Name: ____________________ **Class: 16S**_________ **Reg Number:** ______

MERIDIAN JUNIOR COLLEGE
JC2 Preliminary Examination
Higher 2

Chemistry 9729/01

Paper 1 Multiple–Choice Questions **22 September 2017**

1 hour

Additional Materials: *Data Booklet*
OMR Answer Sheet

INSTRUCTIONS TO CANDIDATES

Write your name, class and register number in the spaces provided at the top of this page.

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

Read very carefully the instructions on the OMR answer sheet.

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

Use of OMR Answer Sheet

Ensure you have written your name, class register number and class on the OMR Answer Sheet. Use a **2B** pencil to shade your answers on the OMR sheet; erase any mistakes cleanly. Multiple shaded answers to a question will not be accepted.

For shading of class register number on the ***OMR sheet***, please follow the given examples:
If your register number is **1**, then shade **01** in the index number column.
If your register number is **21**, then shade **21** in the index number column.

This document consists of **14** printed pages

1 *The use of Data Booklet is relevant to this question.*

Scientists have been comparing the stability of isotopes using the neutron:proton ratio. Nuclei are considered to be stable if the neutron:proton ratio is between 1:1 to 1.5:1. Stable nuclei within these ratios are known to be in the *'band of stability'*.

Which one of these elements do not lie within the *'band of stability'* ?

A ^{91}Zr **B** ^{133}Cs **C** ^{165}Ho **D** ^{209}Bi

2 The information on two particles, $\mathbf{Q}^+$ and $\mathbf{R}^+$, are given in the table below.

particles	number of electrons	number of neutrons	angle of deflection in an electric field
$\mathbf{Q}^+$	20	25	2.0°
$\mathbf{R}^+$	▨	20	2.3°

Which of the following pairs of particles are isoelectronic?

A **Q** and **R**

B **Q** and $\mathbf{R}^+$

C $\mathbf{Q}^+$ and **R**

D $\mathbf{Q}^+$ and $\mathbf{R}^+$

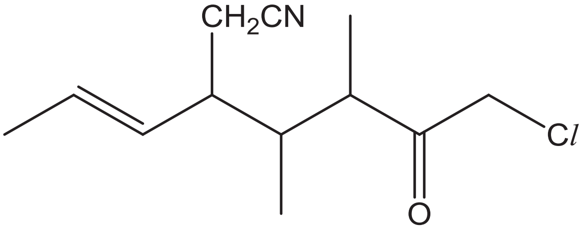
3 Three substances **D**, **E** and **F** have the following physical properties.

substance	melting point / °C	boiling point / °C	electrical conductivity in	
			solid state	liquid state
D	1538	2862	good	good
E	2852	3600	poor	good
F	3550	3825	good	not known

What could be the identities of **D**, **E** and **F**?

	D	**E**	**F**
A	Fe	NaC*l*	SiO_2
B	Fe	MgO	C (graphite)
C	NaC*l*	MgO	C (diamond)
D	Fe	SiO_2	C (graphite)

4 What is the number of sp, sp^2 and sp^3 hybridised carbons present in compound **H**?

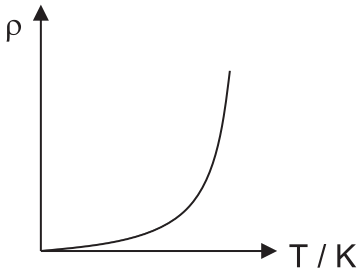


compound **H**

	sp hybridised C	sp^2 hybridised C	sp^3 hybridised C
A	0	3	7
B	1	3	7
C	1	3	8
D	1	4	8

5 Which of the following graphs show the correct relationship for an ideal gas under constant pressure, *P* ?

A



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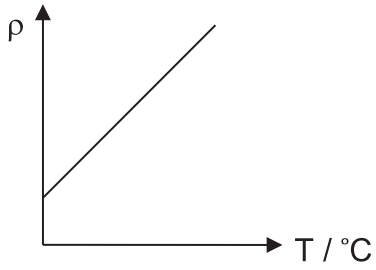
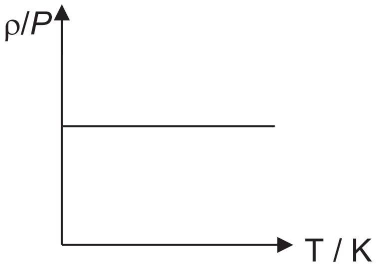
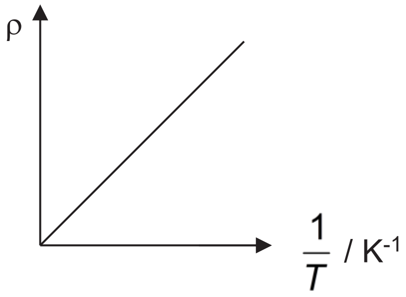


C



D



6 In which reaction does ammonia behave as a Lewis base?

1 $HCl + NH_3 \longrightarrow NH_4Cl$

2 $NaH + NH_3 \longrightarrow NaNH_2 + H_2$

3 $Zn^{2+} + 4NH_3 \longrightarrow [Zn(NH_3)_4]^{2+}$

A 1 only

B 3 only

C 1 and 3 only

D 1, 2 and 3

7 A chloride and an oxide of the elements in the third period of the Periodic Table are dissolved in two separate portions of water to form aqueous solutions.

Both of the resulting solutions can be used to dissolve Al_2O_3 but only one of the two can be used to dissolve SiO_2.

Which of the following could be the chloride and the oxide used?

A	$NaCl$	MgO
B	$MgCl_2$	SO_3
C	$SiCl_4$	Na_2O
D	PCl_5	P_4O_{10}

8 Three solutions containing the halogens **X**$_2$, **Y**$_2$ and **Z**$_2$ were added to three aqueous solutions of **X**$^-$, **Y**$^-$ and **Z**$^-$ ions separately. The experimental results are shown in the following table.

	X$^-$	**Y**$^-$	**Z**$^-$
X$_2$	No reaction	No reaction	**X**$^-$ formed
Y$_2$	**Y**$^-$ formed	No reaction	**Y**$^-$ formed
Z$_2$	No reaction	No reaction	No reaction

Which of the following statements is correct?

A **Y**$_2$ is a stronger oxidising agent than **X**$_2$.

B **X**$_2$ is a weaker oxidising agent than **Z**$_2$.

C **Y**$^-$ is a stronger reducing agent than **Z**$^-$.

D **Z**$^-$ is a weaker reducing agent than **X**$^-$.

9 **W** is a compound containing only Fe, C and H. When 1.888 g of **W** was subjected to complete combustion, 4.47 g of CO_2 and 0.914 g of H_2O were formed.

What is the empirical formula of **W**?

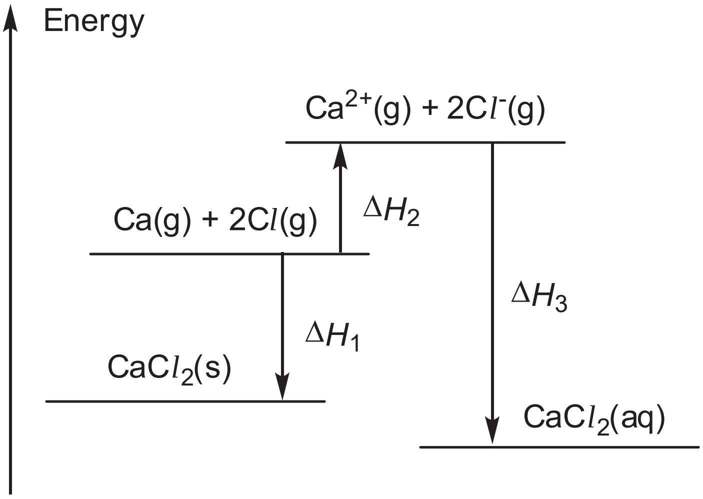
A FeCH

B FeC_2H

C $FeC_{10}H_{10}$

D $Fe_2C_5H_2$

10 The energy level diagram shown represents the dissolution of $CaCl_2$ in water.



Which of the following statements about the diagram is correct?

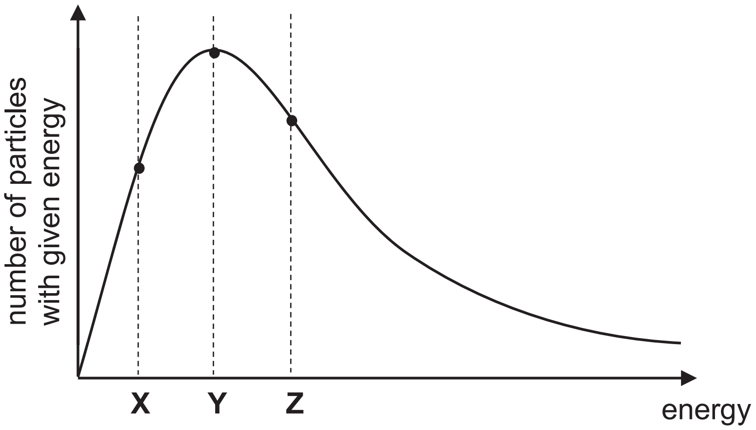
A The enthalpy change of formation of $CaCl_2$ is given by ΔH_1.

B The enthalpy change of dissolving $CaCl_2$ is given by $\Delta H_1+\Delta H_2+\Delta H_3$.

C The sum of the first and second ionisation energies of Ca is given by ΔH_2.

D The sum of the enthalpy change of hydration of Ca^{2+} and Cl^- is given by ΔH_3.

11 The Maxwell–Boltzmann distribution for a gas at constant temperature is shown below.



How would the number of particles change at the kinetic energies **X**, **Y** and **Z** when temperature is lowered by 5 °C.

	X	**Y**	**Z**
A	lower	lower	higher
B	lower	higher	higher
C	higher	lower	lower
D	higher	higher	lower

12 The reaction of nitric oxide with hydrogen can be monitored by the initial rate method and the overall kinetics is found to be third order.

$$2NO\,(g) + 2H_2\,(g) \longrightarrow N_2\,(g) + 2H_2O(l)$$

A proposed mechanism of the reaction is given below.

Step 1: $NO + NO \longrightarrow N_2O_2$

Step 2: $N_2O_2 + H_2 \longrightarrow N_2O + H_2O$

Step 3: $N_2O + H_2 \longrightarrow N_2 + H_2O$

What is the slow step in the mechanism?

A Step 1

B Step 2

C Step 3

D No conclusion can be drawn from the mechanism

13 Fe_3O_4 is found naturally in the mineral magnetite. It can be reduced to iron metal using hydrogen according to the following equilibrium.

$$Fe_3O_4\ (s) + 4H_2\ (g) \rightleftharpoons 3Fe\ (s) + 4H_2O\ (g) \qquad \Delta H = +50.4\ kJ\ mol^{-1}$$

Which of the following statements are correct about the reaction?

1 A reduction in the total pressure will increase the production of Fe.

2 The numerical values of K_c and K_p are equal.

3 An increase in temperature will increase the value of K_c.

A 1, 2 and 3

B 1 and 2 only

C 2 and 3 only

D 3 only

14 An equal volume of 0.1 mol dm^{-3} $Pb(NO_3)_2$ is added to a mixture containing 0.1 mol dm^{-3} of $NaCl$ and 0.1 mol dm^{-3} NaI.

What is the most probable observation?

K_{sp} of $PbCl_2$ (white ppt) = 1.7×10^{-4} $mol^3\ dm^{-9}$
K_{sp} of PbI_2 (yellow ppt) = 4.1×10^{-9} $mol^3\ dm^{-9}$

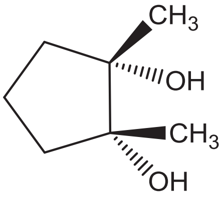
A A white and yellow ppt is formed.

B A yellow ppt is formed.

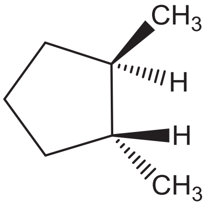
C A white ppt is formed.

D No ppt is formed.

15 Which molecules are optically active?



1



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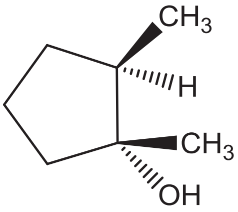


3

A 3 only

B 1 and 2 only

C 2 and 3 only

D 1, 2 and 3 only

16 One mole of methylcyclobutane reacts with one mole of halogen in the presence of ultra–violet light.

Which statements are true about this reaction?

1 There are only four possible mono–substituted products.
2 Hydrogen is a side product formed in the reaction.
3 Homolytic fission occurs only in the initiation step.

A 1 only

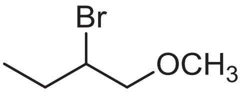
B 1 and 2 only

C 1 and 3 only

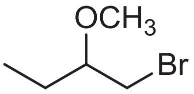
D 2 and 3 only

17 Which of the following is the major product when but–1–ene reacts with $BrCl$ in pure methanol?

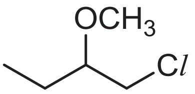
A



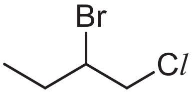
B



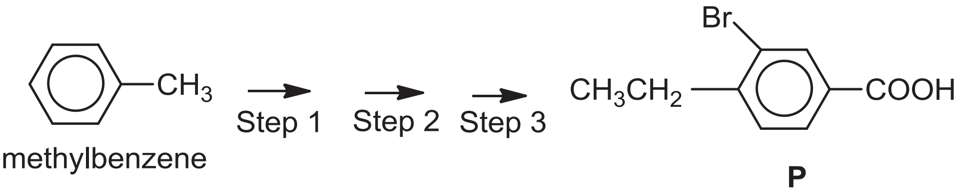
C



D



18 Compound **P** can be synthesised from methylbenzene as shown below.



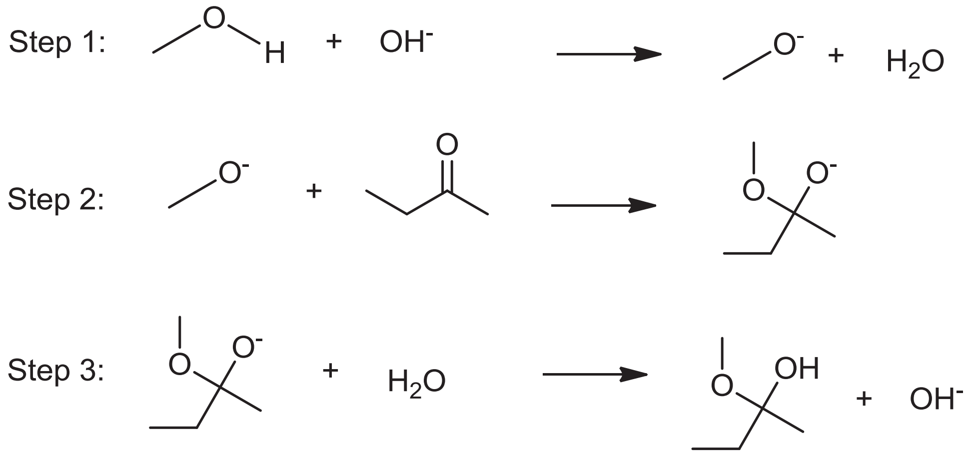
P

Which of the following could be a sequence for converting methylbenzene to compound **P**?

	step 1	step 2	step 3
A	CH_3CH_2Cl, $AlCl_3$, r.t.p.	Br_2 in $AlBr_3$, in the dark	$KMnO_4$, dilute H_2SO_4, heat
B	$KMnO_4$, dilute H_2SO_4, heat	Br_2 in $AlBr_3$, heat	CH_3CH_2Cl, $AlCl_3$, r.t.p
C	Br_2 in $AlBr_3$, heat	CH_3CH_2Cl, $AlCl_3$, r.t.p	$K_2Cr_2O_7$, dilute H_2SO_4, heat
D	$K_2Cr_2O_7$, dilute H_2SO_4, heat	CH_3CH_2Cl, $AlCl_3$, r.t.p.	Br_2 in $AlBr_3$, in the dark

19 1–methoxybutan–2–ol is an organic compound which has an alcohol and an ether (R–O–R) attached to the same carbon atom. It is formed when butan–2–one reacts with methanol in the presence of a catalyst.

The reaction follows the mechanism below.



1-methoxybutan-2-ol

Which of the following statements about the reaction is **not** correct?

A Methanol acts as a Lewis acid in step 1.

B Step 2 is a nucleophilic addition reaction across the C=O bond.

C Methanol can be used in step 3 instead of water.

D KOH can be used as a catalyst for this reaction.

20 0.5 g of each of the following compounds was heated with NaOH (aq).

$CH_2{=}CHCl$ CH_3CH_2I CH_3COBr C_6H_5Br

Each of the mixtures was then acidified with dilute nitric acid, followed by the subsequent addition of $AgNO_3$ (aq).

Which statement is correct?

A The reaction with C_6H_5Br gave a cream precipitate.

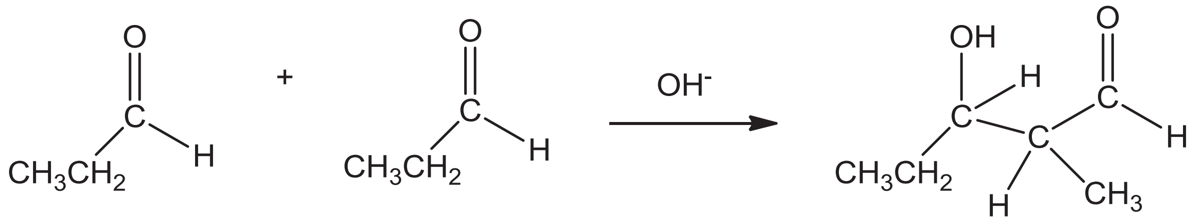
B The reaction with CH_3CH_2I gave a precipitate that dissolved completely in dilute aqueous ammonia.

C The rate of reaction with $CH_2{=}CHCl$ would be the slowest.

D The reaction with CH_3COBr gave the largest mass of precipitate.

21 In the presence of a strong base, aldehydes and ketones may undergo addition reaction to form an *aldo* compound (hydroxycarbonyl).

A reaction of propanal with sodium hydroxide to form an *aldo* compound is as shown below.

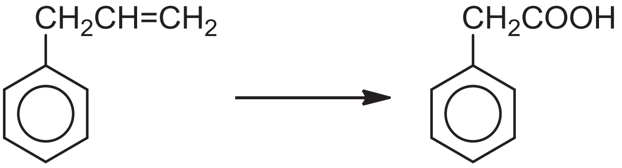


aldol compound

Which product can be formed when sodium hydroxide is added to a mixture of butanal, $CH_3CH_2CH_2CHO$, and propanone, CH_3COCH_3?

A $CH_3CH_2CH_2CH(OH)CH_2CH_2CH_2CHO$
B $(CH_3)_2C(OH)CH_2CH_2CH_2CHO$
C $(CH_3CH_2)_2C(OH)CH_2COCH_3$
D $CH_3CH_2CH_2CH(OH)CH_2COCH_3$

22 Alkenes can undergo oxidation to form carboxylic acids. The following conversion occurs in a multiple–step reaction.



Which of the following reagents is involved in the above conversion?

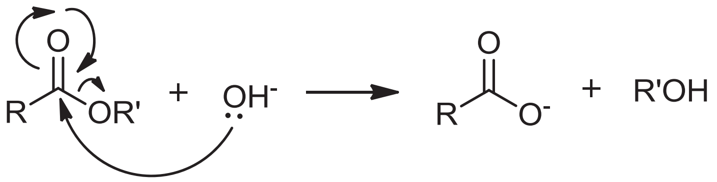
A concentrated H_2SO_4

B acidified $K_2Cr_2O_7$

C acidified $KMnO_4$

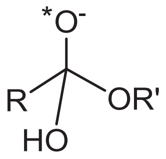
D alkaline I_2

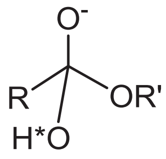
23 Esters can be hydrolysed under basic conditions according to the following mechanism.

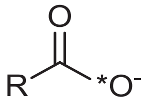


In an isotope labelling experiment, oxygen–18–labeled hydroxide, *OH⁻, is used.

Which of the following are produced as an intermediate or product?

1 

2 

3 

4 R'—O*H

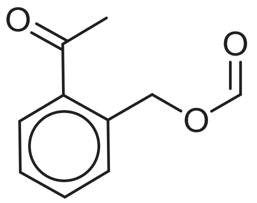
A 1 and 2 only

B 1 and 4 only

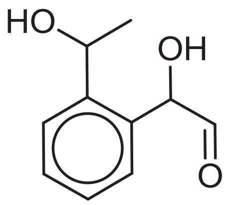
C 2 and 3 only

D 3 and 4 only

24 Compounds **V** and **W** have the following structures.



compound **V**



compound **W**

Which of the following reagents can be used to distinguish between compounds **V** and **W**?

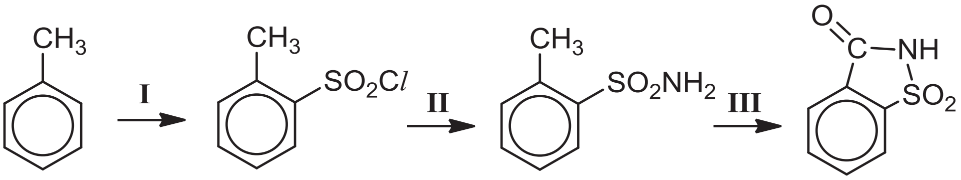
A iodine and aqueous sodium hydroxide

B 2,4–dinitrophenylhydrazine

C acidified aqueous potassium dichromate(VI)

D aqueous silver nitrate and aqueous ammonia

25 Saccharin is an artificial sweetener which can be synthesised from methylbenzene through a series of reactions below.



Which of the following statements is correct about the above synthesis?

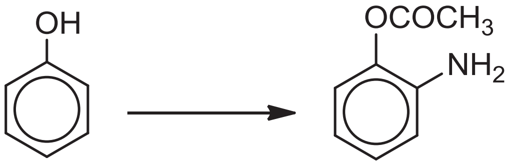
A Reaction **I** involves methylbenzene as an electrophile.

B Reaction **II** is a nucleophilic substitution reaction.

C Reaction **III** does not involve oxidation.

D Reaction **III** does not involve the elimination of water.

26 Phenols are widely used in household products and as intermediates for industrial synthesis. Compound **X** can produced from phenol in three steps.

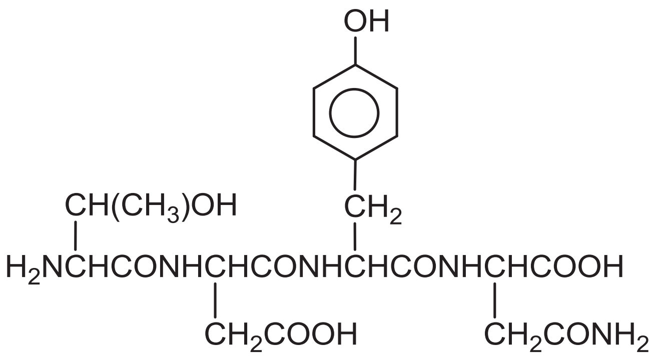


compound **X**

What are the reagents required in this three–step synthesis?

	stage 1	stage 2	stage 3
A	concentrated HNO_3, concentrated H_2SO_4	$NaBH_4$	CH_3COCl
B	aqueous HNO_3	Sn, concentrated HC*l* followed by NaOH (aq)	CH_3COCl
C	aqueous HNO_3	CH_3COCl	Sn, concentrated HC*l*, followed by NaOH (aq)
D	aqueous HNO_3	$NaBH_4$	CH_3COCl

27 Compound **Y** is formed from the partial hydrolysis of a hormone molecule.



Compound **Y**

Which of the following statement is **incorrect**?

A Prolonged heating of compound **Y** with dilute NaOH produces three carbon–containing products.

B Prolonged heating of compound **Y** with dilute NaOH liberates an alkaline gas.

C One mole of Na_2CO_3 is needed for complete reaction with one mole of compound **Y**.

D Two moles of Na is needed for complete reaction with one mole of compound **Y**.

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

A galvanic cell consists of a Mg^{2+}/Mg half–cell and a Cu^{2+}/Cu half–cell.

Which of the following statements is correct?

A Reducing the size of the magnesium electrode decreases the e.m.f of the cell.

B Increasing the temperature has no effect on the e.m.f. of the cell.

C Adding aqueous sodium hydroxide to the Cu^{2+}/Cu half–cell increases the e.m.f. of the cell.

D Adding water to the the Mg^{2+}/Mg half–cell increases the e.m.f. of the cell.

29 Methanol can be synthesised according to the reaction below. Cr_2O_3 is used as a catalyst to increase the rate of this reaction.

$$CO\,(g) + 2H_2\,(g) \rightarrow CH_3OH\,(l)$$

Which of the following statements are correct about the synthesis of methanol?

1 Cr_2O_3 is used as a catalyst because Cr can exhibit variable oxidation states in its compounds.

2 Cr_2O_3 lowers the activation energy by using its partially filled 3d orbitals for the adsorption of reactant molecules.

3 There is a decrease in the oxidation number of carbon.

A 1, 2 and 3

B 1 and 2 only

C 2 and 3 only

D 1 only

30 A reaction scheme starting from aqueous copper(II) nitrate solution is shown below.

Both **J** and **K** are copper–containing species.

$$Cu(NO_3)_2(aq) \xrightarrow[\mathbf{I}]{NH_3(aq)} \mathbf{J} \xrightarrow[\mathbf{II}]{\text{excess } NH_3(aq)} \mathbf{K} \xrightarrow[\mathbf{III}]{KCN(aq)} [Cu(CN)_6]^{4-}(aq)$$

Which of the following statements are correct about the above reaction scheme?

1 One of the reactions involves a redox reaction.

2 CN^- is a stronger ligand than NH_3.

3 Precipitation occurs in step **I**.

A 1, 2 and 3

B 2 and 3 only

C 1 and 2 only

D 2 only

End of Paper 1

2017 MJC H2 Chemistry Prelim Paper 2

1 Concepts of acids and bases are important aspects in Chemistry which can be applied to many areas in our daily life.

(a) There are three theories of acids and bases. In 1887, Svante Arrhenius proposed that acids are substances that produce H^+ in water and bases are those which produce OH^- in water. In 1923, Johannes N Brønsted and Thomas M Lowry proposed another set of definitions for acids and bases. Later in the same year, Gilbert N Lewis defined acids and bases in terms of electron pair acceptors and donors respectively.

(i) State the *Bronsted–Lowry theory* of acids and bases.

[1]

(ii) There are several limitations to Arrhenius' theory of acids and bases. Give an example to illustrate one of its limitations.

[1]

(b) The pK_a values and solubilities of some weak acids in methanol and water at 25 ˚C are given in **Table 1.1**.

Table 1.1

compound	p*K*a in methanol	p*K*a in water	solubility/ per 100 g of water
CH_3COOH ethanoic acid	9.71	4.88	100 g
$CH_2(CN)COOH$ 2–cyanoethanoic acid	7.50	2.46	More than 100 g

(i) Two samples of 2–cyanoethanoic acid of identical concentrations were dissolved in water and methanol separately. Calculate the ratio of H^+ ions formed in water and in methanol.

[1]

(ii) Suggest a reason why both acids in **Table 1.1** have lower pK_a in water than in methanol.

[1]

(iii) Explain why 2–cyanoethanoic acid has a higher solubility in water than ethanoic acid.

[1]

(c) The base dissociation constants of some weak bases are given in **Table 1.2**.

Table 1.2

compound	K_b value at 25˚C
methylamine CH_3NH_2	4.6×10^{-4}
dimethylamine $(CH_3)_2NH$	5.4×10^{-4}
trimethylamine $(CH_3)_3N$	6.3×10^{-5}

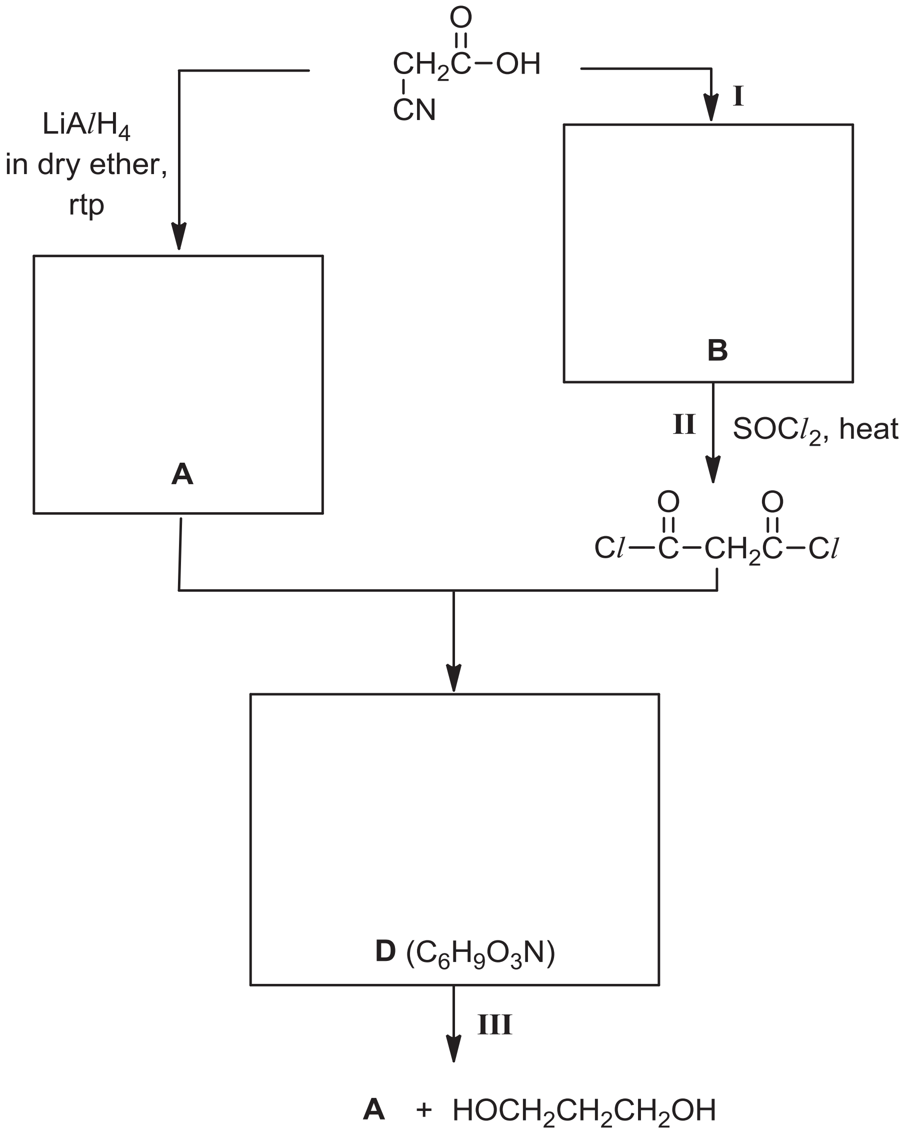
(i) Explain why dimethylamine is more basic than methylamine.

[1]

(ii) Among the three compounds, trimethylamine is the least basic, which is unusual. Suggest a reason for this.

[1]

(d) 2–cyanoethanoic acid can undergo a series of reactions to form a neutral cyclic compound **D**. Compound **D** can further react to produce compound **A** and a diol**.**



(i) Draw the structures of compounds **A**, **B** and **D** in the boxes above.

[3]

(ii) State the types of reaction in step **I** and **II.**

[1]

Step **I**: ……………………………………….

Step **II**: ……………………………………….

(iii) State the reagents and conditions required in Step **I** and **III**.

[2]

Step **I**: ……………………………………….

Step **III**: ……………………………………..

[Total: 13]

2 Vitamins and minerals are essential nutrients that perform many roles in the body. They help to build bones, heal wounds, bolster the immune system and convert food into energy. Young children require many essential minerals such as calcium, magnesium, iodine, iron and zinc to develop and grow.

Table 2.1 shows the recommended daily intake of some essential minerals for children.

Table 2.1

Mineral	**Recommended daily intake for children / mg**	
	Age group	
	1 – 3 years	**4 – 8 years**
Calcium	500	700
Iodine	0.090	0.090
Iron	9	10
Magnesium	80	130
Phosphorus	460	500
Zinc	3	4

Table 2.2 shows part of a nutrition label on a tin of powdered milk formula.

Table 2.2

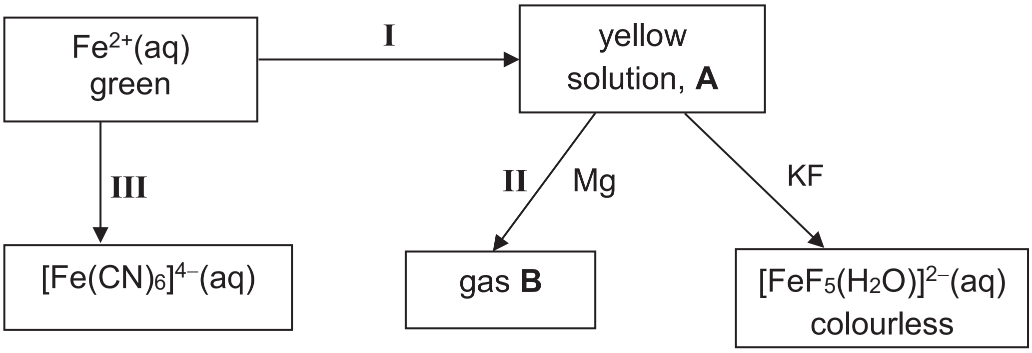
Nutrition Information **Standard Dilution (per 100 ml)**	
Nutrients:	
Protein	2.2 g
Fat	5.1 g
Carbohydrate	11.2 g
Minerals:	
Sodium	39 mg
Potassium	106 mg
Chloride	79 mg
Calcium	119 mg
Phosphorus	69 mg
Magnesium	7.8 mg
Iron	1.03 mg
Zinc	0.7 mg
Copper	0.056 mg
Manganese	0.0094 mg
Iodine	0.011 mg

(a) Zinc helps the immune system fight off invading bacteria and viruses. A 2–year old child takes an average of 3 feeds of milk formula per day, with a quantity of 180 ml per feed.

Using the information provided, determine if the zinc obtained from the milk formula meets the recommended quantity for daily intake. Comment on whether there is a need for the child to supplement his diet with zinc from other sources.

[2]

(b) Iron is an essential mineral used to carry oxygen in the blood.
The following flowchart shows the reactions of iron and its compounds.



(i) Name the types of reactions taking place in **I** and **II**.

[2]

I: ……………………………………….

II: ……………………………………….

(ii) Write the formula of the cation present in **A** and identify gas **B**.
By considering the nature of this cation present, explain fully why gas **B** is formed when Mg is added to **A** in reaction **II**.

[3]

(iii) What is the type of reaction taking place in **III**? Write a balanced equation for the reaction.

[2]

(iv) $Fe^{2+}(aq)$ appears to be green whereas $[FeF_5(H_2O)]^{2-}(aq)$ is colourless.

1. Explain why $Fe^{2+}(aq)$ appears to be green.

[3]

2. Write the full electronic configuration of iron in $[FeF_5(H_2O)]^{2-}$.

[1]

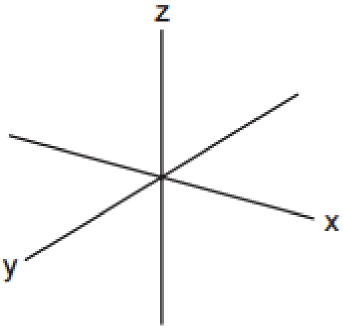
3. Suggest why $[FeF_5(H_2O)]^{2-}$ is colourless.

[1]

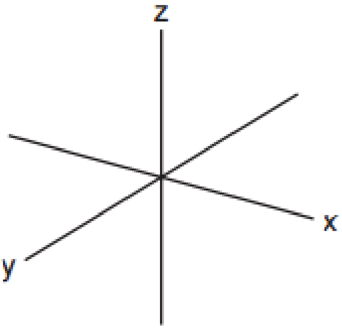
(v) Iron forms many octahedral complexes, of which $[Fe(CN)_6]^{4-}$ is an example. On the axes below, sketch the shapes of a d orbital from the lower energy level and a d orbital from the higher energy level in an octahedral complex.

[2]

lower energy level



higher energy level



(c) Calcium is the most abundant mineral present in milk formula. It is essential for healthy bones and teeth. In the blood, it also helps to regulate the heartbeat, blood pressure and neural transmission.

Table 2.3 gives data about some physical properties of calcium and iron.

Table 2.3

property	calcium	iron
relative atomic mass	40.1	55.8
atomic radius (metallic)/ nm	0.197	0.126
ionic radius (2+)/ nm	0.099	0.076
melting point / °C	839	1538
density / g cm^{-3}	1.54	7.86

(i) Explain why the atomic radius of iron is less than that of calcium.

[2]

(ii) Use relevant data from **Table 2.3** to explain qualitatively why the density of iron is significantly greater than that of calcium.

[1]

(d) Magnesium, phosphorus and chlorides are also minerals found in milk formula.

(i) Write relevant chemical equations to illustrate the reactions of magnesium chloride and phosphorus pentachloride with water. Suggest the approximate pH of any solutions formed.

[2]

(ii) Like magnesium, phosphorus and chlorine, element **Z** is also a Period 3 element. The first six ionisation energies of **Z** are shown in **Figure 2.1** while the 2nd ionisation energies of seven consecutive elements **A – G** (one of which is **Z**) is shown in **Figure 2.2**.

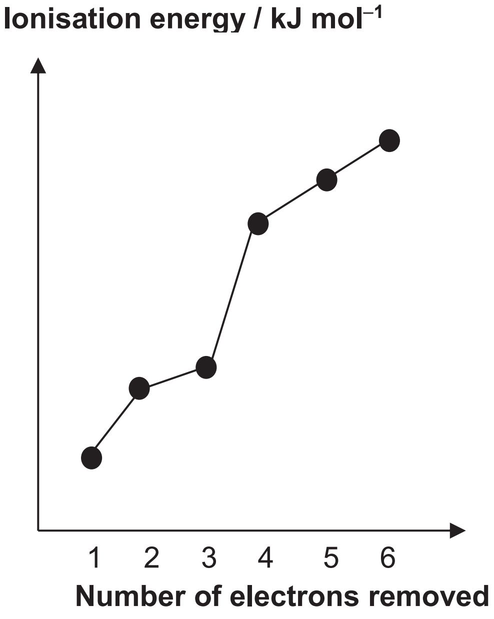


Figure 2.1

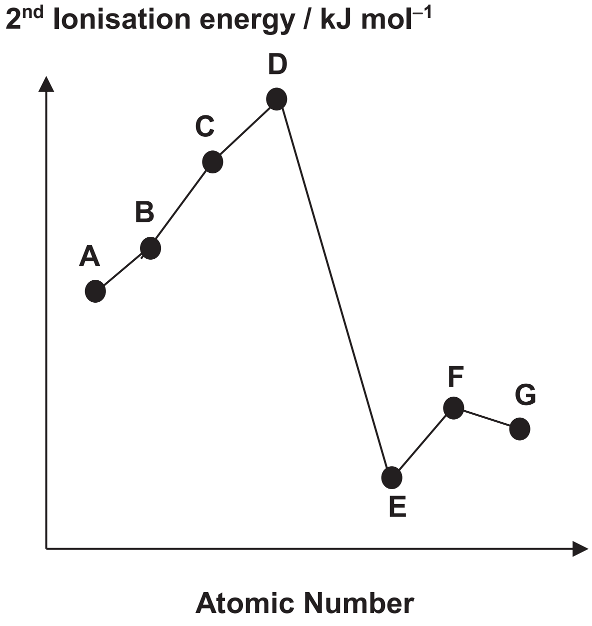


Figure 2.2

Identify element **Z**. Hence, state which element **A – G** in **Figure 2.2**, could be **Z**.

[1]

[Total: 22]

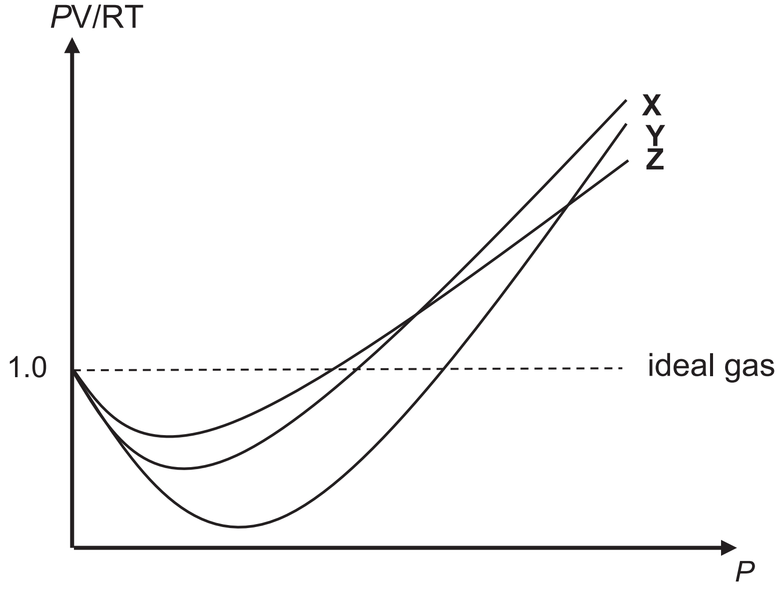
3 Nitrosyl chloride, NOC*l*, is a toxic gas that has caused several industrial accidents.

At 250 °C, NOC*l* readily dissociates into NO and Cl_2.

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

(a) The graphs of *P*V/RT against *P* for 1 mole each of NO, Cl_2 and NOC*l* at room temperature are plotted below.

Figure 3.1



With reference to **Figure 3.1**, deduce which of the graphs is the plot for NOC*l*.

[2]

(b) The dissociation was investigated by adding 5 moles of NOC*l* into a 5.0 dm^3 sealed vessel, and equilibrium was established at 250 °C under a pressure of 5.80×10^6 Pa.

(i) Assuming ideal gas behaviour, determine the total amount of gas in moles, at equilibrium.

[1]

(ii) Write the expression for the equilibrium constant, K_p, for the dissociation of NOC*l*, including units.

[1]

(iii) Calculate a value for K_p under the stated conditions.

[3]

(c) Standard Gibbs free energy change, $\Delta G^\ominus$ is related to K_c by the following equation.

$$\Delta G^\ominus = -\,RT \ln K_c$$

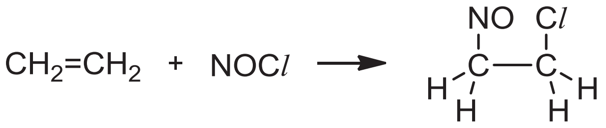
$\Delta G^\ominus$ for the dissociation of NOC*l* at 250 °C is –1.47 kJ mol^{-1}.

(i) Using the above information, calculate K_c for the dissociation of NOC*l* at 250 °C. [1]

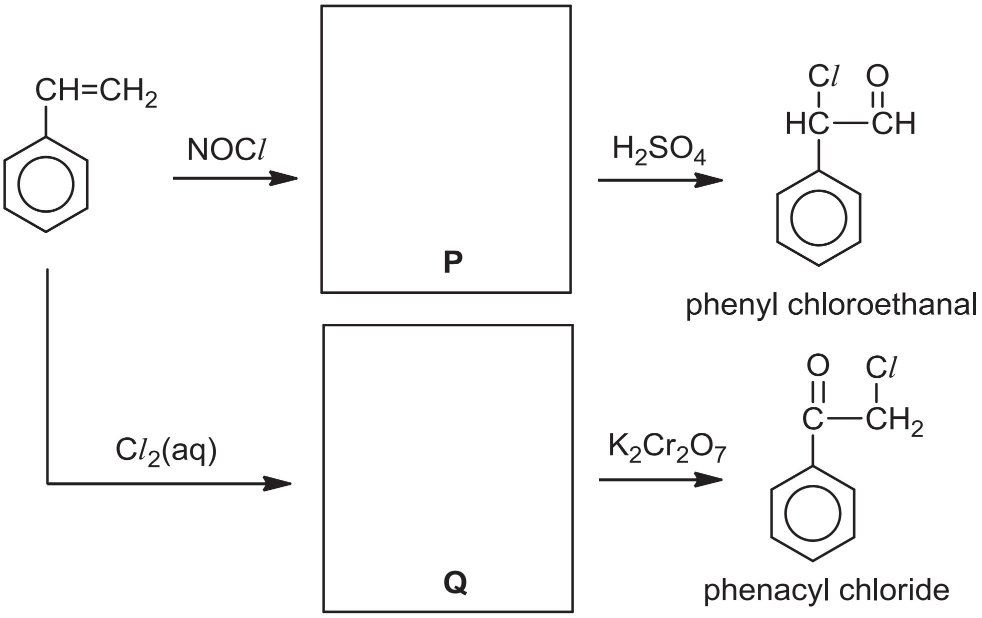
(ii) Suggest how K_c will change when the temperature is raised. [1]

(iii) Hence, using *Le Chatelier's Principle*, deduce whether the dissociation reaction is exothermic or endothermic. [2]

(d) NOC*l* is sometimes used in organic synthesis. It can react with alkenes to form chloro–nitroso compounds according to the following equation.



A reaction scheme involving the use of NOC*l* for the synthesis of phenyl chloroethanal and phenacyl chloride is given below



(i) Draw the structures of compounds **P** and **Q**.

[2]

(ii) State a reagent which can distinguish between phenyl chloroethanal and phenacyl chloride. Write a balanced equation for the reaction.

[2]

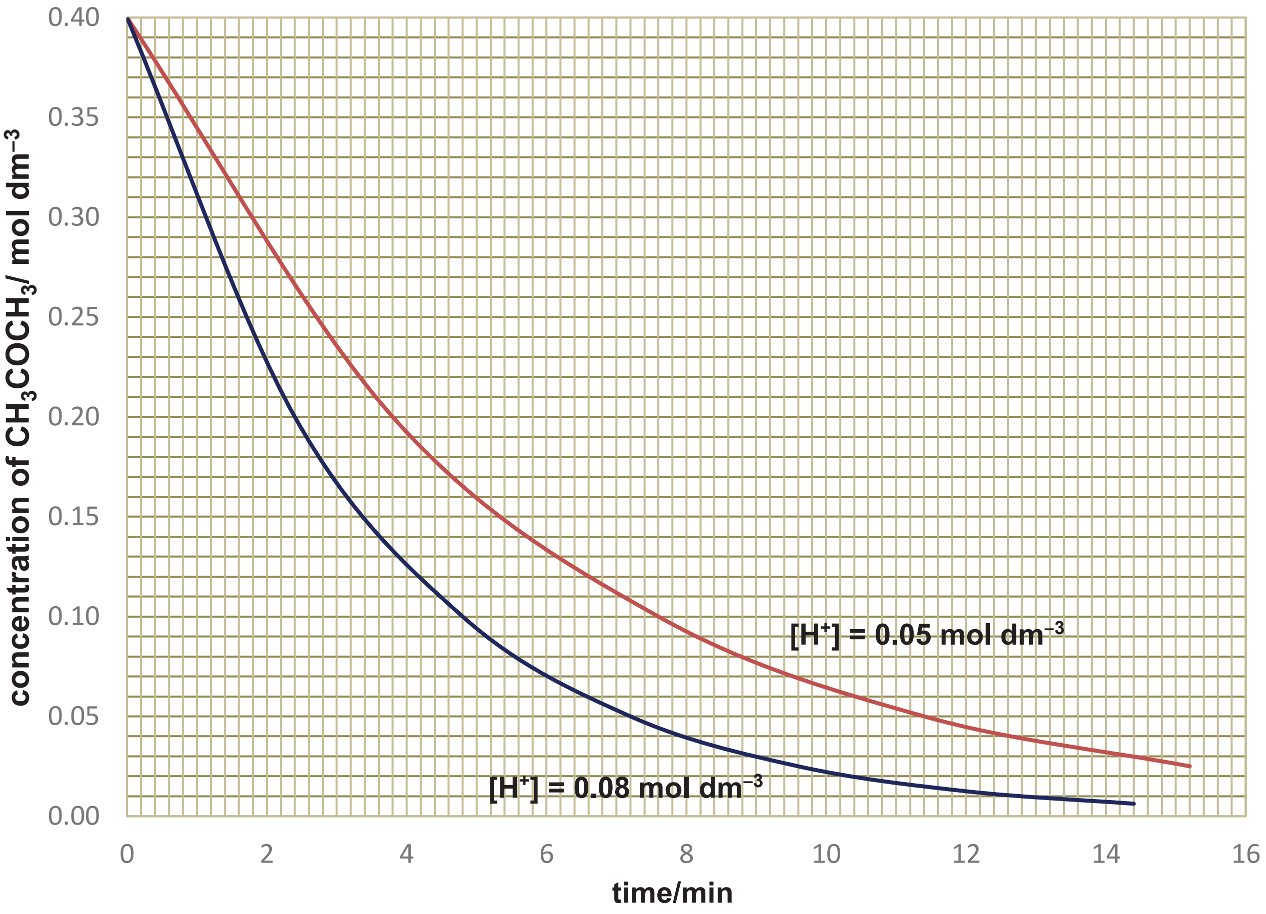
[Total: 15]

4 The bromination of propanone is an acid–catalysed reaction which produces bromopropanone. The equation for the reaction is given below.

$$CH_3COCH_3 + Br_2 \xrightarrow{H^+} CH_2BrCOCH_3 + H^+ + Br^-$$

(a) Two experiments on the kinetics of the reaction are conducted with [Br_2] being kept constant. The [CH_3COCH_3] is monitored and the following graphs are obtained.

Graph of concentration of CH_3COCH_3 with time



(i) Using the information above, deduce the order of reaction with respect to CH_3COCH_3 and H^+. Show your working on the graph.

[3]

(ii) Another experiment was conducted with a different [Br_2]. It was determined that changing [Br_2] has no effect of the rate of reaction. Sketch a graph to show how [Br_2] varies with time.

[1]

(iii) Using your answers from **(a)(i)** and **(a)(ii)**, construct the rate equation for the bromination of CH_3COCH_3.

[1]

(iv) Given that the initial rate of reaction is 7.6×10^{-5} mol dm^{-3} min^{-1} when [H^+] is 0.05 mol dm^{-3}, calculate the rate constant, *k*, for the reaction. State its units.

[1]

(b) Bromopropanone, $CH_2BrCOCH_3$, can also be synthesised via organic reactions.

(i) Devise a 3–step synthesis to produce $CH_2BrCOCH_3$ from the allyl alcohol, $CH_2{=}CHCH_2OH$.

[3]

(ii) Other than the use of an oxidising agent, suggest a chemical test to determine if the synthesis reaction in **(b)(i)** is complete.

[2]

(c) $CH_2BrCOCH_3$ undergoes hydrolysis with aqueous NaOH to form $CH_2(OH)COCH_3$. The reaction follows a second order kinetics.

(i) Outline the mechanism for this reaction, showing all the charges and using curly arrows to represent the movement of electron pairs.

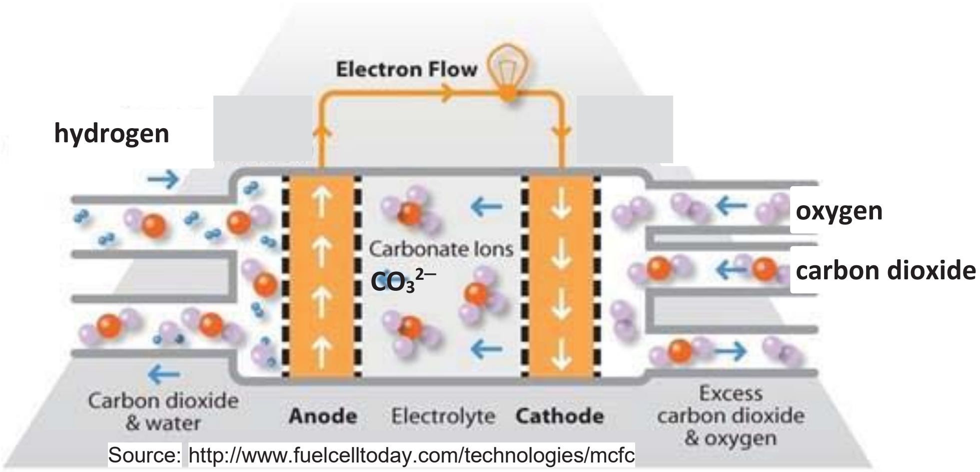
[2]

(ii) CH_3CH_2COBr is an isomer of bromopropanone, $CH_2BrCOCH_3$. The rate of hydrolysis for each of the two compounds is different. State and explain which isomer has a faster rate of hydrolysis.

[2]

[Total: 15]

5 A fuel cell is an electrochemical cell that converts the chemical energy from a fuel into electricity. One example is molten–carbonate fuel cells (MCFCs) developed for natural gas power plants.



Source: http://www.fuelcelltoday.com/technologies/mcfc

(a) At the anode, water and carbon dioxide are formed whereas carbonate ions are formed at the cathode.

(i) Construct the half–equations at the electrodes of this MCFC electrochemical cell. Hence, give the balanced equation for the reaction that occurs during discharge of the MCFC.

[2]

(ii) Draw a fully labelled diagram of the electrochemical cell to determine the standard electrode potential of the $O_2(g)/OH^-(aq)$ electrode system.

[2]

(b) Another example of a fuel cell is direct–formic acid fuel cells (DFAFCs).
It has the overall reaction similar to the combustion of formic acid in oxygen. The following reactions take place at the electrodes.

$CO_2 + 2H^+ + 2e \rightleftharpoons HCOOH \qquad E^\theta = -0.61\ V$

$\frac{1}{2}O_2 + 2H^+ + 2e \rightleftharpoons H_2O \qquad E^\theta = +1.23\ V$

By using one of the phrases *more positive, more negative* or *no change,* deduce the effect of increasing $[OH^-]$ on the electrode potential of the cathode.

[1]

(c) **Table 5.1** shows the different enthalpies of various compounds. The data will be useful for this question.

Table 5.1

	ΔH^θ / kJ mol^{-1}
standard molar enthalpy of formation of CO_2 (g)	−394
standard molar enthalpy of formation of H_2O (*l*)	−286
standard molar enthalpy of formation of CH_3OH (aq)	−246
standard molar enthalpy of formation of HCHO (aq)	−150
standard molar enthalpy of combustion of formic acid, CH_2O_2 (*l*)	−211

(i) Define the term *standard enthalpy change of formation*, ΔH_f^θ of formic acid, CH_2O_2.

[1]

(ii) Using Hess's law and information from **Table 5.1**, construct an energy cycle to calculate the $\Delta H_f^\ominus$ of formic acid.

[3]

(iii) Methanol, CH_3OH is toxic because liver enzymes oxidise it to formaldehyde, HCHO.

Using **Table 5.1**, calculate the standard enthalpy change, $\Delta H^\ominus$ for the following reaction.

$$CH_3OH\ (aq) + \tfrac{1}{2}O_2\ (g) \longrightarrow HCHO\ (aq) + H_2O\ (l)$$

[1]

[Total: 10]

End of Paper 2

Name ________________________ **Class: 16S**_______ **Reg Number:** _____

MERIDIAN JUNIOR COLLEGE
JC 2 Preliminary Examination
Higher 2

Chemistry 9729/03

Paper 3 Free Response **13 September 2017**

2 hours

Additional Materials: *Data Booklet*
Writing Paper

INSTRUCTIONS TO CANDIDATES

Write your name, class and register number in the spaces provided at the top of this page.

Answer all questions in Section A and one question from Section B.

Begin each question on a fresh page of writing paper.

Fasten the writing papers behind the given **Cover Page for Questions 1 & 2** and **Cover Page for Questions 3 & 4 or 5** respectively.

Hand in Questions **1 & 2** and **3 & 4 or 5** **separately**.

You are advised to spend about 30 minutes per question only.

INFORMATION FOR CANDIDATES

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

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

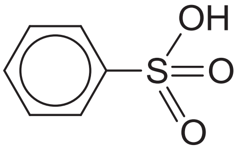
This document consists of **20** printed pages.

Section A

Answer **all** questions in this section.

1 Sulfa drugs are a class of sulfur containing compounds. These drugs have a variety of uses and can be classified as antibiotics and non–antibiotic drugs. They were the "wonder drugs" before penicillin was discovered.

A precursor to synthesising such sulfa drugs is aryl sulfonic acid with the general structure shown below.



Aryl sulfuric acids may be synthesised from the electrophilic substitution reaction between concentrated sulfuric acid and an aromatic compound.

(a) In an experiment to investigate the rate of reaction between concentrated sulfuric acid and benzene to form sulfonic acid, different volumes of sulfuric acid and benzene were used and the time taken for a complete reaction was recorded in **Table 1.1**.

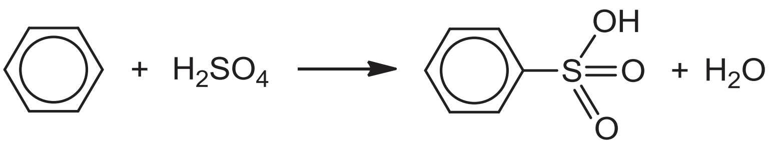
Table 1.1

Experiment	**Volume of concentrated sulfuric acid / cm^3**	**Volume of benzene / cm^3**	**Volume of water / cm^3**	**Time taken for complete reaction / s**
1	10	20	30	60
2	20	20	20	15
3	20	30	10	10

(i) Use the data above to deduce the order of reaction with respect to concentrated sulfuric acid and benzene, showing how you arrive at your answer. [3]

(ii) Hence, construct the rate equation for the reaction. [1]

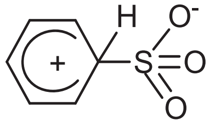
(b) The overall equation for the formation of the aryl sulfonic acid, $C_6H_5SO_3H$, through electrophilic substitution is given below.

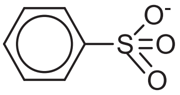


This reaction proceeds via a four–step mechanism.

- **Step 1**: The SO_3 electrophile is first generated from concentrated sulfuric acid given by the following equation.

  $$2H_2SO_4 \rightleftharpoons SO_3 + H_3O^+ + HSO_4^-$$

- **Step 2**: The SO_3 electrophile is then attacked by benzene to form an intermediate  .

- **Step 3**: When the intermediate from **Step 2** is deprotonated, an anion  is formed and the sulfuric acid is regenerated.

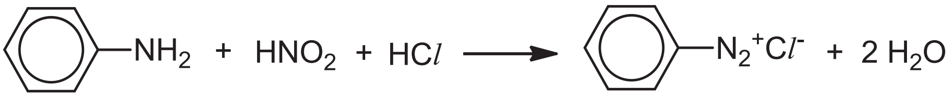
- **Step 4**: The $C_6H_5SO_3^-$ anion is then protonated by a hydronium ion, H_3O^+, to form the products, $C_6H_5SO_3H$ and water.

(i) Use the information given above to outline the mechanism for **Steps 2 to 4**, showing all charges and using curly arrows to show the movement of electron pairs. You are required to show the displayed formulae of all species. [3]

(ii) With reference to your answer in **(a)(ii)**, suggest which step corresponds to the rate determining step of the mechanism. [1]

(c) Another application of aryl sulfonic acid is in coupling with diazonium salts to form useful compounds.

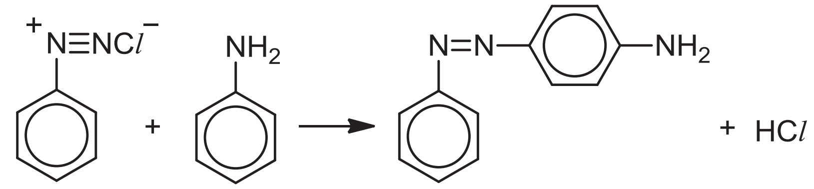
The diazonium salt is first produced by reacting phenylamine with cold nitrous acid and hydrochloric acid. This process is called diazotisation.



diazonium salt

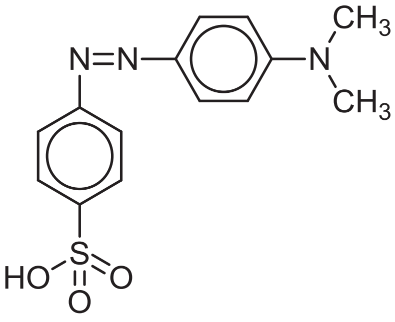
(i) Describe how you will carry out a simple chemical test to distinguish between phenylamine and the diazonium salt. [2]

The diazonium salt obtained from the diazotisation can undergo coupling with another phenylamine to form an azo compound, which is a useful dye. An example of a coupling reaction is given below.



diazonium salt azo compound

Methyl orange, which is used as an acid–base indicator, is formed using coupling reaction between a phenylamine derivative and a sulfonic acid containing diazonium salt.



methyl orange

(ii) Draw the structures of the two reactants used in the coupling reaction to synthesise methyl orange. State which of these two reactants is the electrophile. [3]

(d) Similar to sulfuric acid, concentrated sulfonic acids can be used as a catalyst in the synthesis of esters.

Compound **P**, $C_7H_{13}O_2Br$, is formed from the reaction between compounds **Q** and **R**, using concentrated sulfonic acid as a catalyst. Both compounds **Q** and **R** are able to rotate plane–polarised light.

Upon combustion with excess oxygen, 0.1 mole of compound **Q** produces 0.5 mole of carbon dioxide gas and 0.5 mole of water. Effervescence is observed when two moles of compound **Q** reacts with one mole of sodium carbonate.

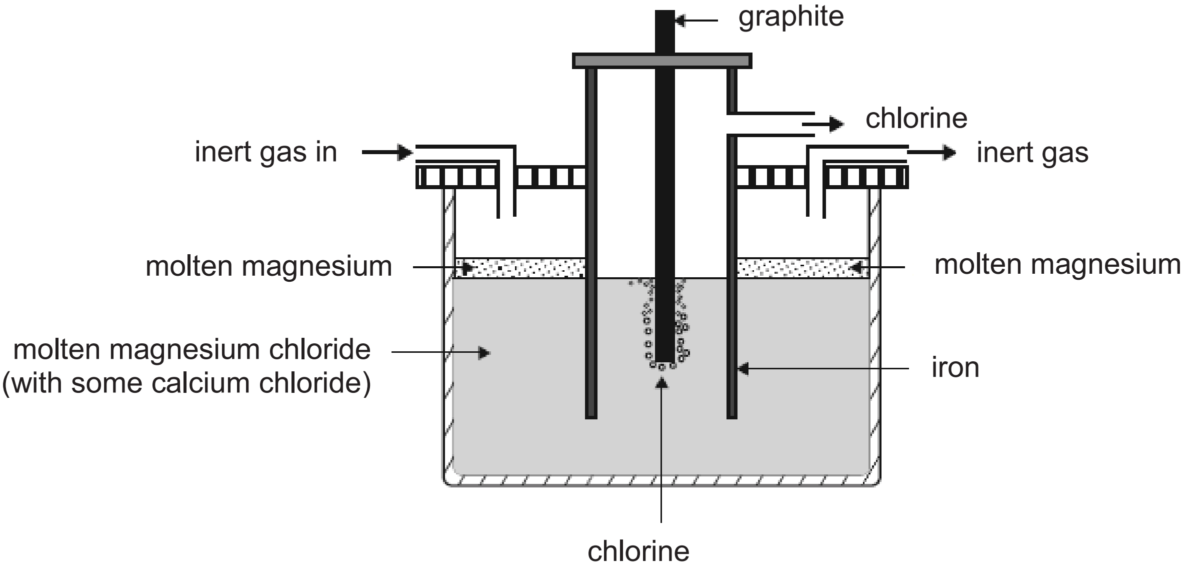
Compound **R** gives a yellow precipitate when heated in an alkaline solution of iodine. Upon heating with sodium hydroxide, followed by the addition of aqueous silver nitrate, a cream precipitate was formed.

Deduce the structures of **P**, **Q** and **R**, explaining the chemistry of the reactions described. [7]

[Total: 20]

2 Magnesium–containing compounds are important substances that have found many applications in our daily life.

(a) Magnesium metal is one of the most abundant elements on Earth. It is produced by the electrolysis of molten magnesium chloride. An example of such an electrolytic cell to form molten magnesium is shown below.



(i) Write the half equations, with state symbols, for the reactions at the graphite and iron electrodes. [2]

(ii) Explain why an inert gas is constantly blown into the compartment. [1]

(iii) Generally, to reduce energy consumption, $CaCl_2$ and $ZnCl_2$ can be added to lower the melting point of $MgCl_2$. However, in this electrolytic cell, only $CaCl_2$ can be used for this purpose.

With reference to $E^\ominus$ values in the *Data Booklet*, explain why only $CaCl_2$ can be used to lower the melting point of $MgCl_2$ in this electrolytic cell and not $ZnCl_2$. [2]

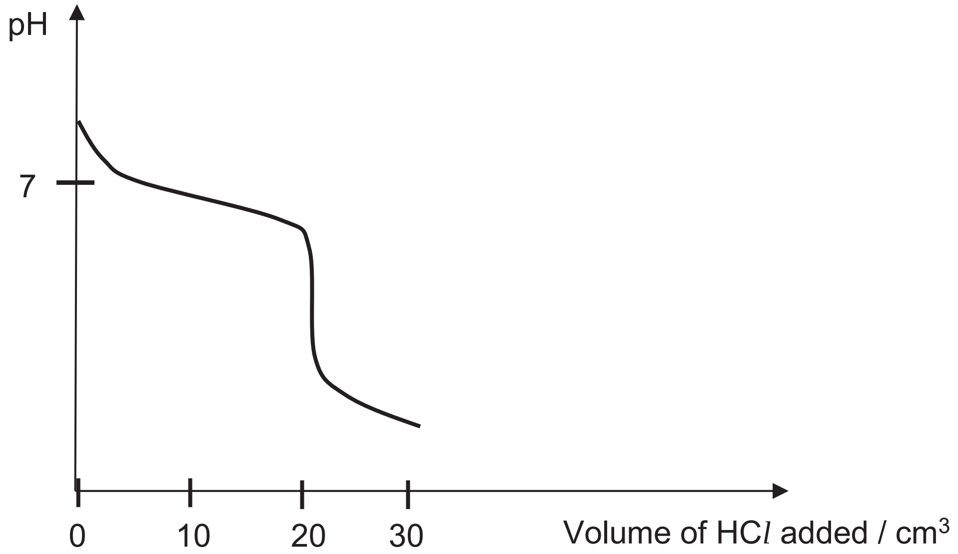
(iv) By quoting relevant $E^\ominus$ values, explain whether an iron electrode is a suitable replacement for the graphite electrode for the above electrolytic cell. [2]

(v) Another metal, **M**, is obtained by using the same electrolytic cell above. During the electrolysis, a current of 1.5 A was applied for 6 hours. The amount of metal **M** obtained was 1.12×10^{-1} mole. Determine the charge of the molten metal ion, $\mathbf{M}^{x+}$. [2]

(b) Magnesium hydrogencarbonate, $Mg(HCO_3)_2$, is a bicarbonate salt of magnesium with $K_b = 2.4 \times 10^{-8}$ mol dm^{-3}.

A sample of 0.10 mol dm^{-3} $Mg(HCO_3)_2$ solution was titrated against a 0.10 mol dm^{-3} solution of hydrochloric acid. The following titration curve was obtained.

Graph 2.1



(i) With the aid of the titration curve, calculate the volume of the sample of $Mg(HCO_3)_2$ solution. [1]

(ii) Calculate the initial pH on the titration curve. [2]

(iii) With the aid of an equation, explain why the pH value obtained at equivalence point is acidic. No calculations are required. [2]

(iv) Given the pH transition ranges of some indicators in **Table 2.1**, suggest with reasoning, an appropriate indicator for the titration between aqueous $Mg(HCO_3)_2$ and hydrochloric acid.

Table 2.1

Name of indicator	pH transition range
bromocresol green	4 – 6
thymolphthalein	9 – 11

[2]

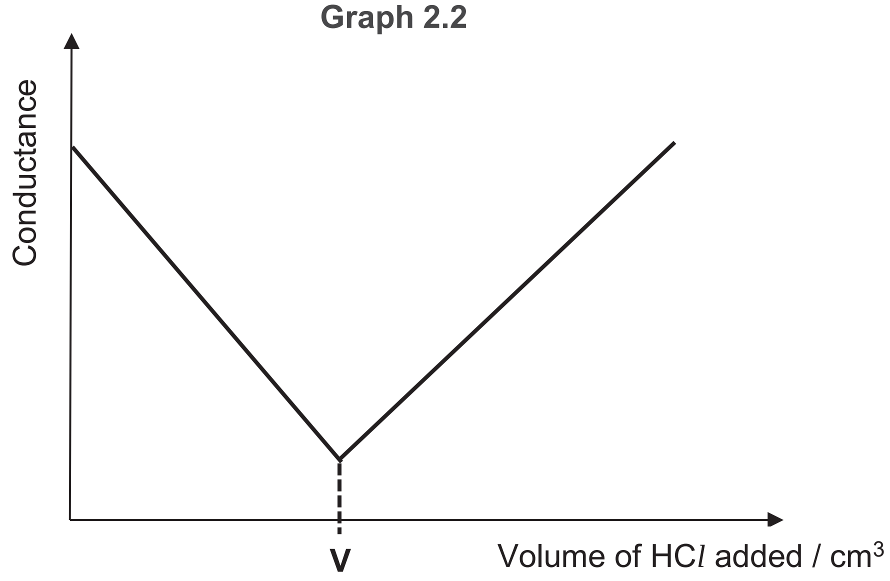
(v) State the volume of hydrochloric acid and calculate the pH at which the buffer operates at its maximum buffer capacity. [2]

(vi) As compared to magnesium hydrogencarbonate, magnesium carbonate has a K_b value of 2.10×10^{-4}. Explain why magnesium carbonate is a stronger base than magnesium hydrogencarbonate. [1]

(c) Instead of monitoring the pH change during the titration, the electrolytic conductivity of the reaction mixture is continuously monitored. The equivalence point is the point at which conductivity undergoes a sudden change.

The conductometric titration curve shown in **Graph 2.2** is obtained when 20 cm^3 of 0.10 mol dm^{-3} aqueous sodium hydroxide was titrated against 0.10 mol dm^{-3} aqueous hydrochloric acid. The change in conductance may be assumed to be only due to the changes in the amount of hydrogen ions and hydroxide ions.

Graph 2.2



Using your understanding of the titration between sodium hydroxide and hydrochloric acid, determine the volume **V** in the above conductometric titration curve. Explain the change in conductance as an increasing volume of HC*l* is added.

[3]

[Total: 22]

3 This question is about the chemistry of oxygen containing compounds.

(a) "Elephant's toothpaste" is a foamy substance caused by the rapid decomposition of hydrogen peroxide as shown by the equation:

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

(i) The decomposition of H_2O_2 results in the formation of a highly reactive species, •OH, with an unpaired electron. With the aid of an equation and the use of curly arrows to represent the movement of electrons, show how this reactive species may be formed from H_2O_2. [1]

(ii) Using data from the *Data Booklet*, calculate $E^{\ominus}_{cell}$ for the decomposition of hydrogen peroxide. [1]

(iii) Hence, calculate $\Delta G^{\ominus}$ for the decomposition of hydrogen peroxide. Explain the significance of your answer. [2]

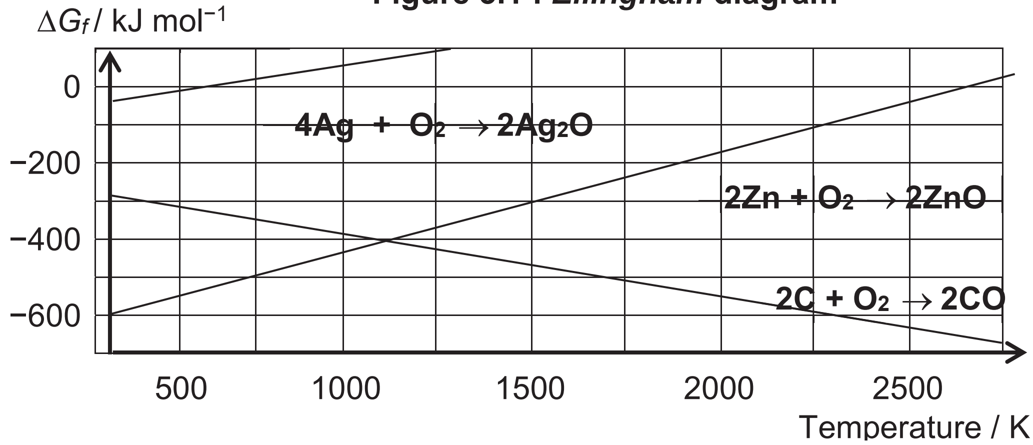
(iv) $Fe^{2+}(aq)$ ions can be used to catalyse the decomposition of hydrogen peroxide. Using relevant data from the *Data Booklet*, describe and explain the role of $Fe^{2+}(aq)$ ions in this reaction. You should support your answers with relevant equations. [3]

(b) ΔG, ΔH and ΔS are related by the following equation.

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

Figure 3.1 is an *Ellingham* diagram, which shows the variation in the Gibbs free energy change of **formation**, ΔG_f, with temperature, T, for some oxides.

Figure 3.1 : *Ellingham* diagram



(i) With reference to the gradient of the graph for the formation of zinc oxide, ZnO, explain with reasoning, the sign of ΔS. [2]

(ii) The *Ellingham* diagram in **Figure 3.1** can also be used to deduce the ease of decomposition of silver oxide and zinc oxide. Suggest which metal oxide is thermally less stable at 1000 K. Explain your answer. [2]

(iii) Similar to enthalpy change of reaction, the Gibbs free energy, ΔG, of a reaction can be calculated using the following expression.

$$\Delta G = \sum \Delta G_f\text{(products)} - \sum \Delta G_f\text{(reactants)}$$

Calculate the ΔG value for the reduction of zinc oxide by carbon at 2250 K. Hence, comment on the feasibility of this reaction at 2250 K. [2]

(c) The zinc–air battery is commonly used as small button cells in watches and hearing aids. When a gas permeable and liquid–tight membrane sealing tab in the button cell is removed, oxygen in the air is absorbed into an alkaline electrolyte.

The positive electrode is made of porous carbon and the negative electrode consists of zinc. The zinc electrode slowly dissolves to form a colourless solution. The electrolyte used is a paste of potassium hydroxide.

(i) Write equations, with state symbols, for the reactions that occur at the anode and the cathode respectively. [2]

(ii) The zinc–air battery has a cell potential of +1.59 V. Using relevant data from the *Data Booklet*, calculate the electrode potential for the reaction at the anode. [1]

(iii) The zinc electrode of a new zinc–air button cell weighs 1.85 g. The cell can run until 80% of the zinc is consumed.

Calculate the maximum amount of current that can be drawn from the cell if it is expected to last for 365 days. [1]

(iv) Common alkaline batteries contain zinc and manganese(IV) oxide in a paste of potassium hydroxide. The overall equation is as shown.

$$Zn\,(s) + MnO_2\,(s) + H_2O\,(l) \rightarrow ZnO\,(s) + Mn(OH)_2\,(s)$$

Based on this information, suggest an advantage, other than lower cost that the zinc–air battery has over the common alkaline battery of a similar mass. Explain your answer. [1]

[Total: 18]

Section B

Answer **one** question from this section.

4 Barium hydroxide is a compound that can exist in the anhydrous or hydrated forms. Its main uses are as a precursor for the manufacture of other barium compounds and as a substance to remove sulfates from various products.

(a) **(i)** Draw the dot–and–cross diagram for sulfate(VI) ion. In your diagram, use the symbol 'x' and '•' to distinguish between the electrons from sulfur and oxygen, and the symbol '∆' for any additional electrons responsible for the overall negative charge. [1]

(ii) Using the *Valence Shell Electron Pair Repulsion* theory, explain the shape of sulfate(VI) ion. [2]

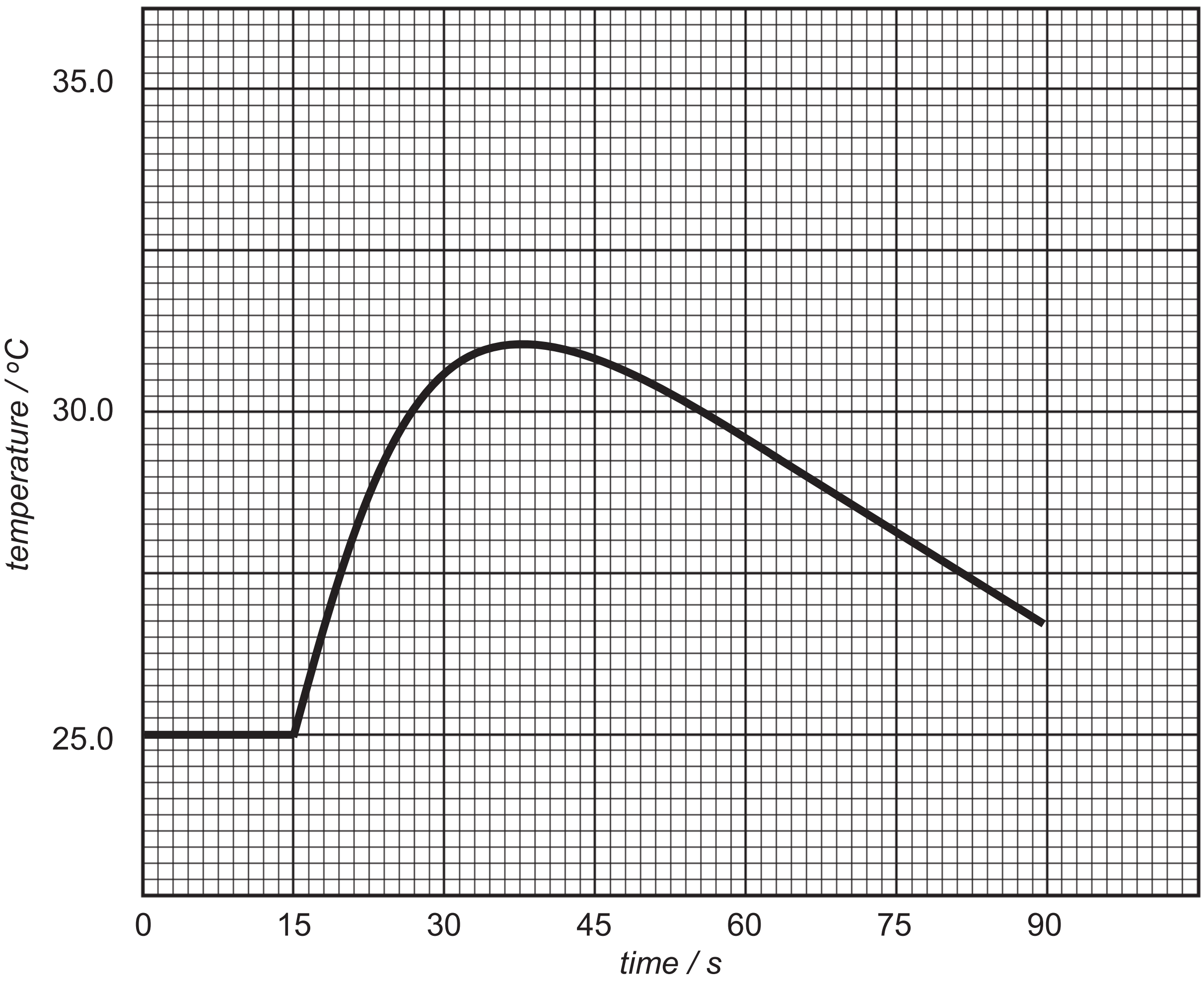
(b) Barium ion most commonly exists in the octahydrate form while magnesium ion usually exists in the hexahydrate form. When a 3.00 g solid sample of $Ba(OH)_2.8H_2O$ is strongly heated, the experimental loss in mass is 1.54 g.

$$Ba(OH)_2.8H_2O\ (s) \rightarrow BaO\ (s) + 9H_2O\ (g)$$

(i) By means of calculations, explain whether the decomposition of the $Ba(OH)_2.8H_2O$ sample is complete. [2]

(ii) Explain whether the thermal decomposition temperature of the anhydrous form of barium hydroxide is higher or lower than that of anhydrous magnesium hydroxide. [2]

(c) A temperature probe is used to measure the temperature of 100 cm^3 of 0.8 mol dm^{-3} barium hydroxide in a polystyrene cup. At 15 seconds, 120 cm^3 of 2.0 mol dm^{-3} hydrochloric acid is added. The temperature readings are recorded using a data logger for 90 seconds. The results are shown below.



(i) Construct appropriate lines on the graph above and determine the temperature rise of the reaction. [1]

(ii) Using your answer in **(c)(i)**, calculate a value for the enthalpy change of neutralisation for the reaction. [2]

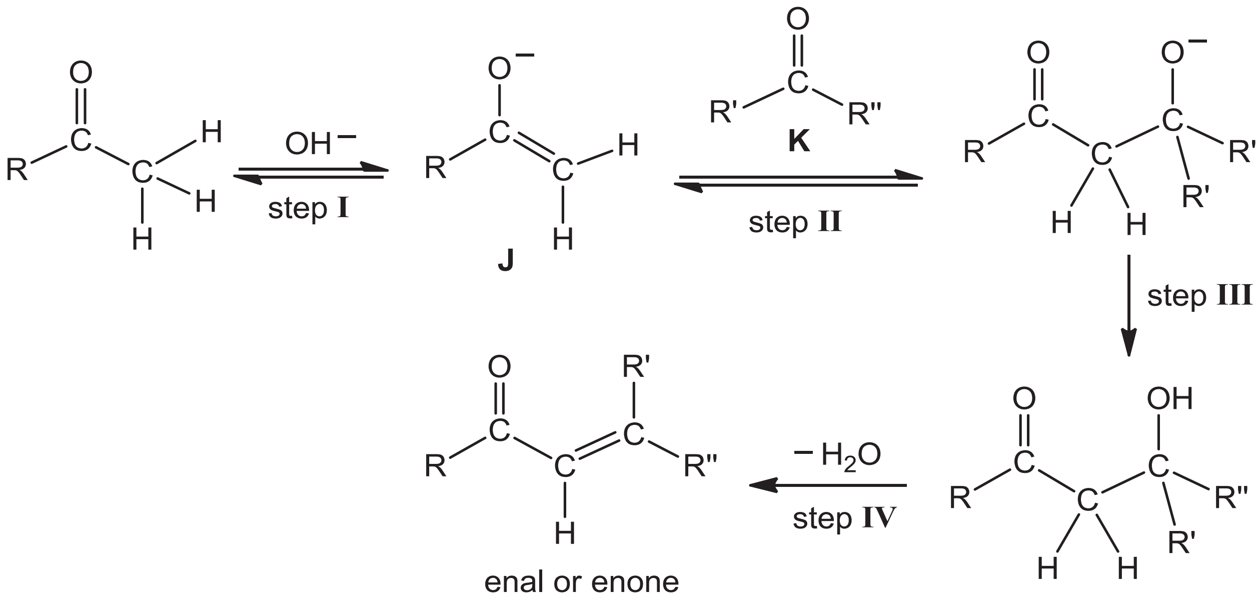
(d) Using the following data, calculate a value for the lattice energy of barium hydroxide by means of a *Born–Haber* cycle.

enthalpy change of atomisation of barium	= +182 kJ mol^{-1}
enthalpy change of formation of barium hydroxide	= –940 kJ mol^{-1}
$\frac{1}{2}O_2\,(g) + \frac{1}{2}H_2\,(g) + e^- \rightarrow OH^-\,(g)$	= +230 kJ mol^{-1}

[3]

(e) Barium hydroxide may be used as a strong base for the first step of the *aldol condensation* reaction to produce an 'enal' or an 'enone'. An 'enal' is a molecule with an alkene group adjacent to an aldehyde group. An 'enone' is a molecule with an alkene group adjacent to a ketone group.

The following flowchart shows the *aldol condensation* reaction.

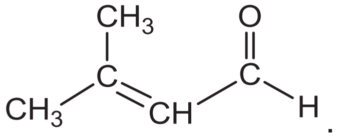


(R, R' and R'' = alkyl group or H atom)

(i) State the roles of species **J** and **K** in step **II**. [1]

(ii) State the type of reactions for steps **III** and **IV**. [1]

(iii) Suggest the structures of the two reactants required to synthesise the 'enal',


. [2]

(iv) In certain organic chemistry reactions, concentrated sulfuric acid and concentrated phosphoric acid may be used interchangeably.

Using the above information, propose a two–step synthesis route to convert the enal $(CH_3)_2C{=}CHCHO$, as the only available organic reactant, to compound **Q**.

Q

State the reagents and conditions required as well as the structures of the intermediates formed. [3]

[Total: 20]

5 Hydrogen cyanide, HCN, is extremely toxic and with sufficient concentrations it leads to rapid death. During the Second World War, a form of hydrogen cyanide known as *Zyklon B* was used in the Nazi gas chambers.

(a) Draw a dot–and–cross diagram to illustrate the bonding in HCN. [1]

(b) The synthesis of HCN was developed in the early 1900s. The most commonly used procedure is the *Andrussow* process. A less common method is the *BMA* process.

Andrussow process: $CH_4\,(g) + NH_3\,(g) + \frac{3}{2}\,O_2\,(g) \rightarrow HCN\,(g) + 3\,H_2O\,(g)$

BMA process: $CH_4\,(g) + NH_3\,(g) \rightarrow HCN\,(g) + 3\,H_2\,(g)$

(i) Using information from the *Data Booklet*, calculate the enthalpy change of reaction for each of the two processes above. [2]

(ii) Hence, comment on why the *Andrussow* process is the preferred procedure. [1]

(c) Other than gaseous HCN, sodium cyanide and potassium cyanide are used in the powder form in many homicide incidents.

It was predicted that salts like zinc cyanide, $Zn(CN)_2$, are harmless. The solubility data of some of these cyanides are given below.

solubility of NaCN at 25 °C = 1.3 mol dm^{-3}
solubility of KCN at 25 °C = 1.1 mol dm^{-3}
K_{sp} of $Zn(CN)_2$ = 8.0×10^{-12} mol^3 dm^{-9}

Using the above information, explain why it was predicted that $Zn(CN)_2$ is harmless. [2]

(d) When cyanide is transported to the body's tissues, it binds irreversibly to an enzyme called *cytochrome c oxidase* and stops cells from being able to use oxygen for respiration. *Cytochrome c oxidase*, which contains Fe^{2+}, converts oxygen to water during respiration.

The United States standard cyanide antidote kit was developed in the last decade as a first aid tool. It comprises of a three step process.

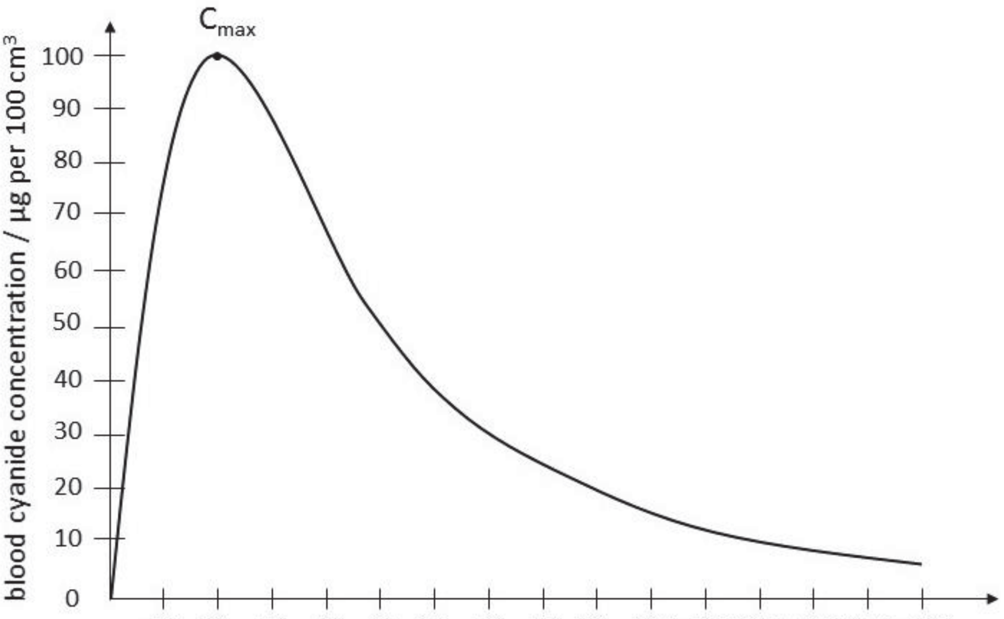
Step 1: Inhalation of a small dosage of amyl nitrite.
Step 2: Intravenous delivery of sodium nitrite, $NaNO_2$.
Step 3: Intravenous delivery of sodium thiosulfate.

(i) The nitrite oxidises some of the Fe^{2+} in haemoglobin in the red blood cells to Fe^{3+}, where Fe^{3+} has a higher affinity for cyanide. Suggest an advantage and a disadvantage of using nitrite as an antidote for cyanide poisoning. [2]

(ii) The sodium thiosulfate converts cyanide into thiocyanate ions, SCN^-, which is relatively harmless to the human body. Suggest, using coordination chemistry, how this conversion serves as an antidote. [1]

The human body has a mechanism which rapidly converts cyanide into the harmless thiocyanate via a first order kinetics when small doses are ingested. The cyanide concentration can be traced and represented by the **Graph 5.1**. **C_{max}** refers to the maximum concentration of cyanide in the body after ingestion. After which, it is eliminated by converting it to thiocyanate.

Graph 5.1



(iii) The safe level of cyanide concentration in blood is 20 μg per 100 cm^3 and below. From 20 to 200 μg per 100 cm^3, it is at a toxic level where the body may develop complications if the level is not brought back to safety after more than 60 minutes. (*Note: 1 μg = 1 x 10^{-6} g.*)

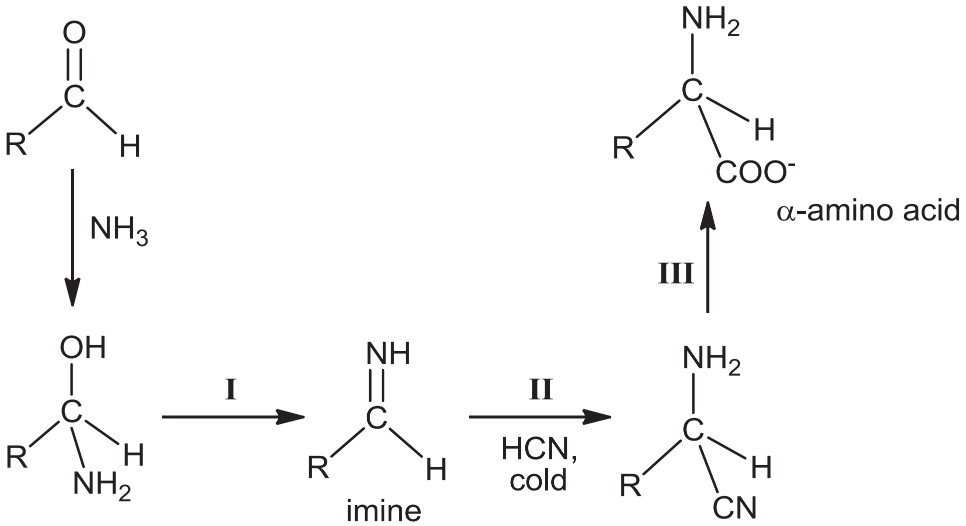
Using the graph and the above information, calculate the maximum cyanide blood concentration a victim can tolerate before complication occurs. [2]

In the octahedral complex, the d–subshell of the Fe^{3+} ion is split into two energy levels. In a 'high spin' state, the electrons occupy all the d–orbitals singly before pairing up in the lower energy d–orbitals. In a 'low spin' state, the lower energy d–orbitals are filled first, by pairing, before the higher energy d–orbitals are used.

(iv) Explain why splitting of the d–subshell occurs in the octahedral complex. [1]

(v) When cyanide binds with Fe^{3+}, it forms an octahedral complex which is at a 'low spin' state. Draw the electronic distribution of Fe^{3+} ion in its d–orbitals, showing the two energy levels. [1]

(e) Despite its lethal effect, hydrogen cyanide is often used in organic synthesis as a precursor to many important products like amino acids. It was first used by German chemist Adolph Strecker in 1850 to produce α–amino acids.



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

(ii) Suggest the reagent and condition for step **III**. [1]

(iii) Suggest why a low temperature condition is used in step **II**. [1]

(iv) Step **II** proceeds via 2 stages:

1. acid–base reaction between N in the imine and HCN
2. followed by a nucleophilic attack on C by CN^-

Outline a mechanism for step **II**, showing all charges and using curly arrows to represent the movement of electron pairs. [2]

(v) Suggest why the amino acid synthesised by *Strecker's* method shows no optical activity while that of a naturally occurring amino acid rotates plane polarised light. [2]

[Total: 20]

End of Paper 3

2017 MJC H2 Chemistry Prelim Paper 4

1 Magnesium carbonate is a white solid that is readily found in nature. In this experiment, you will determine the percentage purity of a sample impure magnesium carbonate.

FA 1 is a sample of impure magnesium carbonate. You may assume that only the magnesium carbonate present in the sample will react with the acid. You will first dissolve **FA 1** in excess hydrochloric acid.

$$\mathrm{MgCO_3(s) + 2HC}l\mathrm{(aq) \rightarrow MgC}l_2\mathrm{(aq) + H_2O(}l\mathrm{) + CO_2(g)}$$

The resulting solution will then be titrated using sodium hydroxide. You may assume that no compounds present in **FA 1** will react with the sodium hydroxide.

$$\mathrm{NaOH(aq) + HC}l\mathrm{(aq) \rightarrow NaC}l\mathrm{(aq) + H_2O(}l\mathrm{)}$$

FA 1 is impure magnesium carbonate.
FA 2 is 2.0 mol dm^{-3} hydrochloric acid, $\mathrm{HC}l$.
FA 4 is 0.20 mol dm^{-3} sodium hydroxide, NaOH.
methyl orange indicator

(a) Procedure

Preparation of standard solution

1. Fill a burette with **FA 2**.
2. Run between 47.50 and 48.50 cm^3 of **FA 2** into a 250 cm^3 beaker.
3. Record your burette readings and the volume of **FA 2** in the space below.

4. Weigh accurately about 2.0 g of **FA 1** in a weighing bottle.
5. Transfer the **FA 1** from the weighing bottle as fully as you can into the beaker containing **FA 2**.
6. Reweigh the weighing bottle and record all masses in the space below.

7. Stir the mixture carefully until all the solid has reacted.
8. Transfer the contents of the beaker into the volumetric flask.
9. Rinse the beaker with distilled water and add it to the volumetric flask. Make the solution up to 250 cm^3 with distilled water and mix thoroughly. Label this solution as **FA 3**.

Titration

1. Fill another burette with **FA 3** from the volumetric flask.
2. Pipette 25.0 cm^3 of **FA 4** into a conical flask.
3. Add a few drops of methyl orange indicator.
4. Titrate **FA 4** with **FA 3** until the end-point is reached.
5. Repeat the titration as many times as you think necessary to obtain consistent results.
6. Record your titration results in the space provided below.

[7]

M1	M2	M3	M4	M5	M6	M7

(b) From your titration results, obtain a suitable volume of **FA 3** to be used in your calculations. Show clearly how you obtained this volume.

volume of **FA 3** = ……………………………… [1]

(c) Calculations

(i) Calculate the amount of hydrochloric acid present in the volume of **FA 3** obtained in **(b)**.

amount of HC*l* = …………..……………….[1]

(ii) Calculate the amount of hydrochloric acid present in 250 cm^3 of **FA 3**.

amount of HC*l* in 250 cm^3 **FA 3** = …………..……………….[1]

(iii) Calculate the amount of hydrochloric acid in **FA 2** that has reacted with magnesium carbonate in **FA 1**.

amount of HC*l* reacted with $MgCO_3$ = ……………………………[1]

(iv) Calculate the percentage purity of magnesium carbonate present in **FA 1**.
[A_r: C, 12.0; O, 16.0; Mg, 24.3]

percentage purity of **FA1** = …………………….. [1]

(d) **(i)** The maximum error in a single burette reading is ±0.05 cm^3.

Student X, carrying out this experiment, recorded that 48.50 cm^3 of **FA 2** was added to **FA 1**.

What are the smallest and largest possible volumes of **FA 2** that were added?

smallest volume used = ……………………………………

largest volume used = ……………………………………

[1]

(ii) Student Y used an identical mass of **FA 1** but added 47.70 cm^3 of **FA 2** instead. How would the percentage purity of **FA 1** calculated by student Y compare to that obtained by student X? Explain your answer.

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

[1]
[Total: 14]

2 Determination of the enthalpy change of neutralisation, *ΔH_n*

The enthalpy change of neutralisation, ΔH_n, is the enthalpy change when one mole of water is formed during a neutralisation reaction as shown in the equation.

$$H^+ (aq) + OH^- (aq) \rightarrow H_2O\ (l)$$

FA 5 is a solution of sulfuric acid, H_2SO_4
FA 6 is 1.50 mol dm^{-3} potassium hydroxide, KOH

You will perform a series of experiments using different volumes of **FA 5** and **FA 6**. The change in temperature, ΔT, for each experiment will be determined and used to plot a graph of ΔT against volume of **FA 5** used.

You will then use data from the graph to determine a value for the enthalpy change of neutralisation, ΔH_n.

(a) Determining the change in temperature for a series of reactions between FA 5 and FA 6

(i) Procedure

1. Support the Styrofoam cup in a 250 cm^3 beaker.
2. Add 10.0 cm^3 of **FA 5** from a measuring cylinder into the Styrofoam cup.
3. Measure the temperature of **FA 5** in the Styrofoam cup. Record the initial temperature of the solution of **FA 5** as $\mathbf{T_{FA5}}$.
4. Wash and dry the thermometer.
5. Measure 40.0 cm^3 of **FA 6** into another measuring cylinder.
6. Measure the temperature of **FA 6** solution using the thermometer and record the initial temperature of the solution of **FA 6** as $\mathbf{T_{FA6}}$.
7. Tip the **FA 6** in the measuring cylinder into the Styrofoam cup, stir and record the maximum temperature obtained in the reaction as $\mathbf{T_{max}}$.
8. Rinse and dry the Styrofoam cup and the thermometer.
9. Repeat steps 2 to 8 using 20.0 cm^3 and 30.0 cm^3 of **FA 5** and appropriate volumes of **FA 6** each time such that the total volume of the reacting mixture is 50 cm^3.

In an appropriate format in the space provided, record:

- all measurements of volumes used,
- all temperatures measured and the change in temperature, **ΔT**.

$\Delta\mathbf{T} = \mathbf{T}_{max} - \mathbf{T}_{weighted\ initial}$

$$\mathbf{T}_{weighted\ initial} = \frac{(\text{Volume of FA 5} \times T_{\text{FA 5}}) + (\text{Volume of FA 6} \times T_{\text{FA 6}})}{\text{Volume of FA 5} + \text{Volume of FA 6}}$$

These data should be recorded for the experiments described in **(a)(i)**, together with additional experiments described in **(a)(ii)**.

Results

[5]

M1	M2	M3	M4	M5

(a)(ii) On the grid provided, plot a graph of Δ**T** (y–axis) against volume of **FA 5** (x–axis) using the data you obtained in **(a)(i)**.

Consider your plotted plots. Carry out four more experiments which will enable you to identify the volume of **FA 5** which gives the maximum change in temperature, Δ**T***max*. In each case, the total volume of the reaction mixture must be 50 cm^3.

You may find it useful to consider the results obtained from each experiment before choosing the volumes of solutions for the next experiment.

(iii) Draw a line of best fit through the points where the temperature rise is increasing and another best fit line through the points where the temperature rise is decreasing. Extrapolate these two lines until they cross.

[3]

M1	M2	M3

(iv) Determine from your graph, the maximum change in temperature, Δ**T***max*, and the volume**, V***max*, of **FA 5** required to obtain this value.

Δ**T***max* = …………………………… **V***max* = ………………………… [2]

(b) Using your answers in **(a)(iv)**, calculate

(i) the concentration, in mol dm^{-3}, of H_2SO_4 in **FA 5**.

concentration of H_2SO_4 in **FA 5** = ………..……………………… [1]

(ii) the heat change for the neutralisation reaction at $\Delta\mathbf{T}_{max}$.

You should assume that the specific heat capacity of the final solution is 4.18 J g^{-1} K^{-1}, and the density of the final solution is 1.00 g cm^{-3}.

heat change = ………………………………… [1]

(c) Using your answers from **(b)(i)** and **(b)(ii)**, calculate a value for the enthalpy change of neutralisation, ΔH_n.

ΔH_n =…………………………..[3]

M1	M2	M3

(d) When the experiment is done in the way described, the results are not very accurate.

Apart from limitations due to the accuracy of the measuring equipment, suggest why the temperature rises are more inaccurate as they approach their maximum value.

....

....

....

[1]

(e) In another experiment, 1.50 mol dm^{-3} aqueous ammonia is used instead of the 1.50 mol dm^{-3} aqueous potassium hydroxide.

Draw on your graph another pair of lines to show the results you would expect to obtain. Explain your answer.

....

....

....

....

....

....

....

[2]

(f) Planning

Barium carbonate, $BaCO_3$, is widely used in the ceramics industry as an ingredient in glazes. $BaCO_3$ can be formed from the reaction between barium oxide and carbon dioxide as shown in *Reaction 1*.

Reaction 1 : $BaO\,(s) + CO_2\,(g) \rightarrow BaCO_3\,(s)$ ΔH_1

Experimentally, it is difficult to measure the enthalpy change of reaction, ΔH_1 directly. Instead, Hess's Law can be used to calculate ΔH_1 using experimentally determined values of ΔH_2 and ΔH_3 for the following reactions as shown below.

Reaction 2 : $BaO\,(s) + 2HNO_3\,(aq) \rightarrow Ba(NO_3)_2(aq) + H_2O(l)$ ΔH_2

Reaction 3 : $BaCO_3\,(s) + 2HNO_3\,(aq) \rightarrow Ba(NO_3)_2(aq) + H_2O(l) + CO_2\,(g)$ ΔH_3

(i) Construct an energy cycle using the information in the question to show how the enthalpy change of reaction, ΔH_1, can be calculated from ΔH_2 and ΔH_3.

[1]

(ii) You are to plan an experiment that will allow you to determine the enthalpy change of *Reaction 2*, ΔH_2. Your plan must enable you to plot a graph that includes data from the experiment. You may assume that all solutions have a density of 1 g cm^{-3} and the specific heat capacity of water is 4.18 J g^{-1} K^{-1}.

You may also assume that the following are provided:

- 3 g solid barium oxide
- 120 cm^3 of 0.500 mol dm^{-3} aqueous nitric acid, HNO_3
- Styrofoam cup
- stop-watch
- thermometer
- apparatus and materials normally found in a school laboratory.

YOU ARE NOT REQUIRED TO PERFORM THIS EXPERIMENT.

In your plan, you should include details of:

- calculations of suitable quantities of reagents used;
- an outline of all essential experimental procedures;
- a sketch of the graph you expect to obtain and
- an outline of the calculations you would perform to find ΔH_2 in kJ mol^{-1}.

[6]
[Total: 25]

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3 Inorganic and Organic Analysis

(a) You are provided with **FA 7** and **FA 8**.

In all tests, the reagents should be added gradually until no further change is observed, with shaking after each addition.

At each stage of any test you are to record details of the following.

- colour changes seen
- the formation of any precipitate
- the solubility of such precipitates in an excess of the reagent added

Where gases are released they should be identified by a test, described in the appropriate place in your observations.

Record your observations in the spaces provided. You should indicate clearly at which stage in a test a change occurs.

1. **FA 7** is a sodium compound containing one anion listed on page 20. Dissolve the **FA 7** provided in about 15 cm^3 of distilled water in a boiling tube.

Carry out the following tests and record your observations in the table below.

Test	Observations
(i) To a 1 cm depth of the solution of **FA 7** in a test-tube, add a few drops of aqueous barium nitrate followed by dilute nitric acid.	
(ii) To a 1 cm depth of the solution of **FA 7** in a test-tube, add an equal volume of aqueous hydrogen peroxide, then	
add a few drops of aqueous barium nitrate, followed by dilute nitric acid.	
(iii) To a 2 cm depth of the solution of **FA 7** in a test tube, add an equal volume of sulfuric acid, then heat the mixture gently and cautiously.	

Test	Observations
(iv) To a 1 cm depth of the solution of **FA 7** in a test-tube, add an equal volume of aqueous sodium hydroxide, then	
add a few drops of aqueous potassium manganate(VII),	
followed by sulfuric acid.	

(v) Identify the anion in **FA 7**, and state the evidences for your identification.

anion ....

evidence ....

....

....

....

....

....

[6]

2. **FA 8** solution contains two cations from those listed in the Qualitative Analysis Notes on page 19. Carry out tests using reagents that will allow you to identify which ions are present.

(i) In the space below, draw a single table to record details of the tests performed and observations made.

[4]

(ii) Identify the cations in **FA 8**, and state the evidences for your identification.

cation ....

evidence ....

....

....

cation ....

evidence ....

....

....

[2]

(b) You are provided with an organic solution **FA 9** which contains one functional group.

FA 9 gives a positive test with 2,4-dinitrophenylhydrazine. Devise two other confirmatory tests using the **bench reagents provided** to identify the functional group present in **FA 9**.

(i) In the space below, draw a single table to record details of the tests performed and observations made.

(ii) Identify the functional group in **FA 9**, and state the evidences for your identification.

Functional group in **FA 9** ....

evidence ....

....

....

....

[4]
[Total : 16]

Answers for 2017 H2 Chemistry P1

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

2017 MJC H2 Chemistry Prelim Suggested Answers

1(a) (i) An acid is a substance that can donate a proton (H^+) to another substance/proton donor.

A base is a substance that can accept a proton (H^+) from another substance/proton acceptor.

(ii) *Arrhenius theory* of acids and bases applies to aqueous system only.
or
Arrhenius theory of acids and bases does not apply to acids/bases that do not dissociate H^+/OH^- from itself.

(b) (i)

$$\frac{[H^+]_{water}}{[H^+]_{methanol}} = \frac{\sqrt{10^{-2.45}}}{\sqrt{10^{-7.50}}} = 331$$

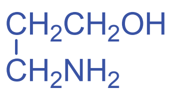
(ii) Water is a more polar solvent than methanol. (hence the both H^+ and conjugates bases can better stabilized through the formation of stronger ion-dipole interations).

(iii) $CH_2(CN)COOH$, can form more extensive hydrogen bonding with water due to its additional –CN group .

(c) (i) In dimethylamine, there are more electron–donating $-CH_3$ groups that increases the electron density of the lone pair on N atom which increases the availability of the lone pair on N to accept H^+.

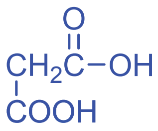
(ii) Trimethylamine have 3 bulky methyl groups that causes steric hindrance. Hence it reduces the availability of lone pair of electron on N atom to accept H^+.

(d) (i)



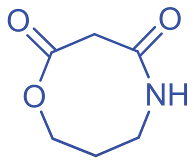
$$\begin{array}{l} CH_2CH_2OH \\ | \\ CH_2NH_2 \end{array}$$

A



$$\begin{array}{l} \qquad\; O \\ \qquad\; \| \\ CH_2C-OH \\ | \\ COOH \end{array}$$

B



D

(ii) Step **I**: acidic hydrolysis
Step **II**: Nucleophilic acyl substitution

(iii) Step **I**: dilute sulfuric acid, heat
Step **III**: dilute sulfuric acid, heat followed by $LiAlH_4$, dry ether, rtp

2(a) Zn obtained from daily feed = 0.7 × 180 × 3 / 100 = 3.78 mg

(It meets the recommended quantity for daily intake)

(b) **(i)** **I**: oxidation

II: acid–metal displacement

(ii) Cation in **A**: $[Fe(H_2O)_6]^{3+}$

Gas **B** is H_2.

$[Fe(H_2O)_6]^{3+}$ has very high charge density , it polarises the electron cloud of the surrounding water molecules, weakens and breaks the O–H bond, which results in the release of a proton.

(iii) Ligand exchange

$[Fe(H_2O)_6]^{2+} + 6CN^- \rightarrow [Fe(CN)_6]^{4-} + 6H_2O$

(iv) ***1.*** Fe^{2+} has partially–filled d–orbitals.

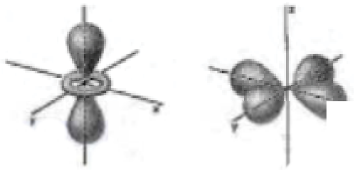
In $[Fe(H_2O)_6]^{2+,}$ the d orbitals are split into two groups due to the ability of the ligands to split them.

A lower energy d electron undergoes d–d transition and is promoted to a higher energy d orbital. During the transition, the d electron absorbs the red wavelength of light from the visible region of the electromagnetic spectrum and the remaining wavelengths not absorbed appear as the green colour.

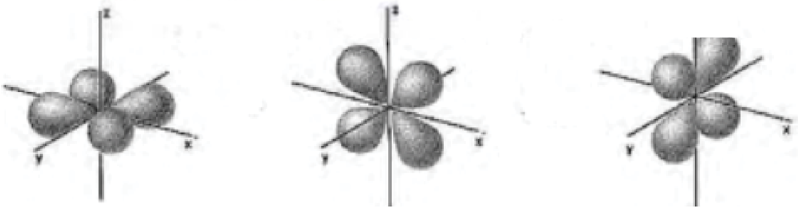
2. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$

3. $[FeF_5(H_2O)]^{2-}(aq)$ is colourless because the energy absorbed for d–d transition is out of the range of the visible spectrum.

(v) **correct upper** orbital diagram



correct lower orbital diagram



Any one from each category

(c) **(i)** Fe has more protons and hence has greater nuclear charge than Ca. But there is only slight increase in screening effect as electrons are added to the inner 3d orbitals that provide shielding effect for the 4s electrons from Ca to Fe.

Hence, Fe has greater effective nuclear charge and has increased electrostatic attraction between the nucleus and the valence 4s electrons compared to Ca. Therefore, atomic radius of iron is less than calcium.

(ii) The relative atomic mass of Fe is larger than that of Ca and the atomic radius of Fe (0.126) is smaller than that of Ca (0.197 nm) thus the densities of Fe and Cu is greater than that of Ca.

(d) **(i)** $\mathrm{MgC}l_2$ solution: pH = 6.5 $\mathrm{PC}l_5$ solution: pH = 2.0

$$\mathrm{MgC}l_2\,(s) + 6\mathrm{H_2O}\,(l) \longrightarrow [\mathrm{Mg(H_2O)_6}]^{2+}\,(aq) + 2\mathrm{C}l^-\,(aq)$$

$$[\mathrm{Mg(H_2O)_6}]^{2+}\,(aq) \rightleftharpoons [\mathrm{Mg(H_2O)_5(OH)}]^{+}\,(aq) + \mathrm{H}^+\,(aq)$$

$$\mathrm{PC}l_5\,(s) + 4\mathrm{H_2O}\,(l) \rightarrow \mathrm{H_3PO_4}\,(aq) + 5\mathrm{HC}l\,(aq)$$

(ii) Element **Z** belongs to Group 13. => **Z** is A*l*.
Element **F** could be element **Z**.

3(a) **Y** is the plot for NOC*l*. This is because of its permanent dipole–permanent dipole interaction between its molecules which is most significant, hence it deviates most from ideal gas .

(b) (i) $$n = \frac{5.80\times10^{6}\times5.0\times10^{-3}}{8.31\times(250+273)} = 6.67$$

(ii) $$K_p = \frac{(P_{NO})^2(P_{Cl_2})}{(P_{NOCl})^2}\ \mathbf{Pa}$$

(iii) Let x be the change in number of moles of gas.
Total number of moles of gases at equilibrium = $5 - 2x + 2x + x$
$x = 1.673$
At equilibrium,
No. of moles of NOC*l* = 1.65
No. of moles of NO = 3.35
No. of moles of $\mathrm{C}l_2$ = 1.67

$K_p = 5.95 \times 10^6$ Pa

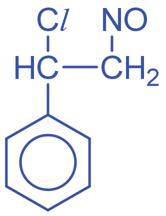
(c) **(i)** $K_c = 1.40$

(ii) When T increases, K_c decreases .

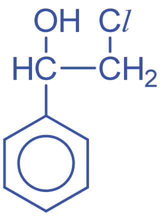
(iii) Since K_c decreases, the amount of reactants will increases and products will decrease .

By *Le Chatelier's* Principle, when temperature is raised and equilibrium position shifts left , the backward reaction is endothermic so as to absorb heat . Therefore the forward reaction is exothermic .

(d) **(i)**

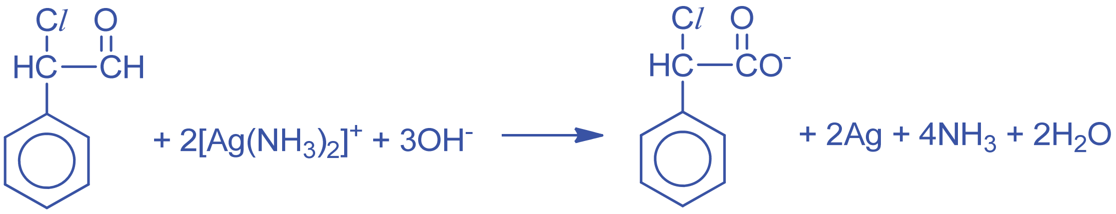


P



Q

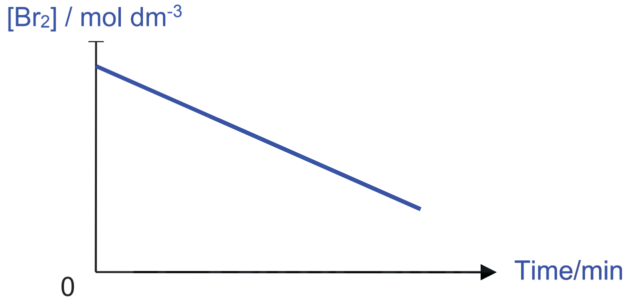
(ii) Tollens' reagent



Accept alternative reagents

4(a) **(i)** Order of reaction w.r.t to CH_3COCH_3 is 1 .
Order of reaction w.r.t to H^+ is 1

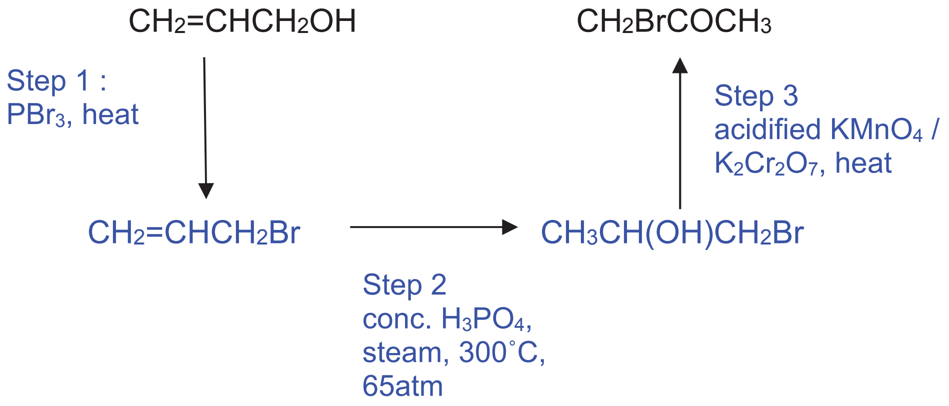
(ii)



(iii) Rate = $k[CH_3COCH_3][H^+]$

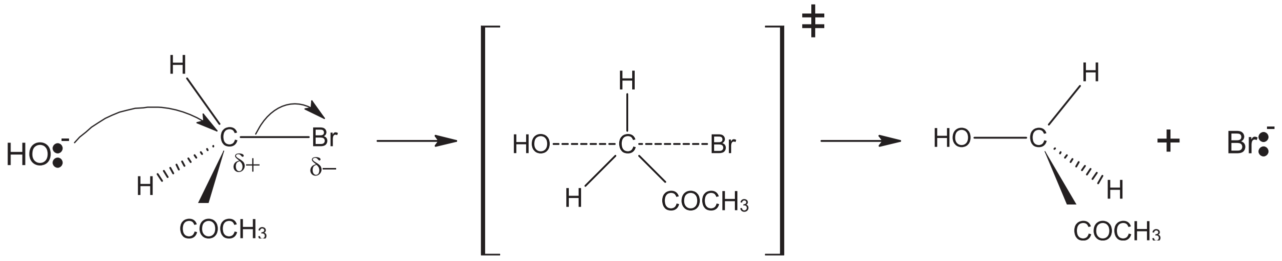
(iv) $k = 3.80 \times 10^{-3}$ $mol^{-1}\ dm^3\ min^{-1}$

(b) **(i)**



(ii) Add aqueous Br_2, r.t.p to the sample.
If the orange Br_2 decolourises, $CH_2=CHCH_2OH$ is present, reaction is not complete .

(c) **(i)** Nucleophilic substitution S_N2



(ii) CH_3CH_2COBr has a faster rate of hydrolysis.

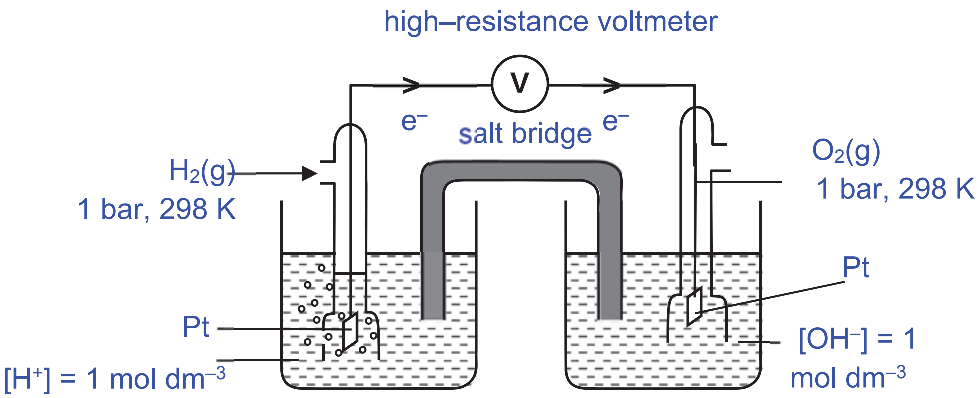
The carbonyl C atom in CH_3CH_2COBr is bonded to two electronegative atoms O and Br which makes the carbonyl C atom highly electron–deficient and is very susceptible to nucleophilic substitution.

5(a) **(i)** Anode: $H_2 + CO_3^{2-} \longrightarrow H_2O + CO_2 + 2e$

Cathode: $\frac{1}{2} O_2 + CO_2 + 2e \longrightarrow CO_3^{2-}$

$H_2 + \frac{1}{2} O_2 \longrightarrow H_2O$

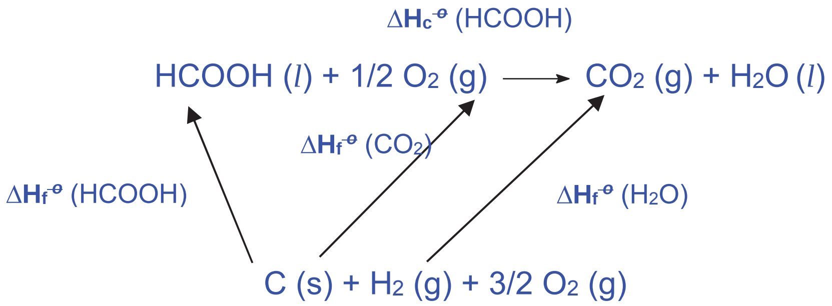
(ii)



(b) more negative

(c) **(i)** $H_f^\ominus$ of formic acid is the energy change when one mole of the formic acid is formed from its elements at standard conditions of 298K and 1 bar.

(ii)



$\Delta H_f^\ominus$ (HCOOH) = –469 kJ mol^{-1}

(iii) $\Delta H_{rxn}^\ominus$ = (–150) + (–286) – (–246) = –190 kJ mol^{-1}

2017 MJC H2 Chemistry Prelim P3 Suggested Answers

MERIDIAN JUNIOR COLLEGE
JC 2 Preliminary Examination
H2 Chemistry Paper 3

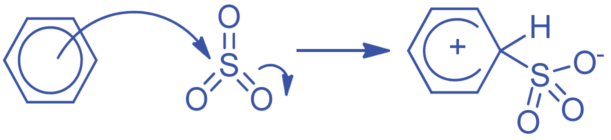
1(a) **(i)** Comparing experiments 1 and 2,
When [H_2SO_4] is doubled and [C_6H_6] is kept constant
Rate of reaction increased 4 times
Order of reaction with respect to H_2SO_4 is 2

Comparing experiments 2 and 3,
When [C_6H_6] is increased 1.5 times and [H_2SO_4] is kept constant
Rate of reaction increased 1.5 times
Order of reaction with respect to C_6H_6 is 1

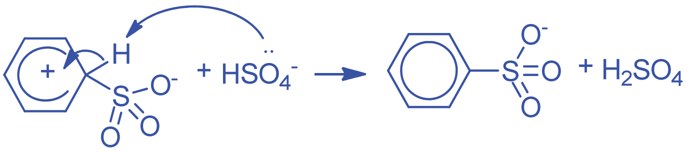
(ii) Rate = k [C_6H_6] [H_2SO_4]^2

(b) **(i)**

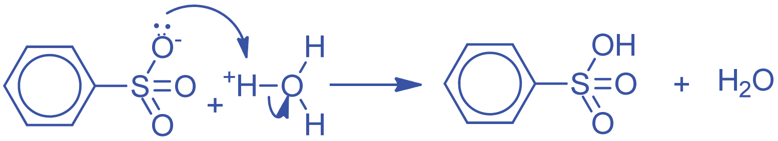
Step 2:



Step 3:



Step 4:

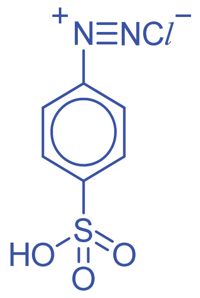


(ii) Step 2

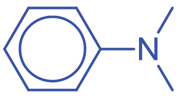
(c) **(i)** Test: Br_2 (aq), r.t.p.

- Phenylamine: Decolourisation of orange bromine solution with the formation of a white precipitate.
- Diazonium salt: No decolourisation of orange bromine solution.

(ii)



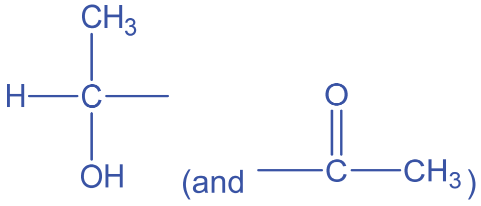
diazonium salt



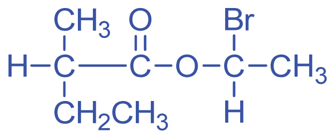
phenylamine derivative

Electrophile is the diazonium salt

(d)

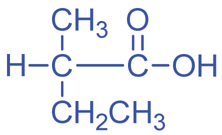
Reaction	Deduction
Q and R can rotate plane–polarized light.	Q and R contains chiral carbon and has no plane of symmetry.
0.1 mol of compound Q produces 0.5 mol of carbon dioxide gas and 0.5 mol of water.	Q contains 5 C atoms and 10 H atoms.
2 mol of Q undergoes acid–base reaction reaction with 1 mol of Na_2CO_3	Q contains 1 carboxylic acid functional group.
R undergoes oxidation when heated in an alkaline solution of iodine to give a yellow precipitate.	Yellow precipitate is CHI_3. R contains structure 
R undergoes nucleophilic substitution when heated with sodium hydroxide, followed by the addition of dilute and aqueous silver nitrate, a cream precipitate was formed.	R contains a bromoalkane / halogenoalkane functional group. Cream precipitate is AgBr.
Q and R undergo nucleophilic acyl substitution to form P.	P contains an ester functional group

Structure of **P**:



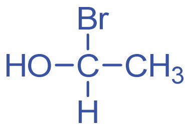
$H{-}\overset{CH_3}{\underset{CH_2CH_3}{C}}{-}\overset{O}{\overset{||}{C}}{-}O{-}\overset{Br}{\underset{H}{C}}{-}CH_3$

Structure of **Q**:



$H{-}\overset{CH_3}{\underset{CH_2CH_3}{C}}{-}\overset{O}{\overset{||}{C}}{-}OH$

Structure of **R**:



$HO{-}\overset{Br}{\underset{H}{C}}{-}CH_3$

2(a) **(i)** Iron electrode: $Mg^{2+}(l) + 2e \rightarrow Mg\ (l)$

Graphite electrode: $2Cl^{-}\ (l) \rightarrow Cl_2\ (g) + 2e$

(ii) To prevent Mg from reaction with oxygen in the air.

(iii) Iron electrode is the cathode in which Mg is formed from molten Mg^{2+}.

As $E^{\ominus}_{Zn2+/Zn}$ is more positive than $E^{\ominus}_{Mg2+/Mg}$, Zn^{2+} is preferentially discharged to form Zn. Thus, the addition of $ZnCl_2$ will interfere with the production of Mg at the cathode.

As $E^{\ominus}_{Ca2+/Ca}$ is less positive than that of Mg^{2+}, Ca^{2+} will not be preferentially discharged to form Mg (or Mg^{2+} will be preferentially discharged instead) . Thus, the addition of $CaCl_2$ will not interfere with the production of Mg at the cathode.

(iv) An iron electrode is not a suitable replacement.

Fe undergoes oxidation to form Fe^{2+}/ Fe^{3+} instead of Cl^{-} oxidising to Cl_2 since $E^{\ominus}_{Fe2+/Fe}$ (-0.44) or $E^{\ominus}_{Fe3+/Fe}$ (-0.04) is less positive than $E^{\ominus}_{Cl2/Cl-}$ (+1.36).

Fe^{2+}/ Fe^{3+} formed could be reduced instead of Mg^{2+} at cathode electrode.

(v) $1.12 \times 10^{-1} = \dfrac{1.5\times6\times60\times60}{n_e\times96500}$

$n_e = 3$

Therefore, the charge = +3

(b) **(i)** $n_{HCl} = 0.10 \times \frac{20}{1000} = 2 \times 10^{-3}$ mol

$n_{Mg(HCO3)2} = \frac{2 \times 10^{-3}}{2} = 1 \times 10^{-3}$ mol

$V_{Mg(HCO3)2} = \frac{1 \times 10^{-3}}{0.10} = 10 \text{ cm}^3$

(ii) $K_b = \frac{[OH^-]^2}{[HCO_3^-]}$

$2.4 \times 10^{-8} = \frac{[OH^-]^2}{0.10 \times 2}$

$[OH^-] = 6.93 \times 10^{-5}$ mol dm^{-3}

pH = 14 – 4.31

pH = 9.84

(iii) $H_2CO_3 \rightleftharpoons HCO_3^- + H^+$ OR $CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$

H_2CO_3 dissociates (partially) in water or undergoes hydrolysis to produce H^+ and HCO_3^-.

(iv) Bromocresol green.

The pH transition range of the indicator (around 4 – 6) lies within the sharp pH change (around 3 – 6 from graph) over the equivalence point.

(v) 10 cm^3

pOH = pK_b = - lg (2.4 x 10^{-8})

pOH = 7.62

pH = 6.38

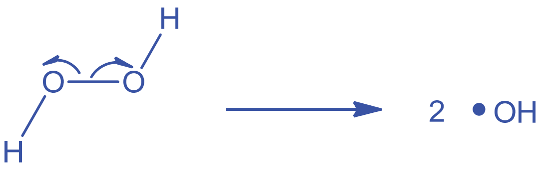
(vi) CO_3^{2-} has higher charge than HCO_3^- hence greater tendency to attract H^+.

(c) Volume V = 20 cm^3

From 0 to V cm^3, the conductance decreases due to the decreasing amount of (OH^-) ions in the solution as H^+ ions react with OH^- ions to form (undissociated) water.

At V cm^3, the conductance is the lowest as all the OH^- ions present have reacted with the added H^+ ions. After V cm^3, as more H^+ ions are present due to the addition of hydrochloric acid, the conductance increases.

3(a) **(i)**



(ii) $E^{\ominus}_{cell}$ = +1.77 – (+0.68) = + 1.09 V

(iii) $\Delta G^{\ominus}$ = – (2)(96500)(1.09) = – 210 kJ mol^{-1}

Since $\Delta G < 0$, decomposition is spontaneous.

(iv) Fe^{2+} acts as a homogenous catalyst because of the ability to exist in various oxidation states, thus facilitating the formation of reaction intermediates via alternative pathways of lower E_a.

$H_2O_2 + 2H^+ + 2Fe^{2+} \rightarrow 2Fe^{3+} + 2H_2O$ --- (1)
$E^{\ominus}_{cell}$ = +1.77 – (+0.77) = + 1.00 V > 0

$Fe^{3+} + H_2O_2 \rightarrow Fe^{3+} + O_2 + 2H^+$ --- (2)
$E^{\ominus}_{cell}$ = +0.77 – (+0.68) = + 0.09 V > 0

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

- Both steps are spontaneous since their $E^{\ominus} > 0$
- Activation energy is lower and thus reaction is faster.

(b) **(i)** ΔS is negative as there is a decrease in disorder due to decrease in the number of moles of gas molecules from 1 to 0.

(ii) Ag_2O

Since $\Delta G_f > 0$ for formation of Ag_2O, $\Delta G < 0$ for the decomposition of Ag_2O.
$2Ag_2O \rightarrow 4Ag + O_2$
Hence, the decomposition of Ag_2O is spontaneous at 1000 K

(iii) At 2250 K,
(1) $C + O_2 \rightarrow 2CO$ ΔG_f = – 600 kJ mol^{-1}
(2) $Zn + O_2 \rightarrow 2ZnO$ ΔG_f = – 150 kJ mol^{-1}
(3) $ZnO \rightarrow 2Zn + O_2$ $-\Delta G_f$ = + 150 kJ mol^{-1}

(1) + (3) : $2ZnO + 2C \rightarrow 2Zn + 2CO$
ΔG = –600 + 150 = –450 kJ mol^{-1}
Since $\Delta G < 0$, the reaction is therefore thermodynamically feasible at 2250 K.

(c) **(i)** $Zn\,(s) + 4OH^-\,(aq) \rightarrow Zn(OH)_4^{2-}\,(aq) + 2e$

$O_2\,(g) + 2H_2O\,(l) + 4e \rightarrow 4OH^-\,(aq)$

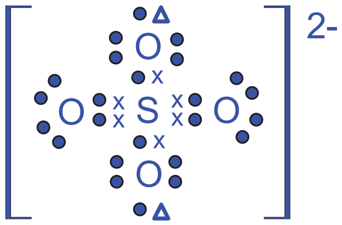
(ii) $1.59 = 0.40 - E^\theta_{oxd}$ hence $E^\theta_{oxd} = -1.19$ V

(iii) $$\frac{80}{100}\times\frac{1.85}{65.4}=\frac{I\times365\times24\times60\times60}{2\times96500}$$

$I = 1.38 \times 10^{-4}$ A

(iv) Zinc-air battery has a higher energy density or power over mass ratio as it uses air as an oxidising agent unlike the heavier oxidising agent MnO_2 used in the alkaline battery.

4(a) (i)



(ii) There are 4 bond pairs and 0 lone pair around S. To minimise repulsion, the 4 electron pairs are directed towards corners of a tetrahedron hence tetrahedral shape.

(b) (i) Amount = $\frac{3.0}{137.3 + 2(16.0 + 1.0) + 8(18.0)} = \frac{3.0}{315.3}$ = 9.515 x 10^{-3} mol

Amount of H_2O lost = 9.515 x 10^{-3} x 9 = 8.563 x 10^{-2} mol
Theoretical mass of H_2O lost = 8.563 x 10^{-2} x 18.0 = 1.54 g
Decomposition is complete.

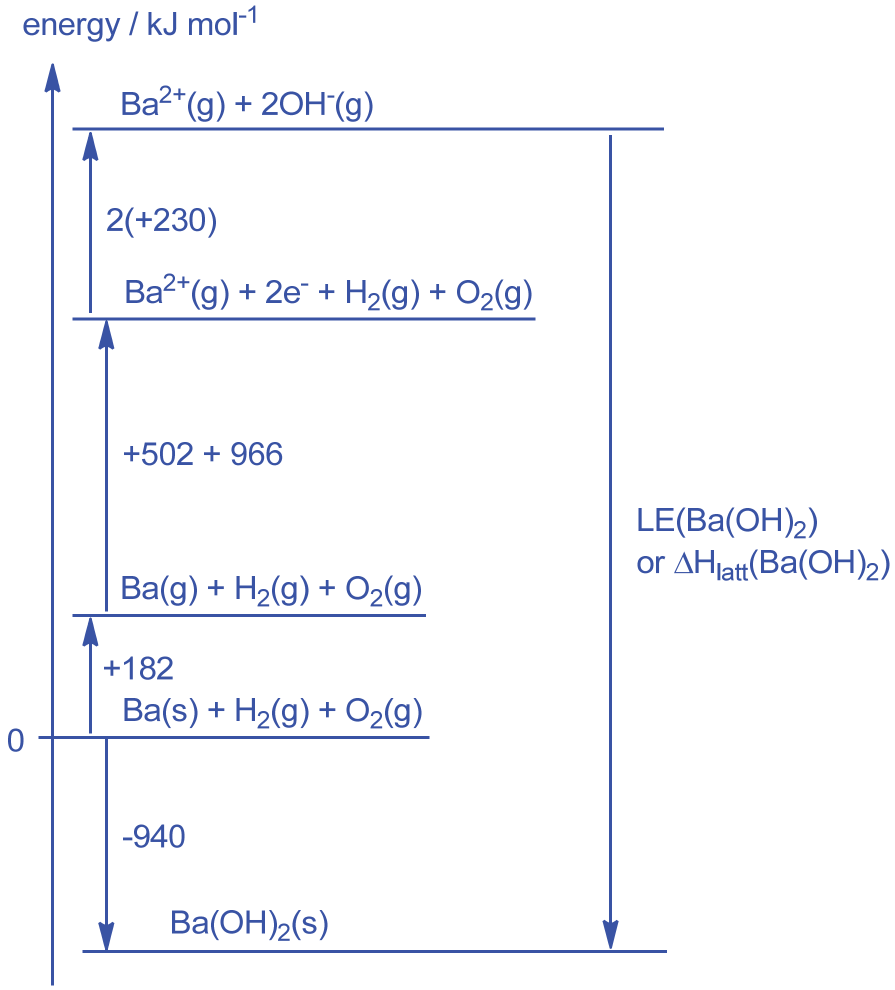
(ii) Ionic radius: $Ba^{2+} > Mg^{2+}$
Charge density and polarising power: $Ba^{2+} < Mg^{2+}$
Ability of cation to polarise, weaken and break O–H bond: $Ba^{2+} < Mg^{2+}$
Thermal stability: $Ba(OH)_2 > Mg(OH)_2$

(c) (i) 34.0 – 25.0 = 9.0 °C

(ii) Amount of H_2O formed = $\frac{100}{1000}$ 0.8 x 2 = 0.16 mol
Heat absorbed by solution = 220 x 4.18 x 9.0 = 8276.4 J

$$\Delta H_n = -\frac{8276.4}{0.16} = -51.7 \text{ kJ mol}^{-1}$$

(d)



182 + 502 + 966 + 2(230) + LE($Ba(OH)_2$) = –940

$\Delta H_{latt}(Ba(OH)_2)$ = –3050 kJ mol^{-1}

(e) **(i)** J: nucleophile

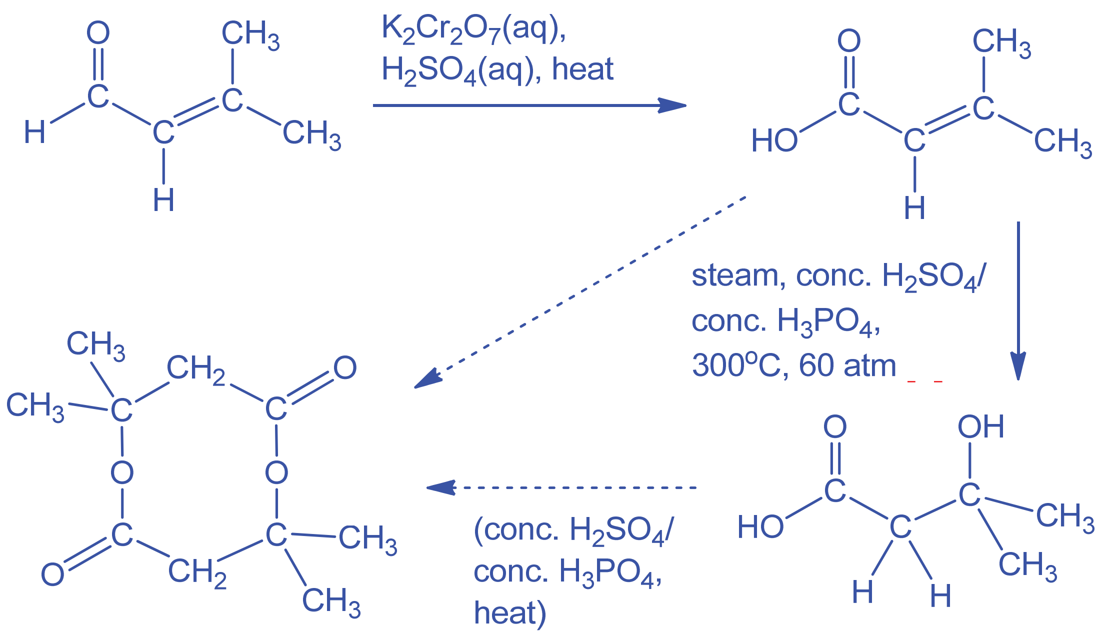
K: electrophile

(ii) III: acid-base / Lewis base

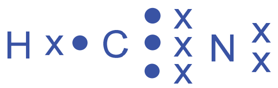
IV: elimination / Lewis acid

(iii) CH_3CHO and CH_3COCH_3

(iv)



5(a)



(b) **(i)** $\Delta H = 4 \times 410 + 3 \times 390 + \frac{3}{2} \times 496 - [410 + 890 + 6 \times 460] = -506 \text{ kJ mol}^{-1}$

ΔH *(BMA process)*

$= 4 \times 410 + 3 \times 390 - [410 + 890 + 3 \times 436]$

$= +202 \text{ kJ mol}^{-1}$

(ii) The Andrussow process is exothermic which is energetically more favourable

(c) Ksp $= s \times (2s)^2$

Solubility $= \sqrt[3]{\frac{8.0 \times 10^{-12}}{4}}$

$= 1.26 \times 10^{-4}$ mol dm^{-3}

$Zn(CN)_2$ has very low solubility in water , hence the CN^- ions will not be dissociated to cause harm.

(d) **(i)** Advantage: nitrite is soluble in water and hence can be transported to the body tissues quickly OR nitrite oxidises Fe^{2+} in haemoglobin to Fe^{3+} which can remove cyanide easily.

Disadvantage: the body will be starved of oxyhaemoglobin that is able to transport oxygen to the cell.

(ii) The SCN^- is a weaker ligandthat will not bind strongly to the Fe^{2+} in cytochrome c oxidase.

(iii) Half-life = 30 min

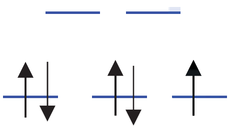
No. of half-lives before complication occurs $= \frac{60}{30} = 2$

Maximum blood cyanide concentration = 20 x 2 x 2 = 80 μg per 100 cm^3

(iv) Two orbitals have their lobes pointing at the ligands along the x, y and z axis, hence they experienced greater repulsion from the ligands OR the ligands split the d orbitals into two energy levels.

The other three orbitals experienced less repulsion since their lobes do not point at the ligands along the axes. Hence, there are two energy levels.

(v)

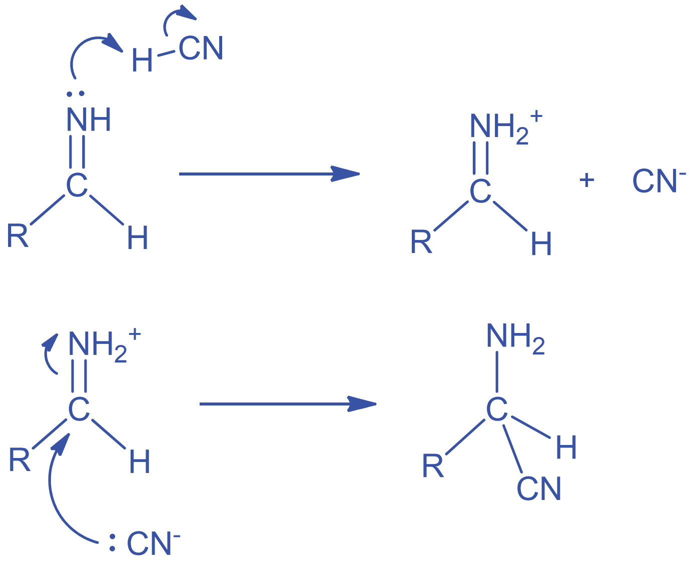


(e) **(i)** Elimination

(ii) NaOH (aq), heat under reflux

(iii) Prevent poisonous HCN from vapourising into the environment.

(iv)



(v) CN^- nucleophile attacks the trigonal planar carbonyl C from either side of the plane with equal probability, producing a racemic mixture.Naturally occurring amino acid is present as one of the enantiomers and will rotate plane polarised light.

MERIDIAN JUNIOR COLLEGE
JC 2 Preliminary Examination
H2 Chemistry Paper 4

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1 (a) Procedure

Burette readings

Final burette reading / cm^3	48.00
Initial burette reading / cm^3	0.00
Volume of FA 2 / cm^3	48.00

Mass Readings

Mass of weighing bottle and FA 1 / g	6.789
Mass of weighing bottle and residual solid / g	4.789
Mass of FA 1 added / g	2.000

Titration

	1	2
Final burette reading / cm^3	21.30	21.30
Initial burette reading / cm^3	0.00	0.00
Volume of FA 3 / cm^3	21.30	21.30
	✓	✓

(b) Average volume of FA3 used $= \dfrac{21.30 + 21.30}{2} = 21.30\ cm^3$

(c) **(i)**

Amount of HC*l* in FA3 in 21.30 cm^3

$$= \frac{25.0}{1000} \times 0.2 = 5.00 \times 10^{-3}\ mol$$

(ii) Amount of HC*l* remaining in FA3 (in 250 cm^3)

$$= \frac{250}{17.50} \times 5 \times 10^{-3} = 0.0587\ mol$$

(iii) Initial amount of HC*l* $= \dfrac{48.00}{1000} \times 2.0 = 0.0960\ mol$

Amount of HC*l* in FA3 that has reacted = 0.0960 – 0.0587
= 0.0373 mol

(iv) Amount of $MgCO_3 = \dfrac{0.0373}{2}$

$= 0.01865$ mol

Mass of $MgCO_3 = 0.01865 \times (24.3 + 12 + 48) = 1.57$ g

Percentage purity of FA1 $= \dfrac{1.57}{2.00} \times 100\% = 78.6\%$

(d) (i)

smallest volume used = 48.40 cm^3

largest volume used = 48.60 cm^3

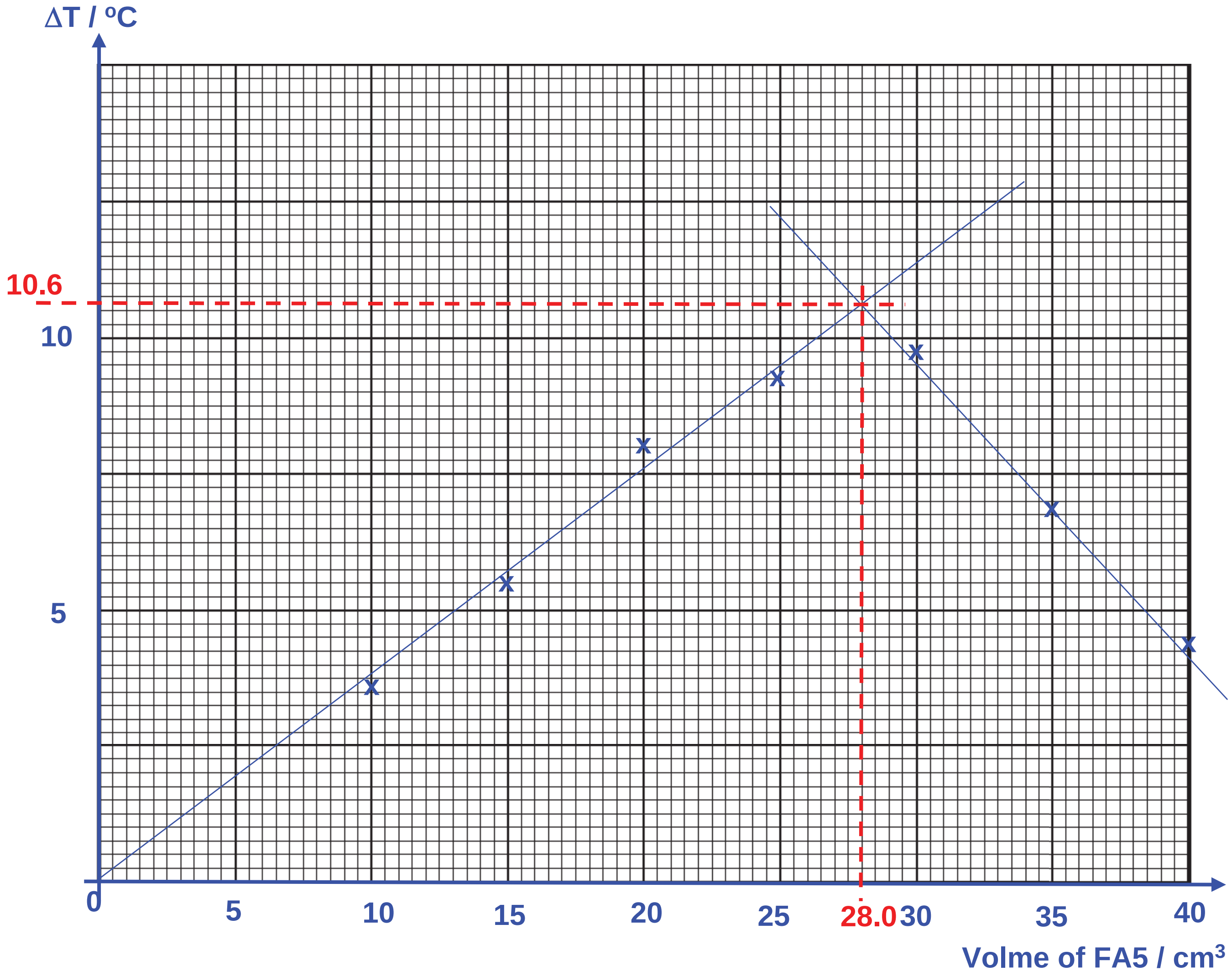
(ii) The percentage purity of FA 1 should be the same for student X and student Y since FA2 (hydrochloric acid) is added in excess to completely react with FA1 (magnesium carbonate).

2 Results

Expt	**Volume of FA 5 / cm^3**	**Volume of FA 6 / cm^3**	**T_{FA5} /°C**	**T_{FA6} /°C**	**$T_{weighted\ initial}$ /°C**	**T_{max}/°C**	**ΔT / °C**
1	10.0	40.0	28.0	32.0	31.2	34.5	3.3
2	20.0	30.0	30.0	32.0	31.2	38.0	6.8
3	30.0	20.0	31.0	31.5	31.2	41.0	9.8
4	**40.0**	**10.0**	31.0	31.5	31.1	35.5	4.4
5	**15.0**	**35.0**	29.5	31.5	30.9	36.0	5.1
6	**25.0**	**25.0**	30.5	31.5	31.0	40.0	9.0
7	**35.0**	**15.0**	31.0	31.5	31.2	38.0	6.8

[5]

(ii)



(iv)

ΔT_{max} = 10.6 °C …………………………… V_{max} = 28.0 cm^3 ……………………………

(b **(i)** No of moles of KOH = [(50 – 28) / 1000] x 1.50 = 0.0330 mol

No of moles of H_2SO_4 = 0.0375 × ½ = 0.0165 mol

$[H_2SO_4]$ in FA 5 = = $\dfrac{0.0165}{28.00/1000}$

= 0.589 mol dm^{-3}

(ii) Q = (50) (4.18)(10.6)= 2215 J

(c) ΔH_n = $= -\dfrac{2215}{2\times[0.589]\times\dfrac{28.00}{1000}} =$ – 67.1 kJ mol^{-1}

(d) As the temperature rises to the maximum value, there is a greater temperature difference between the solution and the surrounding. Hence, there is greater heat loss to the surrounding or there is a greater temperature gradient.

Hence, the temperature is more inaccurate as they approach the maximum value.

(e) **for graph**

Maximum is reached at the same V_{max} of sulfuric acid as the experiment with potassium hydroxide.

for explanation

Lower temperature rise, ΔT_{max}, as some heat that would have been released is used to dissociate the weak base completely. Maximum is reached at the same number of moles of sulfuric acid as the reacting mole ratio remains the same. Hence, V_{max} is the same.

(f) **Planning**

(i)

$$\begin{tikzcd}
BaO\ (s) + CO_2\ (g) \arrow[rr, "\Delta H_1"'] \arrow[dr, "2HNO_3\ (aq)\ \ \Delta H_2"'] & & BaCO_3\ (s) \arrow[dl, "2HNO_3\ (aq)\ \ \Delta H_3"] \\
& Ba(NO_3)_2\ (aq) + H_2O(l) + CO_2\ (g) &
\end{tikzcd}$$

By *Hess Law*, $\Delta H_1 = \Delta H_2 - \Delta H_3$

(ii) Pre-calculations

If mass of BaO used is 1.00 g, amount of BaO $= \dfrac{1.00}{137.0+16.0} = 0.006536$ mol

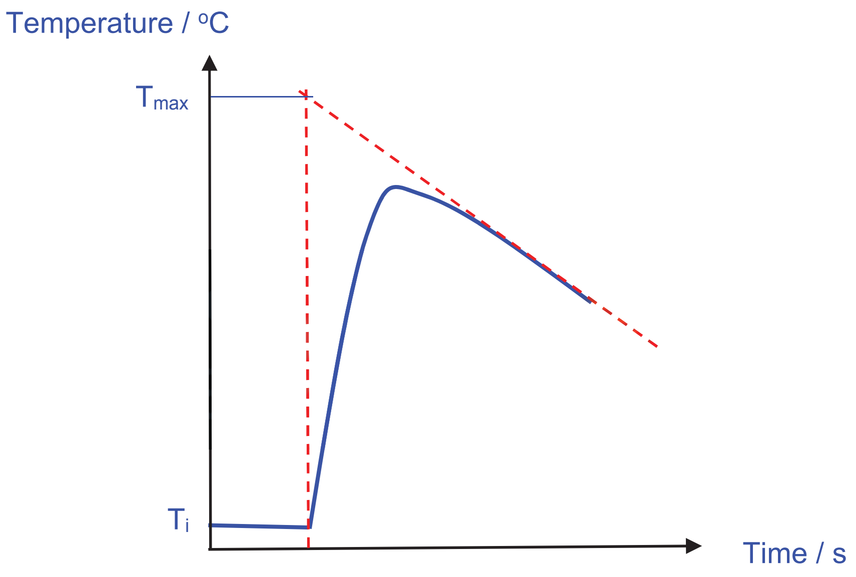
Amount of HNO_3 = 2 x 0.006536 = 0.01307 mol

Minimum volume of HNO_3 required to dissolve the BaO solid $= \dfrac{0.01307}{0.500} = 26.14\ cm^3$

Experimental Procedure

1. Weigh out about 1 g of BaO into a dry weighing bottle. Record the mass readings in a table.
2. Using a 50 cm^3 measuring cylinder, transfer 40 cm^3 of HNO_3 into the styrofoam cup supported in a glass beaker.
3. Measure and record the initial temperature of the HNO_3. Start the stop-watch and stir the solution gently with the thermometer. Record the temperature of the solution every 30 seconds for 2.0 minutes.
4. At 2.0 minutes, transfer the BaO solid into the styrofoam cup. Continuously stir the mixture thoroughly, and read the temperature at 2.5 minutes. Following this, record the temperature every 30 seconds from 3.0 minutes to 8.0 minutes.
5. At the end of the experiment, reweigh the weighing bottle and record the actual mass of BaO used.
6. Plot a graph of temperature against time to obtain a cooling curve. Obtain the maximum temperature change by extrapolation.

Method 1 : Cooling curve



To calculate ΔH_2

Quantity of heat absorbed by solution, Q = $(V_{HNO3}) \times 4.18 \times (T_i - T_{max})$

$= \boldsymbol{x}$ J

$$\Delta H_2 = -x \quad \div \frac{1.00}{137.0+16.0} / 1000$$

$$= -y \quad \text{kJ mol}^{-1}$$

Other methods possible: *Fixed volume of HNO_3 and change mass of BaO* ***OR*** *Fixed mass of BaO and change volume of HNO_3*

3 Inorganic and Organic Analysis

(a) 1. Test on FA 7

Test	Observations
(i) To a 1 cm depth of the solution of **FA 7** in a test-tube, add a few drops of aqueous barium nitrate followed by dilute nitric acid.	White precipitate formed dissolves in (excess) HNO_3 to form a colourless solution.
(ii) To a 1 cm depth of the solution of **FA 7** in a test-tube, add an equal volume of aqueous hydrogen peroxide, then	No effervescence OR a colourless solution is obtained.
add a few drops of aqueous barium nitrate, followed by dilute nitric acid.	White precipitate formed does not dissolve in (excess) HNO_3.
(iii) To a 2 cm depth of the solution of **FA 7** in a test tube, add an equal volume of sulfuric acid, then heat the mixture gently and cautiously.	When heated, gas produced decolourises purple $KMnO_4$.
(iv) To a 1 cm depth of the solution of **FA 7** in a test-tube, add an equal volume of aqueous sodium hydroxide, then	No ppt formed.
add a few drops of aqueous potassium manganate(VII),	Green solution formed when $KMnO_4$ added.
followed by sulfuric acid.	Green solution (or yellow or brown) turned colourless on adding sulfuric acid.

(v) anion: SO_3^{2-}
evidences (any two):

1. FA 7 reacts with sulfuric acid / in test (iii) to give SO_2 gas which decolourises $KMnO_4$.
2. FA 7 formed white precipitate of $BaSO_3$ formed which dissolves in excess acid.
3. The SO_3^{2-} in FA 7 is oxidised to SO_4^{2-} in test (ii) by H_2O_2 which formed white ppt $BaSO_4$ that is insoluble in excess acid.
4. FA7 reduced purple MnO_4^- to green MnO_4^{2-} under alkaline condition OR to colourless Mn^{2+} under acidic condition.

2. (i) Test on FA 8

Test	Observations
(i) To a 1 cm depth of FA 8 in a test-tube, add aqueous sodium hydroxide drop wise till excess. Heat the mixture.	White ppt is soluble in excess NaOH(aq) to form a colourless solution. Gas evolved turned moist red litmus blue.
(ii) To a 1 cm depth of FA 8 in a test-tube, add aqueous ammonia drop wise till excess.	White ppt is soluble in excess NH_3(aq) to form a colourless solution.

(ii) Cation: Zn^{2+}
Evidence: FA 8 forms a white ppt of $Zn(OH)_2$ which is soluble in excess NaOH to form $Zn(OH)_4^{2-}$. FA 8 forms a white ppt of $Zn(OH)_2$ which is soluble in excess NH_3 to form $Zn(NH_3)_4^{2+}$
Cation: NH_4^+
Evidence: FA 8 evolved NH_3 gas upon heating with NaOH(aq). Hence, NH_4^+ ion is present.

(b) (i) Test on FA 9

Tests	Observation
(i) To a 1 cm depth of FA 9 in a test-tube, add 1 cm^3 of dilute sulfuric acid. Add one drop or 2 drops of aqueous potassium manganate (VII). Place the test-tube in the water bath for several minutes.	Purple $KMnO_4$ decolourised.
(ii) To a 1 cm depth of FA 9 in a test-tube, add 1 cm^3 (or a few drops) of Fehling's solution.	Brick red ppt formed.

Place the test-tube in the water bath for several minutes.	

(ii) Functional group in **FA 9** (aliphatic) aldehyde

Evidence: FA 9 undergoes oxidation as it decolorised purple with $KMnO_4$.This shows that it cannot be a ketone.

FA 9 undergoes a positive Fehling's test (or oxidation) as it formed a brick red ppt.

Hence, FA9 is an (aliphatic) aldehyde.