CANDIDATE'S NAME: ________________________________ **CTG:** ____________

YISHUN JUNIOR COLLEGE

2017 JC2 PRELIMINARY EXAMINATION

CHEMISTRY **9729/01**
HIGHER 2
Paper 1 Multiple Choice Questions **FRIDAY 15 SEPTEMBER 2017**
0800hrs − 0900hrs
(1 hour)

Additional Materials: Optical Mark Sheet (OMS)
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Write your name, CTG, and NRIC / FIN number on the Optical Mark Sheet (OMS), and shade the corresponding boxes for your NRIC / FIN number.

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

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
Any rough working should be done in this booklet.

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

This question paper consists of **13** printed pages.

1 An element R can exist in a few oxidation states. 0.01 mol of R^{2+} requires 0.004 mol of acidified $KMnO_4$ for complete reaction. The half equation for reduction of MnO_4^- is

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

What is the final oxidation state of R?

A	+4	**B**	+3	**C**	0	**D**	−1

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

Which of the following particles would, on gaining an electron, have a half-filled set of p orbitals?

1	B^-	2	C	3	N	4	N^+

A 1, 2 and 3

B 1, 2 and 4

C 3 only

D 2 and 4

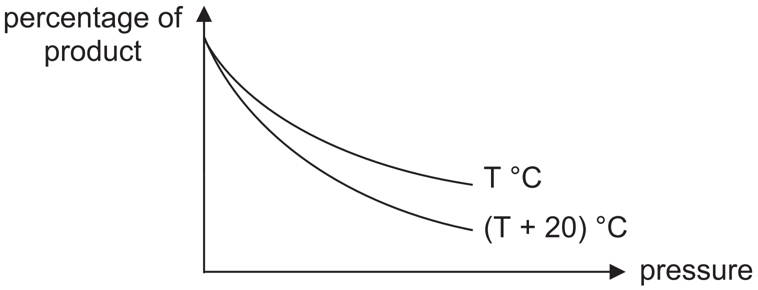
4 Which gas shows the greatest deviation from ideality?

A	CH_4	**B**	SO_3	**C**	C_2H_2	**D**	O_2

5 A gas at a pressure of 4.50 atm is heated from 25 °C to 480 °C and simultaneously compressed to one-third of its original volume. What will be the final pressure?

A	3.79 atm	**B**	34.1 atm	**C**	86.4 atm	**D**	259 atm

6 The graph below shows how the percentage of product present at equilibrium varies with temperature and pressure for a reaction.



Which reaction could the graph represent?

A $4Fe(s) + 3O_2(g) \rightleftharpoons 2Fe_2O_3(s)$ $\Delta H = -1644$ kJ mol^{-1}

B $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $\Delta H = +57$ kJ mol^{-1}

C $2C(s) + O_2(g) \rightleftharpoons 2CO(g)$ $\Delta H = -222$ kJ mol^{-1}

D $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(s)$ $\Delta H = +86$ kJ mol^{-1}

7 Values for the ionic product of water, K_w, at two different temperatures are given below.

Temperature / °C	K_w / mol^2 dm^{-6}
25	1.00×10^{-14}
50	5.48×10^{-14}

What is correct for pure water at 50 °C?

A $[H^+] > [OH^-]$

B pH = 2.34×10^{-7}

C pH > 7

D pH < 7

8 What is a satisfactory indicator for the titration of 0.10 mol dm^{-3} aqueous methylamine with 0.10 mol dm^{-3} ethanoic acid?

A methyl red (pH range 4.2 − 6.3)

B bromothymol blue (pH range 6.0 − 7.6)

C thymol blue (pH range 8.0 − 9.6)

D there is no suitable indicator

9 The uncatalysed reaction between SO_2 and O_2 is slow.

$$2SO_2 + O_2 \rightarrow 2SO_3$$

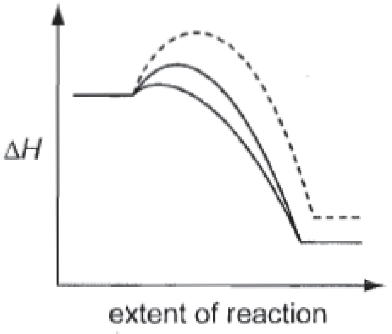
The reaction is speeded up in the presence of the homogeneous catalyst NO, which participates as follows.

$$2NO + O_2 \rightarrow 2NO_2$$

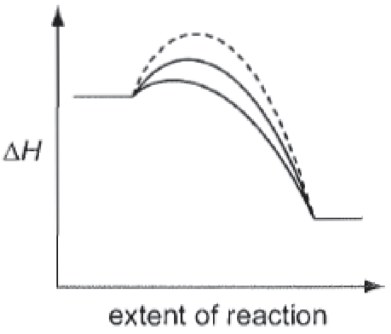
$$2NO_2 + 2SO_2 \rightarrow 2NO + 2SO_3$$

Which reaction pathway diagram is most appropriate for describing the enthalpy changes occurring during the catalysed reaction? In each case the reaction pathway for the uncatalysed reaction is shown as a dashed line.

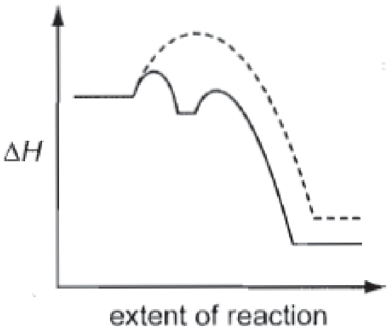
A



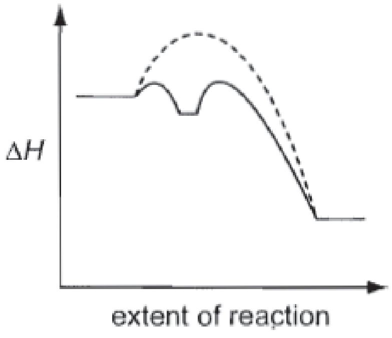
B



C



D



10 The enthalpy change of formation of rubidium bromide, RbBr, can be calculated using a Born-Haber cycle.

The relevant enthalpy changes are shown in the table.

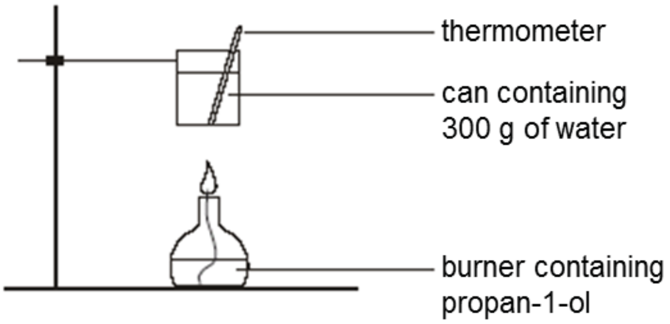
	enthalpy change / kJ mol^{-1}
$Rb(s) \rightarrow Rb(g)$	+81
$Br_2(l) \rightarrow 2Br(g)$	+224
$Rb(g) \rightarrow Rb^+(g) + e^-$	+403
$Br(g) + e^- \rightarrow Br^-(g)$	−324
$Rb^+(g) + Br^-(g) \rightarrow RbBr(s)$	−687

What is the enthalpy change of formation of RbBr?

A −303 kJ mol^{-1} **B** −415 kJ mol^{-1}

C −577 kJ mol^{-1} **D** −627 kJ mol^{-1}

11 A student used the set-up below to heat a can containing 300 g of water.



The following data were recorded:
mass of propan-1-ol burnt = m g
change in temperature of water = ΔT °C

Given that:
relative molecular mass of propan-1-ol = 60.0
enthalpy change of combustion of propan-1-ol = -2021 kJ mol^{-1}
specific heat capacity of water = c J g^{-1} K^{-1}

What is the efficiency of this heating process?

A $\dfrac{m \times 2021 \times 1000}{300 \times c \times \Delta T \times 60.0} \times 100\%$

B $\dfrac{m \times c \times \Delta T \times 60.0}{300 \times 2021 \times 1000} \times 100\%$

C $\dfrac{300 \times c \times \Delta T \times 60.0}{m \times 2021} \times 100\%$

D $\dfrac{300 \times c \times \Delta T \times 60.0}{m \times 2021 \times 1000} \times 100\%$

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

Peroxodisulfate(VI), $S_2O_8^{2-}$, is capable of oxidising iodide as shown in the following equation.

$$2I^- + S_2O_8^{2-} \rightarrow I_2 + 2SO_4^{2-}$$

Which metal ion can be a suitable catalyst for this reaction?

1 Cu^{2+} 2 Co^{2+} 3 Mn^{2+} 4 V^{2+}

A 1, 2 and 3

B 2 and 3

C 2 only

D 4 only

13 Consider the reaction $2A + 2B \rightarrow A_2B_2$.
The mechanism involves the following steps:

$2A \rightleftharpoons C$	fast
$B + C \rightarrow D$	slow
$B + D \rightarrow A_2B_2$	fast

Based on the information, what is the rate equation for this reaction?

A rate = $k\,[A]^2\,[B]^2$

B rate = $k\,[B]\,[C]$

C rate = $k\,[A]^2\,[B]$

D rate = $k\,[A]\,[B]^2$

14 Element J is in Period 3 of the Periodic Table. The following four statements were made about the properties of element J or its compounds.

Three statements are correct descriptions and one is false.

Which statement does **not** fit with the other three?

A Adding NaOH(aq) to the solution resulting from the reaction of a chloride of J with water produces a white precipitate which is soluble in an excess of NaOH(aq).

B Element J is a solid at room temperature.

C Element J has the highest melting point among the period 3 elements.

D The oxide of element J is soluble in hydrochloric acid.

15 A student was given a sample of strontium carbonate that was mixed with strontium nitrate. He carried out two separate experiments using the same mass of the solid mixture.

Strontium nitrate decomposes according to the following equation.

$$Sr(NO_3)_2(s) \rightarrow SrO(s) + 2NO_2(g) + \tfrac{1}{2}O_2(g)$$

Experiment 1: The sample was heated strongly to constant mass and the volume of gas evolved was found to be 200 cm^3.

Experiment 2: Excess dilute sulfuric acid was added to the sample and the volume of gas evolved was found to be 75 cm^3.

All volumes were measured at the same temperature and pressure.

What is the mole ratio of strontium carbonate to strontium nitrate in the sample?

A 3 : 2 **B** 3 : 5 **C** 6 : 5 **D** 8 : 5

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

By using the relevant $E^\ominus$ values, what are the vanadium containing products formed when chlorine is passed through a solution that contains $VO^{2+}(aq)$?

A V^{3+}

B VO_2^+

C VO_2^+, VO_3^- and V^{3+}

D VO_2^+ and VO_3^-

17 Element Y has the following electronic configuration.

$$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^7\,4s^2$$

Which compounds do **not** exist?

1 YO_2Cl_2

2 $[Y(C_2O_4)_2(H_2O)_2]Cl$

3 $Na_2[Y(CN)_6]$

4 YCl_2

A 1 only

B 1, 2 and 3

C 2 and 3

D 2, 3 and 4

18 Platinum(IV) chloride is combined with ammonia to form a single product. The product is a different platinum(IV) compound which contains a cation with a 2+ charge and has a co-ordination number of 6.

What is the formula of this product?

A $Pt(NH_3)_6Cl_2$

B $Pt(NH_3)_3Cl_4$

C $Pt(NH_3)_4Cl_4$

D $Pt(NH_3)_6Cl_4$

19 The C−H bond lengths of three hydrocarbons are given in the table below.

compound	structural formula	C−H bond length / nm
ethane	CH_3CH_3	0.110
ethene	$CH_2=CH_2$	0.108
ethyne	$CH\equiv CH$	0.106

Which statement best explains the shortest C−H bond length observed in ethyne?

A The carbon-carbon triple bond in ethyne has the greatest bond energy.

B The bond angle around the carbon atom in ethyne is the largest.

C The orbital that carbon used in formation of the C−H bond in ethyne has the greatest s orbital character.

D A sp-sp overlap occurs between the two carbon atoms in ethyne.

20 Which statements best describe the reaction mechanism involved in the conversion of chloroethane to ethanol?

1 The reaction mechanism involves a carbocation.

2 The reaction mechanism involves nucleophilic attack of OH^- in an overall second order reaction.

3 The reaction mechanism involves heterolytic fission of the C−C*l* bond, followed by a reaction with OH^-.

4 The activation energy of the first step of the mechanism is greater than the activation energy of the second step of the mechanism.

A 1 and 3 only

B 2 only

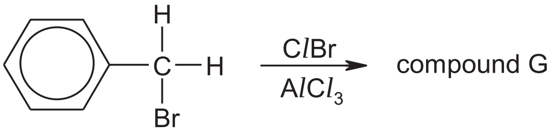
C 1, 3 and 4 only

D 2 and 4 only

21 How many constitutional isomers can C_4H_9Cl form?

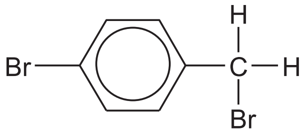
A 3 **B** 4 **C** 5 **D** 6

22 Bromine, in the presence of anhydrous aluminium chloride, undergoes a substitution reaction with benzene forming bromobenzene. When bromomethylbenzene reacts with C*l*Br, in the presence of anhydrous aluminium chloride, a similar reaction occurs and compound G is formed.

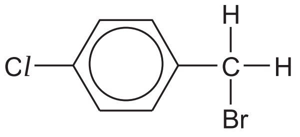


What could compound G be?

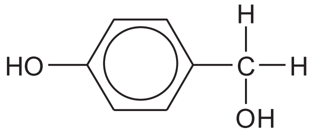
A



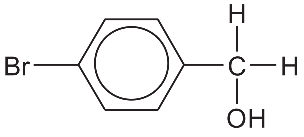
B



C



D



23 An alcohol D has the molecular formula of $C_5H_{11}OH$. On heating D with concentrated sulfuric acid, two products E and F are formed, E being the minor product. On heating E with hot acidified potassium manganate(VII), one of the products gives a pale yellow precipitate with alkaline aqueous iodine.

What could D be?

A $CH_3CH(OH)CH_2CH_2CH_3$

B $CH_3CH_2CH(OH)CH_2CH_3$

C $CH_3CH(CH_3)CH(OH)CH_3$

D $(CH_3)_2C(OH)CH_2CH_3$

24 Which of the following reagents **cannot** be used to distinguish between ethanol and propanone?

A alkaline aqueous iodine

B acidified potassium dichromate(VI)

C 2,4-dinitrophenylhydrazine

D sodium metal

25 Which reaction yields a carbon compound containing deuterium, D? [D = ^2H]

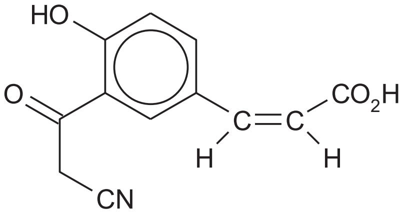
A $CH_3CH_2CN \xrightarrow{\substack{\text{NaOD} \\ D_2O}}$

B $CH_3CH(OH)CH_3 \xrightarrow{\substack{\text{KMnO}_4 \\ D_2SO_4\text{(aq)}}}$

C $CH_3CO_2H \xrightarrow{\substack{C_2H_5OD \\ \text{conc } D_2SO_4}}$

D $C_6H_5ONa \xrightarrow{D_2O}$

26 Which statements about compound P are correct?



compound P

1 4 moles of hydrogen gas will react completely with 1 mole of compound P in the presence of platinum metal.

2 It will exist as a pair of stereoisomers.

3 It reacts with ethanoic acid in the presence of concentrated sulfuric acid to form a sweet-smelling product.

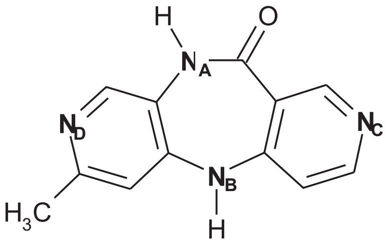
A 1, 2 and 3

B 2 only

C 1 and 2 only

D 2 and 3 only

27 An analogue of Nevirapine which is a synthetic antiviral drug is shown below.



The four nitrogen atoms are labelled as N_A, N_B, N_C and N_D.

N_c and N_D are part of the pyridine rings where the lone pair of electrons on the nitrogen atoms are not delocalised into the pyridine rings.

Which sequence shows the four nitrogen atoms in decreasing order of basicity?

A $N_B > N_D > N_C > N_A$

B $N_D > N_C > N_A > N_B$

C $N_C > N_D > N_B > N_A$

D $N_D > N_C > N_B > N_A$

28 Which statement about 2-aminopropanoic acid extracted from silkworms is correct?

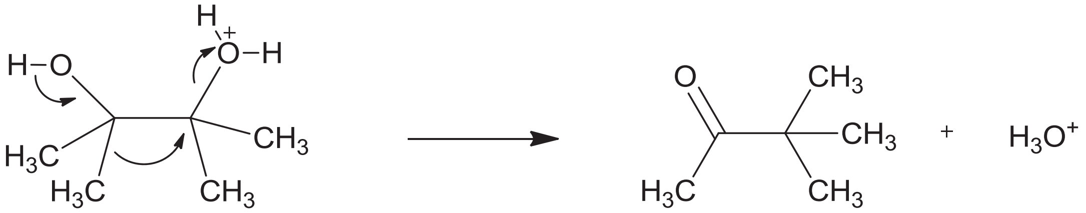
A It is able to rotate plane polarised light.

B It reacts with ethanoic acid to form an amide.

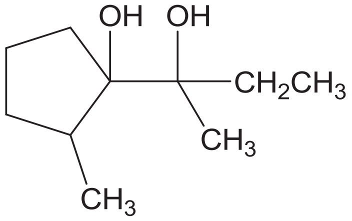
C pH of its aqueous solution drops drastically when a small amount of hydrochloric acid is added.

D It decolourises orange aqueous bromine.

29 When a 1, 2–diol is treated with a dilute acid, the protonated diol undergoes pinacol rearrangement as shown.

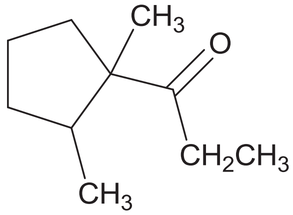


Which of the following products is **not** formed via pinacol rearrangement by adding dilute acid to diol Z?

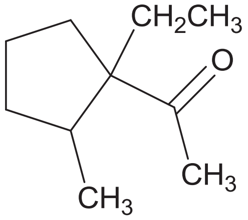


diol Z

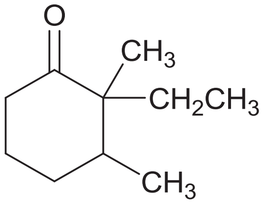
A



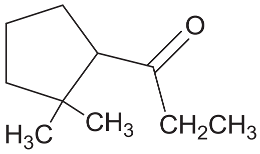
B



C



D



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

An experiment was conducted to compare the rate of hydrolysis of four halogen-containing compounds. 1 mole of the 4 compounds K, L, M and N are each heated separately with excess NaOH(aq) for 30 seconds and then acidified with HNO_3(aq). Excess $AgNO_3$(aq) is added and the precipitate formed is filtered, dried and weighed.

CH_3CH_2COCl	C_6H_5Cl	$(CH_3)_3CCl$	$(CH_3)_3CBr$
K	L	M	N

71.1 g of the precipitate is obtained from compound M. What are the possible masses of the precipitates obtained from the other three halogen-containing compounds?

	mass of precipitate from K / g	mass of precipitate from L / g	mass of precipitate from N / g
A	128.1	0	112.9
B	120.2	0	60.7
C	126.2	40.2	112.9
D	65.2	0	57.3

~ END OF PAPER ~

Parent's Signature:

CANDIDATE'S NAME: ______________________________ **CTG:** _________

YISHUN JUNIOR COLLEGE

2017 JC2 PRELIMINARY EXAMINATION

CHEMISTRY 9729/02
HIGHER 2

Paper 2 Structured Questions **THURSDAY 24 AUGUST 2017**
1400 hrs − 1600hrs
(2 hours)

Candidates answer on the Question Paper
Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and CTG on all the work that 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 paper clips, highlighters, glue or correction fluid.

Answer **all** questions.
A Data Booklet is provided.

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

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

For Examiner's Use	
Paper 1	
Total	**/ 30**
Paper 2	
1	/ 15
2	/ 12
3	/ 10
4	/ 19
5	/ 19
Total	**/ 75**
Paper 3	
Total	**/ 80**
Paper 4	
Total	**/ 55**

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

Answer **all** the questions.

1 Antacids neutralise stomach acid and relieve the symptoms of indigestion, heartburn or stomach ulcer. One of the active ingredient in antacid is calcium carbonate, $CaCO_3$. There are also other ingredients such as binders present in each tablet. On average, a 1.3 g tablet contains 0.5 g of $CaCO_3$.

Calcium carbonate undergoes neutralisation reaction with hydrochloric acid as shown in the following equation.

$$CaCO_3(aq) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

A student was given an antacid tablet. She was asked to determine the volume of stomach acid that can be neutralised by 1 tablet. She crushed the antacid tablet and dissolved it with 50.0 cm^3 of 0.100 mol dm^{-3} of HCl in a 50.0 cm^3 graduated flask. She pipetted 25.0 cm^3 of this sample and boiled gently for 5 minutes. She then titrated the boiled sample with 20.0 cm^3 of 0.0500 mol dm^{-3} sodium hydroxide for complete neutralisation.

(a) Suggest a reason why the 25.0 cm^3 sample was boiled before titrating with NaOH.

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

(b) **(i)** Calculate the amount of HCl present initially in the graduated flask.

[1]

(ii) Calculate the amount of HCl reacted with NaOH.

[1]

(iii) Using your answer in **(b)(i)** and **(b)(ii),** calculate the amount of HC*l* neutralised by one antacid tablet.

[2]

(iv) A patient with a hyperacidic stomach has a HC*l* concentration of 0.0300 mol dm^{-3}. The volume of liquid in the stomach is 375 cm^3.

Using your answer in **(b)(iii)**, calculate the minimum number of antacid tablets that the patient with hyperacidic stomach would have to take to bring the concentration of HC*l* in the stomach to the normal level of 0.000300 mol dm^{-3}.

[2]

(c) The following diagram shows the nutrition fact label of the antacid used for the student's analysis.

Drug Facts

Active ingredient (in each tablet) **Purpose**

Calcium carbonate 500 mg............................Antacid

Uses relieves ■ heartburn ■ sour stomach ■ acid indigestion

Warnings

Ask a doctor or pharmacist before use if you are now taking a prescription drug. Antacids may interact with certain prescription drugs.

When using this product do not exceed 15 tablets daily or use the maximum dosage for more than 2 weeks

Keep out of reach of children.

Directions chew 2 to 4 tablets as symptoms occur

Other information

- **each tablet contains:** calcium 215 mg and magnesium 5 mg
- store at 20°-25°C (68°-77°F)

Inactive ingredients adipic acid, dextrose, FD&C blue #1 aluminum lake, FD&C red #40 aluminum lake, FD&C yellow #5 aluminum lake (tartrazine), FD&C yellow #6 aluminum lake, flavors, maltodextrin, mineral oil, polyethylene glycol, powdered cellulose, talc

Verify by calculation if there are 500 mg of $CaCO_3$ in each antacid tablet.

[2]

(d) Magnesium oxide, MgO and aluminium oxide, Al_2O_3 can also act as antacids. The oxides MgO and Al_2O_3 have the melting points 2852°C and 2072°C respectively.

(i) Both MgO and Al_2O_3 have giant ionic structure. Explain the difference between the melting points of MgO and Al_2O_3.

....

....

....

....[2]

(ii) Describe the reactions of MgO and Al_2O_3 with water. Give the approximate pH of any solution formed.

……………………………………………………………………………………………

……………………………………………………………………………………………

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

(iii) When NaOH(aq) is added to separate solutions containing Mg^{2+}(aq) and Al^{3+}(aq), a white precipitate is formed in each case. When an excess of NaOH(aq) is added, **one** of these precipitates dissolves.

Construct ionic equations, with state symbols, for the formation of the white precipitate, and its subsequent dissolving.

……………………………………………………………………………………………

……………………………………………………………………………………………

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

[Total: 15]

2 The halogens, found in group 17 of the Periodic Table, and their compounds are useful laboratory reagents.

The table below shows some properties of the halogens and their compounds.

halogen	chlorine	bromine	iodine
standard enthalpy change of vapourisation ($\Delta H_v^\ominus$) of X_2 / kJ mol^{-1}	0	+15	+30
electronegativity	3.2	3.0	2.7
standard enthalpy change of reaction ($\Delta H_r^\ominus$) for thermal decomposition of HX / kJ mol^{-1}	+183	+103	+11
solubility of $PbX_2(s)$ / g dm^{-3}	4.7	4.3	0.6

(a) Describe and explain the trend in the volatility of the halogens.

....

....

....

....

....

....[2]

(b) By quoting relevant data from the *Data Booklet*, explain the relative thermal stabilities of the hydrides of the Group 17 elements.

....

....

....

....

....

....[2]

(c) **(i)** Write an expression for K_{sp} of $PbCl_2$, stating the units.

K_{sp} = ... units .... [1]

(ii) Using relevant data from the table and your expression for K_{sp} in **(c)(i)**, calculate the solubility product of $PbCl_2$.

Give your answer to **two** significant figures.

[2]

(d) Astatine, At, is found below iodine in group 17 of the Periodic Table. Using your knowledge of the chemistry of group 17, predict the changes (if any) that you may observe when the following reagents are mixed.

If nothing is formed, write “no reaction” and where there is a reaction predicted, write an ionic equation with state symbols.

(i) aqueous bromine and aqueous sodium astatide

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

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

(ii) astatine and aqueous sodium chloride

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

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

(e) In 1886, Henri Moissan succeeded in obtaining fluorine by the electrolysis of molten potassium hydrogen difluoride, KHF_2, which is an ionic compound containing **one** cation and **one** anion.

(i) Write the formulae of the ions present in KHF_2.

cation: ……………………………………….

anion: ………………………………………

[1]

(ii) Draw the structure for the anion and indicate the types of bonding that occur within it in your diagram.

[2]

[Total: 12]

3 **(a)** **(i)** Describe and explain how the thermal stability of magnesium carbonate might compare to calcium carbonate.

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

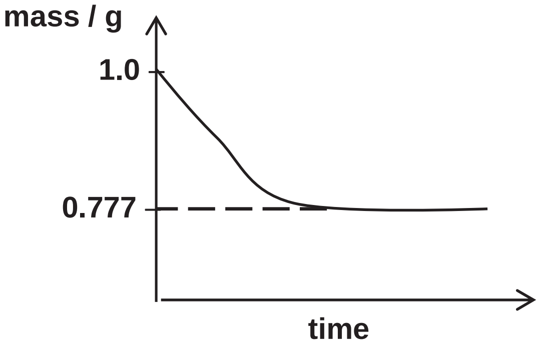
…………………………………………………………………………………………

…………………………………………………………………………………………[3]

(ii) Write an equation for the decomposition of $MgCO_3$.

…………………………………………………………………………………………[1]

(b) The graph represents the change in mass that occurs when 1.0 g of powdered carbonate of another group 2 element, **Z,** is decomposed at a temperature T.



Using the above graph, calculate and determine the identity of **Z**.

Identity of **Z** : ……………………….. [3]

(c) Beryllium, the first member of the group 2 elements was discovered in 1798 by a chemist named Vaquelin when he was working with emeralds. Cutting edge computers require an alloy of beryllium and copper to meet the demands placed on microprocessor connectors.

(i) Beryllium chloride reacts with ammonia in a 1:2 ratio to form a product. Draw dot–and–cross diagrams showing the bonding in beryllium chloride and ammonia.

beryllium chloride

ammonia

[1]

(ii) Draw a diagram to illustrate the shape of the product around the Be atom formed from the reaction between beryllium chloride and ammonia.

[2]

[Total: 10]

4 Energy density is the amount of energy that can be stored in a given mass of a substance or system. The higher the energy density of a substance or system, the greater the amount of energy stored in its mass. In fuel, energy density can be measured as the amount of energy released in megajoules per gram of fuel (MJ/g).
(1 MJ = 10^3 kJ)

The table below provides information on the standard enthalpy change of combustion of some commonly used fuel today.

fuel	formula	standard enthalpy change of combustion (ΔH_c°) / kJ mol^{-1}
hydrogen	H_2	– 286
coal	C	– 393
ethanol	CH_3CH_2OH	– 1367
ethene	$CH_2{=}CH_2$	– 1410

(a) An average household was found to consume an average energy of 108 MJ per day.

(i) Using relevant data from the table above, determine the mass of the coal required to supply energy for an average household a day.

Hence, determine the energy density of coal.

[2]

(ii) The energy density of ethanol was found to be 0.0297 MJ/g. With reference to your answer in **(a)(i)**, state and explain which fuel is more efficient in supplying energy to the average household.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

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

(iii) Ethanol, ethene and liquid hydrogen are possible alternative sources of fuel that may be used in replacement of coal as the burning of coal releases toxic carbon monoxide gas into the atmosphere.

Explain why carbon monoxide gas, CO, is toxic.

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

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

(b) **(i)** Using relevant data from the table, determine the standard enthalpy change of formation of liquid ethanol.

[1]

(ii) Using relevant data from the *Data Booklet*, determine the standard enthalpy change of combustion of liquid ethanol.

[2]

(iii) Suggest a reason for the discrepancy between the value in **(b)(ii)** and the one given in the table.

…………………………………………………………………………………………………

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

(c) The direct oxidation of alcohols such as ethanol in a fuel cell represents potentially the most efficient method of obtaining useful energy from a renewable fuel.

(i) Given that carbon dioxide is formed at the anode while water is produced at the cathode, construct the relevant half-equations for the reactions occurring at the electrodes and hence the equation for the overall reaction, assuming acidic conditions.

cathode: ……………………………………………………………………………

anode: ……………………………………………………………………………

overall: …………………………………………………………………………...

[2]

(ii) The value for the $E^{\ominus}$ for the reaction occurring at the anode was determined to be +0.08 V. Using suitable data from the *Data Booklet*, determine the e.m.f produced by the ethanol fuel cell.

[2]

(iii) Hence, determine the value of $\Delta G^{\ominus}$ of the ethanol fuel cell.

[1]

(d) Ethanol can be readily synthesised from ethene industrially.

(i) State the reagents and conditions for the industrial synthesis of ethanol from ethene.

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

(ii) Identify the type of hybridisation that exists in the carbon atoms of ethene and hence explain the bonding that occurs in a molecule of ethene in terms of orbitals overlap.

Type of hybridization in C: ………………….

Explanation of bonding:

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

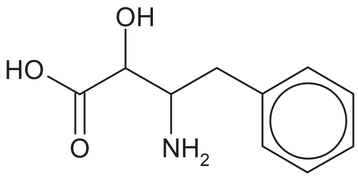
…………………………………………………………………………………………

…………………………………………………………………………………………

………………………………………………………………………………….……[3]

[Total: 19]

5 **(a)** Compound **Y** is an intermediate in the production of a drug which is being developed to reduce the effects of the HIV virus.



compound **Y**

(i) Name three functional groups in compound **Y**, other than the phenyl group.

……………………………………………………………………………………………………

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

(ii) On the structure above, indicate with an asterisk (*) any chiral carbon present, and state the total possible number of stereoisomers that compound **Y** can have.

total possible number of stereoisomers = ……………… [2]

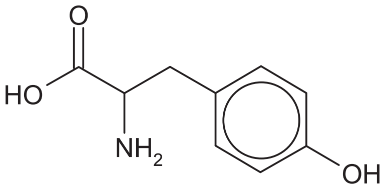
(iii) Draw the structural formula of the organic products that will be formed when compound **Y** is treated with

- hot acidified $K_2Cr_2O_7(aq)$

- anhydrous $PBr_3(l)$

[3]

(b) Compound **Y** is similar in structure to tyrosine, one of the twenty α-amino acids found in proteins.



tyrosine

At pH = 5.7, compound **Y** exists as a *zwitterion*.

(i) Define the term *zwitterion*.

……………………………………………………………………………………………

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

(ii) Draw the structural formula of the zwitterionic form of tyrosine.

[1]

Another potential anti-HIV drug can be synthesised by combining tyrosine with another α-amino acid, glycine, $H_2NCH_2CO_2H$.

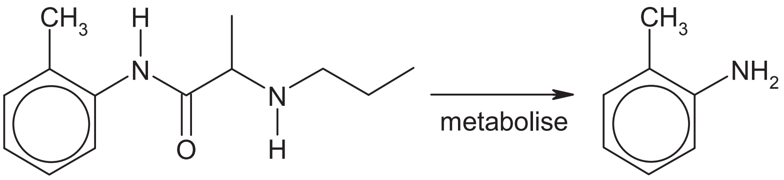
(iii) State the type of linkage that will be formed between tyrosine and glycine.

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

(iv) Draw the structures of two different dipeptides that could be formed when one molecule of tyrosine reacts with one molecule of glycine.

[2]

(c) Prilocain, a widely used local anaesthetic, is metabolised in the liver by enzymes to form 2-methylphenylamine.



prilocain 2-methylphenylamine

(i) State the reagents and conditions required to produce 2-methylphenylamine from prilocain in the laboratory.

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

In the aqueous medium, 2-methylphenylamine is a weak Bronsted base.

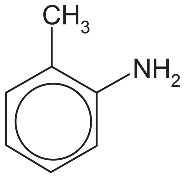
(ii) Write an expression for the base dissociation constant, K_b, for 2-methylphenylamine.

[1]

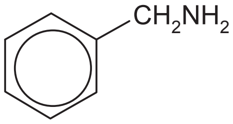
(iii) The pK_b value for 2-methylphenylamine is 9.6. Use this value to calculate the pH of a 0.10 mol dm^{-3} solution of 2-methylphenylamine.

[2]

(d) 2-methylphenylamine and benzylamine are isomers.



2-methylphenylamine



benzylamine

Suggest how the pK_b value of benzylamine might compare to that of 2-methylphenylamine.

Explain your answer in terms of their structures.

……

……

……

……

……

……

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

[Total: 19]

~ END OF PAPER ~

CANDIDATE'S NAME: ________________________________ **CTG:** ____________

YISHUN JUNIOR COLLEGE

2017 JC2 PRELIMINARY EXAMINATION

CHEMISTRY **9729/03**
HIGHER 2

Paper 3 Free Response Questions **MONDAY 11 SEPTEMBER 2017**
1400hrs − 1600hrs
(2 hours)

Candidates answer in separate paper.

Additional Materials: Writing Papers
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and CTG on all the work that 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 paper clips, highlighters, glue or correction fluid.

Section A
Answer **all** questions.

Section B
Answer **one** question.

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

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 for Section A **separately** from Section B with the respective cover sheet on top.

This question paper consists of **12** printed pages.

Section A

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

1 **(a)** Copper often occurs in the Earth's crust as copper(I) sulfide, Cu_2S, associated with the sulfides of zinc, ZnS, and silver, Ag_2S. The first stage of the extraction of copper from its ore involves the partial air-oxidation to copper(I) oxide, Cu_2O, and sulfur dioxide, SO_2, followed by the reaction between this copper(I) oxide and unreacted copper(I) sulfide to give copper and more sulfur dioxide.

(i) Write balanced chemical equations for these two reactions. [2]

(ii) Suggest how the melting point of copper(I) sulfide might compare to that of copper(I) oxide. Explain your answer. [2]

(iii) This first stage produces copper containing some zinc and silver as impurities. The solid impure copper is purified by electrolysis.

Describe, with reference to the $E^\ominus$ values, the electrode reactions that take place during this electrolysis, and explain in detail how each of the two impurity metals is removed from the copper. [3]

(iv) Using inert electrodes, a current was passed through two beakers containing aqueous silver nitrate and aqueous copper(II) sulfate, connected in series. After 30 minutes, 0.100 g of silver was deposited from the first solution.

Calculate the current passed and the mass of copper deposited from the aqueous copper(II) sulfate. [2]

(b) When KI(aq) is added to a solution containing Cu^{2+}(aq), a white precipitate of the highly insoluble copper(I) iodide and a brown solution is formed.

(i) By selecting appropriate $E^\ominus$ values from the *Data Booklet*, explain why it would be expected that this redox reaction would **not** occur. [1]

(ii) Suggest a possible reason for why it does in fact occur. [1]

(c) Copper(I) iodide is used in the synthesis of Gilman reagents, $R_2Cu^-Li^+$, which are very useful in organic synthesis because larger molecules can be prepared from smaller ones.

$$2RLi + CuI \rightarrow \underset{\text{Gilman reagent}}{R_2Cu^-Li^+} + LiI$$

For example, lithium dimethylcopper reacts with 1-chlorodecane to give undecane.

$$(CH_3)_2Cu^-Li^+ + CH_3(CH_2)_8CH_2Cl \rightarrow CH_3(CH_2)_8CH_2CH_3 + LiCl + CH_3Cu$$

The above reaction is called organometallic coupling reaction.

Similarly, organometallic coupling reaction can be used to synthesise ketones by reacting suitable Gilman reagents and acid chlorides.

Suggest a suitable Gilman reagent and an acid chloride that can be used to synthesise 5,6-dimethyldecan-3-one. [2]

(d) Carbonyl compounds can be converted into alkanes by reacting the carbonyl compounds with hydrazine, H_2NNH_2, in the presence of KOH. This reaction is named as the Wolff-Kishner reaction, which is named by the two chemists, Ludwig Wolff and N.M. Kishner, who discovered it in 1911.

$$RCOR' + H_2NNH_2 \xrightarrow{OH^-} RCH_2R' + N_2 + H_2O$$

For example, ethane can be synthesised from ethanal and hydrazine, according to the following equation.

$$\underset{\text{ethanal}}{CH_3CHO(g)} + H_2NNH_2(l) \longrightarrow \underset{\text{ethane}}{CH_3CH_3(g)} + N_2(g) + H_2O(l)$$

For this reaction, $\Delta S^\ominus = +191.5\ \text{J K}^{-1}\ \text{mol}^{-1}$ at 298 K.

(i) Explain what is meant by the term *entropy* of a chemical system. [1]

(ii) Suggest what is the significance of the sign of the entropy change with respect to the reaction between ethanal and hydrazine. [1]

The following table lists some $\Delta H_f^\ominus$ values.

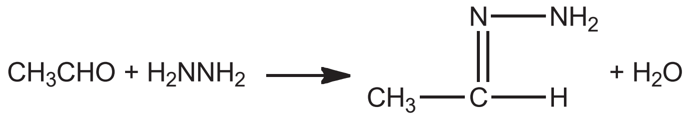
compound	$\Delta H_f^\ominus$ / kJ mol^{-1}
$CH_3CHO(g)$	−196.4
$H_2NNH_2(l)$	+50.6
$CH_3CH_3(g)$	−84.7
$H_2O(l)$	−285.8

(iii) Use the data above to calculate $\Delta H^\ominus$ for the reaction between ethanal and hydrazine.

Hence calculate the $\Delta G^\ominus$ for the reaction between ethanal and hydrazine.

Leave all your answers to one decimal place. [2]

(iv) The first step of the Wolff-Kishner reaction involves the formation of a hydrazone intermediate.

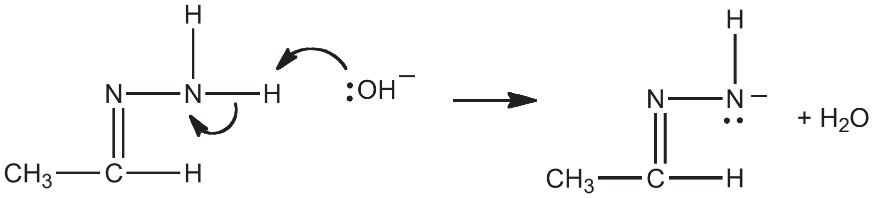


$$CH_3CHO + H_2NNH_2 \longrightarrow CH_3-C(=N-NH_2)-H + H_2O$$

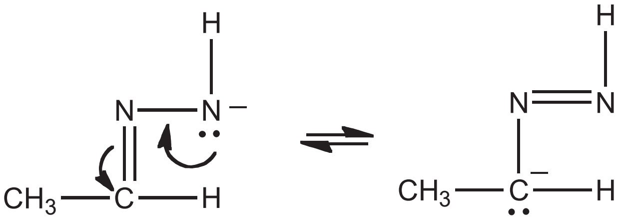
State the type of reaction that has occurred. [1]

(v) After the formation of the hydrazone, the reaction occurs via a five-step mechanism to obtain ethane as the product.

step 1: abstraction of one of the weakly acidic protons from the −NH_2 group by OH^-, to form a hydrazone anion.



step 2: the hydrazone anion has a resonance form that places the negative charge on the carbon atom and has a double bond between the two nitrogen atoms.



step 3: protonation of the carbon atom of the resonance form of the hydrazone anion by H_2O to yield a neutral intermediate.

step 4: abstraction of a proton from the neutral intermediate by OH^- to form N_2, an ethyl anion, $CH_3CH_2^-$, and H_2O.

step 5: protonation of the carbon atom of the ethyl anion by H_2O to yield ethane and OH^-.

Using the information given above, suggest the mechanism for steps 3, 4 and 5.

Show any relevant lone pairs and charges, and indicate the movement of electron pairs with curly arrows. [3]

[Total: 21]

2 Manganate(VII) and dichromate(VI) ions are oxidising agents that are commonly used in organic synthesis.

(a) In aqueous solution, dichromate(VI) ions exist in equilibrium with chromate(VI) ions.

$$\underset{\text{orange}}{Cr_2O_7^{2-}(aq)} + H_2O(l) \rightleftharpoons \underset{\text{yellow}}{2CrO_4^{2-}(aq)} + 2H^+(aq)$$

(i) State Le Chatelier's Principle. [1]

(ii) Explain why a solution of potassium chromate turns from yellow to orange on the addition of dilute hydrochloric acid. [1]

Following the addition of dilute hydrochloric acid, the solution was warmed. This caused the colour to change from orange back to yellow.

(iii) State whether the forward reaction is exothermic or endothermic.

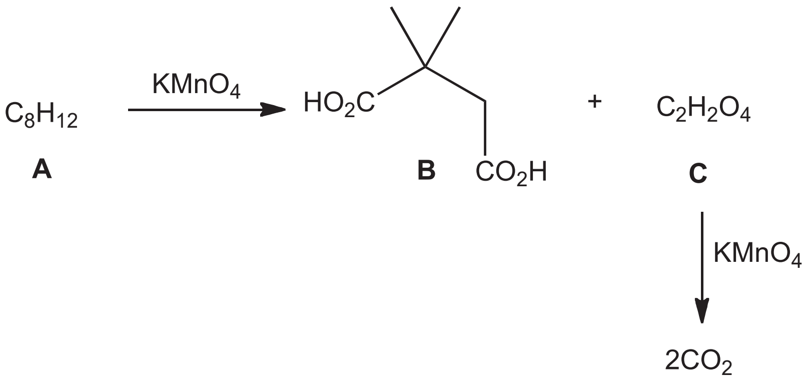
Explain your answer. [2]

At 25 °C, the equilibrium constant, K_c, for the above equilibrium has a value of 1.31×10^{-13}.

(iv) Calculate a value for the ratio $\frac{[CrO_4^{2-}]^2}{[Cr_2O_7^{2-}]}$ at pH 8. [1]

(v) Use your answer for **(a)(iv)** to deduce the colour of the solution at pH 8. [1]

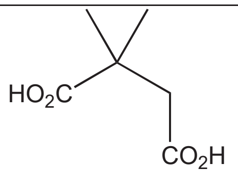
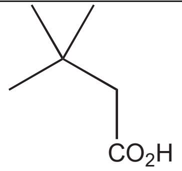
(b) Hot, acidified concentrated potassium manganate(VII) can oxidise various functional groups to ketones, carboxylic acids and carbon dioxide, allowing the structures to be determined. The following scheme shows the reaction of compound **A**.



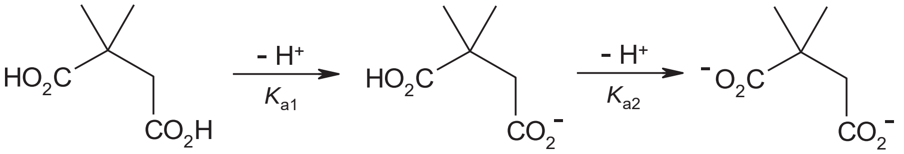
(i) Suggest the structures of compounds **A** and **C**. [2]

(ii) Explain why compound **A** does not exhibit *cis–trans* isomerism. [1]

(iii) Compound **B** and 3,3-dimethylbutanoic acid and are both weak acids.

acid	formula
compound **B**	
3,3-dimethylbutanoic acid	

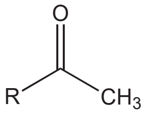
Compound **B** is a dicarboxylic acid which ionises in two stages.



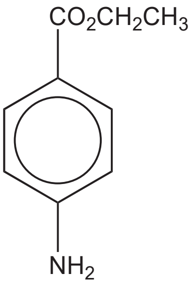
Suggest a reason why the K_{a1} value of compound **B** is much higher than the K_a value of 3,3-dimethylbutanoic acid. [1]

(c) Hydroxynitriles can be synthesised from ketones, and they are useful intermediates in the synthesis of amino acids.

Name and outline the mechanism for the synthesis of hydroxynitrile from a ketone. In your answer, show any relevant lone pairs, dipoles and charges, and use curly arrows to indicate the movement of electron pairs.

You may use  to represent a ketone. [3]

(d) Benzocaine is well known for its local anaesthetic properties and is commonly used in antiseptic creams and sunburn remedies.



benzocaine

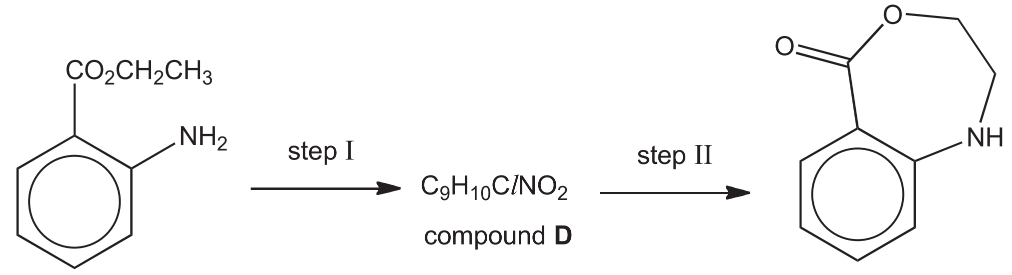
The preparation of benzocaine from methylbenzene involves the use of potassium manganate(VII) in one of the steps.

(i) *Use of the Data Booklet is relevant to this question.*

Suggest how methylbenzene can be converted to benzocaine. Give reagents, conditions and the structural formulae of the compounds obtained for each stage of the conversion. [4]

(ii) Describe a simple chemical test that could be used to distinguish methylbenzene from benzocaine, other than the use of $KMnO_4$. State your observations clearly. [2]

(e) Methyl anthranilate is an isomer of benzocaine and it is used as a bird repellent to protect crops. It can be used in the following organic synthesis.



methyl anthranilate

(i) Suggest the reagents and conditions needed for step I. [1]

(ii) Suggest the structure of compound **D**. [1]

[Total: 21]

3 This question is about reactions involving some *d*-block elements and their ions.

(a) Ammonia is a reagent commonly used to react with copper and silver ions. The metal ions can be precipitated from their solutions in some instances.

With the aid of relevant equations, explain the following observations as fully as you can.

(i) When aqueous ammonia is added to a solution containing copper(II) ions, a pale blue precipitate is obtained. This precipitate dissolves to form a deep blue solution when excess ammonia is added. [3]

(ii) When aqueous ammonia is added to Ag*Cl*, the precipitate dissolves. However, if aqueous ammonia is added to AgBr, the precipitate remains insoluble. [3]

(b) Iron forms compounds mainly in the +2 and +3 oxidation states. Iron complexes are usually coloured.

(i) Explain why iron exhibits variable oxidation states. [2]

(ii) State the full electronic configuration of an iron(III) ion and draw fully-labelled diagrams of **all** the orbitals in the 3*d*-subshell of an iron(III) ion. [3]

(iii) Using your diagrams in **(b)(ii)**, briefly explain why splitting of the *d*-subshell occurs in an octahedral complex.

Hence, explain why iron(III) complexes are usually coloured. [3]

(iv) In 2012, a group of scientists synthesised two iron(III) complexes with different colours. The iron(III) complex bonded to N,N-diethylethylenediamine ligands is red in colour and the one bonded to N-ethylethylenediamine ligands is blue in colour. The energy gap between the *d*-orbitals is inversely proportional to the wavelength of the light absorbed.

Given that red light has a longer wavelength than blue light, deduce whether the red complex or the blue complex has a larger energy gap between the *d*-orbitals. [2]

(v) The arrangement of electrons in the *d*-orbitals depends on the spin states of complexes.

In a ‘high spin’ state, the electrons occupy all the *d*-orbitals singly, before starting to pair up in the lower energy *d*-orbitals.

In a ‘low spin’ state, the lower energy *d*-orbitals are filled first, by pairing up if necessary, before the higher energy *d*-orbitals are used.

It was found that the two iron(III) complexes in **(b)(iv)** have different ‘spin’ state for the Fe^{3+} ion.

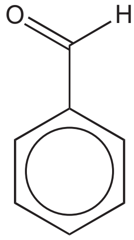
Use appropriate diagrams and your answer to **(b)(iv)** to show the electronic configuration of a Fe^{3+} ion in the red complex and the blue complex respectively. Your diagrams should indicate clearly the relative size of the energy gap for each complex. [2]

[Total: 18]

Section B

Answer **one** question from this section.

4 Benzaldehye contains an aromatic benzene ring and has the following structure.



(a) Benzaldehyde undergoes disproportionation reaction in the presence of a strong base such as potassium hydroxide to produce potassium benzoate and phenylmethanol. Potassium benzoate can be acidified to obtain benzoic acid as one of the final products.

The disproportionation reaction is as follows:

$$2C_6H_5CHO + KOH \rightarrow C_6H_5CH_2OH + C_6H_5CO_2K$$

The rate of disappearance of potassium hydroxide was measured for several different concentrations of benzaldehyde and potassium hydroxide at a certain temperature.

experiment number	$[C_6H_5CHO]$ / mol dm^{-3}	[KOH] / mol dm^{-3}	rate of disappearance of KOH / mol dm^{-3} s^{-1}
1	0.300	0.050	5.7×10^{-5}
2	0.300	0.100	1.1×10^{-4}
3	0.600	0.200	9.2×10^{-4}

(i) With reference to the above reaction, explain why it is a disproportionation reaction. [1]

(ii) From the experimental data given in the table, determine the order of reaction with respect to C_6H_5CHO and KOH. Explain your reasoning. [2]

(iii) Hence write the rate equation for the disproportionation of benzaldehyde, and calculate the rate constant, giving its units. [2]

(iv) Calculate the half-life of the reaction when the concentration of C_6H_5CHO is increased to 1.60 mol dm^{-3}. [2]

(v) With the aid of a sketch of the Boltzmann distribution, explain the effect of increasing temperature on the rate of reaction. [3]

(b) The disproportionation reaction in **(a)** produces a low yield of phenylmethanol and benzoic acid.

Two other separate reactions could be carried out to convert benzaldehyde to phenylmethanol and to benzoic acid.

State the reagents and conditions needed to convert benzaldehyde to

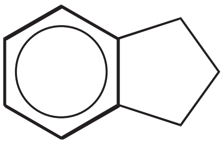
(i) phenylmenthanol, and [1]

(ii) benzoic acid. [1]

(c) Suggest a chemical test that could be used to distinguish between benzaldehyde and phenylmethanol. You should state what you would observe for **each** compound. [2]

(d) Aromatic hydrocarbon **R** and **S** are structural isomers, with molecular formula C_9H_{10}.

The structure of **S** is shown below.



S

R is found to exhibit stereoisomerism. When aqueous bromine was added to both **R** and **S** separately, only **R** decolourised orange aqueous bromine. When hot acidified potassium manganate(VII) solution was added to **R** and **S** separately, both decolourised purple potassium manganate(VII) to form compounds **T** and **U** respectively.

1.0 mol of compound **T** reacts with exactly 0.5 mol of sodium carbonate while 1.0 mol of compound **U** reacts with exactly 1.0 mol of sodium carbonate.

Deduce the structures of compounds **R**, **T** and **U**. Explain the chemistry of the reactions described. [6]

[Total: 20]

5 This question is about reactions involving acids and bases.

(a) **(i)** Draw a dot-and-cross diagram to show the bonding in a carbonate anion, CO_3^{2-}.

You should distinguish carefully between electrons originating from the central atom and those from the outermost atoms.

Include all lone pairs in your diagram. [1]

(ii) Use the VSEPR (valence shell electron pair repulsion) theory to predict the shape of the carbonate ion, giving a reason for your answer. [2]

(b) The carbonate ion is a diacidic base. When sodium carbonate reacts with hydrochloric acid, the neutralisation reaction occurs in two stages.

Stage 1: $Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$

Stage 2: $NaHCO_3 + HCl \rightarrow CO_2 + NaCl + H_2O$

(i) Explain why **Stage 1** is considered to be a Bronsted-Lowry acid-base reaction. [1]

(ii) Explain, with the help of an equation, why the pH at the end of **stage 1** is slightly higher than 7. [2]

(c) The major buffer system that is used to control the pH of blood is the carbonic acid, H_2CO_3, and hydrogen carbonate, HCO_3^-, buffer system.

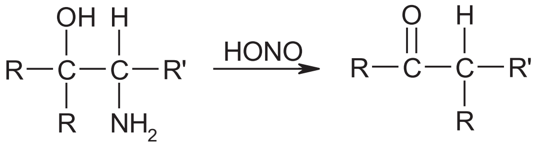
Explain, with the aid of relevant equations, how the pH of blood is maintained when a small amount of acid or alkali is added. [2]

(d) **(i)** State **two** assumptions of the kinetic theory of gases. [2]

(ii) When excess hydrochloric acid is added to a 20.0 cm^3 sample of aqueous sodium carbonate, 56.0 cm^3 of carbon dioxide gas was collected at 1.1 atm and 30 °C.

Determine the concentration of the sample of aqueous sodium carbonate. [2]

(e) A carbonyl compound, **H**, $C_6H_{10}O$, can be synthesised from 1-aminoalcohol, **G**, $C_6H_{13}ON$, in the presence of nitrous acid, HONO, via Tiffeneau-Demjanov Rearrangement. The simplified illustration of the rearrangement is illustrated below.

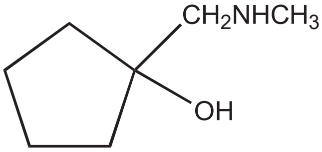


$$R{-}C(OH)(R){-}CH(NH_2){-}R' \xrightarrow{HONO} R{-}C(=O){-}CH(R){-}R'$$

H produces a yellow precipitate with iodine in alkaline solution. Treatment of **H** with hot acidified solution of potassium manganate(VII) produces **J,** $C_5H_8O_3$, along with a gas that forms white precipitate in limewater. **H** was also observed to decolourise bromine in tetrachloromethane readily.

Explain the chemistry of the reactions described and deduce the structures of **G**, **H** and **J**. [5]

(f) Starting from a suitable carbonyl compound of your choice, devise a 3-step synthesis of the compound below.



Suggest reagents and conditions for each step, and draw the structural formula of every intermediate compound. [3]

[Total: 20]

~ END OF PAPER ~

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

1 Determination of the concentration of sodium thiosulfate in solution Z

Sodium thiosulfate is commonly used in an alternative method for the extraction of gold from its ores, through the formation of a stable and soluble complex of gold(I) ions, $[Au(S_2O_3)_2]^{3-}$. One of your tasks is to determine the concentration of sodium thiosulfate in a commercially produced solution **Z** used in the extraction process.

Solution **Z** contains sodium thiosulfate in deionised water. You are not provided with solution **Z**, as it is too concentrated for use in this experiment. A diluted solution of **Z** has been prepared for you. This diluted solution is **FA 5**.

FA 1 is 0.0230 mol dm^{-3} of aqueous potassium iodate(V), KIO_3
FA 2 is 0.50 mol dm^{-3} potassium iodide, KI
FA 3 is 0.75 mol dm^{-3} sulfuric acid, H_2SO_4
FA 4 is a solution of sodium thiosulfate, $Na_2S_2O_3$ of an unknown concentration
FA 5 a diluted solution of **Z**, in which 31.00 cm^3 of solution **Z** was made up to 250 cm^3 with deionised water in a volumetric flask

You are also provided with starch solution.

In acidic medium, iodate(V) ions oxidise iodide ions to iodine

$$IO_3^-(aq) + 5I^-(aq) + 6H^+(aq) \rightarrow 3I_2(aq) + 3H_2O(l) \qquad \textbf{reaction 1}$$

If an excess of sodium thiosulfate is present in the reaction mixture, the iodine produced in **reaction 1** is immediately reduced back to iodide ions, as shown in **reaction 2**, and the dark brown colour of iodine does not form.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq) \qquad \textbf{reaction 2}$$

In the experiments that you will perform, insufficient volumes of the first sodium thiosulfate solution will be added initially, and some iodine will remain in the solution. The amount of iodine left-over can be determined by titration with the second solution of sodium thiosulfate, as shown in **reaction 2**.

You will prepare a number of reaction mixtures, each of which will contain:

- a fixed volume of **FA 1**,
- excess amounts of **FA 2** and **FA 3**,
- a different volume of **FA 4**.

All reaction mixtures will contain some iodine, produced in **reaction 1**, that will be titrated against the **FA 5** solution.

You are required to use a graphical method to determine the concentrations of sodium thiosulfate in **FA 4**, **FA 5** and solution **Z**.

(a) Titration of iodine produced against FA 5

Note: You will perform each titration only **once**. Great care must be taken to ensure that you do not overshoot the end-point.

You will be using two burettes in this task, and each of the burette will contain different sodium thiosulfate solutions, so care must be taken that the right one is used each time.

(i) Experiment 1

1. Fill the burette labelled "**FA 4**" with **FA 4** solution.
2. Fill the burette labelled "**FA 5**" with **FA 5** solution.
3. Using a pipette, transfer 25.0 cm^3 of **FA 1** into a 250 cm^3 conical flask.
4. From the burette labelled "**FA 4**", transfer 9.50 cm^3 of **FA 4** to the same conical flask.

If you accidentally added an incorrect volume of **FA 4** for any of your titrations, record the actual volume of **FA 4** added in your table on the next page, and use that volume for the plotting of the graph later

5. Use appropriate measuring cylinders to add to this flask:
   - 10 cm^3 of **FA 2**,
   - 10 cm^3 of **FA 3**.
6. Titrate the iodine liberated with **FA 5** until the solution fades to a pale yellow colour.
7. Add about 1 cm^3 of starch indicator to this flask. Continue adding **FA 5** until the blue-black colour **just** disappears.
8. Record your titration results in the section "Table of results" on page 3. Make sure that your recorded results show the precision of your working.

(ii) Experiment 2

9. Repeat steps 3 to 8 but add 22.00 cm^3 of **FA 4** at step 4.

(iii) Experiment 3 to 5

10. Choose three further volumes of **FA 4** between 9.50 cm^3 and 22.00 cm^3.
11. Repeat steps 3 to 8 using each of your chosen volumes of **FA 4** at step 4.

Recording

Prepare a table in the space provided on the next page to record:

- the volumes of **FA 4** added for each experiment.
- the burette readings and the volumes of **FA 5** used for each experiment.

Table of results

[4]

(b) Graphical determination of the concentration of sodium thiosulfate in FA 4, FA 5 and solution Z.

(i) Plot a graph of the volume of **FA 5** added (*y-axis*) against the volume of **FA 4** added (*x-axis*) on the grid below. When choosing the scale, you should ensure that the graph line can be extrapolated to intersect both the *x-axis* and the *y-axis*.

Draw a straight line of best fit, taking into account all of your plotted points.

Extrapolate your graph line so that it intersects both the *x-axis* and the *y-axis*.

[3]

(ii) It is possible to react all the iodine produced by the reaction between 25.0 cm^3 of **FA 1** and 10 cm^3 of **FA 2** and **FA 3** by using **FA 4** only.

From your graph, determine the volume of **FA 4** required to do this.

volume of **FA 4** required = ... [3]

(iii) Calculate the gradient of your graph line, showing clearly how you did this.

gradient = ... [1]

(c) Calculations

(i) The amount of iodate(V) ions, IO_3^-, present in 25.0 cm^3 of **FA 1** is 5.75×10^{-4} mol.

Use this value, together with data obtained from your graph in **(b)(i)**, to calculate the concentration of thiosulfate ions in **FA 4**.

$[S_2O_3^{2-}]$ in **FA 4** = ... [2]

(ii) The concentration of $S_2O_3^{2-}$ in **FA 4** and **FA 5** are related to the gradient of the graph obtained in **(b)(iii)** by the following equation:

$$[S_2O_3^{2-}]_{\textbf{FA 5}} = \frac{[S_2O_3^{2-}]_{\textbf{FA 4}}}{|\text{gradient}|}$$

Using the equation, or otherwise, calculate the concentration of thiosulfate ions in **FA 5**.

$[S_2O_3^{2-}]$ in **FA 5** = ... [1]

(iii) Calculate the concentration of thiosulfate ions in the commercially produced solution **Z**.

$[S_2O_3^{2-}]$ in solution **Z** = ... [1]

(d) A student suggested using burettes, rather than using measuring cylinders, to measure the volume of **FA 2** and **FA 3** used in **(a)** so as to improve on the accuracy of the titration data.

State whether you agree with the student and briefly explain why.

....

....

....

.... [1]

(e) In a private institution, a laboratory assistant made the mistake in the preparation of the **FA 5** solution by diluting 21.00 cm^3 of solution **Z** to 250 cm^3, rather than the specified volume of 31.00 cm^3.

State and explain how using this incorrect sample of **FA 5** will affect the gradient of your graph.

....

....

....

.... [1]

[Total: 17]

2 Determination of the enthalpy change for the thermal decomposition of sodium hydrogen carbonate

FA 6 is solid anhydrous sodium carbonate, Na_2CO_3
FA 7 is solid sodium hydrogen carbonate, $NaHCO_3$

You will need access to the **FA 3** solution that you have used earlier.

Sodium hydrogen carbonate is commonly used as a raising agent in baking, as it undergoes thermal decomposition at temperatures above 80 °C, according to the equation:

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(l) \qquad \textbf{reaction 1}$$

Due to the high temperature involved, the enthalpy change of this reaction cannot be measured directly using a coffee-cup calorimeter.

In the experiments that you will perform, the coffee-cup calorimeter will be used to determine the enthalpy change, ΔH_2, for the reaction:

$$Na_2CO_3(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + CO_2(g) + H_2O(l) \qquad \textbf{reaction 2}$$

and the enthalpy change, ΔH_3, for the reaction:

$$2NaHCO_3(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2CO_2(g) + 2H_2O(l) \qquad \textbf{reaction 3}$$

You will then use your results of your experiments to calculate the enthalpy change, ΔH_1, for the thermal decomposition of sodium hydrogen carbonate.

(a) Determining enthalpy change for the reaction between Na_2CO_3 and H_2SO_4, ΔH_2

1. Place the styrofoam cup inside a 250 cm^3 beaker to prevent it from toppling over.
2. Using a measuring cylinder, place 40 cm^3 of **FA 3** into the styrofoam cup.
3. Stir the solution in the cup gently with the thermometer, and measure its temperature. Record the initial temperature of **FA 3** in your table.
4. Weigh the weighing bottle labelled "**FA 6**" and its contents using a weighing scale, without the cap. The bottle has been pre-weighed to contain between 4.50 g and 5.00 g of solid sodium carbonate.
5. Pour **FA 6** from the weighing bottle into the styrofoam cup, place the lid onto the cup, and insert the thermometer through the lid.
6. Stir the mixture using the thermometer and record the maximum temperature reached.
7. Reweigh the weighing bottle.

(i) In an appropriate format in the space below, record:

- all mass readings, including the mass of **FA 6** added to the styrofoam cup
- all temperatures measured and the temperature rise.

[1]

(ii) Calculate the heat change for **reaction 2**.

Assume that the specific heat capacity of the final solution is 3.75 J g^{-1} K^{-1} and that its density is 1.00 g cm^{-3}.

heat change = ... [1]

(iii) By calculating the number of moles of each reagent that was added to the styrofoam cup, and with reference to the equation for the reaction, show which of the reagents, **FA 3** or **FA 6**, is added in excess.

[A_r: Na, 23.0; C, 12.0; O, 16.0]

reagent added in excess = ... [1]

(iv) Calculate enthalpy change for **reaction 2**, ΔH_2:

$$Na_2CO_3(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + CO_2(g) + H_2O(l)$$

ΔH_2 = ... [1]

(b) **Determining enthalpy change for the reaction between $NaHCO_3$ and H_2SO_4, ΔH_3**

1. Empty and rinse the styrofoam cup used in **(a)**, and place the cup back in the 250 cm^3 beaker.
2. Using the same measuring cylinder used in **(a)**, place 40 cm^3 of **FA 3** into the styrofoam cup.
3. Wash and dry the thermometer used in **(a)**, before using it to stir the solution in the cup gently, and measure its temperature. Record the initial temperature of **FA 3** in your table.
4. Weigh the weighing bottle labelled "**FA 7**" and its contents using a weighing scale, without the cap. The bottle has been pre-weighed to contain between 3.50 g and 4.00 g of solid sodium hydrogen carbonate.
5. Pour **FA 7** from the weighing bottle into the styrofoam cup, place the lid onto the cup, and insert the thermometer through the lid.
6. Stir the mixture using the thermometer and record the minimum temperature reached.
7. Reweigh the weighing bottle.

(i) In an appropriate format in the space below, record:

- all mass readings, including the mass of **FA 7** added to the styrofoam cup
- all temperatures measured and the temperature fall.

[3]

(ii) Calculate the heat change for **reaction 3**.

Assume that the specific heat capacity of the final solution is 3.75 J g^{-1} K^{-1} and that its density is 1.00 g cm^{-3}.

heat change = ... [1]

(iii) By calculating the number of moles of each reagent that was added to the styrofoam cup, and with reference to the equation for the reaction, show which of the reagents, **FA 3** or **FA 7**, is added in excess.

[A_r: Na, 23.0; H, 1.0; C, 12.0; O, 16.0]

reagent added in excess = ... [1]

(iv) Calculate enthalpy change for **reaction 3**, ΔH_3:

$$2NaHCO_3(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2CO_2(g) + 2H_2O(l)$$

ΔH_3 = ... [1]

(c) Use your answer to **(a)(iv)** and **(b)(iv)** to calculate enthalpy change for **reaction 1**, ΔH_1:

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(l)$$

ΔH_1 = ... [4]

(d) In **(a)**, one of the significant sources of errors that will affect the accuracy of the enthalpy change for the reaction between Na_2CO_3 and H_2SO_4, ΔH_2, is that the heat capacity of the styrofoam cup is not taken into account.

Explain the effect of this error on your calculated value of ΔH_2.

[1]

[Total: 15]

3 Planning

A sample of solid anhydrous sodium carbonate is believed to be contaminated with sodium chloride, Na*Cl*.

The percentage purity of sodium carbonate in the sample can be determined by measuring the volume of carbon dioxide formed when sodium carbonate is reacted with an excess of sulfuric acid.

$$Na_2CO_3(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + CO_2(g) + H_2O(l)$$

You are to plan an experiment that will enable you to:

- react a pre-weighed impure sample of sodium carbonate with a pre-determined volume of the **FA 3** solution that you have used earlier for Question 1 and 2,
- collect and measure the volume of the carbon dioxide gas evolved.

(a) Draw a diagram of the apparatus that you would use to carry out this experiment.

[2]

(b) By considering the capacity of the apparatus that you have drawn in **(a)** to measure the volume of the carbon dioxide gas, calculate the maximum mass of the impure sample of sodium carbonate that you would use in your experiment.

[A_r: Na, 23.0; C, 12.0; O, 16.0 and 1 mole of gas occupies a volume of 24.0 dm^3 under the conditions present in the laboratory]

maximum mass of impure sample of sodium carbonate used = ______________ [2]

(c) A student suggested that 40.0 cm^3 of **FA 3** solution is sufficient for the experiment.

State whether you agree with the student, and explain your answer.

____

____

____ [1]

(d) State how you would ensure that all the carbon dioxide gas given off in the reaction between the impure sample of sodium carbonate and **FA 3** solution was collected and that none escaped from the apparatus.

____

____

____ [1]

(e) Other than this method that involves the collection of carbon dioxide gas, the percentage purity of sodium carbonate in the sample can also be determined using a titration.

In a typical experiment, a pre-weighed mass of the impure sample of sodium carbonate is dissolved in water and made up to 250 cm^3 in a volumetric flask, and 25.0 cm^3 of this solution is titrated against a standard solution of hydrochloric acid using methyl orange as indicator.

State which of the two methods you would expect to give the more accurate results. Explain your choice.

[2]

[Total: 8]

4 Inorganic Qualitative Analysis

You are provided with **FA 8**, which is a mixture of two solids, **FA 9**, which is soluble in water and **FA 10**, which is insoluble in water. Each contains **one cation** and **one anion** from the lists on page 17 and 18.

In this question you will perform a series of test-tube reactions, make observations and deduce the identities of the cations and anions present in **FA 9** and **FA 10**.

If the evolution of a gas is observed at any stage, the gas should be tested and identified.

You are advised that the reagent should be added gradually in all tests, with shaking after each addition.

(a) Tests on FA 8

Perform the test-tube experiments described below and record your observations in the spaces provided in the table.

	Test	**Observations**
(i)	Place all of the solid, **FA 8**, into a 100 cm^3 beaker. Add 25 cm^3 of distilled water and warm to dissolve the **FA 9**. Filter the mixture and use the filtrate for tests **(a)(ii)** to **(a)(iv)**. Wash the residue, **FA 10**, and use it for tests **(a)(v)** to **(a)(vii)**.	

Tests on Filtrate, FA 9

	Test	**Observations**
(ii)	Place about 1 cm depth of **FA 9** into a test-tube. Add a few drops of dilute sulfuric acid.	
(iii)	Place about 1 cm depth of **FA 9** into a test-tube. Add a few drops of aqueous barium chloride, followed by a few drops of dilute hydrochloric acid.	
(iv)	Place about 1 cm depth of **FA 9** into a test-tube. Add a few drops of aqueous silver nitrate. followed by a few drops of aqueous ammonia.	

Tests on Residue, FA 10

	Test	**Observations**
(v)	Using a spatula, transfer as much of the residue on the filter paper as you can into a test-tube. Add dilute sulfuric acid drop-wise into the test-tube to dissolve the residue. Filter if necessary. Use the resultant solution for test **(a)(vi)** and **(a)(vii)**.	
(vi)	Place about 1 cm depth of the **filtrate** from **(a)(v)** in a test-tube. Add aqueous sodium hydroxide drop-wise with shaking, until no further change is seen.	
(vii)	Place about 1 cm depth of the **filtrate** from **(a)(v)** into a test-tube. Add aqueous ammonia, drop-wise with shaking, until no further change is seen.	

[5]

(b) Based on your observations to **(a)(ii)**, suggest a possible identity of the cation in **FA 9**.

cation in **FA 9**: .... [1]

(c) From your remaining observations, state the identities of the one anion in both **FA 9** and **FA 10**, and the one cation in **FA 10**.

In each case, give evidence to support your conclusion.

	identity		evidence
FA 9	anion:		
FA 10	cation:		
	anion:		

[3]

[Total: 9]

5 Planning

In this question, you will devise a plan, using test-tube reactions, to distinguish between four organic compounds, so that each is identified.

Consider 4 unlabelled bottles and each bottle contains one of the following colourless liquids:

ethanal propanone propan-2-ol ethanoic acid

Plan an investigation, using test tube reactions, which would allow you to identify each of these organic compounds.

Each compound should be identified by at least one positive test. It is not sufficient to identify a compound simply by eliminating all the others.

Your plan should include:

- details of the reagents and conditions to be used,
- an outline of the sequence of steps you would follow,
- an explanation of how you would analyse your results in order to identify each compound.

Once a compound has been clearly identified, your plan should concentrate on distinguishing the remaining compounds.

[Total: 6]

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. insoluble in excess	green ppt. 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. insoluble in excess	off-white ppt. insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

ions	*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 with dilute acids; gives white ppt. with $Ba^{2+}(aq)$ (soluble in dilute strong acids)

(c) Test for gases

ions	*reaction*
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

END OF PAPER 4

Paper 1 Worked Solutions

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

1 $MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$

0.004 mol MnO_4^- gains 0.004 × 5
= 0.020 mol of e^-.

0.01 mol $\mathbf{R}^{2+}$ loses 0.020 mol of e^-.

$\Rightarrow$ 1 mol $\mathbf{R}^{2+}$ loses 2 mol of e^-.

O.S. of **R** increases from +2 to +4.

Ans: A

2 **A**: Incorrect. The equation corresponds to the sum of 1st, 2nd and 3rd I.E.

B: Incorrect. Ti^{2+} needs to be in gaseous state, not solid state.

C: Correct. Third ionisation of Ti is the energy required to remove one mole of electrons from one mole of $Ti^{2+}(g)$ to form one mole of $Ti^{3+}(g)$.

D: Incorrect. The equation corresponds to the reverse of 3rd I.E.

Ans: C

3 **1**: Correct. B^{2-} has an electronic configuration of $1s^2\,2s^2\,2p^3$.

2: Correct. C^- has an electronic configuration of $1s^2\,2s^2\,2p^3$.

3: Incorrect. N^- has an electronic configuration of $1s^2\,2s^2\,\mathbf{2p^4}$.

4: Correct. N has an electronic configuration of $1s^2\,2s^2\,2p^3$.

Ans: B

4 As all four gases consist of non-polar molecules (the dipole moments cancel out completely in SO_3 as it has a trigonal planar shape), only id-id interactions exist between their respective molecules.

Since SO_3 has the biggest and most polarisable electron cloud, the id-id interaction between its molecules is the strongest (and the volume of its molecules will be the most significant compared to the volume of the container), and so SO_3 shows the greatest deviation from ideality among the 4 gases.

Ans: B

5 $p_1V_1 = nRT_1$

$p_2V_2 = nRT_2$

Rearranging,

$$\frac{p_1V_1}{T_1} = nR = \frac{p_2V_2}{T_2}$$

$$\Rightarrow \frac{(4.50)V}{298} = \frac{P_2(\frac{1}{3}V)}{753}$$

$\Rightarrow P_2 = 34.1$ atm

Ans: B

6 As pressure increases, equilibrium position will shifts to the side with a smaller number of moles of gas to reduce pressure; and as seen from the graph, percentage of the product decreases. This implies that the reactants contain fewer moles of gas than the products (option **B** or **C**).

When temperature is increased from T °C to (T + 20) °C, the endothermic reaction will occur to a greater extent to remove heat; and as seen from the graph, percentage of the product decreases. This implies that the forward reaction is exothermic (option **A** or **C**).

Ans: C

7 $K_w = [H^+]\,[OH^-]$ (by definition)

At 50 °C, $K_w = 5.48 \times 10^{-14}$ mol^2 dm^{-6}
$\Rightarrow [H^+]\,[OH^-] = 5.48 \times 10^{-14}$ mol^2 dm^{-6}

Since $[H^+] = [OH^-]$ for pure water,
$\Rightarrow [H^+]^2 = 5.48 \times 10^{-14}$ mol^2 dm^{-6}
$\Rightarrow [H^+] = 2.34 \times 10^{-7}$ mol dm^{-3}

$pH = -\log [H^+] = -\log (2.34 \times 10^{-7}) = 6.63\ (< 7)$

Answer: **D**

8 For a weak acid-weak base (methylamine) titration, the pH will change gradually as the titrant is added to the aliquot even when it is near to the equivalence point (i.e.no sharp colour change will be observed), and so there is no suitable indicator that can be used for the titration.

Answer: **D**

9 In the presence of the homogeneous catalyst NO, the reaction proceed via a two-step mechanism (i.e. the reaction pathway diagram has two humps) with lower activation energy (option **C** and **D**).

In addition, the use of a catalyst <u>does not alter the energy level of the reactants and the products</u> (options **B** and **D**).

Answer: **D**

10

$$\begin{tikzcd}
Rb(s) & + & \tfrac{1}{2}Br_2(l) \arrow[rr, "\Delta H_f"] \arrow[d, "\tfrac{1}{2}(+224)"] & & RbBr(s) \\
Rb(g) \arrow[from=1-1, "+81"] \arrow[d, "+403"] & + & Br(g) \arrow[d, "-324"] & & \\
Rb^+(g) & + & Br^-(g) \arrow[rr, dash] & & {} \arrow[uu, "-687"']
\end{tikzcd}$$

$\Delta H_f = +81 + \tfrac{1}{2}(+224) + 403 + (-324) + (-687)$

$= -415 \text{ kJ mol}^{-1}$

Answer: **B**

11 Heat evolved = (300 x c x ΔT) J

No. of moles of propan-1-ol = (m / 60.0) mol

Maximum amount of heat evolved
= (2021 x 1000 x m / 60.0) J

Efficiency of heating process

$$= \frac{300 \times c \times \Delta T \times 60.0}{m \times 2021 \times 1000} \times 100\%$$

Ans: D

12 From the Data Booklet,
$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$ $E^\ominus = +2.01$ V
$I_2 + 2e^- \rightleftharpoons 2I^-$ $E^\ominus = +0.54$ V

In order for the metal ion to catalyse the reaction, $E^\ominus_{cell}$ must be positive. Hence the $E^\ominus$ value should be between +0.54 V and +2.01 V.

1: Incorrect. $E^\ominus(Cu^{2+}/Cu^+) = +0.15$ V

2: Correct. $E^\ominus(Co^{3+}/Co^{2+}) = +1.89$ V

3: Correct. $E^\ominus(Mn^{3+}/Mn^{2+}) = +1.54$ V

4: Incorrect. $E^\ominus(V^{3+}/V^{2+}) = -0.26$ V

Ans: B

13 The rate of the reaction depends on the rate of the slow step.
⇒ rate = k [B] [C]

However, the rate equation for the overall reaction should be in terms of concentrations of only the reactants (note that C and D are reaction intermediates).

Since step 1 of the mechanism is an equilibrium, $2A \rightleftharpoons C$, we can write an expression for the equilibrium constant:

$$K = \frac{[C]}{[A]^2}$$

rearranging, we get: $[C] = K[A]^2$

The rate equation then becomes
Rate = k [B] K $[A]^2$
$= k'\,[A]^2\,[B]$

Ans: C

14. Option **A** suggest that element J is A*l*. Since in the aqueous solution Al^{3+} first form a white ppt with OH^-: $Al(OH)_3$ which dissolves in excess NaOH due to the formation of $Al(OH)_4^-$

Options **B** and **D** agrees with the suggestion that element J is A*l*.

Option **C** is **incorrect** as Si has the highest melting point among the period 3 elements.

Answer: C

15 Expt 1:
$SrCO_3(s) \rightarrow SrO(s) + CO_2(g)$
$Sr(NO_3)_2(s) \rightarrow SrO(s) + 2NO_2(g) + \tfrac{1}{2}O_2(g)$

Expt 2:
$SrCO_3(s) + H_2SO_4 \rightarrow SrSO_4(s) + CO_2(g) + H_2O(l)$

No. of moles of $CO_2(g) = \dfrac{75}{V_m}$ mol

(where V_m = molar volume at a certain temperature and pressure)

Let amount of $SrCO_3$ be a mol and amount of $Sr(NO_3)_2$ be b mol.

From expt 1, a + 2.5b = $200/V_m$ ----- eqn 1
From expt 2, a = $75/V_m$

Subst a = $75/V_m$ into eqn 1 gives
b = $50/V_m$ mol

⇒ Mole ratio of $SrCO_3 : Sr(NO_3)_2$
= $75/V_m : 50/V_m$ = 3 : 2

Ans: A

16

	$E^\ominus$
$\mathbf{Cl_2} + 2e^- \rightleftharpoons 2Cl^-$	+1.36
$VO_3^- + 4H^+ + e^- \rightleftharpoons \mathbf{VO^{2+}} + 2H_2O$	+1.00
$VO_2^+ + 2H^+ + e^- \rightleftharpoons \mathbf{VO^{2+}} + H_2O$	+1.00
VO_2^+ + 2H+ + $e^- \rightleftharpoons V^{3+}$ + H2O	+0.34

Cl_2 can only be reduced and VO^{2+} can only be oxidised.

Hence, VO^{2+} can be oxidised to either VO_3^- or VO_2^+ since the $E^\ominus$ values of $E^\ominus(Cl_2/Cl^-)$ is more positive than $E^\ominus(VO_2^+/VO^{2+})$ and $E^\ominus(VO_3^-/VO^{2+})$.

Answer: **D**

17 **Highest oxidation state = number of 4s electrons + number of unpaired 3d electrons**

Given electronic configuration to be:
$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^7\,4s^2$

There are a total of two 4s electrons and three unpaired 3d electrons. Hence maximum oxidation state is +5.

O.S of Y in compound 1 is +6.
O.S of Y in compound 2 is +5.
O.S of Y in compound 1 is +4.
O.S of Y in compound 1 is +2.

Ans: A

18 Since the product is a platinum(IV) compound which contains a cation with a 2+ charge and has a co-ordination number of 6, this means that the cation contains two Cl^- ligands and four NH_3 ligands, i.e. $[Pt(NH_3)_4Cl_2]^{2+}$.

Since the reaction is between $PtCl_4$ and NH_3 only, and so the anion of the product is Cl^- ions, i.e. the product is made up of $[Pt(NH_3)_4Cl_2]^{2+}$ & $2Cl^-$.

Hence the formula of the product is: $Pt(NH_3)_4Cl_4$.

Ans: C

19 The shortest C−H bonds are associated with those carbon hybrid orbitals with the greatest s character. With greater s character, the hybrid orbital can pull the electron density closer to the nucleus and results in shorter bond length.

A, **B** and **D** are correct statements but do not explain the C-H bond length.

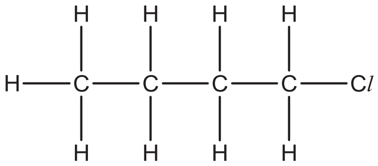
Ans: C

20 Chloroethane undergoes the S_N2 mechanism to give ethanol as it is a primary halogenoalkane. The mechanism involves an OH^- nucleophilic attack from the opposite end of the Cl leaving group and it is an overall second order reaction.

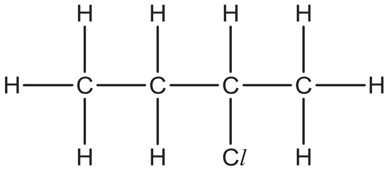
1, 3 and 4 are statements which describes S_N1 mechanism.

Ans: B

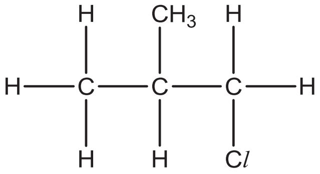
21 In total, there are 4 constitutional isomers that C_4H_9Cl can form. The isomers are as follows:



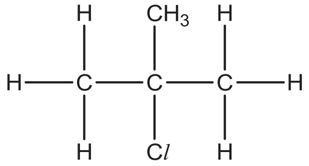
1-chlorobutane



2-chlorobutane



1-chloro-2-methylpropane



2-chloro-2-methylpropane

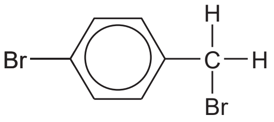
Ans: B

22 Since Br is less electronegative than Cl, the δ+ charge will reside on the Br-atom in the Cl−Br molecule. The molecule will therefore react with $AlCl_3$ to produce the electrophile Br^+:

$$Cl{-}Br + AlCl_3 \rightarrow Br^+ + AlCl_4^-$$

Br^+ then acts as the electrophile to attack the benzene ring.

Structure of G is therefore:



Ans: A

23 D undergoes dehydration to give alkenes E and F. E being the minor product as it is the less substituted alkene (i.e. less stable). Upon oxidation, E gives a ketone with $-COCH_3$ group.

A: Minor product obtained upon dehydration is $CH_2=CHCH_2CH_2CH_3$. It is oxidised to give CO_2, H_2O and $CH_3CH_2CH_2CO_2H$.

B: The only product obtained upon dehydration is $CH_3CH=CHCH_2CH_3$. It is oxidised to give CH_3CO_2H and $CH_3CH_2CO_2H$.

C: Minor product obtained upon dehydration is $CH_3CH(CH_3)CH=CH_2$. It is oxidised to give $CH_3CH(CH_3)CO_2H$, CO_2 and H_2O.

D: Minor product obtained upon dehydration is $CH_2=C(CH_3)CH_2CH_3$. It is oxidised to give CO_2, H_2O and $CH_3COCH_2CH_3$. $CH_3COCH_2CH_3$ gives yellow ppt with I_2/OH^-

Ans: D

24 **A**: Both ethanol ($-CH(OH)CH_3$) and propanone ($-COCH_3$) give yellow ppt with aqueous alkaline iodine.

B: Ethanol will be oxidised to ethanoic acid and turns acidified potassium dichromate(VI) from orange to green. Propanone cannot be oxidised and so acidified potassium dichromate (VI) will remain orange.

C: Propanone will give a yellow or orange ppt with 2,4 DNPH and ethanol will not give a ppt with 2,4 DNPH.

D: Effervescence of H_2 gas which 'pops' with lighted splint will be observed for ethanol reacting with sodium metal. No gas will be evolved when sodium metal is added to propanone.

Ans: A

25

A: $CH_3CH_2CN \xrightarrow[D_2O]{NaOD} CH_3CH_2CO_2^-Na^+$

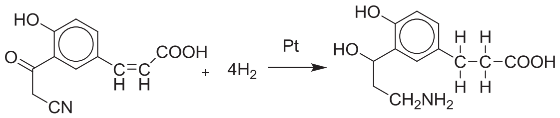
B: $CH_3CH(OH)CH_3 \xrightarrow[D_2SO_4(aq)]{KMnO_4} CH_3COCH_3$

C: $CH_3CO_2H \xrightarrow[\text{conc } D_2SO_4]{C_2H_5OD} CH_3CO_2C_2H_5$

D: $C_6H_5ONa \xrightarrow{D_2O} C_6H_5OD$

Ans: D

26 1: **Correct**



1 mole of compound **P** reacts completely with 4 moles of H_2 gas.

2: **Correct**
It has 1 C=C which can exhibit cis-trans isomerism and no chiral carbon.
Total number of stereoisomers = $2^1 = 2$

3: **Incorrect**
Phenol does not react with ethanoic acid in the presence of concentrated sulfuric acid. Acid chloride is needed to react with phenol to form ester.

Ans: C

27 N_D is the most basic as it has an electron donating methyl group on the adjacent carbon which makes the lone pair of electrons more available for donation to a proton. Hence, N_D is more basic than N_C.

Lone pair of electrons on N_B is delocalised into the pyridine rings (similar to phenylamine) which makes the lone pair of electron less available for donation to a proton. Hence, N_B is less basic than N_C and N_D where the lone pair of electrons are not delocalised into the pyridine rings.

N_A is an amide nitrogen with the lone pair of electron being delocalised into the adjacent carbonyl group. Hence the lone pair is not available for donation to a proton. Amide is neutral.

Order of basicity is $N_D > N_C > N_B > N_A$

Ans: **D**

28 **A**: Correct. 2-aminopropanoic acid isolated from silkworm has a chiral centre and is optically pure and is able to rotate plane polarised light.

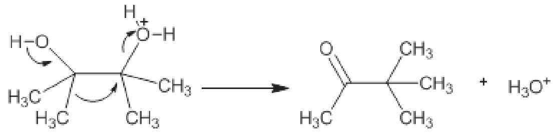
B: Incorrect. Amine cannot react with ethanoic acid to form an amide. Acyl chloride which is more reactive has to be used to react with amine.

C: Incorrect. An aqueous solution of 2-aminopropanoic acid exists as zwitterions and has buffering capacity.

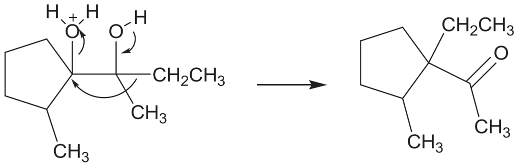
D: Incorrect. Aqueous bromine is decolourised only when alkene, phenol or phenylamine is present (and is absent in 2-aminopropanoic acid)

Ans: A

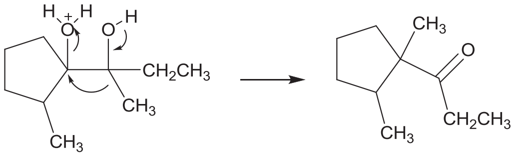
29 The pinacol rearrangement works via the mechanism as shown.



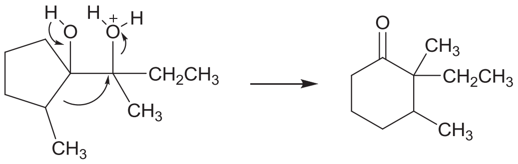
A:



B:



C:



Compound **A**, **B** and **C** can be obtained via pinacol rearrangement.

Ans: D

30 Rate of hydrolysis is in the following order:

K > N > M > L

K is acid chloride and undergoes hydrolysis most readily due to the presence of 2 electronegative atoms (C*l* and O atoms) attached to the carbon.

For halogenoalkane, rate of hydrolysis depends on the strength of the C−Hal bond. C−Br bond is weaker than C−C*l* bond and hence is broken more readily.

L is a chlorobenzene and the C−C*l* bond is not broken in the presence of NaOH(aq). The lone pair of electrons on C*l* is partially delocalised into the benzene ring, leading to partial double character and strengthen the C−C*l* bond.

71.1 g of AgC*l* is equivalent to 0.5 mol of AgC*l*. W will give more AgC*l* as it is more reactive than M.

N will give more than 0.5 mol of AgBr which is equivalent to 93.9 g of AgBr.

L will not give any precipitate.

Ans: A

2017 H2 Chemistry 9729 Preliminary Examinations Suggested solutions

Paper 2: Structured Questions

1 (a) To drive off the CO_2

(b) (i) Amount of HC*l* = $50.0 \times 10^{-3} \times 0.100 = 5.00 \times 10^{-3}$ mol

(ii) Amount of HC*l* = $20.0 \times 10^{-3} \times 0.0500 = 1.00 \times 10^{-3}$ mol

(iii) Amount of HC*l* unreacted in graduated flask = $2 \times 1.00 \times 10^{-3} = 2.00 \times 10^{-3}$mol
Amount of HC*l* neutralised = $5.00 \times 10^{-3} - 2.00 \times 10^{-3} = 3.00 \times 10^{-3}$ mol

(iv) Amount of excess stomach acid
= $(375 \times 10^{-3} \times 0.0300) - (375 \times 10^{-3} \times 0.000300) = 0.011138$ mol

1 tablet is able to neutralise 3.00×10^{-3} mol of HC*l*.
To neutralise 0.011138 mol of HC*l*, minimum of 4 tablets is needed.

(c) Amount of $CaCO_3$ in 1 tablet = ½ x $3.00 \times 10^{-3} = 1.50 \times 10^{-3}$ mol

Mass of $CaCO_3$ in 1 tablet = $1.50 \times 10^{-3} \times 100.1 = 0.150$ g = 150 mg.

There are only 150 mg of $CaCO_3$ in 1 tablet.

(d) **(i)** For Al_2O_3, there is a **decrease** in **ionic character/ increase in covalent character**

due to the **high polarising power of Al^{3+} ion** which distorts the electron cloud of O^{2-} ion to a greater extent compared to Mg^{2+} ion. Thus the melting point is lower than MgO.

(ii) MgO is only **slightly soluble in water.** pH = 9 (accepts 8 to 10)

Al_2O_3 remains **insoluble** in water. pH = 7.

(iii) $Al^{3+}(aq) + 3OH^-(aq) \rightarrow Al(OH)_3(s)$
$Al(OH)_3(s) + OH^-(aq) \rightarrow Al(OH)_4^-(aq)$

2 **(a)** The volatility of the halogens **decreases** down the group.

The halogens have simple molecular structure and are non-polar.

The **instantaneous dipole-induced dipole interactions between the molecules of each halogen become stronger** due to the **increasing size and polarisability of the electron cloud of the halogens down the group.**

Hence more energy is required to overcome the stronger instantaneous dipole-induced dipole interactions between the molecules of each halogen.

(b)

hydrogen halides	H−C*l*	H−Br	H−I
bond energy / kJ mol^{-1}	431	366	299

The thermal stability of the hydrides of the Group 17 elements **decreases** down the group as the **H−X bond strength decreases** down the group. Hence less energy is required to overcome the H−X covalent bond.

(c) **(i)** $K_{sp} = [Pb^{2+}][Cl^{-}]^2$ mol^3 dm^{-9}

correct expression and units

(ii) $[PbCl_2] = 4.7 \div 278.2 =$ **0.016894 mol dm^{-3}**

$K_{sp} = (0.016894) \times (2 \times 0.016894)^2 =$ **1.9×10^{-5}** mol^3 dm^{-9}

[1] for correct calculation of solubility in mol dm^{-3}
[1] for correct numerical answer and leave the answer to 2 significant figures

(d) **(i)** Decolourisation of orange/yellow/reddish brown Br_2(aq) and a black solid is formed.

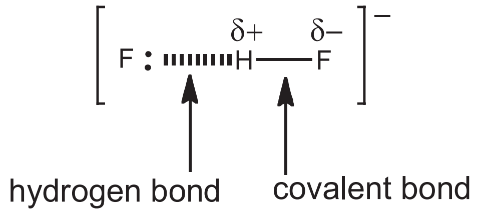
$Br_2(aq) + 2At^{-}(aq) \rightarrow 2Br^{-}(aq) + At_2(s)$

(ii) no reaction

(e) **(i)** cation: K^+

anion: HF_2^-

(ii)



[1] for covalent bond; [1] for hydrogen bond

[Total:12]

3 **(a)** **(i)**

- Mg^{2+} has a smaller ionic radii and thus a higher charge density and polarising power.
- Ease of distortion of electron cloud of carbonate increases, weakening of C–O covalent bond occurs to a greater extent.
- thermal stability of magnesium carbonate is lower than calcium carbonate.

(ii) $MgCO_3 \rightarrow MgO + CO_2$

(b) $Mass\ \ of\ \ CO_2 = 1.00 - 0.777 = 0.223g$

$$n_{\ CO_2} = \frac{0.223}{(12+16\times2)} = 5.0682\times10^{-3}mol$$

$$n_{\ ZCO_3} = 5.0682\ \times10^{-3}mol$$

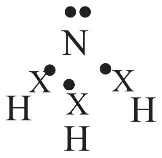
$$5.0682\times10^{-3} = \frac{1.0}{M_{MCO3}} \quad \Rightarrow \quad M_{\ ZCO_3} = 197.3\,gmol^{-1}$$

$$M_Z + (12+16\times3) = 197.3$$

$$M_Z = 137.3\,gmol^{-1}$$

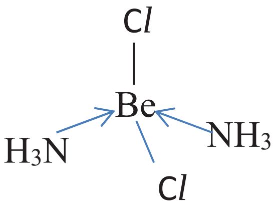
Identity of **Z** : **Barium**

(c) **(i)**



Both correct [1]

(ii)



Tetrahedral shape around Be.

[Total:10]

4 **(a)** **(i)** Amount of coal required

$= \dfrac{108 \times 10^3}{393}$

$= 274.81$ mol

Mass of coal required

$= 274.81 \times 12.0$

$= 3297.7$ g

Energy density of coal

$= \dfrac{108}{3297.7}$

$= 0.0327$ MJ/g

(ii)

- Coal is a **more efficient fuel.**
- The energy density of coal (0.0327 MJ/g) **is larger than the energy of density of ethanol.** Thus for the **same amount of energy supplied**, **lesser amount of coal is required.**

(iii)

- CO undergoes **<u>ligand exchange reaction</u>** and **<u>binded more strongly via dative bond</u> to haemoglobin than O_2**.
- Thus, this **<u>displaces O_2 from oxyhaemoglobin</u>** and **<u>reduces the amount of haemoglobin available for carrying O_2.</u>**

(b) **(i)** $2C\,(s) + 3H_2\,(g) + \frac{1}{2}O_2\,(g) \rightarrow CH_3CH_2OH\,(l)$

$\Delta H^{\ominus}_{f}\ \square = \square\Delta H^{\ominus}_{c}\,(C) + 3\square\Delta H^{\ominus}_{c}\,(H_2) + \frac{1}{2}\Delta H^{\ominus}_{c}\,(O_2) - \Delta H^{\ominus}_{c}\,(CH_3CH_2OH)$

$= 2 \times (-393) + 3(-286) + 0 - (-1367)$

$=$ **-277 kJmol^{-1}** [1]

(ii) $\Delta H^{\ominus}_{r}$= Energy absorbed to break bonds + Energy released to form bonds

$CH_3CH_2OH\ (l) + 3\ O_2\ (g) \rightarrow 2\ CO_2\ (g) + 3\ H_2O\ (l)$

bonds broken	(endothermic)	bonds formed	(exothermic)
5 × C–H	**5 × (+410)**	**4 × C=O**	**4 × (−805)**
1 × C–O	**1 × (+360)**	**6 × O–H**	**6 x ($\underline{-460}$)**
1 × C–C	**1 x (+350)**		
1 × O–H	**1 x (+460)**		
3 O=O	**3 × (+496)**		
total energy absorbed	**+4708**	**total energy evolved**	**− 5980**

$\Delta H^{\ominus}_{c}$ = +4708 – 5980
$\Delta H^{\ominus}_{c}$ = **– 1272 kJ mol^{-1}**

✓ Bond energy data from data booklet [1]
✓ Final answer + units [1]

(iii) ✓ **Bond energy values in the Data Booklet are averages**, so it would not apply exactly to a particular compound.

Or

✓ In the calculation in **(b)(ii)**, it is assumed that all the reactants and products are in the gaseous state. However, **ethanol is a liquid at standard conditions**

(c) **(i)** **Anode:** $\mathbf{CH_3CH_2OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^-}$
Cathode: $\mathbf{O_2 + 4H^+ + 4e^- \rightarrow 2H_2O}$
Overall: $\mathbf{CH_3CH_2OH + 3O_2 \rightarrow 2CO_2 + 3H_2O}$

(ii) $E^{\ominus}_{cell} = E^{\ominus}_{cathode} - E^{\ominus}_{anode}$
= +$\underline{\mathbf{1.23}}$ – (+0.08)
= **+ 1.15V**

✓ Correct value for $E^{\ominus}_{cathode}$ [1]
(allow for e.c.f if student wrote the wrong equation at the anode as :
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$, $E^{\ominus}_{cathode}$ = +0.40)

✓ Correct value for $E^{\ominus}_{cell}$ [1]

(iii) $\Delta G^{\ominus} = -nFE^{\ominus}_{cell}$
= –12 x 96500 x 1.15
= –1.33 x 10^6 Jmol^{-1}

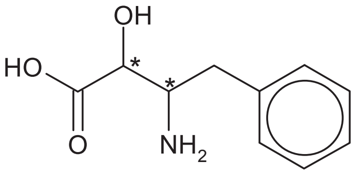
= –1.33 x 10^3 kJmol^{-1} (correct units)

(d) (i) **$H_2O(g)$ (steam), H_3PO_4 catalyst, heat, high pressure**

(ii)
1. In ethene, each of the carbon atom is **sp^2 hybridised**.
2. Each carbon atoms forms **two σ-bonds with hydrogen atoms** through **the head on overlap** of two of **its sp^2 orbitals with the 1s orbitals** of the **hydrogen atoms**.
3. Another **σ-bond** is formed when the remaining **sp^2 orbital of the two carbon atoms overlap with each other**.
4. The **remaining unhybridised p orbital** of the two carbon atoms, which is perpendicular to the plane of sp^2 hybrid orbitals, **overlaps laterally or sideways to form a π bond.**

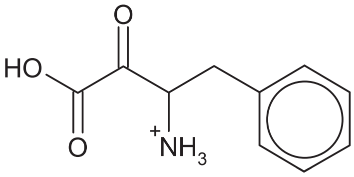
5 (a) (i) carboxylic acid , (secondary) alcohol , and (primary) amine .

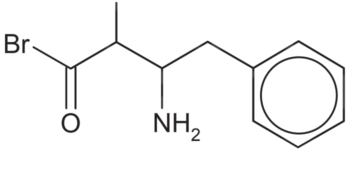
(ii)



total possible number of stereoisomers = 2^2 = **<u>4</u>**

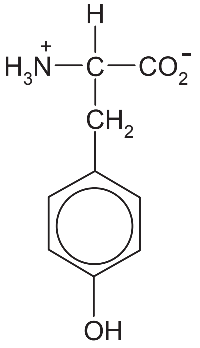
(iii)





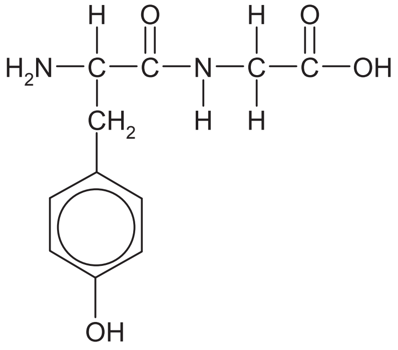
(b) **(i)** A zwitterion is a molecule that is **neutral overall**, but **contains a positive charge** on one part of the molecule (usually $-NH_3^+$) **and a negative charge** on another part of the molecule (usually $-CO_2^-$).

(ii)

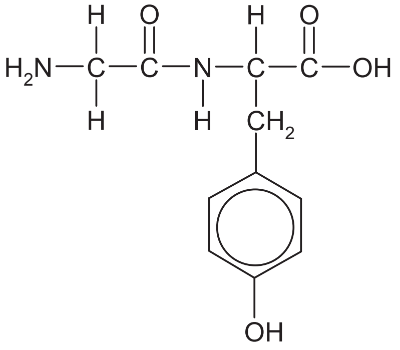


(iii) peptide or amide linkage

(iv)

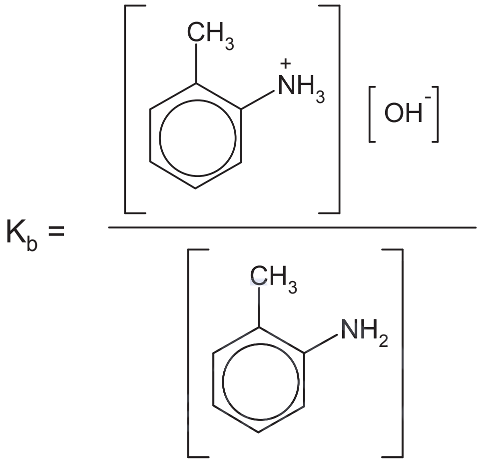


and



(c) **(i)** NaOH(aq), reflux
or
HC*l*(aq), reflux, followed by NaOH(aq)

(ii)



(iii) $K_b = 10^{-pK_b} = 10^{-9.6} = 2.5119 \times 10^{-10}\ \text{mol dm}^{-3}$

$[OH^-] = \sqrt{K_b \times c_{base}} = \sqrt{2.5119 \times 10^{-10} \times 0.10} = 5.0119 \times 10^{-6}\ \text{mol dm}^{-3}$

$pOH = -\log[OH^-] = -\log(5.0119 \times 10^{-6}) = 5.30$

$pH = 14.0 - 5.30 = 8.70$

(d) The pK_b of benzylamine will be **<u>lower</u>** than that for 2-methylphenylamine

Benzylamine is a stronger base as **<u>the phenylmethyl group is electron donating</u>**, **<u>making the lone pair of electrons on N more available for donation</u>** to a proton (or H^+ ion).

2-methylphenylamine is a weaker base as the **<u>lone pair of electrons on the N</u>** of the amine is **<u>delocalised into the benzene ring</u>**, making them **<u>less available for donation</u>** to a proton (or H^+ ion).

Worked solutions for 2017 9729 H2 Chemistry Preliminary Examination Paper 3

1 **(a)** **(i)** $2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$

$2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$

(ii) Both compounds have giant ionic lattice structure. While the charge and size of the cation as well as the charge of the anion are the same in both ionic compounds, **S^{2-} is bigger than O^{2-}**.

Consequently, **the electrostatic forces of attraction between Cu^+ and S^{2-} are weaker than that between Cu^+ and O^{2-}**. Hence, **lesser amount of energy is required** to overcome the weaker ionic bonds in Cu_2S. The melting point of **Cu_2S will be lower than that of Cu_2O**.

[1]: correct comparison of the size of S^{2-} and O^{2-}
[1]: Cu_2S has a lower melting point than Cu_2O

(iii) anode: impure copper
cathode: pure copper
electrolyte: $CuSO_4(aq)$

$Ag^+ + e^- \rightleftharpoons Ag$ $\quad E^\ominus = +0.80V$
$Cu^{2+} + 2e^- \rightleftharpoons Cu$ $\quad E^\ominus = +0.34V$
$Zn^{2+} + 2e^- \rightleftharpoons Zn$ $\quad E^\ominus = -0.76V$

reaction at the anode
By controlling the voltage, when the current runs through the circuit, copper and zinc metals will be oxidised to form aqueous cations at the anode.

$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

Ag will not be oxidised due to its more positive $E^\ominus$ reduction potential (compared to Cu), and will drop to the bottom as sludge.

reaction at the cathode
Subsequently both Cu^{2+} and Zn^{2+} will migrate to the cathode but only Cu^{2+} will be reduced to Cu as it has a more positive $E^\ominus$ reduction potential than Zn.

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Hence, the copper cathode would grow in size with pure copper deposited, while Zn^{2+} remains in solution.

[1]: description of anode, cathode and electrolyte
[1]: correct electrode reactions (both anode and cathode) with reference to relevant $E^\ominus$ values (correct state symbols must be given for the equations)
[1]: Ag dropping to the bottom as sludge and Zn^{2+} remaining in the solution

(iv) Amount of Ag deposited = $0.100 \div 107.9 = 9.2678 \times 10^{-4}$ mol

$Ag^+(aq) + e^- \rightarrow Ag(s)$

Amount of electrons = 9.2678×10^{-4} mol

$Q = (9.2678 \times 10^{-4}) \times 96500 = 89.436$ C

$I = 89.436 \div (30 \times 60) = 0.0497$ A

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Amount of copper deposited = ½ × (9.2678×10^{-4}) = 4.6339×10^{-4} mol
Mass of copper deposited = (4.6339×10^{-4}) × 63.5 = 0.029425 = 0.0294 g

(b) **(i)** $2Cu^{2+}(aq) + 4I^{-}(aq) \rightarrow 2CuI(s) + I_2(aq)$

$E^{\ominus}_{cell}$ = +0.15 − (+0.54) **= –0.39V**

Since the $E^{\ominus}_{cell}$ **is negative, the reaction is not feasible**.

(ii) The precipitation of CuI reduces the concentration $Cu^{+}(aq)$, shifting the Cu^{2+}/Cu^{+} equilibrium ($Cu^{2+} + e^{-} \rightleftharpoons Cu^{+}$) to the right, favouring the reduction process and hence making the reduction potential of Cu^{2+}/Cu^{+} more positive.
As such, $E^{\ominus}_{cell}$ becomes positive and the redox reaction becomes spontaneous.

(c) CH_3CH_2COCl and $(CH_3CH_2CH_2CH(CH_3)CH(CH_3)CH_2)_2Cu^{-}Li^{+}$
or
$CH_3CH_2CH_2CH(CH_3)CH(CH_3)CH_2COCl$ and $(CH_3CH_2)_2Cu^{-}Li^{+}$

[1] for a suitable Gilman reagent, and [1] for the corresponding acid chloride

(d) **(i)** Entropy (S) is a measure of the degree of disorder or randomness in a system.

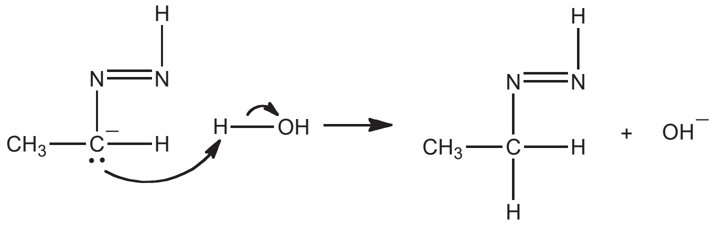
(ii) ΔS is **positive** as the forward reaction is **accompanied by an increase in the number of moles of gases**. Hence, there is an increase in the number of ways of distributing the gaseous particles and entropy increases.

(iii) $\Delta H^{\ominus} = [(-84.7) + (-285.8)] - [(-196.4) + 50.6] = -224.7$ kJ mol^{-1}

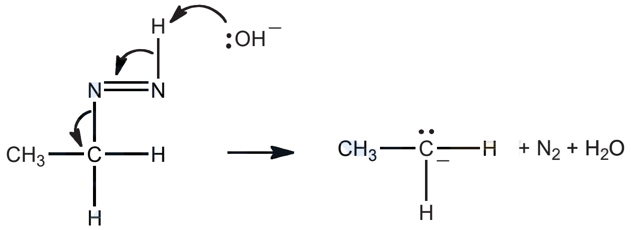
$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus} = -224.7 - (298)(0.1915) = -281.8$ kJ mol^{-1}

(iv) condensation (or addition-elimination) reaction

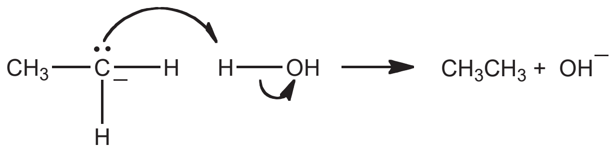
(v) step 3:



step 4:



step 5:



[Total: 21]

2 **(a)** **(i)** Le Chatelier's principle states that when a **system at equilibrium** is subjected to **external disturbance**, the **position of equilibrium will shift** to **counteract the change** imposed to re−establish the equilibrium.

(ii) As [H^+] is increased, the **position of equilibrium shifts to the left** to **reduce [H^+]**, producing **higher concentration of $Cr_2O_7^{2-}$** and turning the solution orange.

(iii) The colour change implies that the **position of equilibrium has shifted** to the **right** to **absorb** some of the **added heat.**

Hence, the forward reaction is **endothermic**.

(iv)

$$K_c = \frac{[CrO_4^{2-}]^2[H^+]^2}{[Cr_2O_7^{2-}]}$$

$$= \frac{[CrO_4^{2-}]^2(10^{-8})^2}{[Cr_2O_7^{2-}]} = 1.31\times10^{-13}$$

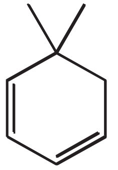
$$\frac{[CrO_4^{2-}]^2}{[Cr_2O_7^{2-}]} = 1310$$

(v) The high ratio of $\frac{[CrO_4^{2-}]^2}{[Cr_2O_7^{2-}]}$ indicates a much **higher proportion of CrO_4^{2-}** compared to $Cr_2O_7^{2-}$.

The solution will appear **yellow**.

(allow for ecf from **(iii)**)

(b) **(i)**

	$(COOH)_2$
A	**C**

(ii) **A** does **not** exhibit ***cis-trans*** **isomerim** because only the *cis*-form can exist due to **ring strain**.

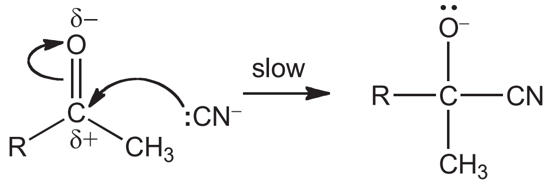
(iii) Compound **B** is a stronger acid than 3,3-dimethylbutanoic acid, because the conjugate base of compound **B** is **more stable** than the conjugate base of 3,3-dimethylbutanoic acid due to the **additional stabilisation of the hydrogen bond formed between the $-COO^-$ group of the mono-anion with the unionised –COOH group.**

(c) nucleophilic addition

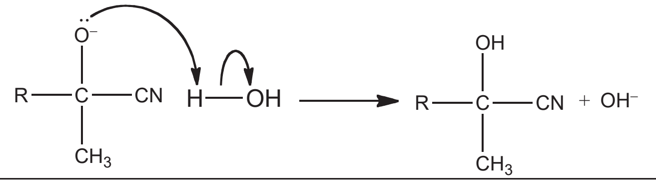
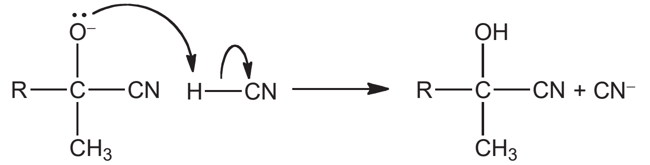
step 1:

NaOH(aq) used	$HCN + OH^- \rightarrow H_2O + CN^-$
NaCN(s) used	$NaCN(s) + aq \rightarrow Na^+(aq) + CN^-(aq)$

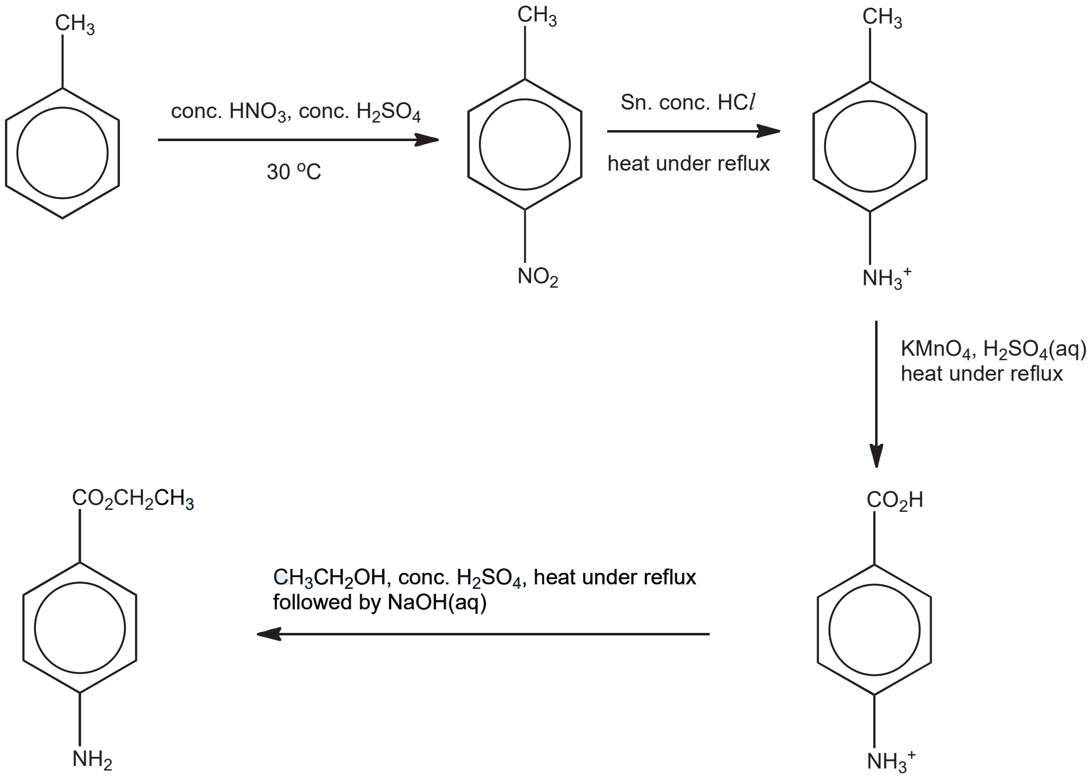
step 2:



step 3:

NaOH(aq) used	
NaCN(s) used	

(d) (i)

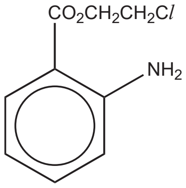


(ii) To a sample of the unknown in a test−tube, add **Br_2(aq)** until in excess.

If the sample is benzocaine, **orange Br_2** will be **decolourised** and a **white precipitate** is formed.
If the sample is methylbenzene, orange Br_2 will **not be decolourised** and **no white precipitate** is formed.

(e) (i) (limited) Cl_2, uv

(ii)



[Total: 21]

3 (a) (i) $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$
$Cu^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Cu(OH)_2(s)$ -------- (1)

NH_3(aq) undergoes **hydrolysis in water** to form OH^-. When a **small amount of NH_3** is added, a **blue precipitate** of **$Cu(OH)_2$** is formed.

$[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 4H_2O(l)$

Addition of **excess ammonia** causes the formation of the more stable **deep blue $[Cu(NH_3)_4(H_2O)_2]^{2+}$** complex ion through a **ligand-exchange reaction**.

The reaction **lowers the concentration of Cu^{2+}(aq)** causing $Cu(OH)_2$ to dissolve. The **position of equilibrium (1) shifts to the left** and the **ionic product < K_{sp}**.

(ii) When NH_3(aq) is added, it reacts with Ag^+ to form $[Ag(NH_3)_2]^+$(aq).
$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq)$

The concentration of Ag^+(aq) decreases and the equilibrium position shifts left and ionic product $[Ag^+][Cl^-]$ becomes lower than K_{sp} ($AgCl$)

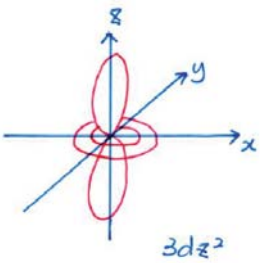
$Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$

As the **K_{sp} of AgBr is lower than K_{sp} of AgCl**, the **ionic product $[Ag^+][Br^-]$ remains higher than K_{sp} of AgBr** upon addition of NH_3(aq). Hence, the precipitate remains insoluble.

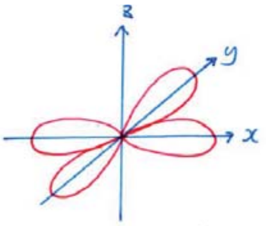
(b) (i) The **energy difference between the 3d and 4s subshells in Fe is relatively small**.

This means with sufficient energy, **both the 4s and some / all of the inner 3d electrons can be removed** to form stable compounds and ions of various oxidation states.

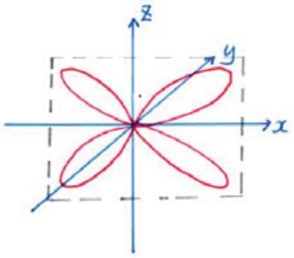
(ii) Fe^{3+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$



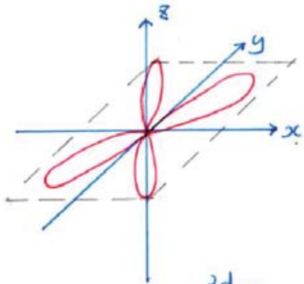
3d$_{z^2}$



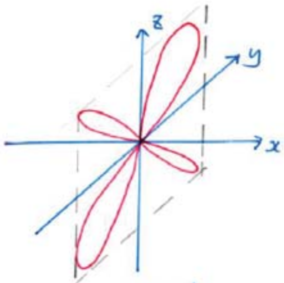
3d$_{x^2-y^2}$



3d$_{xz}$



3d$_{xy}$



3d$_{yz}$

(iii) As the lobes of the 3d$_{x^2-y^2}$ and 3d$_{z^2}$ orbitals lie along the axes, the electrons in these two d-orbitals are pointing towards the lone pairs of electrons of the ligands in an octahedral complex.
Repulsion between the lone pair of electrons of the ligands and the 3*d* electrons in these orbitals is stronger. Thus, 3d$_{x^2-y^2}$ and 3d$_{z^2}$ orbitals form the higher energy set.

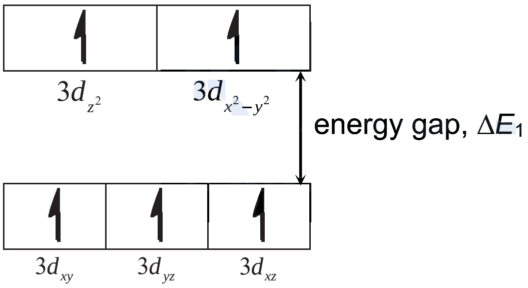
As the 3d orbitals in Fe^{3+} are **partially filled**, d-d transition, where the **electron is promoted from a lower energy orbital to a higher energy orbital**, is possible.

Energy that corresponds to the frequency of light in the visible region of the electromagnetic spectrum is absorbed. Colours that are complementary to those frequency of light absorbed are seen.

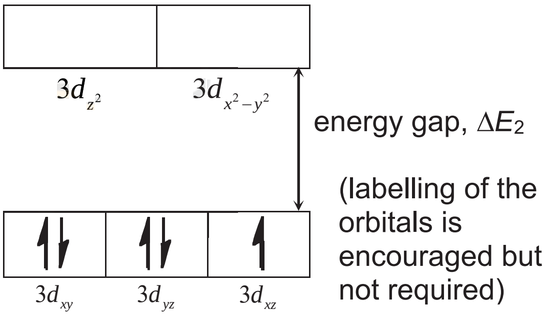
(iv) The **red complex absorbs visible light in the blue region** while the blue complex absorbs in the red region,

i.e. the red complex absorbs light with a shorter wavelength, and so **the red complex has a larger energy gap** between the d-orbitals.

(v) high spin state for the blue complex



low spin state for the red complex



(labelling of the orbitals is encouraged but not required)

- [1] for each correctly drawn spin state
- [1] for indicating the energy gap size in the diagram such that $\Delta E_1 < \Delta E_2$

[Total: 18]

4 **(a) (i)** Benzaldehyde is simultaneously oxidised to benzoic acid and reduced to phenylmethanol.

(Or carbon is simultaneously oxidised as its oxidation state is increased from +1 in benzaldehyde to +3 in benzoic acid and reduced, as its oxidation state is decreased from +1 in benzaldehyde to −1 in phenylmethanol.)

(ii) Comparing experiments 1 and 2, concentration of C_6H_5CHO is kept constant, when concentration of KOH doubles, the rate doubles. Hence order of reaction with respect to KOH is 1.

Comparing experiments 2 and 3, as the order w.r.t. KOH is one, when the concentration of KOH is doubled, the rate should be doubled. However, when both the concentration of KOH and C_6H_5CHO is doubled, the rate increased by 8 times. This means that when the concentration of C_6H_5CHO is doubled, the rate is quadrupled. Hence order of reaction with respect to C_6H_5CHO is 2.

(iii) rate = $k\,[C_6H_5CHO]^2[KOH]$

For experiment 1: k = **0.0127 mol^{-2} dm^6 s^{-1}**
For experiment 2: k = **0.0122 mol^{-2} dm^6 s^{-1}**
For experiment 3: k = **0.0128 mol^{-2} dm^6 s^{-1}**

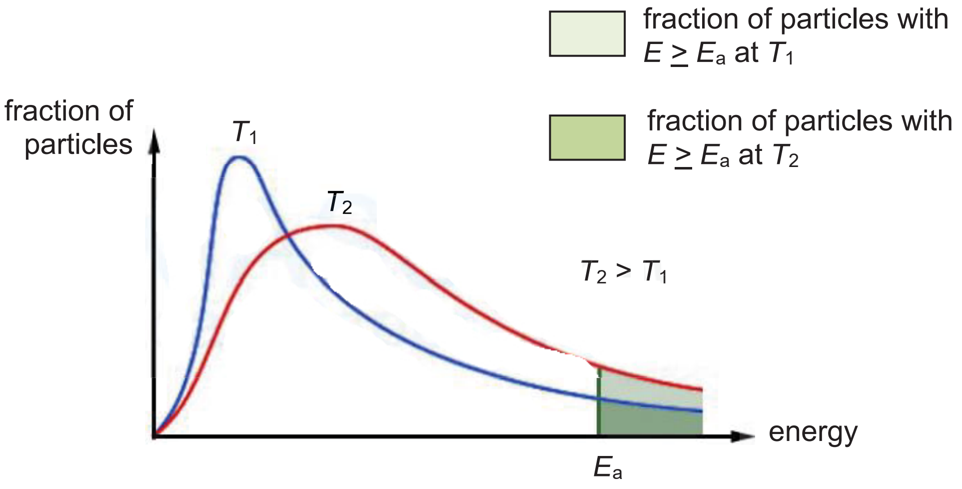
- [1] for any one out of the three

(iv) rate = k' [KOH] where $k' = k[C_6H_5CHO]^2$

$$t_{½} = \frac{\ln 2}{k[C_6H_5CHO]^2} = \frac{\ln 2}{(0.012667)(1.60)^2} = 21.4\text{ s}$$

(v) When temperature increases, **molecular speed and average kinetic energies of reactant particles increases.** Hence, there will be a **higher frequency of collisions and** a **greater fraction** of the particles will have energy **greater than the activation energy** required for reaction. This will lead to a **higher frequency of effective collisions**.

The **rate constant *k* increases** as the temperature increases, hence **rate of reaction increases.**



(b) (i) LiA/H4 in dry ether / $NaBH_4$ in methanol, room temperature

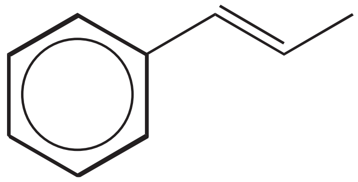
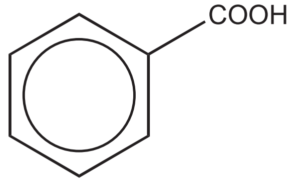
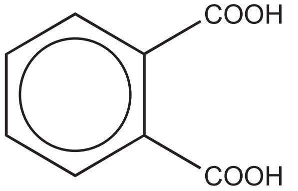
(ii) $KMnO_4$ / $K_2Cr_2O_7$, dilute H_2SO_4, reflux

(c)

test	benzaldehyde	phenylmethanol
anhydrous PCl_5 / $SOCl_2$	no white fumes	white fumes
Tollens' regent, warm	silver mirror	no silver mirror
2,4-DNPH	orange precipitate	no orange precipitate
Na	no effervescence	effervescence and the gas evolved 'pops' with a lighted splint

[1] for correct reagents and conditions, and [1] for correct observations for both benzaldehyde and phenylmethanol

(d)

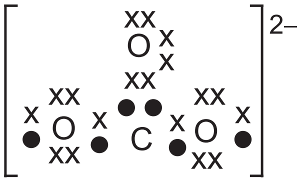
		
R	**T**	**U**

[1] for each correct structure

information	deduction
R exhibits stereoisomerism.	**R** exhibits **cis-trans isomerism** (it cannot exhibit enantiomerism as the side chain contains only three C-atoms). **R contains C=C group** (with two different groups attached to each C-atom)
R is found to decolourise orange aqueous bromine but **S** does not.	**R** undergoes **electrophilic addition** with aqueous bromine. **R contains C=C group**
When hot acidified potassium managate solution is added to 1 mol of **R** and **S,** both decolourised the purple potassium managate to form compound **T** and **U** respectively.	**R** and **S** undergoes **oxidation** Presence of benzylic H on both **R** and **S** both **T** and **U contains −COOH group**
1.0 mol of compound **T** exactly reacts with 0.5 mol of sodium carbonate while compound 1.0 mol of compound **U** reacts with exactly 1.0 mol of sodium carbonate to give out carbon dioxide gas.	**T** and **U** undergoes **neutralisation** reaction with sodium carbonate. **T** contains **one −COOH group** **U** contains **two −COOH groups**

[Total: 20]

5 (a) (i)



(ii) trigonal planar

the **3 bond pairs and 0 lone pair** of electrons **will space themselves out as far apart as possible to minimise repulsion**.

(b) (i) The reaction between Na_2CO_3 and HC*l* is an acid-base reaction as HC*l* functions as a **Bronsted acid** and **donates** a **proton** to Na_2CO_3. Hence, Na_2CO_3 functions as a **Bronsted base** and **accepts** a **proton** from HC*l*.

(ii) $HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$

The pH is weakly basic as HCO_3^- undergoes hydrolysis in water to produce OH^-.

(c) When **a small amount of acid** is added,
$HCO_3^-(aq) + H_3O^+(aq) \rightarrow H_2CO_3(aq) + H_2O(l)$

When **a small amount of alkali** is added:
$H_2CO_3(aq) + OH^-(aq) \rightarrow HCO_3^-(aq) + H_2O(l)$

(d) (i) Ideal gas particles take up zero (or negligible) volume (as compared to the volume of the container)

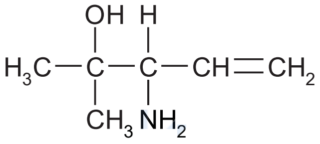
There are no (or negligible) intermolecular forces of attraction between the particles of an ideal gas.

(ii) pV = nRT
$1.1 \times 101325 \times 56.0 \times 10^{-6} = n \times 8.31 \times (30 + 273)$
No. of moles of CO_2 produced = **2.4789×10^{-3} mol**

No. of moles of $Na_2CO_3 = 2.4789 \times 10^{-3}$ mol
$[Na_2CO_3] = [(2.4789 \times 10^{-3}) \div 0.02]$ = **0.124 mol dm^{-3}**

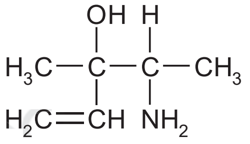
(e)

G is:



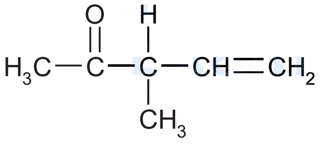
$H_3C-C(OH)(CH_3)-CH(NH_2)-CH=CH_2$

(but also accept:



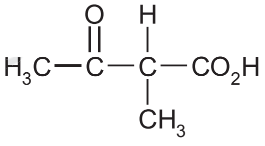
$H_3C-C(OH)(CH=CH_2)-CH(NH_2)-CH_3$)

H is:



$H_3C-C(=O)-CH(CH_3)-CH=CH_2$

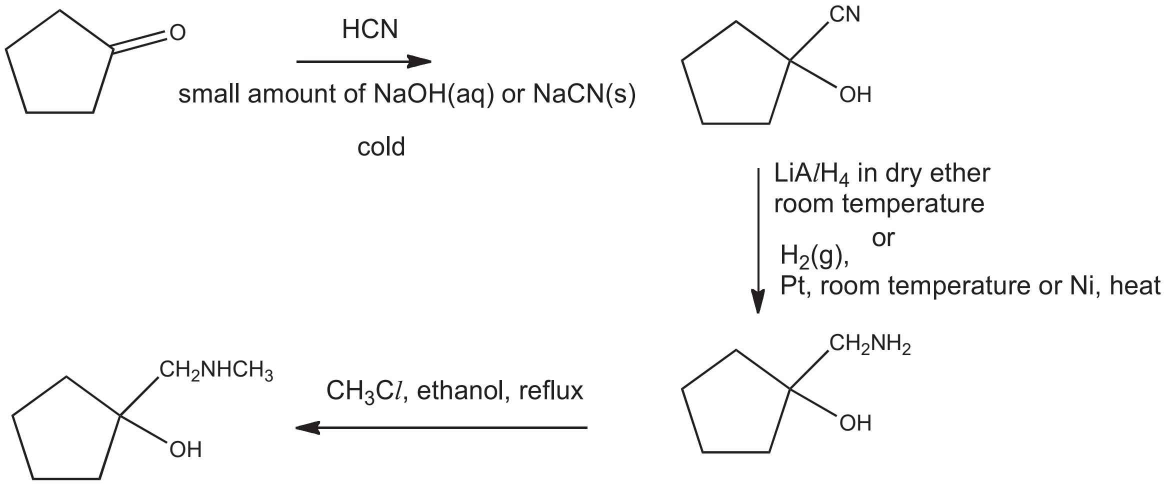
J is:



$H_3C-C(=O)-CH(CH_3)-CO_2H$

information	deduction
H produces a yellow precipitate with iodine in alkaline solution.	**H** undergoes **oxidation**. **H** contains **CH_3CO- group**.
Treatment of **H** with hot acidified solution of potassium maganate(VII) produces **J,** $C_5H_8O_3$, along with a gas that forms white precipitate in limewater.	**H** undergoes **oxidation (or oxidative cleavage)** with hot acidified potassium maganate(VII) to produce $CO_2(g)$ **H** contains a **terminal alkene**
H was also observed to be able to readily decolourise bromine in tetrachloromethane	**H** undergoes **electrophilic addition** with Br_2 in CCl_4 **H** contains a **alkene**

(f)



[Total: 20]

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

1 Determination of the concentration of sodium thiosulfate in solution Z

Sodium thiosulfate is commonly used in an alternative method for the extraction of gold from its ores, through the formation of a stable and soluble complex of gold(I) ions, $[Au(S_2O_3)_2]^{3-}$. One of your tasks is to determine the concentration of sodium thiosulfate in a commercially produced solution **Z** used in the extraction process.

Solution **Z** contains sodium thiosulfate in deionised water. You are not provided with solution **Z**, as it is too concentrated for use in this experiment. A diluted solution of **Z** has been prepared for you. This diluted solution is **FA 5**.

FA 1 is 0.0230 mol dm^{-3} of aqueous potassium iodate(V), KIO_3
FA 2 is 0.50 mol dm^{-3} potassium iodide, KI
FA 3 is 0.75 mol dm^{-3} sulfuric acid, H_2SO_4
FA 4 is a solution of sodium thiosulfate, $Na_2S_2O_3$ of an unknown concentration
FA 5 a diluted solution of **Z**, in which 31.00 cm^3 of solution **Z** was made up to 250 cm^3 with deionised water in a volumetric flask

You are also provided with starch solution.

In acidic medium, iodate(V) ions oxidise iodide ions to iodine

$$IO_3^-(aq) + 5I^-(aq) + 6H^+(aq) \rightarrow 3I_2(aq) + 3H_2O(l) \qquad \textbf{reaction 1}$$

If an excess of sodium thiosulfate is present in the reaction mixture, the iodine produced in **reaction 1** is immediately reduced back to iodide ions, as shown in **reaction 2**, and the dark brown colour of iodine does not form.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq) \qquad \textbf{reaction 2}$$

In the experiments that you will perform, insufficient volumes of the first sodium thiosulfate solution will be added initially, and some iodine will remain in the solution. The amount of iodine left-over can be determined by titration with the second solution of sodium thiosulfate, as shown in **reaction 2**.

You will prepare a number of reaction mixtures, each of which will contain:

- a fixed volume of **FA 1**,
- excess amounts of **FA 2** and **FA 3**,
- a different volume of **FA 4**.

All reaction mixtures will contain some iodine, produced in **reaction 1**, that will be titrated against the **FA 5** solution.

You are required to use a graphical method to determine the concentrations of sodium thiosulfate in **FA 4**, **FA 5** and solution **Z**.

(a) Titration of iodine produced against FA 5

Note: You will perform each titration only **once**. Great care must be taken to ensure that you do not overshoot the end-point.

You will be using two burettes in this task, and each of the burette will contain different sodium thiosulfate solutions, so care must be taken that the right one is used each time.

(i) Experiment 1

1. Fill the burette labelled "**FA 4**" with **FA 4** solution.
2. Fill the burette labelled "**FA 5**" with **FA 5** solution.
3. Using a pipette, transfer 25.0 cm^3 of **FA 1** into a 250 cm^3 conical flask.
   From the burette, transfer 9.50 cm^3 of **FA 4** to the same conical flask.

   If you accidentally added an incorrect volume of **FA 4** for any of your titrations, record the actual volume of **FA 4** added in your table on the next page, and use that volume for the plotting of the graph later
4. Use appropriate measuring cylinders to add to this flask:
   - 10 cm^3 of **FA 2**,
   - 10 cm^3 of **FA 3**.
5. Titrate the iodine liberated with **FA 5** until the solution fades to a pale yellow colour.
6. Add about 1 cm^3 (about 10 drops) of starch indicator to this flask. Continue adding **FA 5** until the blue-black colour **just** disappears.
7. Record your titration results in the section "Recording" on page 3. Make sure that your recorded results show the precision of your working.

(ii) Experiment 2

8. Repeat steps 3 to 8 but add 22.00 cm^3 of **FA 4** at step 4.

(iii) Experiment 3 to 5

9. Choose three further volumes of **FA 4** between 9.50 cm^3 and 22.00 cm^3.
10. Repeat steps 3 to 8 using each of your chosen volumes of **FA 4** at step 4.

Recording

Prepare a table in the space provided on the next page to record:

- the volumes of **FA 4** added for each experiment.
- the burette readings and the volumes of **FA 5** used for each experiment.

Table of results

Titration number		**1**	**3**	**4**	**5**	**2**
Volume of **FA 4**	/cm^3	**9.50**	**12.50**	**15.50**	**18.50**	**22.00**
Final burette reading	/cm^3	31.30	28.75	24.10	44.90	46.80
Initial burette reading	/cm^3	0.10	1.00	0.00	24.10	30.00
Volume of **FA 5** added	/cm^3	31.20	27.75	24.10	20.80	16.80

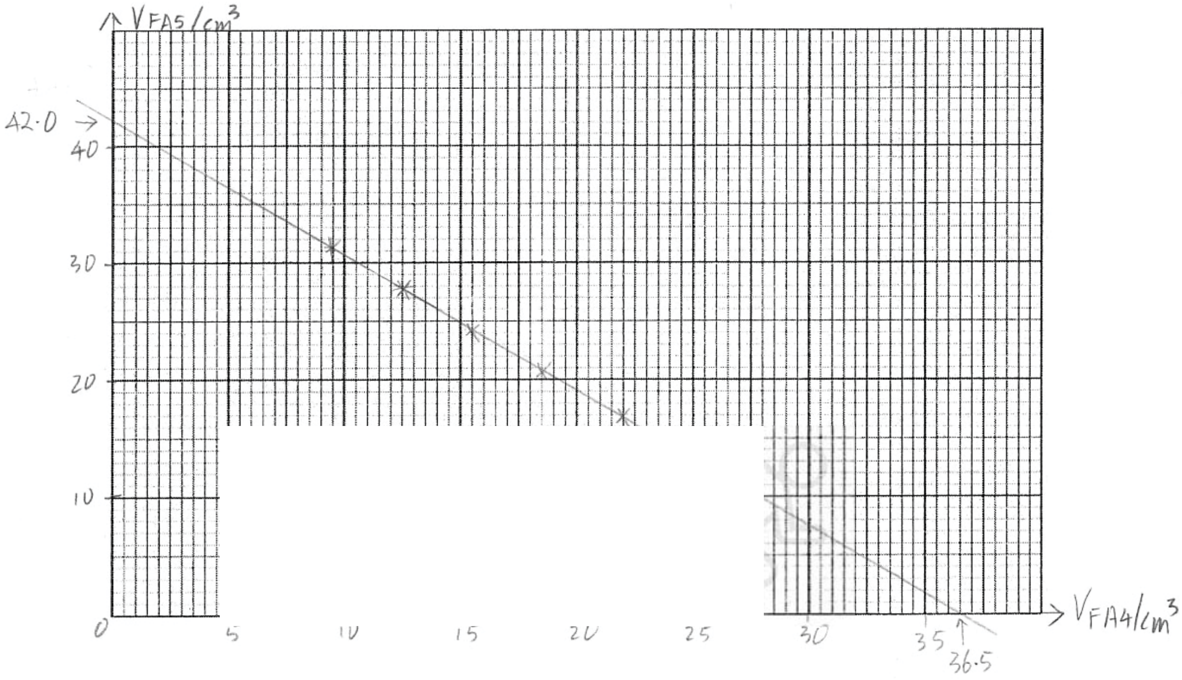
[4]

(b) Graphical determination to determine concentration of sodium thiosulfate in FA 4, FA 5 and solution Z.

(i) Plot a graph of the volume of **FA 5** added (*y-axis*) against the volume of **FA 4** added (*x-axis*) on the grid below. When choosing the scale, you should ensure that the graph line can be extrapolated to intersect both the *x-axis* and the *y-axis*.

Draw a straight line of best fit, taking into account all of your plotted points.

Extrapolate your graph line so that it intersects both the *x-axis* and the *y-axis*.



[3]

(ii) It is possible to react all the iodine produced by the reaction between 25.0 cm^3 of **FA 1** and 10 cm^3 of **FA 2** and **FA 3** by using **FA 4** only.

From your graph, determine the volume of **FA 4** required to do this.

volume of **FA 4** required = 36.5 cm^3 [3]

(iii) Calculate the gradient of your graph line, showing clearly how you did this.

gradient = $\frac{0-42.0}{36.5-0} = -1.1507 = -1.15$

gradient = −1.15 [1]

(c) Calculations

(i) The amount of iodate(V) ions, IO_3^-, present in 25.0 cm^3 of **FA 1** is 5.75 × 10^{-4} mol.

Use this value, together with data obtained from your graph, to calculate the concentration of thiosulfate ions in **FA 4**.

Number of moles of iodine produced = $3 \times n_{IO_3^-} = 3 \times 5.75 \times 10^{-4} = 1.725 \times 10^{-3}$ mol

Number of moles of $S_2O_3^{2-}$ required = $2 \times n_{I_2} = 2 \times 1.725 \times 10^{-3} = 3.45 \times 10^{-3}$ mol

concentration of $S_2O_3^{2-}$ in **FA4** = $\frac{n_{S_2O_3^{2-}}}{V_{\mathbf{FA4}}} = \frac{3.45 \times 10^{-3}}{36.5 \times 10^{-3}} = 0.094521 = 0.0945 \text{ mol dm}^{-3}$

[$S_2O_3^{2-}$] in **FA 4** = 0.0945 mol dm^{-3} [2]

(ii) The concentration of $S_2O_3^{2-}$ in **FA 4** and **FA 5** are related to the gradient of the graph obtained in **(b)(iii)** by the following equation:

$$[S_2O_3^{2-}]_{\mathbf{FA\,5}} = \frac{[S_2O_3^{2-}]_{\mathbf{FA\,4}}}{|\text{gradient}|}$$

Using the equation, or otherwise, calculate the concentration of thiosulfate ions in **FA 5**.

$$[S_2O_3^{2-}]_{\mathbf{FA5}} = \frac{[S_2O_3^{2-}]_{\mathbf{FA4}}}{|\text{gradient}|} = \frac{0.094521}{1.1507} = 0.082142 = 0.0821 \text{ mol dm}^{-3}$$

[$S_2O_3^{2-}$] in **FA 5** = 0.0821 mol dm^{-3} [1]

(iii) Calculate the concentration of thiosulfate ions in the commercially produced solution **Z**.

$$[S_2O_3^{2-}]_z \times 31.00\times10^{-3} = [S_2O_3^{2-}]_{\mathbf{FA5}} \times 250\times10^{-3}$$

$$\Rightarrow [S_2O_3^{2-}]_{\mathbf{z}} = \frac{[S_2O_3^{2-}]_{\mathbf{FA5}}\times 250\times10^{-3}}{31.00\times10^{-3}} = \frac{0.082142\times 250\times10^{-3}}{31.00\times10^{-3}} = 0.662 \text{ mol dm}^{-3}$$

$[S_2O_3^{2-}]$ in solution **Z** = 0.622 mol dm^{-3} [1]

(d) A student suggested using burettes, rather than using measuring cylinders, to measure the volume of **FA 2** and **FA 3** used in **(a)** so as to improve on the accuracy of the titration data.

State whether you agree with the student and briefly explain why.

No. Since both solutions are in excess, using a burette (which has a higher precision than measuring cylinders) does not improve the accuracy of the experiment.

[1]

(e) In a private institution, a laboratory assistant made the mistake in the preparation of the **FA 5** solution by diluting 21.00 cm^3 of solution **Z** to 250 cm^3, rather than the specified volume of 31.00 cm^3.

State and explain how using this incorrect sample of **FA 5** will affect the gradient of your graph.

As the concentration of $S_2O_3^{2-}$ in the incorrect sample of **FA 5** will be **lower** than the intended value, and since $[S_2O_3^{2-}]_{\mathbf{FA\,5}} = \frac{[S_2O_3^{2-}]_{\mathbf{FA\,4}}}{|\text{gradient}|}$, the **magnitude of the gradient** will be **larger**.

Or

As the concentration of $S_2O_3^{2-}$ in the incorrect sample of **FA 5** will be lower than the intended value, a larger volume of **FA 5** would be required for each titration, leading to a larger magnitude for the gradient.

[1]

[Total: 17]

2 Determination of the enthalpy change for the thermal decomposition of sodium hydrogen carbonate

FA 6 is solid anhydrous sodium carbonate, Na_2CO_3
FA 7 is solid sodium hydrogen carbonate, $NaHCO_3$

You will need access to the **FA 3** solution that you have used earlier.

Sodium hydrogen carbonate is commonly used as a raising agent in baking, as it undergoes thermal decomposition at temperatures above 80 °C, according to the equation:

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(l) \qquad \textbf{reaction 1}$$

Due to the high temperature involved, the enthalpy change of this reaction cannot be measured directly using a coffee-cup calorimeter.

In the experiments that you will perform, the coffee-cup calorimeter will be used to determine the enthalpy change, ΔH_2, for the reaction:

$$Na_2CO_3(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + CO_2(g) + H_2O(l) \qquad \textbf{reaction 2}$$

and the enthalpy change, ΔH_3, for the reaction:

$$2NaHCO_3(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2CO_2(g) + 2H_2O(l) \qquad \textbf{reaction 3}$$

You will then use your results of your experiments to calculate the enthalpy change, ΔH_1, for the thermal decomposition of sodium hydrogen carbonate.

(a) Determining enthalpy change for the reaction between Na_2CO_3 and H_2SO_4, ΔH_2

1. Place the styrofoam cup inside a 250 cm^3 beaker to prevent it from toppling over.
2. Using a measuring cylinder, place 40 cm^3 of **FA 3** into the styrofoam cup.
3. Stir the solution in the cup gently with the thermometer, and measure its temperature. Record the initial temperature of **FA 3** in your table.
4. Weigh the weighing bottle labelled "**FA 6**" and its contents using a weighing scale, without the cap. The bottle has been pre-weighed to contain between 4.50 g and 5.00 g of solid sodium carbonate.
5. Pour **FA 6** from the weighing bottle into the styrofoam cup, place the lid onto the cup, and insert the thermometer through the lid.
6. Stir the mixture using the thermometer and record the maximum temperature reached.
7. Reweigh the weighing bottle.

(i) In an appropriate format in the space below, record:

- all mass readings, including the mass of **FA 6** added to the styrofoam cup
- all temperatures measured and the temperature rise.

Mass of weighing bottle and **FA 6**	/ g	8.104
Mass of weighing bottle and residual **FA 6**	/ g	3.542
Mass of **FA 6** added to the styrofoam cup	/ g	4.562
Initial temperature of **FA 3**	/ °C	30.2
Maximum temperature reached	/ °C	39.2
Temperature rise	/ °C	9.0

[1]

(ii) Calculate the heat change for **reaction 2**.

Assume that the specific heat capacity of the final solution is 3.75 J g^{-1} K^{-1} and that its density is 1.00 g cm^{-3}.

$$q = (40.0 \times 1.00) \times 3.75 \times 9.0 = 1350 \text{ J} = 1.35 \text{ kJ}$$

heat change = 1.35 kJ [1]

(iii) By calculating the number of moles of each reagent that was added to the styrofoam cup, and with reference to the equation for the reaction, show which of the reagents, **FA 3** or **FA 6**, is added in excess.

[A_r: Na, 23.0; C, 12.0; O, 16.0]

$$n_{H_2SO_4} = 0.75 \times 40.0 \times 10^{-3} = 0.0300 \text{ mol}$$

$$n_{Na_2CO_3} = \frac{4.562}{2(23.0) + 12.0 + 3(16.0)} = \frac{4.562}{106.0} = 0.043038 \text{ mol}$$

From the balanced equation, $\frac{n_{H_2SO_4}}{n_{Na_2CO_3}} = \frac{1}{1}$,

0.0300 mol of H_2SO_4 will require only 0.0300 mol of Na_2CO_3 for complete reaction, and since the number of moles of Na_2CO_3 added is more than 0.0300 mol, Na_2CO_3 is added in excess.

reagent added in excess = Na_2CO_3 [1]

(iv) Calculate enthalpy change for **reaction 2**, ΔH_2:

$$Na_2CO_3(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + CO_2(g) + H_2O(l)$$

$$\Delta H_{rxn} = -\frac{1.35}{0.0300} = -45.0 \text{ kJ mol}^{-1}$$

ΔH_2 = −45.0 kJ mol^{-1} [1]

(b) **Determining enthalpy change for the reaction between $NaHCO_3$ and H_2SO_4, ΔH_2**

1. Empty and rinse the styrofoam cup used in **(a)**, and replace the cup in the 250 cm^3 beaker.
2. Using the same measuring cylinder used in **(a)**, place 40 cm^3 of **FA 3** into the styrofoam cup.
3. Wash and dry the thermometer used in **(a)**, before using it to stir the solution in the cup gently, and measure its temperature. Record the initial temperature of **FA 3** in your table.
4. Weigh the weighing bottle labelled "**FA 7**" and its contents using a weighing scale, without the cap. The bottle has been pre-weighed to contain between 3.50 g and 4.00 g of solid sodium hydrogen carbonate.
5. Pour **FA 7** from the weighing bottle into the styrofoam cup, place the lid onto the cup, and insert the thermometer through the lid.
6. Stir the mixture using the thermometer and record the minimum temperature reached.
7. Reweigh the weighing bottle.

(i) In an appropriate format in the space below, record:

- all mass readings, including the mass of **FA 7** added to the styrofoam cup
- all temperatures measured and the temperature fall.

Mass of weighing bottle and **FA 7**	/ g	7.428
Mass of weighing bottle and residual **FA 7**	/ g	3.463
Mass of **FA 7** added to the styrofoam cup	/ g	3.965
Initial temperature of **FA 3**	/ °C	30.2
Minimum temperature reached	/ °C	37.8
Temperature fall	/ °C	7.6

[3]

(ii) Calculate the heat change for **reaction 3**.

Assume that the specific heat capacity of the final solution is 3.75 J g^{-1} K^{-1} and that its density is 1.00 g cm^{-3}.

$$q = (40.0 \times 1.00) \times 3.75 \times 7.6 = 1140 \text{ J} = 1.14 \text{ kJ}$$

heat change = 1.14 kJ [1]

(iii) By calculating the number of moles of each reagent that was added to the styrofoam cup, and with reference to the equation for the reaction, show which of the reagents, **FA 3** or **FA 7**, is added in excess.

[A_r: Na, 23.0; H, 1.0; C, 12.0; O, 16.0]

$$n_{H_2SO_4} = 0.75 \times 40.0 \times 10^{-3} = 0.0300 \text{ mol}$$

$$n_{NaHCO_3} = \frac{3.965}{23.0 + 1.0 + 12.0 + 3(16.0)} = \frac{3.965}{84.0} = 0.047202 \text{ mol}$$

From the balanced equation, $\frac{n_{H_2SO_4}}{n_{NaHCO_3}} = \frac{1}{2}$,

0.0300 mol of H_2SO_4 will require 0.0600 mol of $NaHCO_3$ for complete reaction, and since the number of moles of $NaHCO_3$ added is less than 0.0600 mol, H_2SO_4 is added in excess.

reagent added in excess = H_2SO_4 [1]

(iv) Calculate enthalpy change for **reaction 3**, ΔH_3:

$$2NaHCO_3(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2CO_2(g) + 2H_2O(l)$$

$$\Delta H_{rxn} = +\frac{1.14}{0.047202} \times 2 = +48.303 = +48.3 \text{ kJ mol}^{-1}$$

ΔH_3 = +48.3 kJ mol^{-1} [1]

(c) Use your answer to **(a)(iv)** and **(b)(iv)** to calculate enthalpy change for **reaction 1**, ΔH_1:

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(l)$$

$$\begin{tikzcd}
2NaHCO_3(s) \arrow[rr, "\Delta H_1"] \arrow[dr, "\Delta H_3"', "+ H_2SO_4(aq)"] & & Na_2CO_3(s) + CO_2(g) + H_2O(l) \arrow[dl, "\Delta H_2"', "+ H_2SO_4(aq)"] \\
& Na_2SO_4(aq) + 2CO_2(g) + 2H_2O(l) &
\end{tikzcd}$$

Hence, $\Delta H_1 = \Delta H_3 - \Delta H_2 = +48.303 - (-45.0) = +93.303 = +93.3 \text{ kJ mol}^{-1}$

ΔH_1 = +93.3 kJ mol^{-1} [4]

(d) In **(a)**, one of the significant sources of errors that will affect the accuracy of the enthalpy change for the reaction between Na_2CO_3 and H_2SO_4, ΔH_2, is that the heat capacity of the styrofoam cup is not taken into account.

Explain the effect of this error on your calculated value of ΔH_2.

As some of the **heat produced** in the reaction **is absorbed** by the styrofoam cup, the **maximum temperature** measured is **lower** than expected, and so the **magnitude** of ΔH_2 calculated will be **lower** than the theoretical value

[1]

[Total: 15]

3 Planning

A sample of solid anhydrous sodium carbonate is believed to be contaminated with 5 to 10% of sodium chloride, NaC*l*.

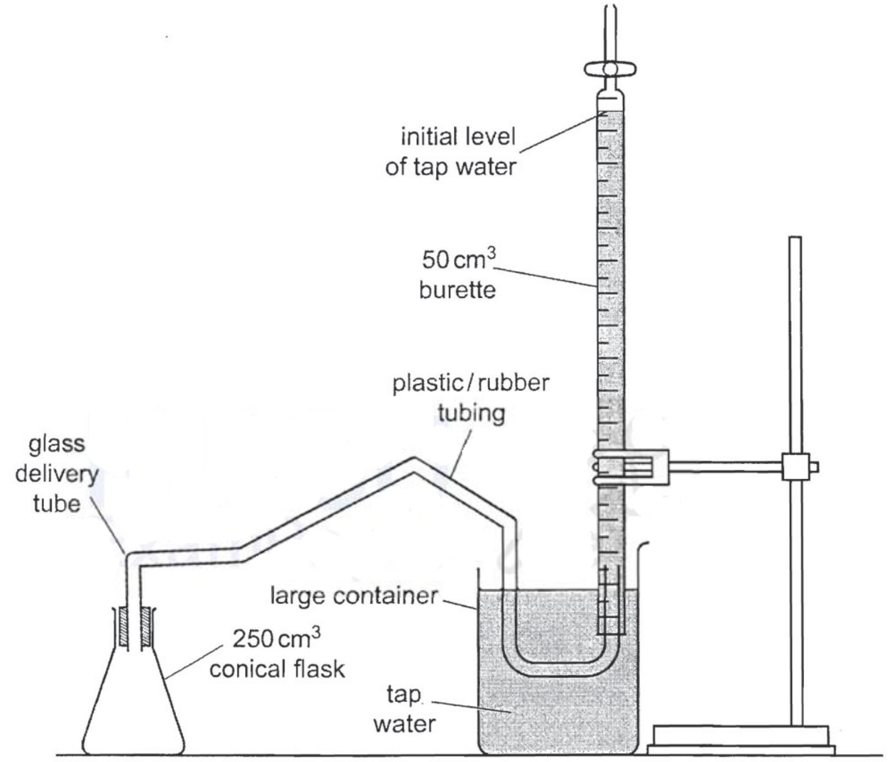
The percentage purity of sodium carbonate in the sample can be determined by measuring the volume of carbon dioxide formed when sodium carbonate is reacted with an excess of sulfuric acid.

$$Na_2CO_3(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + CO_2(g) + H_2O(l)$$

You are to plan an experiment that will enable you to:

- react a pre-weighed impure sample of sodium carbonate with a pre-determined volume of the **FA 3** solution that you have used earlier for Question 1 and 2,
- collect and measure the volume of the carbon dioxide gas evolved.

(a) Draw a diagram of the apparatus that you would use to carry out this experiment.



[2]

(b) By considering the capacity of the apparatus that you have drawn in **(a)** to measure the volume of the carbon dioxide gas, calculate the maximum mass of the impure sample of sodium carbonate that you would use in your experiment.

[A_r: Na, 23.0; C, 12.0; O, 16.0 and 1 mole of gas occupies a volume of 24.0 dm^3 under the conditions present in the laboratory]

Taking the maximum volume of $CO_2(g)$ collected to be 50 cm^3,

$$n_{CO_2} = \frac{50}{24000} = 2.0833 \times 10^{-3} \text{ mol}$$

$$\Rightarrow n_{Na_2CO_3} = 2.0833 \times 10^{-3} \text{ mol}$$

$$m_{Na_2CO_3} = 2.0833 \times 10^{-3} \times \{2(23.0) + 12.0 + 3(16.0)\} = 2.0833 \times 10^{-3} \times \{106.0\} = 0.22083 = 0.221 \text{ g}$$

maximum mass of impure sample of sodium carbonate used = 0.221 g [2]

(c) A student suggested that 40.0 cm^3 of **FA 3** solution is sufficient for the experiment.

State whether you agree with the student, and explain your answer.

Yes, I agree with the student. The number of moles of H_2SO_4 present in 40.0 cm^3 of **FA 3** {0.0300 mol, calculated in **2(a)(iii)** and **2(b)(iii)**} is more than enough to react with the amount of Na_2CO_3 calculated in **3(b)**.

[1]

(d) Describe briefly how you would ensure that all the carbon dioxide gas given off in the reaction between the impure sample of sodium carbonate and **FA 3** solution was collected and that none escaped from the apparatus.

Place the weighed sample of sodium carbonate in the conical flask, and stopper the flask. Introduce the measured volume of **FA 3** solution using a thistle funnel (the volume of **FA 3** introduced need to be subtracted from the volume of gas collected).

or

Place the weighing bottle that contains the weighed sample of sodium carbonate (carefully) into the conical flask that contains the measured volume of **FA 3** solution. Stopper the conical flask. Tilt the conical flask such that the weighing bottle is tipped over in order to start the reaction.

[1]

(e) Other than this method that involves the collection of carbon dioxide gas, the percentage purity of sodium carbonate in the sample can also be determined using a titration.

In a typical experiment, a pre-weighed mass of the impure sample of sodium carbonate is dissolved in water and made up to 250 cm^3 in a volumetric flask, and 25.0 cm^3 of this solution is titrated against a standard solution of hydrochloric acid using methyl orange as indicator.

State which of the two methods you would expect to give the more accurate results. Explain your choice.

Titration method.

Source of error for the collection of CO_2 gas method:

- The volume of the CO_2 gas may not be measured under standard conditions (the volume collected will be lower than the actual volume produced, as the gas syringe may not be perfectly frictionless; or the volume measured will be higher than the actual volume as the water level inside the burette is higher than the water level in the beaker for the downward displacement of water).

Other sources of errors if downward displacement of water method was used:

- CO_2 gas is slightly soluble in water (the volume collected will be lower than the actual volume produced, as some of the CO_2 produced may be dissolved in the water used for downward displacement of water).
- The rubber tubing contains a certain volume of water at the start of the experiment that must first be displaced before the CO_2 gas can be collected (the volume collected will be lower than the actual volume produced).

[2]

[Total: 8]

4 Inorganic Qualitative Analysis

You are provided with **FA 8**, which is a mixture of two solids, **FA 9**, which is soluble in water and **FA 10**, which is insoluble in water. Each contains **one cation** and **one anion** from the lists on page 16 and 17.

In this question you will perform a series of test-tube reactions, make observations and deduce the identities of the cations and anions present in **FA 9** and **FA 10**.

If the evolution of a gas is observed at any stage, the gas should be tested and identified.

You are advised that the reagent should be added gradually in all tests, with shaking after each addition.

If it appears that no reaction has taken place, this should be clearly recorded.

(a) Tests on FA 8

Perform the test-tube experiments described below and record your observations in the spaces provided in the table.

	Test	**Observations**
(i)	Place all of the solid, **FA 8**, into a 100 cm^3 beaker. Add 25 cm^3 of distilled water and warm to dissolve the **FA 9**. Filter the mixture and use the filtrate for tests **(a)(ii)** to **(a)(iv)**. Wash the residue, **FA 10**, and use it for tests **(a)(v)** to **(a)(vii)**.	A green residue **[✓1]** and a colourless filtrate was obtained **[✓2]**.

Tests on Filtrate, FA 9

	Test	**Observations**
(ii)	Place about 1 cm depth of **FA 9** into a test-tube. Add a few drops of dilute sulfuric acid.	A white ppt is formed **[✓3]**.
(iii)	Place about 1 cm depth of **FA 9** into a test-tube. Add a few drops of aqueous barium chloride,	No ppt is formed **[✓4]**.
	followed by a few drops of dilute hydrochloric acid.	No ppt is formed / no gas is produced **[✓5]**.
(iv)	Place about 1 cm depth of **FA 9** into a test-tube. Add a few drops of aqueous silver nitrate.	A white ppt is formed **[✓6]**.
	followed by a few drops of aqueous ammonia.	The ppt dissolves to give a colourless solution **[✓7]**.

Tests on Residue, FA 10

	Test	**Observations**
(v)	Using a spatula, transfer as much of the residue on the filter paper as you can into a test-tube. Add dilute sulfuric acid drop-wise into the test-tube to dissolve the residue. Filter if necessary. Use the resultant solution for test **(a)(vi)** and **(a)(vii)**.	Effervescence produced **[✓8]**, the gas gives white ppt with limewater **[✓9]**. A pale green / blue solution is produced **[✓10]**.
(vi)	Place about 1 cm depth of the **filtrate** from **(a)(v)** in a test-tube. Add aqueous sodium hydroxide drop-wise with shaking, until no further change is seen.	A (pale) blue ppt is formed that is insoluble in excess NaOH(aq) **[✓11]**.
(vii)	Place about 1 cm depth of the **filtrate** from **(a)(v)** into a test-tube. Add aqueous ammonia, drop-wise with shaking, until no further change is seen.	A blue ppt is formed **[✓12]** that is soluble in excess NH_3(aq) to form a dark blue solution **[✓13]**.

[5]

(b) Based on your observations to **(a)(ii)**, suggest a possible identity of the cation in **FA 9**.

cation in **FA 9**: Ba^{2+} [1]

(c) From your remaining observations, state the identities of the one anion in both **FA 9** and **FA 10**, and the one cation in **FA 10**.

In each case, give evidence to support your conclusion.

	identity		evidence
FA 9	anion:	Cl^-	A white ppt is formed with $AgNO_3$(aq), that is soluble in NH_3(aq) in **(a)(iv)**.
FA 10	cation:	Cu^{2+}	A (pale) blue ppt is formed with NaOH(aq) that is insoluble in excess in **(a)(vi)**. **<u>Or</u>** A blue ppt is formed with NH_3(aq) that is soluble in excess to form a dark blue solution in **(a)(vii)**.
	anion:	CO_3^{2-}	CO_2(g) produced with H_2SO_4(aq) in **(a)(v)**.

[3]

[Total: 9]

5 Planning

In this question, you will devise a plan, using test-tube reactions, to distinguish between four organic compounds, so that each is identified.

Consider 4 unlabelled bottles and each bottle contains one of the following colourless liquids:

ethanal propanone propan-2-ol ethanoic acid

Plan an investigation, using test tube reactions, which would allow you to identify each of these organic compounds.

Each compound should be identified by at least one positive test. It is not sufficient to identify a compound simply by eliminating all the others.

Your plan should include:

- details of the reagents and conditions to be used,
- an outline of the sequence of steps you would follow,
- an explanation of how you would analyse your results in order to identify each compound.

Once a compound has been clearly identified, your plan should concentrate on distinguishing the remaining compounds.

	Test	**Expected Observations**
1	Place about 1 cm depth of each of the four samples into four separate test tubes. Add a few drops aqueous sodium carbonate.	If effervescence is produced, and the gas gives a white ppt with limewater, the sample is ethanoic acid. If no effervescence is produced, the sample is ethanal, propanone or propan-2-ol.
2	Place about 1 cm depth of a fresh sample for each of the three remaining samples into three separate test tubes. Add a few drops of Tollen’s reagent, and warm in a hot water bath.	If a grey ppt or a silver mirror is formed, the sample is ethanal. If no grey ppt or silver mirror is obtained, the sample is propanone or propan-2-ol.
3	Place about 1 cm depth of a fresh sample for each of the two remaining samples into two separate test-tubes. Add a few drops of 2,4-dinitrophenylhydrazine.	If a yellow / orange ppt is formed, the sample is propanone If no ppt is formed, the same is probably propan-2-ol.
4	Place about 1 cm depth of a fresh sample for the last sample in a test-tube. Add 10 drops of dilute sulfuric acid, followed by 2 drops of potassium manganate(VII) and warm in the water bath.	If the purple $KMnO_4$ is decolourised, the sample is propan-2-ol.

[Total: 6]

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. insoluble in excess	green ppt. 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. insoluble in excess	off-white ppt. insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

ions	*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 Al foil
nitrite, $NO_2^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and Al 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 with dilute acids; gives white ppt. with $Ba^{2+}(aq)$ (soluble in dilute strong acids)

(c) Test for gases

ions	*reaction*
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

END OF PAPER 4

Preparation list

Chemicals:

FA 1 is 0.0230 mol dm^{-3} of potassium iodate(V), KIO_3 (about 150 cm^3 per student)
FA 2 is 0.500 mol dm^{-3} potassium iodide, KI (about 70 cm^3 per student)
FA 3 is 0.750 mol dm^{-3} dilute sulfuric acid (about 230 cm^3 per student)
FA 4 is 0.100 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$ (about 120 cm^3 per student)
FA 5 is 0.0869 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$ (about 180 cm^3 per student)

starch solution containing 20 g dm^{-3} of soluble starch (about 10 cm^3 per student)

FA 6 is solid anhydrous sodium carbonate, Na_2CO_3 (preweighed 4.50 − 5.00 g)
FA 7 is solid sodium hydrogen carbonate, $NaHCO_3$ (preweighed 3.50 − 4.00 g)

FA 8 is a 10 : 1 solid mixture of $CuCO_3{\cdot}Cu(OH)_2{\cdot}H_2O$ and $BaCl_2{\cdot}2H_2O$ (preweighed 2.00 − 2.50 g, mixture should be thoroughly mixed)

Apparatus:

1 × 50 cm^3 burette labelled **FA 4**
1 × 50 cm^3 burette labelled **FA 5**
1 × 25.0 cm^3 pipette with pipette filler
2 × 250 cm^3 conical flask
1 × 10 cm^3 measuring cylinder
1 × 25 cm^3 measuring cylinder
1 × 50 cm^3 measuring cylinder
1 × 100 cm^3 beaker
1 × 250 cm^3 beaker
1 × 250 cm^3 beaker labelled "waste"

2 × glass filter funnel
1 × Styrofoam cup with lid
1 × thermometer (0.2 °C graduation)
1 × distilled water bottle (with access to additional supplies of deionised water)
1 × retort stand with double clamps
1 × paper towel

6 × test-tubes
2 × small test-tubes
1 × boiling tube
6 × dropper / teat pipette
1 × glass rod and spatula
1 × set of blue / red litmus paper + filter paper strips and box of filter paper
1 × tripod stand, wire gauze, and heat-proof mat
1 × bunsen burner and lighter

weighing scale (for weighing / reweighing of **FA 6** & **FA 7**, about 1 per 8-12 candidates)

Bench Reagents:

aqueous sodium hydroxide (approximately 2.0 mol dm^{-3})
aqueous ammonia (approximately 2.0 mol dm^{-3})
hydrochloric acid (approximately 2.0 mol dm^{-3})
nitric acid (approximately 2.0 mol dm^{-3})
sulfuric acid (approximately 1.0 mol dm^{-3})
aqueous silver nitrate (approximately 0.05 mol dm^{-3})
aqueous barium chloride (approximately 0.2 mol dm^{-3})
limewater (saturated solution of calcium hydroxide)