INNOVA JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION
in preparation for General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME			
CLASS		INDEX NUMBER	

CHEMISTRY

9729/01

Paper 1 Multiple Choice

15 September 2017

1 hour

Additional Materials: *Data Booklet*
Multiple Choice Answer Sheet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in soft pencil.
Do not use staples, paper clips, highlighters, glue or correction fluid.

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.

This document consists of **13** printed pages and **1** blank page.

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

1 A given mass of ideal gas occupies a volume V and exerts a pressure p at 30 °C.

At which temperature will the same mass of the ideal gas occupy a volume $\frac{V}{3}$ and exert a pressure $2p$?

A 20 °C

B 20 K

C 202 °C

D 202 K

2 Which equation corresponds to the third ionisation energy of titanium (Ti)?

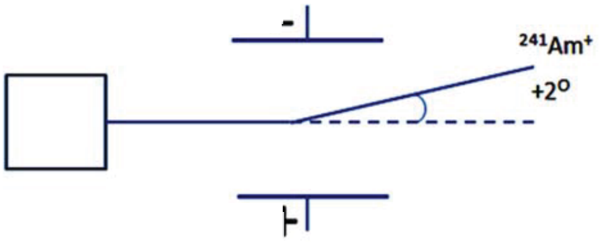
A $Ti(g) \rightarrow Ti^{3+}(g) + 3e^-$

B $Ti^{2+}(s) \rightarrow Ti^{3+}(g) + e^-$

C $Ti^{2+}(g) \rightarrow Ti^{3+}(g) + e^-$

D $Ti^{3+}(g) + e^- \rightarrow Ti^{2+}(g)$

3 A sample of the element Americium (Am) was vaporised, ionised and passed through an electric field. It was observed that a beam of $^{241}Am^+$ particles gave an angle of deflection of +2°.



Assuming an identical set of experimental conditions, by what angle would a beam of $^{32}S^-$ particles be deflected?

A +15.1°

B –15.1°

C +30.1°

D –30.1°

4 Which of the following statements describes a phenomenon which **cannot** be explained by hydrogen bonding?

A Ice floats on water.

B The boiling point of carboxylic acid increases with increasing relative molecular mass.

C 2-nitrophenol is more volatile than 4-nitrophenol.

D Ethanoic acid molecules form dimers when dissolved in benzene.

5 A tertiary amine, R_3N, reacts with boron trifluoride, BF_3 to give an addition product. Which of the following statements is **not** true?

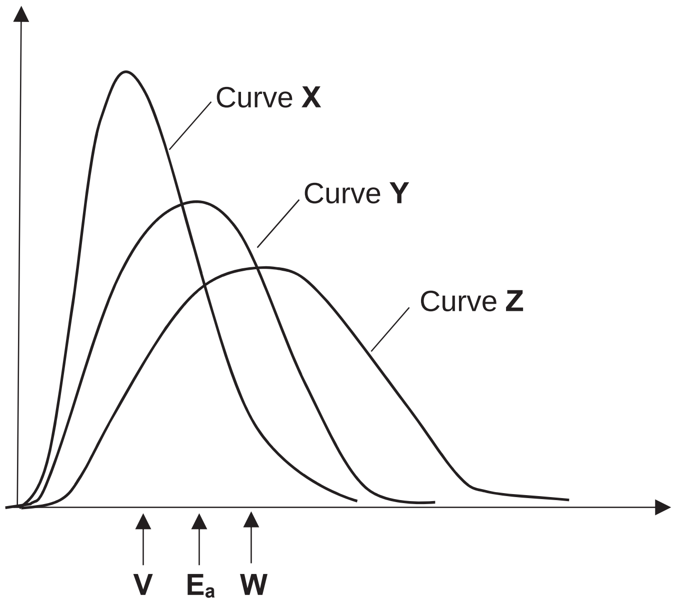
A R_3N acts as a Lewis base.

B The product is a polar molecule.

C There are six σ bonds in the product.

D The product contains a dative covalent bond.

6 The curve **Y** and the value E_a represent the distribution of energies of the molecules and the activation energy for an uncatalysed gaseous reaction.



What is a possible outcome if the reaction is catalysed?

A The distribution of energies will be given by curve **X** and the activation energy by value **V**

B The distribution of energies will be given by curve **Y** and the activation energy by value **V**.

C The distribution of energies will be given by curve **Y** and the activation energy by value **W**.

D The distribution of energies will be given by curve **Z** and the activation energy by value **W**.

7 If the rate of decay of a radioactive isotope decrease from 300 counts per minute to 37.5 counts per minute after 1 day, what is its half-life?

A 4 hours

B 6 hours

C 8 hours

D 12 hours

8 Which of the following statements does **not** describe a reaction at equilibrium?

A Forward and backward reactions occur at equal rate.

B The system must be closed.

C K_c increases as the reaction progresses.

D Concentrations of reactants and products are constant.

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

The enthalpy change of formation of carbon monoxide and carbon dioxide are given below.

$$\Delta H_f \text{ CO} = -110 \text{ kJmol}^{-1}$$
$$\Delta H_f \text{ CO}_2 = -393 \text{ kJmol}^{-1}$$

Which of these statements are correct?

1 CO_2(g) has lower energy content than CO(g).

2 The enthalpy change of combustion of carbon is –393 kJmol^{-1}.

3 CO_2(g) is formed exothermically from CO(g).

4 A larger amount of energy is required to atomise CO_2(g) than CO(g).

A 1, 2, 3 and 4

B 1, 2 and 3 only

C 1, 2 and 4 only

D 2 and 3 only

10 A sparingly soluble calcium salt ionises in aqueous solution according to the equation given:

$$Ca_3X_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2X^{3-}(aq)$$

If the solubility product K_{sp} of Ca_3X_2 is S, what is the value of the concentration of $Ca^{2+}(aq)$ at equilibrium?

A $S^{\frac{1}{2}}$

B $\left[\frac{S}{108}\right]^{\frac{1}{5}}$

C $\left[\frac{3S}{5}\right]^{\frac{1}{2}}$

D $\left[\frac{9S}{4}\right]^{\frac{1}{5}}$

11 The K_{sp} of AgCl and AgI are 1.80×10^{-10} mol^2 dm^{-6} and 8.3×10^{-17} mol^2 dm^{-6} respectively. Which of the following statements is correct when equal volumes of 1×10^{-4} mol dm^{-3} aqueous $AgNO_3$ was added to a mixture containing 3.0×10^{-6} mol dm^{-3} BaCl_2 and 3.0×10^{-6} mol dm^{-3} BaI_2?

A AgCl is precipitated only.

B AgI is precipitated only.

C AgCl is precipitated followed by AgI.

D AgI is precipitated followed by AgCl.

12 The dissociation constant, K_w, for the ionisation of water, $H_2O \rightleftharpoons H^+ + OH^-$, at different temperatures is given below.

Temperature / °C	K_w / mol^2 dm^{-6}
0	1.15×10^{-15}
25	1.00×10^{-14}
50	5.50×10^{-14}

What can be deduced from this information?

A Only at 25 °C are $[H^+]$ and $[OH^-]$ equal.

B The equilibrium lies furthest to the right at 0 °C.

C The forward reaction is exothermic.

D The pH of pure water decreases with temperature.

13 Calculate the standard Gibbs free energy change, $\Delta G^\ominus$ for the following reaction:

$$2Al\,(s) + 3Cu^{2+}(aq) \longrightarrow 2Al^{3+}(aq) + 3Cu(s)$$

A –386 kJ mol^{-1}

B –579 kJ mol^{-1}

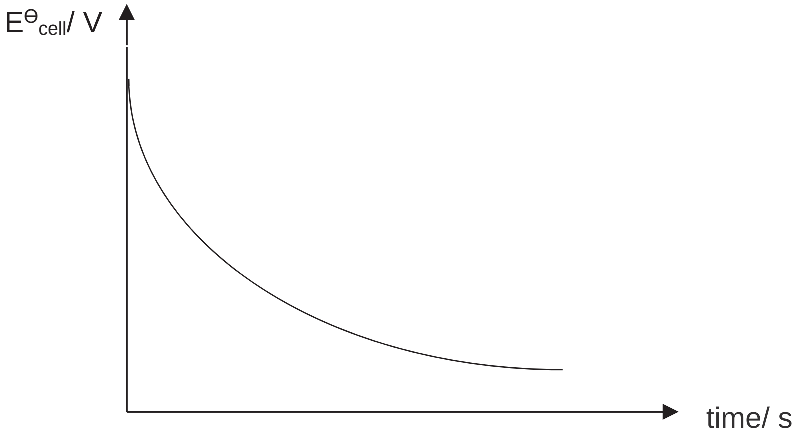
C –1045 kJ mol^{-1}

D –1158 kJ mol^{-1}

14 An experiment is carried out with the following cell.

$$Fe\,(s)\,|\,Fe^{2+}\,(aq)\,||\,Ni^{2+}\,(aq)\,|\,Ni\,(s)$$

The following graph of cell potential against time was obtained when a change was continuously made to the half-cell.



What continuous change could produce these results?

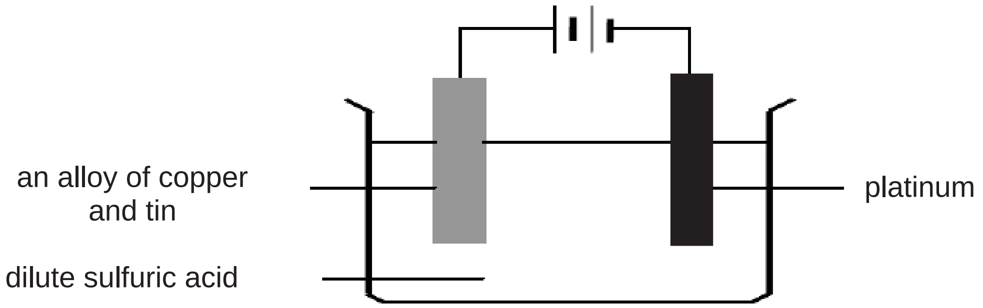
A Add nickel (II) chloride to the nickel half-cell.

B Add aqueous cyanide ions to the iron half-cell.

C Add water to the nickel half-cell.

D Increases the surface area of iron immersed in the solution.

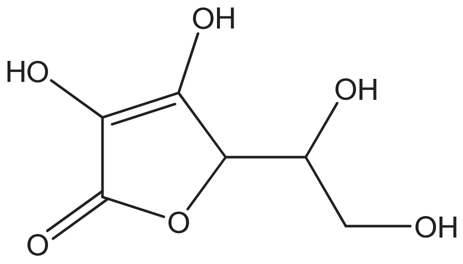
15 The circuit shown in the diagram was set up.



Which reactions will occur at the electrodes?

	anode reaction	*cathode reaction*
A	Oxygen gas is evolved.	Hydrogen gas is evolved.
B	Tin dissolves preferentially.	Hydrogen gas is evolved.
C	Copper dissolves preferentially.	Copper is deposited.
D	Copper and tin both dissolve.	Sulfur dioxide gas is evolved.

16 The diagram shows the structure of vitamin C.



vitamin C

How many stereoisomers are there in one molecule of vitamin C?

A 2 **B** 4 **C** 8 **D** 16

17 Propyne, C_3H_4, has the following structure.

$$H-C\equiv C-CH_3$$

Which row correctly describes the bonding and hybridisation in a molecule of propyne?

	number of π bonds	number of sp C atoms	number of sp^2 C atoms
A	1	1	1
B	2	2	0
C	2	2	1
D	3	3	0

18 During the nitration of benzene, a nitro group substitutes at a carbon atom. Which one of the following gives the arrangement of the bonds at this carbon atom during the reaction?

	at the start of the reaction	*in the intermediate complex*	*at the end of the reaction*
A	planar	planar	planar
B	planar	tetrahedral	tetrahedral
C	planar	tetrahedral	planar
D	tetrahedral	planar	tetrahedral

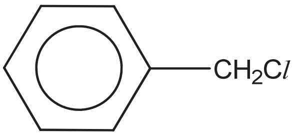
19 When a halogen compound **S** was boiled under reflux for some time with silver nitrate in a mixture of ethanol and water, little or no precipitate was seen.

Which of the following formulae could represent **S**?

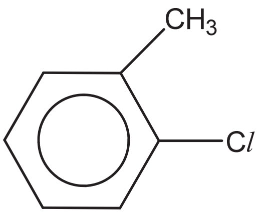
A $CH_3CH_2CHClCH_2CH_3$

B $CH_3CH_2CH_2COCl$

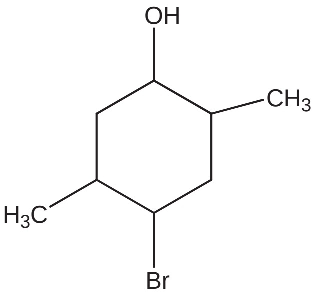
C



D



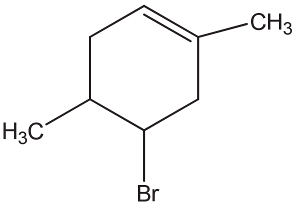
20 Compound **P** was heated with ethanolic potassium hydroxide.



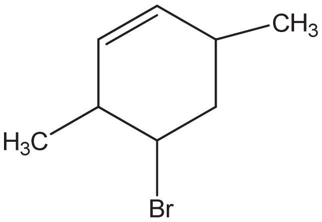
compound **P**

Which of the following would be the major product?

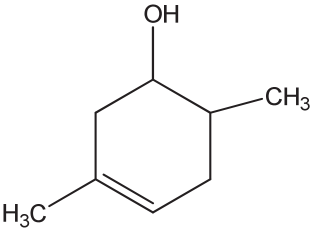
A



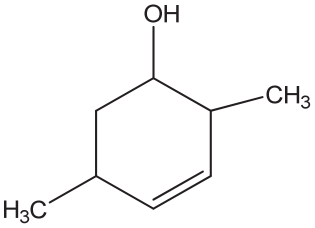
B



C



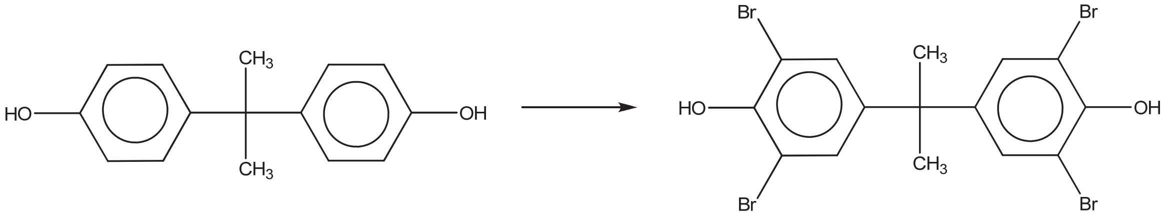
D



21 How many isomers (including both structural isomers and stereoisomers) with molecular formula $C_4H_{10}O$ liberate hydrogen gas on reaction with sodium?

A 2 **B** 3 **C** 4 **D** 5

22 Bisphenol A was used to make products such as plastic polycarbonate baby bottles and food containers. It is now regarded as toxic and has been withdrawn from use.



bisphenol A compound **Q**

Which reagent will convert bisphenol A into compound **Q**?

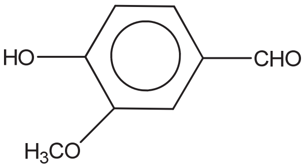
A $AlBr_3(s)$

B $Br_2(aq)$

C HBr(g)

D NaBr(aq)

23 Vanillin is the active ingredient of vanilla.



vanillin

Which of the following will be observed with vanillin?

1 Warm acidified potassium dichromate (VI) turns green.
2 2,4-dinitrophenylhydrazine reagent gives an orange precipitate.
3 A yellow precipitate is formed on warming with aqueous alkaline iodine.

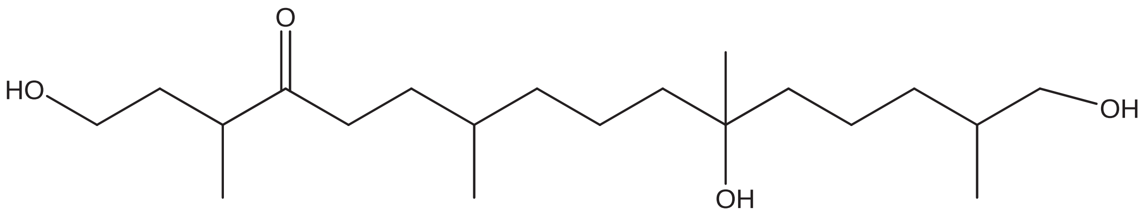
A 1 only

B 2 only

C 1 and 2 only

D 2 and 3 only

24 The mould *Phytophthora* damages many plants, destroying agricultural crops such as potatoes. A hormone-like compound called alpha1 regulates the reproduction of all species of *Phytophthora*. The structure of alpha1 is now known, giving scientist a key to the possible future eradication of the mould.



alpha1

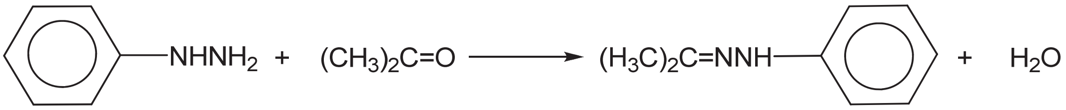
Which of the following reagents will react with alpha1?

1 Br_2
2 $SOCl_2$
3 H_2/Pt

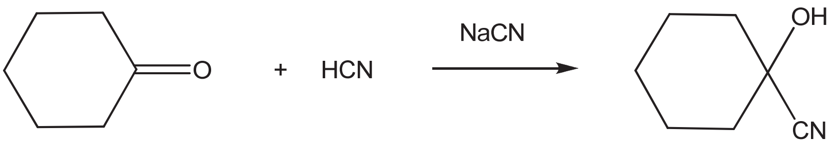
A 1 and 2 only
B 2 and 3 only
C 1 and 3 only
D 1, 2 and 3 only

25 Which transformations involve a nucleophile?

1



2



3 $CH_3CH_2COCl + NH_3 \longrightarrow CH_3CH_2CONH_2 + HCl$

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

26 Which of the following properties are identical for the two enantiomers of 2-hydroxypropanoic acid, $CH_3CH(OH)COOH$?

1 $\Delta H_f^\ominus$

2 pK_a

3 melting point

A 2 only

B 3 only

C 1 and 2 only

D 1, 2 and 3 only

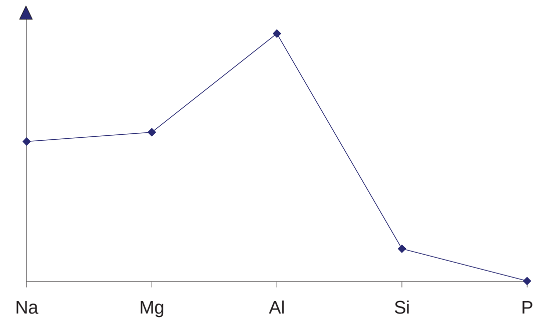
27 When organic compounds **E**, **F**, **G** and **H** are added separately to water, solutions of increasing pH values are obtained. The possible identities of compounds **E** to **H** (not necessarily in that order) are given below.

$CH_3CH_2CO_2H$ CH_3CH_2COCl $(CH_3)_2CHNH_2$ $CH_3CH_2NH_2$

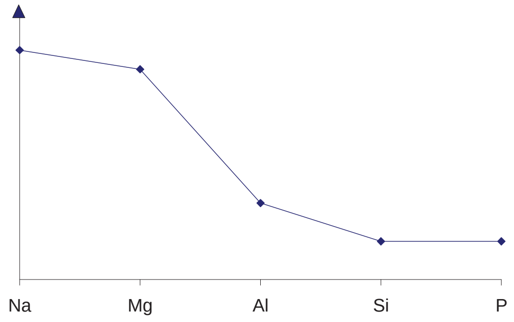
Which is the correct set of identities of compounds **E**, **F**, **G** and **H**?

	E	**F**	**G**	**H**
A	$CH_3CH_2CO_2H$	CH_3CH_2COCl	$CH_3CH_2NH_2$	$(CH_3)_2CHNH_2$
B	$CH_3CH_2CO_2H$	CH_3CH_2COCl	$(CH_3)_2CHNH_2$	$CH_3CH_2NH_2$
C	CH_3CH_2COCl	$CH_3CH_2CO_2H$	$(CH_3)_2CHNH_2$	$CH_3CH_2NH_2$
D	CH_3CH_2COCl	$CH_3CH_2CO_2H$	$CH_3CH_2NH_2$	$(CH_3)_2CHNH_2$

28 The graphs below show the variation in two properties of the elements Na to P and their compounds.



Graph I



Graph II

Which properties are illustrated in Graphs I and II?

	Graph I	Graph II
A	electrical conductivity of the element	pH of the chloride when added to water
B	electrical conductivity of the element	pH of the oxide when added to water
C	melting point of the element	pH of the chloride when added to water
D	melting point of the element	pH of the oxide when added to water

29 Which of the following elements is expected to show the greatest tendency to form some covalent compounds?

A Barium

B Calcium

C Magnesium

D Potassium

30 Why is hydrogen iodide a stronger acid than hydrogen chloride?

A A molecule of hydrogen chloride is more polar than a molecule of hydrogen iodide.

B The enthalpy change of formation of hydrogen iodide is greater than that of hydrogen chloride.

C The covalent bond in the hydrogen iodide molecule is weaker than that in the hydrogen chloride molecule.

D The dissociation of hydrogen chloride molecules is suppressed by the stronger permanent dipole–permanent dipole interactions.

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INNOVA JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION
in preparation for General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME	

CLASS		INDEX NUMBER	

CHEMISTRY

9729/02

Paper 2 Structured Questions

24 August 2017

Candidates answer on the question paper.

2 hours

Additional Materials: *Data Booklet*

READ THESE INSTRUCTIONS FIRST

Write your index number, name and civics group on all the work you hand in.
Write in dark blue or black pen.
You may use pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

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

You are advised to show all working in calculations.
You are reminded of the need for good English and clear presentation in your answers.
You are reminded of the need for good handwriting.
Your final answers should be in 3 significant figures.

You may use a calculator.

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

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

For Examiner's Use	
1	19
2	12
3	10
4	10
5	24
Significant Figures and Units	
Handwriting and Presentation	
Total	75

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

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

1 Halogens are highly reactive and form compounds with many other elements, including metals and non-metals.

(a) Fluorine reacts with bromine to form liquid bromine trifluoride, BrF_3.

Two molecules of BrF_3 react to form ions as shown by the following equation.

$$2BrF_3 \longrightarrow BrF_2^+ + BrF_4^-$$

(i) Draw the structures and suggest the shape of each of these species.

BrF_3

Shape: ……………………………..

BrF_4^-

Shape: ……………………………..

[3]

(ii) BrF_4^- ions are also formed when potassium fluoride, KF dissolves in liquid BrF_3 to form $KBrF_4$. Explain, in terms of structure and bonding, why $KBrF_4$, has a high melting point.

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[2]

(b) Magnesium bromide, $MgBr_2$ is a chemical compound of magnesium and bromine and is often used in the pharmaceutical industries.

In this part of the question, you will construct an energy cycle for magnesium bromide to determine the enthalpy change of hydration of magnesium ions.

(i) Magnesium bromide has a lattice energy of –2440 kJ mol^{-1}.
Define in words the *lattice energy of magnesium bromide*.

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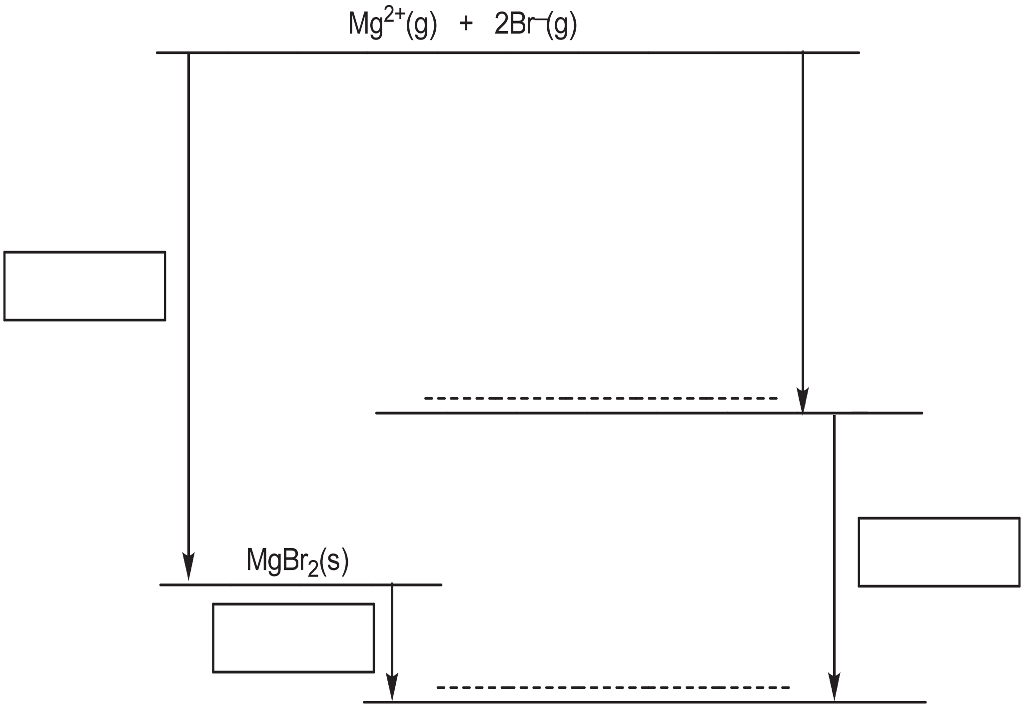
[1]

(ii) The table below shows the enthalpy changes that are needed to determine the enthalpy change of hydration of magnesium ions.

enthalpy change	**energy /kJ mol^{-1}**
lattice energy of magnesium bromide	–2440
enthalpy change of solution of magnesium bromide	–89
enthalpy change of hydration of bromide ions	–304

On the two dotted lines, add the species present and label the numerical values of the three arrows in the boxes provided.



[2]

(iii) Calculate the enthalpy change of hydration of magnesium ions.

[1]

(iv) Given that the enthalpy change of formation of $Mg^{2+}(aq)$ is +413 kJ mol^{-1} , use your answer in **(b)(iii**) as well as relevant values from the *Data Booklet* to calculate the enthalpy change of atomisation of magnesium.

[1]

(v) The enthalpy change of hydration of magnesium ions is more exothermic than the enthalpy change of hydration of calcium ions. Explain why.

…………………………………………………………………………………………

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…………………………………………………………………………………………

[1]

(c) Nickel is a typical transition element in the d-block of the Periodic Table. Many nickel ions are able to interact with ligands to form complex ions, such as $[Ni(H_2O)_6]^{2+}$.

A student dissolves nickel(II) sulfate in water. A green solution forms containing the complex ion $[Ni(H_2O)_6]^{2+}$. The student then reacts separate portions of the green solution of nickel(II) sulfate as outlined below.

- Concentrated hydrochloric acid is added to the green solution of nickel(II) sulfate until there is no further change. The solution turns a lime-green colour and contains the four-coordinate complex ion **A**.
- Aqueous sodium hydroxide is added to the green solution of nickel(II) sulfate. A pale-green precipitate **B** forms.
- Concentrated aqueous ammonia is added to the green solution of nickel(II) sulfate until there is no further change. The solution turns a violet colour and contains the complex ion **C**. **C** has a molar mass of 160.7 g mol^{-1}.

(i) Explain why aqueous nickel(II) sulfate is green.

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[2]

(ii) Draw a three dimensional diagram for the $[Ni(H_2O)_6]^{2+}$ ion.

[1]

(iii) Suggest the formulae of **A**, **B** and **C**.

A: ……………………………………………………………

B: ……………………………………………………………

C: ……………………………………………………………

[3]

(iv) What type of reaction has taken place in the formation of **C** from $[Ni(H_2O)_6]^{2+}$? Write an equation for this reaction.

…………………………………………………………………………………………

…………………………………………………………………………………………

[2]

[Total: 19]

2 **(a)** In a school lab, magnesium strips can be stored in a normal container. However, barium metal has to be submerged in oil when it is stored. With reference to relevant data from the *Data Booklet*, explain the above observation.

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[2]

(b) When solid barium carbonate is heated, no carbon dioxide is detected as it is thermally stable.
However, magnesium carbonate decomposes on heating as shown by the equation below.

$$MgCO_3(s) \longrightarrow MgO(s) + CO_2(g)$$

$$\Delta H^\ominus = +117 \text{ kJ mol}^{-1}; \quad \Delta S^\ominus = +175 \text{ J mol}^{-1} \text{ K}^{-1}$$

(i) Explain why barium carbonate is thermally stable while magnesium carbonate is not.

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……………………………………………………………………………………………

……………………………………………………………………………………………

[2]

(ii) Account for the sign of $\Delta S^\ominus$ in this reaction.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

[1]

(iii) Calculate the standard Gibbs free energy change, $\Delta G^\ominus$, for the decomposition of magnesium carbonate.

[1]

(iv) Assuming that $\Delta H^\ominus$ and $\Delta S^\ominus$ for the reaction are independent of temperature, calculate the temperature at which the decomposition reaction becomes feasible.

[1]

(c) The labels of group 2 metal carbonates fell off the bottles. In an attempt to identify the compound in one of the bottles, the following experiment was carried out.

1.68 g of an insoluble metal carbonate, **D**CO_3 was reacted with 100 cm^3 of hydrochloric acid of concentration 0.500 mol dm^{-3}. The resulting solution was then made up to 250 cm^3 with distilled water. 25.0 cm^3 of this solution required 25 cm^3 of 0.04 mol dm^{-3} sodium hydroxide for titration.

(i) Write a balanced equation for the reaction between the metal carbonate and hydrochloric acid.

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

(ii) Calculate the relative atomic mass of **D** and hence using the Periodic Table, identify **D**.

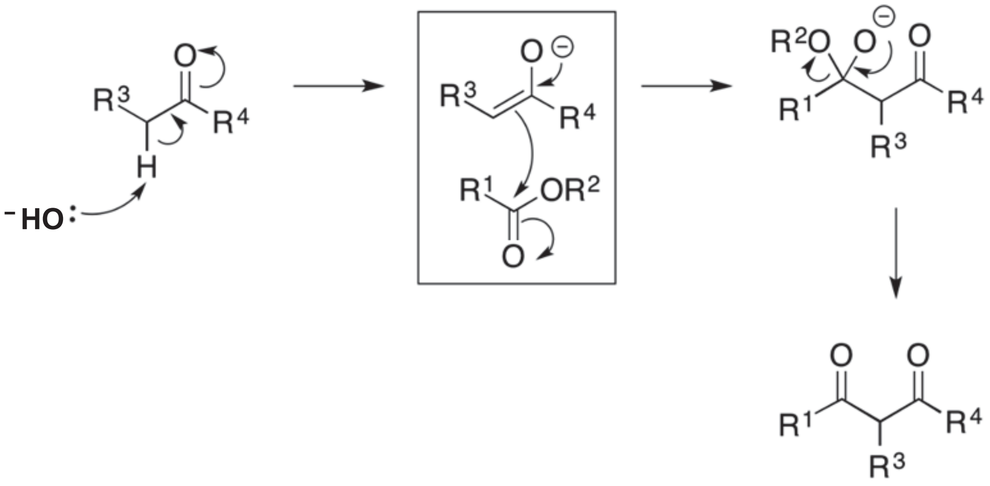
[4]

[Total: 12]

3 Claisen condensation is a carbon-carbon bond forming reaction between 2 esters or an ester and a carbonyl compound in the presence of strong base to form β-ketoesters or diketones respectively.

The following is the general equation for the reaction between an ester and a ketone.

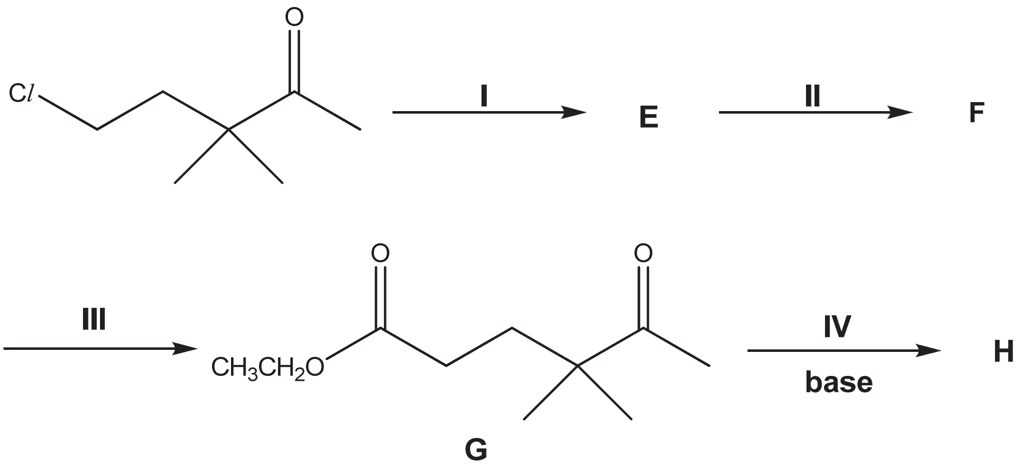
The mechanism of the Claisen condensation reaction is given below.



(a) Name the type of reaction for the step shown in the box above.

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

The Claisen condensation reaction can be used in step **IV** of the following synthesis.



(b) **(i)** Suggest reagents and conditions for steps **I** to **III**.

Step **I**: ……………………………………………………………………………………..

Step **II**: …………………………………………………………………………………….

Step **III**: ……………………………………………………………………………………

[3]

(ii) State the type of reactions for step **I** to **III**

Step **I**: ……………………………………………………………………………………..

Step **II**: …………………………………………………………………………………….

Step **III**: ……………………………………………………………………………………

[3]

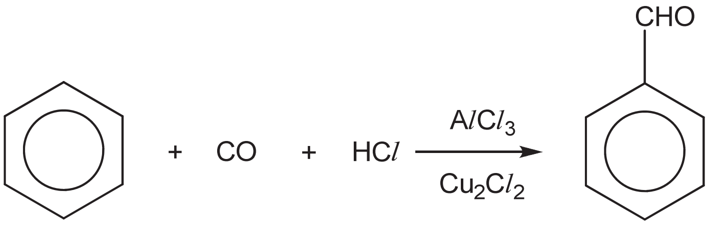
(iii) Propose the structures of compounds **E**, **F** and **H**.

E	**F**	**H**

[3]

[Total: 10]

4 **(a)** The Gattermann-Koch reaction, named after the German chemists Ludwig Gattermann and Julius Arnold Koch in organic chemistry, refers to a Friedel-Crafts acylation reaction in which carbon monoxide and hydrochloric acid are used in-situ with Friedel-Crafts catalyst, namely $AlCl_3$. The reaction involves an acylium ion as an electrophile and tetrachloroaluminate ion, $AlCl_4^-$. An example is provided below.

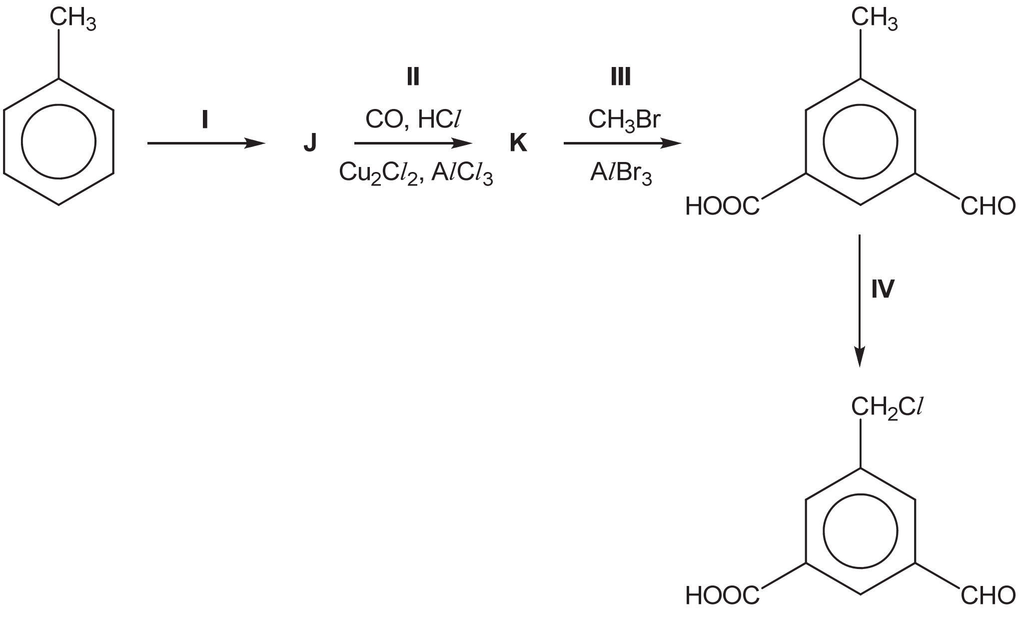


(i) Give the formula of the acylium ion in this reaction.

.... [1]

(ii) The synthesis of compound **L** involves the Gattermann-Koch reaction in Step **II**.

Complete the reaction scheme below by providing the appropriate reagents and conditions for Step **I** and **IV** and give the structural formula for **J** and **K**.



L

Step **I**: ……………………………………………………………………………………

Step **IV**: ……………………………………………………………………………………

J

K

[4]

(b) Three non-cyclic organic compounds, **M**, **N** and **P** each have the same empirical formula CH_2O.
The number of carbon atoms in their molecules are shown in the table below.

compound	number of C atoms
M	2
N	3
P	3

All the carbon atoms are bonded directly to one another in **M** and in **N** but not in **P**.

M and **N** each give a brisk effervescence with Na_2CO_3(aq) but not **P**.

P does not give a silver mirror when treated with Tollens' reagent.

(i) Draw the structural formula of **M**.

[1]

(ii) When **N** is heated under reflux with acidified $K_2Cr_2O_7$, the product, **Q**, gives a orange precipitate with 2,4-dinitrophenylhydrazine.

Draw the structural formulae of **N** and **Q**.

N

Q

[2]

(iii) When **N** is warmed with concentrated sulfuric acid, compound **R** is formed. **R** has the molecular formula $C_6H_8O_4$.

Draw the structural formula of **R.**

[1]

(iv) **P** is optically active. Draw the displayed formula of **P**.

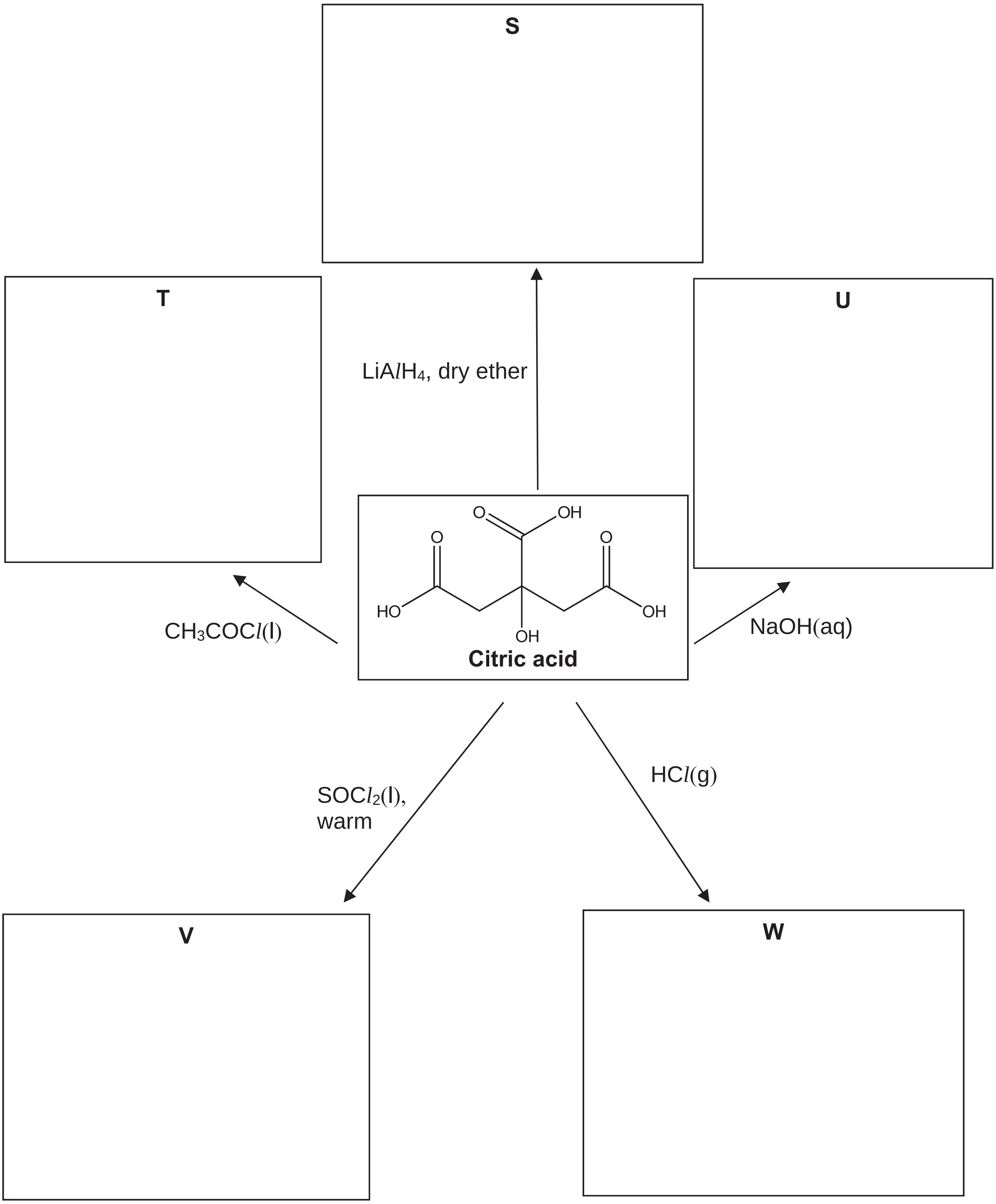
[1]

[Total: 10]

5 Citric acid, $C_6H_8O_7$ is produced commercially by the fermentation of sugars. Citric acid is used in the production of beverages and foods; in detergents; and in cosmetics and pharmaceuticals.

Fruits such as oranges, lemons and strawberries also contain citric acid.

(a) Citric acid can undergo the following reactions:



Suggest structures for the organic compounds **S, T, U, V** and **W**.

[5]

(b) As citric acid is a user-friendly, inexpensive, water-soluble crystalline solid, it is often used for finding the concentration of alkalis e.g. sodium hydroxide and potassium hydroxide.

Citric acid is a tribasic acid with the following pK_a values:

pK_1 = 3.14, pK_2 = 4.75 , pK_3 = 6.40

(i) Explain why citric acid is soluble in water.

…………………………………………………………………………………….

…………………………………………………………………………………….

[1]

(ii) The pK_a value of ethanoic acid, CH_3COOH is 4.76.

Suggest why the pK_1 value of citric acid is lower than the pK_a value of ethanoic acid.

…………………………………………………………………………………….

…………………………………………………………………………………….

…………………………………………………………………………………….

…………………………………………………………………………………….

…………………………………………………………………………………….

…………………………………………………………………………………….

[2]

(iii) Calculate the pH of a solution that is a mixture of equal volumes of 0.100 mol dm^{-3} of citric acid and 0.060 mol dm^{-3} of sodium hydroxide.

[2]

(c) The neutralisation equivalent (N.E.) of a carboxylic acid is defined as the mass in g of the acid required to neutralise one mole of a strong alkali such as sodium hydroxide. Each carboxylic acid has a unique N.E. value.

N.E. values can be used to determine the identity of a carboxylic acid.

A student carried out a titration experiment between a sample of citric acid and sodium hydroxide solution. 3.68 g of the citric acid was dissolved in 500 cm^3 of water in a volumetric flask. It was found that 5.00 cm^3 of the citric acid solution needed 5.29 g of 4.43 g dm^{-3} sodium hydroxide solution for complete reaction.

(i) Calculate the mass, in g, of the citric acid used in the 5 cm^3 sample.

[1]

(ii) Calculate the amount, in moles, of sodium hydroxide that reacted with the 5 cm^3 of citric acid.

The density of the sodium hydroxide solution is 1.01 g cm^{-3}.

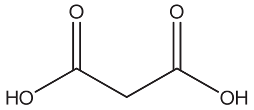
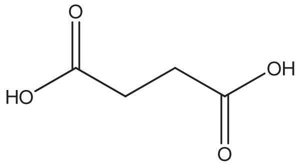
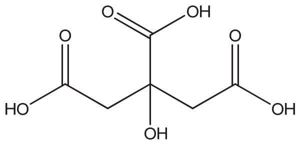
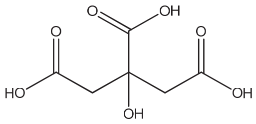
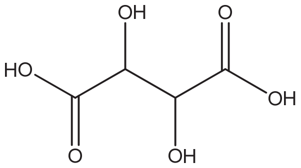
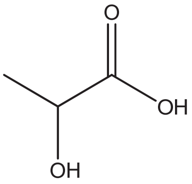
[2]

(iii) Calculate the neutralisation equivalent (N.E.) for this sample of citric acid.

[1]

(d) Table 5.1 gives the neutralisation equivalent (N.E.) values for some organic acids.

Table 5.1

Acid name	**Structure**	**Molar mass/ g mol^{-1}**	**N.E. / g**
Malonic acid		104.0	52.0
Succinic acid		118.0	59.0
Anhydrous citric acid		192.0	64.0
Citric acid monohydrate	 . H_2O	210.0	70.0
Tartaric acid		150.0	*m*
Lactic acid		90.0	90.0

(i) Suggest whether the student's sample of citric acid is a hydrated sample or anhydrous sample. Support your answer with appropriate evidence.

……………………………………………………………………………………

……………………………………………………………………………………

……………………………………………………………………………………
[2]

(ii) Determine the value of *m* in Table 5.1.

[1]

(e) Another student determines the N.E. of an unknown aliphatic acid to be 82.0 g.

The unknown aliphatic acid has the following formula, $C_xH_y(COOH)_n$ where x and y are integers and n = 1, 2 or 3.

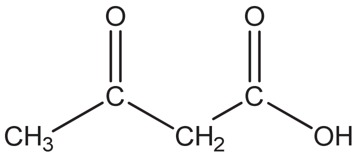
Determine the molecular formula of the unknown aliphatic acid.

[3]

(f) The loss of carbon dioxide from a carboxylic acid is called decarboxylation.

$$RCOOH \longrightarrow RH + CO_2$$

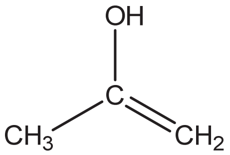
Certain types of carboxylic acids are readily decarboxylated. Beta-keto acids such as acetoacetic acid readily decarboxylate at room temperature in an acidic solution.



acetoacetic acid

The decarboxylation of acetoacetic acid occurs via a two-step mechanism.

- the H atom from the COOH group is transferred to the carbonyl oxygen atom via a cyclic transition state to form CO_2 and the following compound, an enol,



enol

- the enol then extracts a H atom from a H_2O molecule to form a ketone and H^+ and OH^- ions.

Suggest the mechanism for this reaction. Show any relevant lone pairs, dipoles and charges, and indicate the movement of electron pairs with curly arrows.

[4]

[Total: 24]

For
Examiner's
Use

INNOVA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
in preparation for General Certificate of Education Advanced Level
Higher 2

CHEMISTRY 9729/03

Paper 3 Free Response **13 September 2017**
2 hours

Candidates answer on separate paper.

Additional Materials: Writing Papers
Data Booklet
Cover Page

READ THESE INSTRUCTIONS FIRST

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

Section A
Answer **all** questions.

Section B
Answer **one** question.

You are advised to show all working in calculations.
You are reminded of the need for good English and clear presentation in your answers.
You are reminded of the need for good handwriting.
Your final answers should be in 3 significant figures.

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

This document consists of **12** printed pages.

Section A

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

1 Benzoic acid, C_6H_5COOH is a colourless crystalline solid and a simple aromatic carboxylic acid. Benzoic acid occurs naturally in many plants. Salts of benzoic acid are used as food preservatives and benzoic acid is an important precursor for the industrial synthesis of many other organic substances.

(a) In the identification of benzoic acid, a commonly used reagent is neutral iron(III) chloride solution, in which a buff precipitate of iron(III) benzoate, $Fe(C_6H_5CO_2)_3$ is formed. When 50.0 cm^3 of iron(III) chloride solution was added to 50.0 cm^3 of benzoic acid solution, 0.0532 g of the buff precipitate was formed in the mixture.

The reactions that take place are shown below:

$$C_6H_5CO_2H \rightleftharpoons C_6H_5CO_2^- + H^+$$

$$Fe^{3+} + 3C_6H_5CO_2H \longrightarrow Fe(C_6H_5CO_2)_3 + 3H^+$$

(Given: M_r of $Fe(C_6H_5CO_2)_3 = 418.8$)

(i) Calculate the number of moles of benzoic acid that reacted with the neutral iron(III) chloride solution.

[1]

(ii) Given that the pH of the solution after the reaction is 2.33, calculate the number of moles of H^+ in the mixture.

[1]

(iii) Assuming that the H^+ ions in solution are formed only from the dissociation of benzoic acid in solution, as well as the reaction of benzoic acid with iron(III) chloride, calculate the concentration of benzoate ions in the mixture.

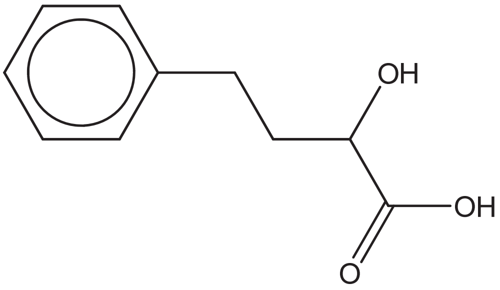
[2]

(iv) Iron(III) benzoate is a sparingly soluble salt.

Calculate the K_{sp} of iron(III) benzoate, given that the concentration of Fe^{3+} in the mixture was 1.83×10^{-3} mol dm^{-3} at equilibrium.

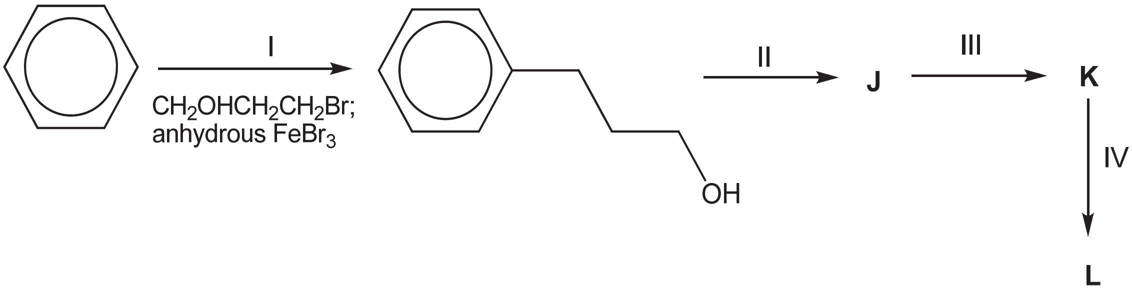
[1]

(b) Benzoic acid can be produced by oxidising compound **L**.



Compound **L**

Compound **L** can be synthesised by the following reaction scheme.



(i) State the *type of reaction* in step I and hence explain the need for $FeBr_3$ to be anhydrous.

[2]

(ii) Suggest the identities of **J** and **K**.

[2]

(iii) State the reagents and conditions for steps II to IV.

[3]

(iv) State the *type of reaction* for stage IV.

[1]

[Total: 13]

[Turn over

2 Sulfur is a chemical element with the symbol S and an atomic number of 16. It is an abundant, multivalent non-metal. It can be found in amino acids and it is a precursor to other chemicals such as H_2SO_4. H_2SO_4 is a common mineral acid with many uses. It can be used as an electrolyte in batteries.

(a) In the cells of a lead-acid car battery the following reactions take place.

anode: $Pb(s) \longrightarrow Pb^{2+}(aq) + 2e^-$

cathode $PbO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Pb^{2+}(aq) + 2H_2O(l)$

(i) Use the *Data Booklet* to calculate E^θ_{cell} for this reaction.

[1]

(ii) Construct an equation for the overall reaction.

[1]

The electrolyte in a lead-acid cell is $H_2SO_4(aq)$. Most of the $Pb^{2+}(aq)$ ions that are produced at the electrodes are precipitated as a highly insoluble $PbSO_4(s)$.

(iii) Construct an equation for the overall cell reaction in the presence of H_2SO_4.

[1]

(iv) By considering the effect of decreasing $[Pb^{2+}(aq)]$ on the electrode potentials of the cathode and the anode, state and explain whether the overall E^θ_{cell} will *increase*, *decrease* or *remain the same*.

[1]

(b) H_2SO_4 is also used as an electrolyte in the anodising of aluminium. Anodising of aluminium is the process of coating aluminium metal with aluminium oxide (Al_2O_3) via electrolysis with the aluminium metal as the anode.

(i) Using $H_2SO_4(aq)$ as the electrolyte and an inert electrode, draw an electrolysis set-up to show how a piece of aluminium metal can be anodised.

[1]

(ii) Write chemical equations to show the reactions at the anode and cathode during anodising. Include in your answers, the overall equation.

[3]

(iii) The aluminum piece to be anodised has a surface area of 29.2 cm^2. Calculate the time taken to form a 0.2 mm protective layer of Al_2O_3 on the aluminum piece if a current of 2.0 A is passed through the set-up.

(Density of Al_2O_3 is 3.95 g cm^{-3})

[4]

(iv) Give one example of an anodised aluminium object, and explain the advantages of anodising it.

[1]

[Turn over

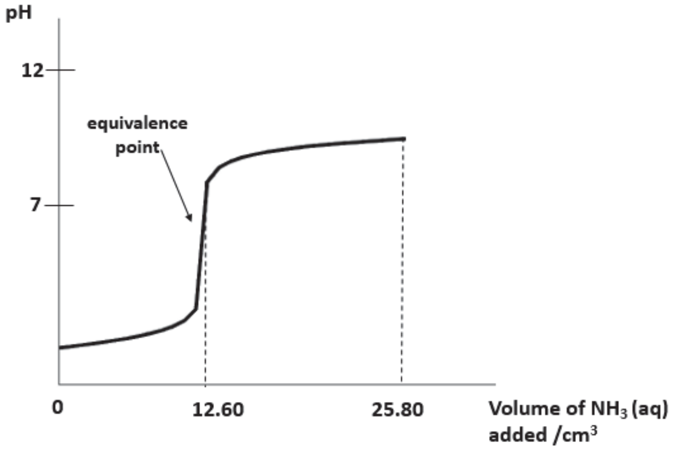
(c) H_2SO_4, can be produced when sulfur trioxide is added to water, according to the following equation:

$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$$

Calculate the volume of gaseous SO_3, under room temperature and pressure, needed to form 30.0 cm^3 of 0.0200 mol dm^{-3} of H_2SO_4.

[1]

(d) 25.0 cm^3 of 0.0200 mol dm^{-3} of H_2SO_4 was titrated against $NH_3(aq)$. The following graph was obtained.



(i) Calculate the initial pH of the sulfuric acid solution.

[1]

(ii) Calculate the concentration of $NH_3(aq)$ used in this titration.

[2]

(iii) Suggest a suitable indicator for this titration, giving a reason for your choice.

[2]

(e) Thiophenol are the sulfur analogue of phenol, that is, sulfur takes the place of oxygen in the hydroxyl group of phenol. A common reaction that phenol and thiophenol have is shown in **Figure 1** below.

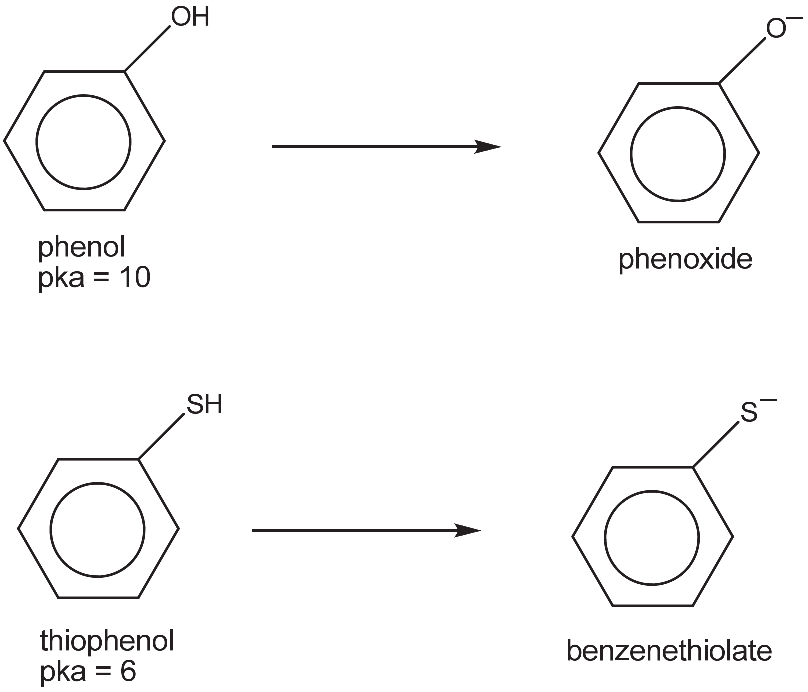
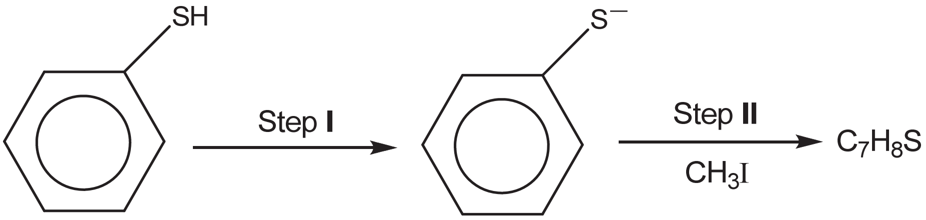


Figure 1

Consider the reaction scheme below.



(i) Suggest reagent and condition for step **I**.

[1]

(ii) What *type of reaction* is step **I** and step **II**?

[2]

(iii) Suggest the structure of C_7H_8S.

[1]

[Total: 23]

3 Halogenated organic compounds are widespread throughout nature and have a vast array of uses in modern industrial processes. They find many uses in the industries such as solvents and pesticides.

The rate of hydrolysis of $CH_3CH_2CH_2CH_2Br$ with aqueous NaOH was studied in a series of 3 experiments in which the initial rate of the reaction was measured. The following results were obtained.

Experiment	$[OH^-]$ / mol dm^{-3}	$[CH_3CH_2CH_2CH_2Br]$ / mol dm^{-3}	Initial Rate / mol dm^{-3} s^{-1}
1	0.100	0.010	4×10^{-6}
2	0.200	0.010	8×10^{-6}
3	0.200	0.020	16×10^{-6}

(a) Explain the meaning of the following terms.

(i) order of reaction

[1]

(ii) half-life

[1]

(iii) Using the data given, derive the rate equation for the hydrolysis of $CH_3CH_2CH_2CH_2Br$.

[3]

(iv) Using your rate equation, determine a value for the rate constant, including units for this reaction.

[2]

(v) Using the Maxwell-Boltzmann distribution curve, explain how the reaction rate might change with an increase in temperature.

[4]

(vi) Given that the rate equation for the hydrolysis of $(CH_3)_3CBr$ is rate = $k[(CH_3)_3CBr]$, suggest possible mechanisms for **both** of the reactions of $(CH_3)_3CBr$ and $CH_3CH_2CH_2CH_2Br$ with aqueous NaOH which are consistent with the observed kinetics.

[6]

(b) Bromine reacts with 2-methylpropane in the presence of sunlight to produce mono-brominated products via a free radical mechanism.

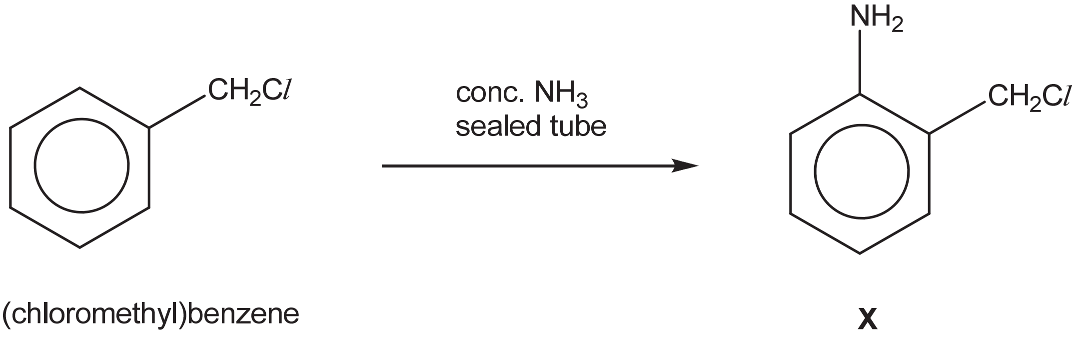
(i) Explain why the mono-bromination of 2-methylpropane results in the formation of two products in unequal amounts.

[1]

(ii) By quoting appropriate data from the *Data Booklet,* explain the difference in the reactivity of fluorine with 2-methylpropane compare with that of bromine.

[2]

(c) A student was not successful in making **X** from (chloromethyl)benzene with the proposed reaction route as shown.



Instead, a different product with molecular formula C_7H_9N was obtained.

(i) Draw the displayed formula of the product obtained.

[1]

(ii) Suggest how **X** can be synthesised from (chloromethyl)benzene. You should include the reagents, conditions and intermediate(s) formed in your answer.

[3]

[Total: 24]

Section B

Answer **one** question from this section

4 Hydrogen gas is needed in a large number of processes in the chemical industries such as hydrocracking of petroleum, production of margarine and production of ammonia.

Hydrogen gas can be produced in many chemical reactions.

(a) One of the reactions that produces hydrogen is the reaction of sodium with ethanol.

$$C_2H_5OH(l) + Na(s) \longrightarrow C_2H_5ONa(s) + \frac{1}{2}H_2(g)$$

This is also a chemical test for the presence of alcohol.

(i) Write the full electronic configuration of Na.

[1]

(ii) Describe how you would use the ionisation energies found in the *Data Booklet* to conclude that sodium is in group 1 of the periodic table.

[1]

(iii) Ethanoic acid reacts with sodium in a similar way. However, when ethanol and ethanoic acid is reacted with solid sodium carbonate separately, only ethanoic acid gives off a gas that forms white precipitate with calcium hydroxide.

Explain the difference in reactions of ethanol and ethanoic acid with sodium carbonate.

[3]

(iv) An unknown compound **M**, $C_8H_{10}O$ was found to be an alcohol when tested with sodium metal.

When **M** is treated with hot acidified potassium dichromate, compound **N**, C_8H_8O is formed. **N** gives a yellow precipitate, **P** when warmed with alkaline aqueous iodine.

When **M** is heated with concentrated H_2SO_4, compound **R**, C_8H_8 is formed. **R** gives compound **S** when reacted with hydrogen chloride gas.

M also gave compound **S** when reacted with phosphorous pentachloride at room temperature.

Deduce the structures of **M**, **N**, **P**, **R** and **S.**

[5]

[Turn over

(b) Another reaction that produces hydrogen is the reaction of methane with steam at 1000–1400 K.

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) \qquad \Delta H = +206 \text{ kJ mol}^{-1}$$

This reaction produces large quantities of hydrogen for industrial use.

(i) State and explain the effect of decreasing the temperature of the reaction on the equilibrium position.

[1]

(ii) Deduce the sign of entropy change for the forward reaction.

[1]

(iii) Hence, or otherwise, predict and explain the spontaneity of the forward reaction at low temperature.

[1]

(iv) Comment and explain if there is any discrepancy in your answers in **b(i)** and **b(iii)**.

[1]

(v) Calculate the enthalpy change of vaporisation of water using the data in **Table 1**.

Table 1

Enthalpy change of formation of carbon monoxide	–111 kJ mol^{-1}
Enthalpy change of formation of methane	–75 kJ mol^{-1}
Enthalpy change of formation of water	–285 kJ mol^{-1}

[2]

(c) Hydrogen gas can also be produced from the reaction of carbon monoxide with steam.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) \quad K_c = 6.40 \times 10^{-1} \text{ at } 1100\text{K}$$

A mixture containing 0.8 mol of CO and 0.8 mol of H_2O was placed in a 2 dm^3 flask and allowed to come to equilibrium at 1100K.

(i) Write an expression for an expression for K_c of this reaction.

[1]

(ii) Calculate the amount of each substance present in the equilibrium mixture at 1100K.

[2]

(iii) State and explain the effect of decreasing pressure on the equilibrium constant.

[1]

[Total: 20]

5 Methanol can be prepared industrially by reacting together carbon monoxide and hydrogen. This is a reversible reaction:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \quad \Delta H = -94 \text{ kJmol}^{-1}$$

A chemist mixes together 0.114 mol CO(g) and 0.152 mol H_2(g) in a container. The container is pressurised and then sealed and the total volume is 200 cm^3. The mixture is heated to 500 K at constant volume and left to reach equilibrium. The chemist analyses the equilibrium mixture and finds that 0.052 mol CH_3OH has formed.

(a) Calculate the value of K_c for the equilibrium at 500 K. [2]

(b) The chemist repeats the experiment using the same initial amounts of CO and H_2. The same procedure is used but the mixture is heated in the 200 cm^3 sealed container to a temperature higher than 500 K.
As the gas volume is kept at 200 cm^3, the increased temperature also increases the pressure.

Explain why it is difficult to predict how the yield of CH_3OH would change and state what happens to the value of K_c. [2]

(c) Methanol can be oxidised to formaldehyde, HCHO, by passing its vapour over copper heated to 300 °C.

Explain why the boiling point of methanol (65 °C) is higher than that of formaldehyde (–19 °C). [2]

(d) State the type of hybridisation shown by the C atom in formaldehyde and draw its hybrid orbitals. [2]

(e) Benzaldehyde, C_6H_5CHO, is the simplest aromatic aldehyde and has a characteristic smell of almonds.
In the presence of a solution of potassium hydroxide, benzaldehyde undergoes disproportionation to give a mixture of two organic products, **E** and **F**. **F** has a higher solubility in water compared to **E**.

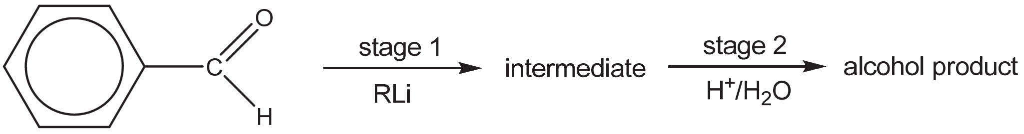
(i) Suggest the structures of **E** and **F**. [2]

(ii) Explain why **F** is soluble in water. [1]

(f) Alkyllithium compounds, RLi, can be used to increase the number of carbon atoms in an organic compound. Different alkyl groups, R, add carbon chains with different chain lengths.

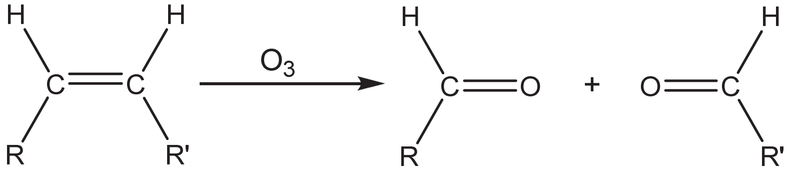
RLi provides a source of R^- ions, which act as a nucleophile.

(i) RLi reacts with benzaldehyde to give an intermediate in stage 1, followed by reaction with aqueous acid to form an alcohol in stage 2.



Describe the mechanism for the above reaction, including curly arrows and relevant dipoles. [3]

(ii) ‘Ozonolysis’ is a technique used in organic chemistry to break open a C=C double bond. During ozonolysis, an alkene reacts with ozone, O_3. The products are carbonyl compounds as shown below.



An aromatic alkene, **A** undergoes ozonolysis to give benzaldehyde and **B**, C_4H_8O. **B** has no reaction with $[Ag(NH_3)_2]^+(aq)$ but gives a yellow precipitate with aqueous alkaline iodine.

B undergoes a reaction with an alkyllithium compound, **C**, followed by reaction with aqueous acid to give an alcohol, **D**, which is optically active. The elimination of H_2O from **D** produces a mixture of four different isomeric alkenes with the formula, C_7H_{14}, only two of which are cis-trans isomers of each other. Suggest the structural formulae of compounds **A** to **D** and the two cis-trans isomers.

[6]

[Total: 20]

CHEMISTRY LAB PREPARATION LIST FOR JC2 H2 CHEMISTRY

2017 PRELIM

APPARATUS

S/N	Apparatus	Quantity
1	25cm^3 Pipette	1
2	Pipette Filler	1
3	Burette stand and clamp	2
4	250cm^3 conical flask	2
5	250cm^3 volumetric flask	1
6	250cm^3 beaker	1
7	Funnel (for filling burette)	1
8	White tile	1
9	spatula	1
10	Wash bottle containing distilled water	1
11	Marker pen or labels(suitable for labelling glassware)	1
12	100cm^3 beaker	2
13	25cm^3 measuring cylinder	1
14	10cm^3 measuring cylinder	2
14	50cm^3 burette	2
15	Glass rod	1
16	Stopwatch	1
17	Paper towels	
18	Dropping pipettes	4
19	**DRY** Boiling tube	4
20	**DRY** Test tubes	8

CHEMICALS NEEDED (PER STUDENT)

S/N	Chemical
1	**FA1**
2	Magnesium Ribbon
3	Bromophenol blue
4	**FA3**
5	**FA4**
6	**FA5**
7	**FA6**
8	Starch indicator
9	**FA7**
10	**FA8**
11	**FA9**

CHEMISTRY LAB PREPARATION LIST FOR JC2 H2 CHEMISTRY

2017 PRELIM

APPARATUS NEEDED (PER STUDENT)

S/N	**Apparatus**	**Quantity**	**Location**	**Remarks**
1	25cm^3 Pipette	1	Student's bench	Reuse
2	Pipette Filler	1	Student's bench	Reuse
3	Burette stand and clamp	2	Student's bench	Reuse
4	250cm^3 conical flask	2	Student's bench	Reuse
5	250cm^3 volumetric flask	1	Student's bench	Reuse
6	250cm^3 beaker	1	Student's bench	Reuse
7	Funnel (for filling burette)	1	Student's bench	Reuse
8	White tile	1	Student's bench	Reuse
9	spatula	1	Student's bench	Reuse
10	Wash bottle containing distilled water	1	Student's bench	Reuse
11	Marker pen or labels(suitable for labelling glassware)	1	Student's bench	Reuse
12	100cm^3 beaker	2	Student's bench	Reuse
13	25cm^3 measuring cylinder	1	Student's bench	Reuse
14	10cm^3 measuring cylinder	2	Student's bench	Reuse
14	50cm^3 burette	2	Student's bench	Reuse
15	Glass rod	1	Student's bench	Reuse
16	Stopwatch	1	Student's bench	Reuse
17	Paper towels		Student's bench	Must change to new one per shift
18	Dropping pipettes	4	Student's bench	Must change to new one per shift
19	Boiling tube	~~3~~ 4	Student's bench	Must change to new one per shift
20	Test tubes	8	Student's bench	Must change to new one per shift
~~21~~	~~Hard glass test tube~~	~~1~~	~~Student's bench~~	~~Must change to new one per shift~~
22	Access to weighing balance			4 per lab

CHEMICALS NEEDED (PER STUDENT)

S/N	Chemical	Concentration	Quantity	Location	Remarks
1	**FA1** Hydrochloric acid **[H]**	2.00 mol dm^{-3}	$40cm^3$	Student's bench	Dilute $170cm^3$ of concentrated (35-37%; approximately 11 mol dm^{-3}) hydrochloric acid to 1 dm^3
2	Magnesium Ribbon **[F]**		0.20g (in one strip) - Place in a ziplock bag and label.	Student's bench - together with FA1 to FA9 **REMOVE the small strips in the bottle found with the common QA reagents	One strip of Mg ribbon, lightly cleaned with emery paper or sand paper if appropriate, of mass 0.20g. All Mg strips supplied to candidates must be cut to the same length, to within 0.2cm, using scissors and a ruler.
3	Bromophenol blue		$5cm^3$	Student's bench/ Shared by two students per bench	Dissolve 0.4g of the solid indicator in $200cm^3$ ethanol and make up to 1 dm^3 with distilled water.
4	**FA3** Sodium hydroxide **[H]**	0.120 mol dm^{-3}	150 cm^3	Student's bench	Dissolve 4.80g of NaOH in each dm^3 of solution.
5	**FA4** Acidified iron(III) chloride **[C][H]**	0.060 mol dm^{-3}	150 cm^3	Student's bench	Dissolve 16.22g of $FeCl_3.6H_2O$ in each dm^3 of 0..20 mol dm^{-3} hydrochloric acid. 0.20 mol dm^{-3} hydrochloric acid made by diluting 2.0 mol dm^{-3} hydrochloric acid 10 fold.(see above in FA1)
6	**FA5** Potassium iodide	0.060 mol dm^{-3}	$80cm^3$	Student's bench	Dissolve 9..96g of KI in each dm^3 of solution.
7	**FA6** Sodium thiosulfate	0.0060 mol dm^{-3}	150 cm^3	Student's bench	Dissolve 29.78g of $Na_2S_2O_3.5H_2O$ in each dm^3 of solution. Dilute this solution 20-fold.
8	Starch indicator	Freshly prepared aqueous starch indicator	$80cm^3$	Student's bench	Mix 2g of soluble starch with a little cold water until a smooth paste is obtained. Add $100cm^3$ of boiling water and stir. Boil until a clear solution is obtained (about 5 minutes).

		(approx. 2% solution w/v)			
9	**FA7**	A mixture of aluminium sulfate and sodium chloride	0.5g	Student's bench	Approximately equal masses of $Al_2(SO_4)_3.16H_2O$ and NaCl thoroughly mixed.
10	**FA8**	A mixture of magnesium carbonate and potassium iodide	0.5g	Student's bench	Approximately equal masses of $MgCO_3$ and KI thoroughly mixed. Note: "basic" forms of magnesium carbonate are suitable.
11	**FA9 [H]**	Ammonium iron(II) sulfate	1.5g	Student's bench	Approximately 1.5g of $(NH_4)_2Fe(SO_4).6H_2O$

STANDARD BENCH REAGENTS

Hazard	Label	Identity	Notes (hazards given in this column are for the raw materials)
[MH]	Dilute hydrochloric acid	2.0 mol dm^{-3} HCl	Dilute 170 cm^3 of concentrated (35 – 37%; approximately 11 mol dm^{-3}) hydrochloric acid to 1 dm^{-3}
[C]	Dilute nitric acid	2.0 mol dm^{-3} HNO_3	Dilute 128 cm^3 of concentrated (70% w/v) nitric acid to 1 dm^3
[MH]	Dilute sulfuric acid	1.0 mol dm^{-3} H_2SO_4	Cautiously pour 55 cm^3 of concentrated (98%) sulfuric acid into 500 cm^3 of distilled water with continuous stirring. Make the solution up to 1 dm^3 with distilled water. **Care:** concentrated H_2SO_4 is very corrosive
[C][MH][N]	Aqueous ammonia	2.0 mol dm^{-3} NH_3	Dilute 112 cm^3 of concentrated (35%) ammonia to 1 dm^3
[C]	Aqueous sodium hydroxide	2.0 mol dm^{-3} NaOH	Dissolve 80.0 g of NaOH in each dm^3 of solution. **Care:** the process of solution is exothermic and any concentrated solution is very corrosive.
[MH]	Aqueous barium nitrate	0.1 mol dm^{-3} barium nitrate	Dissolve 26.1 g of $Ba(NO_3)_2$ in each dm^3 of solution.
[N]	Aqueous silver nitrate	0.05 mol dm^{-3} silver nitrate	Dissolve 8.5g of $AgNO_3$ in each dm^3 of solution.
[MH]	Limewater	Saturated aqueous calcium hydroxide, $Ca(OH)_2$	Prepare fresh limewater by leaving distilled water to stand over solid calcium hydroxide for several days, shaking occasionally. Decant or filter the solution.
	Aqueous potassium iodide	0.1 mol dm^{-3} KI	Dissolve 16.6g of KI in each dm^3 of solution

	Acidified aqueous potassium manganate (VII)	0.02 mol dm^{-3} potassium manganate (VII)	Dissolve 3.16g of $KMnO_4$ in each dm^3 of solution. Mix equal volumes of 0.02 mol dm^{-3} $KMnO_4$ and 1.0 mol dm^{-3} sulfuric acid.
	hexane	Hexane	

The following materials and apparatus should be available **FOR EACH STUDENT**.

Red and blue litmus papers, plain filter strips for use with acidified manganate(VII), aluminium foil for testing nitrate/nitrite, wooden splints and the apparatus normally used in the Centre for use with limewater testing for carbon dioxide.

INNOVA JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION
in preparation for General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME **WORKED SOLUTIONS**

CLASS

INDEX NUMBER

CHEMISTRY

9729/01

Paper 1 Multiple Choice

27 June 2017

1 hour

Additional Materials: *Data Booklet*
Multiple Choice Answer Sheet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in soft pencil.
Do not use staples, paper clips, highlighters, glue or correction fluid.

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.

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

This document consists of **19** printed pages.

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

1 A given mass of ideal gas occupies a volume *V* and exerts a pressure *p* at 30 °C.

At which temperature will the same mass of the ideal gas occupy a volume $\frac{V}{3}$ and exert a pressure 2*p*?

A 20 °C **C** 202 °C

B 20 K **D** 202 K

Answer: **D**

pV = nRT

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\frac{P_1V_1}{T_1} = \frac{2P_1\frac{V_1}{3}}{T_2}$$

$$T_2 = \frac{2}{3}T_1$$

Original T = 30 + 273 = 303 K
New T = $\frac{2}{3}$ × 303 = 202 K

2 Which equation corresponds to the third ionisation energy of titanium (Ti)?

A $Ti(g) \rightarrow Ti^{3+}(g) + 3e^-$

B $Ti^{2+}(s) \rightarrow Ti^{3+}(g) + e^-$

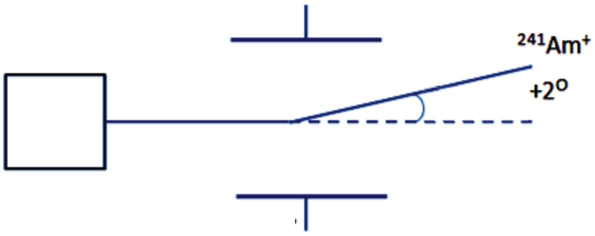
C $Ti^{2+}(g) \rightarrow Ti^{3+}(g) + e^-$

D $Ti^{3+}(g) + e^- \rightarrow Ti^{2+}(g)$

Answer: **C**

Third ionization energy of Ti is defined as the amount of energy required to remove 1 mole of electrons from one mole of doubly charged gaseous Ti (Ti^{2+}) to form one mole of triply charged gaseous Ti (Ti^{3+}).

3 A sample of the element Americium (Am) was vaporised, ionised and passed through an electric field. It was observed that a beam of $^{241}Am^+$ particles gave an angle of deflection of +2°.



Assuming an identical set of experimental conditions, by what angle would a beam of $^{32}S^-$ particles be deflected?

A +15.1°

B –15.1°

C +30.1°

D –30.1°

Answer: **B**

angle of deflection $\alpha \dfrac{\text{charge}}{\text{mass}}$

angle of deflection of $^{241}Am^+$ = +2°

For $^{241}Am^+$, $\dfrac{q}{m}=\dfrac{1}{241}$

$$k\frac{1}{241}=(2)$$
$$k=482$$

For $^{32}S^-$, $\dfrac{q}{m}=\dfrac{1}{32}$

angle of deflection of $^{32}S^-$ = $=\dfrac{1}{32}\times 482$ = –15.1°

4 Which of the following statements describes a phenomenon which **cannot** be explained by hydrogen bonding?

A Ice floats on water.

B The boiling point of carboxylic acid increases with increasing relative molecular mass.

C 2-nitrophenol is more volatile than 4-nitrophenol.

D Ethanoic acid molecules form dimers when dissolved in benzene.

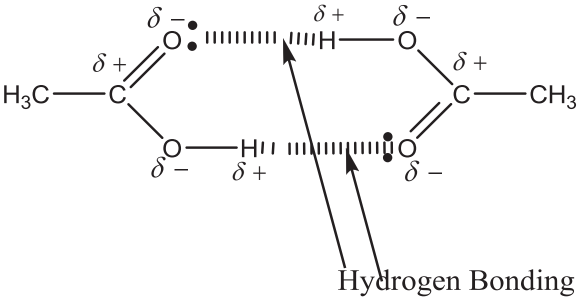
Answer: **B**

Option **A** is incorrect as in ice, each H_2O molecule forms the maximum of **four** hydrogen bonds with 4 other H_2O molecules. This results in an **open structure** of ice and hence ice is **less dense** than water and so, floats on water.

Option **B** is correct as the boiling point of carboxylic acid increases with increasing M_r due to **stronger instantaneous dipole-induced dipole interactions between the non-polar R group** as the size of electron cloud of R group increases and hence become more polarisable.

Option C is incorrect as in 2-nitrophenol, due to close proximity between –OH and $–NO_2$ groups, they can be used for formation of **intramolecular hydrogen bonds.** Hence, there are **fewer available sites** for **intermolecular hydrogen bonds**. Thus, 2-nitrophenol has a lower boiling point (and hence more volatile) as **lesser energy is required** to overcome the **less extensive hydrogen bonds** between molecules.

Option **D** is incorrect as in benzene, CH_3COOH molecules can form a dimer via hydrogen bonding.



5 A tertiary amine, R_3N, reacts with boron trifluoride, BF_3 to give an addition product. Which of the following statements is **not** true?

A R_3N acts as a Lewis base.

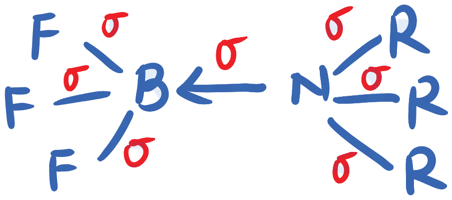
B The product is a polar molecule.

C There are six σ bonds in the product.

D The product contains a dative covalent bond.

Answer: **C**

Addition product:



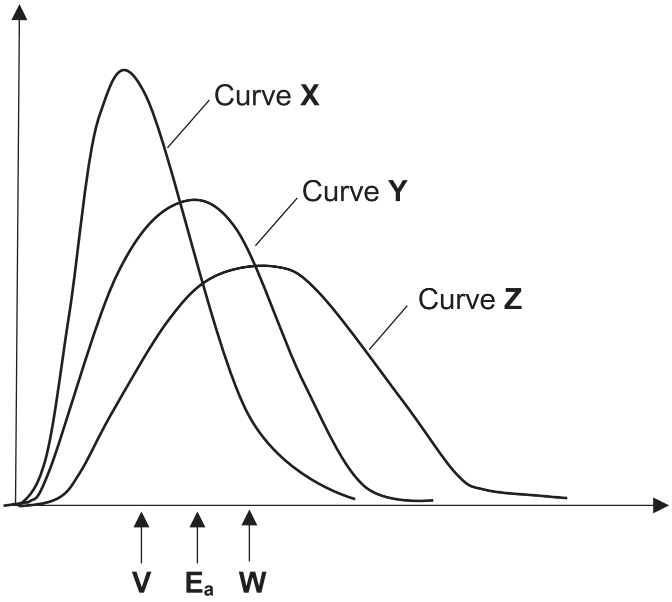
Option **A** is incorrect as R_3N is a lewis base as it **donates an electron pair** to BF_3.

Option **B** is incorrect as the molecule is polar due to presence of **polar bonds** (C–N, B–F and B–N) and the **dipole moments do not cancel out**.

Option **C** is correct as there is a **minimum of 7 σ bonds** in the addition product (not taking into account the C–H and C–C σ bonds present in the R groups).

Option D is correct as there is a **dative covalent bond from N to B**.

6 The curve **Y** and the value E_a represent the distribution of energies of the molecules and the activation energy for an uncatalysed gaseous reaction.



What is a possible outcome if the reaction is catalysed?

A The distribution of energies will be given by curve **X** and the activation energy by value **V**

B The distribution of energies will be given by curve **Y** and the activation energy by value **V**.

C The distribution of energies will be given by curve **Y** and the activation energy by value **W**.

D The distribution of energies will be given by curve **Z** and the activation energy by value **W**.

Answer: **B**

When catalyst is added, the graph distribution of energies of molecules will not change, it is affected only by temperature. Hence the curve should be **Y.**
However, when catalyst is added E_a will become lowered, hence value **V.**

7 If the rate of decay of a radioactive isotope decrease from 300 counts per minute to 37.5 counts per minute after 1 day, what is its half-life?

A 4 hours

B 6 hours

C 8 hours

D 12 hours

Answer: **C**

First half-life occurs when 300 counts per minute is reduced to 150 counts per minute.
Second half-life occurs when 150 counts per minute is reduced to 75 counts per minute.
Third half-life occurs when 75 counts per minute is reduced to 37.5 counts per minute.

3 half-life in 24 hours means each half-life is 8 hours.

8 Which of the following statements does **not** describe a reaction at equilibrium?

A Forward and backward reactions occur at equal rate.

B The system must be closed.

C K_c increases as the reaction progresses.

D Concentrations of reactants and products are constant.

Answer: **C**

At dynamic equilibrium, rate of forward reaction = rate of backward reaction, hence there is no change in concentration of reactants and products.

K_c is only affected by **temperature changes**.

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

The enthalpy change of formation of carbon monoxide and carbon dioxide are given below.

$$\Delta H_f\ CO = -110\ kJmol^{-1}$$
$$\Delta H_f\ CO_2 = -393\ kJmol^{-1}$$

Which of these statements are correct?

1 CO_2(g) has lower energy content than CO(g).

2 The enthalpy change of combustion of carbon is –393 $kJmol^{-1}$.

3 CO_2(g) is formed exothermically from CO(g).

4 A larger amount of energy is required to atomise CO_2(g) than CO(g).

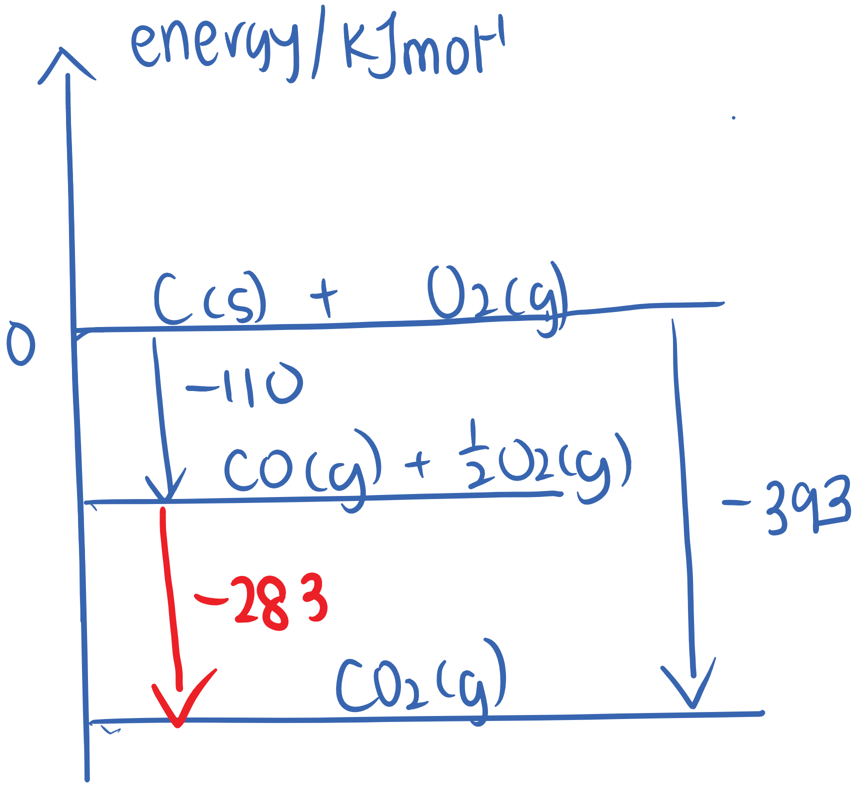
A 1, 2, 3 and 4

B 1, 2 and 3 only

C 1, 2 and 4 only

D 2 and 3 only

Answer: **A**



Option **1** is correct as from the energy level diagram, $CO_2(g)$ has a lower energy content than CO(g).
Option **2** is correct as $\Delta H_c(C) = \Delta H_f(CO_2) = –393$ $kJmol^{-1}$ from the diagram
Option **3** is correct as from the energy level diagram, $CO_2(g)$ is formed exothermically from CO(g). [–283 $kJmol^{-1}$]
Option **4** is correct as atomisation means to produce free gaseous C and O atoms (an endothermic process). More energy is required to atomise $CO_2(g)$ than CO(g) as $CO_2(g)$ has a lower energy content.

10 A sparingly soluble calcium salt ionises in aqueous solution according to the equation given:

$$Ca_3X_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2X^{3-}(aq)$$

If the solubility product K_{sp} of Ca_3X_2 is S, what is the value of the concentration of Ca^{2+} (aq) at equilibrium?

A $S^{\frac{1}{2}}$

B $\left[\dfrac{S}{108}\right]^{\frac{1}{5}}$

C $\left[\dfrac{3S}{5}\right]^{\frac{1}{2}}$

D $\left[\dfrac{9S}{4}\right]^{\frac{1}{5}}$

Answer: **D**

$$\mathrm{Ca_3X_2\ (s) \rightleftharpoons 3\ Ca^{2+}\ (aq)\ +\ 2\ X^{3-}\ (aq)}$$

$K_{sp} = [Ca^{2+}]^3\ [X^{3-}]^2$
$S = (3x)^3\ (2x)^2$
$= (27x^3)\ (4x^2)$
$= 108\ x^5$

$$X = \left(\frac{S}{108}\right)^{\frac{1}{5}}$$

$$[Ca^{2+}] \text{ at eqm} = 3x = 3\left(\frac{S}{108}\right)^{\frac{1}{5}} = \left(\frac{243S}{108}\right)^{\frac{1}{5}} = \left[\frac{9S}{4}\right]^{\frac{1}{5}}$$

11 The K_{sp} of $\mathrm{AgC}l$ and AgI are 1.80×10^{-10} mol^2 dm^{-6} and 8.3×10^{-17} mol^2 dm^{-6} respectively. Which of the following statements is correct when equal volumes of 1×10^{-4} mol dm^{-3} aqueous $AgNO_3$ was added to a mixture containing 3.0×10^{-6} mol dm^{-3} $\mathrm{BaC}l_2$ and 3.0×10^{-6} mol dm^{-3} BaI_2?

A AgC*l* is precipitated only.

B AgI is precipitated only.

C AgC*l* is precipitated followed by AgI.

D AgI is precipitated followed by AgC*l*.

Answer: **B**

$[Ag^+] = [AgNO_3] = 1 \times 10^{-4}$ mol dm^{-3}

$[\mathrm{C}l^-] = 2 \times [\mathrm{BaC}l_2] = 6 \times 10^{-6}$ mol dm^{-3}

$[I^-] = 2 \times [BaI_2] = 6 \times 10^{-6}$ mol dm^{-3}

Take note that the mixture consists of equal volumes of $AgNO_3$ and $\mathrm{BaC}l_2$. Hence, the new concentration will be halved.
$[Ag^+]$ in mixture $= 0.5 \times 10^{-4}$

$[\mathrm{C}l^-]$ in mixture $= 3 \times 10^{-6}$

IP of AgC*l* $= (0.5 \times 10^{-4})(3.0 \times 10^{-6}) = 1.5 \times 10^{-10}$

IP < Ksp → AgC*l* will not ppt out

IP of AgI $= (0.5 \times 10^{-4})(3.0 \times 10^{-6}) = 1.5 \times 10^{-10}$

IP > Ksp → AgI will ppt out

12 The dissociation constant, K_w, for the ionisation of water, $H_2O \rightleftharpoons H^+ + OH^-$, at different temperatures is given below.

Temperature / °C	K_w / mol^2 dm^{-6}
0	1.15×10^{-15}
25	1.00×10^{-14}
50	5.50×10^{-14}

What can be deduced from this information?

A Only at 25 °C are $[H^+]$ and $[OH^-]$ equal.

B The equilibrium lies furthest to the right at 0 °C.

C The forward reaction is exothermic.

D The pH of pure water decreases with temperature.

Answer: **D**

Option **A** is incorrect as the $[H^+]$ and $[OH^-]$ of water are equal at all temperatures.
Option **B** is incorrect as the value of K_w is the smallest at 0 °C. Hence, equilibrium lies most to the left.
Option **C** is incorrect as K_w increases with temperature, the forward reaction is favoured.
Option **D** is correct as an increase in temperature favours the endothermic reaction, hence the forward reaction is endothermic.

Option **D**:
$K_w = [H^+]\,[OH^-]$
$K_w = [H^+]^2$
$pH = -\log \sqrt{(K_w)}$
as K_w increases with temperature, pH will decrease.

13 Calculate the standard Gibbs free energy change, $\Delta G^\ominus$ for the following reaction:

$$2Al\,(s) + 3Cu^{2+}(aq) \longrightarrow 2Al^{3+}(aq) + 3Cu(s)$$

A –386 kJ mol^{-1}

B –579 kJ mol^{-1}

C –1045 kJ mol^{-1}

D –1158 kJ mol^{-1}

Answer: **D**

$E_{cell} = +0.34 - (-1.66) = +2.00$ V

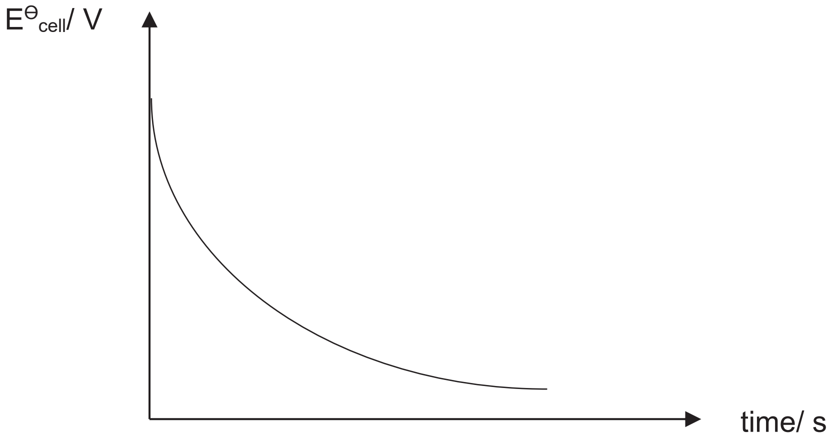
$\Delta G^\ominus = -nFE_{cell} = -6 \times 96500 \times 2.00 = -1158\,000$ J mol^{-1}

$= \underline{\mathbf{-1158\ kJ\ mol^{-1}}}$

14 An experiment is carried out with the following cell.

$$\text{Fe (s)} \mid \text{Fe}^{2+}\text{(aq)} \parallel \text{Ni}^{2+}\text{(aq)} \mid \text{Ni (s)}$$

The following graph of cell potential against time was obtained when a change was continuously made to the half-cell.



What continuous change could produce these results?

A Add nickel (II) chloride to the nickel half-cell.

B Add aqueous cyanide ions to the iron half-cell.

C Add water to the nickel half-cell.

D Increases the surface area of iron immersed in the solution.

Answer: **C**

$E_{cell} = E_{Ni^{2+}/Ni} - E_{Fe^{3+}/Fe^{2+}}$ (graph states that E_{cell} should decrease)

Option **A** is incorrect as

$$Ni^{2+} + 2e^- \rightleftharpoons Ni$$

When nickel (II) chloride is added to the nickel half-cell, $[Ni^{2+}]$ increase, eqm position shift right. $E_{Ni^{2+}/Ni}$ is more positive (incorrect)

Option **B** is incorrect as

$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \qquad +0.77$$

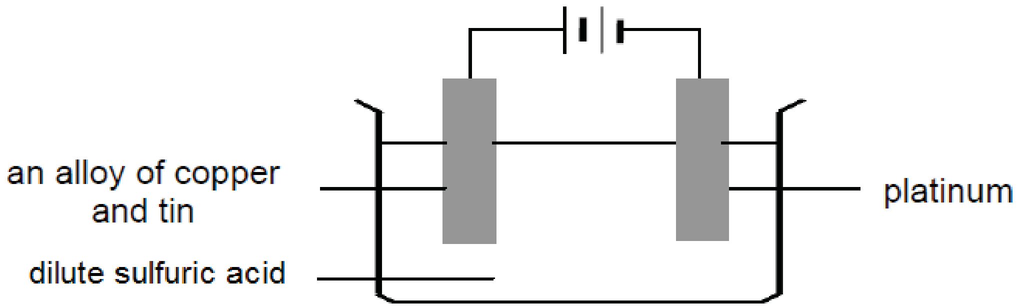
$$[Fe(CN)_6]^{3-} + e^- \rightleftharpoons [Fe(CN)_6]^{4-} \qquad +0.36$$

When aqueous cyanide ions is added to the iron half-cell. $E_{Fe^{3+}/Fe^{2+}}$ is less positive (incorrect)

Option **C** is correct as when water is added to the nickel half-cell, $[Ni^{2+}]$ decrease, eqm position shift left. $E_{Ni^{2+}/Ni}$ is less positive (correct)

Option **D** is incorrect as increases in the surface area of iron affects rate not E values.

15 The circuit shown in the diagram was set up.



Which reactions will occur at the electrodes?

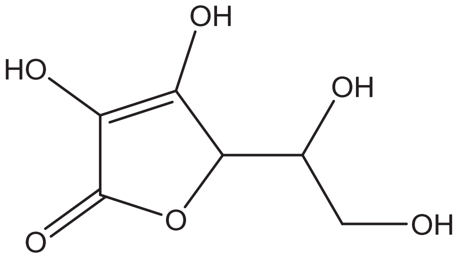
	anode reaction	*cathode reaction*
A	Oxygen gas is evolved.	Hydrogen gas is evolved.
B	Tin dissolves preferentially.	Hydrogen gas is evolved.
C	Copper dissolves preferentially.	Copper is deposited.
D	Copper and tin both dissolve.	Sulfur dioxide gas is evolved.

Answer: **B**

At the anode: (oxidation will occur)
Species present: Cu and Sn
Consider
$Sn^{2+} + 2e^- \longrightarrow Sn$ $\quad$ ***E***⊖/ **V** = - 0.14
$Cu^{2+} + 2e^- \longrightarrow Cu$ $\quad$ ***E***⊖/ **V** = +0.34
Based on the ***E***⊖/ **V** values, a less positive value indicates that tin will be selectively oxidised.

At the cathode: (reduction will occur)
Species present: H_2O and H^+
Consider
$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$ $\quad$ ***E***⊖/ **V** = –0.83
$2H^+ + 2e^- \longrightarrow H_2$ $\quad$ ***E***⊖/ **V** = 0.00
$Sn^{2+} + 2e^- \longrightarrow Sn$ $\quad$ ***E***⊖/ **V** = - 0.14
Based on the ***E***⊖/ **V** values, a more ***E***⊖/ **V** positive value indicates that H^+ will be selectively reduced to produce H_2 gas.

16 The diagram shows the structure of vitamin C.

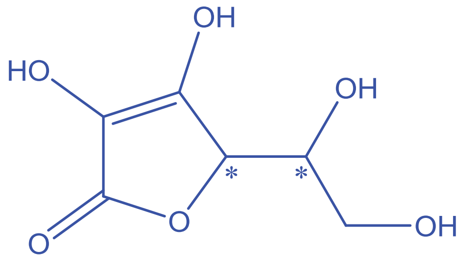


vitamin C

How many stereoisomers are there in one molecule of vitamin C?

A 2 **B** 4 **C** 8 **D** 16

Answer: **B**



2 chiral centres so number of enantiomers are $2^2 = 4$

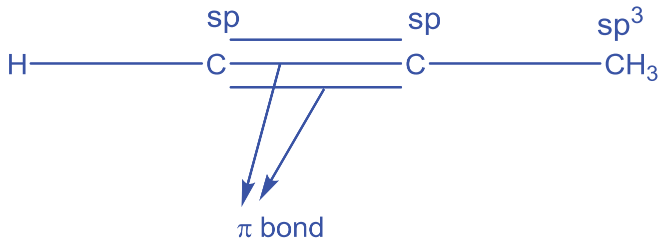
17 Propyne, C_3H_4, has the following structure.

$$H—C\equiv C—CH_3$$

Which row correctly describes the bonding and hybridisation in a molecule of propyne?

	number of π bonds	number of sp C atoms	number of sp^2 C atoms
A	1	1	1
B	2	2	0
C	2	2	1
D	3	3	0

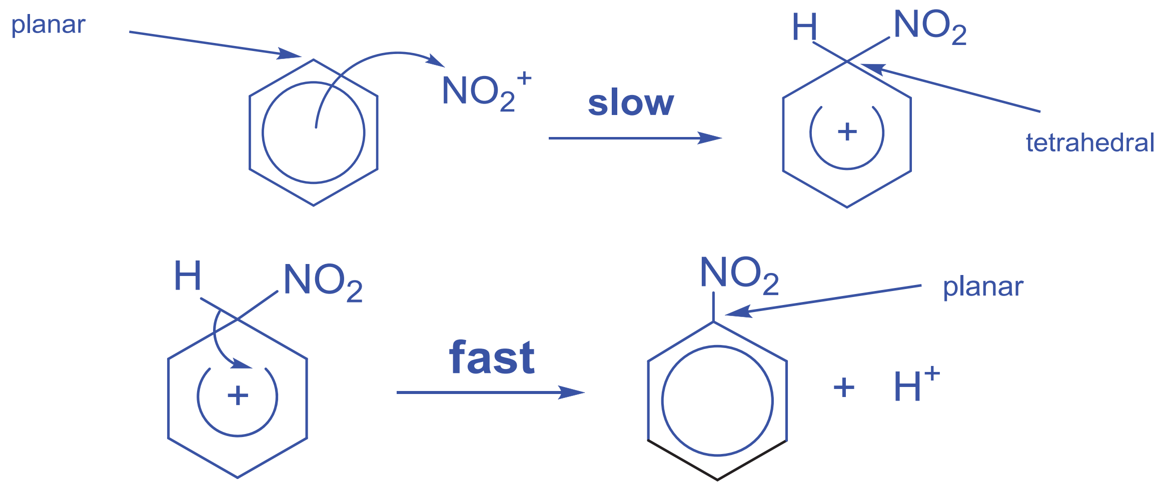
Answer: **B**



18 During the nitration of benzene, a nitro group substitutes at a carbon atom. Which one of the following gives the arrangement of the bonds at this carbon atom during the reaction?

	at the start of the reaction	*in the intermediate complex*	*at the end of the reaction*
A	planar	planar	planar
B	planar	tetrahedral	tetrahedral
C	planar	tetrahedral	planar
D	tetrahedral	planar	tetrahedral

Answer: **C**



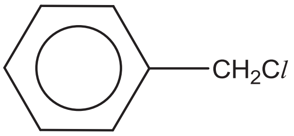
19 When a halogen compound **S** was boiled under reflux for some time with silver nitrate in a mixture of ethanol and water, little or no precipitate was seen.

Which of the following formulae could represent **S**?

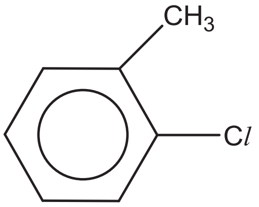
A $CH_3CH_2CHClCH_2CH_3$

B $CH_3CH_2CH_2COCl$

C



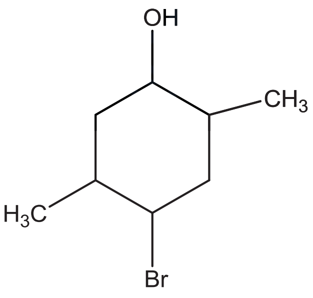
D



Answer: **D**

Given that there is little or no ppt seen, it shows that the C-Cl bond is strong, hence it is referring to the Cl bonded to a benzene ring as the p orbital of Cl will overlap with the π orbital of the benzene ring.

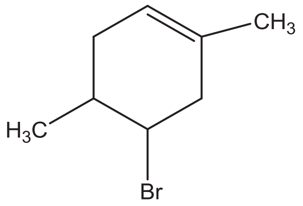
20 Compound **P** was heated with ethanolic potassium hydroxide.



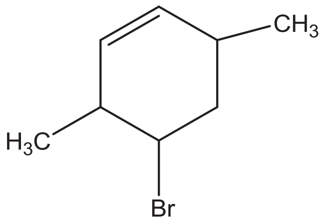
compound **P**

Which of the following would be the major product?

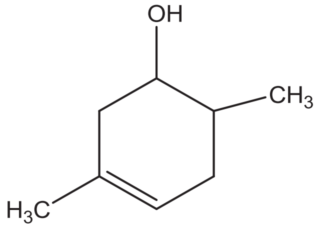
A



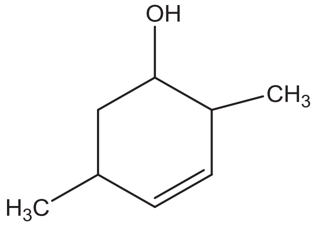
B



C



D



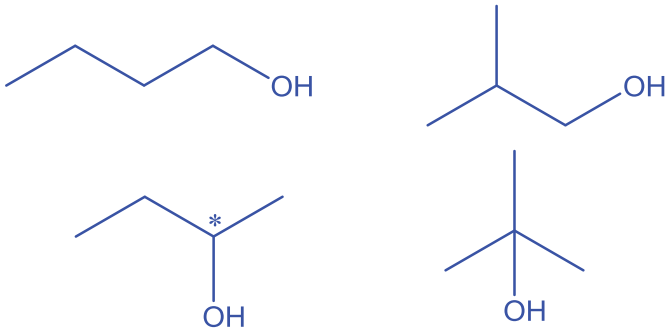
Answer: **C**

Ethanolic KOH is the reagent to eliminate H and Br → **A** and **B** will be wrong
Using Saytzeff rule whereby the "poor get poorer"

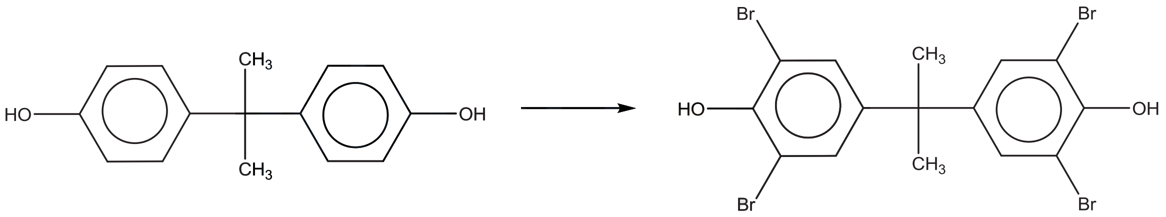
21 How many isomers (including both structural isomers and stereoisomers) with molecular formula $C_4H_{10}O$ liberates hydrogen on reaction with sodium?

A 2 **B** 3 **C** 4 **D** 5

Answer: **D**



22 Bisphenol A was used to make products such as plastic polycarbonate baby bottles and food containers. It is now regarded as toxic and has been withdrawn from use.



bisphenol A compound **Q**

Which reagent will convert bisphenol A into compound **Q**?

A $AlBr_3(s)$

B $Br_2(aq)$

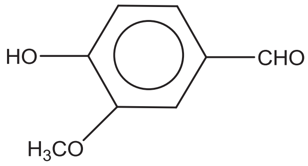
C $HBr(g)$

D $NaBr(aq)$

Answer: **B**

Based on the product, the reaction is electrophilic substitution. Since the starting reactant is a phenol, catalyst will not be necessary. Hence $Br_2(aq)$ will be sufficient.

23 Vanillin is the active ingredient of vanilla.



vanillin

Which of the following will be observed with vanillin?

1 Warm acidified potassium dichromate (VI) turns green.
2 2,4-dinitrophenylhydrazine reagent gives an orange precipitate.
3 A yellow precipitate is formed on warming with aqueous alkaline iodine.

A 1 only

B 2 only

C 1 and 2 only

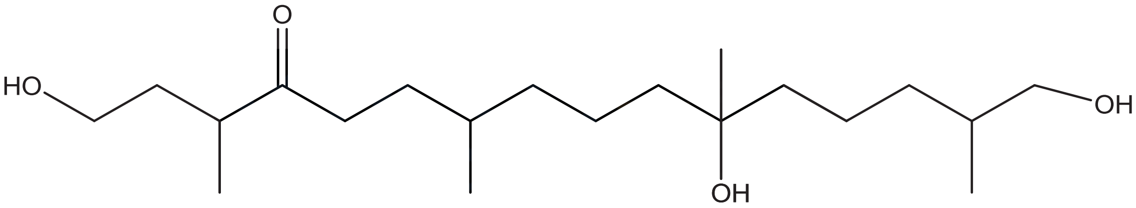
D 2 and 3 only

Answer: **C**

Option **1** and **2** are correct as Vanillin has the aldehyde group which can be oxidised by potassium dichromate and react with 2,4-DNPH.

Option **3** is not correct as there is no presence of CH_3CO- or $CH_3CH(OH)$- group in vanillin hence it does not react with aqueous alkaline iodine.

24 The mould *Phytophthora* damages many plants, destroying agricultural crops such as potatoes. A hormone-like compound called alpha1 regulates the reproduction of all species of *Phytophthora*. The structure of alpha1 is now known, giving scientist a key to the possible future eradication of the mould.



alpha1

Which of the following reagents will react with alpha1?

1 Br_2
2 $SOCl_2$
3 H_2/Pt

A 1 and 2 only

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

Answer: **B**

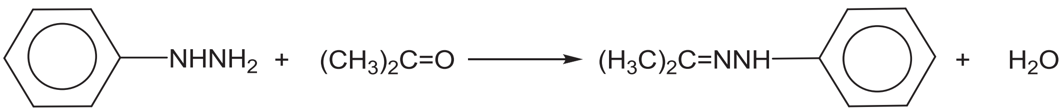
Alpha1 is not able to react with aqueous Br_2 since there is no C=C.

OH group on Alpha1 is able to react with $SOCl_2$ to form halogenoalkane.

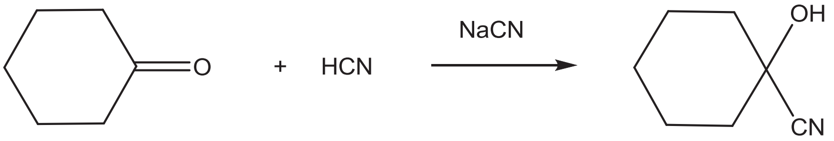
Carbonyl group on alpha1 can be reduced by H_2/Pt to form secondary alcohol.

25 Which transformations involve a nucleophile?

1



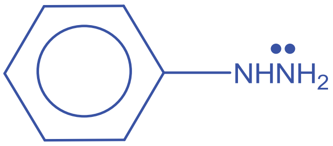
2



3 $CH_3CH_2COCl + NH_3 \longrightarrow CH_3CH_2CONH_2 + HCl$

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

Answer: **D**



Option **1** is correct as is the nucleophile. Similar to 2,4-DNPH
Option **2** is correct as CN^- is the nucleophile. Reaction is nucleophilic addition.
Option **3** is correct as NH_3 is the nucleophile. Reaction is nucleophilic acyl substitution.

26 Which of the following properties are identical for the two enantiomers of 2-hydroxypropanoic acid, $CH_3CH(OH)COOH$?

1 ΔH^o_f
2 pK_a
3 melting point

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

Answer: **D**

Enantiomers will only differ in their biological properties. Given that they have the same functional group, their chemical and physical properties should remain the same.

27 When organic compounds **E**, **F**, **G** and **H** are added separately to water, solutions of increasing pH values are obtained. The possible identities of compounds **E** to **H** (not necessarily in that order) are given below.

$CH_3CH_2CO_2H$ CH_3CH_2COCl $(CH_3)_2CHNH_2$ $CH_3CH_2NH_2$

Which is the correct set of identities of compounds **E**, **F**, **G** and **H**?

	E	**F**	**G**	**H**
A	$CH_3CH_2CO_2H$	CH_3CH_2COCl	$CH_3CH_2NH_2$	$(CH_3)_2CHNH_2$
B	$CH_3CH_2CO_2H$	CH_3CH_2COCl	$(CH_3)_2CHNH_2$	$CH_3CH_2NH_2$
C	CH_3CH_2COCl	$CH_3CH_2CO_2H$	$(CH_3)_2CHNH_2$	$CH_3CH_2NH_2$
D	CH_3CH_2COCl	$CH_3CH_2CO_2H$	$CH_3CH_2NH_2$	$(CH_3)_2CHNH_2$

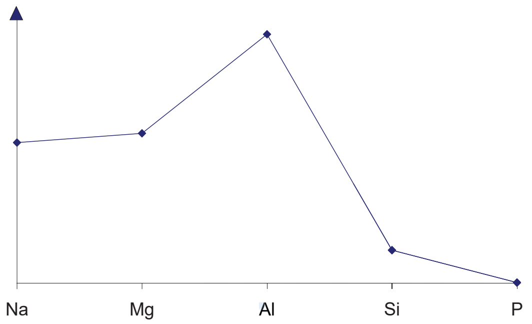
Answer: **D**

Between CH_3CH_2COCl and $CH_3CH_2CO_2H$, $CH_3CH_2CO_2H$ is a weaker acid as one mole of CH_3CH_2COCl will form one mole of CH_3CH_2COOH and one mole of HCl in aqueous solution while CH_3CH_2COOH will only partially dissociate to form H^+. CH_3CH_2COCl will have a lower pH than CH_3CH_2COOH.

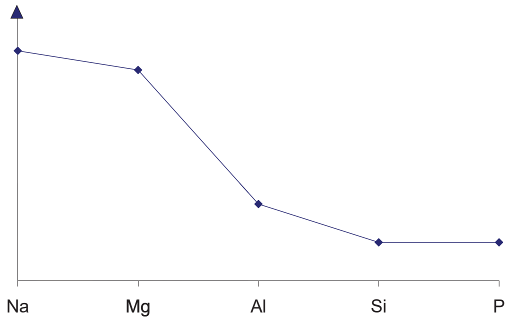
$(CH_3)_2CHNH_2$ is a stronger base as compared to $CH_3CH_2NH_2$ as it has one more methyl electron donating group, hence the lone pair is more available to accept H^+. $(CH_3)_2CHNH_2$ will have a higher pH as compared to $CH_3CH_2NH_2$.

28 The graphs below show the variation in two properties of the elements Na to P and their compounds.

Graph I



Graph II



Which properties are illustrated in Graphs I and II?

	Graph I	Graph II
A	electrical conductivity of the element	pH of the chloride when added to water
B	electrical conductivity of the element	pH of the oxide when added to water
C	melting point of the element	pH of the chloride when added to water

D	melting point of the element	pH of the oxide when added to water

Answer: **A**

Graph 1:
Electrical conductivity increases from Na to A*l* due to the increasing amount of delocalised electrons. Si is a semiconductor / metalloid hence it is able to conduct electricity. Phosphorus is a non-metal with a simple covalent structure. Hence it is unable to conduct electricity.

Melting point of graph should increase from Na to A*l* and peak at Si as Si has a giant covalent structure. Hence, options C and D are eliminated.

Graph 2:
$\mathrm{NaC}l$ - pH 7
$\mathrm{MgC}l_2$ – pH 6.5
$\mathrm{A}l\mathrm{C}l_3$ – pH 3
$\mathrm{SiC}l_4$ – pH 2
$\mathrm{PC}l_5$ – pH 2

$\mathrm{Na_2O}$ – pH 13
MgO – pH 10
$\mathrm{A}l_2\mathrm{O}_3$ – not soluble hence pH 7
$\mathrm{SiO_4}$ – not soluble hence pH 7
$\mathrm{P_4O_{10}}$ – pH 2

29 Which of the following elements is expected to show the greatest tendency to form some covalent compounds?

A Barium

B Calcium

C Magnesium

D Potassium

Answer: **C**

The metal cation with the highest charge density will have the greatest polarising power and hence the greatest tendency to form covalent compounds.

Charge density = charge / ionic radius

Since Mg has a charge of +2 and the smallest size, it has the highest charge density

30 Why is hydrogen iodide a stronger acid than hydrogen chloride?

A A molecule of hydrogen chloride is more polar than a molecule of hydrogen iodide.

B The enthalpy change of formation of hydrogen iodide is greater than that of hydrogen chloride.

C The covalent bond in the hydrogen iodide molecule is weaker than that in the hydrogen chloride molecule.

D The dissociation of hydrogen chloride molecules is suppressed by the stronger permanent dipole–permanent dipole interactions.

Answer: **C**

For HI and HC*l* to form acids, the H – X bond must be broken and the molecules need to dissociate in water to form H^+ and X^- ions.
Hence, the molecule with the weaker H – X bond will be able to dissociate to a greater extent to form more H^+ ions to be the stronger acid.

INNOVA JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION
in preparation for General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME	**WORKED SOLUTIONS**
CLASS	
INDEX NUMBER	

CHEMISTRY

9729/02

Paper 2 Structured Questions

24 August 2017

Candidates answer on the question paper.

2 hours

Additional Materials: *Data Booklet*

READ THESE INSTRUCTIONS FIRST

Write your index number, name and civics group on all the work you hand in.
Write in dark blue or black pen.
You may use pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

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

You are advised to show all working in calculations.
You are reminded of the need for good English and clear presentation in your answers.
You are reminded of the need for good handwriting.
Your final answers should be in 3 significant figures.

You may use a calculator.

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

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

For Examiner's Use	
1	19
2	12
3	10
4	10
5	24
Significant Figures and Units	
Handwriting and Presentation	
Total	75

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

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

1 Halogens are highly reactive and form compounds with many other elements, including metals and non-metals.

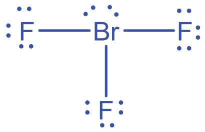
(a) Fluorine reacts with bromine to form liquid bromine trifluoride, BrF_3.

Two molecules of BrF_3 react to form ions as shown by the following equation.

$$2BrF_3 \longrightarrow BrF_2^+ + BrF_4^-$$

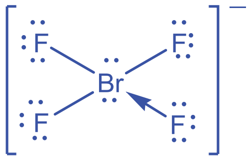
(i) Draw the structures and suggest the shape of each of these species. [3]

BrF_3



T-shaped

BrF_4^-



Square planar

(ii) BrF_4^- ions are also formed when potassium fluoride, KF dissolves in liquid BrF_3 to form $KBrF_4$. Explain, in terms of structure and bonding, why $KBrF_4$, has a high melting point. [2]

$KBrF_4$ has a **giant ionic structure** with **strong electrostatic forces of attraction between oppositely charged ions**, K^+ and BrF_4^-.

Large amount of energy is required to break the strong ionic bonds, thus it has a high melting point.

(b) Magnesium bromide, $MgBr_2$ is a chemical compound of magnesium and bromine and is often used in the pharmaceutical industries.

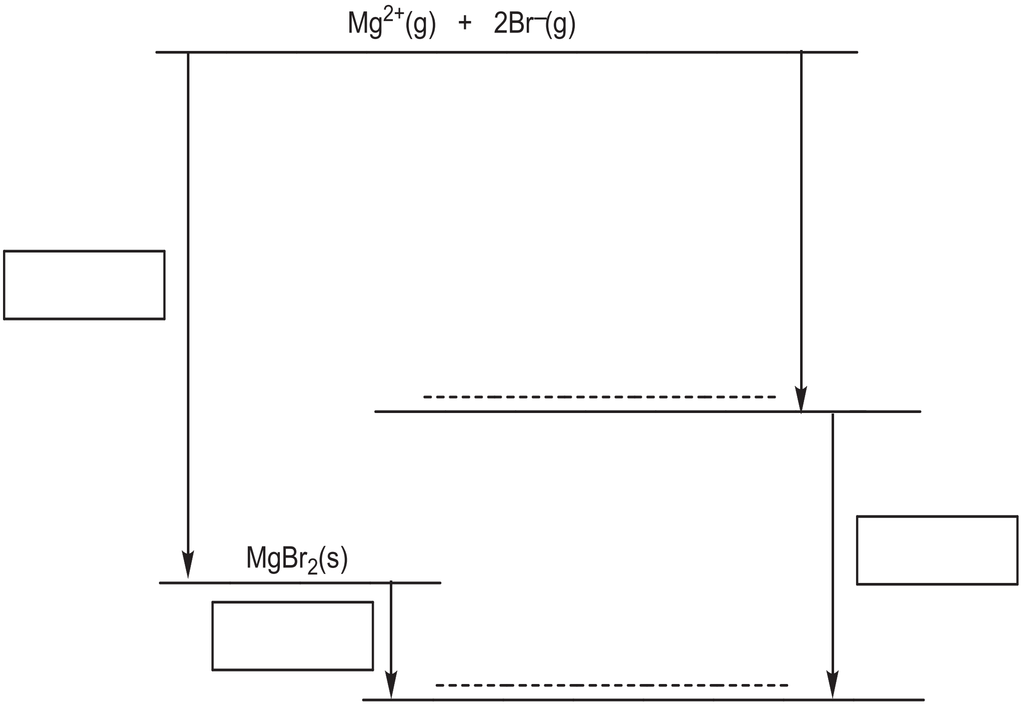
In this part of the question, you will construct an energy cycle for magnesium bromide to determine the enthalpy change of hydration of magnesium ions.

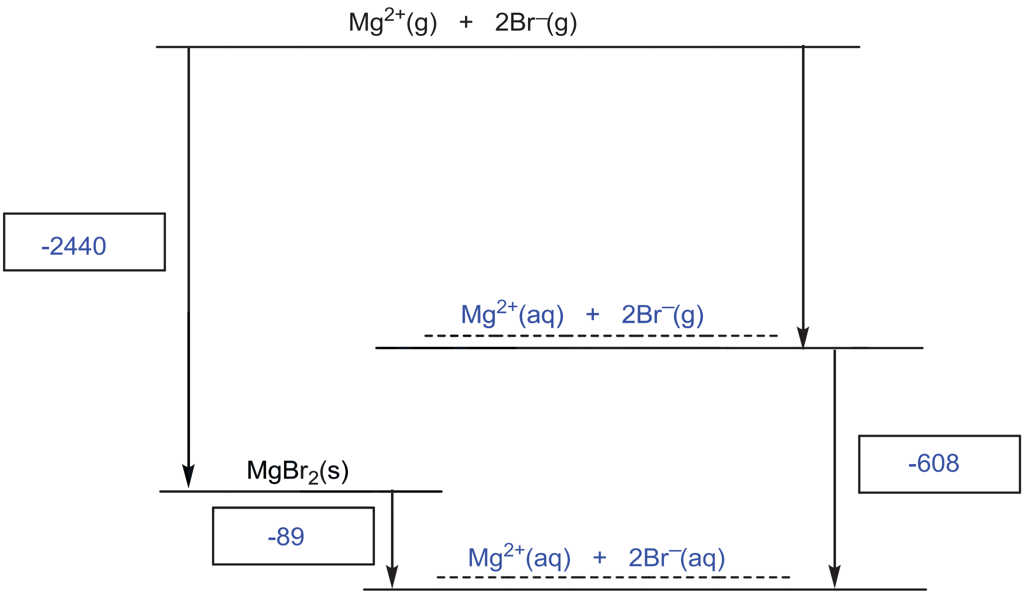
(i) Magnesium bromide has a lattice energy of –2440 kJ mol^{-1}.
Define in words the *lattice energy of magnesium bromide*. [1]
Lattice energy of $MgBr_2$ is the **enthalpy change/ energy released** when **ONE mole of solid $MgBr_2$ is formed from its separate gaseous ions, Mg^{2+}(g) and Br^-(g)**.

(ii) The table below shows the enthalpy changes that are needed to determine the enthalpy change of hydration of magnesium ions.

enthalpy change	**energy /kJ mol^{-1}**
lattice energy of magnesium bromide	–2440
enthalpy change of solution of magnesium bromide	–89
enthalpy change of hydration of bromide ions	–304

On the two dotted lines, add the species present and label the numerical values of the three arrows in the boxes provided. [2]





Species on the 2 dotted lines
Three numerical values

(iii) Calculate the enthalpy change of hydration of magnesium ions. [1]

Enthalpy change of hydration = –2440 – 89 + 608 = –1921
= **<u>–1920 kJ mol^{-1}</u>**

(iv) Given that the enthalpy change of formation of $Mg^{2+}(aq)$ is +413 kJ mol^{-1}, use your answer in **(b)(iii)** as well as relevant values from the *Data Booklet* to calculate the enthalpy change of atomisation of magnesium. [1]

$$\begin{tikzcd}
Mg(s) \arrow[r, "\Delta H_{atom}"] \arrow[dr, "413"'] & Mg(g) \arrow[r, "736 + 1450"] & Mg^{2+}(g) \arrow[dl, "-1921"] \\
& Mg^{2+}(aq) &
\end{tikzcd}$$

$\Delta H_{atomisation} = 413 + 1921 – 736 – 1450$
$= \mathbf{+148\ kJ\ mol^{-1}}$

(v) The enthalpy change of hydration of magnesium ions is more exothermic than the enthalpy change of hydration of calcium ions. Explain why. [1]

- $\Delta H_{hydration}\ \alpha\ \dfrac{q_+}{r_+}$ or in words
- Mg^{2+} has **higher charge density than Ca^{2+} since Mg^{2+} has a smaller ionic size than Ca^{2+}** and hence a more exothermic $\Delta H_{hydration}$.

(c) Nickel is a typical transition element in the d-block of the Periodic Table. Many nickel ions are able to interact with ligands to form complex ions, such as $[Ni(H_2O)_6]^{2+}$.

A student dissolves nickel(II) sulfate in water. A green solution forms containing the complex ion $[Ni(H_2O)_6]^{2+}$. The student then reacts separate portions of the green solution of nickel(II) sulfate as outlined below.

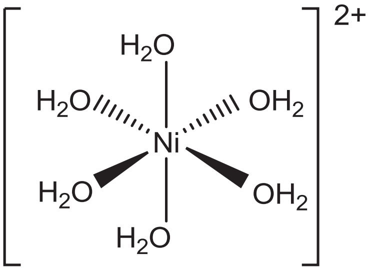
- Concentrated hydrochloric acid is added to the green solution of nickel(II) sulfate until there is no further change. The solution turns a lime-green colour and contains the four-coordinate complex ion **A**.
- Aqueous sodium hydroxide is added to the green solution of nickel(II) sulfate. A pale-green precipitate **B** forms.
- Concentrated aqueous ammonia is added to the green solution of nickel(II) sulfate until there is no further change. The solution turns a violet colour and contains the complex ion **C**. **C** has a molar mass of 160.7 g mol^{-1}.

(i) Explain why aqueous nickel(II) sulfate is green. [2]

$NiSO_4$ (aq) is coloured due to:

- the presence of **partially filled 3d–orbitals** in the Ni^{2+} metal ions.
- In the **presence of ligands**, **3d orbitals split into two groups with small energy gap**
- Some of the **light energy is used to promote an electron from a d-orbital of lower energy into the unfilled/ partially filled d-orbital of higher energy.**
- Green colour seen is the **complement of the red colour absorbed** in the visible region of the spectrum.

(ii) Draw a three dimensional diagram for the $[Ni(H_2O)_6]^{2+}$ ion. [1]



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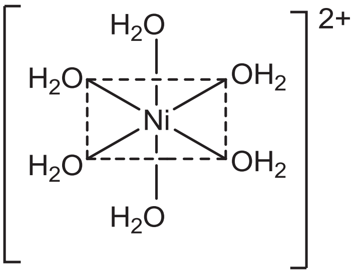


(iii) Suggest the formulae of **A**, **B** and **C**. [3]

A: $[NiCl_4]^{2-}$

B: $Ni(OH)_2$ or $Ni(H_2O)_4(OH)_2$

C: $[Ni(NH_3)_6]^{2+}$, do not allow $[Ni(NH_3)_4(H_2O)_2]^{2+}$ due to M_r of C given

(iv) What type of reaction has taken place in the formation of **C** from $[Ni(H_2O)_6]^{2+}$? Write an equation for this reaction. [2]

Ligand exchange

$[Ni(H_2O)_6]^{2+} + 6NH_3 \rightarrow [Ni(NH_3)_6]^{2+} + 6H_2O$

[Total: 19]

2 **(a)** In a school lab, magnesium strips can be stored in a normal container. However, barium metal has to be submerged in oil when it is stored. With reference to relevant data from the *Data Booklet*, explain the above observation. [2]

Reduction potential for Ba^{2+} **(-2.92V)** **is more negative** than Mg^{2+} **(-2.38V)** . **Ba is more reactive OR undergoes oxidation more readily than Mg**, thus has to be kept in oil to prevent it from reacting OR avoid direct contact with atmospheric O_2 .

(b) When solid barium carbonate is heated, no carbon dioxide is detected as it is thermally stable.

However, magnesium carbonate decomposes on heating as shown by the equation below.

$$MgCO_3(s) \longrightarrow MgO(s) + CO_2(g)$$

$$\Delta H^\ominus = +117 \text{ kJ mol}^{-1}; \quad \Delta S^\ominus = +175 \text{ J mol}^{-1} \text{ K}^{-1}$$

(i) Explain why barium carbonate is thermally stable while magnesium carbonate is not. [2]

Ba^{2+} ion is **larger and has a smaller charge density** than Mg^{2+}.

Ba^{2+} ion (has a smaller polarizing power) is able to **polarize/ distort the large electron cloud of the carbonate ion less effectively** than Mg^{2+} , **weakening the C-O bond to a smaller extent**.

More energy is required to break the C – O bond in $BaCO_3$ than $MgCO_3$.

(ii) Account for the sign of $\Delta S^\ominus$ in this reaction. [1]

There is an **increase in disorderliness** due to increase in the number of **moles** of gaseous particles , resulting in more ways to arrange the particles in the system.

(iii) Calculate the standard Gibbs free energy change, $\Delta G^\ominus$, for the decomposition of magnesium carbonate. [1]

$$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$$

$$= +117 - \left(298 \times \frac{+175}{1000}\right) = +117 - 52.15$$

$$\approx +64.9 \text{ kJ mol}^{-1}$$

(iv) Assuming that $\Delta H^\ominus$ and $\Delta S^\ominus$ for the reaction are independent of temperature, calculate the temperature at which the decomposition reaction becomes feasible. [1]

$$\Delta G^\ominus = 0 = \Delta H^\ominus - T\Delta S^\ominus = +117 - \left(\mathbf{T} \times \frac{+175}{1000}\right)$$

T = 669K = 396^{0}C

At 669K, the decomposition reaction becomes feasible.

(c) The labels of group 2 metal carbonates fell off the bottles. In an attempt to identify the compound in one of the bottles, the following experiment was carried out.

1.68 g of an insoluble metal carbonate, **D**CO_3 was reacted with 100 cm^3 of hydrochloric acid of concentration 0.500 mol dm^{-3}. The resulting solution was then made up to 250 cm^3 with distilled water. 25.0 cm^3 of this solution required 25 cm^3 of 0.04 mol dm^{-3} sodium hydroxide for titration.

(i) Write a balanced equation for the reaction between the metal carbonate and hydrochloric acid. [1]

$DCO_3\,(s) + 2HCl\,(aq) \rightarrow DCl_2\,(aq) + H_2O\,(l) + CO_2\,(g)$

(ii) Calculate the relative atomic mass of **D** and hence using the Periodic Table, identify **D**. [4]

Amount of sodium hydroxide that was used for the titration

= (25/1000) x 0.04

= **1.00 x 10^{-3}** mol (3sf)

Amount of HC*l* present originally = $\frac{100}{1000}$ x 0.500 = 0.05000 mol

Amount of HC*l* in **25.0 cm^3** after reaction with **D**CO_3

= 1.00 x 10^{-3} mol

Amount of unreacted HC*l* in **250 cm^3** = 1.00 x 10^{-3} x $\frac{250}{25.0}$

= 1.00 x 10^{-2} mol

Amount of HC*l* reacted with **D**CO_3

= Amount of HC*l* initially – amount of unreacted HC*l*

= 0.05000 - 1.00 x 10^{-2} = 0.0400 mol

Amount of **D**CO_3 reacted = 0.0400/2 = 0.0200 mol

M_r of **D**CO_3 = 1.68 / 0.0200 = 84

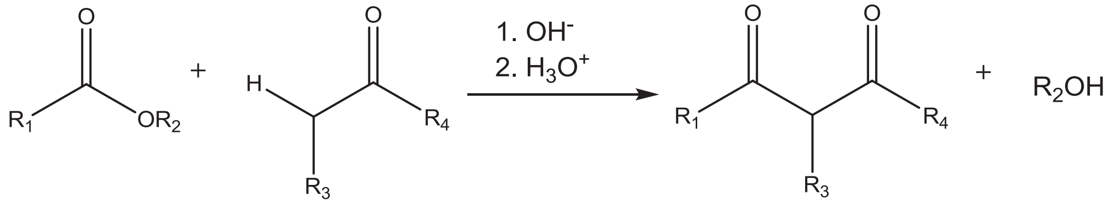
A_r of **D** = 84 – 12.0 – 3 x 16.0 = 24.0 **(must be 1d.p.)**

D = Mg

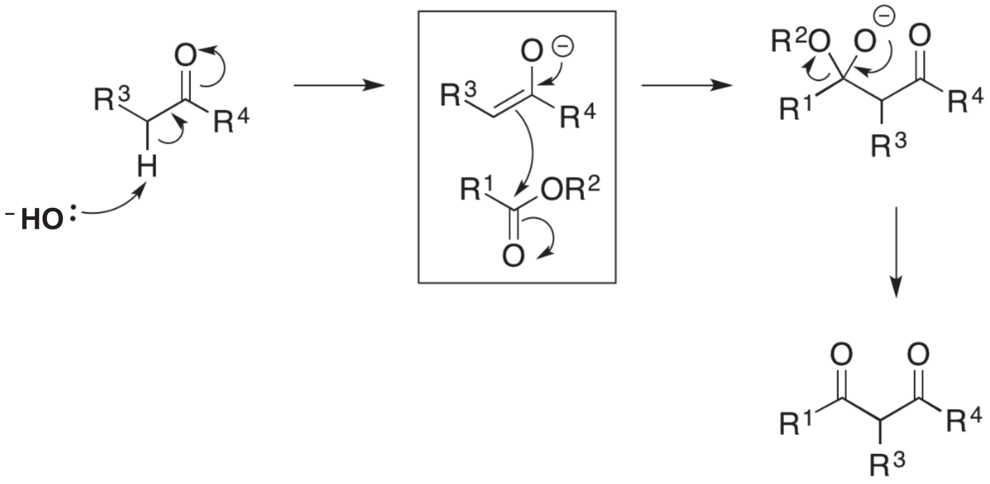
[Total: 12]

3 Claisen condensation is a carbon-carbon bond forming reaction between 2 esters or an ester and a carbonyl compound in the presence of strong base to form β-ketoesters or diketones respectively.

The following is the general equation for the reaction between an ester and a ketone.



The mechanism of the Claisen condensation reaction is given below.

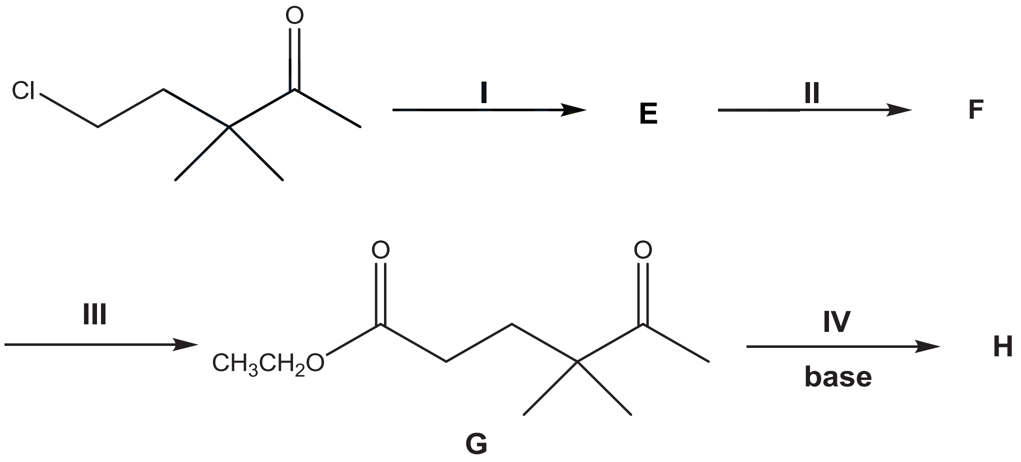


(a) Name the type of reaction for the step shown in the box above.

[1]

Nucleophilic addition

The Claisen condensation reaction can be used in step **IV** of the following synthesis.



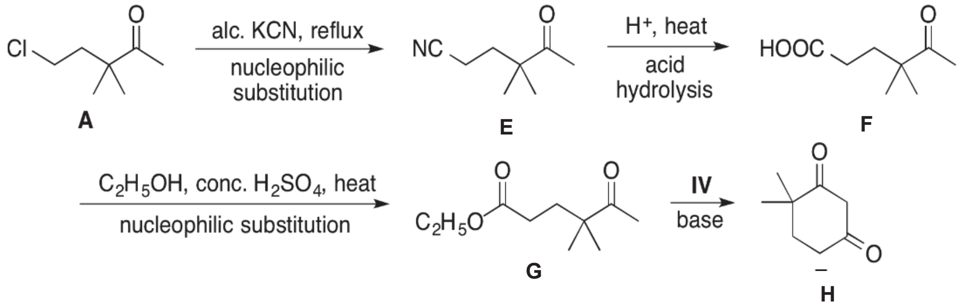
(b) **(i)** Suggest reagents and conditions for steps **I** to **III**. [3]

Step I : ethanolic KCN, heat with reflux
Step II : HC*l* (aq) or H_2SO_4 (aq), heat
Step III : C_2H_5OH, trace amount of conc H_2SO_4, heat with reflux

(ii) State the type of reactions for step **I** to **III** [3]

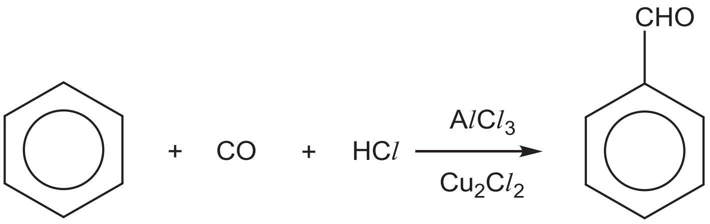
Step I: Nucleophilic substitution
Step II: Acidic hydrolysis
Step III: Condensation or Nucleophilic acyl substitution

(iii) Propose the structures of compounds **E**, **F** and **H**. [3]



[Total: 10m]

4 **(a)** The Gattermann-Koch reaction, named after the German chemists Ludwig Gattermann and Julius Arnold Koch in organic chemistry, refers to a Friedel-Crafts acylation reaction in which carbon monoxide and hydrochloric acid are used in-situ with Friedel-Crafts catalyst, namely $AlCl_3$. The reaction involves an acylium ion as an electrophile and tetrachloroaluminate ion, $AlCl_4^-$. An example is provided below.

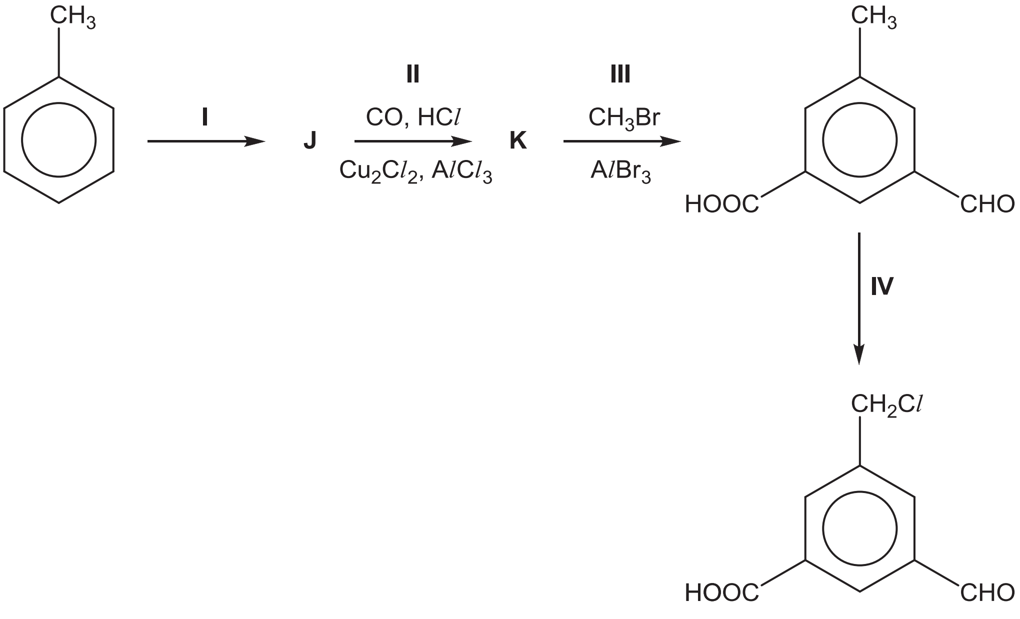


(i) Give the formula of the acylium ion in this reaction. [1]

^+CHO

(ii) The synthesis of compound **L** involves the Gattermann-Koch reaction in Step **II**.

Complete the reaction scheme below by providing the appropriate reagents and conditions for Step **I** and **IV** and give the structural formula for **J** and **K**.



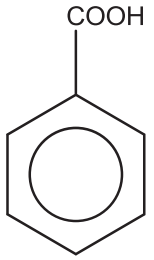
L CHO

[4]

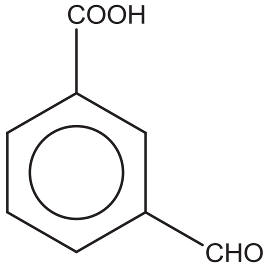
Step I: $KMnO_4$, dil H_2SO_4, heat with reflux

Step IV: limited Cl_2 (g) or limited Cl_2 in CCl_4, UV light

J:



K:



(b) Three non-cyclic organic compounds, **M**, **N** and **P** each have the same empirical formula CH_2O.
The number of carbon atoms in their molecules are shown in the table below.

compound	number of C atoms
M	2
N	3
P	3

All the carbon atoms are bonded directly to one another in **M** and in **N** but not in **P**.

M and **N** each give a brisk effervescence with $Na_2CO_3(aq)$ but not **P**.

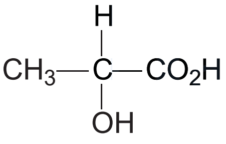
P does not give a silver mirror when treated with Tollens' reagent.

(i) Draw the structural formula of **M**. [1]

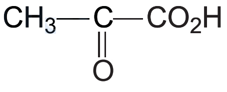
CH_3COOH

(ii) When **N** is heated under reflux with acidified $K_2Cr_2O_7$, the product, **Q**, gives a orange precipitate with 2,4–dinitrophenylhydrazine.

Draw the structural formulae of **N** and **Q**. [2]



$CH_3CH(OH)CO_2H$



CH_3COCO_2H

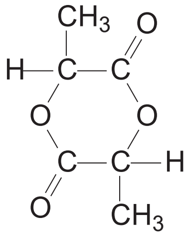
Compound **N**

Compound **Q**

(iii) When **N** is warmed with concentrated sulfuric acid, compound **R** is formed. **R** has the molecular formula $C_6H_8O_4$.

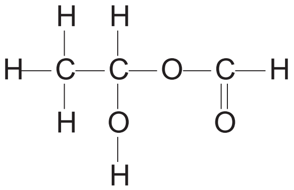
Draw the structural formula of **R.**

[1]



(iv) **P** is optically active. Draw the displayed formula of **P**.

[1]

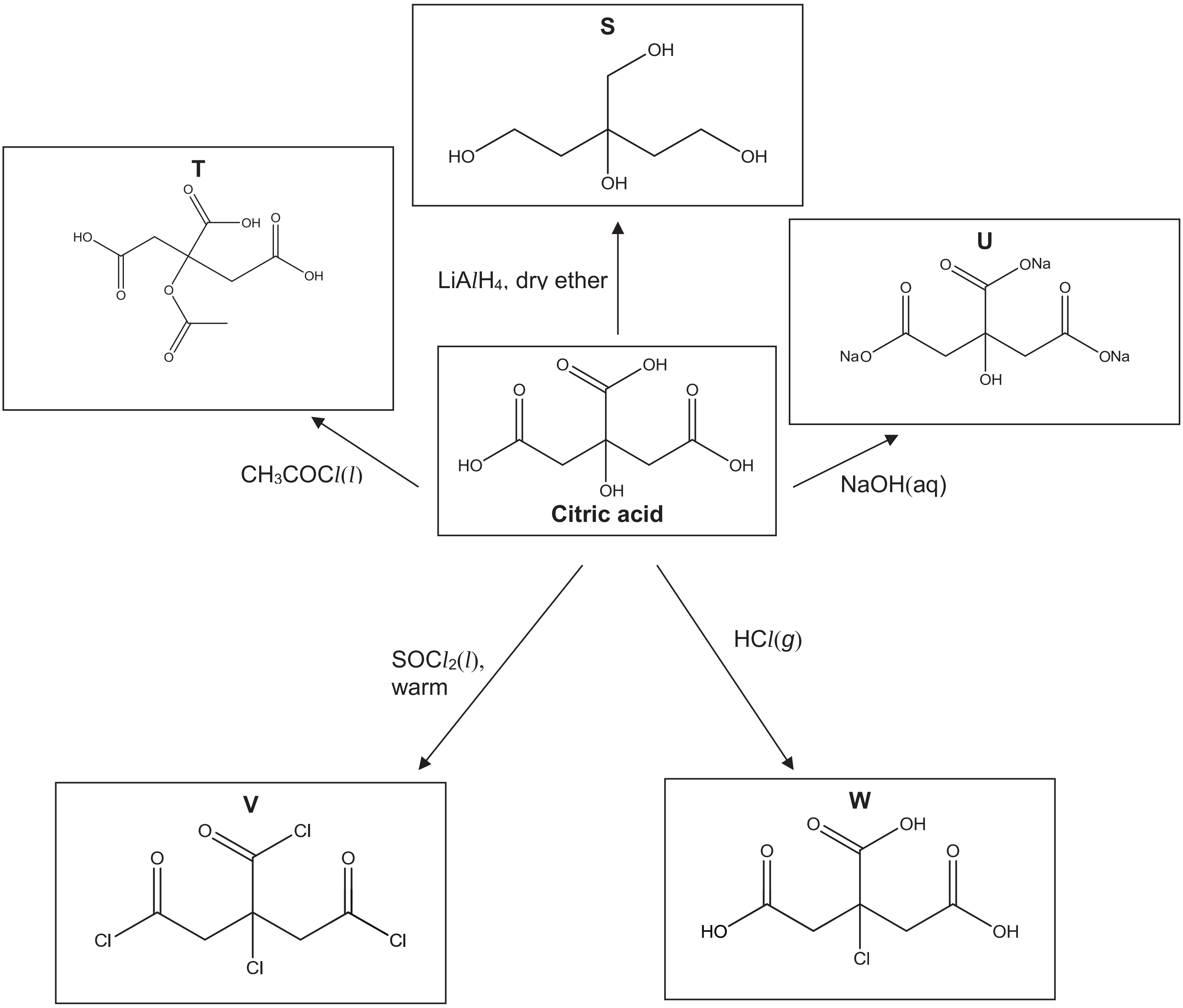


[Total: 10]

5 Citric acid, $C_6H_8O_7$ is produced commercially by the fermentation of sugars. Citric acid is used in the production of beverages and foods; in detergents; and in cosmetics and pharmaceuticals.

Fruits such as oranges, lemons and strawberries also contain citric acid.

(a) Citric acid can undergo the following reactions:



Suggest structures for the organic compounds **S, T, U, V** and **W**.

[5]

(b) As citric acid is a user-friendly, inexpensive, water-soluble crystalline solid, it is often used for finding the concentration of alkalis e.g. sodium hydroxide and potassium hydroxide.

Citric acid is a tribasic acid with the following pK_a values:

pK_1 = 3.14, pK_2 = 4.75 , pK_3 = 6.40

(i) Explain why citric acid is soluble in water.

Citric acid has (3 **COOH groups)** which can form **hydrogen bonds** with water molecules.

[1]

(ii) The pK_a value of ethanoic acid, CH_3COOH is 4.76.

Suggest why the pK_1 value of citric acid is lower than the pK_a value of ethanoic acid.

The anion formed by citric acid contains **two electron withdrawing –COOH group** which **disperses the negative charge** on the oxygen atom of the anion.
Thus, the anion formed by citric acid is **more stable than the ethanoate anion** and hence citric acid is **stronger**/ has a lower pK_a value**.**

OR

The anion formed by citric acid is further **stabilised by intramolecular hydrogen bonding** with the neighbouring COOH groups.
Thus, the anion formed by citric acid is **more stable than the ethanoate anion** and hence citric acid is **stronger**/ has a lower pK_a value .

[2]

(iii) Calculate the pH of a solution that is a mixture of equal volumes of 0.100 mol dm^{-3} of citric acid and 0.060 mol dm^{-3} of sodium hydroxide.

A buffer solution is formed.

New initial concentration of citric acid = 0.100 / 2 = 0.050 mol dm^{-3}

New initial concentration of NaOH = 0.060 / 2 = 0.030 mol dm^{-3}

$C_6H_8O_7 + OH^- \rightarrow C_6H_7O_7^- + H_2O$

After reaction

Final concentration of citric acid salt, $C_6H_7O_7^-$ = **0.030 mol dm^{-3}**

Final concentration of citric acid = 0.050 – 0.030 = **0.020 mol dm^{-3}**

$$\text{pH of solution} = pK_1 + \log_{10}\frac{[C6H7O7-]}{[C6H8O7\,]}$$
$$= 3.14 + \log_{10}\left[\frac{0.030}{0.020}\right] = 3.316 = \mathbf{3.32}$$

[2]

(c) The neutralisation equivalent (N.E.) of a carboxylic acid is defined as the mass in g of the acid required to neutralise one mole of a strong alkali such as sodium hydroxide. Each carboxylic acid has a unique N.E. value.

N.E. values can be used to determine the identity of a carboxylic acid.

A student carried out a titration experiment between a sample of citric acid and sodium hydroxide solution. 3.68 g of the citric acid was dissolved in 500 cm^3 of water in a volumetric flask. It was found that 5.00 cm^3 of the citric acid solution needed 5.29 g of 4.43 g dm^{-3} sodium hydroxide solution for complete reaction.

(i) Calculate the mass, in g, of the citric acid used in the 5 cm^3 sample.

Mass of citric acid = 3.68 x $\frac{5.00}{500}$ = 0.0368 g

[1]

(ii) Calculate the amount, in moles, of sodium hydroxide that reacted with the 5 cm^3 of citric acid.

The density of the sodium hydroxide solution is 1.01 g cm^{-3}.

Concentration of NaOH = $\frac{4.43}{40}$ = 0.11075 mol dm^{-3}

Volume of NaOH used = 5.29/1.01 = 5.2376 cm^3

Moles of NaOH used = $\frac{5.2376}{1000} \times 0.11075$ = 5.801 x 10^{-4} mol (4 s.f.)
= 5.80 x 10^{-4} mol (3 s.f.)

[2]

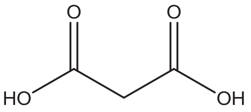
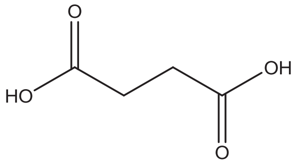
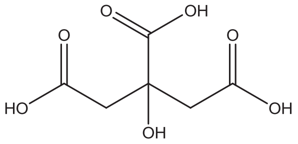
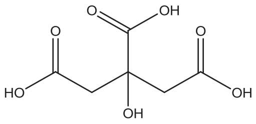
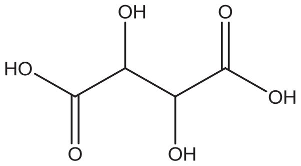
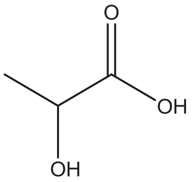
(iii) Calculate the neutralisation equivalent (N.E.) for this sample of citric acid.

Neutralisation Equivalent = $\frac{0.0368}{5.801 \times 10^{-4}}$ = 63.4

[1]

(d) Table 5.1 gives the neutralisation equivalent (N.E.) values for some organic acids.

Table 5.1

Acid name	**Structure**	**Molar mass/ g mol^{-1}**	**N.E. / g**
Malonic acid		104.0	52.0
Succinic acid		118.0	59.0
Anhydrous citric acid		192.0	64.0
Citric acid monohydrate	 . H_2O	210.0	70.0
Tartaric acid		150.0	*m*
Lactic acid		90.0	90.0

(i) Suggest whether the student's sample of citric acid is a hydrated sample or anhydrous sample. Support your answer with appropriate evidence.

Anhydrous citric acid. The calculated value of N.E. is 63.4 and this is close to the theoretical value of 64.0.

[2]

(ii) Determine the value of *m* in Table 5.1.

N.E. for tartaric acid = $\frac{150.0}{2}$ = 75.0

[1]

(e) Another student determines the N.E. of an unknown aliphatic acid to be 82.0 g.

The unknown aliphatic acid has the following formula, $C_xH_y(COOH)_n$ where *x* and *y* are integers and n = 1, 2 or 3.

Determine the molecular formula of the unknown aliphatic acid.

The molar mass of the acid is either:

82.0 g mol^{-1} for a monobasic acid, n = 1
82.0 x 2 = 164.0 g mol^{-1} for a dibasic acid, n = 2
82.0 x 3 = 246.0 g mol^{-1} for a tribasic acid, n= 3

The molar mass of a -COOH group = 12.0 + 2 x 16.0 + 1.0 = 45.0 g mol^{-1}
The molar mass of a $–CH_2–$ group = 12.0 + 2.0 = 14.0 g mol^{-1}

It is a tribasic acid as **246.0 – (3 x 45.0) - (14.0 x 7) = 13.0** g mol^{-1} (equivalent to 1C and 1 H)

The tribasic acid consists of **3 –COOH groups**, **7 $–CH_2–$ groups** and **one C** and one H atom. It is possible to form a molecule using these groups.

The molecular formula is **$C_{11}H_{18}O_6$** or **$C_8H_{15}(COOH)_3$**

Marking guidelines

- 1 mark for calculating the molar mass of the tribasic acid
- 1 mark for explaining why it has to be the tribasic acid using the calculated molar mass
- 1 mark for giving the correct molecular formula
- Working must be shown for the mark to be obtained. No marks to be given if the correct answer is given without any working.

Additional note (not marking points):

It cannot be a monobasic acid as 85.0 = 12.0 + 45.0 + 2 x14.0
There cannot be a structure for 1 –COOH group and 2 $–CH_2–$ groups and 1 C atom. (Molecular formula $C_4H_5O_2$)

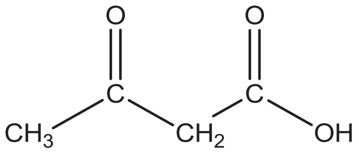
It cannot be a dibasic acid as 164.0 = 2 x 45.0 + 5 x 14.0 + 4.0
There cannot be a structure for 2 –COOH groups and 5 $–CH_2–$ groups and 4 H atoms. (Molecular formula $C_7H_{16}O_4$)

[3]

(f) The loss of carbon dioxide from a carboxylic acid is called decarboxylation.

$$RCOOH \longrightarrow RH + CO_2$$

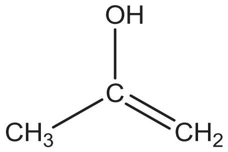
Certain types of carboxylic acids are readily decarboxylated. Beta-keto acids such as acetoacetic acid readily decarboxylate at room temperature in an acidic solution.



acetoacetic acid

The decarboxylation of acetoacetic acid occurs via a two-step mechanism.

- the H atom from the COOH group is transferred to the carbonyl oxygen atom via a cyclic transition state to form CO_2 and the following compound, an enol,

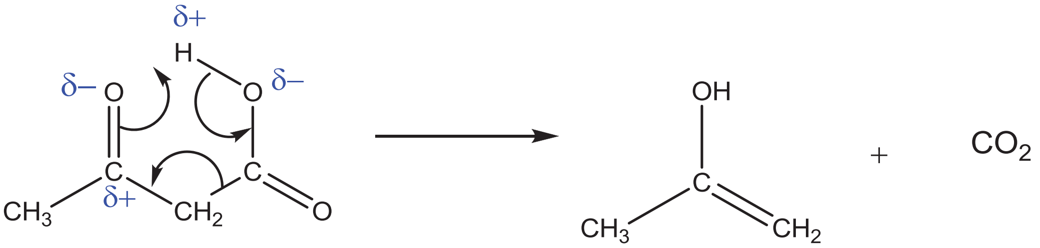


enol

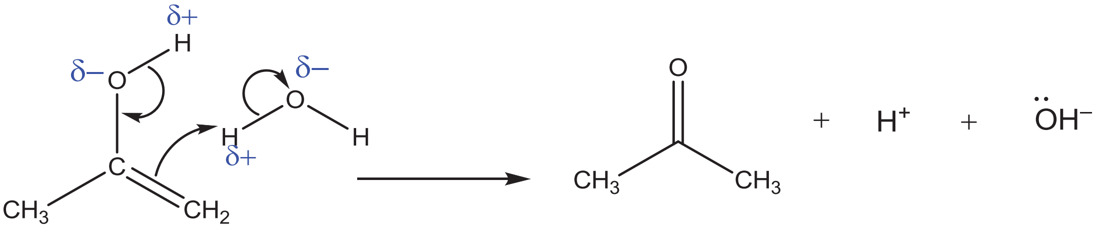
- the enol then extracts a H atom from a H_2O molecule to form a ketone and H^+ and OH^- ions.

Suggest the mechanism for this reaction. Show any relevant lone pairs, dipoles and charges, and indicate the movement of electron pairs with curly arrows.

Step 1



Step 2



[4]

[Total: 24]

INNOVA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
in preparation for General Certificate of Education Advanced Level
Higher 2

CHEMISTRY

9729/03

Paper 3 Free Response

13 September 2017

2 hours

Candidates answer on separate paper.

Additional Materials: Writing Papers
Data Booklet
Cover Page

READ THESE INSTRUCTIONS FIRST

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

Section A
Answer **all** questions.

Section B
Answer **one** question.

You are advised to show all working in calculations.
You are reminded of the need for good English and clear presentation in your answers.
You are reminded of the need for good handwriting.
Your final answers should be in 3 significant figures.

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

This document consists of **20** printed pages.

Section A

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

1 Benzoic acid, C_6H_5COOH is a colourless crystalline solid and a simple aromatic carboxylic acid. Benzoic acid occurs naturally in many plants. Salts of benzoic acid are used as food preservatives and benzoic acid is an important precursor for the industrial synthesis of many other organic substances.

(a) In the identification of benzoic acid, a commonly used reagent is neutral iron(III) chloride solution, in which a buff precipitate of iron(III) benzoate, $Fe(C_6H_5CO_2)_3$ is formed. When 50.0 cm^3 of iron(III) chloride solution was added to 50.0 cm^3 of benzoic acid solution, 0.0532 g of the buff precipitate was formed in the mixture.

The reactions that take place are shown below:

$$C_6H_5CO_2H \rightleftharpoons C_6H_5CO_2^- + H^+$$

$$Fe^{3+} + 3C_6H_5CO_2H \longrightarrow Fe(C_6H_5CO_2)_3 + 3H^+$$

(Given: M_r of $Fe(C_6H_5CO_2)_3 = 418.8$)

(i) Calculate the number of moles of benzoic acid that reacted with the neutral iron(III) chloride solution.

[1]

Number of moles of $Fe(C_6H_5CO_2)_3$ = 0.0532 / 418.8
= 1.2703×10^{-4} mol

$C_6H_5CO_2^- \equiv C_6H_5CO_2H$

Number of moles of benzoic acid reacted = $3 \times 1.2703 \times 10^{-4}$
= 3.8108×10^{-4}
= 3.81×10^{-4} mol

(ii) Given that the pH of the solution after the reaction is 2.33, calculate the number of moles of H^+ in the mixture.

[1]

$[H^+] = 10^{-2.33} = 4.677 \times 10^{-3}$ mol dm^{-3}

Number of moles of H^+ = $0.100 \times 4.677 \times 10^{-3}$
= 4.677×10^{-4}
= 4.68×10^{-4} mol

(iii) Assuming that the H^+ ions in solution are formed only from the dissociation of benzoic acid in solution, as well as the reaction of benzoic acid with iron(III) chloride, calculate the concentration of benzoate ions in the mixture.

[2]

Since the H^+ comes from both dissociation of benzoic acid and reaction of benzoic acid with iron (III) chloride,

Number of moles of benzoate in solution = $4.677 \times 10^{-4} - 3.8108 \times 10^{-4}$
= 8.6655×10^{-5} mol

Concentration of benzoate in solution = moles / volume
= 8.6655×10^{-5} / [(50 + 50)/1000]
= 8.67×10^{-4} mol dm^{-3}

Allow ecf

(iv) Iron(III) benzoate is a sparingly soluble salt.

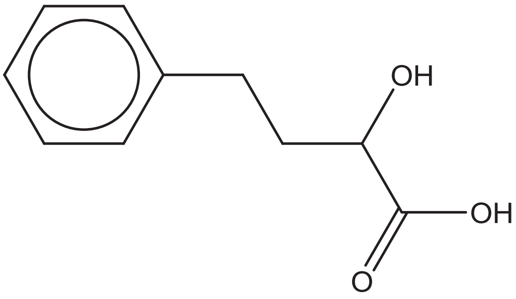
Calculate the K_{sp} of iron(III) benzoate, given that the concentration of Fe^{3+} in the mixture was 1.83×10^{-3} mol dm^{-3} at equilibrium.

[1]

K_{sp} = $[Fe^{3+}][C_6H_5CO_2^-]^3$
= $(1.83 \times 10^{-3})(8.6655 \times 10^{-4})^3$
= 1.1908×10^{-12}
= 1.19×10^{-12} mol^4 dm^{-12}

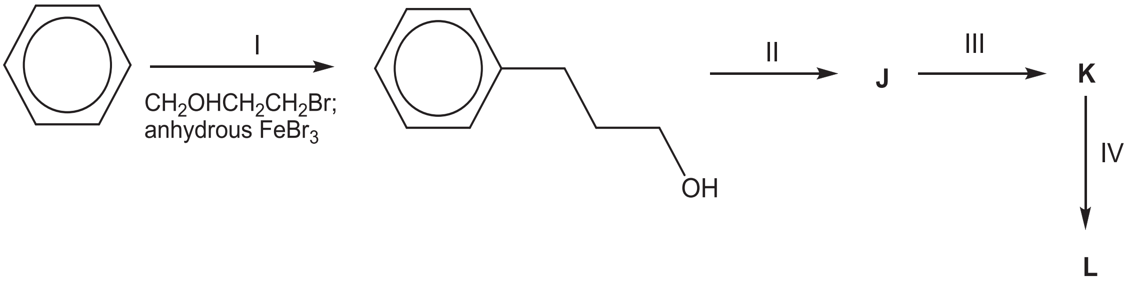
Allow ecf

(b) Benzoic acid can be produced by oxidising compound **L**.



Compound **L**

Compound **L** can be synthesised by the following reaction scheme.



(i) State the *type of reaction* in step I and hence explain the need for $FeBr_3$ to be anhydrous.

[2]

Electrophilic substitution

The catalyst will be hydrolysed and lose its catalytic property if it is dissolved in water.

$FeBr_3$ has to be anhydrous as it has to be electron deficient to accept a lone pair of electron from the Br in $CH_3(CH_2)_3Br$ to form the electrophile $CH_3(CH_2)_3^+$ for electrophilic substitution to take place.

If water is present, $Fe^{3+}(aq)$ will be present and the electrophile $CH_3(CH_2)_3^+$ will not be formed.

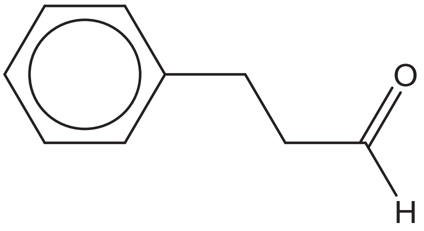
$Fe^{3+}(aq)$ will undergo hydrolysis:

$[Fe(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Fe(H_2O)_5(OH^-)]^{2+} + H_3O^+$

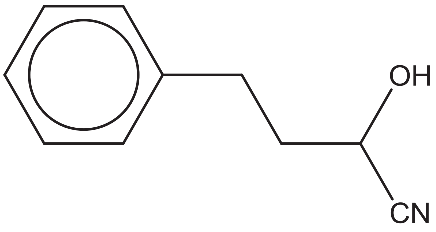
(ii) Suggest the identities of **J** and **K**.

[2]

J:



K:



(iii) State the reagents and conditions for steps II to IV. [3]

II: $K_2Cr_2O_7$, dilute H_2SO_4, heat with immediate distillation

III: HCN, trace amount of NaCN or NaOH, cold

IV: dilute H_2SO_4 or dilute HCl, heat

(iv) State the *type of reaction* for stage IV. [1]

Acidic hydrolysis

[Total: 13]

2 Sulfur is a chemical element with the symbol S and an atomic number of 16. It is an abundant, multivalent non-metal. It can be found in amino acids and as a precursor to other chemicals such as H_2SO_4. H_2SO_4 is a common mineral acid with many uses. It can be used as an electrolyte in batteries.

(a) In the cells of a lead-acid car battery the following reactions take place.

anode: $Pb(s) \longrightarrow Pb^{2+}(aq) + 2e^-$

cathode $PbO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Pb^{2+}(aq) + 2H_2O(l)$

(i) Use the *Data Booklet* to calculate E^θ_{cell} for this reaction. [1]

E^θ cell = 1.47–(–0.13) = +1.60V

(ii) Construct an equation for the overall reaction. [1]

$PbO_2 + Pb + 4H^+ \longrightarrow 2Pb^{2+} + 2H_2O$

The electrolyte in a lead-acid cell is $H_2SO_4(aq)$. Most of the $Pb^{2+}(aq)$ ions that are produced at the electrodes are precipitated as a highly insoluble $PbSO_4(s)$.

(iii) Construct an equation for the overall cell reaction in the presence of H_2SO_4. [1]

$PbO_2 + Pb + 4H^+ + 2SO_4^{2-} \longrightarrow 2PbSO_4 + 2H_2O$

(iv) By considering the effect of decreasing $[Pb^{2+}(aq)]$ on the electrode potentials of the cathode and the anode, state and explain whether the overall E^{θ}_{cell} will *increase*, *decrease* or *remain the same*.

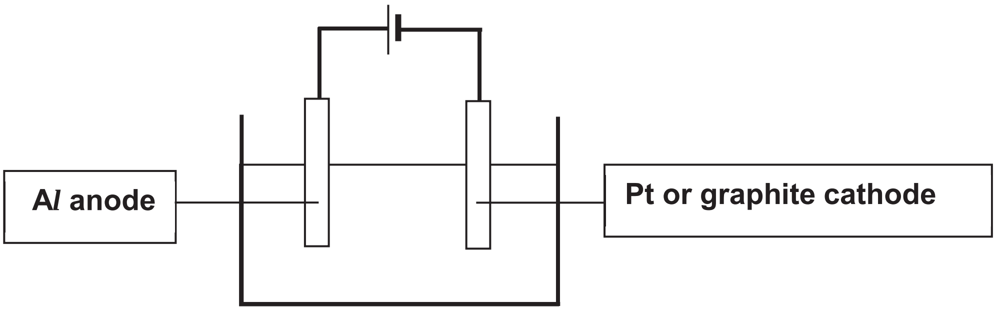
[1]

Overall E^{θ}_{cell} will increase as $[Pb^{2+}]$ decreases, $E^{\theta}(PbO_2/Pb^{2+})$will become more positive, but $E^{\theta}(Pb^{2+}/Pb)$ will become more negative

(b) H_2SO_4 is also used as an electrolyte in the anodising of aluminium. Anodising of aluminium is the process of coating aluminium metal with aluminium oxide (Al_2O_3) via electrolysis with the aluminium metal as the anode.

(i) Using $H_2SO_4(aq)$ as the electrolyte and an inert electrode, draw an electrolysis set-up to show how a piece of aluminium metal can be anodised.

[1]



- Correct orientation of the battery
- Correct labeling of both the electrodes with the material used
- Correct cell. i.e. An electrolytic cell and not a electrochemical cell

(ii) Write chemical equations to show the reactions at the anode and cathode during anodising. Include in your answers, the overall equation.

[3]

Reaction at the A*l* anode:
$2H_2O\ (l) \longrightarrow O_2\ (g) + 4H^+\ (aq) + 4e$
The oxygen liberated then reacts with the aluminium to produce aluminium oxide protective surface.
$4Al\ (s) + 3O_2\ (g) \longrightarrow 2Al_2O_3\ (s)$
Reaction at the Pt cathode:
$2H^+\ (aq) + 2e \longrightarrow H_2\ (g)$

Overall reaction: $2Al\ (s) + 3H_2O\ (l) \longrightarrow Al_2O_3\ (s) + 3H_2\ (g)$

(iii) The aluminium piece to be anodised has a surface area of 29.2 cm^2. Calculate the time taken to form a 0.2 mm protective layer of Al_2O_3 on the aluminium piece if a current of 2.0 A is passed through the set-up.

(Density of Al_2O_3 is 3.95 g cm^{-3})

[4]

Volume of Al_2O_3 layer $= 29.2 \times 0.02$
$= 0.58400\ cm^3$

Mass of $Al_2O_3 = 3.95 \times 0.584$
$= 2.3068$ g

Amount of $Al_2O_3 = \dfrac{2.3068}{2\times27.0+3\times16.0}$

= 0.022616 mol

Amount of O_2 = 0.0226 × 3/2

= 0.033923 mol

Amount of electrons passed through the anode = 0.0339 × 4

= 0.13569 mol

Q = 0.13569 × 96500

= 13094 C

Time needed =13094 ÷ 2.0

= 6547.2 s = 6550 s (3s.f)

Alternatively from here,
It = n_eF approach

t = (n_eF) / I

= (0.13569 × 96500) / 2.0

= 6547.2 s = 6550 s (3s.f)

(iv) Give one example of an anodised aluminium object, and explain the advantages of anodising it.

[1]

Examples of anodized aluminium objects: drink cans, windows frames and grilles

Anodised aluminium objects are more resistant to corrosion. Moreover, they can be decorative as well since the aluminium oxide layer is able to absorb dyes.

(c) H_2SO_4, can be produced when sulfur trioxide is added to water, according to the following equation:

$$SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(aq)$$

Calculate the volume of gaseous SO_3 under room temperature and pressure, needed to form 30.0 cm^3 of 0.0200 mol dm^{-3} of H_2SO_4.

[1]

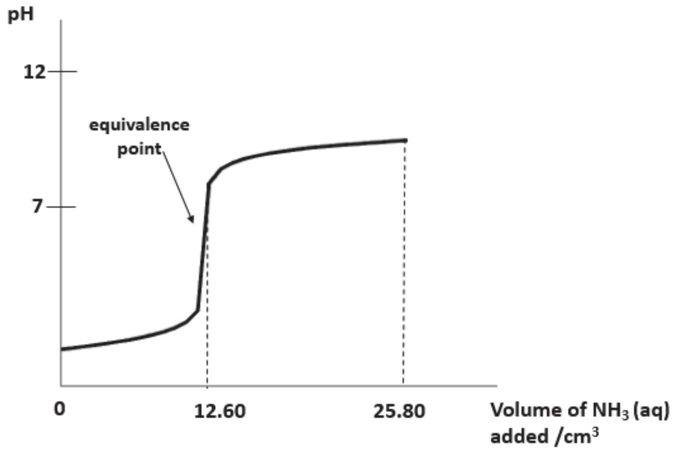
Amount of H_2SO_4 to be produced = $\frac{30}{1000}$ X 0.02 = 6.00 x 10^{-4}

Amount of SO_3 needed = 6.00 x 10^{-4}

Volume of SO_3 needed at r.t.p = 6.00 x 10^{-4} X 24.0 dm^3

= 0.0144 dm^3

(d) 25.0 cm^3 of 0.0200 mol dm^{-3} of H_2SO_4 was titrated against NH_3(aq).The following graph was obtained.



(i) Calculate the initial pH of the sulfuric acid solution.

[1]

$[H_2SO_4] = 0.02$ mol dm^{-3}
$[H^+] = 0.04$ mol dm^{-3}
pH = 1.40

(ii) Calculate the concentration of NH_3 (aq) used in this titration.

[2]

H_2SO_4 (aq) + $2NH_3$ (aq) → $(NH_4)_2SO_4$ (aq)

Amount of H_2SO_4 used in titration = $\frac{25}{1000} \times 0.02 = 5.000 \times 10^{-4}$

Amount of NH_3 used in titration = $\frac{25}{1000} \times 0.02 \times 2 = 1.000 \times 10^{-3}$

$[NH_3] = \dfrac{1 \times 10^{-3}}{12.60/1000} = 0.0794$ mol dm^{-3}

(iii) Suggest a suitable indicator for this titration, giving a reason for your choice.

[2]

Methyl orange.

The working range for methyl orange (is in the region of 3 to 5 and) coincides with the equivalence point of a strong acid-weak base titration (<7).

[5]

(e) Thiophenol are the sulfur analogue of phenol, that is, sulfur takes the place of oxygen in the hydroxyl group of phenol. A common reaction that phenol and thiophenol have is shown in **Figure 1** below.

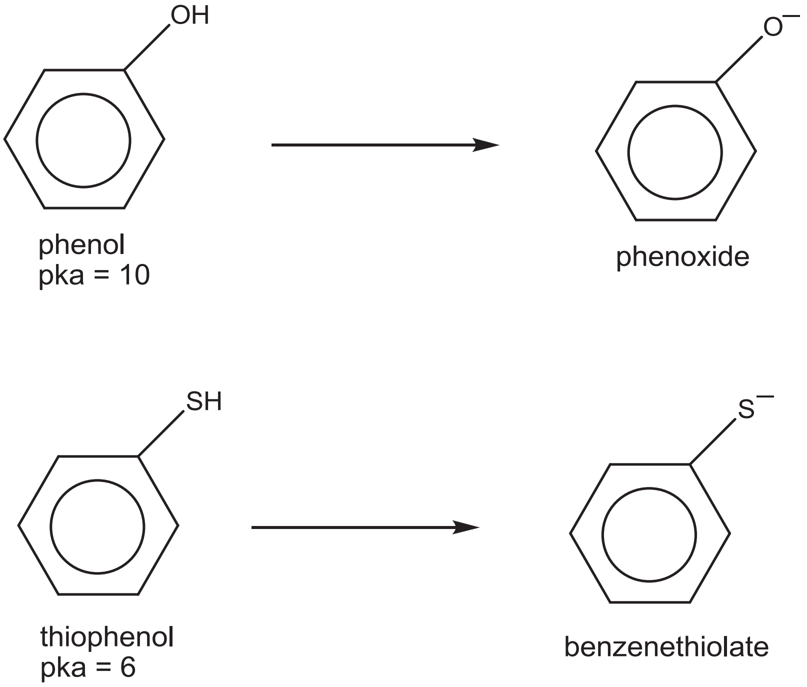
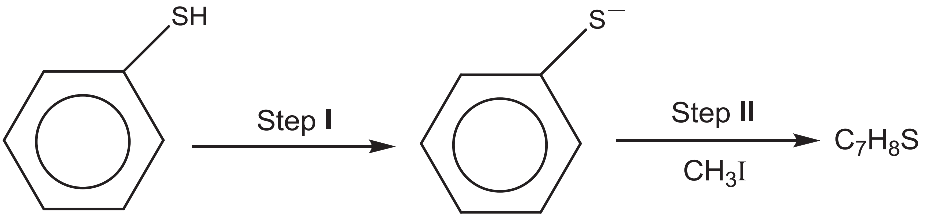


Figure 1

Consider the reaction scheme below.



(i) Suggest reagent and condition for step **I**. [1]

Reagents and Conditions: Na metal at room temperature

OR

Reagents and Conditions: NaOH (aq) at room temperature

(ii) What *type of reaction* is step **I** and step **II**? [2]

Step I

Acid- Metal (if student answer is Na metal)

Accept: Redox

OR

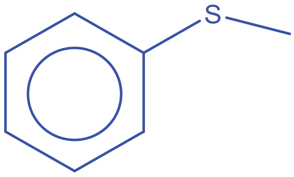
Acid-base if student answer is NaOH(aq)

Step II

Nucleophilic substitution

(iii) Suggest the structure of C_7H_8S.

[1]



[Total: 23]

3 Halogenated organic compounds are widespread throughout nature and have a vast array of uses in modern industrial processes. They find many uses in the industries such as solvents and pesticides.

The rate of hydrolysis of $CH_3CH_2CH_2CH_2Br$ with aqueous NaOH was studied in a series of 3 experiments in which the initial rate of the reaction was measured. The following results were obtained.

Experiment	$[OH^-]$ / mol dm^{-3}	$[CH_3CH_2CH_2CH_2Br]$ / mol dm^{-3}	Initial Rate / mol dm^{-3} s^{-1}
1	0.100	0.010	4×10^{-6}
2	0.200	0.010	8×10^{-6}
3	0.200	0.020	16×10^{-6}

(a) Explain the meaning of the following terms.

(i) order of reaction

(ii) half-life

The order of reaction with respect to a given reactant is the power to which the concentration of that reactant is raised to in the rate equation.

The half-life ($t_{1/2}$) of a reaction is the time taken for the concentration of a reactant to decrease to half its initial value.

[2]

(iii) Using the data given, derive the rate equation for the hydrolysis of $CH_3CH_2CH_2CH_2Br$.

For $CH_3CH_2CH_2CH_2Br$

(inspection method)
Using experiment 1 and 2, when $[OH^-]$ doubles, keeping $[CH_3CH_2CH_2CH_2Br]$ constant, rate doubled. Hence order of reaction with respect to $[OH^-]$ is one.

Using experiment 2 and 3, when $[CH_3CH_2CH_2CH_2Br]$ is doubled, keeping $[OH^-]$ constant, rate doubled. Hence order of reaction with respect to $[CH_3CH_2CH_2CH_2Br]$ is one.

(Substitution method)
Let the rate law be:
Rate = $k[OH^-]^a[CH_3CH_2CH_2CH_2Br]^b$

Using experiment 1 and 2

$$\frac{4\times10^{-6}}{8\times10^{-6}}=\frac{k(0.100)^a(0.010)^b}{k(0.200)^a(0.010)^b}$$

$$(\frac{1}{2})^a=\frac{1}{2}$$

$$a=1$$

Using experiment 2 and 3

$$\frac{8\times10^{-6}}{16\times10^{-6}}=\frac{k(0.010)^b}{k(0.020)^b}$$

$$(\frac{1}{2})^b=\frac{1}{2}$$

$$b=1$$

Rate = k $[OH^-][CH_3CH_2CH_2CH_2Br]$

[3]

(iv) Using your rate equation, determine a value for the rate constant, including units for this reaction.

Rate = k $[OH^-][CH_3CH_2CH_2CH_2Br]$

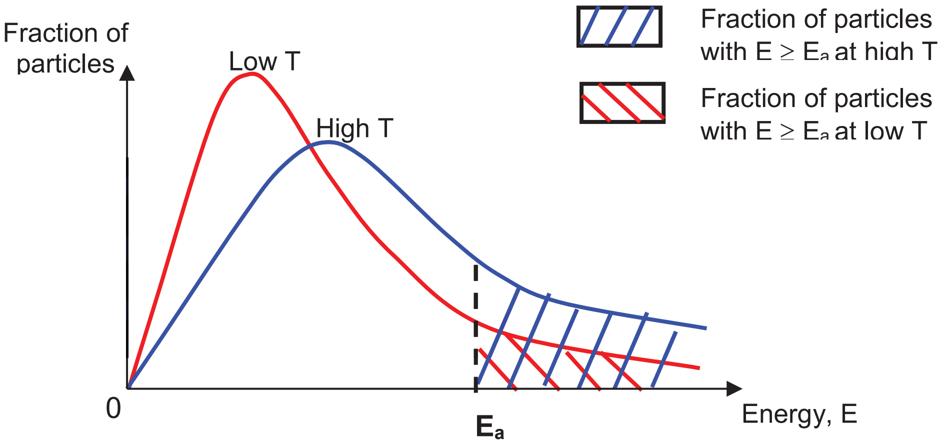
$6 \times 10^{-6} = k(0.100)(0.010)$
$k = 6.00 \times 10^{-3}$ allow ecf

$$k=\frac{Rate}{[CH_3CH_2CH_2CH_2Br][OH^-]}$$

$$k=\frac{mol dm^{-3}s^{-1}}{(mol dm^{-3})^2}=mol^{-1}dm^3s^{-1}[1]$$

[1]

(v) Using the Maxwell-Boltzmann distribution curve, explain how the reaction rate might change with an increase in temperature.



- correct axes
- two graphs with higher temperature graph shifted to the left and lower peak, both graph must start from origin.
- both graphs should be labelled, Ea indicated with shading
- legend of shading provided.

An increase in temperature will result in an increase in the average kinetic energy of the particles.
There is an increase in the fraction of particles with energy equal to or greater than the activation energy, E_a. This is as shown by the larger shaded area at a higher temperature in the above diagram.
This result in an increase in the frequency of effective collisions.
Since rate is proportional to the frequency of effective collision, rate increases.

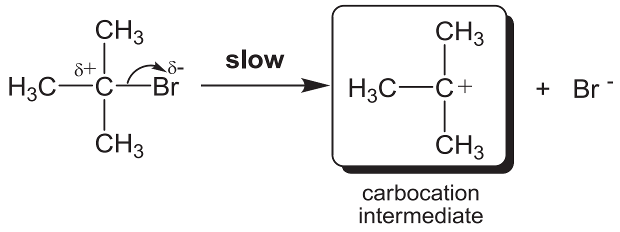
[4]

(vi) Given that the rate equation for the hydrolysis of $(CH_3)_3CBr$ is rate = $k[(CH_3)_3CBr]$, suggest possible mechanisms for **both** of the reactions of $(CH_3)_3CBr$ and $CH_3CH_2CH_2CH_2Br$ with aqueous NaOH which are consistent with the observed kinetics.

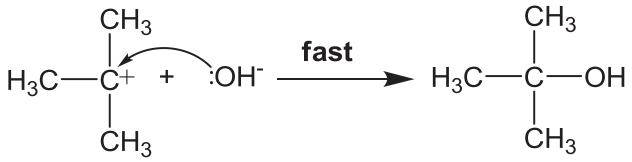
For $(CH_3)_3CBr$

Nucleophilic substitution, S_N1

Step 1 (formation of carbocation):

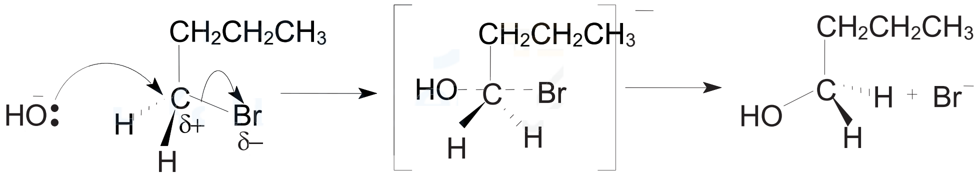


Step 2 (attack by nucleophile)



- δ+ and δ- on C-Br
- arrow to show breaking of C-Br bond, arrow must start from the bond
- slow and fast step
- Correct intermediate and Br^- formed
- lone pair on O of OH–
- arrow starting from lone pair to C+

For $CH_3CH_2CH_2CH_2Br$
Nucleophilic substitution, S_N2



- δ+ and δ- on C-Br
- arrow to show breaking of C-Br bond, arrow must start from the bond
- lone pair on O of OH–
- arrow starting from lone pair to C
- square bracket and negative charge for transition state
- initial reactant and final product should be inversed (solid wedge and dash is not necessary) and Br^- as product

[6]

(b) Bromine reacts with 2-methylpropane in the presence of sunlight to produce mono-brominated products via a free radical mechanism.

(i) Explain why the mono-bromination of 2-methylpropane results in the formation of two products in unequal amounts.

In the propagation step, two alkyl radicals will be formed. Tertiary $(CH_3)C\bullet$ is more stable than primary $(CH_3)_2CCH_2\bullet$. / There are 9 primary H atom and only 1 tertiary H atom.

[1]

(ii) By quoting appropriate data from the *Data Booklet,* explain the difference in the reactivity of fluorine with 2-methylpropane compare with that of bromine.

Bond energy of F_2 = 158kJ mol^{-1} Bond energy of Br_2 = 193 kJ mol^{-1}

Fluorine will react more vigorously/ more reactive because the F-F bond is weaker than Br-Br bond.

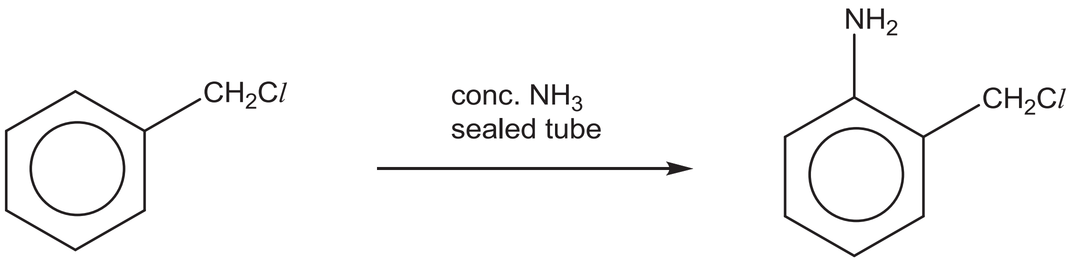
Or

Bond energy of C-F = 485 kJ mol^{-1} Bond Energy of C-Br = 280 kJ mol^{-1}

Fluorine will react more vigorously because C-F bond formed is stronger than C-Br bond.

[2]

(c) A student was not successful in making **X** from (chloromethyl)benzene with the proposed reaction route as shown.

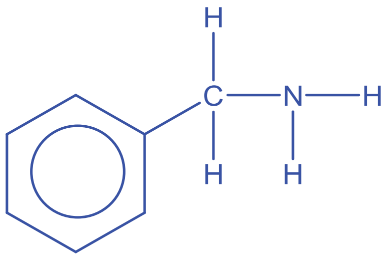


(chloromethyl)benzene

X

Instead, a different product with molecular formula C_7H_9N was obtained.

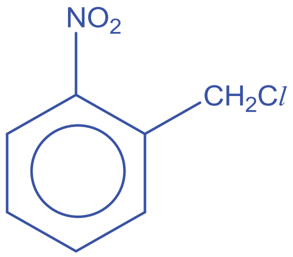
(i) Draw the displayed formula of the product obtained.



[1]

(ii) Suggest how **X** can be synthesised from (chloromethyl)benzene. You should include the reagents, conditions and intermediate(s) formed in your answer.

Step 1: Conc HNO_3, Conc H_2SO_4, **30°C < temp < 55°C (30/55 will not be accepted)**



Step 2:

1) Sn, conc HCl, heat
2) aq NaOH, rtp

[3]

[Total: 24]

Section B

Answer **one** question from this section

4 Hydrogen gas is needed in a large number of processes in the chemical industries such as hydrocracking of petroleum, production of margarine and production of ammonia.

Hydrogen gas can be produced in many chemical reactions.

(a) One of the reactions that produces hydrogen is the reaction of sodium with ethanol.

$$C_2H_5OH(l) + Na(s) \longrightarrow C_2H_5ONa(s) + \frac{1}{2}H_2(g)$$

This is also a chemical test for the presence of alcohol.

(i) Write the full electronic configuration of Na.

Electronic configuration of sodium: $1s^22s^22p^63s^1$

(ii) Describe how you would use the ionisation energies found in the *Data Booklet* to conclude that sodium is in group 1 of the periodic table.

[1]

Since there is a large increase between the first ionisation energy (494 kJ mol^{-1}) and the second ionisation energy (4560 kJ mol^{-1}) of sodium. This means that the second electron is removed from the inner principal quantum shell, hence there is only one valence electron in sodium.

(iii) Ethanoic acid reacts with sodium in a similar way. However, when ethanol and ethanoic acid is reacted with solid sodium carbonate separately, only ethanoic acid gives off a gas that forms white precipitate with calcium hydroxide.

Explain the difference in reactions of ethanol and ethanoic acid with sodium carbonate.

[3]

Reasons: Ethanoic acid is a stronger acid than ethanol hence it is acidic enough to react with sodium carbonate.

$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$
For the ethanoate anion, the negative charge can be delocalised over two electronegative oxygen atoms. This disperses the negative charge on the oxygen atom and leads to a stabilisation of the ethanoate anion.
Hence, ethanoic acid is the more acidic.

$CH_3CH_2OH + H_2O \rightleftharpoons CH_3CH_2O^- + H_3O^+$

For the ethoxide anion, the electron-donating ethyl group intensifies the negative charge on the oxygen atom. Thus, the ethoxide anion is less stable.

(iv) An unknown compound **M**, $C_8H_{10}O$ was found to be an alcohol when tested with sodium metal.

When **M** is treated with hot acidified potassium dichromate, compound **N**, C_8H_8O is formed. **N** gives a yellow precipitate, **P** when warmed with alkaline aqueous iodine.

When **M** is heated with concentrated H_2SO_4, compound **R**, C_8H_8 is formed. **R** gives compound **S** when reacted with hydrogen chloride gas.

M also gave compound **S** when reacted with phosphorous pentachloride at room temperature.

Deduce the structures of **M**, **N**, **P**, **R** and **S.**

[5]

Explanation not required.

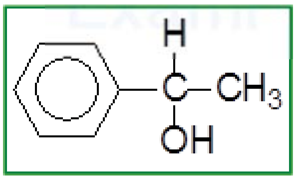
Comparable number of C and H → **M** contained benzene ring.
M undergoes oxidation with hot acidified potassium dichromate → **N** is aldehyde or ketone

N undergoes oxidation with alkaline aqueous iodine to give yellow precipitate,

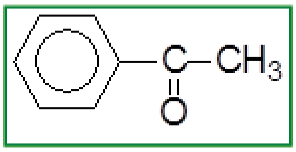
P: <u>CHI_3</u>

→ **N** has structure $-\underset{\underset{\textstyle O}{\|}}{C}-CH_3$ and so **M** has $CH(OH)CH_3$ structure.

M:

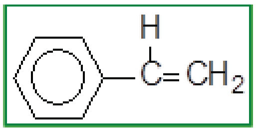


N:



M undergoes dehydration when heated with concentrated H_2SO_4 → **R** is an alkene

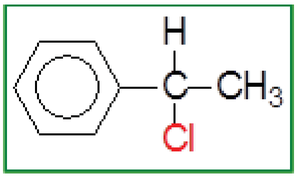
R:



R undergoes electrophilic addition when heated with hydrogen chloride gas → **S** is halogenoalkane

M undergoes substitution with phosphorous pentachloride at room temperature→ **S** is halogenoalkane

S:



(b) Another reaction that produces hydrogen is the reaction of methane with steam at 1000–1400 K.

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) \qquad \Delta H = +206 \text{ kJ mol}^{-1}$$

This reaction produces large quantities of hydrogen for industrial use.

(i) State and explain the effect of decreasing the temperature of the reaction on the equilibrium position.

[1]

When temperature of the system is decreased, by Le Chatelier's Principle, the equilibrium will favour exothermic reaction to release heat. Hence, the backward reaction is favoured and equilibrium position shifted left.

(ii) Deduce the sign of entropy change for the forward reaction.

[1]

Since the no. of moles of gas increases for the forward reaction, disorderness increased as there are more ways to arrange the particles so entropy change (ΔS) is positive.

(iii) Hence, or otherwise, predict and explain the spontaneity of the forward reaction at low temperature.

[1]

Since $\Delta G = \Delta H - T\Delta S$

When temperature is low, magnitude of $-T\Delta S$ will be smaller than that of magnitude of ΔH. or similar reasoning.

Since ΔS is positive and hence $-T\Delta S$ is negative and ΔH is positive, ΔG would be positive and hence the reaction is not spontaneous

(iv) Comment and explain if there is any discrepancy in your answers in **b(i)** and **b(iii)**.

[1]

No. Since at low temperature, forward reaction is not spontaneous (ΔG is positive) hence the position of equilibrium position should be on the left/ forward reaction is not favoured

(v) Calculate the enthalpy change of vaporisation of water of using the data in **Table 1**.

Table 1

Enthalpy change of formation of carbon monoxide	–111 kJ mol^{-1}
Enthalpy change of formation of methane	–75 kJ mol^{-1}
Enthalpy change of formation of water	–285 kJ mol^{-1}

[2]

For $CH_4(g) + H_2O(l) \longrightarrow CO(g) + 3H_2(g)$

Enthalpy change of reaction

$= \Sigma\Delta H_f$ product $- \Sigma\Delta H_f$ reactant

$= (-111 + 3(0)) - (-285 + -75)$
$= +249\ kJmol^{-1}$

$$\begin{tikzcd}
CH_4(g) + H_2O(g) \arrow[rr, "+206\ kJ\ mol^{-1}"] & & CO(g) + 3H_2(g) \\
& CH_4(g) + H_2O(l) \arrow[ul, "\Delta H_{vap}^{\ominus}\ H_2O"] \arrow[ur, "+249\ kJmol^{-1}"'] &
\end{tikzcd}$$

By Hess' law,

$\Delta H_{vap}^{\ominus}\ H_2O = +249\ kJmol^{-1} - (+206\ kJ\ mol^{-1})$
$= +43.0\ kJ\ mol^{-1}$

Or any other possible approaches.

(c) Hydrogen gas can also be produced from the reaction of carbon monoxide with steam.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) \quad K_c = 6.40\times10^{-1} \text{ at } 1100K$$

A mixture containing 0.8 mol of CO and 0.8 mol of H_2O was placed in a 2 dm^3 flask and allowed to come to equilibrium at 1100K.

(i) Write an expression for an expression for K_c of this reaction.

[1]

$$K_c = \frac{[H_2][CO_2]}{[CO][H_2O]}$$

(ii) Calculate the amount of each substance present in the equilibrium mixture at 1100K.

Let the change in number of moles be x.

[2]

	$CO(g) + H_2O(g) \rightleftharpoons$		$CO_2(g) + H_2(g)$	
initial moles	0.80	0.80	0	0
change in moles	–x	–x	+x	+x
eqm moles	(0.80 –x)	(0.80 –x)	+x	+x

$$K_c = \frac{\frac{x^2}{2}}{(\frac{0.80 - x}{2})^2} = 6.40 \times 10^{-1}$$

0.8 x 0.8 – 0.8x = x

x = 0.356

At equilibrium

n(CO) =n(H_2O) = (0.80 – 0.356) = 0.444 mol

n(CO_2) = n(H_2) = 0.356 mol

(iii) State and explain the effect of decreasing pressure on the equilibrium constant. [1]

Decreasing pressure has no effect on the equilibrium constant as it is only affected by change in temperature.

[Total:20]

5 Methanol can be prepared industrially by reacting together carbon monoxide and hydrogen. This is a reversible reaction:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \quad \Delta H = -94 kJmol^{-1}$$

A chemist mixes together 0.114 mol CO(g) and 0.152 mol H_2(g) in a container. The container is pressurised and then sealed and the total volume is 200 cm^3. The mixture is heated to 500 K at constant volume and left to reach equilibrium. The chemist analyses the equilibrium mixture and finds that 0.052 mol CH_3OH has formed.

(a) Calculate the value of K_c for the equilibrium at 500 K. [2]

	CO(g) +	$2H_2(g) \rightleftharpoons$	$CH_3OH(g)$
Initial amount/ mol	0.114	0.152	0
Change in amount/ mol	–0.052	–2(0.052)	+0.052
Equilibrium amount / mol	0.062	0.048	0.052
Equilibrium concentration/ mol dm^{-3}	0.31	0.24	0.26

All three equilibrium concentrations

$$K_c = \frac{[CH_3OH]}{[H_2]^2[CO]} = \frac{[0.26]}{[0.24]^2[0.31]}$$

= 14.6 mol^{-2} dm^6

(b) The chemist repeats the experiment using the same initial amounts of CO and H_2. The same procedure is used but the mixture is heated in the 200 cm^3 sealed container to a temperature higher than 500 K.
As the gas volume is kept at 200 cm^3, the increased temperature also increases the pressure.

Explain why it is difficult to predict how the yield of CH_3OH would change and state what happens to the value of K_c. [2]

At higher pressure, position of equilibrium shifts to the **right** with **fewer gas molecules**.

At higher temperature position of equilibrium shifts to the **left** to favour **endothermic reaction**.

Since **relative effect of pressure and temperature is unknown**, it is difficult to predict how the yield of CH_3OH would change.

The value of K_c **decreases**.

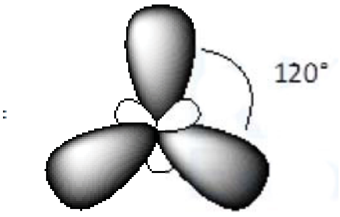
(c) Methanol can be oxidised to formaldehyde, HCHO, by passing its vapour over copper heated to 300 °C.

Explain why the boiling point of methanol (65 °C) is higher than that of formaldehyde (–19 °C). [2]

Both HCHO and CH_3OH have simple molecular structures.
CH_3OH have stronger hydrogen bonds between the molecules while HCHO have weaker permanent dipole-permanent dipole interactions between the molecules .
More energy is required to overcome the stronger hydrogen bonds between CH_3OH molecules, thus CH_3OH has a higher boiling point.

(d) State the type of hybridisation shown by the C atom in formaldehyde and draw its hybrid orbitals. [2]

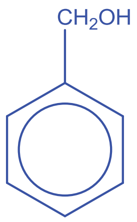
Type of hybridisation: sp^2



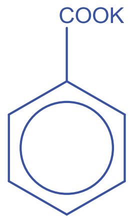
three sp^2 hybrid orbitals with correct shape

(e) Benzaldehyde, C_6H_5CHO, is the simplest aromatic aldehyde and has a characteristic smell of almonds.
In the presence of a solution of potassium hydroxide, benzaldehyde undergoes disproportionation to give a mixture of two organic products, **E** and **F**. **F** has a higher solubility in water compared to **E**.

(i) Suggest the structures of **E** and **F**. [2]



E



F

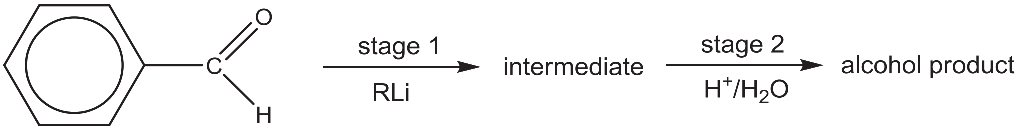
(ii) Explain why **F** is soluble in water. [1]

Ionic salt **F** is able to form ion-dipole interactions with water molecules .

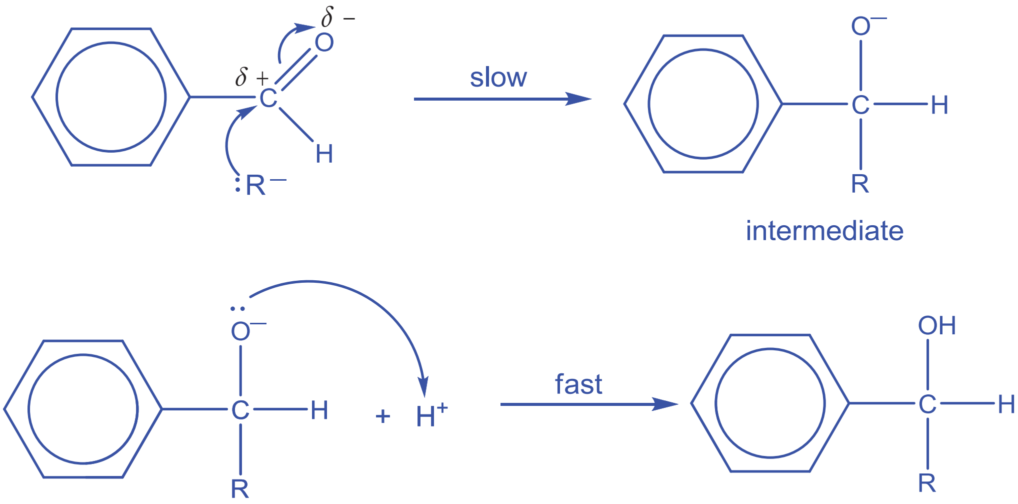
(f) Alkyllithium compounds, RLi, can be used to increase the number of carbon atoms in an organic compound. Different alkyl groups, R, add carbon chains with different chain lengths.

RLi provides a source of R^- ions, which act as a nucleophile.

(i) RLi reacts with benzaldehyde to give an intermediate in stage 1, followed by reaction with aqueous acid to form an alcohol in stage 2.

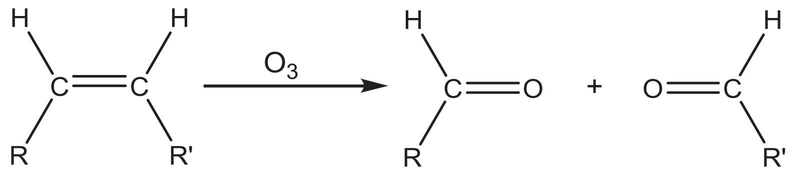


Describe the mechanism for the above reaction, including curly arrows and relevant dipoles. [3]



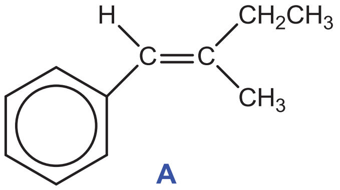
- dipoles on C = O bond & lone pair of electrons on R^- nucleophile
- 2 electron arrows in step 1
- slow and fast step
- correct intermediate
- lone pair of electrons on O^- and electron arrow in step 2
- alcohol product

(ii) 'Ozonolysis' is a technique used in Organic Chemistry to break open a C=C double bond. During ozonolysis, an alkene reacts with ozone, O_3. The products are carbonyl compounds as shown below.

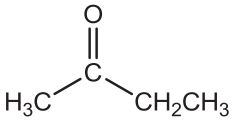


An aromatic alkene, **A** undergoes ozonolysis to give benzaldehyde and **B**, C_4H_8O. **B** has no reaction with $[Ag(NH_3)_2]^+(aq)$ but gives a yellow precipitate with aqueous alkaline iodine.

B undergoes a reaction with an alkyllithium compound, **C**, followed by reaction with aqueous acid to give an alcohol, **D**, which is optically active. The elimination of H_2O from **D** produces a mixture of four different isomeric alkenes with the formula, C_7H_{14}, only two of which are cis-trans isomers of each other. Suggest the structural formulae of compounds **A** to **D** and the two cis-trans isomers. [6]



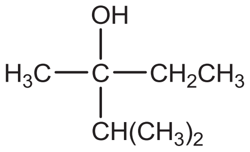
A



B

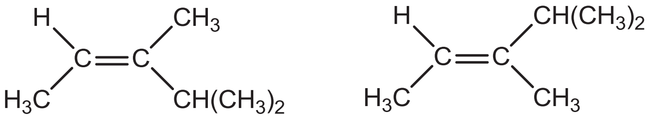
$(CH_3)_2CHLi$

C



$$H_3C-\overset{OH}{\underset{CH(CH_3)_2}{C}}-CH_2CH_3$$

D



Cis and trans isomers

[Total: 20]

INNOVA JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION
in preparation for General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME	
CLASS	
INDEX NUMBER	

CHEMISTRY

9729/04

Paper 4 Practical

15 Aug 2017

2 hours 30 minutes

Candidates answer on the Question Paper.

READ THESE INSTRUCTIONS FIRST

Write your index number, name and class on all the work you hand in.
Give details of the practical shift and laboratory when appropriate, in the boxes provided.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages 18 and 19.

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

Shift
Laboratory

For Examiner's Use	
1	13
2	23
3	19
Total	55

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

1 In this experiment you will determine the relative atomic mass, A_r, of magnesium by a titration method.

FA 1 is 2.00 mol dm^{-3} hydrochloric acid, HC*l*.
FA 3 is 0.120 mol dm^{-3} sodium hydroxide, NaOH
magnesium ribbon
bromophenol blue indicator

(a) Method

Reaction of magnesium with FA 1

- Pipette 25.0 cm^3 of **FA 1** into the 250 cm^3 beaker.
- Weigh the strip of magnesium ribbon and record its mass.

mass of magnesium = ……………g

- Coil the strip of magnesium ribbon loosely and then add it to the **FA 1** in the beaker.
- Stir the mixture occasionally and wait until the reaction has finished.

Dilution of the excess acid

- Transfer all the solution from the beaker into the volumetric flask.
- Make up the solution up to the mark using distilled water.
- Shake the flask to mix the solution before using it for your titrations.
- Label this solution of hydrochloric acid **FA 2**.

Titration

- Fill the burette with **FA 2**.
- Rinse the pipette out thoroughly. Then pipette 25.0 cm^3 of **FA 3** into a conical flask.
- Add several drops of bromophenol blue indicator.
- Run **FA 2** from the burette into this flask until the mixture just becomes yellow.
- Carry out as many titrations as you think necessary to obtain consistent results.
- Make certain that your recorded results show the precision of your working.
- Record in a suitable form below all your burette readings and the volume of **FA 2** added in each accurate titration.

Results

M1	
M2	
M3	
M4	
M5	
M6	

[6]

(b) From your titrations, obtain a suitable volume of **FA 2** to be used in your calculations. Show clearly how you obtained this volume.

M7	

Volume of **FA 2** = ……………………………..[1]

(c) Calculations

Show your working and appropriate significant figures in the final answer to **each** step of your calculations.

(i) Deduce the amount of hydrochloric acid in the volume of **FA 2** you calculated in **(b)**

M8	

Amount of $\mathrm{HC}l$ = ………………… [1]

(ii) In **(a)**, you reacted 25.0 cm^3 of **FA 1** with your weighed piece of magnesium. After the reaction, the unreacted hydrochloric acid was used to prepare 250 cm^3 of **FA 2**.

Calculate the amount of hydrochloric acid that reacted with the magnesium ribbon.

M9	
M10	

Amount of $\mathrm{HC}l$ reacting with Mg = ……………………[2]

(iii) Hence, calculate the relative atomic mass , A_r, of magnesium.

M11	

A_r of Mg = ……………………[1]

(d) A student carried out the same experiment but used 1.00 g of magnesium ribbon. State and explain why the student's experiment could not be used to determine the value for the A_r of magnesium.
Include a calculation in your answer.

[A_r: Mg, 24.3]

M12	
M13	

…………………………………………………………………………………………………

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

[Total: 13]

2 You will investigate the rate of reaction between iron(III) ions, Fe^{3+}, and iodide ions, I^-.

$$2Fe^{3+}(aq) + 2I^{-}(aq) \longrightarrow 2Fe^{2+}(aq) + I_2(aq)$$

The iodine, I_2, produced can be reacted immediately with thiosulfate ions, $S_2O_3^{2-}$.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \longrightarrow 2I^{-}(aq) + S_4O_6^{2-}(aq)$$

When all the thiosulfate has been used, the iodine produced will turn starch indicator blue-black.

The rate of the reaction can therefore be measured by finding the time for the blue-black colour to appear.

FA 4 is aqueous iron(III) chloride, $FeCl_3$.
FA 5 is aqueous potassium iodide, KI.
FA 6 is 0.0060 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$.
starch indicator

You are advised to read the instructions before starting any practical work and draw a table for your results in the space on page **6**.

(a) Method

Experiment 1

- Fill a burette with **FA 4**.
- Run 20.00 cm^3 of **FA 4** into a 100 cm^3 beaker.
- Use the measuring cylinder to place the following in a second 100 cm^3 beaker.
  - 10 cm^3 of **FA 5**
  - 20 cm^3 of **FA 6**
  - 10 cm^3 of starch indicator
- Add the contents of the second beaker to the first beaker and start timing.
- Stir the mixture once and place the beaker on the white tile.
- The mixture turns brown and then yellow before turning a blue-black colour. Stop timing when this **blue-black colour** appears.
- Record in your table the volume of **FA 4** used, the volume of distilled water used and the time to the **nearest second** for the blue-black colour to appear.
- Wash both beakers.

For each of **Experiments 1 - 6** you should complete your results table to show the volume of **FA 4** used, the volume of distilled water used and the time taken to the **nearest second** for the blue-black colour to appear.

Experiment 2

- Fill the other burette with distilled water.
- Run 10.00 cm^3 of **FA 4** into a 100 cm^3 beaker.
- Run 10.00 cm^3 of distilled water into the same beaker.
- Use the measuring cylinder to place the following in a second 100 cm^3 beaker.
  - 10 cm^3 of **FA 5**
  - 20 cm^3 of **FA 6**
  - 10 cm^3 of starch indicator
- Add the contents of the second beaker to the first beaker and start timing.
- Stir the mixture once and place the beaker on the white tile.
- Stop timing when a blue-black colour appears.

- Wash both beakers.

Experiments 3 - 6

Carry out **four** further experiments to investigate the effect of changing the concentration of Fe^{3+} (aq) by altering the volume of aqueous $FeCl_3$, **FA 4**, used.

You should not use a volume of **FA 4** that is less than 6.00 cm^3 and the total volume of the reaction mixture must always be 60 cm^3.

M14	
M15	
M16	
M17	
M18	
M19	

[6]

Calculations

The rate of reaction can be found by calculating the change in concentration of Fe^{3+}(aq) that occurred when enough iodine was produced to change the colour of the indicator to blue-black.

Use your data and the equations on page **5** to carry out the following calculations.

Show your working and appropriate significant figures in the final answer to **each** step of your calculations.

(b) **(i)** Calculate the amount of thiosulfate ions, $S_2O_3^{2-}$ used in each experiment.

M20	

Amount of $S_2O_3^{2-}$ ……………………..[1]

(ii) Calculate the amount of iron(III) ions, Fe^{3+}, that were used to produce the amount of iodine that react with the amount of $S_2O_3^{2-}$ in **(i)**.

M21	

Amount of Fe^{3+} …………………….. [1]

(iii) Using your answer to **(ii)**, calculate the change in Fe^{3+} up to the time of appearance of the blue black colour.

M22	

Change in concentration of Fe^{3+} ……………………..[1]

(iv) The following formula can be used as a measure of the 'rate of reaction'.

$$\text{'rate of reaction'} = \frac{\text{change in concentration of Fe}^{3+}\text{(aq)}}{\text{reaction time}} \times 10^{6}$$

Complete the table to show the volume of **FA 4**, the reaction time and the rate in **Experiments 1- 6**. You should include units.

If you were unable to calculate a value for the change in concentration of Fe^{3+}(aq) in **(iv)**, you should assume it is 2.50×10^{-3} mol dm^{-3}. (Note: this is not the correct value.)

Experiment			
1			
2			
3			
4			
5			
6			

M23

[1]

(c) On the grid, plot the rate (*y*-axis) against the volume of **FA 4** (*x*-axis). Draw a line of best fit through the points. You should identify any points you consider anomalous.

M24	
M25	
M26	

[3]

(d) Using your graph, what conclusion can you reach about the effect of changing the concentration of $FeCl_3$ on the rate of the reaction between $Fe^{3+}(aq)$ and $I^-(aq)$?

……………………………………………………………………………………………………

……………………………………………………………………………………………………

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

M27	
M28	

(e) It was found, by carrying out experiments similar to those used in **(a)**, that increasing the concentration of I^- increased the rate of the reaction.

The student suggested a modification to the method by using the same volumes of all reagents but with the concentration of **FA4** and **FA 5** being doubled their original values. State what the effect would be on the **reaction time** in Experiment 1 and explain how this change would affect any **possible errors** in the measurements.

……………………………………………………………………………………………………

……………………………………………………………………………………………………

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

M29	

(f) Which of the experiments you carried out in **(a)** had the greatest percentage error in the reaction time? Calculate this percentage error. Assume that the error in measuring the reaction time is ±0.5 s.

[1]

M30	

(g) Planning

Aqueous hydrogen peroxide decomposes into oxygen gas and water. The reaction is normally very slow but is catalysed by solid manganese (IV) oxide.

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

You are to plan an experiment to investigate how the rate of the catalysed decomposition of aqueous hydrogen peroxide depends on its concentration.

(i) The rate of decomposition depends on the number of hydrogen peroxide molecules present in a given volume of solution.

Use this information to predict how the rate of decomposition of the hydrogen peroxide depends on the concentration.

Prediction……………………………………………………………………………………

……………………………………………………………………………………………

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

M31

(ii) You are to design a laboratory experiment to test your prediction in **(g) (i)**.

In addition to the standard apparatus present in a laboratory you are provided with the following materials.

- 0.1 mol dm^{-3} aqueous hydrogen peroxide
- A supply of manganese (IV) oxide

Complete the table below to show how you would prepare five solutions of aqueous hydrogen peroxide. Make sure that the correct units are recorded.

expt No.	volume of H_2O_2	volume of H_2O	concentration of H_2O_2
1			
2			
3			
4			
5			

M32

[1]

(iii) Give a step by step description of how you would carry out **one** complete experiment.

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

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

M33	
M34	
M35	

(iv) State a problem which might be experienced by someone having to carry out these experiments alone.

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

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

M36	

[Total: 23]

3 Qualitative Analysis

At each stage of any test you are to record details of the following:

- colour changes seen
- the formation of any precipitate
- the solubility of such precipitates in an excess of the reagent added

Where gases are released they should be identified by a test, **described in the appropriate place in your observations.**

You should indicate clearly at which stage of the test a change occurs.
Marks are **not** given for chemical equations.
No additional tests for ions present should be attempted.

If any solution is warmed, a boiling tube MUST be used.

Rinse and reuse test-tubes and boiling tubes where possible.

Where reagents are selected for use in a test, the name or correct formula of the element or compound must be given.

(a) **FA 7** and **FA 8** are mixtures. Each mixture contains one cation and two anions from those listed on pages 18 and 19.

Carry out the following tests and record all your observations in the table below.

Test	Observations	
	FA 7	**FA 8**
(i) Place two spatula measure of **FA 7** into a boiling tube, then add approximately 5 cm^3 of dilute nitric acid using the measuring cylinder. You are to repeat the steps for **FA 8**. Then		
add about 5 cm^3 of distilled water and shake to mix the solution. Use a 1 cm depth of the solution obtained in a test-tube for each of tests **(ii) – (v)**.	No observation required.	
(ii) Add aqueous sodium hydroxide. Then add dilute nitric acid dropwise until in excess.		Do not carry out this test.
(iii) Add aqueous ammonia.		Do not carry out this test.

Test	Observations	
	FA7	**FA8**
(iv) Add aqueous barium nitrate followed by dilute nitric acid.		

M37

	FA7	**FA8**
(v) Add aqueous silver nitrate followed by aqueous ammonia.		

M38	
M39	
M40	

[4]

(vi) Use your observations to identify the following ions.

FA 7 contains cation ……………………………….

FA 7 contains anions ……………………………… and ………………………………
FA 8 contains anions ……………………………. and ………………………………

State and explain all the evidence for your identification of the cation in **FA 7**.

…………………………………………………………………………………………………

…………………………………………………………………………………………………

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

M41	
M42	
M43	

(b) **FA 9** contains two cations from the list on page 18.

(i) Transfer approximately half of the **FA 9** into a hard-glass test-tube and heat gently at first, and then strongly, until no further change is seen.
Test with litmus papers while you are heating.
Record all your observations below.

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

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

M44	

(ii) Carry out further tests that will enable you to identify **both** cations in **FA 9**.
Describe your tests briefly and state your observations.

FA 9 contains cations ……………………………… and ………………………………
[2]

M45	
M46	

(c) Planning

A solder is an alloy of metals which is used to join other metal pieces together.

A specialist solder that can be used to join together pieces of aluminium is made from a mixture by mass of 65% zinc, 20% aluminium and 15% copper.

You are to plan an experimental procedure to confirm the composition of a powdered sample of this solder, by adding reagents and then extracting from the mixture each of the following in sequence;

- (i) the copper metal,
- (ii) the aluminium as aluminium hydroxide,
- (iii) the zinc as zinc hydroxide

You are provided with

- a sample of this solder, with approximate mass 4 g,
- 1.00 mol dm^{-3} sulfuric acid,
- 1.00 mol dm^{-3} ammonia

No other reagents should be used. Standard laboratory equipment is available including a balance, accurate to two decimal places.

(i) Complete the flowchart below to show the order in which the reagents would be added to the solder to allow you to extract and separate the components as copper metal, (**Step 1**), aluminium hydroxide, **(Step 2)**, and zinc hydroxide, **(Step 3)**.
You are reminded that aqueous ammonia contains both the base OH$^-$ and the complex-forming molecule NH_3.

Step 1	**Step 2**	**Step 3**
reagent(s) added	reagent(s) added	reagent(s) added
……………………………..	………………………….	…………………………….
……………………………..	………………………….	…………………………….
substance(s) present at the end of the reaction	substance(s) present at the end of the reaction	substance(s) present at the end of the reaction
……………………………..	………………………………	…………………………….
……………………………..	………………………………	…………………………….
……………………………..	………………………………	…………………………….
substance(s) removed by filtration (if any)	substance(s) removed by filtration (if any)	substance(s) removed by filtration (if any)
……………………………..	………………………………	…………………………….
……………………………..	………………………………	…………………………….

M47	
M48	
M49	
M50	
M51	

[5]

(ii) For some of the steps in the procedure you would need to be careful to add an appropriate quantity of a reagent.
For each step of your procedure explain why particular quantities of reagent should be chosen.

Step 1

…………………………………………………………………………………………………

…………………………………………………………………………………………………

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

M52

Step 2

…………………………………………………………………………………………………

…………………………………………………………………………………………………

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

M53

Step 3

…………………………………………………………………………………………………

…………………………………………………………………………………………………

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

M54

(iii) If the mass of aluminium hydroxide obtained was 1.50 g, calculate the mass of aluminium that was present in the solder.
[A_r: A*l*, 27.0; O, 16.0]

[1]

M55

[Total: 19]

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

ion	*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

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H

INNOVA JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION
in preparation for General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME	WORKED SOLUTIONS

CLASS		INDEX NUMBER	

CHEMISTRY

9729/04

Paper 4 Practical

15 Aug 2017

2 hours 30 minutes

Candidates answer on the Question Paper.

READ THESE INSTRUCTIONS FIRST

Write your index number, name and class on all the work you hand in.
Give details of the practical shift and laboratory when appropriate, in the boxes provided.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages 18 and 19.

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

Shift
Laboratory

For Examiner's Use	
1	17
2	24
3	14
Total	55

This document consists of **15** printed pages.

1 In this experiment you will determine the relative atomic mass, A_r, of magnesium by a titration method.

FA 1 is 2.00 mol dm^{-3} hydrochloric acid, HC*l*.
FA 3 is 0.120 mol dm^{-3} sodium hydroxide, NaOH
magnesium ribbon
bromophenol blue indicator

(a) Method

Reaction of magnesium with FA 1

- Pipette 25.0 cm^3 of **FA 1** into the 250 cm^3 beaker.
- Weigh the strip of magnesium ribbon and record its mass.

mass of magnesium = ……………g

- Coil the strip of magnesium ribbon loosely and then add it to the **FA 1** in the beaker.
- Stir the mixture occasionally and wait until the reaction has finished.

Dilution of the excess acid

- Transfer all the solution from the beaker into the volumetric flask.
- Make up the solution up to the mark using distilled water.
- Shake the flask to mix the solution before using it for your titrations.
- Label this solution of hydrochloric acid **FA 2**.

Titration

- Fill the burette with **FA 2**.
- Rinse the pipette out thoroughly. Then pipette 25.0 cm^3 of **FA 3** into a conical flask.
- Add several drops of bromophenol blue indicator.
- Run **FA 2** from the burette into this flask until the mixture just becomes yellow.
- Carry out as many titrations as you think necessary to obtain consistent results.
- Make certain that your recorded results show the precision of your working.
- Record in a suitable form on below all your burette readings and the volume of **FA 2** added in each accurate titration.

Results

The following readings are recorded

- Mass of Mg used
- Initial and final burette reading for two (or more) accurate titrations **M1**

Titre values recorded for accurate titrations and appropriate headings for the accurate titration tables and cm^3 units.

- Initial (burette) reading
- Final (burette) reading
- Titre or volume of **FA 2** used/added (*not “difference” or “total”*)
- Unit: cm^3(for each heading)

If cm^3 units are not given in the headings, every entry in the table must have the correct unit. **M2**

All accurate burette reading are to the nearest 0.05 cm^3. *Do **not** award this mark if:*

- $50.00 cm^3$ is used as an initial burette reading
- Any burette reading is greater than $50.00 cm^3$
- There is only one accurate titration **M3**

There are two uncorrected **accurate** titres within $0.10 cm^3$. *Do not award this mark if, having performed two titre within 0.10 cm a further titration is performed.* **M4**

Calculate the student's mean titre based on the following hierarchy:

- Value of 2 identical titres
- Average of titres within $0.05 cm^3$
- Average of titres within $0.1 cm^3$

Award based on the difference, *Δtitre*, between Student's and Supervisor's mean titre.
Give 2 marks if $\Delta titre \leq 0.20 cm^3$
Give 1 marks if $0.20 < \Delta titre \leq 0.50 cm^3$ **M5,M6**

[6]

(b) From your titrations, obtain a suitable volume of **FA 2** to be used in your calculations. Show clearly how you obtained this volume.

Student obtains appropriate "average" to 2 d.p., from any experiments with uncorrected end – point titre values within $0.10 cm^3$
Do not award this mark if the titres used are not identified either in the table (by, for example, a tick) or in a calculation.
*Do **not** award this mark if there are arithmetic error in the table.* **M7**

Volume of **FA 2** = ……………………………..[1]

(c) Calculations

Show your working and appropriate significant figures in the final answer to **each** step of your calculations.

Units should be either in final calculation **or** dotted line.
Sf will be deducted ½ for overall, max 1 mark
Units will be deducted ½ for overall, max 1 mark
Working must be shown for all parts.

(i) Deduce the amount of hydrochloric acid in the volume of **FA 2** you calculated in **(b)**

Amount of NaOH = $0.120 \times \frac{25.0}{1000} = 0.003000 mol$

$NaOH + HCl \rightarrow NaCl + H_2O$

Amount of HCl = amount of NaOH
= 0.00300 mol **M8**

Amount of HC*l* = ………………… [1]

(ii) In **(a)**, you reacted $25.0 cm^3$ of **FA 1** with your weighed piece of magnesium. After the reaction, the unreacted hydrochloric acid was used to prepare $250 cm^3$ of **FA 2**.

Calculate the amount of hydrochloric acid that reacted with the magnesium ribbon.

Amount of HCl in volumetric flask = $0.00300 \times \dfrac{250}{(b)}$ = **a** mol

Amount of HCl used initially = $2.00 \times \dfrac{25.0}{1000} = 0.0500\,mol$ **M9**

Amount of hydrochloric acid that reacted with Mg = 0.0500 – **a**
= **b** mol **M10**

Amount of HC*l* reacting with Mg = ……………………[2]

(iii) Hence, calculate the relative atomic mass , A_r, of magnesium.

$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$
Amount of Mg = **b** /2 mol
A_r = mass of Mg / (**b**/2)
$= \dfrac{2 \times \text{mass of Mg}}{\text{b}}$ (1dp) **M11**
Must be 1dp otherwise 0 mark.

A_r of Mg = ……………………[1]

(d) A student carried out the same experiment but used 1.00 g of magnesium ribbon. State and explain why the student's experiment could not be used to determine the value for the A_r of magnesium.
Include a calculation in your answer.

[A_r: Mg, 24.3]
Amount of Mg = 1/24.3 = 0.0412 mol
Amount of HCl needed = 0.0412 x 2 = 0.0824 mol but only 0.05 mol present **M12**

If 1.0g of Mg is used, Mg would be in excess/ acid would be the limiting reagent/ all the acid would be used up. **M13**

[2]

[Total: 13]

2 You will investigate the rate of reaction between iron(III) ions, Fe^{3+}, and iodide ions, I^-.

$$2Fe^{3+}(aq) + 2I^-(aq) \longrightarrow 2Fe^{2+}(aq) + I_2(aq)$$

The iodine, I_2, produced can be reacted immediately with thiosulfate ions, $S_2O_3^{2-}$.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \longrightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

When all the thiosulfate has been used, the iodine produced will turn starch indicator blue-black.

The rate of the reaction can therefore be measured by finding the time for the blue-black colour to appear.

FA 4 is aqueous iron(III) chloride, $FeCl_3$.
FA 5 is aqueous potassium iodide, KI.
FA 6 is 0.0060 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$.
starch indicator

You are advised to read the instructions before starting any practical work and draw a table for your results in the space on page **6**.

(a) Method

Experiment 1

- Fill a burette with **FA 4**.
- Run 20.00 cm^3 of **FA 4** into a 100 cm^3 beaker.
- Use the measuring cylinder to place the following in a second 100 cm^3 beaker.
  - o 10 cm^3 of **FA 5**
  - o 20 cm^3 of **FA 6**
  - o 10 cm^3 of starch indicator
- Add the contents of the second beaker to the first beaker and start timing.
- Stir the mixture once and place the beaker on the white tile.
- The mixture turns brown and then yellow before turning a blue-black colour. Stop timing when this **blue-black colour** appears.
- Record in your table the volume of **FA 4** used, the volume of distilled water used and the time to the **nearest second** for the blue-black colour to appear.
- Wash both beakers.

For each of **Experiments 1 - 6** you should complete your results table to show the volume of **FA 4** used, the volume of distilled water used and the time taken to the **nearest second** for the blue-black colour to appear.

Experiment 2

- Fill the other burette with distilled water.
- Run 10.00 cm^3 of **FA 4** into a 100 cm^3 beaker.
- Run 10.00 cm^3 of distilled water into the same beaker.
- Use the measuring cylinder to place the following in a second 100 cm^3 beaker.
  - o 10 cm^3 of **FA 5**
  - o 20 cm^3 of **FA 6**
  - o 10 cm^3 of starch indicator
- Add the contents of the second beaker to the first beaker and start timing.
- Stir the mixture once and place the beaker on the white tile.
- Stop timing when a blue-black colour appears.
- Wash both beakers.

Experiments 3 - 6

Carry out **four** further experiments to investigate the effect of changing the concentration of Fe^{3+}(aq) by altering the volume of aqueous $FeCl_3$, **FA 4**, used.

You should not use a volume of **FA 4** that is less than 6.00 cm^3 and the total volume of the reaction mixture must always be 60 cm^3.

Experiment	**Vol. of FA4/ cm^3**	**Vol. of water/ cm^3**	**Time taken/s**
1	20.00	0.00	20
2	10.00	10.00	27
3	7.00	13.00	32
4	13.00	7.00	24
5	15.00	5.00	22
6	18.00	2.00	21

Recording:

- Constructs a table for 6 results. **M14**
- Correct headings and units for FA4, distilled water and time. Volumes / V/vol in cm^3 or / cm^3 or (cm^3), time / t in seconds or / s or (s). **M15**

Precision:

- All times recorded to the nearest second and volumes of FA4 and distilled water to 0.05 cm^3. **M16**

Decision:

- Four further experiments chosen with intervals not less than 2 cm^3 and no volume less than 6 cm^3. At least one volume must be **less than 10 cm^3** and **at least one must be more than 10 cm^3. M17**

- Water added to make total volume of FA 4 and water 20 cm^3 in each experiment and no other changes in volume. **M18**

M17 and M18 penalised if students change volume of other reagents other than FA4 and water.

Accuracy:

- Times increase with decrease in volume FA 4.
- Examiner rounds times to nearest second and calculates (time for expt 2) / (time for expt 1) to 2 decimal place. Ratio is compared with that of Supervisor.
  Award marks as follows:
  if ratio within 0.2 of Supervisor. **M19**

[6]

Calculations

The rate of reaction can be found by calculating the change in concentration of $Fe^{3+}(aq)$ that occurred when enough iodine was produced to change the colour of the indicator to blue-black.

Use your data and the equations on page **5** to carry out the following calculations.

Show your working and appropriate significant figures in the final answer to **each** step of your calculations.

(b) **(i)** Calculate the amount of thiosulfate ions, $S_2O_3^{2-}$ used in each experiment.

$$\text{Amount } S_2O_3^{2-} = \frac{20}{1000} \times 0.0060$$

$= 1.20 \times 10^{-4}$ mol **M20**

Amount of $S_2O_3^{2-}$ ....[1]

(ii) Calculate the amount of iron(III) ions, Fe^{3+}, that were used to produce the amount of iodine that react with the amount of $S_2O_3^{2-}$ in **(i)**.

$2Fe^{3+} \equiv I_2 \equiv 2\ S_2O_3^{2-}$

Amount of Fe^{3+} $= 1.20 \times 10^{-4}$ mol **M21**

OR

Amount of iodine $= \frac{1}{2} \times 1.2 \times 10^{-4}$

$=0.600 \times 10^{-4}$ mol

Amount of Fe^{3+} $= 2 \times 0.600 \times 10^{-4}$
$= 1.20 \times 10^{-4}$ mol **M21**

Amount of Fe^{3+} .... [1]

(iii) Using your answer to **(ii)**, calculate the change in Fe^{3+} up to the time of appearance of the blue black colour.

Change in concentration of Fe^{3+} $= \dfrac{1.20\times10^{-4}}{\frac{60}{1000}} = 0.00200$ mol dm^{-3} **M22**

Change in concentration of Fe^{3+} ....[1]

(iv) The following formula can be used as a measure of the 'rate of reaction'.

$$\text{'rate of reaction'} = \frac{\text{change in concentration of } Fe^{3+}(aq)}{\text{reaction time}} \times 10^6$$

Complete the table to show the volume of **FA 4**, the reaction time and the rate in **Experiments 1- 6**. You should include units.

If you **were unable** to calculate a value for the change in concentration of Fe^{3+}(aq) in **(iv)**, you should assume it is 2.50×10^{-3} mol dm^{-3}. (Note: this is not the correct value.)

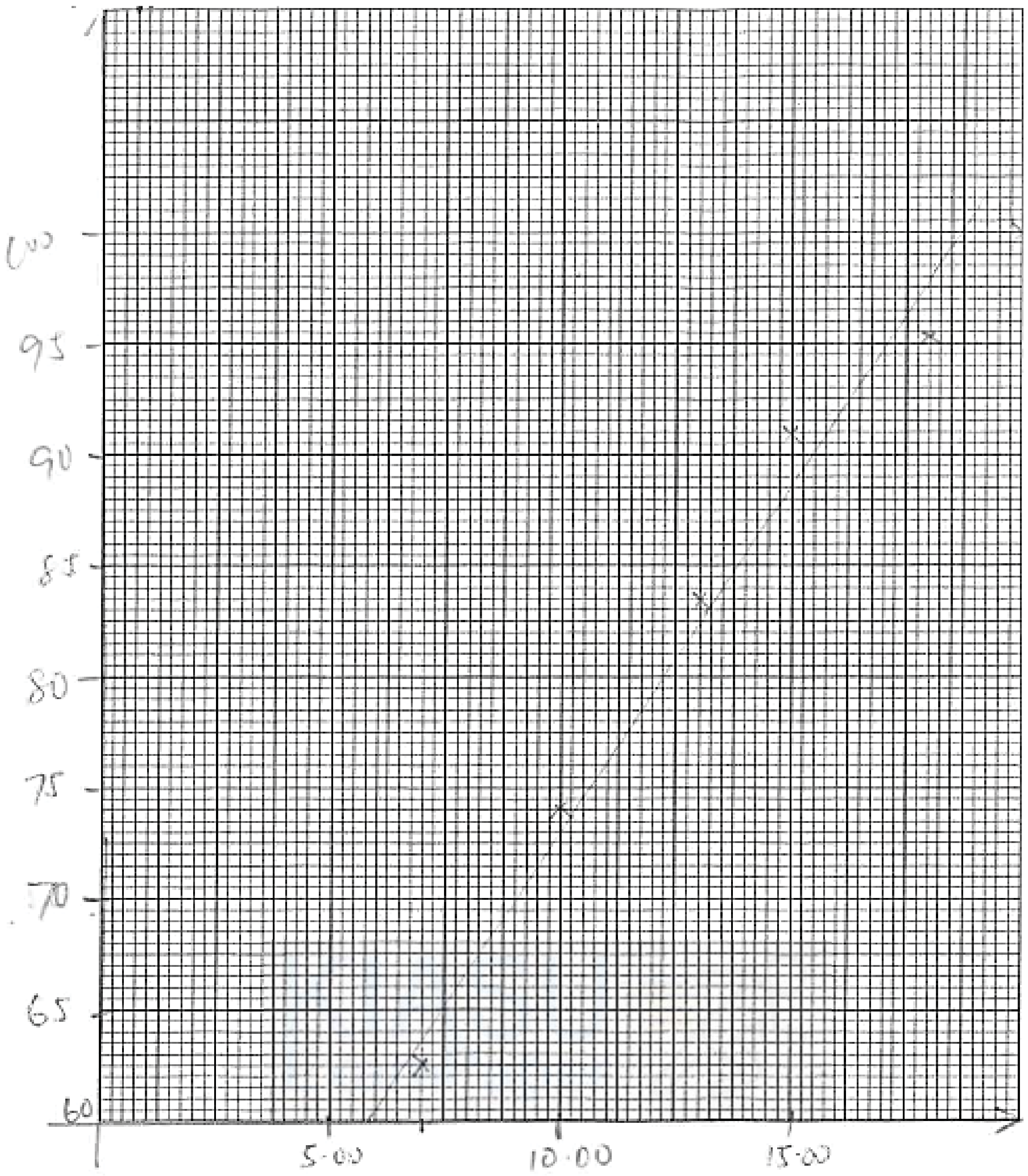
Experiment	Vol. of FA4/ cm^3	Time taken/s	Rate/ mol dm^{-3} s^{-1}
1	20.00	20	100
2	10.00	27	74.0
3	7.00	32	62.5
4	13.00	24	83.3
5	15.00	22	90.9
6	18.00	21	95.2

Rates correctly calculated using $\frac{0.00200}{\text{reaction time}} \times 10^6$

Units for volume given as cm^3. Units for time given as s. Units for rate given as mol dm^{-3} s^{-1}, 3 correct columns used and 3 sig fig. Ignore precision for volume of FA4 and time. **M23**

[1]

(c) On the grid, plot the rate (*y*-axis) against the volume of **FA 4** (*x*-axis). Draw a line of best fit through the points. You should identify any points you consider anomalous.



Axes labelled – rate/ mol dm^{-3} s^{-1} on *y*-axis and volume or FA 4 / cm^3 on *x*-axis. Scales to use at least half of each axis including 0.0 if point plotted. **M24**

Correct plotting – **all** points recorded plotted and within half a small square and within correct small square. Scale must be drawn correctly. **M25**

Draws a line of best fit (can be straight line or curve). Straight lines must be straight (single line with no kinks, drawn using a ruler) or a smooth curve (gradual change in gradient).
Points not on the line must be balanced on either side of the best fit line but any points ringed or labelled as anomalous should be ignored. **M26**

[3]

(d) Using your graph, what conclusion can you reach about the effect of changing the concentration of $FeCl_3$ on the rate of the reaction between Fe^{3+}(aq) and I^-(aq)?

Rate increases as concentration of Fe^{3+} increases/ rate directly proportional to concentration **M27** since **either straight line that pass through the origin shows** rate is directly proportional to concentration **or gradient is positive** **M28** shows that rate increase with increase in concentration (or other words to that effect).

[2]

(e) It was found, by carrying out experiments similar to those used in **(a)**, that increasing the concentration of I^- increased the rate of the reaction.

The student suggested a modification to the method by using the same volumes of all reagents but with the concentration of **FA4** and **FA 5** being doubled their original values. State what the effect would be on the **reaction time** in Experiment 1 and explain how this change would affect any **possible errors** in the measurements.

Reaction time less/shorter. (**Less accurate) since larger % error** (in time). **M29**
Not "Reaction time faster".

[1]

(f) Which of the experiments you carried out in **(a)** had the greatest percentage error in the reaction time? Calculate this percentage error. Assume that the error in measuring the reaction time is ±0.5 s.

Experiment 1.

percentage error = $\frac{0.5}{20} \times 100\%$ **M30**

[1]

(g) **Planning**

Aqueous hydrogen peroxide decomposes into oxygen gas and water. The reaction is normally very slow but is catalysed by solid manganese (IV) oxide.

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

You are to plan an experiment to investigate how the rate of the catalysed decomposition of aqueous hydrogen peroxide depends on its concentration.

(i) The rate of decomposition depends on the number of hydrogen peroxide molecules present in a given volume of solution.

Use this information to predict how the rate of decomposition of the hydrogen peroxide depends on the concentration.

Prediction

Prediction: Predicts **any** direct proportionality e.g. Increasing concentration increases rate or doubling the molecules per unit volume (concentration) doubles the rate. **M31**

[1]

(ii) You are to design a laboratory experiment to test your prediction in **(g) (i)**.

In addition to the standard apparatus present in a laboratory you are provided with the following materials.

- 0.1 mol dm^{-3} aqueous hydrogen peroxide
- A supply of manganese (IV) oxide

Complete the table below to show how you would prepare five solutions of aqueous hydrogen peroxide. Make sure that the correct units are recorded.

expt No.	volume of H_2O_2 / cm^3	volume of H_2O / cm^3	concentration of H_2O_2 / mol dm^{-3}
1	40.00	0.00	0.100
2	35.00	5.00	0.0875
3	30.00	10.00	0.0750
4	25.00	15.00	0.0625
5	20.00	20.00	0.0500

Whole table completed. Correct units required for each column. 0 cm^3 of H_2O_2 not accepted. Total volume of solutions need not be constant. **M32**

Pre-calculation
Assuming burette is used, maximum volume of O_2 that can be collected will be 50 cm^3.

Amount of O_2 = 50/24000 = 2.0833 x 10^{-3} mol
Amount of H_2O_2 = 2 x 2.0833 x 10^{-3} = 4.1667 x 10^{-3} mol

Volume of original H_2O_2 = (4.1667 x 10^{-3})/ 0.1
= 41.67 cm^3

Note: If gas syringe is used in planning, maximum volume of original H_2O_2 will be around 80 cm^3.

[1]

(ii) Give a step by step description of how you would carry out **one** complete experiment.

1. Using a burette, introduce 35.00cm^3 of H_2O_2 solution into a 100 cm^3 conical flask.
2. Using another burette, introduce 5.00 cm^3 of distilled water into the same conical flask.
3. Attach a small tube containing some solid manganese (IV) oxide with a string and stopper it.
4. Record initial volume reading of the syringe.
5. Let the manganese (IV) oxide comes in contact with the solution by loosening the stopper.
6. Start the stopwatch immediately. Swirl to mix gently.
7. Stop the stopwatch once 20 cm^3 of gas has been collected.

Give marks for shaking to react the catalyst and solution present. If a thistle or dropping funnel used the mark is for adding the liquid reagent to the catalyst. In other situations give marks for adding solid catalyst to the solution and closing the vessel. **M33**

Start the reaction and a stopwatch simultaneously. **M34**

Recording the time taken to produce a chosen/fixed volume of gas. **M35**

[3]

(iii) State a problem which might be experienced by someone having to carry out these experiments alone.

Starting the reaction and the stopwatch simultaneously is difficult. Accept any reaction starting process in conjunction with starting the clock. Accept closing the apparatus and starting the clock. **M36**

[1]

[Total: 23]

3 Qualitative Analysis

At each stage of any test you are to record details of the following:
- colour changes seen
- the formation of any precipitate
- the solubility of such precipitates in an excess of the reagent added

Where gases are released they should be identified by a test, **described in the appropriate place in your observations.**

You should indicate clearly at which stage of the test a change occurs.
Marks are **not** given for chemical equations.
No additional tests for ions present should be attempted.

If any solution is warmed, a boiling tube MUST be used.

Rinse and reuse test-tubes and boiling tubes where possible.

Where reagents are selected for use in a test, the name or correct formula of the element or compound must be given.

(a) **FA 7** and **FA 8** are mixtures. Each mixture contains one cation and two anions from those listed on pages 18 and 19.

Carry out the following tests and record all your observations in the table below.

FA 7 is $Al_2(SO_4)_3$ + NaCl; **FA 8** is $MgCO_3$ + KI; **FA 9** is $(NH_4)_2Fe(SO_4)_2$

Test	Observations	
	FA 7	**FA 8**
(i) Place two spatula measure of **FA 7** into a boiling tube, then add approximately 5 cm^3 of dilute nitric acid using the measuring cylinder. You are to repeat the steps for **FA 8**. Then	**FA 7** dissolves/ A colourless solution is formed. [√]	**FA 8** dissolves and effervescence seen. Gas produced gives a white ppt. with $Ca(OH)_2(aq)$. [√]
add about 5 cm^3 of distilled water and shake to mix the solution. Use a 1 cm depth of the solution obtained in a test-tube for each of tests **(ii)** – **(v)**.	No observation required.	
(ii) Add aqueous sodium hydroxide. Then add dilute nitric acid dropwise until in excess.	White ppt. formed, soluble in excess [√] White ppt. re-forms, soluble in excess $HNO_3(aq)$ [√]	Do not carry out this test.
(iii) Add aqueous ammonia.	White ppt. formed, insoluble in excess [√]	Do not carry out this test.
Test	Observations	
	FA7	**FA8**
(iv) Add aqueous barium nitrate followed by dilute nitric acid.	White ppt. formed, insoluble in dilute HNO_3 [√]	No ppt or no observable change [√]

(v) Add aqueous silver nitrate followed by aqueous ammonia.	White ppt formed, soluble in $NH_3(aq)$ [√]	Yellow ppt formed, insoluble in $NH_3(aq)$ [√]

[4]

2 [√] – [1], max [4] M37, M38, M39, M40

(vi) Use your observations to identify the following ions.
FA 7 contains cation ……………………………….…

FA 7 contains anions ……………………………….… and ……………………………….…
FA 8 contains anions ……………………………….… and ……………………………….…

State and explain all the evidence for your identification of the cation in **FA 7**.
M41 cation is Al^{3+} and while ppt with $NH_3(aq)$ insoluble in excess, white ppt with NaOH soluble in excess.
M42 FA 7 anions: SO_4^{2-} and Cl^-
M43 FA 8 anions: CO_3^{2-} and I^-

[3]

(b) **FA 9** contains two cations from the list on page 18.

(i) Transfer approximately half of the **FA 9** into a hard-glass test-tube and heat gently at first, and then strongly, until no further change is seen.
Test with litmus papers while you are heating.
Record all your observations below.

Any two observations correct **M44**

- **FA 9** is (pale) green
- steam/ vapour/ condensation/ water liquid
- damp litmus paper turns blue
- yellow/ white/ brown residue formed
- white smoke (produced on strong heating)
- damp litmus turns red on strong heating

[1]

(ii) Carry out further tests that will enable you to identify **both** cations in **FA 9**.
Describe your tests briefly and state your observations.

With NaOH or NH_3, dirty green ppt formed which turns brown on contact with air and Fe^{2+} identified. **M45**
With NaOH(aq) and heat, pungent gas (NH_3) turns damp red litmus paper blue and NH_4^+ identified. **M46**

FA 9 contains cations ……… Fe^{2+}……………… and ……… NH_4^+ ……………

[2]

(c) **Planning**

A solder is an alloy of metals which is used to join other metal pieces together.

A specialist solder that can be used to join together pieces of aluminium is made from a mixture by mass of 65% zinc, 20% aluminium and 15% copper.

You are to plan an experimental procedure to confirm the composition of a powdered sample of this solder, by adding reagents and then extracting from the mixture each of the following in sequence;

(i) the copper metal,
(ii) the aluminium as aluminium hydroxide,
(iii) the zinc as zinc hydroxide

You are provided with

- a sample of this solder, with approximate mass 4 g,
- 1.00 mol dm^{-3} sulfuric acid,
- 1.00 mol dm^{-3} ammonia

No other reagents should be used. Standard laboratory equipment is available including a balance, accurate to two decimal places.

(i) Complete the flowchart below to show the order in which the reagents would be added to the solder to allow you to extract and separate the components as copper metal, (**Step 1**), aluminium hydroxide, **(Step 2)**, and zinc hydroxide, **(Step 3)**.
You are reminded that aqueous ammonia contains both the base OH$^-$ and the complex-forming molecule NH$_3$.

Step 1	Step 2	Step 3
reagent(s) added	reagent(s) added	reagent(s) added
sulfuric acid **[√]**	(excess, aqueous) ammonia **[√]**	sulfuric acid **[√]**
substance(s) present at the end of the reaction	substance(s) present at the end of the reaction	substance(s) present at the end of the reaction
zinc sulfate **[√]** and aluminium sulfate **[√]** (copper)	zinc (tetra) ammine **[√]** (ions) (aluminium hydroxide)	ammonium sulfate **[√]** (zinc hydroxide)
substance(s) removed by filtration (if any)	substance(s) removed by filtration (if any)	substance(s) removed by filtration (if any)
copper **[√]**	aluminium hydroxide **[√]**	zinc hydroxide **[√]**

Allow: Correct formulae or ions instead of names.
2**[√] – 1 mark; max [5] M47, M48, M49, M50, M51**

Substances present for each step is conditional based on correct reagent added.

[5]

(ii) For some of the steps in the procedure you would need to be careful to add an appropriate quantity of a reagent.
For each step of your procedure explain why particular quantities of reagent should be chosen.

Step 1
Sufficient/ enough/ excess sulfuric acid to dissolve the zinc and aluminium **M52**

Step 2
Sufficient/ enough/ excess aqueous ammonia (to precipitate aluminium hydroxide) and to completely dissolve the zinc hydroxide **M53**

Step 3
Sufficient/ enough sulfuric acid to:
Neutralise ammonia **M54** **OR**
(re)precipitate the zinc hydroxide but not so much that the zinc hydroxide reacts/ dissolves **M54**

[3]

(iii) If the mass of aluminium hydroxide obtained was 1.50 g, calculate the mass of aluminium that was present in the solder.
[A_r: A*l*, 27.0; O, 16.0]

Mass of A*l* in solder = $\frac{27}{27 + 17 \times 3}$ x 1.50 g = **<u>0.519 g</u>** **M55**

[1]

[Total: 19]