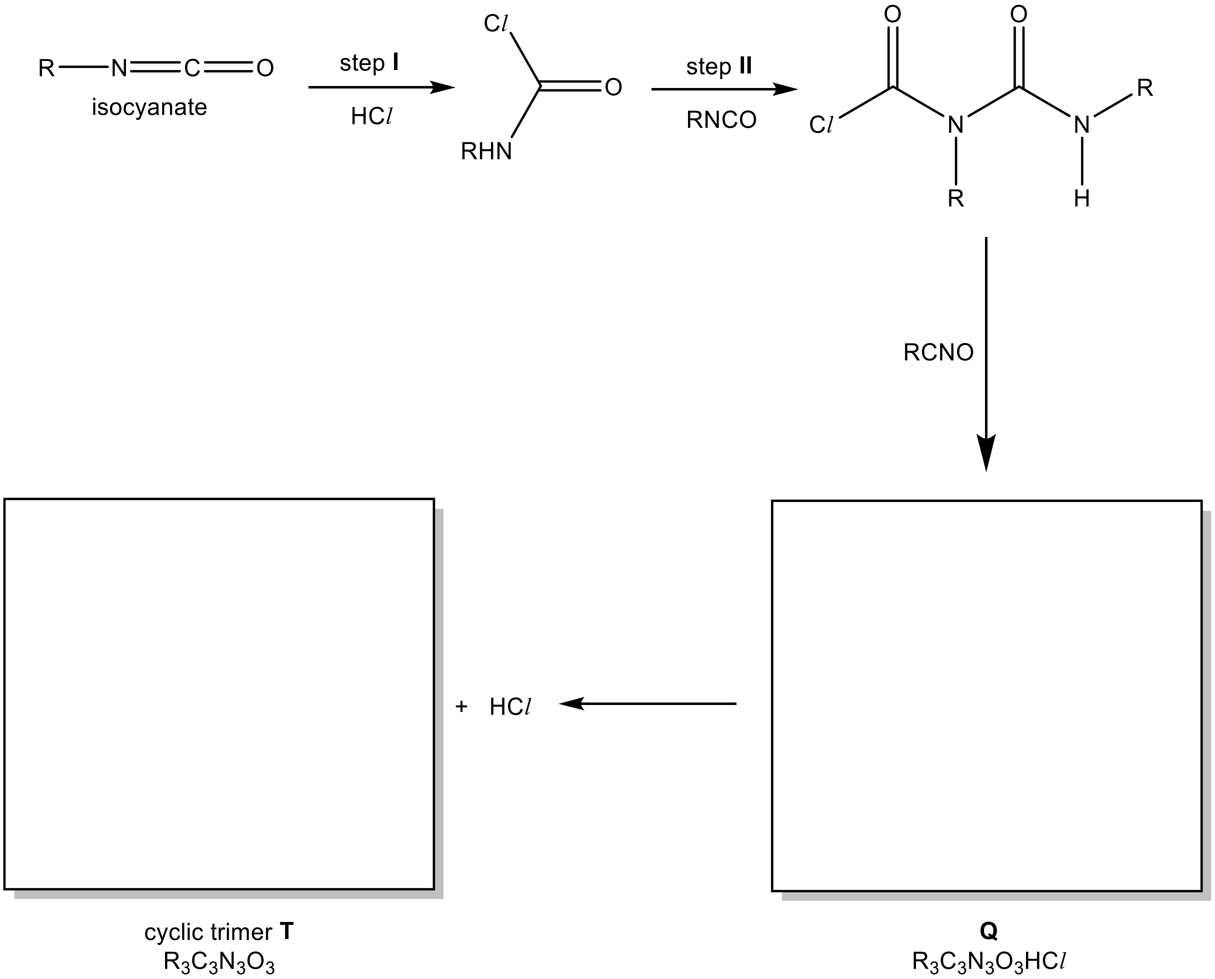
(i) State the type of reaction in step **I**. [1]

Electrophilic substitution.

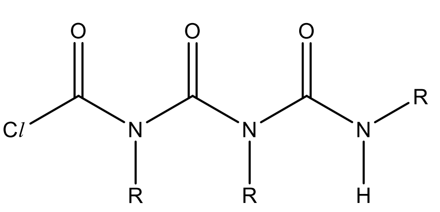
(ii) Draw the structure of **M**. [1]

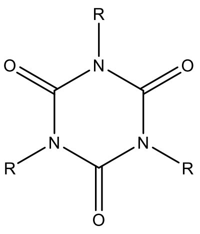


6	**(a)**	**(iii)**	Draw the structure of the isomer of **M** which is formed as a side-product in step **I**. [1] 
		(iv)	Explain the purpose of KOH in step **II**. [1] It is to liberate the amine from its protonated form. It is to form the amine from its protonated form.
		(v)	Write a balanced equation for the overall reaction in step **II**. You are to use [H] to balance the equation. [1] 
		(vi)	State the type of reaction in step **III**. [1] Condensation / addition-elimination
6	**(b)**	Examine the synthetic route below.	

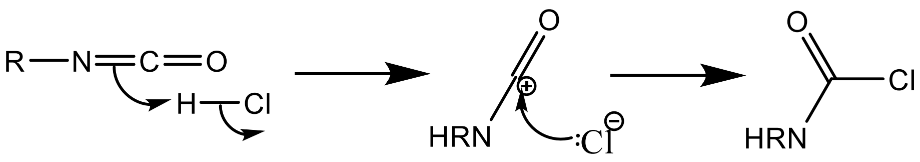


(i) Draw the skeletal formulae of **Q** and the cyclic trimer **T** in the boxes provided. [2]





(ii) Step **I** is an electrophilic addition reaction. Draw the mechanism of step **I**. [3]



6 **(c)** When heated with HC*l* (aq), organic isocyanates (RNCO) are hydrolysed to the amine salt ($RNH_3^+Cl^-$) and carbon dioxide.

$$RNCO + HCl + H_2O \rightarrow RNH_3^+Cl^- + CO_2$$

A 1.13 g sample of an organic isocyanate was treated in this way, and the carbon dioxide produced was absorbed in an excess of aqueous $Ba(OH)_2$, according to the equation shown.

$$Ba(OH)_2\,(aq) + CO_2\,(g) \longrightarrow H_2O\,(l) + BaCO_3\,(s)$$

The mixture was filtered and the residue $BaCO_3$ washed and dried thoroughly. The mass of the residue was 1.97 g.

(i) Show that the molecular mass of the organic isocyanate is 113 g mol^{-1}. [1]

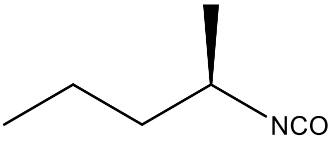
n(org. isocyanate) = 1.97 / 197.3 = 1.00×10^{-2}
molecular mass of org. isocyanate = 1.13 / (1.00×10^{-2}) = 113.2 g mol^{-1}

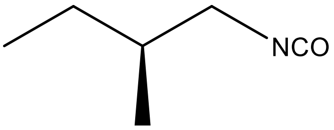
(ii) The R group in RNCO and $RNH_3^+Cl^-$ contains only carbon and hydrogen.

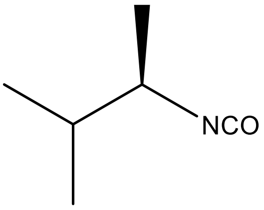
Use the molecular mass mentioned in **(i)** to suggest the molecular formula of the organic isocyanate. [1]

$C_6H_{11}NO$

(iii) Given that a pure sample of this organic isocyanate rotates plane-polarised light, draw a possible stereochemical formula of it. [1]







[Total: 14]

~ End of Paper ~

ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY H2 9729/03

Paper 3 Free Response

2 September 2019
2 hours

Candidates answer on separate paper.

Additional Materials: Cover Page
Answer Paper
Insert

READ THESE INSTRUCTIONS FIRST

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

Section A
Answer **all** questions.

Section B
Answer **one** question.

Start each question on a new page of writing paper.
Fasten the insert in front of all writing paper at the end of the examination.

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

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

This document consists of **14** printed pages.

Section A

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

1 **(a)** *Use of the insert is necessary for this question.*
Fasten the insert in front of all writing paper at the end of the examination.

An iodoalkane, RI, is hydrolysed by aqueous sodium hydroxide. The results obtained from two experiments are plotted on the insert. In each experiment, the overall [NaOH(aq)] remained virtually constant at the value given beside each graph.

(i) Use the graphs on the insert to determine the following. Show all workings clearly.

I Use the half-life method to deduce the order of reaction with respect to the iodoalkane.

II Use the initial rates method to deduce the order of reaction with respect to sodium hydroxide.

III Construct a rate equation for the reaction and use it to calculate a value for the rate constant. Include its units. [7]

(ii) Hence draw a fully labelled energy profile diagram of the reaction. [3]

(b) Silver(I) iodide and iodine are two solids which have low solubility in water. However when both are mixed together with water and left to stand, they dissolve completely to give a coloured solution of silver(I) triiodide.

(i) State the expected colour of the silver(I) triiodide solution. [1]

(ii) Write three relevant equilibria equations and use them to explain how the two solids can completely dissolve when mixed with water. [3]

(c) Another triiodide compound, nitrogen triiodide, NI_3 is a simple covalent molecule that is very sensitive to shock and will decompose rapidly. A touch of a feather or even alpha particles from radioactive decay can trigger an explosion.

$$2NI_3(s) \longrightarrow N_2(g) + 3I_2(g) \qquad \Delta H = -290 \text{ kJ mol}^{-1}$$

76.5 kJ mol^{-1} of energy is needed to convert solid NI_3 to gaseous NI_3.

Use the above information and relevant information from the *Data Booklet* to calculate the N–I bond energy. [2]

(d) Alpha particles, ${}^{4}_{2}He^{2+}$ are produced from the radioactive decay of certain isotopes. An example of one is from the decay of Americium-241.

$$ {}^{241}_{95}Am \rightarrow {}^{4}_{2}He^{2+} + \textbf{M} $$

(i) Use the *Data Booklet* to identify species **M** that is formed. [1]

(ii) Calculate the angle of deflection for **M** in a uniform electric field if the angle of deflection for ${}^{4}_{2}He^{2+}$ is +7.11°. [1]

Americium is often used in smoke detectors as the compound AmO_2 and is made from the thermal decomposition of americium(III) ethanedioate, $Am_2(C_2O_4)_3$.

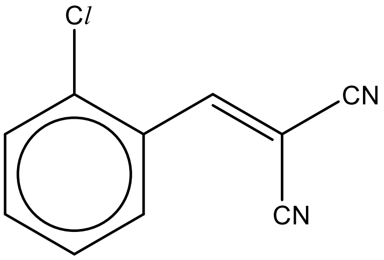
$$ Am_2(C_2O_4)_3 \longrightarrow 2AmO_2 + 4CO + 2CO_2 $$

(iii) Explain why the thermal decomposition is a redox reaction in terms of oxidation state changes. [2]

[Total: 20]

2 **(a)** On 12 June 2019, Hong Kong police fired tear gas into the crowds as many took to the streets to protest against a proposed extradition Bill.

The active compound in tear gas is 2-chlorobenzalmalononitrile.

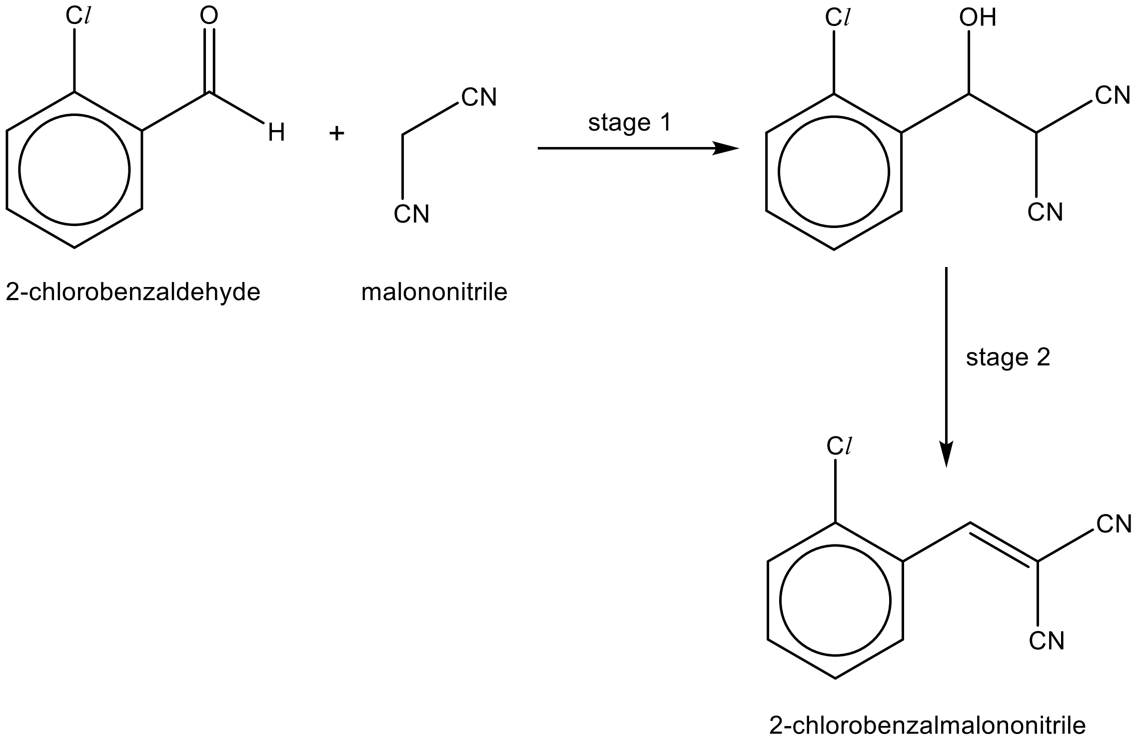


2-chlorobenzalmalononitrile

2-chlorobenzalmalononitrile is a solid at room temperature and is dispersed as an aerosol dissolved in a suitable organic solvent, typically dichloromethane, CH_2Cl_2. Its effects are felt when the solvent evaporates in air and the dry powder touches the eyes, nose and mouth.

(i) Suggest, with reasoning, two physical properties that make dichloromethane a suitable solvent. [2]

2-chlorobenzalmalononitrile can be synthesised via the 2-stage Knoevenagel condensation.

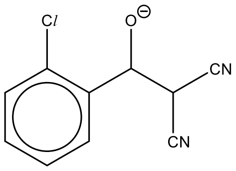


(ii) State the type of the reaction in stage 2. [1]

(iii) Instead of purchasing malononitrile as a starting reagent, it can be made from dichloromethane.

Suggest the reagent and conditions needed to convert dichloromethane to malononitrile. [1]

The following 3-step mechanism illustrates stage 1.

- Malononitrile is deprotonated by a weak base, R_2NH to form its conjugate base, $(NC)_2CH^-$.
- The conjugate base of malononitrile undergoes nucleophilic addition with 2-chlorobenzaldehyde to give  as an intermediate.

- The conjugate acid of R_2NH is deprotonated by the intermediate.

(iv) Describe the 3-step mechanism illustrated above.

Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows. [3]

(v) Suggest another role of the weak base, R_2NH. [1]

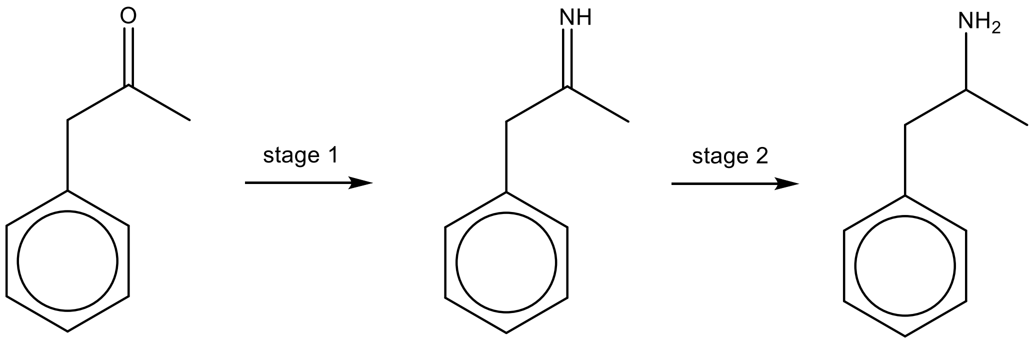
(vi) Compare, and explain, the relative acidities of dichloromethane and malononitrile. [2]

(vii) Draw the **only two** organic products formed when 2-chlorobenzalmalononitrile is heated with acidified potassium manganate(VII). [2]

(b) During World War II, amphetamine pills were issued to the German army as they promoted alertness and self-confidence while reducing pain, hunger and the need for sleep.

Study the two methods of synthesis and answer the questions below.

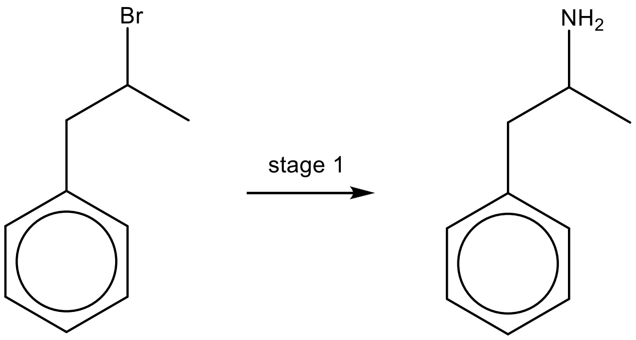
Method 1



phenylpropanone

amphetamine

Method 2



(2-bromopropyl)benzene

amphetamine

(i) State the reagent used in stage 1 for both methods of synthesis. [1]

(ii) One would think that Method 2 would give better yield of amphetamine during synthesis since it only involves one stage as compared to two stages in Method 1, but this is not true.

Suggest why the yield of amphetamine via Method 2 would be poor. [1]

(iii) Only half of the product formed via Method 1 was biologically active in the body.

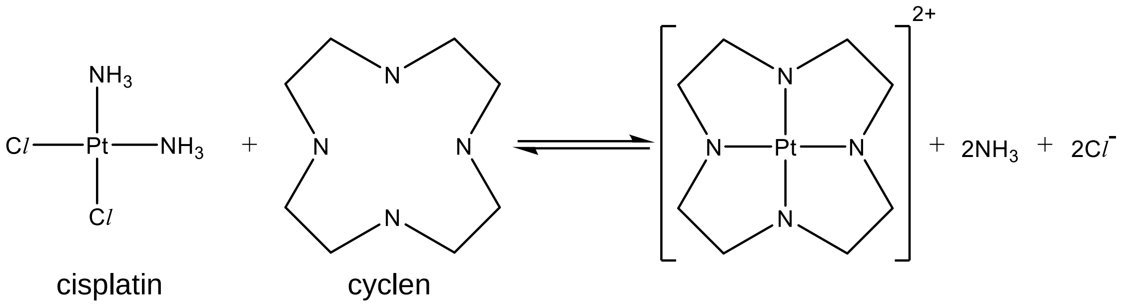
Account for this observation. [2]

(iv) Stage 2 of Method 1 employs the use of platinum metal as a catalyst.

State the type of catalysis involved and briefly outline the stages involved in the reaction. [3]

(v) Explain why transition metals are useful as catalysts. [1]

(c) Cisplatin is an anti-cancer drug containing a platinum centre and appears as a light yellow powder. When cisplatin is dissolved in water and allowed to react with the cyclen *ligand*, the position of equilibrium lies strongly to the right hand side.



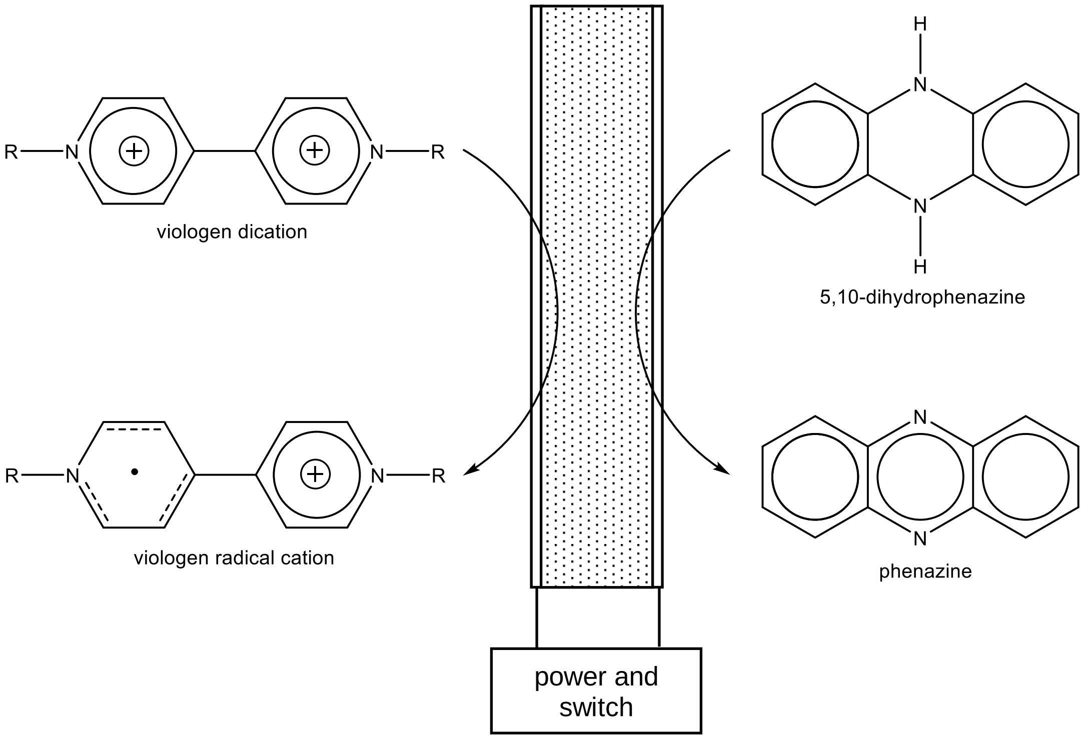
(i) Define the term *ligand*. [1]

(ii) Suggest signs for the enthalpy change of reaction and entropy change of reaction for the forward reaction, and comment on the spontaneity of the reaction across different temperatures. [2]

(iii) Explain why transition metal compounds are coloured. [2]

[Total: 25]

3 **(a)** Boeing 787-9 Dreamliners are equipped with electronically dimmable windows. When a constant current is applied, electrochemical reactions happen within a panel and the conversion of colourless viologen dication to viologen radical cation forms an intense dark purple that shields out sunlight. A simplified diagram together with the chemical changes is shown.



The viologen dication and phenazine are aromatic species. Hückel's rule states that planar cyclic species with 4n+2 pi electrons, where n = 0, 1, 2 ..., are considered aromatic.

(i) State the hybridisation of the nitrogen atoms in the viologen dication. [1]

(ii) State the number of pi electrons in phenazine. [1]

(iii) State the electrode at which the conversion of 5,10-dihydrophenazine to phenazine occurs. [1]

(iv) Write the half-equation for the reaction of 5,10-dihydrophenazine to phenazine in alkaline medium. You may write the names of both compounds respectively. [1]

(v) 0.0300 g of 5,10-dihydrophenazine is finely coated on to one side of the panel.

Calculate the time needed to react all of the coated 5,10-dihydrophenazine to completely darken a window panel, given that a constant current of 0.150 A is supplied. [4]

(b) It is mandatory for all aircrafts to provide an inflatable life vest for every passenger. One particular model of life vests uses a rapid inflation system of compressed CO_2 in a canister.

A student read that the canisters typically pack 11.0 g of CO_2 and commented that the amount of CO_2 present will inflate a life vest fully to 6.00 dm^3 in capacity.

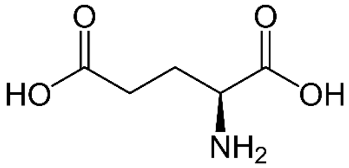
(i) Show how the student obtained 6.00 dm^3 as the capacity of the life vest and state the assumption made in the calculation. [2]

(ii) State two assumptions of the ideal gas law which allowed the student to make the calculations. [2]

(c) Passengers on planes often find that they are more drawn to *umami*-rich flavours as the sweet and salty tastes are dulled due to changes in altitude.

Monosodium glutamate (MSG) is one compound responsible for providing *umami* flavouring and it is the monosodium salt of glutamic acid.

The pK_a values associated with glutamic acid are 2.19, 4.25 and 9.67.



glutamic acid

(i) Draw the structure of glutamic acid at pH 1 and assign the three pK_a values. [2]

(ii) Draw the structure of monosodium glutamate. [1]

[Total: 15]

Section B

Answer **one** question from this section.

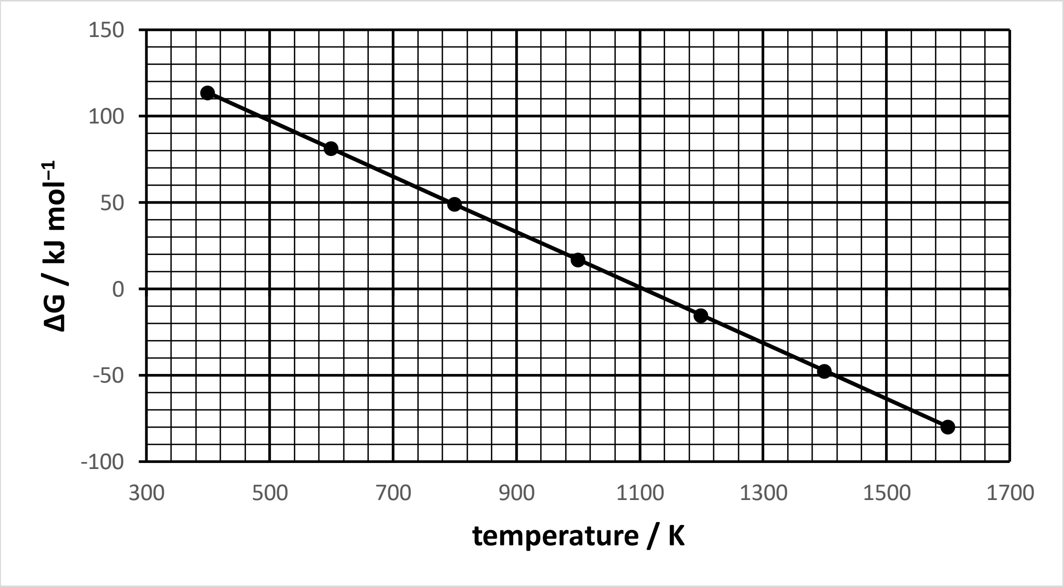
4 **(a)** The thermal decomposition reactions for calcium ethanoate and calcium methanoate are given as follows:

$Ca(HCOO)_2 \rightarrow CaCO_3 + HCHO$

$Ca(CH_3COO)_2 \rightarrow CaCO_3 + CH_3COCH_3$

Predict the organic product, other than propanone and methanal, when a mixture of calcium methanoate and calcium ethanoate undergoes thermal decomposition. [1]

(b) The following Ellingham diagram shows the variation of Gibbs free energy change with temperature for the thermal decomposition of calcium carbonate.



(i) State the range of temperatures where solid calcium carbonate would decompose upon heating. [1]

(ii) Calculate the entropy change of the reaction. [1]

(iii) Hence, calculate the enthalpy change of the reaction. [1]

(c) Dolomite consists of $CaCO_3$ and $MgCO_3$ with the formula $CaMg(CO_3)_2$. It can be added to soil or marine aquarium as a pH buffer.

(i) Write a balanced equation for the action of heat on dolomite. [1]

(ii) Each carbonate is heated separately.

Predict and explain the difference in the thermal decomposition temperatures of the two carbonates. [3]

(iii) Explain why Li_2CO_3 decomposes in a similar way compared to these two carbonates. [1]

(d) **(i)** Predict and explain the difference in melting points of calcium oxide and magnesium oxide. [2]

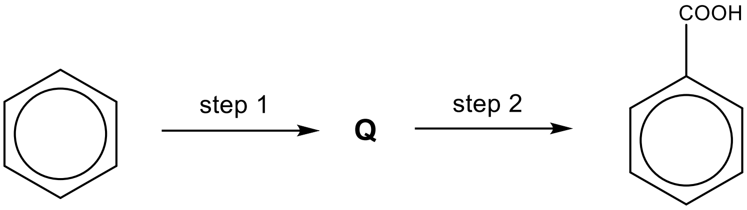
(ii) In power plant or trash incineration plant, large quantities of sulfur dioxide gas are produced. Calcium oxide can be used to remove sulfur dioxide from these exhaust gases in a process called flue-gas desulfurisation.

$$CaO + SO_2 \rightarrow CaSO_3$$

State the type of reaction for the above reaction. [1]

(e) Benzoic acid is an important precursor for the industrial synthesis of many other organic substances. Its salts are also used as food preservatives.

(i) Benzoic acid can be made from benzene by a two-step synthesis.



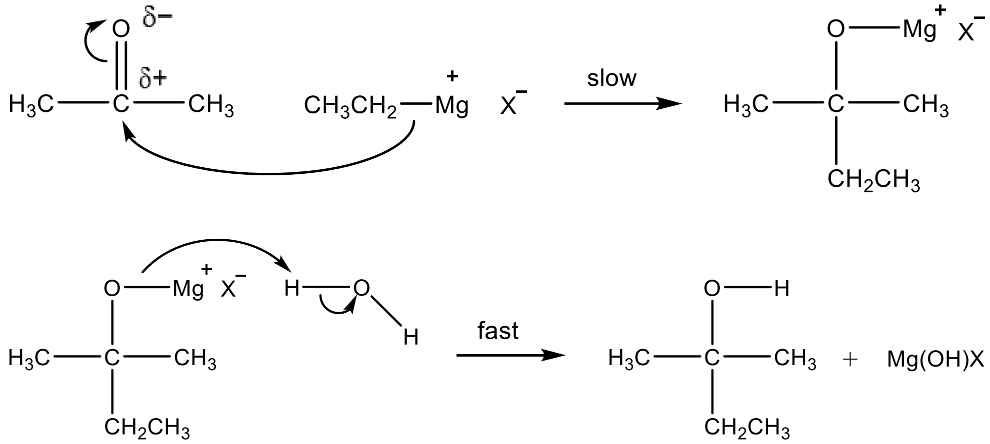
For steps 1 and 2, state the
- reagents and conditions, and
- type of reaction. [4]

(ii) Group 2 elements are known to form organometallic compounds. One example is the Grignard reagent with general formula RMgX. It is produced by reacting an alkyl halide or aryl halide with magnesium.

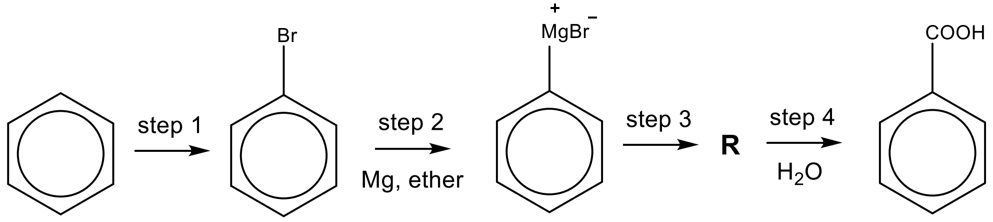
$RX + Mg \rightarrow R\text{–}Mg^{+}\,X^{-}$ where X can be C*l* or Br.

The carbon-magnesium covalent bond is polarised as such; $\overset{\delta-}{C}-\overset{\delta+}{Mg}$.

Grignard reaction is important in making a new C–C bond. The mechanism for the reaction of ethylmagnesium bromide with propanone is shown as follows.



Benzoic acid can also be made from benzene by a four-step synthesis, using the Grignard reagent.



For step 3, state the reagent and intermediate **R**.

For steps 3 and 4, state the type of reaction. [4]

[Total: 20]

5 **(a)** **(i)** A compound **X** consists only of carbon, hydrogen and oxygen. During the complete combustion of 4 g of the compound, 8 g of carbon dioxide and 3.273 g of water were produced.

Determine the empirical formula of the compound **X**. [2]

(ii) Another 4 g sample of compound **X** was vaporised at 160 °C and 101 kPa, and found to occupy a volume of 1620 cm^3.

Determine the relative molecular mass of this compound. [1]

(iii) Hence determine the molecular formula of compound **X**. Show your working clearly. [1]

(b) Butanoic acid is used in the preparation of various esters. These esters have pleasant aromas or tastes. As a consequence, they are used as food and perfume additives.

(i) Biological methods have been developed to produce methane from waste organic matter using bacteria.

Based on the changes in oxidation numbers of carbon, construct a balanced equation for the disproportionation of **aqueous** butanoic acid to produce methane and carbon dioxide only. [1]

(ii) Given the following data,

- Enthalpy change of combustion of butanoic acid is −2184 kJ mol^{-1}.
- Enthalpy change of combustion of methane is −890 kJ mol^{-1}.

Calculate the enthalpy change for the reaction in **(b)(i)** for **liquid** butanoic acid instead of aqueous butanoic acid. [1]

(iii) Given that

$$CH_3CH_2CH_2COOH(l) \rightarrow CH_3CH_2CH_2COOH(aq) \qquad \Delta H^{\ominus}_{soln} = -16.7 \text{ kJ mol}^{-1}$$

Use you answer in **(b)(ii)** to calculate the enthalpy change of reaction in **(b)(i)**. [2]

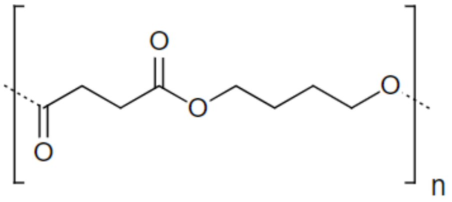
(iv) Butanoic acid boils at 117.7 °C. During boiling, the liquid phase is at equilibrium with the gas phase.

Calculate the entropy change of vaporisation of butanoic acid, given that the enthalpy change of vaporisation of butanoic acid is +52.0 kJ mol^{-1}. [1]

(v) Trouton's Rule states that the entropy change of vaporisation of many liquids, such as benzene and propanone, is about +88 J mol^{-1} K^{-1}.

Compare and explain the calculated result in **(b)(iv)** in relation to Trouton's Rule. [1]

(c) Polybutylene succinate (PBS) is a polyester used in packaging. It is receiving renewed interest due to increased demand for biodegradable polymers.



Polybutylene succinate

Hydrolysis of PBS produces two monomers **E** and **F**.

E can be reduced to **F**.

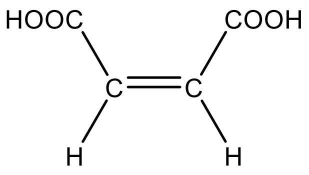
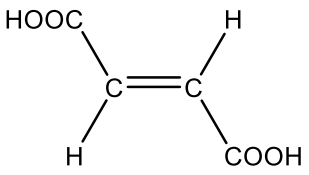
When an organic compound **D**, $C_{10}H_{18}O_2$ is heated with acidified potassium manganate (VII), two products, **E**, $C_4H_6O_4$ and **G**, $C_6H_{12}O$ are formed.

G produces a yellow precipitate on warming with iodine in aqueous sodium hydroxide, and rotates the plane of polarised light.

Upon gentle heating, **E** produces a neutral compound **H**, $C_4H_4O_3$, which does not react with sodium metal or give a precipitate with 2,4-dinitrophenylhydrazine.

Suggest structures for **D** to **H**, and explain the observations described above. [7]

(d) Maleic acid and fumaric acid are two isomers with the same molecular and structural formulae, but with very different physical properties.

	 maleic acid	 fumaric acid
melting point / ^oC	130	287
pKa$_1$	1.9	3.0
pKa$_2$	6.5	4.5

(i) Give two reasons to explain why maleic acid has a lower melting point than fumaric acid. [2]

(ii) Explain why maleic acid has a lower pKa$_1$ value than fumaric acid. [1]

[Total: 20]

End of Paper

ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY H2 9729/03

Paper 3 Free Response

2 September 2019
2 hours

Candidates answer on separate paper.

Additional Materials: Cover Page
Answer Paper
Insert

READ THESE INSTRUCTIONS FIRST

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

Section A
Answer **all** questions.

Section B
Answer **one** question.

Start each question on a new page of writing paper.
Fasten the insert in front of all writing paper at the end of the examination.

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

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

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

Section A

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

1 **(a)** *Use of the insert is necessary for this question.*
Fasten the insert in front of all writing paper at the end of the examination.

An iodoalkane, RI, is hydrolysed by aqueous sodium hydroxide. The results obtained from two experiments are plotted on the insert. In each experiment, the overall [NaOH(aq)] remained virtually constant at the value given beside each graph.

(i) Use the graphs on the insert to determine the following. Show all workings clearly.

I Use the half-life method to deduce the order of reaction with respect to the iodoalkane.

II Use the initial rates method to deduce the order of reaction with respect to sodium hydroxide.

III Construct a rate equation for the reaction and use it to calculate a value for the rate constant. Include its units. [7]

From working on graph, when $[OH^-] = 0.10$ M, half-life = 58 min OR
From working on graph, when $[OH^-] = 0.15$ M, half-life = 39 min [1]
∴ reaction is first order w.r.t. RI. [1]

From working on graph, when $[OH^-] = 0.10$ M,
initial rate = 0.0100/96 = 0.000104 mol dm^{-3} min^{-1} &
From working on graph, when $[OH^-] = 0.15$ M,
initial rate = 0.0100/64 = 0.000156 mol dm^{-3} min^{-1} [1]
When $[OH^-]$ x1.5, rate x1.5, ∴ reaction is first order w.r.t. OH^-. [1]

rate = $k[RI][OH^-]$ [1] (if S_N1, do not award this mark)

$k = \frac{0.000104}{[0.010][0.10]} = 0.104\ mol^{-1}\ dm^3\ min^{-1}$ OR

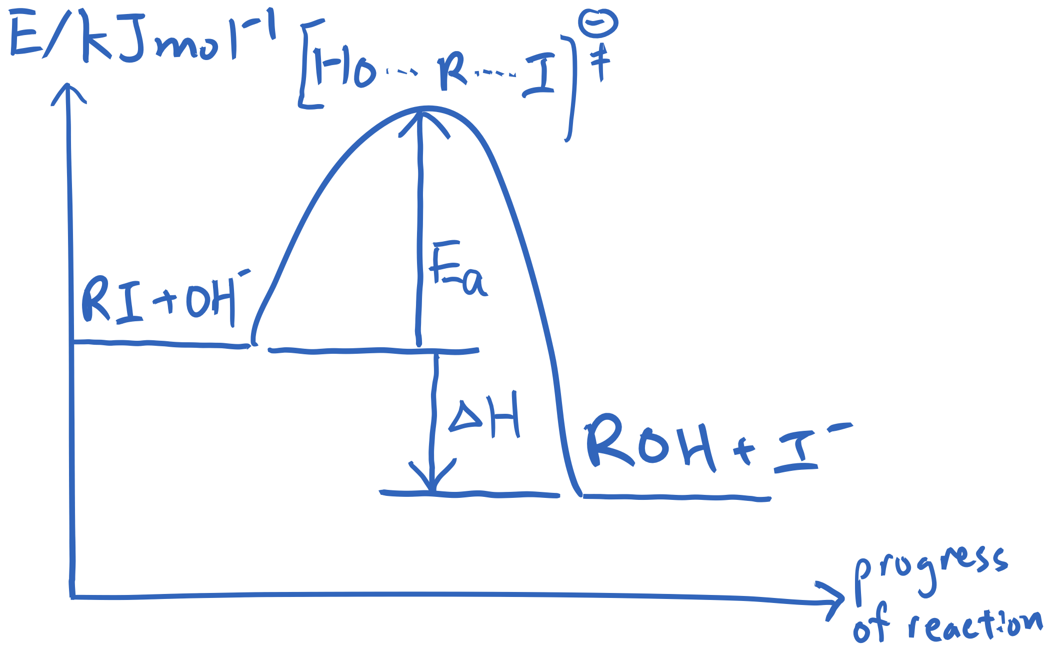
$k = \frac{0.000156}{[0.010][0.15]} = 0.104\ mol^{-1}\ dm^3\ min^{-1}$ [1+1]

Allow ecf if rate equation is rate = $k[RI]$, then

$k = \frac{0.000104}{[0.010]} = 0.0104\ mol^{-1}\ dm^3\ min^{-1}$ OR

$k = \frac{0.000156}{[0.010]} = 0.0156\ mol^{-1}\ dm^3\ min^{-1}$ [1+1] (D.N.A. if rate = $k[OH^-]$)

(ii) Hence draw a fully labelled energy profile diagram of the reaction. [3]



Shape and axes [1]
Reactants, Products [1] (if S_N1, mark for intermediate)
Ea and ΔH [1]
Allow ecf if deduced S_N1 in part (i)

(b) Silver(I) iodide and iodine are two solids which have low solubility in water. However when both are mixed together with water and left to stand, they dissolve completely to give a coloured solution of silver(I) triiodide.

(i) State the expected colour of the silver(I) triiodide solution. [1]

Yellow or Brown (answer is concentration dependent)

(ii) Write three relevant equilibria equations and use them to explain how the two solids can completely dissolve when mixed with water. [3]

$AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$--------- (1) [✓]
$I_2(s) + aq \rightleftharpoons I_2(aq)$------------------ (2) [✓]
$I^-(aq) + I_2(aq) \rightleftharpoons I_3^-(aq)$----------- (3) [✓]

Equilibria (1) and (2) exist for each of the poorly soluble compounds. However, equilibrium (3) is set up in the presence of $I^-(aq)$ and $I_2(aq)$ in solution and the position of equilibrium lies strongly to the right hand side[✓]. With $[I^-]$ and $[I_2]$ constantly falling in (1) and (2), their positions of equilibria will constantly shift to the right[✓][✓] as well, causing AgI(s) and $I_2(s)$ to dissolve. OWTTE

[✓] for each eqn and [✓] for accompanying POE shift.
6[✓]-3m, 4[✓]-2m, 2[✓]-1m

(c) Another triiodide compound, nitrogen triiodide, NI_3 is a simple covalent molecule that is very sensitive to shock and will decompose rapidly. A touch of a feather or even alpha particles from radioactive decay can trigger an explosion.

$$2NI_3(s) \longrightarrow N_2(g) + 3I_2(g) \qquad \Delta H = -290\ \mathrm{kJ\ mol^{-1}}$$

76.5 kJ $\mathrm{mol^{-1}}$ of energy is needed to convert solid NI_3 to gaseous NI_3.

Use the above information and relevant information from the *Data Booklet* to calculate the N–I bond energy. [2]

$$\begin{tikzcd}
2NI_3(s) \arrow[r, "-290"] \arrow[d, "2(+76.5)"'] & N_2(g) \arrow[r, phantom, "+"] & 3I_2(g) \\
2NI_3(g) \arrow[r, "6\mathrm{BDE}(N\text{–}I)"'] & 2N(g) \arrow[u, "2(-944)"] \arrow[r, phantom, "+"] & 6I(g) \arrow[u, "3(-151)"']
\end{tikzcd}$$

$-290 = 2(+76.5) + 6\mathrm{BDE}(N\text{–}I) + (-944) + 3(-151)$

$\mathrm{BDE}(N\text{–}I) = 159\ \mathrm{kJ\ mol^{-1}}$

[1] using –290, +76.5, –944 & –151, no need coefficients and sign.

[1] answer 159, no ECF

(d) Alpha particles, ${}^{4}_{2}He^{2+}$ are produced from the radioactive decay of certain isotopes. An example of one is from the decay of Americium-241.

$${}^{241}_{95}Am \rightarrow {}^{4}_{2}He^{2+} + \mathbf{M}$$

(i) Use the *Data Booklet* to identify species **M** that is formed. [1]

${}^{237}_{93}Np^{2-}$, ${}^{237}Np^{2-}$ minimally, no need for $_{93}$.

(ii) Calculate the angle of deflection for **M** in a uniform electric field if the angle of deflection for ${}^{4}_{2}He^{2+}$ is +7.11°. [1]

Angle of deflection, AOD = $k\frac{Q}{m}$

$\frac{AOD_1 m_1}{Q_1} = \frac{AOD_2 m_2}{Q_2}$

$AOD_{Np^{2-}} = \frac{+7.11 \times 4 \times (-2)}{(+2)237} = -0.12^{\circ}$ (2 or 3 sf)

Americium is often used in smoke detectors as the compound AmO_2 and is made from the thermal decomposition of americium(III) ethanedioate, $Am_2(C_2O_4)_3$.

$$Am_2(C_2O_4)_3 \longrightarrow 2AmO_2 + 4CO + 2CO_2$$

(iii) Explain why the thermal decomposition is a redox reaction in terms of oxidation state changes. [2]

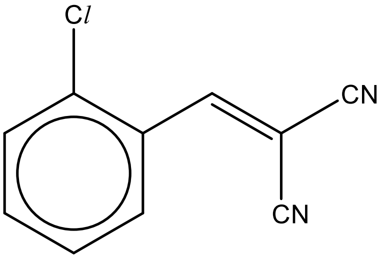
Am in $Am_2(C_2O_4)_3$ is oxidised from +3 oxidation state to +4 in AmO_2. [1]

C in $Am_2(C_2O_4)_3$ is reduced from +3 oxidation state to +2 in CO and oxidised +4 in CO_2. [1]

[Total: 20]

2 **(a)** On 12 June 2019, Hong Kong police fired tear gas into the crowds as many took to the streets to protest against a proposed extradition Bill.

The active compound in tear gas is 2-chlorobenzalmalononitrile.



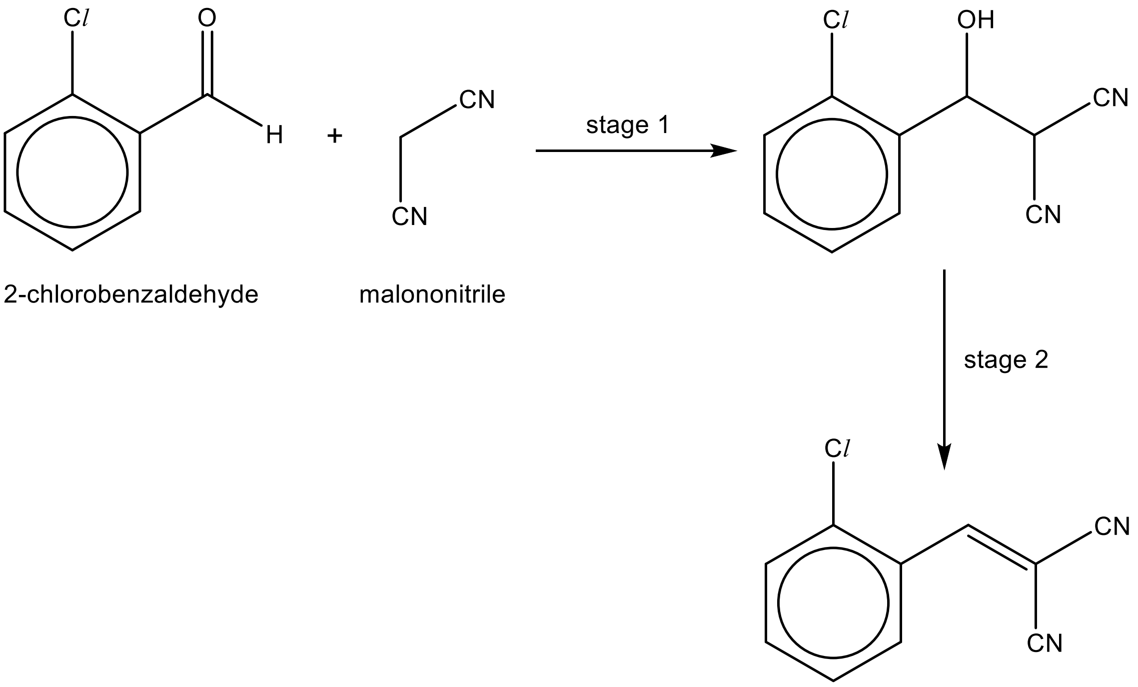
2-chlorobenzalmalononitrile

2-chlorobenzalmalononitrile is a solid at room temperature and is dispersed as an aerosol dissolved in a suitable organic solvent, typically dichloromethane, CH_2Cl_2. Its effects are felt when the solvent evaporates in air and the dry powder touches the eyes, nose and mouth.

(i) Suggest, with reasoning, two physical properties that make dichloromethane a suitable solvent. [2]

1. Polar to favour pd-pd interactions.
2. High volatility/low BP to dry/evaporate in the air.

2-chlorobenzalmalononitrile can be synthesised via the 2-stage Knoevenagel condensation.



2-chlorobenzaldehyde

malononitrile

2-chlorobenzalmalononitrile

(ii) State the type of the reaction in stage 2. [1]

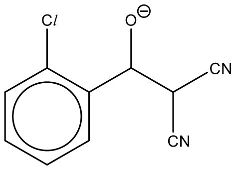
Elimination

(iii) Instead of purchasing malononitrile as a starting reagent, it can be made from dichloromethane.

Suggest the reagent and conditions needed to convert dichloromethane to malononitrile. [1]

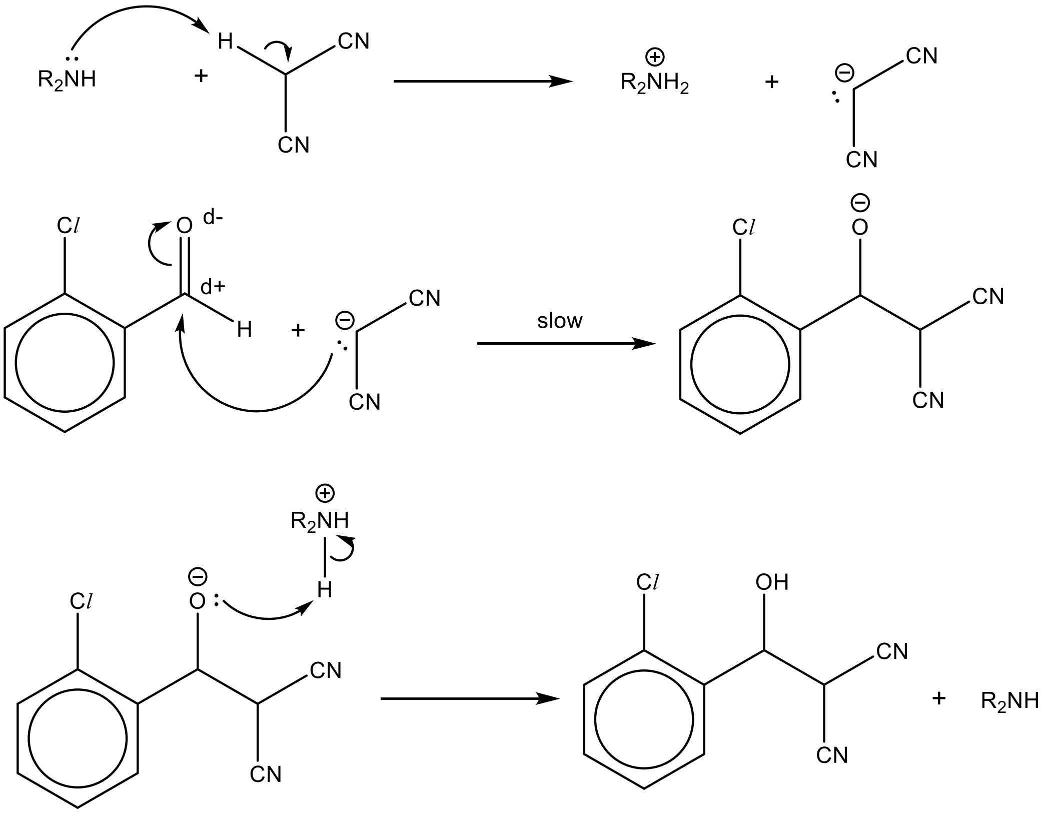
KCN (alc), heat under reflux

The following 3-step mechanism illustrates stage 1.

- Malononitrile is deprotonated by a weak base, R_2NH to form its conjugate base, $(NC)_2CH^-$.
- The conjugate base of malononitrile undergoes nucleophilic addition with 2-chlorobenzaldehyde to give  as an intermediate.
- The conjugate acid of R_2NH is deprotonated by the intermediate.

(iv) Describe the 3-step mechanism illustrated above.

Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows. [3]



Step 1:
2 correct arrows – [√]
$R_2NH_2^+$ & $(NC)_2CH^-$ – [√]

Step 2:
2 correct arrows – [√]
δ+ & δ– – [√]
slow – [√]

Step 3:
2 correct arrows – [√]

6[√] – 3m
4[√] – 2m
2[√] – 1m

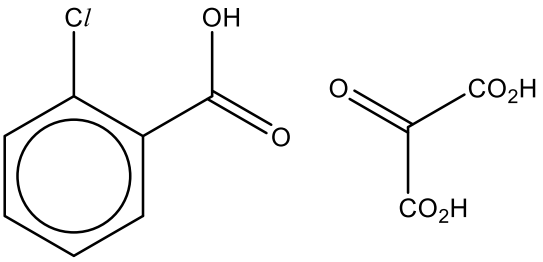
(v) Suggest another role of the weak base, R_2NH. [1]

Catalyst

(vi) Compare, and explain, the relative acidities of dichloromethane and malononitrile. [2]

Malononitrile is more acidic than dichloromethane. The two nitrile groups are more electron withdrawing than the two chloro groups and they stabilise the negative charge on the conjugate base of malononitrile better than dichloromethane.

(vii) Draw the **only two** organic products formed when 2-chlorobenzalmalononitrile is heated with acidified potassium manganate(VII). [2]

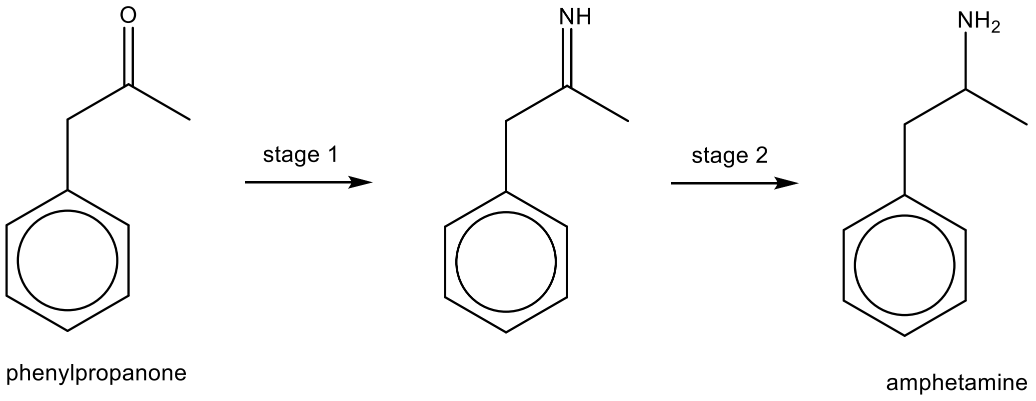


Note: Mesoxalic acid product is thermally stable and will not give 3 CO_2. More appropriately, it will be further hydrated in aqueous medium to form dihydroxymalonic acid, $(HO)_2C(CO_2H)_2$, but we can accept mesoxalic acid as the answer.

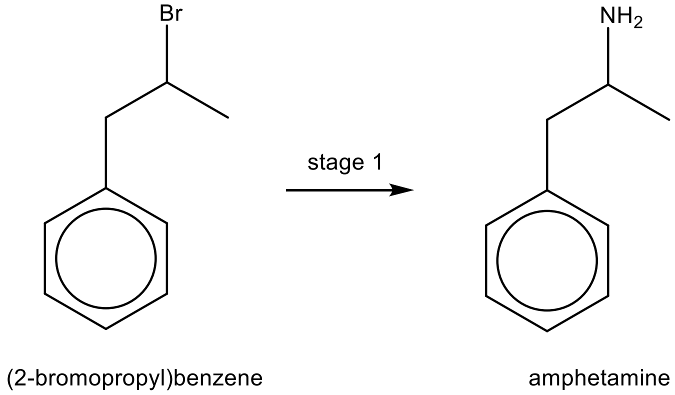
(b) During World War II, amphetamine pills were issued to the German army as they promoted alertness and self-confidence while reducing pain, hunger and the need for sleep.

Study the two methods of synthesis and answer the questions below.

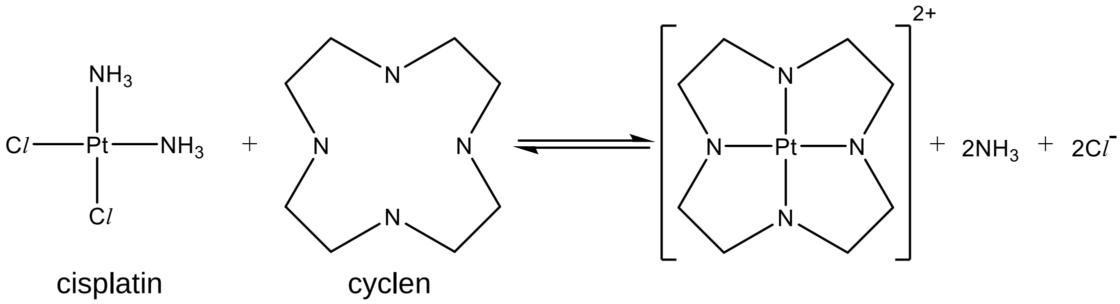
Method 1



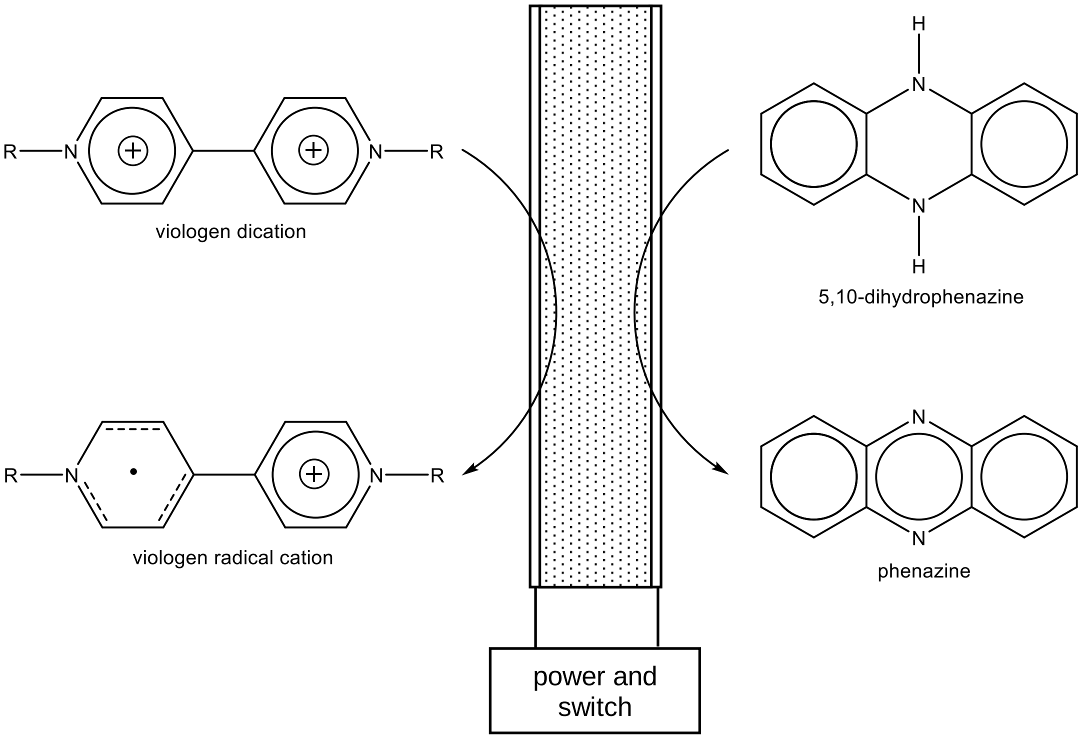
Method 2



		(i)	State the reagent used in stage 1 for both methods of synthesis. [1] NH_3
		(ii)	One would think that Method 2 would give better yield of amphetamine during synthesis since it only involves one stage as compared to two stages in Method 1, but this is not true. Suggests why the yield of amphetamine via Method 2 would be poor. [1] Amphetamine synthesised via Method 2 can react further with more (2-bromopropyl)benzene to undergo polysubstitution/polyalkylation. OWTTE
		(iii)	Only half of the product formed via Method 1 was biologically active in the body. Account for this observation. [2] Amphetamine produced exists as a racemic mixture (idea of 50:50) and only one of the enantiomers possesses the correct configuration to be biologically active. OWTTE
		(iv)	Stage 2 of Method 1 employs the use of platinum metal as a catalyst. State the type of catalysis involved and briefly outline the stages involved in the reaction. [3]

			Heterogeneous catalyst. [1] Diffusion – adsorption – reaction (bond breaking and forming) – desorption – diffusion. [2] OWTTE
		(v)	Explain why transition metals are useful as catalysts. [1] Variable oxidation state OR ability for substances to adsorb on to/form dative bonds on their surface for reaction. OWTTE.
	(c)	Cisplatin is an anti-cancer drug containing a platinum centre and appears as a light yellow powder. When cisplatin is dissolved in water and allowed to react with the cyclen *ligand*, the position of equilibrium lies strongly to the right hand side.  	
		(i)	Define the term *ligand*. [1] A ligand is a neutral molecule or anion with at least one lone pair of electrons capable of dative bonding to the central metal atom or ion.
		(ii)	Suggest signs for the enthalpy change of reaction and entropy change of reaction for the forward reaction, and comment on the spontaneity of the reaction across different temperatures. [2] Sign for ΔH is negative and sign for ΔS is positive. [1] Thus the reaction is spontaneous for all temperatures. [1]
		(iii)	Explain why transition metal compounds are coloured. [2] In presence of ligands, degenerate d-orbitals split into two energy levels with difference of ΔE. [✓] When white/visible light falls on the complex ion, a particular wavelength of light with energy equal to ΔE is absorbed [✓] by the transition metal ion and the electron is promoted from a lower-energy d-orbital to a higher-energy d-orbital. [✓] The colour observed is complementary in colour to the light that is absorbed. [✓] [✓] ligands cause degenerate levels to split [✓] energy gap absorbs visible wavelength / promote e$^-$ lower to higher level [✓] colour seen is complementary 3[✓] – 2m, 2[✓] – 1m
			[Total: 25]

3 **(a)** Boeing 787-9 Dreamliners are equipped with electronically dimmable windows. When a constant current is applied, electrochemical reactions happen within a panel and the conversion of colourless viologen dication to viologen radical cation forms an intense dark purple that shields out sunlight. A simplified diagram together with the chemical changes is shown.



The viologen dication and phenazine are aromatic species. Hückel's rule states that planar cyclic species with 4n+2 pi electrons, where n = 0, 1, 2 ..., are considered aromatic.

(i) State the hybridisation of the nitrogen atoms in the viologen dication. [1]

sp^2

(ii) State the number of pi electrons in phenazine. [1]

14

(iii) State the electrode at which the conversion of 5,10-dihydrophenazine to phenazine occurs. [1]

Anode

(iv) Write the half-equation for the reaction of 5,10-dihydrophenazine to phenazine in alkaline medium. You may write the names of both compounds respectively. [1]

5,10-dihydrophenazine + $2OH^- \longrightarrow$ phenazine + $2H_2O + 2e^-$

(v) 0.0300 g of 5,10-dihydrophenazine is finely coated on to one side of the panel.

Calculate the time needed to react all of the coated 5,10-dihydrophenazine to completely darken a window panel, given that a constant current of 0.150 A is supplied. [4]

M_r of 5,10-dihydrophenazine = 182.0 [1]

$n_{5,10\text{-dihydrophenazine}} = \frac{0.0300}{182.0} = 0.000165$ mol
$n_e = 0.000165 \times 2 = 0.000330$ mol [1] (allow ecf from (iv))

$Q = n_eF = 0.000330 \times 96500 = 31.8$ C [1]

$Q = It$
$t = Q/I = 31.8/0.150 = 212$ s [1]

(b) It is mandatory for all aircrafts to provide an inflatable life vest for every passenger. One particular model of life vests uses a rapid inflation system of compressed CO_2 in a canister.

A student read that the canisters typically pack 11.0 g of CO_2 and commented that the amount of CO_2 present will inflate a life vest fully to 6.00 dm^3 in capacity.

(i) Show how the student obtained 6.00 dm^3 as the capacity of the life vest and state the assumption made in the calculation. [2]

Vol. $CO_2 = \frac{11.0}{44.0}$ mol x 24.0 $dm^3\ mol^{-1}$ = 6.00 dm^3 [1]

Assumption is that the life vest was inflated at r.t.p. conditions (1 atm, 293 K). [1]

Don't penalise 3sf.

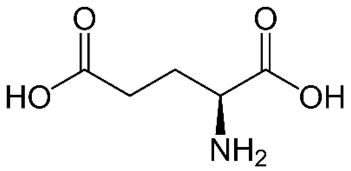
(ii) State two assumptions of the ideal gas law which allowed the student to make the calculations. [2]

1. Volume occupied by particles is negligible compared to the volume of space around them.
2. Negligible intermolecular forces exist between the particles.
3. Collisions are elastic and of negligible duration. (3 choose 2)

(c) Passengers on planes often find that they are more drawn to *umami*-rich flavours as the sweet and salty tastes are dulled due to changes in altitude.

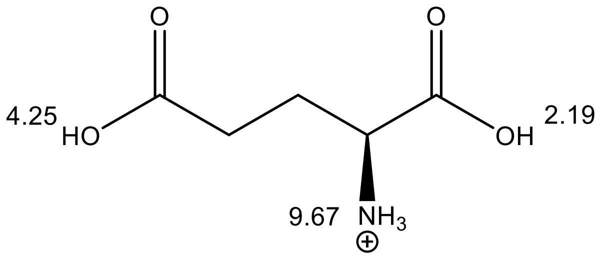
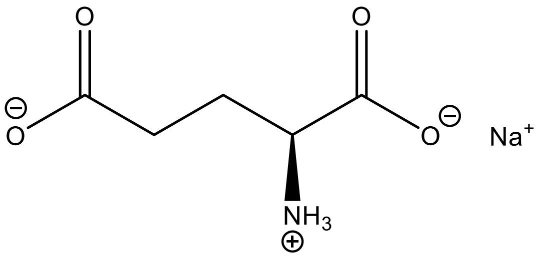
Monosodium glutamate (MSG) is one compound responsible for providing *umami* flavouring and it is the monosodium salt of glutamic acid.

The pK_a values associated with glutamic acid are 2.19, 4.25 and 9.67.



glutamic acid

(i) Draw the structure of glutamic acid at pH 1 and assign the three pK_a values. [2]

			 Structure [1]. 3 correct [1].
		(ii)	Draw the structure of monosodium glutamate. [1]  Na^+ can be anywhere. Allow molecular form and 1 COO^- group. ECF pk_{a1} from previous structure.
			[Total: 15]

Section B

Answer **one** question from this section.

4 **(a)** The thermal decomposition reactions for calcium ethanoate and calcium methanoate are given as follows:

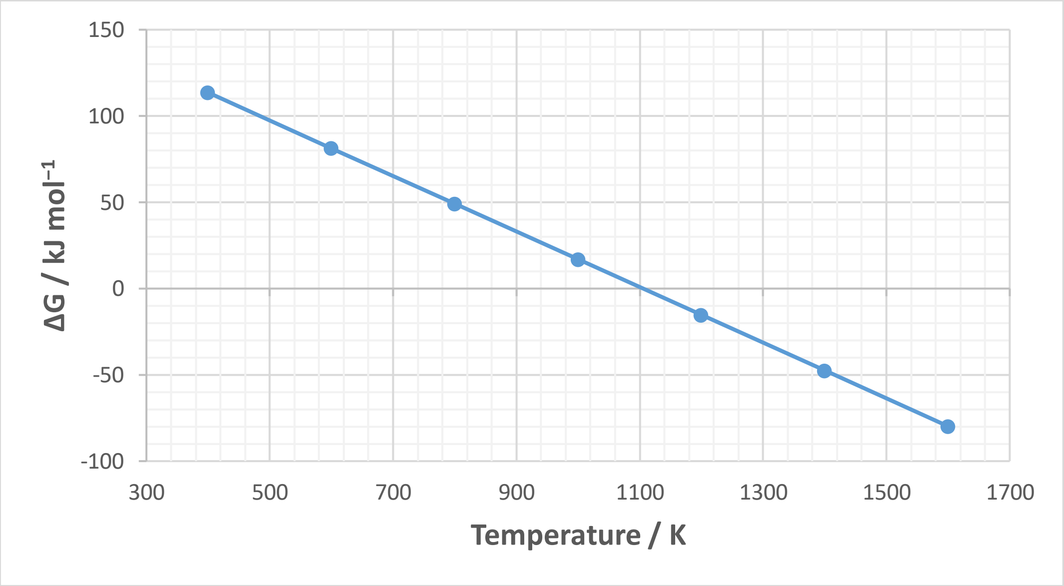
$Ca(HCOO)_2 \rightarrow CaCO_3 + HCHO$

$Ca(CH_3COO)_2 \rightarrow CaCO_3 + CH_3COCH_3$

Predict the organic product, other than propanone and methanal, when a mixture of calcium methanoate and calcium ethanoate undergoes thermal decomposition. [1]

CH_3CHO **[1]**

(b) The following Ellingham diagram shows the variation of Gibbs free energy change with temperature for the thermal decomposition of calcium carbonate.



(i) State the range of temperatures where solid calcium carbonate would decompose upon heating. [1]

T > 1100 Kelvin or T ≥ 1000 K (where $\Delta G < 0$ kJ mol^{-1}), cancel upper bound.

(ii) Calculate the entropy change of the reaction. [1]

Gradient of Line = $-\Delta S$

$[115 - (-80)] \div (400 - 1600) = -\Delta S$

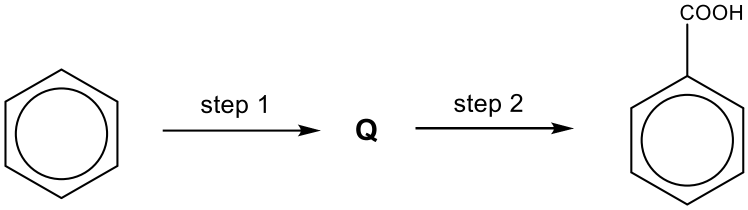
$\Delta S = +0.1625$ kJ mol^{-1} K^{-1} = +163 J mol^{-1} K^{-1} (3sf)

(iii) Hence, calculate the enthalpy change of the reaction. [1]

$\Delta G = \Delta H - T\Delta S$
$0 = \Delta H - (1100)(+163)$ [Choose any data point.]
$\Delta H = +179{,}300$ J mol^{-1} = +179 kJ mol^{-1} (3sf)

	(c)	Dolomite consists of $CaCO_3$ and $MgCO_3$ with the formula $CaMg(CO_3)_2$. It can be added to soil or marine aquarium as a pH buffer.	
		(i)	Write a balanced equation for the action of heat on dolomite. [1] $CaMg(CO_3)_2 \rightarrow CaO + MgO + 2CO_2$
		(ii)	Each carbonate is heated separately. Predict and explain the difference in the thermal decomposition temperatures of the two carbonates. [3] $MgCO_3$ has lower thermal decomposition temperature than $CaCO_3$. **[1]** Mg^{2+} is smaller than Ca^{2+}. Mg^{2+} has greater charge density (and hence greater polarising power) than Ca^{2+}. **[1]** Mg^{2+} polarised the CO_3^{2-} ion to a greater extent compared to Ca^{2+}. The C−O bond is weakened more. Less energy is needed to break it. **[1]** Hence $MgCO_3$ has lower thermal decomposition temperature.
		(iii)	Explain why Li_2CO_3 decomposes in a similar way compared to these two carbonates. [1] Li^+ is smaller than Mg^{2+}, though Li^+ has smaller charge than Mg^{2+}. Li^+ has the similar charge density (and hence similar polarising power) as Mg^{2+}. **[1]**
	(d)	**(i)**	Predict and explain the difference in melting points of calcium oxide and magnesium oxide. [2] $Lattice\ Energy \propto \left\lvert\frac{Q_+Q_-}{r_+ + r_-}\right\rvert$ Mg^{2+} is smaller **[√]** than Ca^{2+}. The electrostatic attraction between Mg^{2+} and O^{2-} is stronger **[√]** than that between Ca^{2+} and O^{2-}. More energy is required to separate the Mg^{2+} and O^{2-} ions. **Two [√]: [1]** Hence MgO has higher melting point and boiling point than CaO. **[1]**
		(ii)	In power plant or trash incineration plant, large quantities of sulfur dioxide gas are produced. Calcium oxide can be used to remove sulfur dioxide from these exhaust gases in a process called flue-gas desulfurisation. $CaO + SO_2 \rightarrow CaSO_3$ State the type of reaction for the above reaction. [1] Acid-Base **[1]**
	(e)	Benzoic acid is an important precursor for the industrial synthesis of many other organic substances. Its salts are also used as food preservatives.	

(i) Benzoic acid can be made from benzene by a two-step synthesis.



For steps 1 and 2, state the

- reagents and conditions, and
- type of reaction.

[4]

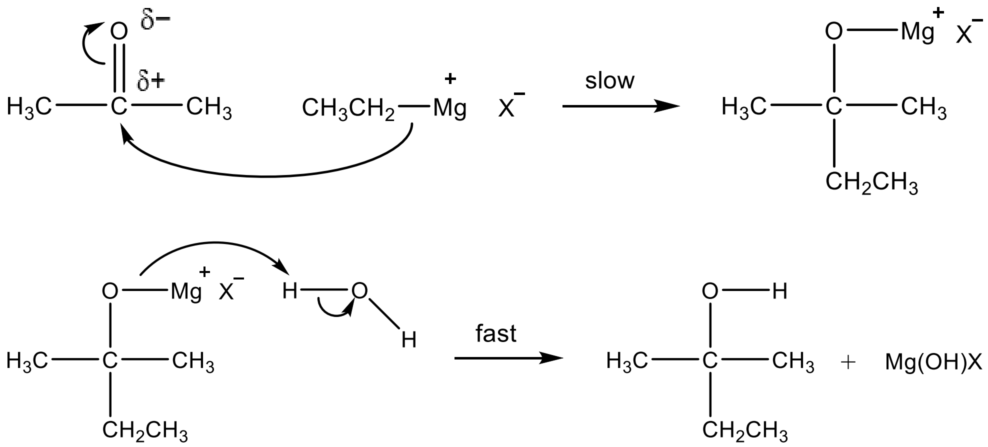
	Step 1	Step 2
Reagents and Conditions	CH_3Br and $FeBr_3$ **[1]** Room Temperature	$KMnO_4$(aq) **[1]** Dilute H_2SO_4(aq) Heat under reflux
Type of Reaction	Electrophilic Substitution **[1]**	Strong Oxidation **[1]**

(ii) Group 2 elements are known to form organometallic compounds. One example is the Grignard reagent with general formula RMgX. It is produced by reacting an alkyl halide or aryl halide with magnesium.

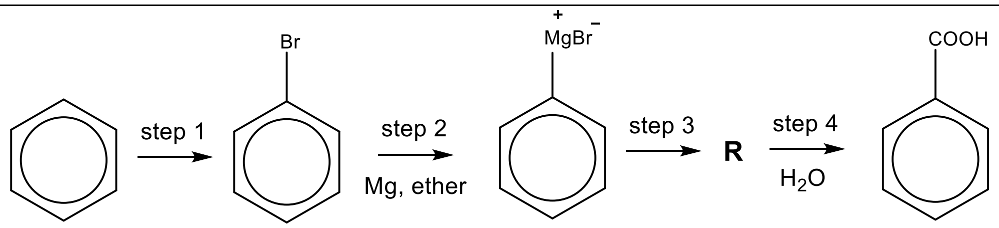
$RX + Mg \rightarrow R\text{–}Mg^+ X^-$ where X can be C*l* or Br.

The carbon-magnesium covalent bond is polarised as such; $\overset{\delta-}{C}-\overset{\delta+}{Mg}$.

Grignard reaction is important in making a new C–C bond. The mechanism for the reaction of ethylmagnesium bromide with propanone is shown as follows.

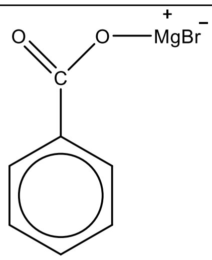


Benzoic acid can also be made from benzene by a four-step synthesis, using the Grignard reagent.



For step 3, state the reagent and intermediate **R**.

For steps 3 and 4, state the type of reaction. [4]

	Step 3	Step 4
Reagent	CO_2 **[1]**	
Intermediate **R**	 **[1]**	
Type of Reaction	Nucleophilic Addition **[1]**	Hydrolysis **[1]**

[Total: 20]

5 (a) (i) A compound **X** consists only of carbon, hydrogen and oxygen. During the complete combustion of 4 g of the compound, 8 g of carbon dioxide and 3.273 g of water were produced.

Determine the empirical formula of the compound **X**. [2]

	C	H	O
Mass / gram	(8)(12.0/44.0) = 2.182	(3.273)(2/18.0) = 0.3637	4 – 2.182 – 0.3637 = 1.454
Amount / mole	0.1818	0.3637	0.09088
Simplest Ratio	2	4	1

Empirical Formula: C_2H_4O **[1]** **Table [1]**

(ii) Another 4 g sample of compound **X** was vaporised at 160 °C and 101 kPa, and found to occupy a volume of 1620 cm^3.

Determine the relative molecular mass of this compound. [1]

PV = nRT
$(101{,}000)(1620 \div 10^{-6}) = (8.31)(160+273)(4 \div Mr)$
Mr = 88.0

(iii) Hence determine the molecular formula of compound **X**. Show your working clearly. [1]

(M_r of C_2H_4O) x n = 88.0
n = 2
Molecular Formula of X is $C_4H_8O_2$.

(b) Butanoic acid is used in the preparation of various esters. These esters have pleasant aromas or tastes. As a consequence, they are used as food and perfume additives.

(i) Biological methods have been developed to produce methane from waste organic matter using bacteria.

Based on the changes in oxidation numbers of carbon, construct a balanced equation for the disproportionation of **aqueous** butanoic acid to produce methane and carbon dioxide only. [1]

$2CH_3CH_2CH_2COOH + 2H_2O \rightarrow 5CH_4 + 3CO_2$

(ii) Given the following data,

- Enthalpy change of combustion of butanoic acid is −2184 kJ mol^{-1}.
- Enthalpy change of combustion of methane is −890 kJ mol^{-1}.

Calculate the enthalpy change for the reaction in **(b)(i)** for **liquid** butanoic acid instead of aqueous butanoic acid. [1]

$2CH_3CH_2CH_2COOH(l) + 2H_2O(l) \rightarrow 5CH_4(g) + 3CO_2(g)$
$\Delta H^{e}_{r} = (2)(-2184) - (5)(-890) = +82$ kJ mol^{-1}

(iii) Given that

$CH_3CH_2CH_2COOH(l) \rightarrow CH_3CH_2CH_2COOH(aq)$ $\Delta H^{\ominus}_{soln} = -16.7\ kJ\ mol^{-1}$

Use you answer in **(b)(ii)** to calculate the enthalpy change of reaction in **(b)(i)**. [2]

$$\begin{tikzcd}
2CH_3CH_2CH_2COOH(aq) + 2H_2O(l) \arrow[r, "\Delta H^{\ominus}_r"] & 5CH_4(g) + 3CO_2(g) \\
2CH_3CH_2CH_2COOH(l) + 2H_2O(l) \arrow[u, "(-16.7)(2)"'] \arrow[ur, "+82"'] &
\end{tikzcd}$$

[1] cycle

By Hess's Law,

$\Delta H^{\ominus}_r = -(-16.7)(2) + (+82) = +115\ kJ\ mol^{-1}$ (3sf) **[1]**

(iv) Butanoic acid boils at 117.7 ºC. During boiling, the liquid phase is at equilibrium with the gas phase.

Calculate the entropy change of vaporisation of butanoic acid, given that the enthalpy change of vaporisation of butanoic acid is $+52.0\ kJ\ mol^{-1}$. [1]

At boiling, $\Delta G_{vap} = 0$

$\Delta H_{vap} - T\Delta S_{vap} = 0$

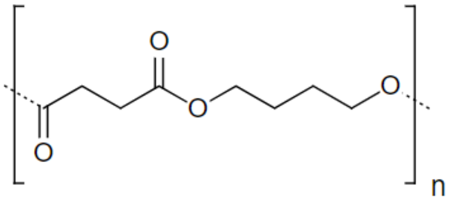
$\Delta S_{vap} = \Delta H_{vap} \div T = +52{,}000 \div (117.7 + 273) = +133\ J\ mol^{-1}\ K^{-1}$

(v) Trouton's Rule states that the entropy change of vaporisation of many liquids, such as benzene and propanone, is about $+88\ J\ mol^{-1}\ K^{-1}$.

Compare and explain the calculated result in **(b)(iv)** in relation to Trouton's Rule. [1]

$\Delta S^{\ominus}_{vap}$(butanoic acid) is more positive than $+85\ J\ mol^{-1}\ K^{-1}$, as hydrogen bonds between butanoic acid molecules reduces its entropy in the liquid state.

(c) Polybutylene succinate (PBS) is a polyester used in packaging. It is receiving renewed interest due to increased demand for biodegradable polymers.



Polybutylene succinate

Hydrolysis of PBS produces two monomers **E** and **F**.

E can be reduced to **F**.

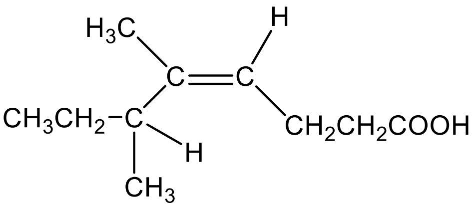
When an organic compound **D**, $C_{10}H_{18}O_2$ is heated with acidified potassium manganate (VII), two products, **E**, $C_4H_6O_4$ and **G**, $C_6H_{12}O$ are formed.

G produces a yellow precipitate on warming with iodine in aqueous sodium hydroxide, and rotates the plane of polarised light.

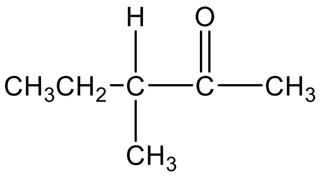
Upon gentle heating, **E** produces a neutral compound **H**, $C_4H_4O_3$, which does not react with sodium metal or give a precipitate with 2,4-dinitrophenylhydrazine.

Suggest structures for **D** to **H**, and explain the observations described above. [7]

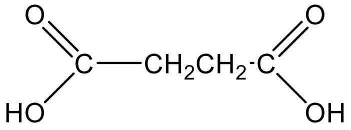
D :



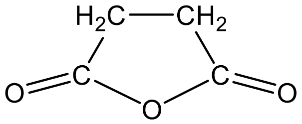
G :



E :

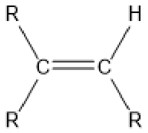
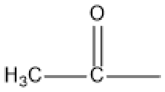


H :



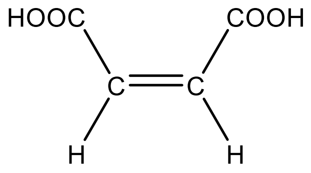
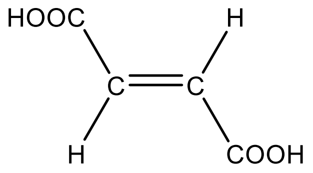
F : $HO—CH_2CH_2CH_2CH_2−OH$

Structures: [1] each. Total = [5]

Information	Type of Reaction	Deduction
D, $C_{10}H_{18}O_2$ is heated with acidified potassium manganate (VII), two products, **E**, $C_4H_6O_4$ and **G**, $C_6H_{12}O$ are formed.	Strong Oxidation	**D** has trisubstituted alkene:  √
G produces a yellow precipitate on heating with iodine in aqueous sodium hydroxide.	Mild Oxidation	**G** has this:  √
G rotates the plane of polarised light.		**G** has chiral carbon. √
Upon gentle heating, **E** produces a neutral compound **H**, $C_4H_4O_3$, which does not react with sodium metal or give a precipitate with 2,4-dinitrophenylhydrazine.	Dehydration	**H** is not carboxylic acid, alcohol, ketone, or aldehyde. OR **H** is anhydride. √

Deduction: 4 ticks: [2] ; 2 or 3 ticks: [1] ; 1 tick : [0]

(d) Maleic acid and fumaric acid are two isomers with the same molecular and structural formulae, but with very different physical properties.

	 maleic acid	 fumaric acid
melting point / ºC	130	287
pKa$_1$	1.9	3.0
pKa$_2$	6.5	4.5

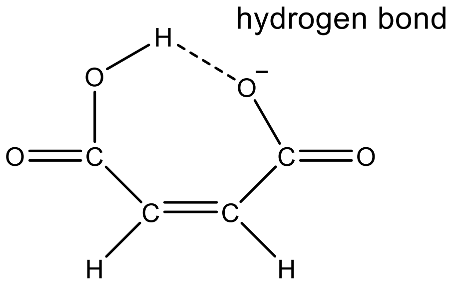
(i) Give two reasons to explain why maleic acid has a lower melting point than fumaric acid. [2]

Maleic acid has intra-molecular hydrogen bonds due to close proximity of its two –COOH groups. It has less inter-molecular hydrogen bonds. **[1]**

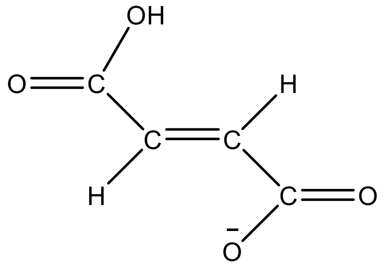
Maleic acid has lower packing efficiency of molecules in the solid state. **[1]** The molecules are further apart. There will be weaker forces of attraction between molecules.

Hence less energy needed to separate the molecules. Maleic acid has lower melting point.

(ii) Explain why maleic acid has a lower pKa$_1$ value than fumaric acid. [1]



Carboxylate ion of Maleic acid



Carboxylate ion of Fumaric acid

Due to close proximity of the two –COOH groups, intra-molecular hydrogen bond can be formed in the carboxylate ion of maleic acid **[√]**. But such intra-molecular hydrogen bond is not possible in the carboxylate ion of fumaric acid.

This ion of maleic acid is more stable **[√]** and more readily formed than that of fumaric acid. Hence pKa$_1$ value of maleic acid is lower than that of fumaric acid.

Two [√] : 1 mark

[Total: 20]

ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY H2 **9729/03**

Paper 3 Free Response **2 September 2019**
2 hours

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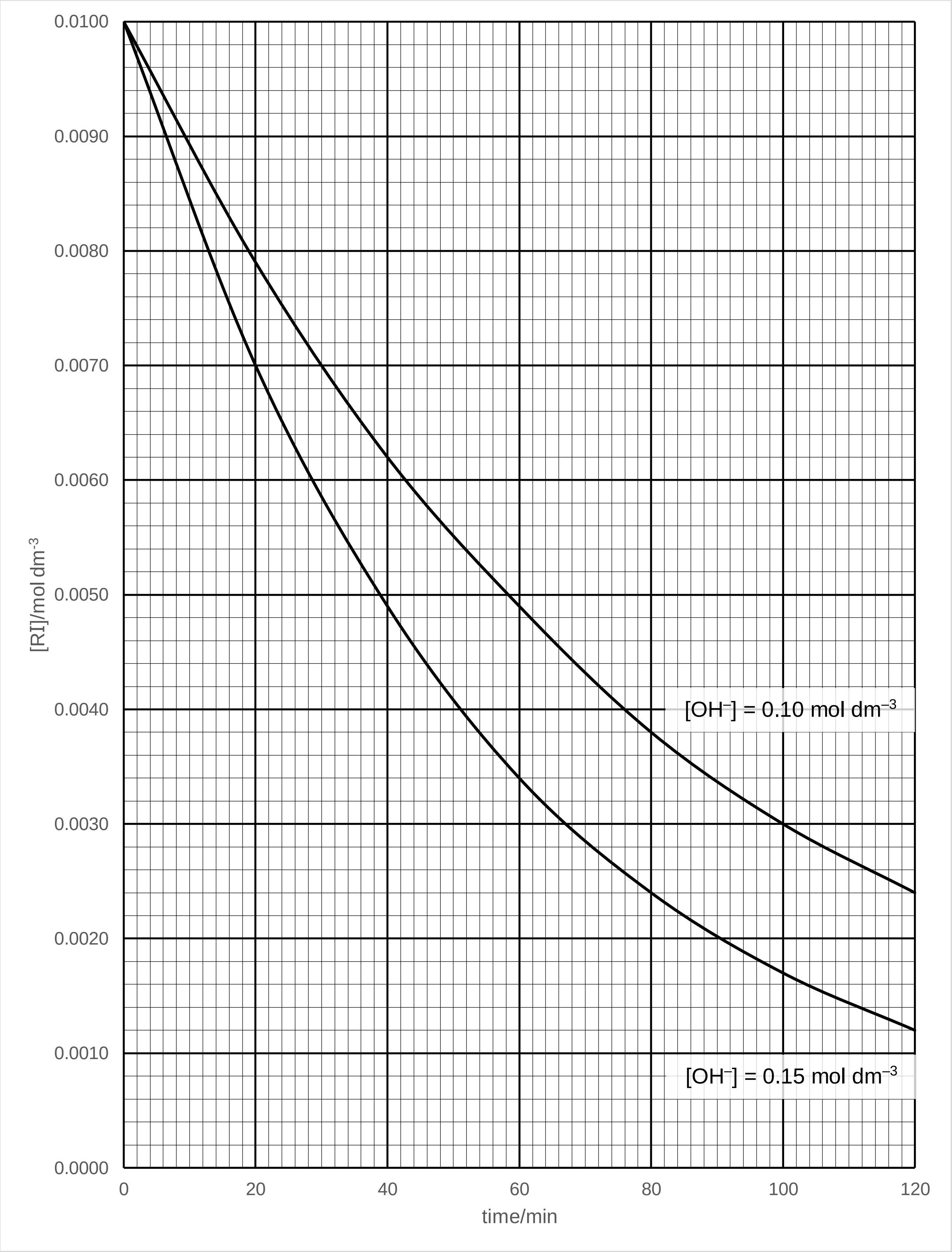

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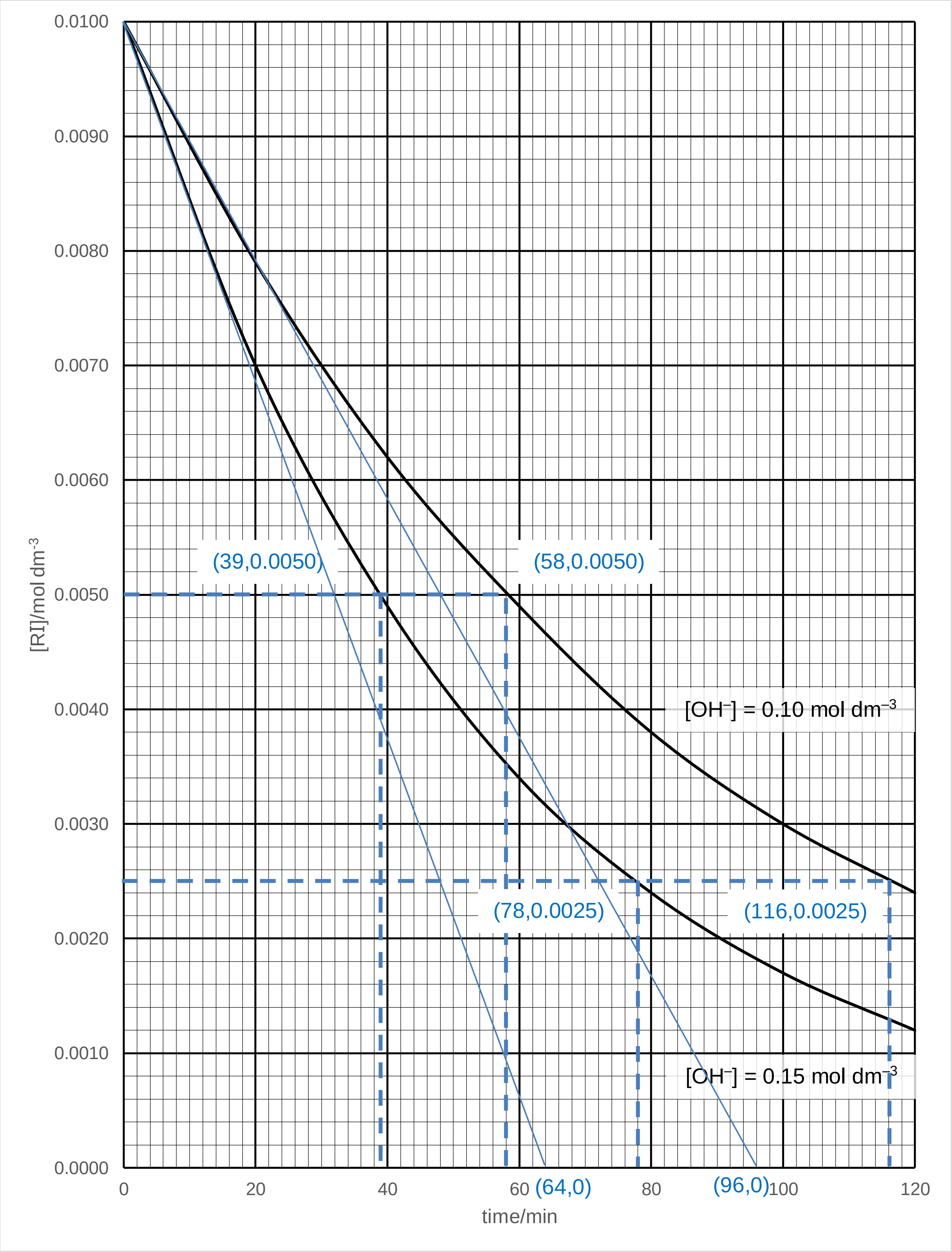


1 Determination of solubility product, K_{sp}, of magnesium carbonate

Magnesium carbonate is basic and sparingly soluble in water, resulting in its use as drying agents in sports and antacids.

You are to carry out a titrimetric analysis to determine the solubility product of magnesium carbonate.

A saturated solution of magnesium carbonate can be prepared by dissolving excess solid magnesium carbonate into a measured volume of water. The mixture will be left to stand for some time before filtering. The filtrate can then be analysed through titration with a standard solution of hydrochloric acid.

The saturated solution of magnesium carbonate, FA 1, has been prepared for you, according to the procedure in **(a)**.

(a) Preparation of FA 1

1. Use a measuring cylinder to transfer 50 cm^3 of deionised water into a 100 cm^3 beaker.
2. Use a spatula to add solid magnesium carbonate into the same beaker, a little at a time with stirring until no more can dissolve.
3. Leave to stand for five minutes.
4. Filter the mixture to obtain the filtrate in a 250 cm^3 conical flask. Ensure that the filtrate is clear. Do not wash the residue.
5. The filtrate is **FA 1**.

You are provided with:
FA 1 saturated solution of magnesium carbonate
FA 2 0.0300 mol dm^{-3} hydrochloric acid solution
Methyl orange indicator

(b) (i) Dilution of FA 2

The concentration of **FA 2** is too high to be used in the titration. You will dilute **FA 2** before using it in **(c)**.

1. Pipette 25.0 cm^3 of **FA 2** into a 250 cm^3 volumetric flask.
2. Top up to the mark with deionised water.
3. Stopper and shake thoroughly.

(b) **(ii)** Calculate the concentration of hydrochloric acid in **diluted FA 2**.

Conc = 0.025 x 0.03 / 0.25 = 0.00300 mol dm^{-3}

[HC*l*] in **diluted FA 2** = ………………………………… [1]

(c) **(i)** **Titration of FA 1 against diluted FA 2**

1. Fill the burette with **diluted FA 2** from **(b)**.
2. Use a pipette to transfer 10.0 cm^3 of **FA 1** into a 100 cm^3 conical flask.
3. Add 1 – 2 drops of methyl orange indicator into the conical flask.
4. Run **diluted FA 2** from the burette into this flask until the appropriate colour change is observed.
5. Record your titration results, to an appropriate level of precision, in the space provided.
6. Repeat steps 1 to 5 until consistent results are obtained.

Results

Final burette reading / cm^3	**17.00**	**34.00**	
Initial burette reading / cm^3	**0.00**	**17.00**	
Vol of diluted FA 2 used / cm^3	**17.00**	**17.00**	

[3]

(c) **(ii)** From your titrations, obtain a suitable volume of **diluted FA 2**, to be used in your calculations. Show clearly how you obtained this volume.

(17.00 + 17.00) / 2 = 17.00 cm^3

Volume of **diluted FA 2** = ... [3]

(d) **(i)** Calculate the concentration of carbonate ions in **FA 1**, using your answers in **(b)(ii)** and **(c)(ii).**

Amount of H$^+$ = ans in (b)(ii) x ans in (c)(ii)/1000

Amount of CO_3^{2-} = amount of H$^+$ / 2

Concentration of CO_3^{2-} = Amount of CO_3^{2-} / 0.0100
= 0.5 [ans in (b)(ii) x ans in (c)(ii)/1000] / 0.0100

$[CO_3^{2-}]$ in **FA 1** = ... [2]

(ii) Hence, calculate the solubility product of magnesium carbonate. State its units.

K_{sp} = $[Mg^{2+}][CO_3^{2-}]$ = [ans from (d)(i)]^2

Units = mol^2 dm^{-6}

K_{sp} of magnesium carbonate = ...

units .... [1]

(e) In **(a)**, it was instructed that the filtrate had to be clear and that the residue should not be washed.

(i) State and explain the effect on titre volume if the filtrate was **not** clear.

effect on titre volume **Titre volume will be larger**

explanation **The residual carbonate will react with the HC*l* added**

[1]

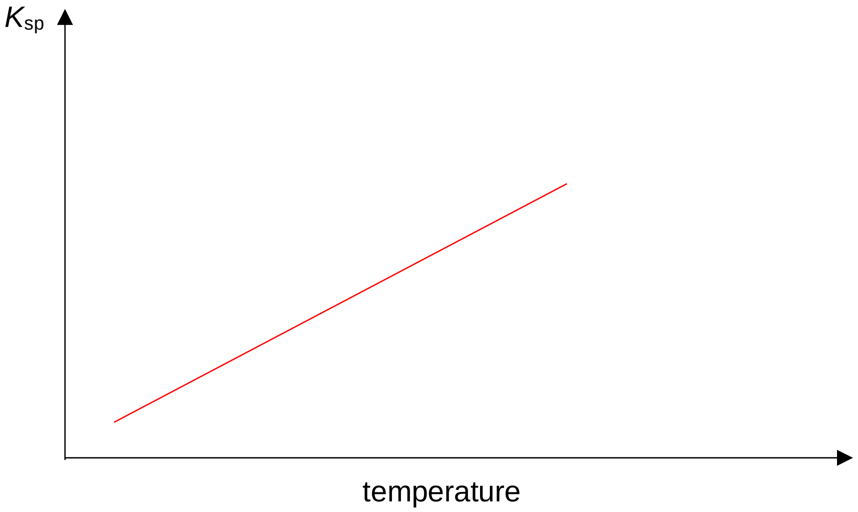
(ii) Explain why the residue should not be washed.

Washing the residue will disturb the equilibrium and cause the solution to be below saturation point (and the titration results will be lower than actual, leading to lower than expected K_{sp}).

[1]

(f) The dissociation of magnesium carbonate in water is endothermic.

Sketch a graph to show how the solubility product of magnesium carbonate varies with temperature. Explain your answer.



explanation

As dissociation is endothermic, increase in temperature cause POE of $MgCO_3(s) \leftrightarrow Mg^{2+}(aq) + CO_3^{2-}(aq)$ to shift right to favour reaction that absorbs heat, increasing concentration of ions, increasing K_{sp}

OR

When temperature increases, there is greater kinetic energy for the ions to break away from the ionic lattice, hence increasing concentration of ions, increasing K_{sp}

OR

Since reaction is endothermic, and entropy change is positive, when temperature is higher, reaction is more spontaneous, hence more $MgCO_3$ dissolves.

[2]

(g) Planning

The technique of gravimetry includes all analytical methods in which the analytical property is a measurement of mass or a change in mass. This technique can also be used in determining the solubility product of magnesium carbonate.

One of the possible approaches is to determine the mass of precipitate formed after mixing two solutions of known concentration. After preparing a mixture of saturated solution containing the precipitate, it can be passed through a pre-weighed filter paper that retains the precipitate. Residual moisture can be removed by drying the filter paper and the precipitate. The amount of precipitate can be determined, from which the concentration of ions in the saturated solution and hence solubility product can be determined.

(i) Plan an investigation to determine the solubility product of magnesium carbonate using the approach outlined above.

You are provided with the following:

- 0.400 mol dm^{-3} sodium carbonate solution
- 0.400 mol dm^{-3} magnesium nitrate solution
- apparatus and equipment normally found in a school laboratory

In your plan you should include brief details of:

- the apparatus you would use,
- the quantities you would use,
- the procedure you would follow,
- the measurements you would make to allow for gravimetric analysis.

- **Measure 50.00 cm^3 of sodium carbonate solution and 50.00 cm^3 magnesium nitrate solution using two separate 50.00 cm^3 burettes into a 250 cm^3 beaker (and place the beaker in a temperature controlled water bath)**
- **Stir the mixture and leave to stand for some time.**
- **Filter the mixture using a pre-weighed filter paper (M1 g)**
- **Dry precipitated $MgCO_3$ together with filter paper**
- **Weigh the dried precipitated $MgCO_3$ together with the filter paper (M2 g).**

[4]

(ii) Show how the measurements recorded in **(g)(i)** can be used to calculate the concentration of Mg^{2+} and CO_3^{2-}, in mol dm^{-3}, in the saturated solution.

Amount of ppt = (M2-M1)/ Mr of $MgCO_3$ = amount of Mg^{2+} not dissolved = amount of CO_3^{2-} not dissolved

Therefore, amount of Mg^{2+} dissolved = 0.4 x 50/1000 - (M2-M1)/Mr of $MgCO_3$
amount of CO_3^{2-} dissolved = 0.4 x 50/1000 - (M2-M1)/Mr of $MgCO_3$

concentration of Mg^{2+} = [0.4 x 50/1000 - (M2-M1)/ Mr of $MgCO_3$]/100/1000
concentration of CO_3^{2-} = [0.4 x 50/1000 - (M2-M1)/ Mr of $MgCO_3$]/100/1000

***depends on mass and volume used in g(i)**

[2]

[Total: 20]

2 Determination of the concentration of $NaHCO_3$ and the value for the enthalpy change of reaction of $NaHCO_3$ and NaOH

FA 3 is a solution of sodium hydrogencarbonate, $NaHCO_3$, of unknown concentration.
FA 4 is 1.50 mol dm^{-3} sodium hydroxide, NaOH.

In this experiment, you will perform a thermometric titration to determine the equivalence point for the reaction of **FA 3** and **FA 4**, where maximum heat is evolved, without the use of an indicator.

You will follow the reaction by measuring the temperature as volumes of **FA 4** are added in regular portions from a burette to a fixed volume of **FA 3** placed in a Styrofoam cup.

The data obtained will allow you to determine the temperature change and then analyse your results graphically in order to determine the equivalence point of the reaction.

In an appropriate format in the space provided on the next page, prepare a table in which you may record the following after each addition of **FA 4**:

- Total volume of **FA 4** added from the burette, starting from 0.00 cm^3, up to the point in time
- Total volume of solution in the cup, V_{total}
- Temperature measured, T

In the same table, you also need to calculate the corresponding values of:

- $\Delta T = T - T_0$, where T_0 is the initial temperature of **FA 3**
- ($V_{total} \times \Delta T$) to 3 significant figures

State clearly the units of each parameter on the header of the column.

Procedure

1. Fill the burette to the 0.00 cm^3 mark with **FA 4**.
2. Place the Styrofoam cup in a 250 cm^3 beaker to provide support for the cup.
3. Use a measuring cylinder to transfer 40.0 cm^3 of **FA 3** into the cup.
4. Measure and record the initial temperature of **FA 3**, T_0.
5. Run 3.00 cm^3 of **FA 4** from the burette into the cup, stir the solution with the thermometer and record the maximum temperature, T.
6. Immediately run a further 3.00 cm^3 of **FA 4** from the burette into the cup, stir and record the maximum temperature as before.
7. Continue the addition of **FA 4** in 3.00 cm^3 and record the maximum or minimum temperature reached after each addition. Do this until a total of 45.00 cm^3 of solution have been run from the burette.

(a) (i) Results

Total volume of FA 4 added, V_{FA4} / cm^3	Total volume of solution in the cup, V_{total} / cm^3	Temperature measured, T / °C	$\Delta T = T - T_0$ / °C	($V_{total} \times \Delta T$) / cm^3 °C
0.00	40.0			
3.00	43.0			
6.00	46.0			
9.00	49.0			
12.00	52.0			
15.00	55.0			
18.00	58.0			
21.00	61.0			
24.00	64.0			
27.00	67.0			
30.00	70.0			
33.00	73.0			
36.00	76.0			
39.00	79.0			
42.00	82.0			
45.00	85.0			

Precision:

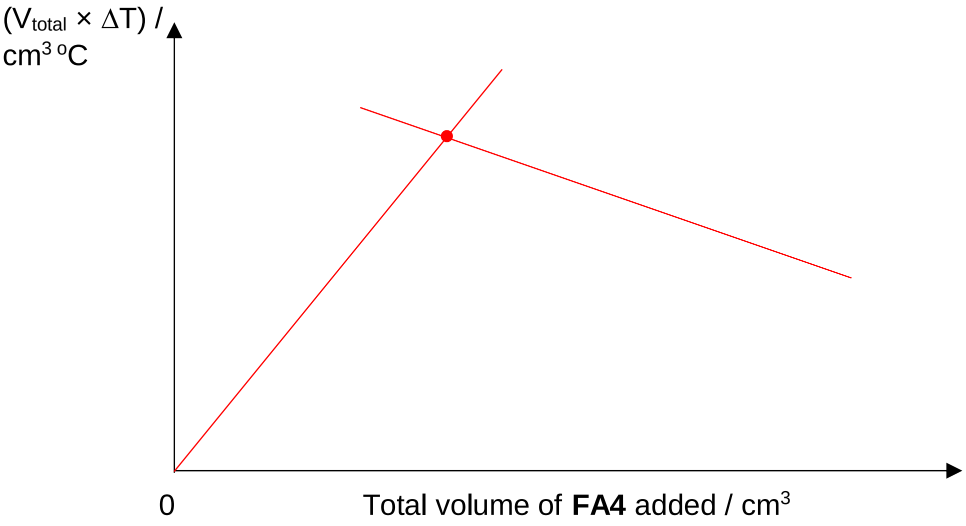
- 2 d.p. for V_{FA4}
- 1 d.p. for T and ΔT
- 3 s.f. for ($V_{total} \times \Delta T$)

[3]

(a) **(ii)** Plot a graph of (V_{total} × ΔT) against total volume of **FA 4** added.

Draw two best-fit straight lines for the ascending and descending points respectively. Extrapolate both lines until they intersect to determine the:

- equivalence point of the reaction, V_{eq}
- maximum value of (V_{total} × ΔT)



V_{eq} = ...

Value of (V_{total} × ΔT) = ... [5]

(b) **(i)** Write down the chemical equation, with state symbols, for the reaction of $NaHCO_3$ and NaOH.

$NaHCO_3\ (aq) + NaOH\ (aq) \rightarrow Na_2CO_3\ (aq) + H_2O\ (l)$

[1]

(ii) Calculate the concentration of $NaHCO_3$ in **FA 3**.

n_{NaOH} = (V_{eq}/1000 x 1.50) mol
$n_{NaHCO3} = n_{NaOH}$
[$NaHCO_3$] = (n_{NaHCO3} ÷ 40.0/1000) mol dm^{-3}

***obtained from the intersection point in (a)(ii)**

[$NaHCO_3$] in **FA 3** = ... [2]

(iii) Given that the heat capacity of solution is 4.2 J K^{-1} cm^{-3}, calculate the enthalpy change of the reaction of $NaHCO_3$ and NaOH, ΔH_r.

Heat released, q = mcΔT = 4.2(V_{total} × ΔT) J
ΔH_r = (-q/n_{NaHCO3}) J mol^{-1}

***obtained from the intersection point in (a)(ii)**

ΔH_r = ... [2]

(c) You plotted a graph of (V_{total} × ΔT) against total volume of **FA 4** added in **(a)(ii)**. Suggest, with explanation, whether plotting a graph of ΔT against total volume of **FA 4** instead is likely to yield a more accurate result for the equivalence point.

Doing so is unlikely to yield a more accurate result. As V_{total} is not constant (or increasing) throughout the experiment,

- **ΔT will vary less linearly with (or not be directly proportional to) the total volume of FA4 added**
  OR
- **curves may be obtained instead since the same amount of heat energy released is distributed over a larger volume**

[2]

(d) Performing the same experiment using a burette instead of a measuring cylinder to transfer **FA 3** into the Styrofoam cup is **not** expected to improve the accuracy of the results obtained. Suggest a reason why is this so.

Heat loss to the surroundings throughout the experiment outweighs the improved accuracy of using a burette to transfer FA3.

[1]

(e) You are provided with methyl orange indicator in **Question 1**.

Explain whether methyl orange indicator can be used to determine the end-point of the titration of $NaHCO_3$ against NaOH instead of performing thermometric titration.

$NaHCO_3$ acts as a weak acid in the presence of a strong alkali of NaOH, as such the equivalence point (at a relatively high pH) lies outside of the (relatively low) working pH range of methyl orange indicator.

[2]

[Total: 18]

3 Qualitative Analysis and Planning

You are provided with four different compounds labelled **FA 5**, **FA 6**, **FA 7** and **FA 8**. Each of these four bottles contains one of the following:

primary alcohol aldehyde monocarboxylic acid metal halide

You will identify **FA 5**, **FA 6**, **FA 7** and **FA 8** by carrying out the prescribed experiments, as well as planning and conducting your own experiments.

For the prescribed experiments, record your observations in Table 3.1 below carefully. Unless otherwise stated, the volumes given below are approximate and should be estimated rather than measured.

You are advised to carry out the experiments in test (a) and (b) on each unknown compound one at a time. You are not required to carry out experiments in test (c) as the results are provided.

Table 3.1

Test		*Observations*			
		FA 5	**FA 6**	**FA 7**	**FA 8**
(a)	To 1 cm depth of the unknown in a test-tube, add 1 cm depth of sodium nitrite. **Test and determine if any gas is evolved.**	**effervescence** **pungent brown/ yellow gas evolved** **blue litmus paper turned red**	**effervescence** **pungent brown/ yellow gas evolved** **blue litmus paper turned red**	**no gas evolved**	**no gas evolved**
(b)	To 1 cm depth of the unknown in a test-tube, add 1 cm depth of dilute sulfuric acid, followed by 5 drops of potassium manganate(VII) solution. Place the test-tube in the hot water bath.	**purple $KMnO_4$ decolourised/ discharged upon standing in hot water bath**	**purple $KMnO_4$ turned brown/ yellow/ formed brown ppt/ decolourised/ discharged upon standing in hot water bath**	**purple $KMnO_4$ decolourised/ discharged / turned brown / turned colourless upon standing in the hot water bath**	**purple $KMnO_4$ decolourised/ discharged / turned colourless upon standing in the hot water bath**

	Test and determine if any gas is evolved.	**colourless odourless gas evolved** **blue litmus turned paper red** **gas produced white ppt with aqueous $Ca(OH)_2$**	**pungent gas evolved** **blue litmus turned red and bleached**	**no gas evolved**	**no gas evolved**
(c)	To 1 cm depth of aqueous iodine, add aqueous sodium hydroxide dropwise until a permanent yellow colour is obtained. Then add 3 drops of the unknown into the same test-tube. Place the test-tube in the hot water bath.	No yellow precipitate	No yellow precipitate	Yellow precipitate obtained	Yellow precipitate obtained

[4]

(d) **Identifying unknown metal halide**

(i) From your observations in Table 3.1, suggest which one of the unknown compounds is the metal halide. [1]

FA …**6**…

explanation… **It decolourised purple $KMnO_4$ with the production of a pungent gas which turns blue litmus paper red and then bleaches.** …

(ii) Suggest the reagent and carry out the test to confirm the identity of the halide in the metal halide. [2]

reagent … **silver nitrate** …

observations … **white ppt formed …**

FA …**6**……… contains …**chloride/ Cl^-** …anion.

(d) **(iii)** In Table 3.2 below, describe two tests that will allow you to identify the cation in the metal halide. Perform the tests and record the observations in the same table. Use only bench reagents provided. [3]

Table 3.2

Test	*Observations*
	FA … 6 …
Add NaOH(aq) dropwise until no further change is observed/ until in excess.	**White ppt formed soluble in excess NaOH.**
Add NH_3(aq) dropwise until no further change is observed/ until in excess.	**White ppt formed insoluble in excess NH_3(aq).**

The cation in metal halide is … **Al^{3+}** …

(iv) The nature of the cation of the metal halide in aqueous solution accounts for its observations in test **(a)**. Describe and explain the nature of the cation by means of an equation. [2]

equation … **$[Al(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Al(H_2O)_5(OH)]^{2+} + H_3O^+$**

explanation … **Since <u>Al^{3+} is small and highly charged/ has high charge density</u>, it undergoes <u>hydrolysis with water</u> to produce an acidic solution.**

(e) **Identifying organic liquids**

(i) The three unknown organic compounds are primary alcohol, aldehyde and monocarboxylic acid.

Based on your observations in tests **(a)** and **(b)**, identify which is the monocarboxylic acid. Suggest the identity of the monocarboxylic acid and support your answer by giving the evidence. [3]

FA …**5** …

The identity of monobasic carboxylic acid is …**methanoic acid/ HCOOH** …

evidence … **<u>In test (b), oxidation of methanoic acid by $KMnO_4$ produced CO_2 which turned blue litmus paper red/ white ppt with limewater.</u>**

(ii) Describe how you would conduct a chemical test, using only the bench reagents provided, to distinguish between the remaining two unknown organic compounds.

Carry out the chemical test.

With aid of your observations and results provided in test **(c)**, identify which is the primary alcohol and the aldehyde. [3]

chemical test … **Tollens' reagent (To 1 cm depth of $AgNO_3$, add NaOH(aq) dropwise till a ppt is formed. Then add NH_3(aq) dropwise till ppt dissolves completely.)**

observations … **silver mirror formed with FA8 but not FA7**

The primary alcohol is **FA** …**7**…

The identity of the primary alcohol is …**ethanol/ CH_3CH_2OH**…

The aldehyde is **FA** …**8**…

The identity of the aldehyde is …**ethanal/ CH_3CHO** …

[Total: 17]

END OF PAPER

Qualitative Analysis Notes
[ppt. = precipitate]

(a) Reactions of aqueous cations

cation	*reaction with*	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt. turning brown on contact with air insoluble in excess	green ppt. turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt. rapidly turning brown on contact with air insoluble in excess	off-white ppt. rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

anion	***reaction***
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, Cl^- (aq)	gives white ppt. with Ag^+(aq) (soluble in NH_3(aq))
bromide, Br^- (aq)	gives pale cream ppt. with Ag^+(aq) (partially soluble in NH_3(aq))
iodide, I^- (aq)	gives yellow ppt. with Ag^+(aq) (insoluble in NH_3(aq))
nitrate, NO_3^- (aq)	NH_3 liberated on heating with OH^-(aq) and A*l* foil
nitrite, NO_2^- (aq)	NH_3 liberated on heating with OH^-(aq) and A*l* foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, SO_4^{2-} (aq)	gives white ppt. with Ba^{2+}(aq) (insoluble in excess dilute strong acids)
sulfite, SO_3^{2-} (aq)	SO_2 liberated on warming with dilute acids; gives white ppt. with Ba^{2+}(aq) (soluble in dilute strong acids)

(c) Tests for gases

gas	***test and test result***
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	“pops” with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	***colour of element***	***colour in aqueous solution***	***colour in hexane***
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

1 Determination of solubility product, K_{sp}, of magnesium carbonate

Magnesium carbonate is basic and sparingly soluble in water, resulting in its use as drying agents in sports and antacids.

You are to carry out a titrimetric analysis to determine the solubility product of magnesium carbonate.

A saturated solution of magnesium carbonate can be prepared by dissolving excess solid magnesium carbonate into a measured volume of water. The mixture will be left to stand for some time before filtering. The filtrate can then be analysed through titration with a standard solution of hydrochloric acid.

The saturated solution of magnesium carbonate, FA 1, has been prepared for you, according to the procedure in **(a)**.

(a) Preparation of FA 1

1. Use a measuring cylinder to transfer 50 cm^3 of deionised water into a 100 cm^3 beaker.
2. Use a spatula to add solid magnesium carbonate into the same beaker, a little at a time with stirring until no more can dissolve.
3. Leave to stand for five minutes.
4. Filter the mixture to obtain the filtrate in a 250 cm^3 conical flask. Ensure that the filtrate is clear. Do not wash the residue.
5. The filtrate is **FA 1**.

You are provided with:
FA 1 saturated solution of magnesium carbonate
FA 2 0.0300 mol dm^{-3} hydrochloric acid solution
Methyl orange indicator

(b) (i) Dilution of FA 2

The concentration of **FA 2** is too high to be used in the titration. You will dilute **FA 2** before using it in **(c)**.

1. Pipette 25.0 cm^3 of **FA 2** into a 250 cm^3 volumetric flask.
2. Top up to the mark with deionised water.
3. Stopper and shake thoroughly.

(b) **(ii)** Calculate the concentration of hydrochloric acid in **diluted FA 2**.

[HC*l*] in **diluted FA 2** = ………………………………… [1]

(c) **(i)** **Titration of FA 1 against diluted FA 2**

1. Fill the burette with **diluted FA 2** from **(b)**.
2. Use a pipette to transfer 10.0 cm^3 of **FA 1** into a 100 cm^3 conical flask.
3. Add 1 – 2 drops of methyl orange indicator into the conical flask.
4. Run **diluted FA 2** from the burette into this flask until the appropriate colour change is observed.
5. Record your titration results, to an appropriate level of precision, in the space provided.
6. Repeat steps 1 to 5 until consistent results are obtained.

Results

[3]

(c) **(ii)** From your titrations, obtain a suitable volume of **diluted FA 2**, to be used in your calculations. Show clearly how you obtained this volume.

Volume of **diluted FA 2** = ……………………………… [3]

(d) **(i)** Calculate the concentration of carbonate ions in **FA 1**, using your answers in **(b)(ii)** and **(c)(ii).**

$[CO_3^{2-}]$ in **FA 1 =** ……………………………… [2]

(ii) Hence, calculate the solubility product of magnesium carbonate. State its units.

K_{sp} of magnesium carbonate = ………………………………….

units ……………………………… [1]

(e) In **(a)**, it was instructed that the filtrate had to be clear and that the residue should not be washed.

(i) State and explain the effect on titre volume if the filtrate was **not** clear.

effect on titre volume …………………………………………………………………

explanation ………………………………………………………………………

…………………………………………………………………………………………

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

(ii) Explain why the residue should not be washed.

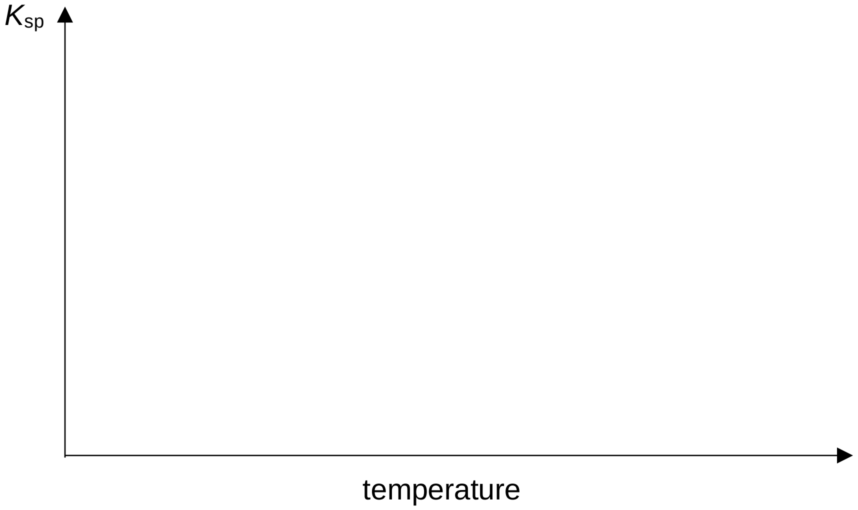
…………………………………………………………………………………………

…………………………………………………………………………………………

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

(f) The dissociation of magnesium carbonate in water is endothermic.

Sketch a graph to show how the solubility product of magnesium carbonate varies with temperature. Explain your answer.



explanation ……………………………………………………………………………………

……………………………………………………………………………………………………

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

(g) **Planning**

The technique of gravimetry includes all analytical methods in which the analytical property is a measurement of mass or a change in mass. This technique can also be used in determining the solubility product of magnesium carbonate.

One of the possible approaches is to determine the mass of precipitate formed after mixing two solutions of known concentration. After preparing a mixture of saturated solution containing the precipitate, it can be passed through a pre-weighed filter paper that retains the precipitate. Residual moisture can be removed by drying the filter paper and the precipitate. The amount of precipitate can be determined, from which the concentration of ions in the saturated solution and hence solubility product can be determined.

(i) Plan an investigation to determine the solubility product of magnesium carbonate using the approach outlined above.

You are provided with the following:

- 0.400 mol dm^{-3} sodium carbonate solution
- 0.400 mol dm^{-3} magnesium nitrate solution
- apparatus and equipment normally found in a school laboratory

In your plan you should include brief details of:

- the apparatus you would use,
- the quantities you would use,
- the procedure you would follow,
- the measurements you would make to allow for gravimetric analysis.

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…………………………………………………………………………………… [4]

(ii) Show how the measurements recorded in **(g)(i)** can be used to calculate the concentration of Mg^{2+} and CO_3^{2-}, in mol dm^{-3}, in the saturated solution.

[2]

[Total: 20]

2 Determination of the concentration of $NaHCO_3$ and the value for the enthalpy change of reaction of $NaHCO_3$ and NaOH

FA 3 is a solution of sodium hydrogencarbonate, $NaHCO_3$, of unknown concentration.
FA 4 is 1.50 mol dm^{-3} sodium hydroxide, NaOH.

In this experiment, you will perform a thermometric titration to determine the equivalence point for the reaction of **FA 3** and **FA 4**, where maximum heat is evolved, without the use of an indicator.

You will follow the reaction by measuring the temperature as volumes of **FA 4** are added in regular portions from a burette to a fixed volume of **FA 3** placed in a Styrofoam cup.

The data obtained will allow you to determine the temperature change and then analyse your results graphically in order to determine the equivalence point of the reaction.

In an appropriate format in the space provided on the next page, prepare a table in which you may record the following after each addition of **FA 4**:

- Total volume of **FA 4** added from the burette, starting from 0.00 cm^3, up to the point in time
- Total volume of solution in the cup, V_{total}
- Temperature measured, T

In the same table, you also need to calculate the corresponding values of:

- $\Delta T = T - T_0$, where T_0 is the initial temperature of **FA 3**
- ($V_{total} \times \Delta T$) to 3 significant figures

State clearly the units of each parameter on the header of the column.

Procedure

1. Fill the burette to the 0.00 cm^3 mark with **FA 4**.
2. Place the Styrofoam cup in a 250 cm^3 beaker to provide support for the cup.
3. Use a measuring cylinder to transfer 40.0 cm^3 of **FA 3** into the cup.
4. Measure and record the initial temperature of **FA 3**, T_0.
5. Run 3.00 cm^3 of **FA 4** from the burette into the cup, stir the solution with the thermometer and record the maximum temperature, T.
6. Immediately run a further 3.00 cm^3 of **FA 4** from the burette into the cup, stir and record the maximum temperature as before.
7. Continue the addition of **FA 4** in 3.00 cm^3 and record the maximum or minimum temperature reached after each addition. Do this until a total of 45.00 cm^3 of solution have been run from the burette.

(a) (i) Results

[3]

(a) **(ii)** Plot a graph of ($V_{total} \times \Delta T$) against total volume of **FA 4** added.

Draw two best-fit straight lines for the ascending and descending points respectively. Extrapolate both lines until they intersect to determine the:

- equivalence point of the reaction, V_{eq}
- maximum value of ($V_{total} \times \Delta T$)

V_{eq} = ……………………………………

Value of ($V_{total} \times \Delta T$) = …………………………….. [5]

(b) **(i)** Write down the chemical equation, with state symbols, for the reaction of $NaHCO_3$ and NaOH.

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

(ii) Calculate the concentration of $NaHCO_3$ in **FA 3**.

$[NaHCO_3]$ in **FA 3** = ………………………………… [2]

(iii) Given that the heat capacity of solution is 4.2 J K^{-1} cm^{-3}, calculate the enthalpy change of the reaction of $NaHCO_3$ and NaOH, ΔH_r.

ΔH_r = ………………………………… [2]

(c) You plotted a graph of ($V_{total} \times \Delta T$) against total volume of **FA 4** added in **(a)(ii)**. Suggest, with explanation, whether plotting a graph of ΔT against total volume of **FA 4** instead is likely to yield a more accurate result for the equivalence point.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

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

(d) Performing the same experiment using a burette instead of a measuring cylinder to transfer **FA 3** into the Styrofoam cup is **not** expected to improve the accuracy of the results obtained. Suggest a reason why is this so.

……………………………………………………………………………………………..

……………………………………………………………………………………………..

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

(e) You are provided with methyl orange indicator in **Question 1**.

Explain whether methyl orange indicator can be used to determine the end-point of the titration of $NaHCO_3$ against NaOH instead of performing thermometric titration.

……………………………………………………………………………………………..

……………………………………………………………………………………………..

……………………………………………………………………………………………..

……………………………………………………………………………………………..

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

[Total: 18]

3 Qualitative Analysis and Planning

You are provided with four different compounds labelled **FA 5**, **FA 6**, **FA 7** and **FA 8**. Each of these four bottles contains one of the following:

primary alcohol aldehyde monocarboxylic acid metal halide

You will identify **FA 5**, **FA 6**, **FA 7** and **FA 8** by carrying out the prescribed experiments, as well as planning and conducting your own experiments.

For the prescribed experiments, record your observations in Table 3.1 below carefully. Unless otherwise stated, the volumes given below are approximate and should be estimated rather than measured.

You are advised to carry out the experiments in test (a) and (b) on each unknown compound one at a time. You are not required to carry out experiments in test (c) as the results are provided.

Table 3.1

Test		*Observations*			
		FA 5	**FA 6**	**FA 7**	**FA 8**
(a)	To 1 cm depth of the unknown in a test-tube, add 1 cm depth of sodium nitrite. **Test and determine if any gas is evolved.**				
(b)	To 1 cm depth of the unknown in a test-tube, add 1 cm depth of dilute sulfuric acid, followed by 5 drops of potassium manganate(VII) solution. Place the test-tube in the hot water bath. **Test and determine if any gas is evolved.**				

(c)	To 1 cm depth of aqueous iodine, add aqueous sodium hydroxide dropwise until a permanent yellow colour is obtained. Then add 3 drops of the unknown into the same test-tube. Place the test-tube in the hot water bath.	No yellow precipitate	No yellow precipitate	Yellow precipitate obtained	Yellow precipitate obtained

[4]

(d) **Identifying unknown metal halide**

(i) From your observations in Table 3.1, suggest which one of the unknown compounds is the metal halide.

FA …………

explanation ……………………………………………………………………………..

…………………………………………………………………………………………

………………………………………………………………………………….. [1]

(ii) Suggest the reagent and carry out the test to confirm the identity of the halide in the metal halide.

reagent ……………………………………………………………………………

observations ………………………………………………………………………………

………………………………………………………………………………………

FA ………… contains …………………….. anion. [2]

(d) **(iii)** In Table 3.2 below, describe two tests that will allow you to identify the cation in the metal halide. Perform the tests and record the observations in the same table. Use only bench reagents provided.

Table 3.2

Test	*Observations*
	FA …………

The cation in metal halide is ..………………………… [3]

(iv) The nature of the cation of the metal halide in aqueous solution accounts for its observations in test **(a)**. Describe and explain the nature of the cation by means of an equation.

equation ………………………………………………………………………………..

explanation ……………………………………………………………………………..

……………………………………………………………………………………………

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

(e) **Identifying organic liquids**

(i) The three unknown organic compounds are primary alcohol, aldehyde and monocarboxylic acid.

Based on your observations in tests **(a)** and **(b)**, identify which is the monocarboxylic acid. Suggest the identity of the monocarboxylic acid and support your answer by giving the evidence.

FA …………

The identity of monocarboxylic acid is ……………………………………….

evidence ………………………………….……………………………….…………….

…………………………………….……………………………………….…………….

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

(ii) Describe how you would conduct a chemical test, using only the bench reagents provided, to distinguish between the remaining two unknown organic compounds.

Carry out the chemical test.

With aid of your observations and results provided in test **(c)**, identify which is the primary alcohol and the aldehyde.

chemical test ………………………………………………………………………...

…………………………………………………………………………………………

observations ……………………………………………………………………………

…………………………………………………………………….…………………………

The primary alcohol is **FA** …………

The identity of the primary alcohol is ……………………………………….

The aldehyde is **FA** …………

The identity of the aldehyde is ………………………………………. [3]

[Total: 17]

END OF PAPER

Qualitative Analysis Notes
[ppt. = precipitate]

(a) Reactions of aqueous cations

cation	***reaction with***	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt. turning brown on contact with air insoluble in excess	green ppt. turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt. rapidly turning brown on contact with air insoluble in excess	off-white ppt. rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

anion	***reaction***
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, Cl^- (aq)	gives white ppt. with Ag^+(aq) (soluble in NH_3(aq))
bromide, Br^- (aq)	gives pale cream ppt. with Ag^+(aq) (partially soluble in NH_3(aq))
iodide, I^- (aq)	gives yellow ppt. with Ag^+(aq) (insoluble in NH_3(aq))
nitrate, NO_3^- (aq)	NH_3 liberated on heating with OH^-(aq) and A*l* foil
nitrite, NO_2^- (aq)	NH_3 liberated on heating with OH^-(aq) and A*l* foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, SO_4^{2-} (aq)	gives white ppt. with Ba^{2+}(aq) (insoluble in excess dilute strong acids)
sulfite, SO_3^{2-} (aq)	SO_2 liberated on warming with dilute acids; gives white ppt. with Ba^{2+}(aq) (soluble in dilute strong acids)

(c) Tests for gases

gas	***test and test result***
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	“pops” with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	***colour of element***	***colour in aqueous solution***	***colour in hexane***
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple