JURONG JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION 2018

CANDIDATE NAME

CLASS **18S**

EXAM INDEX

CHEMISTRY
Higher 2

9729/01

Paper 1 Multiple Choice

13 September 2018
1 hour

Candidates answer on separate paper.

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

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

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

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
Any rough working should be done in this booklet.
The use of an approved scientific calculator is expected, where appropriate.

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

1 The successive ionisation energies (IE) of two elements, **E** and **J**, are given below:

IE/ kJ mol^{-1}	1st	2nd	3rd	4th	5th	6th	7th	8th
E	550	1065	4138	5500	6910	8760	10230	11800
J	1140	2103	3470	4560	5760	8550	9940	18600

What is the likely formula of the compound that is formed when **E** reacts with **J**?

A EJ_2 **B** EJ

C E_2J **D** E_2J_3

2 Carbon, silicon and germanium are Group 14 elements and they all exist in a structure similar to diamond.

The given table shows the bond lengths in these structures.

Element **X**	C	Si	Ge
Bond length **X**–**X** / nm	0.154	0.234	0.244

Which of the following explain why the bond length increases down the group?

1 Degree of orbital overlap decreases down the group.
2 Atomic radius increases down the group.
3 Nuclear charge increases down the group.
4 Electronegativity decreases down the group.

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

3 Which of the following **cannot** be explained by hydrogen bonding?

A the existence of the hydrogen-difluoride anion, HF_2^-
B the difference in volatility between pentan-1-ol and hexan-1-ol
C the difference in melting point between 2-nitrophenol and 4-nitrophenol
D the higher than expected relative molecular mass of ethanoic acid in benzene

4 The percentage by mass of magnesium in a mixture of magnesium chloride and magnesium nitrate was found to be 21.25%.

What is the mass of magnesium chloride present in 100 g of the mixture?

A	47 g	**B**	51 g
C	53 g	**D**	56 g

5 When 10 cm^3 of a gaseous hydrocarbon **X** was burned in 70 cm^3 of oxygen, the final gaseous mixture contained 30 cm^3 of carbon dioxide and 20 cm^3 of unreacted oxygen.

What is the formula of hydrocarbon **X**?

[All gaseous volumes are measured under identical conditions.]

A	C_2H_6	**B**	C_3H_6
C	C_3H_8	**D**	C_4H_{10}

6 An ion of metal **L** can be oxidised by potassium manganate(VII) in acid solution to form $\mathbf{L}O_3^-$. In an experiment, 1.25×10^{-3} mol of the ion of **L** required 37.5 cm^3 of 0.0200 mol dm^{-3} potassium manganate(VII) for complete reaction.

What is the initial oxidation state of the ion of **L** given that potassium manganate(VII) is reduced to Mn^{2+}?

A	+1	**B**	+2
C	+3	**D**	+4

7 Given the following standard enthalpy changes,

$C(s) + O_2(g) \rightarrow CO_2(g)$ –394 kJ mol^{-1}

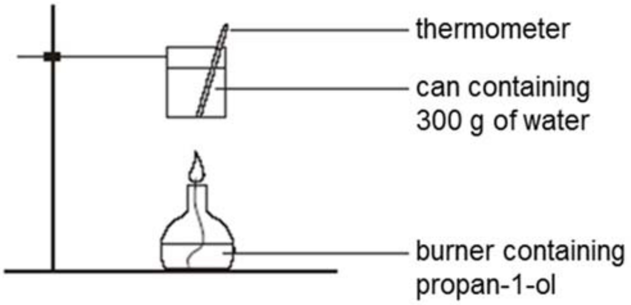
$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ –286 kJ mol^{-1}

$2C(s) + 3H_2(g) + \frac{1}{2}O_2(g) \rightarrow C_2H_5OH(l)$ –278 kJ mol^{-1}

What is the standard enthalpy change of combustion of liquid ethanol, C_2H_5OH?

A	–402 kJ mol^{-1}	**B**	–758 kJ mol^{-1}
C	–1368 kJ mol^{-1}	**D**	–1924 kJ mol^{-1}

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



The following data were recorded:

mass of propan–1–ol burnt = m g
change in temperature of water = ΔT °C

Given that:

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

What is the efficiency of this heating process?

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

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

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

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

9 The experimental results obtained for the reaction between **X** and **Y** at constant temperature are given in the table below.

Experiment	[**X**] / mol dm^{-3}	[**Y**] / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	0.3	0.2	4.00×10^{-4}
2	0.6	0.4	1.60×10^{-3}
3	0.6	1.2	1.44×10^{-2}

What is the rate equation for this reaction?

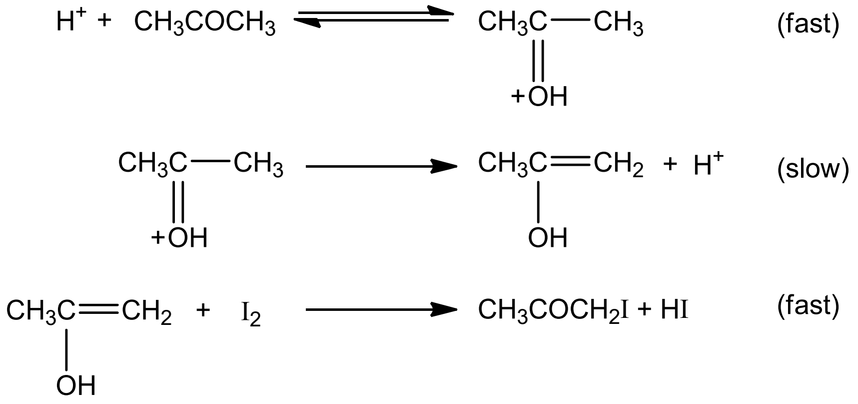
A Rate = $k[\mathbf{Y}]^2$

B Rate = $k[\mathbf{X}]^2$

C Rate = $k[\mathbf{X}]^2[\mathbf{Y}]$

D Rate = $k[\mathbf{X}][\mathbf{Y}]^2$

10 The mechanism for the iodination of propanone in aqueous acid involves the following steps.



$$H^+ + CH_3COCH_3 \rightleftharpoons CH_3C(=\overset{+}{O}H)CH_3 \quad \text{(fast)}$$

$$CH_3C(=\overset{+}{O}H)CH_3 \longrightarrow CH_3C(OH)=CH_2 + H^+ \quad \text{(slow)}$$

$$CH_3C(OH)=CH_2 + I_2 \longrightarrow CH_3COCH_2I + HI \quad \text{(fast)}$$

Which of the following statements are true?

1 The overall order of the reaction is 1.

2 The acid acts as a catalyst.

3 The rate equation is rate = $k[CH_3COCH_3][H^+]$

4 The rate of the reaction is not affected by a change in the iodine concentration.

A 1, 2 and 4 only

B 2, 3 and 4 only

C 1 and 2 only

D 2 and 3 only

11 The rate of removal of *Aspirin*, a pain-killer drug, from the body is a first order reaction with a half-life of 2.0 h.

How long does it take for 87.5% of *Aspirin* to be removed from the body?

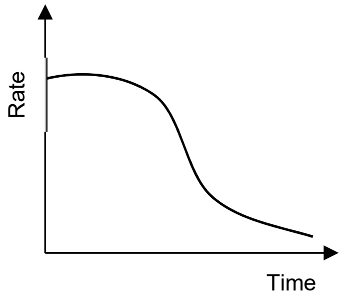
A	6.0 hours	**B**	2.0 hours
C	1.0 hours	**D**	0.4 hours

12 The reaction between potassium manganate(VII) and ethanedioic acid is an example of auto-catalytic reactions, in which one of the products catalyses the reaction.

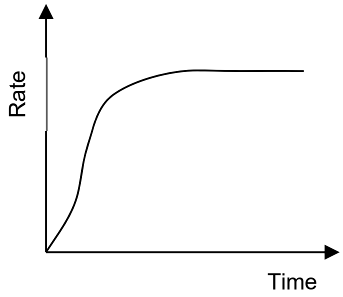
$$2MnO_4^-(aq) + 5H_2C_2O_4(aq) + 6H_3O^+(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 14\ H_2O(l)$$

Which graph correctly represents the kinetics of this reaction?

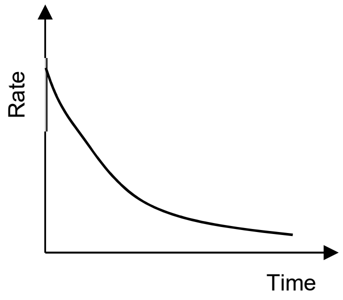
A



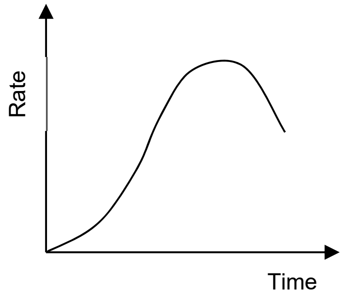
B



C



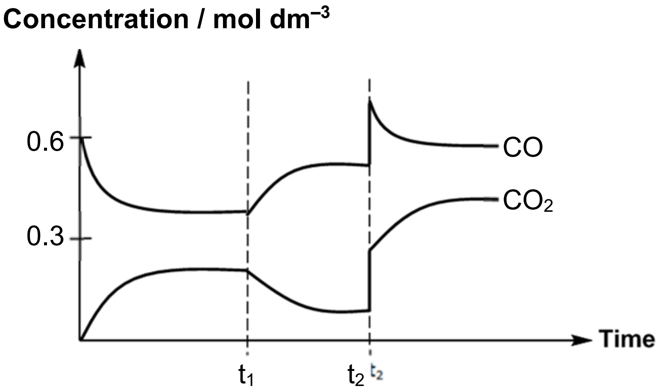
D



13 At a temperature *T* K, 0.60 mol dm^{-3} of CO and 0.30 mol dm^{-3} of O_2 were introduced into a 5 dm^3 vessel and allowed to reach equilibrium.

$$2\ CO\ (g) + O_2\ (g) \ll 2CO_2\ (g) \qquad \Delta H < 0$$

The graph below shows the changes in the concentration of CO and CO_2 in the system with time. A change was made to the system at time, t_1 and t_2.



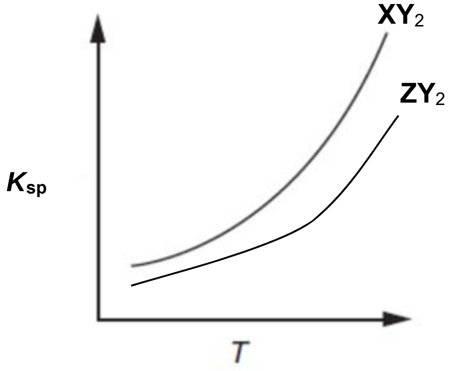
What were the changes made at time, t_1 and t_2?

	t_1	t_2
A	A catalyst was added	Volume of the system is increased
B	The temperature was increased	Volume of the system is decreased
C	Some O_2 was removed	An inert gas was added at constant volume

D	The temperature was decreased	More O_2 was added

14 $\mathbf{XY}_2$ and $\mathbf{ZY}_2$ are sparingly soluble salts containing $\mathbf{Z}^{2+}$, $\mathbf{X}^{2+}$ and $\mathbf{Y}^{-}$ ions.

The solubility product, K_{sp}, of both sparingly soluble salts varies with temperature as shown in the diagram below.



Which conclusions can be drawn from the information?

1 The enthalpy change of solution for both salts is endothermic.

2 Adding $\mathbf{Y}^{-}$ to the solution of $\mathbf{XY}_2$ decreases the K_{sp} of $\mathbf{XY}_2$.

3 Adding $\mathbf{Y}^{-}$ to the solution of $\mathbf{ZY}_2$ decreases the solubility of $\mathbf{ZY}_2$.

4 Given a solution with $[\mathbf{X}^{2+}] = [\mathbf{Z}^{2+}]$, $\mathbf{ZY}_2$ is precipitated out first on adding $\mathbf{Y}^{-}$.

A 1 and 3 only

B 3 and 4 only

C 1, 2 and 4 only

D 1, 3 and 4 only

15 A metal object was electroplated with chromium using an aqueous electrolyte of chromium(III) chloride and a graphite electrode. A current of 2.0 A was passed through the electroplating cell for 45 minutes.

What may be derived from the information given above?

1 The object to be electroplated was connected to the negative terminal of the battery.

2 The object increased in mass by 0.97 g.

3 Oxygen gas was evolved at the anode.

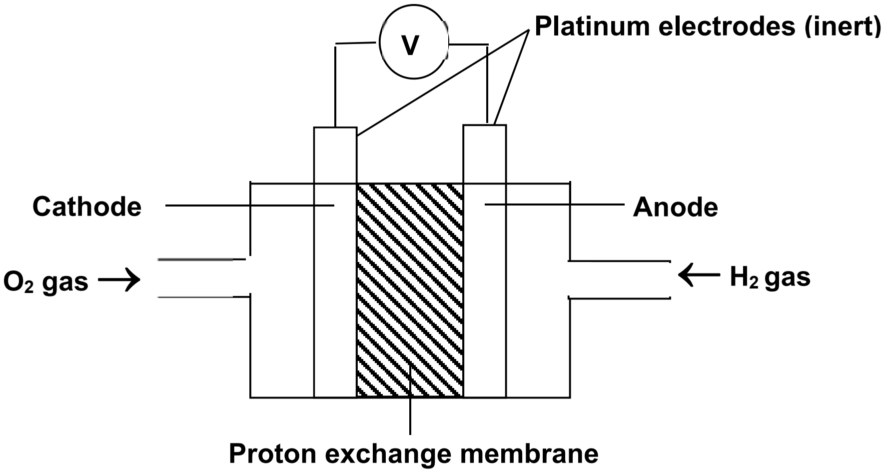
A 1, 2 and 3

B 1 and 2 only

C 2 and 3 only

D 1 only

16 A hydrogen fuel cell as illustrated below has a typical e.m.f. of 1.23 V.



Which of the following is true regarding the operation of this fuel cell?

1 The e.m.f can be increased by increasing the pressure of oxygen gas to 2 atm.

2 The electrode is platinised to increase the rate of reaction, but e.m.f. is not affected.

3 The proton exchange membrane allows the passage of H^+ ions in order to complete the circuit and maintains electrical neutrality.

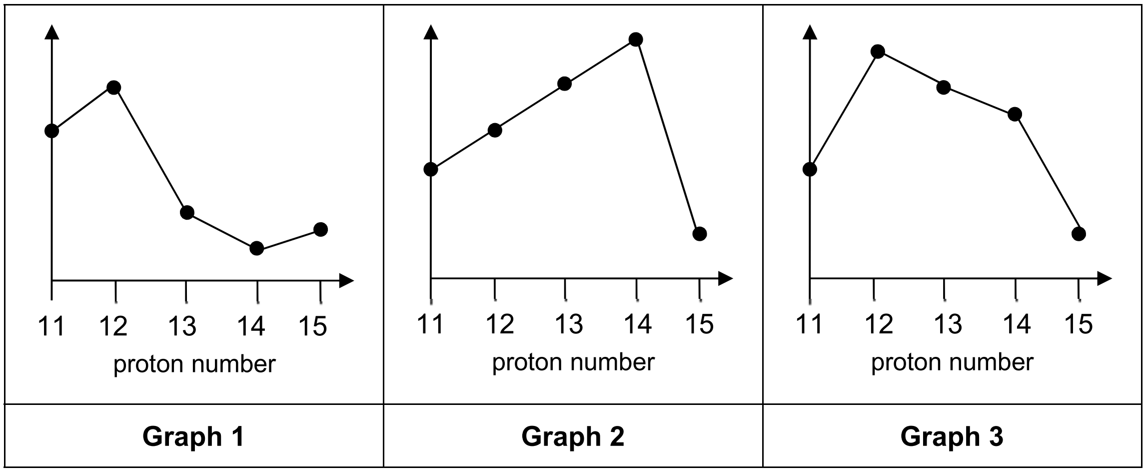
A 1, 2 and 3

B 1 and 2 only

C 2 and 3 only

D 1 only

17 The following graphs show how three properties of the elements, Na to P, and their compounds, vary with proton number.



What properties are shown by the three graphs?

	Graph 1	Graph 2	Graph 3
A	Melting point of oxide	Melting point of chloride	Electrical conductivity of element
B	Melting point of oxide	Melting point of element	Melting point of chloride
C	Melting point of chloride	Electrical conductivity of element	Melting point of oxide
D	Melting point of chloride	Melting point of element	Melting point of oxide

18 Which property of Group 2 elements (magnesium to barium) or their compounds increases with increasing proton number?

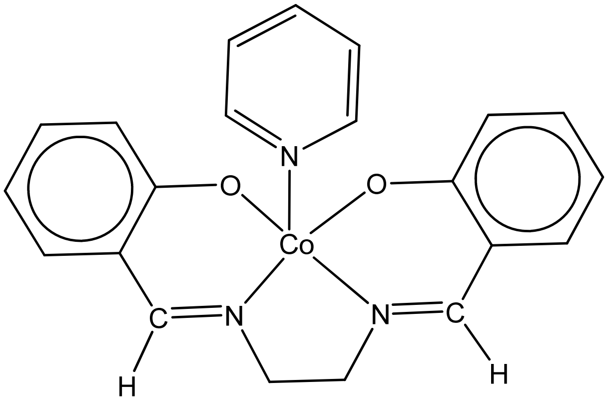
A the stability of the carbonates to heat
B the magnitude of the enthalpy change of hydration of the metal ions
C the acidity of aqueous solutions of the chlorides
D the melting points of the elements

19 For the sequence hydrogen iodide, hydrogen bromide and hydrogen chloride, which of the following properties show a decreasing trend?

1 thermal stability
2 acidity
3 ease of oxidation

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

20 The following cobalt complex is known to be the functional model for biological oxygen carrier.



What is the electronic configuration of the cobalt cation in the above complex?

A [Ar] $3d^6$

B [Ar] $3d^7$

C [Ar] $3d^5 4s^2$

D [Ar] $3d^7 4s^2$

21 Transition metals like platinum and rhodium are found in catalytic converters fitted into cars. Which of the following properties best explains the role of transition metals in this use?

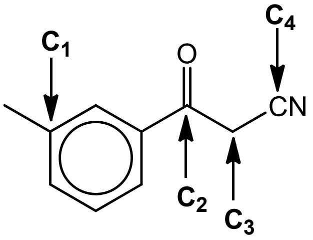
A Transition metals can exhibit variable oxidation states in their compounds as 3d and 4s electrons have similar energies.

B Transition metals form coloured ions due to absorption of energy in the visible light region to promote an electron from a lower to a higher energy 3d orbital.

C Transition metals have very high melting points because both 3d and 4s electrons are involved in forming strong metallic bond.

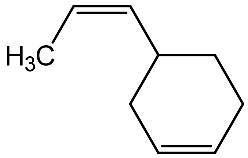
D Transition metals have partially filled 3d orbitals which are available for adsorption of reactant molecules.

22 What is the hybridisation of the various carbon atoms in the following molecule?



	C_1	C_2	C_3	C_4
A	sp^2	sp^3	sp	sp^2
B	sp^2	sp^2	sp^3	sp
C	sp^2	sp^2	sp	sp^3
D	sp^3	sp^2	sp^3	sp

23



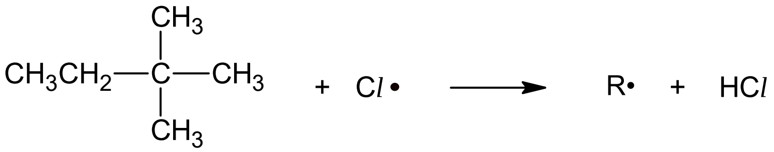
How many stereoisomers does the above molecule have?

A 2 **B** 4

C 6 **D** 8

24 When heated with chlorine, the hydrocarbon 2,2-dimethylbutane undergoes free radical substitution.

In a propagation step, the free alkyl radical R• is formed.



$$CH_3CH_2C(CH_3)_2CH_3 + Cl\bullet \longrightarrow R\bullet + HCl$$

How many different forms of R• are possible?

A 1 **B** 2

C 3 **D** 4

25 Which one of the following statements regarding organic reaction mechanisms is **correct**?

1 Electrophilic addition of alkenes involves a carbocation intermediate.

2 Electrophilic substitution of benzene involves an intermediate with 4 π electrons.

3 Nucleophilic substitution of tertiary halogenoalkanes involves a carbocation intermediate.

4 Nucleophilic addition of a carbonyl compound involves an alkoxide intermediate.

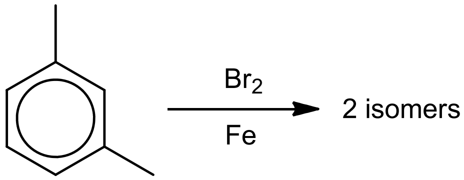
A 1, 2, 3 and 4

B 1 and 2 only

C 2 and 3 only

D 3 and 4 only

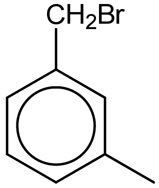
26 When 3-methyltoluene is treated with bromine in the presence of iron filings in the dark, a mixture of two mono-brominated isomers is formed.



3-methyltoluene

What are the structures of these two isomers?

A



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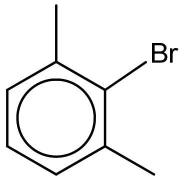

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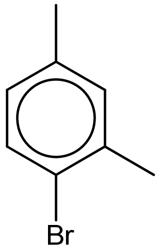

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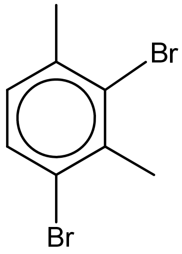

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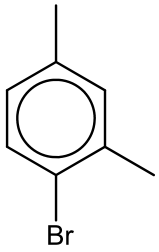

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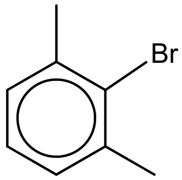

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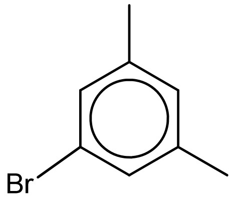

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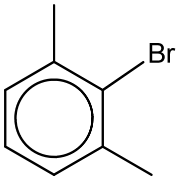


27 When ethyl ethanoate undergoes hydrolysis with dilute sulfuric acid in the presence of $H_2{}^{18}\mathbf{O}$, a mixture of two products is formed. Which of the following pairs correctly gives the structures of the two products?

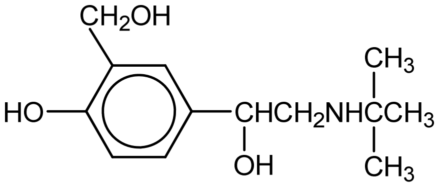
A $CH_3CO^{18}\mathbf{O}H$ and $CH_3CH_2{}^{18}\mathbf{O}H$

B CH_3COOH and $CH_3CH_2{}^{18}\mathbf{O}H$

C $CH_3C^{18}\mathbf{O}OH$ and CH_3CH_2OH

D $CH_3CO^{18}\mathbf{O}H$ and CH_3CH_2OH

28 Albuterol dilates the airways of the lung and is used for treating asthma and other conditions of the lung.



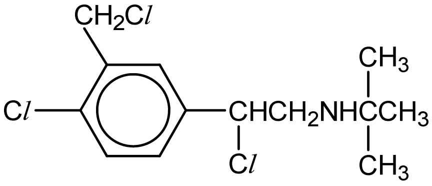
Albuterol

Which of the following statements is true about albuterol?

1 On addition of Na_2CO_3(aq), effervescence of CO_2 is produced.

2 On heating one mole of albuterol with NaOH(aq), one mole of NaOH is used up.

3 On reacting with phosphorus pentachloride,



is one of the products.

A 1 only

B 2 only

C 1 and 3 only

D 2 and 3 only

29 A sample of bromoethane was warmed with ethanolic silver nitrate, and a cream precipitate was observed after about 4 minutes.

Under similar reaction conditions, which one of the following compounds will result in precipitate formation only after 8 minutes?

A iodoethane

B ethanoyl bromide

C bromobenzene

D chloroethane

30 Which of the following gives the correct order of decreasing basic strength?

A $CH_3CH_2NH_2$, NH_3, $(CH_3CH_2)_2NH$

B $CH_3CH_2NH_2$, $(CH_3CH_2)_2NH$, $C_6H_5NH_2$

C $(CH_3CH_2)_2NH$, NH_3, $C_6H_5NH_2$

D $C_6H_5NH_2$, NH_3, $CH_3CH_2NH_2$

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2018 Paper 1 answer key

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

JURONG JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION 2018

CANDIDATE NAME			
CLASS	**18S**	EXAM INDEX	

CHEMISTRY
9729/02

Higher 2

Paper 2 Structured Questions

29 August 2018
2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

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

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

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

For Examiner's Use	
1	/ **13**
2	/ **13**
3	/ **11**
4	/ **10**
5	/ **17**
6	/ **11**
Penalty (delete accordingly)	
Lack **3sf** in final ans	**–1 / NA**
Missing/wrong **units** in final ans	**–1 / NA**
Bond linkages	**–1 / NA**
Total	

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

Answer **all** the questions.

1 Nickel is an important transition metal used in the manufacture of stainless steel alloys. It is first isolated from the mineral ore niccolite by Swedish chemist Axel Fredrik Cronstedt in 1751.

(a) Nickel exists naturally as a mixture of five stable isotopes, each with their own relative isotopic mass. The information about four of these isotopes is given.

isotope	percentage abundance
^{58}Ni	68.1
^{61}Ni	1.14
^{62}Ni	3.63
^{64}Ni	0.93

The relative atomic mass of nickel is 58.7.

Calculate the relative isotopic mass of the fifth isotope of nickel.

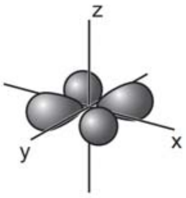
Give your answer to the **nearest whole number**.

[2]

(b) Nickel can form complexes with H_2O ligands.

In a $[Ni(H_2O)_6]^{2+}$ complex, the presence of the H_2O ligands causes the d orbitals to split into two groups at different energy levels.

(i) On the diagram below, tick the box under each of the orbitals of the higher energy level.



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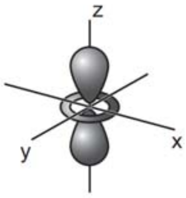

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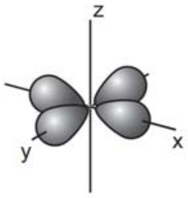

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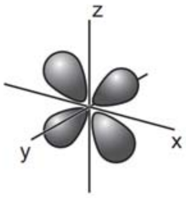

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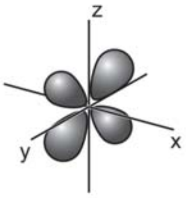


☐

[2]

(ii) Explain why a solution of $[Ni(H_2O)_6]^{2+}$ is coloured.

…………………………………………………………………………………..

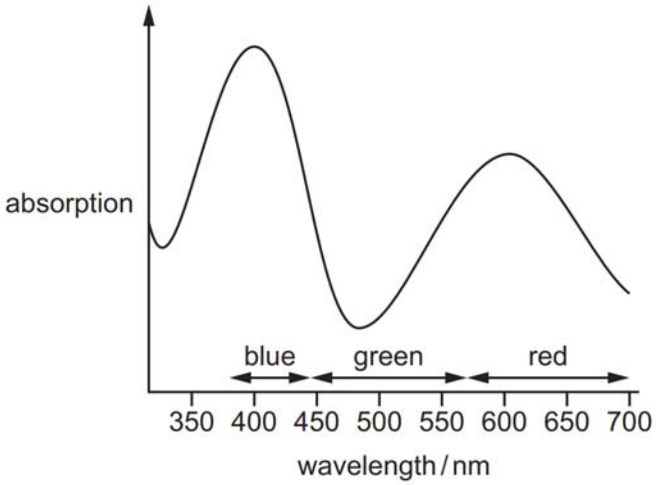
…………………………………………………………………………………..

…………………………………………………………………………………..

…………………………………………………………………………………..

………………………………………………………………………………….. [2]

(iii) The visible spectrum of a solution of $[Ni(H_2O)_6]^{2+}$ is shown below.



State and explain the colour of the solution.

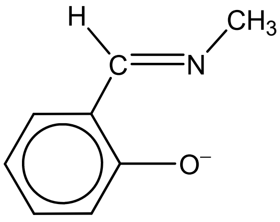
colour of the solution ………………………………..

explanation ……………………………………………………………………….

…………………………………………………………………………………..

………………………………………………………………………………….. [2]

(c) Nickel can form a complex with ligand **X**⁻, which has the structure shown below.



ligand **X**⁻

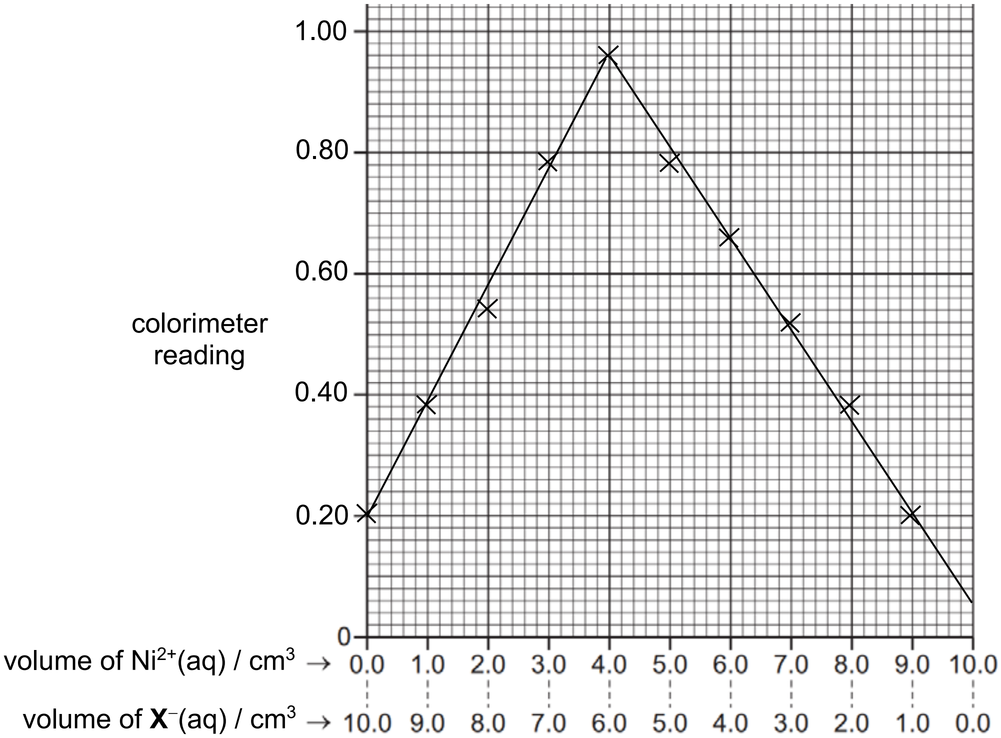
X⁻ is a bidentate ligand. On the structure above, draw circles around the atoms that bind to nickel when **X**⁻ behaves as a ligand. [1]

(d) The formula of a complex can be determined using colorimetry.

In colorimetry, light of a certain wavelength is passed through a complex ion solution. The absorbance of the light is proportional to the intensity of the colour of the solution. The more concentrated the complex ion solution, the more intense its colour and so the higher the absorbance.

An experiment is carried out to determine the formula of the complex formed between nickel and ligand **X**$^-$ having the structure given in **(c)**.

The following graph was obtained when the colour intensities of mixtures of a 3×10^{-3} mol dm^{-3} solution of nickel(II) chloride and a 4×10^{-3} mol dm^{-3} solution containing **X**$^-$ were measured using a colorimeter at room temperature.



Determine the stoichiometry of the complex and suggest its structural formula.

[2]

(e) Like nickel, platinum can also forms complexes in which the central atom is surrounded by four ligands.

A and **B** are isomeric complexes of the same shape with the formula of $Pt(PR_3)_2I_2$.
[The PR_3 ligand has the same shape as NH_3. R is a phenyl group.]

Given that isomer **A** has a dipole moment, draw the structures of **A** and **B**.

isomer **A**	isomer **B**

[2]

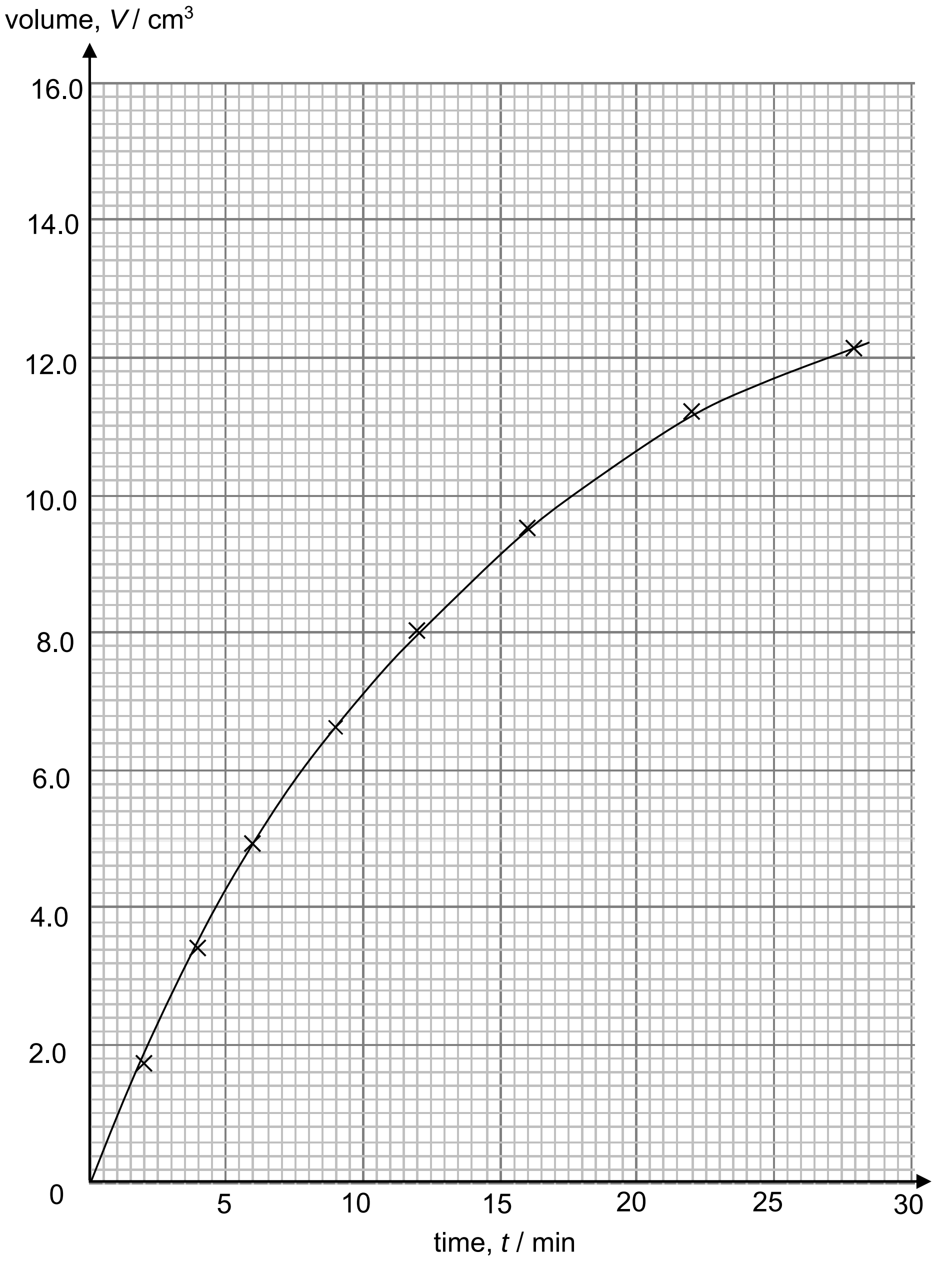
[Total: 13]

2 **(a)** Benzenediazonium chloride, $C_6H_5N_2Cl$, decomposes at 50 °C and 101 kPa, according to the equation below.

$$C_6H_5N_2Cl(aq) \rightarrow C_6H_5Cl(aq) + N_2(g)$$

The progress of the decomposition reaction of a 500 cm^3 sample of $C_6H_5N_2Cl(aq)$ solution was studied by measuring the volume of gas produced over time.

The volume of gas produced, V, after time, t, is proportional to the amount of benzenediazonium chloride that has decomposed. The final volume of gas produced, V_{final}, is 14.6 cm^3 and it is directly proportional to the original concentration of benzenediazonium chloride. The results are recorded in the graph below.



(i) Use the graph to determine the order of the reaction with respect to benzenediazonium chloride.

Show all your working, and draw clearly any construction lines on your graph.

Order of reaction with respect to benzenediazonium chloride: …………….

explanation ……………………………………………………………………

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

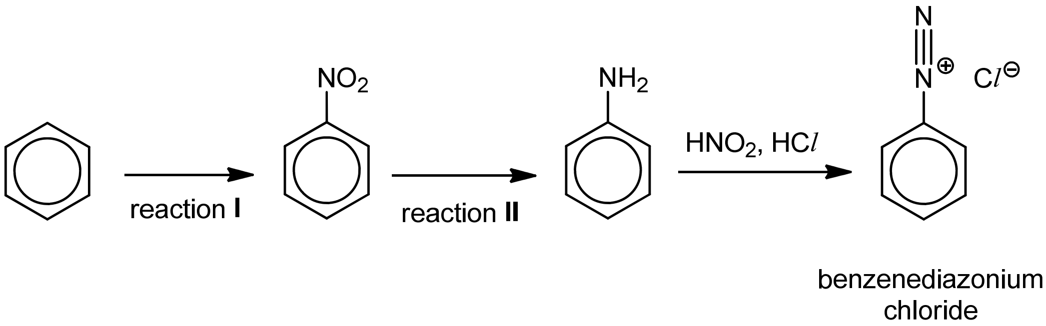
(ii) Calculate the rate constant, stating its units.

[2]

(iii) Assuming nitrogen behaves ideally, calculate the original concentration, in mol dm^{-3}, of benzenediazonium chloride.

[3]

(b) Benzenediazonium chloride is an important intermediate for the production of dyes. The following scheme shows the synthesis of benzenediazonium chloride from benzene.



(i) State the type of reaction and suggest the reagents and conditions for reaction **I**.

type of reaction: ……………………………………………….

reagents: ……………………………………………………….

conditions: …………………………………………………….. [3]

In reaction **II**, nitrobenzene is reduced to phenylamine via two steps.

During step 1, granulated Sn and concentrated HC*l* are added to nitrobenzene and the mixture is heated under reflux in a hot water bath for about half an hour. Sn, which acts as the reducing agent, is converted to Sn^{4+} ions.

(ii) Balance the following half-equation for the reduction of nitrobenzene in acid solution to give $C_6H_5NH_3^+$ in step 1.

.... $C_6H_5NO_2$ + ... H^+ + …. e^- $\rightarrow$ ………………………………………….. [1]

(iii) Hence, by considering electron transfer, write a balanced overall equation for the reaction of nitrobenzene, Sn and concentrated HC*l* in step 1.

…. $C_6H_5NO_2$ + …. Sn + …. HC*l* $\rightarrow$ ………………………………………………. [1]

Step 2 involves the addition of aqueous sodium hydroxide to the resulting mixture.

(iv) Suggest the purpose of this stage.

……………………………………………………………………………………..

……………………………………………………………………………………..

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

[Total: 13]

3 Metals have properties that make them well suited to serve as battery anodes.

They are easily oxidised from their metallic state to produce ions and electrons, where the electrons liberated are conducted throughout the external circuit. The fact that metals are physically strong and easily fashioned into any desired shape adds to their attractiveness as anodes.

Metals commonly employed as anodes in commercial batteries are listed in **Table 3.1**. The tabulated properties give clues as to the ability of each metal to play this role.

Metal	relative atomic mass	density / g cm^{-3}	standard electrode potential, *E* / V	electrochemical capacity / A h g^{-1}
lithium	6.9	0.53	–3.04	3.86
sodium	23.0	0.97	–2.71	1.17
magnesium	24.3	1.74	–2.38	2.21
iron	55.8	7.86	–0.44	0.96
zinc	65.4	7.14	–0.76	0.82
lead	207.2	11.3	–0.13	0.26

Table 3.1

(a) Suggest **two** reasons why lithium is the best choice among the metals in **Table 3.1** to be used as a battery anode.

....

....

....

....

.... [2]

(b) A schematic diagram of a lithium-ion battery is shown below. Lithium is the anode whereas a paste of iron disulfide (FeS_2) powder mixed with powdered graphite serves as the cathode.

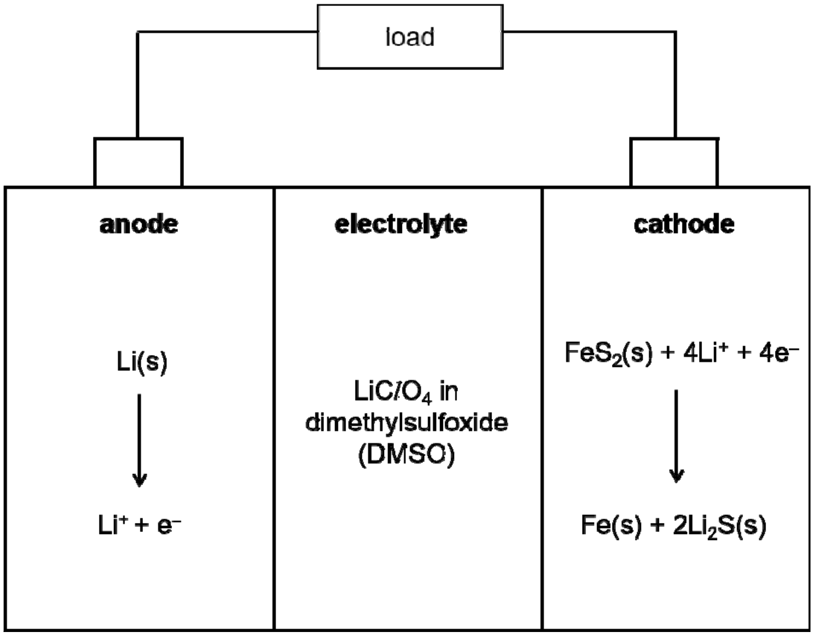


Figure 3.1

(i) On **Figure 3.1**, indicate clearly the direction of electron flow. [1]

(ii) Most batteries use aqueous solutions of ionic salts or ionisable molecules as electrolytes. However, the electrolyte used in this lithium-ion battery must be non-aqueous such as dissolving $LiClO_4$ in dimethylsulfoxide (DMSO), which is an organic solvent. Suggest why.

……………………………………………………………………………………

……………………………………………………………………………………

…………………………………………………………………………………… [1]

(c) Like enthalpy, Gibbs free energy *G* is a state function. Thus, Hess' Law can likewise be applied to calculate the standard Gibbs free energy change of a reaction, ΔG , from relevant data such as the standard Gibbs free energy changes of formation.

Table 3.2 below lists the standard Gibbs free energy change of formation, ΔG_f , for some compounds.

species	ΔG_f / kJ mol^{-1}
$FeS_2(s)$	–160
$Li_2S(s)$	–439

Table 3.2

(i) Use the data in **Table 3.2** above to show that the standard Gibbs free energy change, ΔG_r , of the overall cell reaction in the lithium-ion battery is –718 kJ mol^{-1}.

$$4Li(s) + FeS_2(s) \rightarrow Fe(s) + 2Li_2S(s)$$

[1]

(ii) Use the ΔG_r value given in **(c)(i)** to calculate the E_{cell} of this battery.

[2]

For Examiner's Use

(iii) Use your answer in **(c)(ii)** and relevant E value in **Table 3.1** to calculate the standard electrode potential of the FeS_2(s)/Fe(s) half-cell at the cathode.

[1]

(iv) By using **one** of the phrases *more positive*, *more negative* or *no change*, deduce the effect of increasing [Li^+] on the electrode potential of

- the left-hand electrode (anode) ……………………………………
- The right-hand electrode (cathode) …………………………………

[2]

(v) Hence deduce whether the overall E_{cell} is likely to *increase*, *decrease* or *remain the same*, when [Li^+] increases.

……………………………………………………………………………… [1]

[Total: 11]

For Examiner's Use

4 **(a)** **Figure 4.1** is an incomplete sketch showing the melting points of some of the elements of the Period 3 (sodium to argon). Estimate and indicate, on **Figure 4.1**, the melting points of the four other elements: Mg, A*l*, S and C*l*.

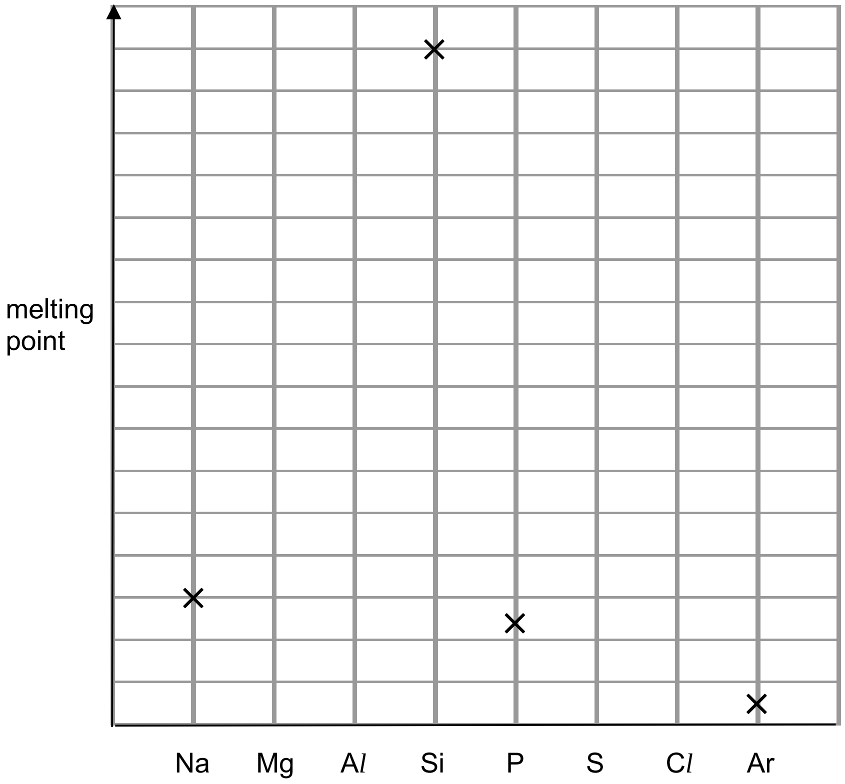
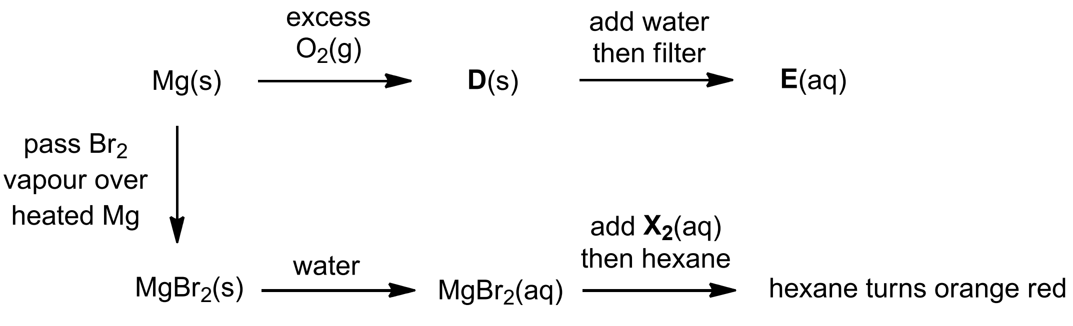


Figure 4.1

[2]

(b) Some reactions of magnesium and its compounds are shown below.



(i) Identify compounds **D** and **E**.

D: ………………….. **E**: ……………………. [2]

(ii) Use appropriate data in the *Data Booklet* to deduce whether $\mathbf{X_2}$ is Cl_2 or I_2.

……………………………………………………………………………………..

……………………………………………………………………………………..

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

(c) Sodium reacts with water to form aqueous sodium hydroxide.

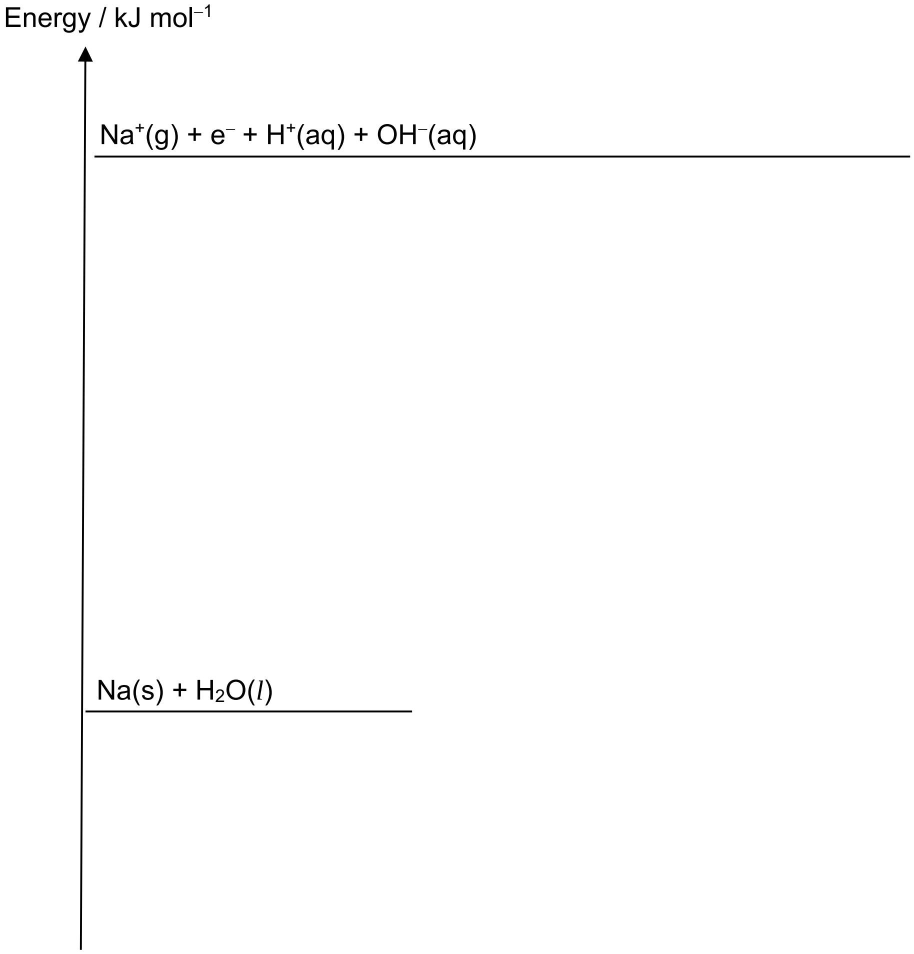
$$Na(s) + H_2O(l) \rightarrow Na^+(aq) + OH^-(aq) + \tfrac{1}{2}H_2(g) \qquad \Delta \boldsymbol{H}_r$$

On the grid below, draw an energy cycle which can be used to calculate $\Delta \boldsymbol{H}_r$, by incorporating the enthalpy changes in **Table 4.1** and any relevant data from the *Data Booklet*.

Hence, calculate $\Delta \boldsymbol{H}_r$.

	value / kJ mol^{-1}
enthalpy change of atomisation of Na(s)	+107
enthalpy change for $Na^+(g) + H^+(aq) + e^- \rightarrow Na^+(aq) + \tfrac{1}{2}H_2(g)$	–850
enthalpy change for $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$	–58

Table 4.1



[4]

[Total: 10]

5 **(a)** But-1-ene reacts with hydrogen bromide to give 2-bromobutane as the major product.

For Examiner's Use

(i) Name and describe the mechanism for this reaction. Show all charges, relevant lone pairs and the movement of electron pairs by using curly arrows.

Name of mechanism: …………………………………………………

[3]

(ii) With reference to the mechanism you have drawn in **(a)(i)**, explain why the major product is 2-bromobutane rather than 1-bromobutane.

………………………………………………………………………………..

………………………………………………………………………………..

……………………………………………………………………………….. [1]

(iii) 2-bromobutane is chiral. However, the product mixture from this reaction does not rotate plane-polarised light.

With reference to the mechanism you have drawn in **(a)(i)**, explain why this is so.

………………………………………………………………………………..

………………………………………………………………………………..

……………………………………………………………………………….. [1]

For Examiner's Use

(b) **Figure 5.1** shows a reaction scheme involving 4-bromobutanone.

Compounds **J** and **K** have the following properties:

- Effervescence is seen when reacted with sodium metal.
- No yellow precipitate is formed when mixed with alkaline aqueous iodine.
- A pale cream precipitate slowly forms when excess HNO_3(aq) is added,

followed by $AgNO_3$(aq).

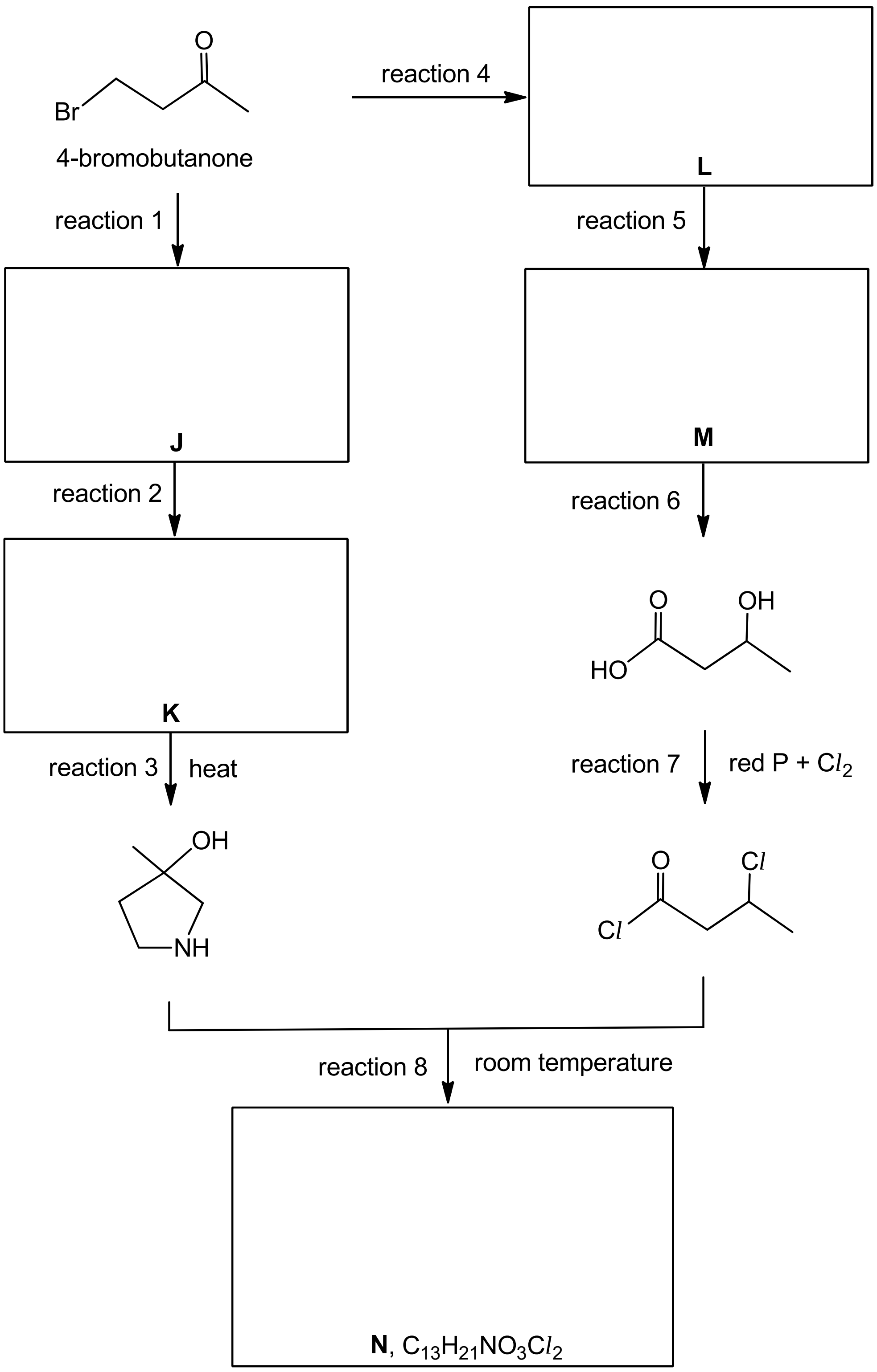


Figure 5.1

(i) Work out the structures for compounds **J**–**N**. Draw their structural formulae in the boxes on the reaction scheme shown in **Figure 5.1**. [5]

For Examiner's Use

(ii) Suggest reagents and conditions for reactions 1, 2, 4, 5 and 6.

reaction 1: ……………………………………………………

reaction 2: ……………………………………………………

reaction 4: ……………………………………………………

reaction 5: ……………………………………………………

reaction 6: …………………………………………………… [5]

(iii) State the types of reaction for reactions 7 and 8.

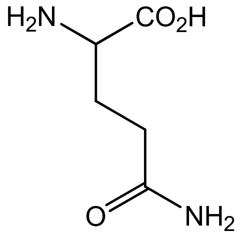
reaction 7: ……………………………………………………

reaction 8: …………………………………………………… [2]

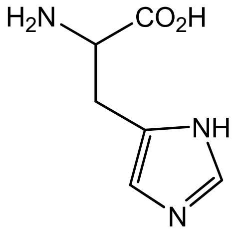
[Total: 17]

6 A pentapeptide comprises the following five amino acids.

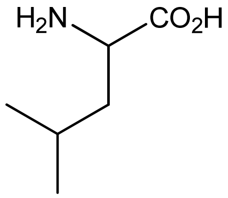
For Examiner's Use



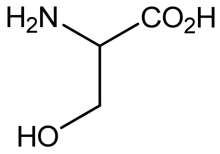
glutamine (gln)
M_r = 146



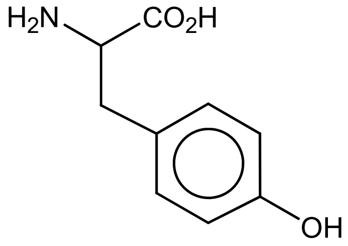
histidine (his)
M_r = 155



leucine (leu)
M_r = 131



serine (ser)
M_r = 105



tyrosine (tyr)
M_r = 181

(a) Calculate the M_r of this pentapeptide. Show your working clearly.

[1]

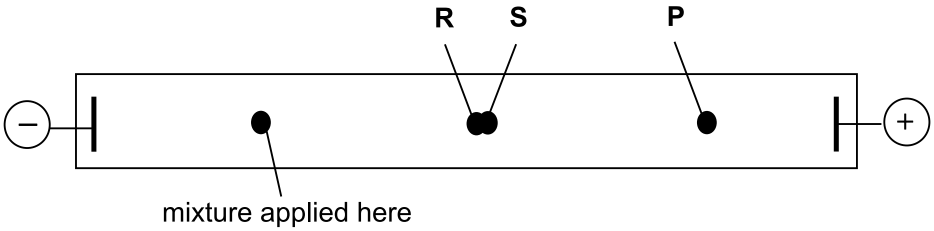
(b) The pentapeptide was broken down by enzymes to form shorter peptides and individual amino acids. One of the peptides is a dipeptide with the sequence

gln-tyr.

(i) Draw the structure of the dipeptide at pH 12.

[2]

A mixture of this dipeptide (gln-tyr) and its two constituent amino acids (gln and tyr) was subjected to electrophoresis in a buffer at pH = 12. At the end of the experiment, the following results were seen. Spots **R** and **S** remained very close together.



The three spots are due to the three species gln, tyr and gln-tyr.

(ii) Which species is responsible for spot **P**? Explain your answer

spot **P**: …………………….

explanation ……………………………………………………………………

……………………………………………………………………………………..

……………………………………………………………………………………..

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

(iii) Suggest why the other two species give spots **R** and **S** that are so close together.

……………..……………………………………………………………………

……………………………………………………………………………………..

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

(c) State a reagent you would use and the observations you would make to distinguish tyrosine (tyr) from glutamine (gln).

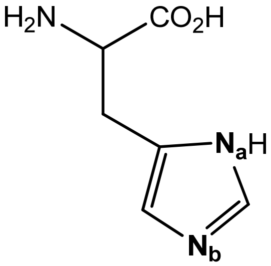
test ………………………………………….

observations …………………………………………………………………..

…………………………………………………………………………………...

……………………………………………………………………………………… [2]

(d) There are two nitrogen atoms, $\mathbf{N_a}$ and $\mathbf{N_b}$, in the side chain of histidine. However, only one of the nitrogen atoms can act as a Bronsted base.



(i) $\mathbf{N_a}$ and $\mathbf{N_b}$ have the same state of hybridisation. State their state of hybridisation.

……………………………… [1]

(ii) Predict which nitrogen atom, $\mathbf{N_a}$ or $\mathbf{N_b}$, can act as a Bronsted base. Explain your answer.

………………………………………………………………………………..

………………………………………………………………………………..

………………………………………………………………………………..

………………………………………………………………………………..

……………………………………………………………………………….. [2]

[Total: 11]

END OF PAPER

Suggested Answers for 2018 H2 Chemistry Preliminary Examination Paper 2

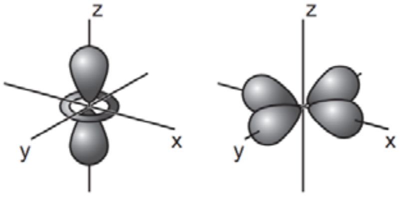
1 **(a)** % abundance of 5th isotope = 100 – (68.1 + 1.14 + 3.63 + 0.93) = 26.2 %

Let relative isotopic mass of 5th isotope be x.

$58.7 = 0.262x + (58 \times 0.681) + (61 \times 0.0114) + (62 \times 0.0363) + (64 \times 0.0093)$

$\therefore\ x = 60$

(b) **(i)**



☑ ☑

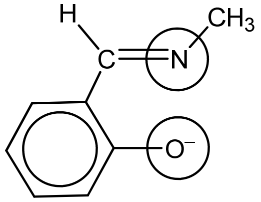
(ii) Visible light is absorbed when an electron transits from a lower energy d orbital to a higher energy d orbital that is partially filled.

Colour seen is the complement of the colours that are absorbed.

(iii) Colour: Green

Wavelengths corresponding to the blue and red regions are most absorbed (or green region is least absorbed).

(c)



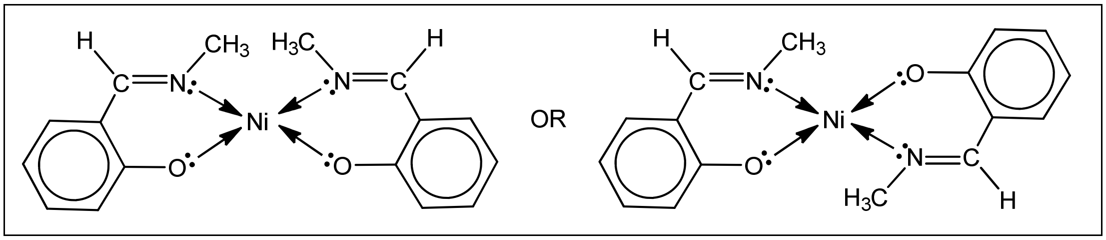
(d) $n(Ni^{2+}) = 4.0 \times 10^{-3} \times 3 \times 10^{-3} = 1.2 \times 10^{-5}$ mol

$n(X^{-}) = 6.0 \times 10^{-3} \times 4 \times 10^{-3} = 2.4 \times 10^{-5}$ mol

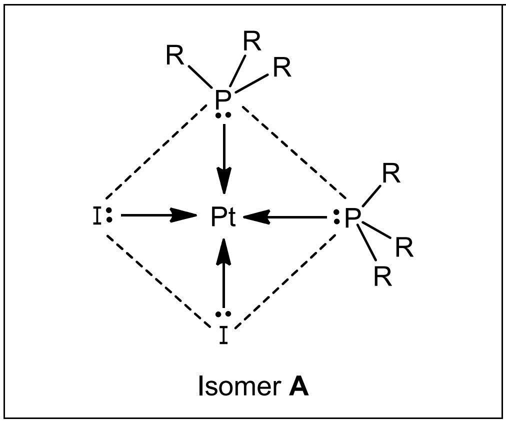
$n(Ni^{2+}) : n(X^{-}) = 1.2 \times 10^{-5} : 2.4 \times 10^{-5} = 1 : 2$

Empirical formula is NiX_2.

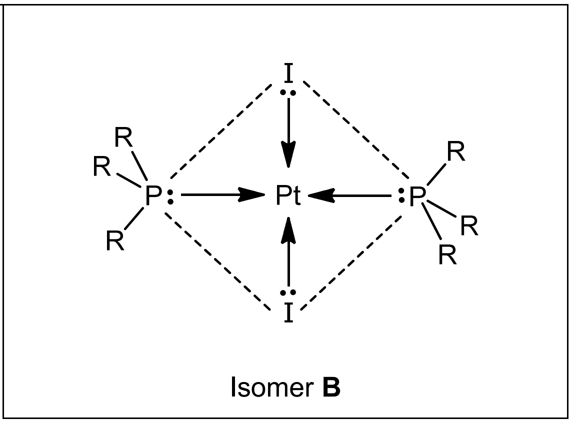
Structural formula of the complex:



(e)

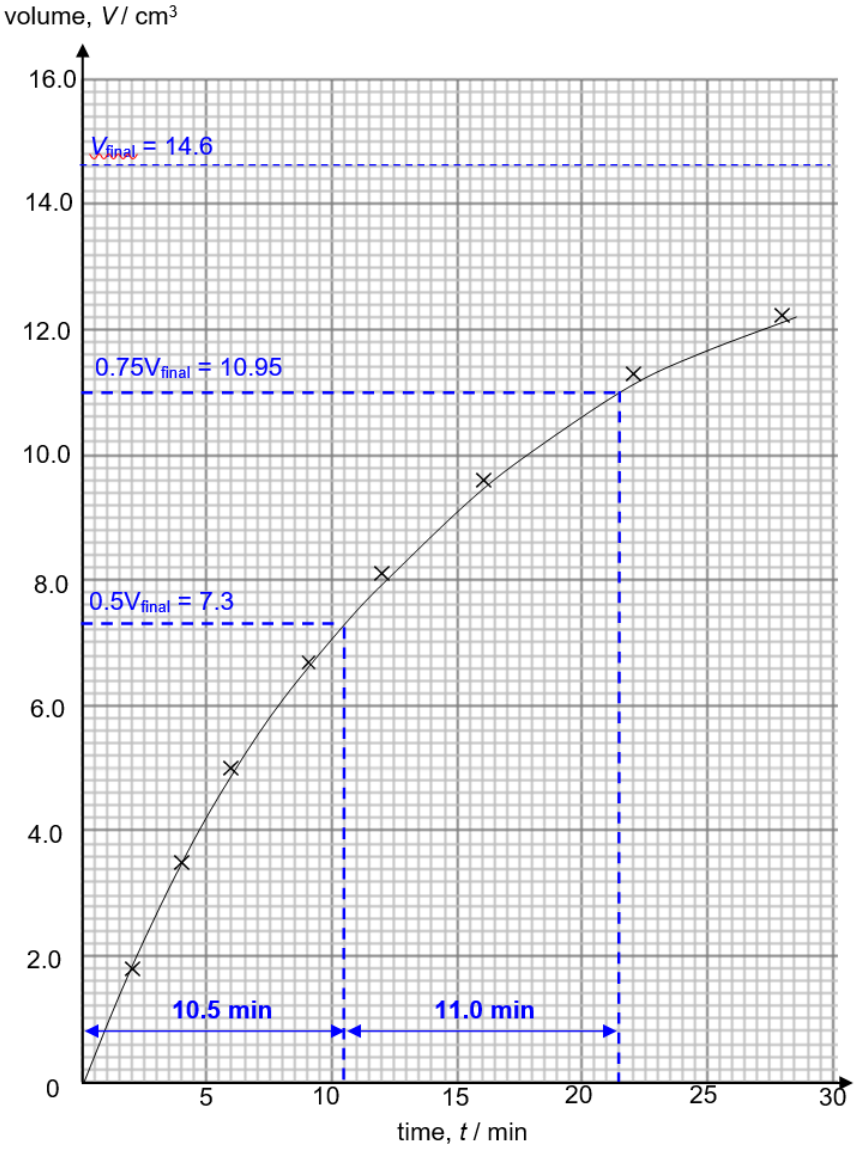


Isomer **A**



Isomer **B**

2 **(a)**



(i) Order of reaction with respect to benzenediazonium chloride: 1

1st $t_{½}$ = 10.5 min; 2nd $t_{½}$ = 11.0 min ⇒ Half-lives are relatively constant.

(ii) Average $t_{½}$ = 0.5 (10.5 + 11.0) = 10.75 min

For overall 1st order reaction, $k = \dfrac{\ln 2}{10.75} = 0.0645 \text{ min}^{-1}$

(iii) $n(N_2) = \dfrac{(101000)(14.7 \times 10^{-6})}{(8.31)(50 + 273)} = 0.000549 \text{ mol}$

$= n(C_6H_5N_2Cl)$ in 500 cm^3 solution

Original [benzenediazonium chloride] = $0.000549 \times \dfrac{1000}{500} = 0.00110 \text{ mol dm}^{-3}$

(b) **(i)** type of reaction: electrophilic substitution

reagents: concentrated HNO_3

conditions: concentrated H_2SO_4, 50 °C

(ii) $1C_6H_5NO_2 + 7H^+ + 6e^- \rightarrow C_6H_5NH_3^+ + 2H_2O$

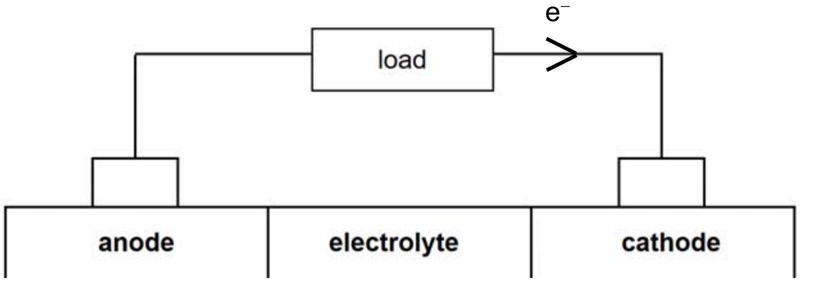
(iii) $2C_6H_5NO_2 + 3Sn + 14HCl \rightarrow 2C_6H_5NH_3Cl + 3SnCl_4 + 4H_2O$

(iv) NaOH will undergo acid-base reaction with $C_6H_5NH_3^+$ (or deprotonate $C_6H_5NH_3^+$) to give $C_6H_5NH_2$.

3 **(a)** Any 2 of the following:

- Li is the lightest/has the lowest density so lithium battery is most portable.
- Li has the most negative E / is most easily oxidised among the metals and thus gives the largest e.m.f./E_{cell}.
- Li has the largest electrochemical capacity so it can produce the largest amount of electrical charge per unit mass of the metal.

(b) **(i)**



(ii) Li is a reactive metal and will undergo redox reaction with water to produce H_2 gas which may cause explosion.

(c) (i)

$$\begin{tikzcd}
4\mathrm{Li(s)} + \mathrm{FeS_2(s)} \arrow[rr, "\Delta G_r"] & & \mathrm{Fe(s)} + 2\mathrm{Li_2S(s)} \\
& 4\mathrm{Li(s)} + \mathrm{Fe(s)} + 2\mathrm{S(s)} \arrow[ul, "\Delta G_f\ (\mathrm{FeS_2})"] \arrow[ur, "2\Delta G_f\ (\mathrm{Li_2S})"'] &
\end{tikzcd}$$

$\Delta G_r = \Sigma\,(a_i \times \Delta G_f\ \text{(products)}) - \Sigma\,(a_i \times \Delta G_f\ \text{(reactants)})$

$= 2(-439) - (-160)$

$= -718$ kJ mol^{-1} (shown)

(ii) $\Delta G = -nFE_{\text{cell}}$

$-718 \times 10^3 = -(4)(96500)(E_{\text{cell}})$

$E_{\text{cell}} = +1.86$ V

(iii) $Li^+ + e^- \ll Li \quad E = -3.04$ V ---[O]

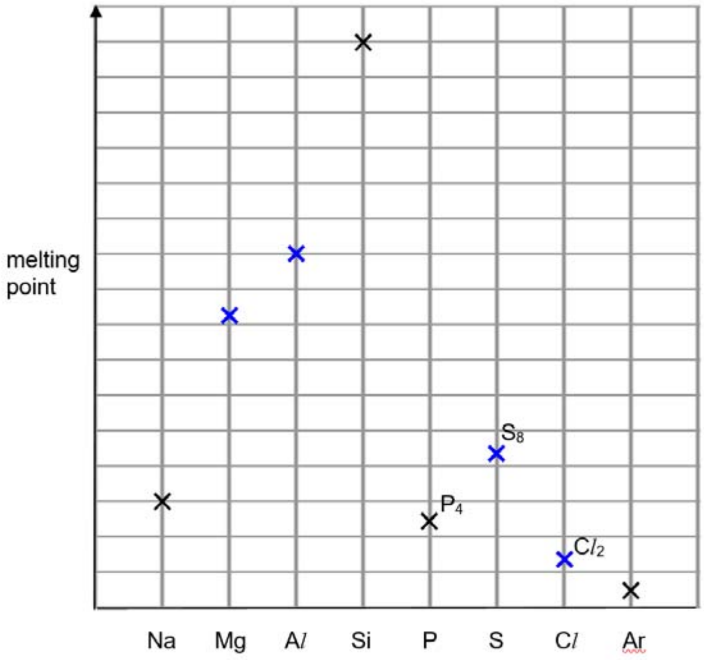
$+1.86 = E\ (FeS_2/Fe) - (-3.04)$

$(FeS_2/Fe) = -1.18$ V

(iv)
- the left-hand electrode (anode): more positive
- The right-hand electrode (cathode): more positive

(v) E_{cell} will remain the same.

4 (a)



(b) (i) **D**: MgO **E**: $Mg(OH)_2$

(ii) X_2 is Cl_2.

E_{cell} for reaction of Cl_2 and Br^- = (+1.36) – (+1.07) = +0.29 V > 0 (energetically feasible).

OR

E_{cell} for reaction of I_2 and Br^- = (+0.54) – (+1.07) = –0.53 V < 0 (energetically not feasible).

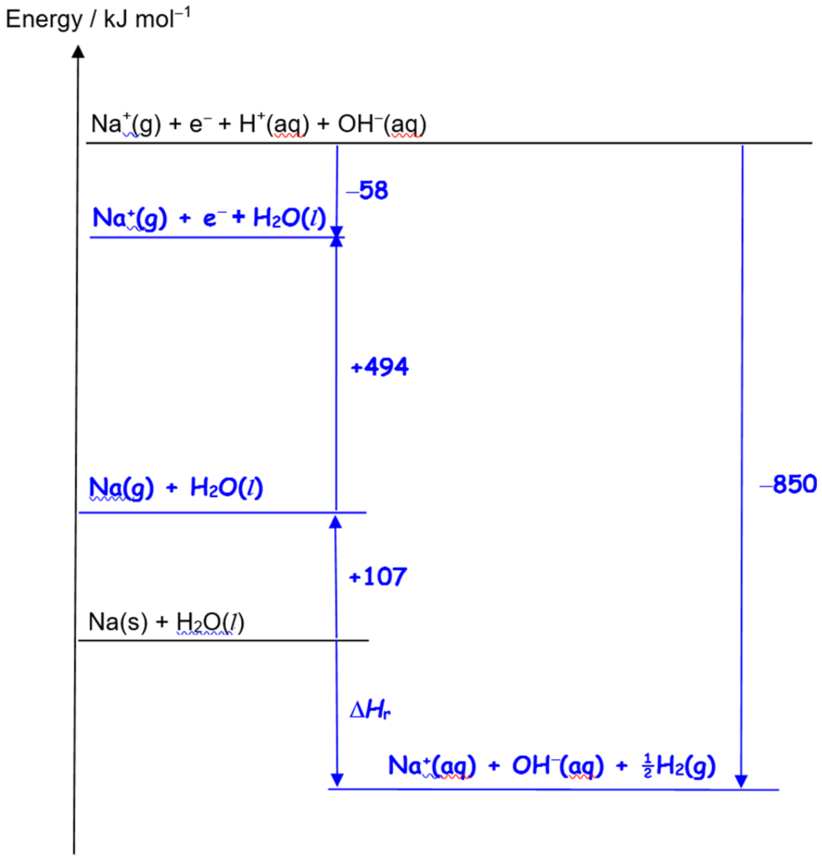
OR

E (Cl_2/Cl^-) > E (Br_2/Br^-) so Cl_2 is a stronger oxidising agent than Br_2 and thus can oxidise Br^- to Br_2.

OR

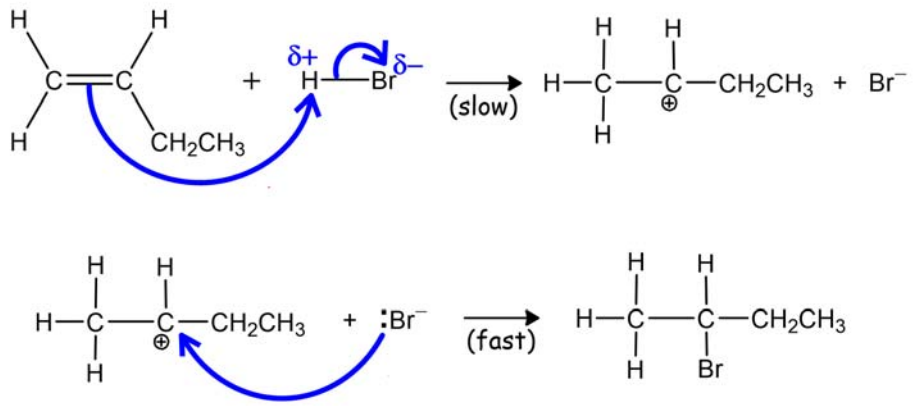
E (Br_2/Br^-) > E (I_2/I^-) so I_2 is a weaker oxidising agent than Br_2 and thus cannot oxidise Br^- to Br_2.

(c)



ΔH_r = (+107) + (+494) – (–58) + (–850) = –191 kJ mol^{-1}

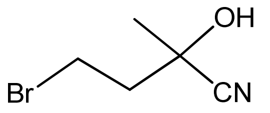
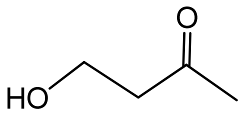
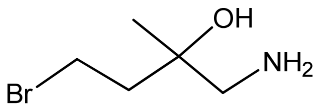
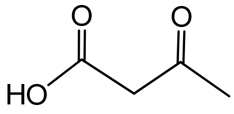
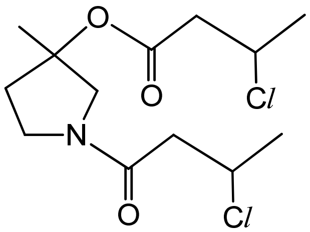
5 **(a)** **(i)** Name of mechanism: electrophilic addition



(ii) In the first step, secondary carbocation, $^{+}CH(CH_3)CH_2CH_3$, (which yields 2-bromobutane) is more stable and thus more readily formed than primary carbocation, $^{+}CH_2CH_2CH_2CH_3$, (which yields 1-bromobutane) as it has one more electron-donating alkyl group which disperses its positive charge more.

(iii) There is equal probability for Br^- to attack either side of the trigonal planar C^+ of carbocation in step 2, forming a racemic mixture.

(b) **(i)**

J: 	**L**: 
K: 	**M**: 
N: 	

(ii) reaction 1: HCN, trace amount of KCN/NaCN

reaction 2: $LiAlH_4$, dry ether OR H_2, Ni, heat

reaction 4: aqueous NaOH/KOH, heat

reaction 5: acidified $K_2Cr_2O_7$/$KMnO_4$, heat

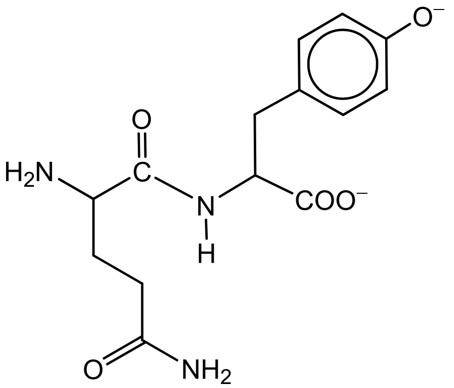
reaction 6: $NaBH_4$, methanol OR H_2, Ni, heat

(iii) reaction 7: nucleophilic substitution

reaction 8: condensation

6 **(a)** $M_r = 146 + 155 + 131 + 105 + 181 - (4 \times 18.0) = 646$

(b) **(i)**



(ii) spot **P**: tyr

Tyrosine has a charge of 2– at pH = 12 and a smaller mass/M_r than gln-tyr. It has the highest $\frac{\text{charge}}{\text{mass}}$ ratio compared to the other two species so it moves the fastest and thus furthest from original position.

(iii) Charge of gln-tyr is twice that of gln and its mass/Mr of is about twice that of gln.

OR

gln and gln-tyr have similar $\frac{\text{charge}}{\text{mass}}$ ratios ($\frac{\text{charge}}{\text{mass}}$ of gln is $\frac{1}{146}$ = 0.00685 whereas $\frac{\text{charge}}{\text{mass}}$ of gln-tyr is $\frac{2}{309}$ = 0.00647).

(c) test: $Br_2(aq)$

observations: Tyr decolourises orange $Br_2(aq)$ and forms a white precipitate while gln will not.

OR

test: neutral $FeCl_3(aq)$

observations: Tyr will give a violet colouration while glu will not.

OR

test: NaOH(aq), heat

observations: Gln will give NH_3 gas which turns damp red litmus paper blue while tyr will not.

(d) **(i)** sp^2

(ii) N_b can act as a Bronsted base.

This is because the lone pair of electron on N_a is in an unhybridised p orbital which is parallel to the adjacent π electron systems so it is delocalised into C=C and $C=N_b$ due to p-p orbital overlap. Hence, the lone pair of electrons is not available for protonation.

However, the lone pair (of electron) on N_b is in a sp^2 orbital which is on the same plane as the ring (or not parallel to adjacent π electron system) and hence it will not be delocalised into the adjacent C=C. Thus, the lone pair of electron is available for protonation.

JURONG JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION 2018

CANDIDATE NAME			
CLASS	**18S**	EXAM INDEX	

CHEMISTRY

9729/03

Higher 2

Paper 3 Free Response

11 September 2018
2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

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

Section A
Answer **all** questions.

Section B
Answer **one** question.

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

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

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

Section A

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

1 **(a)** Peroxides refer to a class of compounds with an oxygen-oxygen single bond.

Hydrogen peroxide, H_2O_2, is the simplest peroxide. It is commonly used in laboratories for both its oxidising and reducing properties.

Sodium peroxide, Na_2O_2, is prepared by burning sodium in air. This reaction also produces sodium oxide, Na_2O.

Compound	Melting point / °C
hydrogen peroxide, H_2O_2	−11
sodium peroxide, Na_2O_2	675
sodium oxide, Na_2O	920

(i) Draw the ‘dot-and-cross’ diagrams for

- hydrogen peroxide, H_2O_2
- sodium peroxide, Na_2O_2. [2]

(ii) Explain the difference in the melting points between

- sodium peroxide (Na_2O_2) and hydrogen peroxide (H_2O_2)
- sodium peroxide (Na_2O_2) and sodium oxide (Na_2O). [2]

(b) The peroxides of the Group 2 elements, MO_2, decompose on heating to produce a single gas and the solid oxide, MO, only.

(i) Write an equation for the thermal decomposition of strontium peroxide, SrO_2. [1]

(ii) Suggest how the temperature at which thermal decomposition of MO_2 occurs varies down Group 2.

Explain your answer. [3]

1 **(c)** Dicarboxylic acids dissociate in stages.

$$HO_2C(CH_2)_nCO_2H \overset{\text{stage 1}}{\ll} HO_2C(CH_2)_nCO_2^- + H^+ \overset{\text{stage 2}}{\ll} {}^-O_2C(CH_2)_nCO_2^- + 2H^+$$

The pK_a values for stage 1 and stage 2 for some dicarboxylic acids are listed below.

n in $HO_2C(CH_2)_nCO_2H$	pK_a(1) for stage 1	pK_a(2) for stage 2
1	2.83	5.69
2	4.16	5.61
3	4.31	5.41

For comparison, the pK_a value of ethanoic acid, CH_3CO_2H, is 4.76.

(i) With reference to the table given, suggest why the pK_a(1) values

- are all smaller than the pK_a of ethanoic acid,
- become larger as n increases. [3]

(ii) Suggest why all the pK_a(2) values in the table above are larger than the pK_a of ethanoic acid. [1]

(iii) Calculate the pH of a 0.10 mol dm^{-3} solution of $HO_2CCH_2CO_2H$. Ignore the effect of pK_a(2) on the pH. [1]

(iv) Sketch the pH-volume added curve you would expect to obtain when 20 cm^3 of 0.10 mol dm^{-3} NaOH is added to 10 cm^3 of 0.10 mol dm^{-3} $HO_2CCH_2CO_2H$.

Mark clearly the initial pH and the point(s) of maximum buffering capacity. Indicate the volume at equivalence point(s). [3]

(v) The monosodium salts of edible dicarboxylic acids can act as buffers.

Write two equations to show how monosodium butanedioate, $HO_2C(CH_2)_2CO_2Na$, acts as a buffer. [2]

(vi) A solution containing both $HO_2C(CH_2)_2CO_2Na$ and $NaO_2C(CH_2)_2CO_2Na$ forms a buffer solution. The following equilibrium is present in the solution.

$$HO_2C(CH_2)_2CO_2^-(aq) \ll {}^-O_2C(CH_2)_2CO_2^-(aq) + H^+(aq)$$

By choosing the correct pK_a value given in the table, calculate the pH of a buffer solution made by mixing 100 cm^3 of 0.5 mol dm^{-3} $HO_2C(CH_2)_2CO_2Na$ and 50 cm^3 of 0.3 mol dm^{-3} $NaO_2C(CH_2)_2CO_2Na$. [2]

[Total: 20]

2 Sulfur is the second member of Group 16 in the Periodic Table.

(a) Explain why sulfur has a lower first ionisation energy than phosphorus. [1]

(b) Natural gas, consisting primarily of methane, is available in large amounts and is used as a fuel. However, direct conversion of alkanes such as methane into useful products is challenging owing to their unreactivity.

(i) Give a reason why alkanes are unreactive. [1]

In 2013, scientists discovered that they could selectively convert methane to alkenes using gaseous sulfur, S_2, over a suitable catalyst. This conversion takes place at over 1000 K, where sulfur exists as $S_2(g)$, as shown in **reaction 1**.

(ii) **reaction 1** $2CH_4(g) + S_2(g) \rightarrow C_2H_4(g) + 2H_2S(g)$

Calculate the enthalpy change of **reaction 1** by drawing an energy cycle using the following information.

$CH_4(g) + 2S_2(g) \rightarrow CS_2(g) + 2H_2S(g)$ $\Delta H_r = +96.0 \text{ kJ mol}^{-1}$

$C_2H_4(g) + 3S_2(g) \rightarrow 2CS_2(g) + 2H_2S(g)$ $\Delta H_r = +91.0 \text{ kJ mol}^{-1}$ [2]

(c) The key stage in the manufacture of sulfuric acid is the reaction between sulfur dioxide and oxygen over a catalyst.

$$2SO_2(g) + O_2(g) \ll 2SO_3(g)$$

(i) When an equimolar mixture of SO_2 and O_2 is passed over a catalyst at T °C at an initial total pressure of 200 kPa, the percentage conversion of $SO_2(g)$ is 98%.

Calculate the equilibrium partial pressure of each of the three gases and hence, the value of K_p at temperature T °C. [3]

(ii) The table below shows values of K_p for this equilibrium at different temperatures.

temperature / °C	K_p / kPa^{-1}
25	4.0×10^{22}
200	2.5×10^{8}
800	1.3×10^{-3}

Using relevant data from the given table, explain in terms of the position of equilibrium,

- the sign of ΔG at 25 °C and
- the sign of ΔH for the forward reaction. [4]

2 **(d)** **(i)** Which of the two gases, SO_2 and O_2, is less ideal? Explain your answer. [1]

(ii) Sketch a graph of volume (V) against temperature (T/ K) for a given mass of an ideal gas at constant pressure. [1]

(e) In the atmosphere, the oxidation of SO_2 to SO_3 can be catalysed by NO_2.

The mechanism for this catalysed oxidation of SO_2 to SO_3 occurs in two steps.

$$\textit{step 1}: \ NO_2(g) + SO_2(g) \xrightarrow{\textit{slow}} NO(g) + SO_3(g) \qquad \Delta H_1 = -88 \text{ kJ mol}^{-1}$$

$$\textit{step 2}: \ NO(g) + \frac{1}{2}O_2(g) \xrightarrow{\textit{fast}} NO_2(g) \qquad \Delta H_2 = -57 \text{ kJ mol}^{-1}$$

Use this information to construct a fully-labelled reaction pathway diagram for the catalysed oxidation of SO_2 to SO_3. Indicate on your diagram, the 'reactants', 'products', ΔH_1 , ΔH_2 and the activation energy, E_a, of the reaction. [3]

(f) Oxides of nitrogen are also used in other applications.

One such oxide is N_2O_5, which exists as $[NO_2^+][NO_3^-]$ in solution.

When benzene is added to a solution of N_2O_5 in CCl_4, an excellent yield of nitrobenzene is obtained in the absence of any added catalyst.

(i) Write a balanced equation for the reaction of benzene and N_2O_5. [1]

(ii) Suggest a mechanism for this reaction, showing all charges and using curly arrows to show the movement of electron pairs. [2]

(iii) Compounds **H** has the molecular formula, C_9H_{12}. Mononitration of **H** produces only one organic product. Suggest the structure of **H**. [1]

[Total: 20]

3 **(a)** Copper has the highest electrical conductivity rating among the non-precious metals. The high conductivity of copper is a consequence of its electronic configuration.

(i) State the electronic configuration of Cu atom. [1]

(ii) Explain why copper is regarded as a *transition element*. [1]

(iii) Suggest why copper is **not** usually used for overhead electrical cables despite its superior conductivity. [1]

(b) Electrical wiring is the most important market for the copper industry. To be used in wiring, copper must be at least 99.9% pure. Chalcopyrite, $CuFeS_2$, is the most common copper ore being used to obtain pure copper in a two-step process.

The first step occurs in a furnace where chalcopyrite is heated strongly with silica, SiO_2, and air. The furnace reduces the copper(II) in chalcopyrite to copper.

The reaction occurring in the blast furnace can be represented by the following **unbalanced** equation.

$$CuFeS_2 + SiO_2 + O_2 \rightarrow Cu + FeSiO_3 + SO_2$$

The copper obtained is nowhere near 99.9% pure as it contains nickel and silver as minor impurities to form an alloy.

The second step occurs in an electrolytic cell where the alloy undergoes electrolysis to produce copper at or above 99.9% purity.

(i) Identify the element that undergoes oxidation in the furnace and state the initial and final oxidation numbers of this element. [1]

(ii) In the furnace, the element O is reduced alongside with the element Cu. Using oxidation numbers or otherwise, write a **balanced** equation for the reaction occurring in the furnace. [1]

(iii) Draw a fully labelled diagram of the electrolytic cell where copper purification occurs. [2]

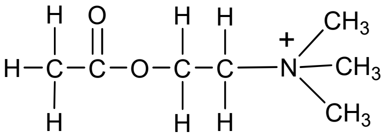
(iv) Explain, by quoting relevant E values, what happens to the nickel and silver impurities during this purification procedure. [4]

(c) When dilute aqueous ammonia was added to copper(II) sulfate solution, a pale blue precipitate was first observed which dissolved to give a dark blue solution when aqueous ammonia was added in excess. In these reactions, the ammonia can act as a *Bronsted-Lowry base* and as a *Lewis base*.

Illustrate the meaning of *Bronsted-Lowry base* and *Lewis base* using the reactions of aqueous copper(II) ions with ammonia. Write equations to account for the observations noted in these reactions. [4]

3 **(d)** In 2013, scientists suggested that too much copper in our diet may contribute to Alzheimer's disease, a neurological disorder in which death of brain cells causes memory loss and cognitive decline. In patients with Alzheimer's disease, the concentration of acetylcholine, a neurotransmitter essential for processing memory and learning, is found to be lower.

The structure of acetylcholine is shown below.

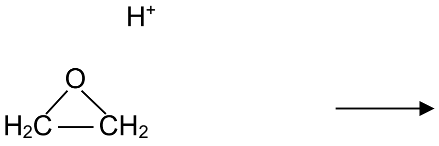


When acetylcholine undergoes hydrolysis in the presence of an enzyme, two products are formed; one of which is a charged species called choline.

(i) Draw the structures of these **two** products. [2]

(ii) As a precursor to the synthesis of acetylcholine, choline is an essential nutrient in our diet. Choline can be produced in a sealed reaction vessel by the reaction of anhydrous trimethylamine, $N(CH_3)_3$, with epoxyethane and HCl under moderate pressure.

Copy and complete the diagram below to suggest a mechanism to show how choline is formed. Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows.



epoxyethane [3]

[Total: 20]

Section B

Answer **one** question from this section.

4 **(a)** Thionyl chloride, $SOCl_2$, is a colourless liquid that is primarily used in the chlorination of organic compounds.

(i) Draw the shape of $SOCl_2$. [1]

(ii) Explain which molecule, $SOCl_2$ or $COCl_2$, is expected to have a larger bond angle. [1]

(b) When $SOCl_2$ is reacted with a carboxylic acid to produce an acyl chloride, two acidic gases are formed.

$$SOCl_2(l) + RCO_2H \rightarrow RCOCl + SO_2(g) + HCl\,(g)$$

A 1.00 g sample of a carboxylic acid RCO_2H was treated in this way, and the gases were absorbed in 60.0 cm^3 of 0.500 mol dm^{-3} NaOH(aq). The excess NaOH was titrated with 0.500 mol dm^{-3} HCl(aq). It required 10.8 cm^3 of the HCl(aq) solution to reach the end-point.

(i) Write equations for the complete reactions between

- NaOH and HCl,
- NaOH and SO_2. [2]

(ii) Calculate the total number of moles of NaOH that reacted with the acidic gases, SO_2 and HCl. [1]

(iii) Calculate the number of moles of RCO_2H that produced the SO_2 and HCl. [1]

(iv) Hence calculate the M_r of the carboxylic acid, RCO_2H. [1]

(v) The R group contains carbon and hydrogen only.

Suggest the structure of RCO_2H. [1]

(c) Using $SOCl_2$ in the initial step, carboxylic acids can be converted into primary amines by the following sequence of reactions.

$$RCO_2H \xrightarrow[\text{step 1}]{SOCl_2} RCOCl \xrightarrow[\text{step 2}]{} \mathbf{D} \xrightarrow[\text{step 3}]{} RCH_2NH_2$$

(i) Identify the structure of **D**. [1]

(ii) Suggest the reagents needed for step 2 and step 3. [2]

(iii) State the *types of reaction* for step 2 and step 3. [1]

4 **(d)** Angelic acid, $C_5H_8O_2$, is a natural product isolated from the roots of the angelica plant.

- Angelic acid reacts with H_2 + Ni to form **T**, $C_5H_{10}O_2$.
- Both angelic acid and **T** exhibit stereoisomerism.
- On treatment with hot acidic $KMnO_4$, angelic acid produces two acidic compounds, **U** and **V**.
- Only **U** gives yellow precipitate with alkaline aqueous iodine.

(i) Suggest structures for **T**, **U**, **V** and angelic acid. Explain the reactions. [6]

(ii) State the types of stereoisomerism shown by angelic acid and compound **T**. [2]

[Total: 20]

5 **(a)** **(i)** Describe the reaction of $SiCl_4$ with water and include any observations you can make. Write an equation for the reaction that occurs. [2]

(ii) Carbon is in the same group as silicon. However, CCl_4 does not react with water. Explain why. [1]

(b) Chlorine-containing organic compounds can also differ in their reactivity towards hydrolysis reactions.

Compounds **A** and **B** are isomers with the molecular formula, C_7H_7Cl. Compound **A** reacts with aqueous NaOH on heating but compound **B** does not.

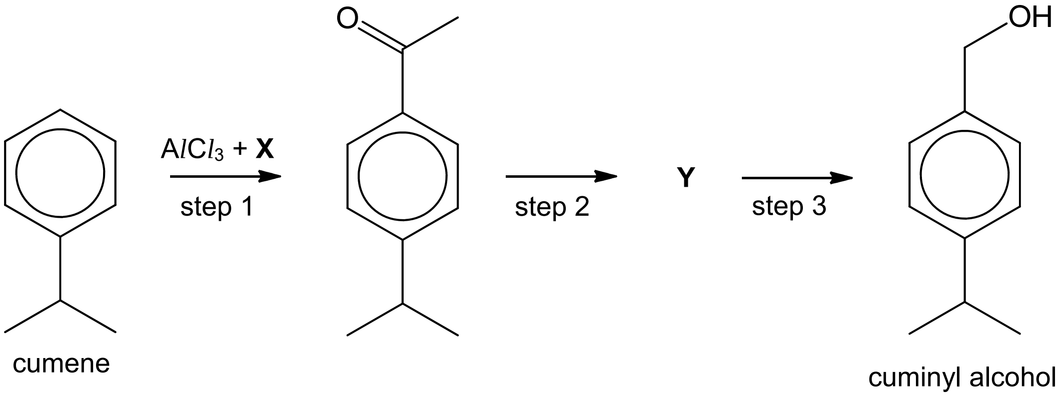
Draw the structures of compounds **A** and **B** and explain the difference in their reactivity towards aqueous NaOH. [2]

(c) Heating tin with hydrochloric acid produces hydrogen gas. Careful removal of water from the resulting product produces white solid $SnCl_2$.

In contrast, passing chlorine gas over heated tin produces colourless liquid $SnCl_4$ as the only product.

Using relevant *E* from the *Data Booklet*, explain the above observations. [2]

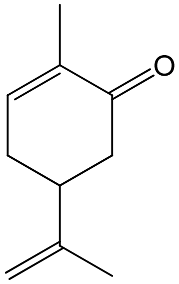
(d) Cumin is a spice used to flavour food. One of the key organic compounds responsible for the smell of cumin is cuminyl alcohol. It can be synthesised from cumene as shown below. Aluminium chloride is used as a catalyst with reagent **X** in step 1.



(i) Suggest the identity of reagent **X**. [1]

(ii) Suggest reagents and conditions for steps 2 and 3 and draw the structure of the intermediate compound **Y**. [3]

5 **(e)** Carvone, an isomer of cuminyl alcohol, is most responsible for the flavour of caraway, dill and spearmint.



carvone

(i) When carvone is treated with $NaBH_4$, compound **M**, $C_{10}H_{16}O$, is produced. Draw the structure of **M** and write an equation to represent this reaction. [2]

(ii) Compound **N** is isomeric with compound **M**.

On treatment with hot concentrated $KMnO_4$, **N** gives two compounds, **P**, C_3H_6O, and **Q**, $C_4H_4O_5$. **P** and **Q** are formed in the mole ratio of 2 : 1.

All three compounds, **N**, **P** and **Q** give an orange precipitate with 2,4-dinitrophenylhydrazine but only **N** forms a silver mirror with Tollens' reagent. One mole of **Q** reacts with two moles of aqueous sodium hydrogencarbonate.

Suggest structures for **N**, **P** and **Q** and explain the observations described above. [7]

[Total: 20]

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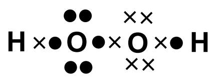
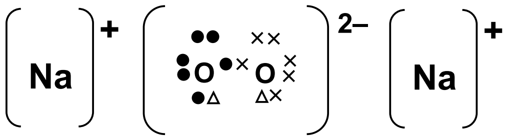
Suggested Answers for 2018 H2 Chemistry Preliminary Examination Paper 3

1 **(a)** **(i)** H_2O_2 :



[1m]

Na_2O_2 :



Accept:
1) 2 [Na]$^+$

Reject:
1) $[Na]_2^+$
2) electrons are drawn around Na^+

[1m]

(ii) Sodium peroxide has a giant ionic structure while hydrogen peroxide has a simple molecular structure.

More energy is needed to overcome the **strong ionic bonds between Na^+ and O_2^{2-}/oppositely charged ions** (✓)

compared to the **weak intermolecular force in H_2O_2/ hydrogen bonds between H_2O_2 molecules**. (✓)

Hence, sodium peroxide has a higher boiling point than hydrogen peroxide.

Both sodium peroxide and sodium oxide have a giant ionic structure.

While O_2^{2-} and O^{2-} have the same ionic charge, **O_2^{2-}** has a **larger radius/ bigger size than O^{2-}** (✓).

Less energy is needed to overcome the **weaker ionic bonds between Na^+ and O_2^{2-} than that between Na^+ and O^{2-}.** (✓)

Hence, sodium peroxide has a lower boiling point than sodium oxide.

4(✓) : **[2m]** ; 2-3(✓) : **[1m]**

Minus 1m if no comparison of the strength of bonds is made.

(b) **(i)** $\mathbf{SrO_2 \rightarrow SrO + \frac{1}{2}O_2}$ or $\mathbf{2SrO_2 \rightarrow 2SrO + O_2}$ **[1m]**

(ii) Down the Group, **decomposition temperature increases**. **[1m]**

Down the Group,

① **radius of M^{2+}/cation increases**
② **charge density** of M^{2+} **decreases**

} **[1m]**

③ **polarising power** of M^{2+} **decreases** / **polarisation of O_2^{2-} anion occurs to smaller extent**
④ **less weakening of O–O bond**
⑤ MO_2 becomes **thermally more stable**, higher temperature is needed to decompose.

} **[1m]**

1 **(c)** **(i)** pK_a(1) values are all smaller than the pK_a of ethanoic acid

[1m] smaller pK_a implies larger K_a, indicating **dicarboxylic acids are more acidic/ stronger acids** than ethanoic acid

[1m] **–CO_2H group is electron-withdrawing**, **disperse the negative charge** and **stabilise** mono**anion**/ $HO_2C(CH_2)_nCO_2^-$

Or mono**anion**/ $HO_2C(CH_2)_nCO_2^-$ is **stabilised by hydrogen bonding** (especially for malonic acid when n=1)

pK_a(1) values become larger as n increases

[1m] electron-withdrawing **–CO_2H group** is **further away from –CO_2^- / ionising –CO_2H / the other –CO_2H group**

Or intervening **additional electron-donating alkyl groups destabilise anion**

(ii) larger pK_a implies smaller K_a with $HO_2C(CH_2)_nCO_2^-$ being a weaker acid than CH_3CO_2H; it is **more difficult to remove** a positively charged **H^+ from a negatively charged** species/ mono**anion** (electrostatically not favourable) **[1m]**

(iii)

$$[H^+] = \sqrt{K_a \times c}$$

$$= \sqrt{10^{-2.83} \times 0.10}$$

$$= \mathbf{0.0122\ mol\ dm^{-3}}$$

pH = -lg [H^+] = **1.92** **[1m]**

(iv)

The following should be clearly marked and labelled:

(✓) Both axes are labelled with units stated for x-axis.

(✓) Curve starts at pH 1.92 (ecf)

(✓) First maximum buffering capacity at 5 cm^3 and pH 2.83.

(✓) Second maximum buffering capacity at 15 cm^3 and pH 5.69.

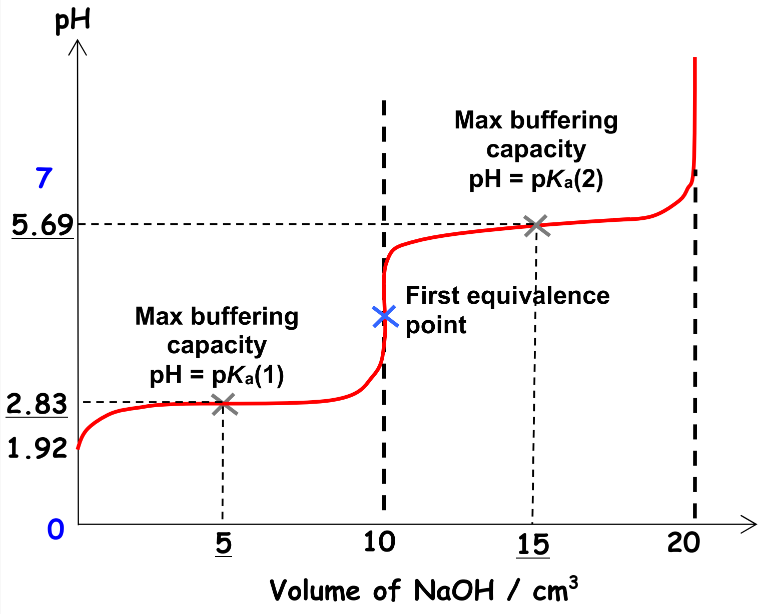
(✓) First equivalence point at 10 cm^3 and graph ends at 20 cm^3

(✓) 2 points of inflection

6(✓) – [3m]

4–5(✓) – [2m]

2–3(✓) – [1m]



(v) **[1m]** $HO_2C(CH_2)_2CO_2Na + H^+ \rightarrow HO_2C(CH_2)_2CO_2H + Na^+$

[1m] $HO_2C(CH_2)_2CO_2Na + OH^- \rightarrow {}^-O_2C(CH_2)_2CO_2Na + H_2O$

allow ionic eqns; reject ≪

1 (c) (vi) System: <u>Acidic Buffer</u>

$$pH = pK_a + \lg\frac{[salt]}{[acid]} = pK_a + \lg\frac{n(salt)}{n(acid)}$$

$$= 5.61 + \lg\left(\frac{\frac{50}{1000}\times 0.3}{\frac{100}{1000}\times 0.5}\right)$$

$$= \underline{5.09}$$

[1m] quote the correct pK_a (5.61) in working
[1m] pH calculation (ecf from wrong pK_a)

2 (a) Inter-electronic **<u>repulsion between paired 3p</u>** **<u>electrons</u>** makes it **<u>easier to remove one of the paired</u>** 3p **<u>electrons</u>** than to remove the unpaired 3p electron from phosphorus. **[1m]**

(b) (i) **[1m]** Either one of the following:

<u>Very strong</u> C–C and C–H <u>bonds</u> / **<u>high bond energies</u>**

<u>Non-polar</u> / **<u>C and H have similar electronegativities</u>**

(ii)

$$\begin{tikzcd}
2CH_4(g) + S_2(g) \arrow[rr] \arrow[dr, "+2(96.0)", "+3S_2(g)"'] & & C_2H_4(g) + 2H_2S(g) \arrow[dl, "+91.0"', "+3S_2(g)"] \\
& 2CS_2(g) + 4H_2S(g) &
\end{tikzcd}$$

[1m] energy cycle

ΔH for reaction 1 = +2(96.0) – 91.0 = +**<u>101 kJ mol^{-1}</u>** **[1m]**

(c) (i)

	$2SO_2(g)$ +	$O_2(g)$ $\ll$	$2SO_3(g)$	
initial partial pressure /kPa	100	100	0	
	$\downarrow$ **–0.98(100)**	$\downarrow$ **–½(98)**		
eqm partial pressure /**<u>kPa</u>**	**2** (✓)	**51** (✓)	**98** (✓)	**2 (✓): [1m]** **3(✓): [2m]**

$$K_P = \frac{(P_{SO_3})^2}{(P_{SO_2})^2(P_{O_2})} = \frac{(98)^2}{(2)^2(51)}$$

$$= \underline{\mathbf{47.1}}\ \text{kPa}^{-1}$$ **[1m]**

(ii) Since ***K*$_p$ at 25 °C** is much **larger than 1**, the **position of equilibrium** in $2SO_2(g) + O_2(g) \ll 2SO_3(g)$ **lies** very much **to the right** **[1m]**, so the **forward reaction is spontaneous** and **Δ*G* is negative**. **[1m]**

As ***K*$_p$ decreases with increasing temperature**, it implies that the **position of equilibrium shifts to the left** **[1m]** with increasing temperature to absorb some heat. Hence, the backward reaction is endothermic and the **forward reaction is exothermic**, so **Δ*H* has a negative sign**. **[1m]**

2 (d) (i) **SO_2** is less ideal.

Either:

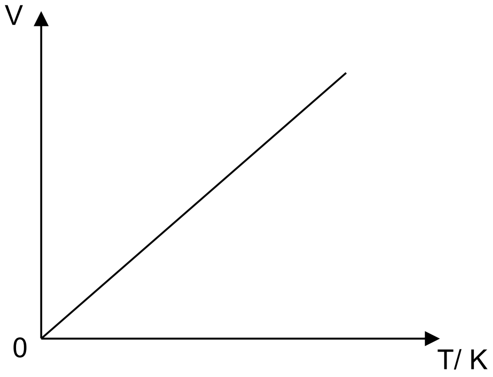
SO_2 has stronger intermolecular forces of attraction between its molecules as it is a **polar molecule / has greater number of electrons per molecule**.

OR

SO_2 is a **larger molecule** than O_2, so the **volume of SO_2 molecules is less negligible compared to the volume of the container/gas**.

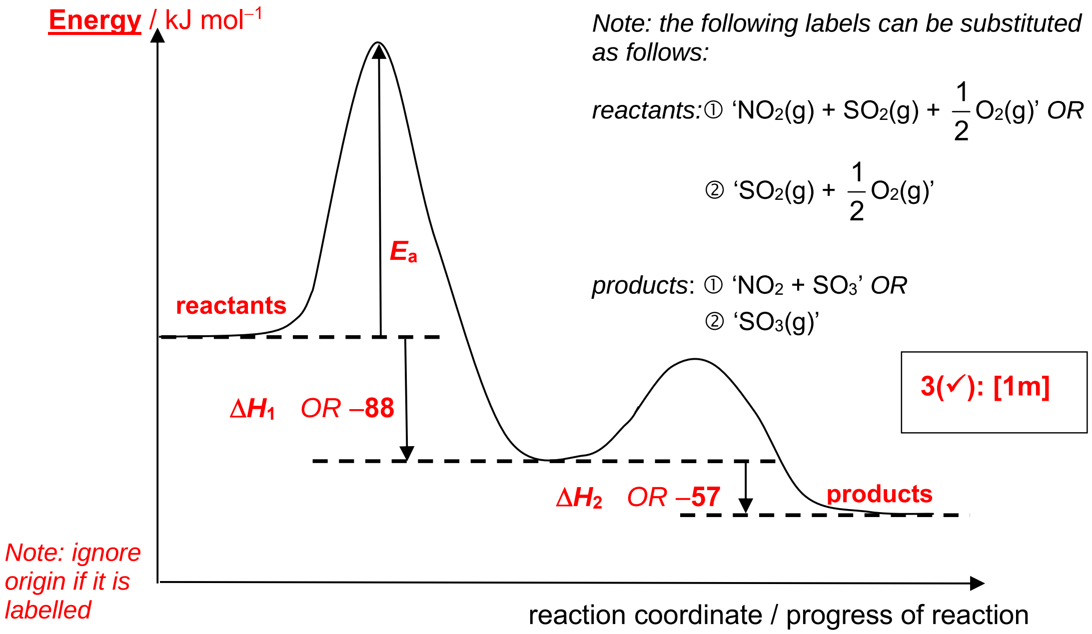
[1m]

(ii)



[1m]

(e)



Note: the following labels can be substituted as follows:

reactants: ① ‘$NO_2(g) + SO_2(g) + \frac{1}{2}O_2(g)$’ *OR*

② ‘$SO_2(g) + \frac{1}{2}O_2(g)$’

products: ① ‘$NO_2 + SO_3$’ *OR*

② ‘$SO_3(g)$’

3(✓): [1m]

Note: ignore origin if it is labelled

(✓): *2 humps.*

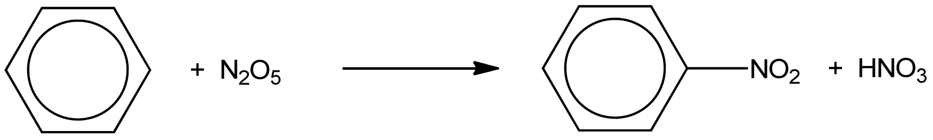
(✓): *label ‘reactants’, ‘products’ OR using appropriate formulae (with balanced species)*

(✓): *label y-axis. Ignore x-axis label. Reject if reactants are labelled at ‘0’ level*

[1m] : *Both ΔH_1 and ΔH_2 shown. Ignore direction of arrows.*

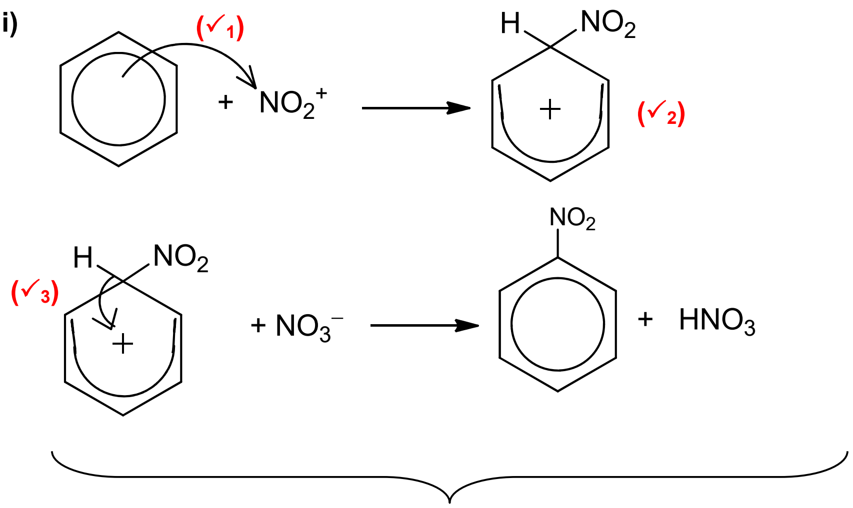
[1m] : *correct labelling of E_a, with $E_{a1} > E_{a2}$. Ignore direction of arrows.*

2 (f) (i)



[1m]

(ii)



(✓4): correct products and balanced equation

(✓1) – *full arrow from π–electron ring of benzene to the N atom of NO_2^+.*

(✓2) – *correct arenium ion with delocalisation of positive charge over the other 5 carbons.*

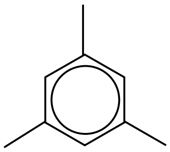
(✓3) – *full arrow from C–H bond to the (+)ve charge of arenium ion*

(✓4) – *correct products formed with* ***balanced equation*** *with HNO_3 as the other product*

Note: *Labelling of* ***"slow/fast"*** *step is* ***not*** *required.*

4(✓): [2m]; 2–3(✓): [1m]

(iii) Structure of **H**:



[1m]

3 **(a)** **(i)** Cu: **$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$** **[1m]**

(**not $3d^9\ 4s^2$** due to the extra stability of $3d^{10}$ and the similar energies of 3d and 4s electron)

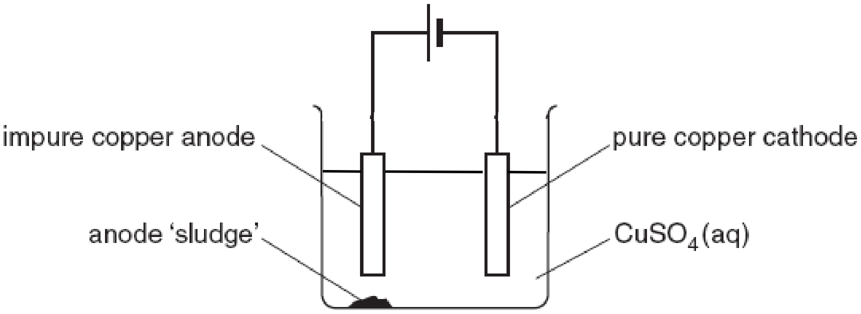
(ii) Copper is a **d-block element** that **forms** one or more **stable ions with incompletely filled d-orbitals**. **[1m]**

(iii) Copper has **high density/** is **too heavy** for overhead use. **[1m]**

(b) **(i)** **S** is oxidised from **–2 to +4** **[1m]**

(ii) **2** $CuFeS_2$ + **2** SiO_2 + **5** O_2 → **2** Cu + **2** $FeSiO_3$ + **4** SO_2 **[1m]**

(iii)



[1m] these labels on the diagram: **impure copper, pure copper, $CuSO_4(aq)$**

[1m] battery with 2 electrodes dipped in a common electrolyte;
battery must show the correct polarity with respect to the impure copper.

(iv) species present:
$Cu^{2+}(aq)$, $SO_4^{2-}(aq)$, $H_2O(l)$, impure Cu (anode) and impurities such as Ag, Ni

$O_2 + 4H^+ + 4e^-$ ≪ **$2H_2O$** E = +1.23 V
$Cu^{2+} + 2e^-$ ≪ **Cu** E = +0.34 V
$Ni^{2+} + 2e^-$ ≪ **Ni** E = –0.25 V
$Ag^+ + e^-$ ≪ **Ag** E = +0.80 V

Note:
The species is more easily oxidised when the E is more negative (*or* less positive).

[1m] **quote E values for Cu^{2+}/Cu, Ni^{2+}/Ni and Ag^+/Ag**

At the **anode**,
Cu(s) is oxidised to $Cu^{2+}(aq)$ in preference over H_2O as E (Cu^{2+}/Cu) is more negative than E (O_2/H_2O). **[1m]**

Ni(s) is also **oxidised to Ni^{2+}**(aq) (which goes into the solution) as **E (Ni^{2+}/Ni) is more negative than E (Cu^{2+}/Cu)**.

Ag(s) **is not oxidised** to Ag^+ as **E (Ag^+/Ag) is more positive than E (Cu^{2+}/Cu)**.
∴ **Ag**(s) **is collected as "anode sludge"**. **[1m]**

$2H_2O$ + $2e^-$ ≪ $H_2 + 2OH^-$ E = –0.83V
Cu^{2+} + $2e^-$ ≪ Cu E = +0.34 V
Ni^{2+} + $2e^-$ ≪ Ni E = –0.25 V

Note:
The species is more easily reduced when the E is more positive (*or* less negative).

At the **cathode**,
$Cu^{2+}(aq)$ is reduced to Cu(s) in preference over H_2O as E (Cu^{2+}/Cu) is more positive than E (H_2O/H_2).

Ni^{2+}(aq) **is not reduced** to Ni(s) **as E (Ni^{2+}/Ni) is more negative than E (Cu^{2+}/Cu)**.
∴ **Ni^{2+}**(aq) **remains in the solution**. **[1m]**

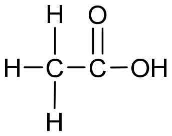
3 **(c)** [1m] ***Bronsted-Lowry base*** is a **proton/H^+ acceptor** as illustrated by **NH_3 accepting a proton/H^+ from H_2O to form OH^-**.
Or $\mathbf{NH_3(aq) + H_2O(\mathit{l}) \ll NH_4^+(aq) + OH^-(aq)}$

[1m] $\mathbf{Cu^{2+}(aq) + 2OH^-(aq) \rightarrow Cu(OH)_2(s)}$
pale blue soln pale blue ppt

[1m] $\mathbf{Cu(OH)_2(s) + 4NH_3(aq) + 2H_2O(\mathit{l}) \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 2OH^-(aq)}$
Or $\mathbf{[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 4H_2O(\mathit{l})}$
dark blue soln

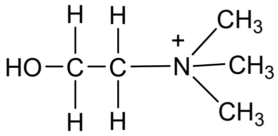
When added in excess, NH_3 acts as a *Lewis base* where N in NH_3 ligand **donates a lone pair** of electrons **to Cu^{2+}**, forming strong dative bonds with Cu^{2+} to give the stable $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex. [1m]

(d) **(i)**



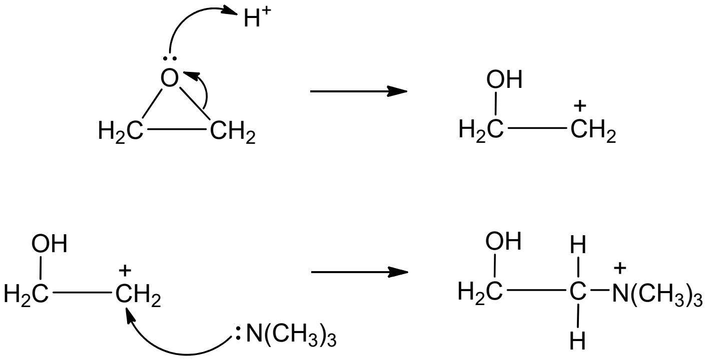
$H-\overset{H}{\underset{H}{C}}-\overset{O}{\overset{\|}{C}}-OH$

[1m] and

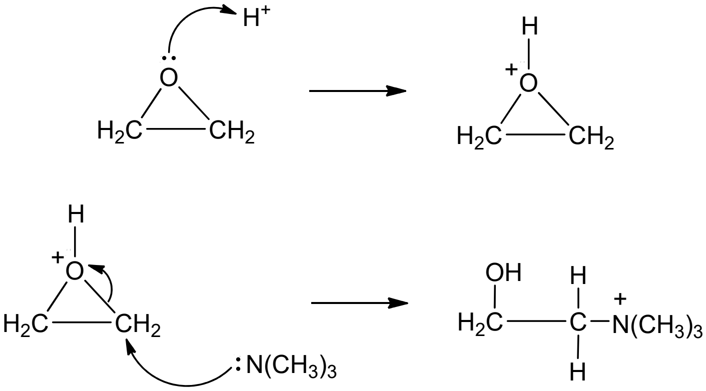


[1m]

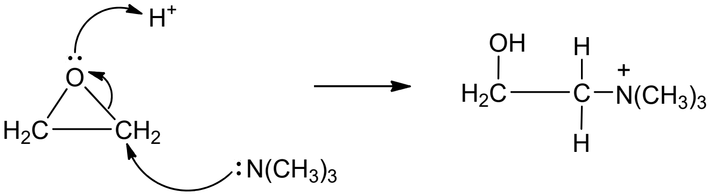
(ii) **Option 1:**



Option 2:

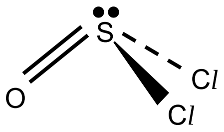


Option 3:

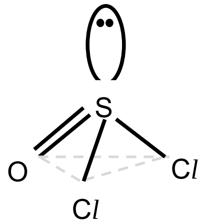


[1m] for each curly arrow with the associated lone pair and any positive charge

4 **(a)** **(i)**



or



[1m] illustrate trigonal pyramidal shape.

(ii) <u>**$COCl_2$**</u> will have a larger bond angle. **[1m] bonus**

<u>**$COCl_2$ has lesser number/ 3**</u> sets of <u>**electron pairs**</u> (or state <u>**3 bp, 0 lp**</u>) which can be <u>**further apart to minimise repulsion**</u> compared to <u>**$SOCl_2$**</u> that <u>**has 4 electron pairs**</u> (or state <u>**3 bp, 1 lp**</u>). **[1m]**

(b) **(i)** $NaOH + HCl \rightarrow NaCl + H_2O$ **[1m]**

$2NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O$ **[1m]**

Allow if 2nd eqn is split into 2 eqns: $SO_2 + H_2O \rightarrow H_2SO_3$
$2NaOH + H_2SO_3 \rightarrow Na_2SO_3 + 2H_2O$

Reject: $NaOH + SO_2 \rightarrow NaHSO_3$ for NaOH is added in excess

(ii) $$\text{n(NaOH) reacted} = \frac{60.0 - 10.8}{1000} \times 0.500$$

$= \underline{\mathbf{0.0246}}$ mol **[1m]**

(iii) RCO_2H : $SO_2 + HCl$: $NaOH$
1 : 1 : 3

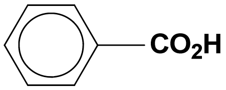
$$n(RCO_2H) = \frac{0.0246}{3} = \underline{\mathbf{0.00820}}\text{ mol}$$ **[1m]**

(iv) $$M_r\,(RCO_2H) = \frac{1.00}{0.0082} = \underline{\mathbf{122}}$$ **[1m] no units, 3 s.f., ecf**

(v) RCO_2H: mass units of $-CO_2H = 45$

mass units of $-R = 122 - 45 = 77$

estimated number of C in $-R = 77/12 = 6.4$ (⇒ R contains 6 carbon atoms)

RCO_2H is 

[1m]

(c) **(i)** **$RCONH_2$** **[1m]**

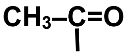
(ii) Step 2: <u>**NH_3**</u>(g) **[1m]** reject (aq)

Step 3: <u>**$LiAlH_4$**</u>, dry ether **[1m]** reject (aq); ignore 'heat'

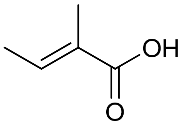
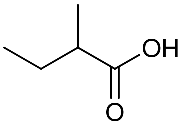
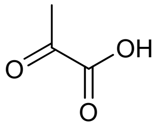
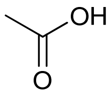
(iii) Step 2: <u>**condensation/ nucleophilic acyl substitution**</u>
Step 3: <u>**reduction**</u>

allow nucleophilic substitution
[1m] each, bonus

4 (d) (i)

Observation	Type of Reaction	Deduction
Angelic acid + H_2 → **T** $C_5H_8O_2$ $C_5H_{10}O_2$	**reduction** (✓)	**Angelic acid** is an **alkene**. (✓)
Angelic acid + $KMnO_4$ → **U** and **V**	**Oxidative cleavage of C=C** /**oxidation** (✓)	**U** and **V** are **carboxylic acids.** (✓)
U + I_2/OH^- → yellow ppt	**Iodoform test/ oxidation** (✓)	**U** has the structure  $CH_3\text{–}\underset{\vert}{C}=O$ (✓)

5-6(✓): [2m]; 3-4(✓): [1m]

angelic acid	**T**	**U**	**V**
			

[1m] for each structure

(ii) angelic acid : **cis-trans isomerism** **[1m]**

compound **T** : **enantiomerism** **[1m]**

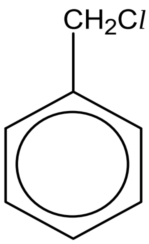
5 (a) (i) **SiC*l*$_4$ reacts with water / hydrolyses** completely in water **to give** a strongly **acidic solution**. **[1m] bonus**

A **white solid/ppt** of SiO_2 will be observed/ **white (or steamy) fumes** of HC*l* will be observed. **[1m]**

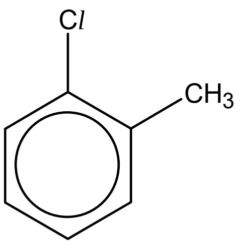
$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$ **[1m]**

(ii) Unlike silicon, **carbon does not have energetically accessible empty 3d orbitals to accept** a lone pair of **electrons from water** molecules. **[1m]**

(b)



A



B (-CH_3 and C*l* groups can be in any position)

[1m] for both structures of **A** and **B**

For compound **B**, **delocalisation of the lone pair** of electrons **on C*l* into the** π-electron cloud of **benzene ring imparts double bond character to the C–C*l*, strengthening the C–C*l* bond**. Hence, **B** does not react with NaOH(aq). **[1m]**

5 **(c)** $2H^+ + 2e^- \ll H_2$ $E = 0.00$ V

$Sn^{2+} + 2e^- \ll Sn$ $E = -0.14$ V

$Sn^{4+} + 2e^- \ll Sn^{2+}$ $E = +0.15$ V

$Cl_2 + 2e^- \ll 2Cl^-$ $E = +1.36$ V

Reaction between H^+ and Sn:

E_{cell} = 0.00 – (–0.14) = +0.14 V > 0 (reaction is energetically feasible) **[1m]**

Reaction between H^+ and Sn^{2+}:

E_{cell} = 0.00 – (+0.15) = –0.15 V < 0

Oxidation of Sn^{2+} to Sn^{4+} by H^+ is NOT energetically feasible.

Reaction between Cl_2 and Sn:

E_{cell} = 1.36 – (–0.14) = +1.50 V > 0

Oxidation of Sn to Sn^{2+} by Cl_2 is energetically feasible. **[1m]**

Reaction between Cl_2 and Sn^{2+}:

E_{cell} = 1.36 – (+0.15) = +1.21 V > 0

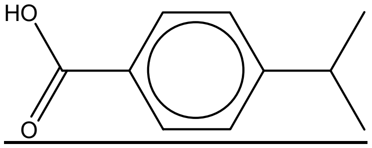
Oxidation of Sn^{2+} to Sn^{4+} by Cl_2 is energetically feasible. **[1m] bonus**

Award max [1m] if three E_{cell} values are calculated without any comment.

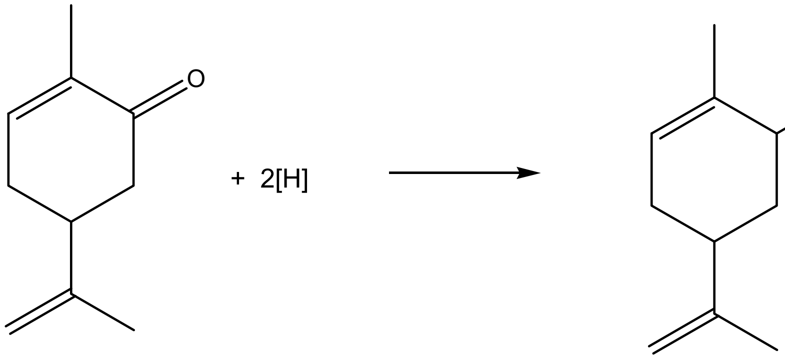
(d) **(i)** **CH_3COCl** **[1m]**

(ii) Step **2**: **alkaline I_2(aq), heat,** followed by H^+(aq) **[1m]**

Step **3**: **$LiAlH_4$, dry ether** **[1m]**

Y:  **[1m]**

(e) **(i)**



M **[1m]**

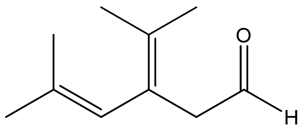
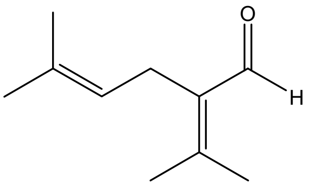
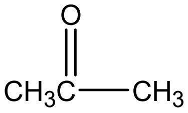
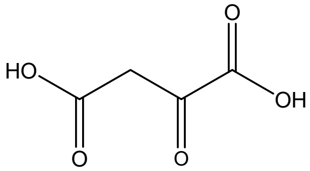
[1m]

5 (e) (ii)

8-9(✓): [4m]
6-7(✓): [3m]
4-5(✓): [2m]
2-3(✓): [1m]

Information from question	Type of reaction	Deduction
N reacts with hot concentrated $KMnO_4$ to give **P** and **Q**	**oxidation** (✓)	**C=C bond in N cleaves** (✓)
N, **P**, **Q** react with 2,4-DNPH	**condensation** (✓)	**N, P and Q contains carbonyl group** / **contains either aldehyde or ketone groups** (✓)
Only **N** gives silver mirror with Tollens' reagent	**oxidation** (✓)	**N contains** aliphatic **aldehyde group** (✓) **P and Q contain ketone group** (✓)
One mole of **Q** reacts with two moles of $NaHCO_3(aq)$	**acid-carbonate reaction** / **acid – hydrogen carbonate reaction** (✓)	**Q contains 2 –CO_2H groups** (✓)

[1m] for each correct structure

 or 	 $CH_3\overset{\overset{O}{\Vert}}{C}-CH_3$	
N	**P**	**Q**

JURONG JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION 2018

CANDIDATE NAME	

CLASS	**18S**	EXAM INDEX	

CHEMISTRY 9729/04

Higher 2

Paper 4 Practical

16 August 2018
2 hours 30 minutes

Candidates answer on the Question paper.

Additional Materials: As listed in the Confidential Instructions

---

READ THESE INSTRUCTIONS FIRST

Write your name, class and exam index number on all the work you hand in.
Give details of the practical shift and laboratory where appropriate, in the boxes provided.
Write in dark blue or black pen.
You may use a HB pencil for any diagrams, graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

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

You may lose marks if you do not show your working or if you do not use appropriate units.

Qualitative Analysis Notes are printed on pages 17 and 18.

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

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

Shift
Laboratory

For Examiner's Use	
1	13
2	16
3	12
4	14
Total	55

This document consists of **18** printed pages and **0** blank page.

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

1 Determination of the A_r of magnesium by a back titration method

FA 1 is an aqueous solution prepared by dissolving 0.215 g of magnesium ribbon in 30.0 cm^3 of 1.00 mol dm^{-3} hydrochloric and made up to 250 cm^3 with deionised water.

FA 2 is aqueous sodium carbonate containing 2.65 g dm^{-3} Na_2CO_3.

In this question, you will titrate **FA 2** with **FA 1** to determine how much hydrochloric acid was left over after the reaction with magnesium.

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

$$Na_2CO_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$$

Using the experimental results, you will determine the A_r of magnesium.

(a) **Method**

1. Fill the burette with **FA 1**.
2. Using a pipette, transfer 25.0 cm^3 of **FA 2** into the conical flask.
3. Add a few drops of methyl orange indicator.
4. Run **FA 1** from the burette into the conical flask until the yellow colour of the solution changes to orange.
5. Record your titration results in the space provided below. Make certain that your recorded results show the precision of your working.
6. Repeat points 1 to 5 as necessary until consistent results are obtained.

Results

[5]

(b) From your titrations, obtain a suitable volume of **FA 1** to be used in your calculations. Show clearly how you obtained this volume.

25.0 cm^3 of **FA 2** requires ………………. of **FA 1** for complete reaction. [1]

(c) **Calculations**

(i) Calculate the amount of sodium carbonate in the 25.0 cm^3 of **FA 2** used in each titration. [A_r: Na, 23.0; C, 12.0; O, 16.0]

Amount of Na_2CO_3 in 25.0 cm^3 of **FA 2** = …………………. [1]

(ii) Use your answer in **(c)(i)** to calculate the amount of hydrochloric acid present in 250 cm^3 of **FA 1**.

[1]

Amount of HC*l* present in 250 cm^3 = ………………….

(iii) Calculate the amount of hydrochloric acid that reacted with the magnesium.

Amount of HC*l* that reacted with the magnesium = …………………. [1]

(iv) Hence calculate the relative atomic mass, A_r, of magnesium.

A_r of magnesium = ………………… [1]

(d) The A_r of magnesium given in the Periodic Table is 24.3. Use this value given in the Periodic Table to calculate the percentage error of your A_r value of Mg obtained in **(c)(iv)**.

% error = ………………… [1]

(e) A solution of sodium hydroxide was prepared at the same concentration, in mol dm^{-3}, as **FA 2**. A student repeated the titration but replaced **FA 2** with this sodium hydroxide.

Explain the effect that replacing **FA 2** with this solution of sodium hydroxide would have on the volume of **FA 1** needed for the titration.

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

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

[Total: 13]

2 Determination of enthalpy change of formation of magnesium oxide.

FA 3 is magnesium ribbon
FA 4 is magnesium oxide
FA 5 is 2.0 mol dm^{-3} hydrochloric acid

The enthalpy change of formation of magnesium oxide, ΔH_f (MgO), is the enthalpy change when one mole of magnesium oxide is formed from its elements in their standard states under standard conditions.

$$Mg(s) + \tfrac{1}{2} O_2(g) \rightarrow MgO(s) \qquad \Delta H_f \text{ (MgO)}$$

To cause magnesium and oxygen to react together, they must be heated. The reaction then proceeds in an uncontrolled and highly exothermic fashion. It is not possible to measure this enthalpy change without the use of equipment such as a bomb calorimeter.

You are to perform an experiment by which you will determine this enthalpy change by an indirect route.

Both magnesium and magnesium oxide react exothermically with hydrochloric acid to form magnesium chloride. You will determine the molar enthalpy changes for **reaction 1** and **reaction 2**.

reaction 1 $Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$ $\Delta H_{rxn\ 1}$

reaction 2 $MgO(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2O(l)$ $\Delta H_{rxn\ 2}$

You will then use Hess's Law to determine a value for the enthalpy change of formation of magnesium oxide, ΔH_f(MgO).

(a) Determining the enthalpy change of reaction 1 between FA 3 and FA 5.

Follow the instructions below to determine the maximum temperature change when a known mass of magnesium, **FA 3**, reacts completely with excess **FA 5**. Record all the mass readings in Table 2.1 and all measurements of time and temperature in the space provided below the table.

Method 1

1. Weigh the stoppered weighing bottle labelled **FA 3** and its contents. Record the total mass of weighing bottle and **FA 3**.
2. Use a 50 cm^3 measuring cylinder to transfer 50.0 cm^3 of **FA 5** into a Styrofoam cup. Place this cup inside a second Styrofoam cup which is held in a 250 cm^3 glass beaker to prevent it tipping over.
3. Stir the solution in the cup with the thermometer and measure its temperature. Record this temperature in your table in **(a)(i)** (this is the temperature at t = 0 min) and start the stop-watch. Repeat this measurement each minute for 3 minutes and record each temperature.
4. At the fourth minute, carefully add **FA 3** from the weighing bottle to **FA 5** in the cup. Quickly stir the mixture with the thermometer but **do not measure the temperature**.
5. Continue to stir the mixture. Measure and record the temperature at 4½ minutes, then **every half minute** until the temperature reaches a maximum, and then **every minute** until the tenth minute.
6. Empty and wash the Styrofoam cup. Rinse the cup with deionised water and dry it using a paper towel.

7. Reweigh the emptied weighing bottle and record its mass. Calculate and record the mass of **FA 3** used.

(a) (i) Results

Record the required mass readings in Table 2.1 and in an appropriate format in the space below, record all measurements of time and temperature.

Table 2.1

Mass of weighing bottle with **FA 3** /g	
Mass of empty weighing bottle / g	
Mass of **FA 3** used / g	

Measurements of time and temperature:

[3]

For Examiner's Use

(a) **(ii)** Plot a graph of temperature (y-axis) against time (x-axis) on the grid below. You will use the graph to determine the theoretical temperature change at 4 minutes. The scale for temperature should extend at least 1 °C above your highest recorded temperature.

1. Draw a straight line of best-fit for the points before the fourth minute. Draw a second straight line of best-fit for the points after the fourth minute. Extrapolate both lines to the fourth minute.
2. From your graph, read the minimum and maximum temperature at the fourth minute. Record these values in the spaces below and determine a value for the maximum temperature rise, $\Delta \boldsymbol{T}$, at the fourth minute.

Temperature at 4th minute

minimum = ………... °C

maximum = ………… °C [4]

temperature rise, $\Delta \boldsymbol{T}$ = ………….. K

(iii) Use your $\Delta \boldsymbol{T}$ from **(a)(ii)** to calculate a value for the molar enthalpy change of **reaction 1** between **FA 3** and **FA 5**, $\Delta H_{\text{rxn 1}}$, in kJ mol^{-1}.
Assume that the specific heat capacity of the final solution is 3.75 J g^{-1} K^{-1} and that its density is 1.05 g cm^{-3}. [A_r: Mg, 24.3]

$\Delta H_{rxn\ 1}$ = …………………… kJ mol^{-1} [2]

(b) Determining the enthalpy change of reaction 2 between FA 4 and FA 5.

A student carried out an experiment to determine the enthalpy change of **reaction 2**, $\Delta H_{\text{rxn 2}}$, using a known mass of **FA 4** that reacts with excess **FA 5**.

The student was provided with five pre-weighed samples of **FA 4**, labelled **v**, **w**, **x**, **y** and **z**, and carried out the experiment according to the following instructions.

Method 2

1. Use a 50 cm^3 measuring cylinder to transfer 50.0 cm^3 of **FA 5** into a Styrofoam cup. Place this cup inside a second Styrofoam cup which is held in a 250 cm^3 glass beaker to prevent it tipping over.
2. Stir the solution in the cup with the thermometer. Read and record its temperature. This is the initial temperature of **FA 4**, T_{initial}.
3. Carefully add sample **v** to the **FA 5** in the cup.
4. Using the thermometer, stir the mixture continuously until it reaches its maximum temperature. Record the maximum temperature reached, T_{max}.
5. Wash and carefully dry the Styrofoam cup.
6. Repeat steps 1 to 5 with the remaining samples **w**, **x**, **y** and **z**.

The student recorded all masses and temperatures in Table 2.2 below.

Table 2.2

	expt **v**	expt **w**	expt **x**	expt **y**	expt **z**
Mass of **FA 4** added to the cup, **m** / g	0.507	0.503	0.487	0.506	0.476
T_{initial} / °C	31.2	31.2	31.0	31.1	31.3
T_{max} / °C	38.7	38.6	38.2	38.2	38.3
Temperature change, ΔT / °C					
$\frac{\Delta T}{\mathbf{m}}$ / °C g^{-1}					

(i) Complete Table 2.2 by calculating values for ΔT and $\Delta T/\mathbf{m}$. Leave values for $\Delta T/\mathbf{m}$ to 3 significant figures.

(ii) Based on the calculated $\Delta T/\mathbf{m}$ values in Table 2.2, determine an appropriate mean maximum temperature change, ΔT_{ave}, and mean mass of **FA 4**, m_{ave}.

ΔT_{ave} = …………………. °C m_{ave} = ……………………. g [2]

(iii) Use your results in **(b)(ii)** to calculate a value for the molar enthalpy change of **reaction 2** between **FA 4** and **FA 5**, $\Delta H_{\text{rxn 2}}$, in kJ mol^{-1}.
Assume that the specific heat capacity of the final solution is 3.75 J g^{-1} K^{-1} and that its density is 1.05 g cm^{-3}. [A_r: Mg, 24.3; O, 16.0]

$\Delta H_{\text{rxn 2}}$ = ……………………. kJ mol^{-1} [2]

(c) Use your values for $\Delta H_{\text{rxn 1}}$ and $\Delta H_{\text{rxn 2}}$, together with the enthalpy change of formation of water, $\Delta H_f(H_2O)$, to calculate a value for the enthalpy change of formation of magnesium oxide, $\Delta H_f(MgO)$.

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad \Delta H_f(H_2O) = -286 \text{ kJ mol}^{-1}$$

Note: If you were unable to calculate the enthalpy changes, assume that the value of $\Delta H_{\text{rxn 1}}$ is –457 kJ mol^{-1} and the value $\Delta H_{\text{rxn 2}}$ is –141 kJ mol^{-1}.

$\Delta H_f(MgO)$ = ………………..…. kJ mol^{-1} [2]

(d) Two methods, **Method 1** and **Method 2**, have been used to determine the maximum temperature change, ΔT, of an exothermic reaction. Which method would give a more accurate ΔT ? Explain your answer.

…………………………………………………………………………………………...

……………………………………………………………………………………………

……………………………………………………………………………………………

[1]

[Total: 16]

3 Planning

The solubility of calcium iodate(V), $Ca(IO_3)_2$, at 20 °C, is approximately 2.4 g dm^{-3}.

When solid calcium iodate(V) is added to water, a small amount dissolves to form a saturated solution, establishing an equilibrium between the undissolved salt and its aqueous ions.

$$Ca(IO_3)_2\,(s) \ll Ca^{2+}\,(aq) + 2IO_3^{-}\,(aq)$$

The equilibrium constant for the above solubility equilibrium, K_{sp}, is also known as the solubility product of calcium iodate.

$$K_{sp} = [Ca^{2+}(aq)]\,[IO_3^{-}(aq)]^2$$

This solubility product can be found by determining the equilibrium concentration of IO_3^- ions in a saturated solution of calcium iodate.

The exact concentration of IO_3^- ions is determined by titration. Excess aqueous KI and aqueous H^+ is first added to a sample of saturated calcium iodate solution to liberate iodine.

$$IO_3^-\,(aq) + 5I^-\,(aq) + 6H^+\,(aq) \rightarrow 3I_2\,(aq) + 3H_2O\,(l)$$

The iodine liberated in the resulting mixture is then titrated with sodium thiosulfate, $Na_2S_2O_3$ of known concentration.

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

(a) Using the information given above, you are required to write a plan to determine the solubility product, K_{sp}, of calcium iodate, $Ca(IO_3)_2$, at 20 °C.

You may assume that you are provided with:

- solid sodium thiosulfate crystals, $Na_2S_2O_3.5H_2O$ (M_r = 248.2)
- solid calcium iodate, $Ca(IO_3)_2$
- aqueous potassium iodide, KI, of about 0.2 mol dm^{-3}
- aqueous hydrochloric acid, HC*l*, of about 1 mol dm^{-3}
- starch indicator
- any other required apparatus normally found in a college laboratory.

Your plan should include details of, including quantities:

- the preparation of 250.0 cm^3 of 0.075 mol dm^{-3} aqueous $Na_2S_2O_3$;
- the preparation of about 100 cm^3 of a saturated solution of calcium iodate, $Ca(IO_3)_2$ at 20 °C;
- the essential details of the titration process;
- an outline of how you would use your mean titre value to determine the solubility product of $Ca(IO_3)_2$.

In your calculations, you should let **V** cm^3 be your mean titre and express your final mathematical expression in terms of **V**.

For Examiner's Use

For Examiner's Use

[8]

…………………………………………………………………………………………

(b) The solubility of calcium iodate(V), $Ca(IO_3)_2$, at 20 °C, is approximately 2.4 g dm^{-3}. Justify, with calculations, that the chosen concentration, 0.075 mol dm^{-3}, of aqueous $Na_2S_2O_3$ solution is appropriate. [M_r of $Ca(IO_3)_2$ = 389.9]

[2]

(c) The experiment described in your plan in **(a)** is repeated using 0.1 mol dm^{-3} aqueous $Ca(NO_3)_2$ solution, instead of deionised water, to prepare a saturated solution of calcium iodate(V).

State and explain how, if at all, the titre values and calculated K_{sp} would be expected to differ from that obtained in **(a)**.

[Assume that both the experiments were carried out under the same conditions.]

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

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…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

[2]

[Total: 12]

4 Qualitative Analysis

(a) You are provided with solid **FA 6** which contains $S_2O_8^{2-}$ anion and one cation from the ions listed in the *Qualitative Analysis Notes*.

You are to perform the tests described in Table 4.1 to deduce the nature of **FA 6** and to identify the cation present in **FA 6**.

Record your observations in Table 4.1. Your answers should include
- details of colour changes and precipitates formed,
- the identity of any gases evolved, and details of the test used to identify each one.

You should indicate clearly at what stage in a test a change occurs.
Marks are not given for chemical equations.
No additional or confirmatory tests for ions present should be attempted.

Table 4.1

Tests	*Observations*
(i) To a spatula measure of **FA 6** in a boiling tube, add 1-2 cm depth of dilute hydrochloric acid and heat cautiously. Retain the solution for **test (ii)**.	
(ii) To the resulting solution from **test (i)**, add barium nitrate(V) solution.	
(iii) To a spatula measure of **FA 6** in a test tube, add 1-2 cm depth of freshly prepared solution of iron(II) sulfate solution and warm.	
(iv) Place a spatula measure of **FA 6** in a boiling tube and add dilute nitric acid to dissolve the solid. Then add 1 cm depth of manganese(II) sulfate solution and 4 drops of silver nitrate(V) solution to act as a catalyst. Heat cautiously to bring the mixture to boiling.	

(v) To a spatula measure of **FA 6** in a boiling tube, add 1 cm depth of aqueous sodium hydroxide. Heat cautiously.	

[5]

(b) **(i)** State, with supporting evidence, the nature of **FA 6**.

nature of **FA 6**: ……………………………………………………

evidence: ………………………………………………………………………..

……………………………………………………………………………………….

……………………………………………………………………………………….

(ii) Identify the cation in **FA 6**. cation: ………………

(iii) Write the ionic equation, including state symbols, for the reaction that occurs in **test (i)**.

……………………………………………………………………………………… [4]

(c) You are provided with an organic solution **FA 7** which contains one functional group.

Care: FA 7 is flammable. Do not use Bunsen burner for heating.
Use the hot water provided.

FA 7 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 7**.

Carry out the tests and record details of the tests performed and observations made in table 4.2.

Table 4.2

Confirmatory Tests	*Observations*

[5]

Functional group present in **FA 7**: …………..………………

[Total: 14]

Qualitative Analysis Notes

[ppt. = precipitate]

(a) Reactions of aqueous cations

cation	***reaction with***	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white ppt. with high [Ca^{2+}(aq)]	no. ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess

copper(II), $Cu^{2+}(aq)$	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), $Fe^{2+}(aq)$	green ppt., turning brown on contact with air insoluble in excess	green ppt., turning brown on contact with air insoluble in excess
iron(III), $Fe^{3+}(aq)$	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, $Mg^{2+}(aq)$	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), $Mn^{2+}(aq)$	off-white ppt., rapidly turning brown on contact with air insoluble in excess	off-white ppt., rapidly turning brown on contact with air insoluble in excess
zinc, $Zn^{2+}(aq)$	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

anion	*reaction*
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, $Cl^-(aq)$	gives white ppt. with $Ag^+(aq)$ (soluble in $NH_3(aq)$)
bromide, $Br^-(aq)$	gives pale cream ppt. with $Ag^+(aq)$ (partially soluble in $NH_3(aq)$)
iodide, $I^-(aq)$	gives yellow ppt. with $Ag^+(aq)$ (insoluble in $NH_3(aq)$)
nitrate, $NO_3^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and A*l* foil
nitrite, $NO_2^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and A*l* foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, $SO_4^{2-}(aq)$	gives white ppt. with $Ba^{2+}(aq)$ (insoluble in excess dilute strong acids)
sulfite, $SO_3^{2-}(aq)$	SO_2 liberated with dilute acids; gives white ppt. with $Ba^{2+}(aq)$ (soluble in excess dilute strong acids)

(c) Tests for gases

gas	*test and test results*
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	"pops" with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	*colour of element*	*colour in aqueous solution*	*colour in hexane*
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

JURONG JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION 2018

CANDIDATE NAME	Mark Scheme		
CLASS	**18S**	EXAM INDEX	

CHEMISTRY

9729/04

Higher 2

Paper 4 Practical

16 August 2018
2 hours 30 minutes

Candidates answer on the Question paper.

Additional Materials: As listed in the Confidential Instructions

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

You may lose marks if you do not show your working or if you do not use appropriate units.

Qualitative Analysis Notes are printed on pages 16 and 17.

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

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

Shift
Laboratory

Mark Scheme:

For calculations, the principle of no double penalty (error carried forward) applies.

For connecting parts, marking from point of first penalty onwards will be based on correct method only.

For Examiner's Use	
1	**13**
2	**16**
3	**12**
4	**14**
Total	**55**

This document consists of **17** printed pages and **0** blank page.

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

1 Determination of the A_r of magnesium by a back titration method

FA 1 is an aqueous solution prepared by dissolving 0.215 g of magnesium ribbon in 30.0 cm^3 of 1.00 mol dm^{-3} hydrochloric and made up to 250 cm^3 with deionised water.

FA 2 is aqueous sodium carbonate containing 2.65 g dm^{-3} Na_2CO_3.

In this question, you will titrate **FA 2** with **FA 1** to determine how much hydrochloric acid was left over after the reaction with magnesium.

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

$$Na_2CO_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$$

Using the experimental results, you will determine the A_r of magnesium.

(a) Method

1. Fill the burette with **FA 1**.
2. Using a pipette, transfer 25.0 cm^3 of **FA 2** into the conical flask.
3. Add a few drops of methyl orange indicator.
4. Run **FA 1** from the burette into the conical flask until the yellow colour of the solution changes to orange.
5. Record your titration results in the space provided below. Make certain that your recorded results show the precision of your working.
6. Repeat points 1 to 5 as necessary until consistent results are obtained.

Results

Titration number	1	2
Final burette reading / cm^3	23.80	47.80
Initial burette reading / cm^3	0.00	24.00
Volume of FA 1 used / cm^3	23.80	23.80
	✓	✓

[1] A proper table with correct headers (must state 'burette') and units. (Do not award if any final and initial burette readings are inverted)

[1] All burette readings are recorded to the nearest 0.05 cm^3 + correct computation of titres.

(Do not award if 50 is used as initial burette reading or burette reading is > 50)

[1] Has two uncorrected titres within 0.10 cm^3 + place ✓ under selected titres within 0.10 cm^3. (Do not award if additional titration is performed after consistent titres are obtained.)

Accuracy: Supervisor's titre, V = 23.80 cm^3

(V ± 0.20) cm^3, 23.60 – 24.00 cm^3 [2]
(V ± 0.40) cm^3, 23.40 – 24.20 cm^3 [1]

[5]

(b) From your titrations, obtain a suitable volume of **FA 1** to be used in your calculations. Show clearly how you obtained this volume.

average volume of FA 1 used = $\dfrac{23.80 + 23.80}{2}$ = $\underline{23.80}$ cm^3

- quotes the selected titres within 0.10 cm^3 in the working
- calculates average titre correctly to 2 d.p. [1]

25.0 cm^3 of **FA 2** requires $\underline{23.80}$ $\underline{cm^3}$ of **FA 1** for complete reaction. [1]

(c) Calculations

(i) Calculate the amount of sodium carbonate in the 25.0 cm^3 of **FA 2** used in each titration. [A_r: Na, 23.0; C, 12.0; O, 16.0]

Amount of Na_2CO_3 = $\underline{\dfrac{2.65}{106.0} \times \dfrac{25.0}{1000}}$ = 6.25×10^{-4} mol [1]

Amount of Na_2CO_3 in 25.0 cm^3 of **FA 2** = $\underline{6.25 \times 10^{-4}}$ $\underline{mol}$ [1]

(ii) Use your answer in **(c)(i)** to calculate the amount of hydrochloric acid present in 250 cm^3 of **FA 1**.

Na_2CO_3 : HCl
1 : 2
(25.0 cm^3) (23.80 cm^3)

Amount of HCl in 250 cm^3

= $\underline{\dfrac{250}{\text{ans.(b)}} \times (2 \times \text{ans.(c)(i)})}$

= $\dfrac{250}{23.80} \times \left(2 \times 6.25 \times 10^{-4}\right)$ = 0.01313 mol [1]

[1]

Amount of HC*l* present in 250 cm^3 = $\underline{0.0131}$ $\underline{mol}$

(iii) Calculate the amount of hydrochloric acid that reacted with the magnesium.

Amount of HCl reacted with Mg

= $\underline{\left(\dfrac{30}{1000} \times 1.00\right) - \text{ans.(c)(ii)}}$

= $\left(\dfrac{30}{1000} \times 1.00\right) - 0.01313$ = 0.01687 mol [1]

Amount of HC*l* that reacted with the magnesium = $\underline{0.0169}$ $\underline{mol}$ [1]

(iv) Hence calculate the relative atomic mass, A_r, of magnesium.

Mg : HCl
1 : 2

A_r of Mg

= $\underline{\dfrac{0.215}{\left(\dfrac{1}{2} \times \text{ans.(c)(iii)}\right)}}$ = $\dfrac{0.215}{\left(\dfrac{1}{2} \times 0.01687\right)}$ = 25.49 [1]

A_r of magnesium = $\underline{25.5}$ $\underline{\text{(no units)}}$ [1]

(d) The A_r of magnesium given in the Periodic Table is 24.3. Use this value given in the Periodic Table to calculate the percentage error of your A_r value of Mg obtained in **(c)(iv)**.

$$\% \text{ error} = \frac{|\text{ans(c)(iv)} - 24.3|}{24.3} \times 100\%$$

$$= \frac{|25.49 - 24.3|}{24.3} \times 100\% = 4.90\ \% \quad [1]$$

% error = 4.90 % [1]

(e) A solution of sodium hydroxide was prepared at the same concentration, in mol dm^{-3}, as **FA 2**. A student repeated the titration but replaced **FA 2** with this sodium hydroxide.

Explain the effect that replacing **FA 2** with this solution of sodium hydroxide would have on the volume of **FA 1** needed for the titration.

Half the volume of FA 1 is required since NaOH and HC*l* react in a mole ratio of 1:1 while Na_2CO_3 and HC*l* react in a mole ratio of 1:2.
[1]

[2]

[1] State correct units in 1(b)[cm^3], (c)(i)(ii)(iii)[mol], (c)(iv)[no units] and 1(d)[%]

Any calculation not attempted loses this mark.

[Total: 13]

2 Determination of enthalpy change of formation of magnesium oxide.

FA 3 is magnesium ribbon
FA 4 is magnesium oxide
FA 5 is 2.0 mol dm^{-3} hydrochloric acid.

The enthalpy change of formation of magnesium oxide, ΔH_f (MgO), is the enthalpy change when one mole of magnesium oxide is formed from its elements in their standard states under standard conditions.

$$Mg(s) + \tfrac{1}{2} O_2(g) \rightarrow MgO(s) \qquad \Delta H_f \text{ (MgO)}$$

To cause magnesium and oxygen to react together, they must be heated. The reaction then proceeds in an uncontrolled and highly exothermic fashion. It is not possible to measure this enthalpy change without the use of equipment such as a bomb calorimeter.

You are to perform an experiment by which you will determine this enthalpy change by an indirect route.

Both magnesium and magnesium oxide react exothermically with hydrochloric acid to form magnesium chloride. You will determine the molar enthalpy changes for **reaction 1** and **reaction 2**.

reaction 1 $Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g) \qquad \Delta H_{rxn\ 1}$

reaction 2 $MgO(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2O(l) \qquad \Delta H_{rxn\ 2}$

You will then use Hess's Law to determine a value for the enthalpy change of formation of magnesium oxide, ΔH_f(MgO).

(a) Determining the enthalpy change of reaction 1 between FA 3 and FA 5.

Follow the instructions below to determine the maximum temperature change when a known mass of magnesium, **FA 3**, reacts completely with excess **FA 5**. Record all the mass readings in Table 2.1 and all measurements of time and temperature in the space provided below the table.

Method 1

1. Weigh the stoppered weighing bottle labelled **FA 3** and its contents. Record the total mass of weighing bottle and **FA 3**.
2. Use a 50 cm^3 measuring cylinder to transfer 50.0 cm^3 of **FA 5** into a Styrofoam cup. Place this cup inside a second Styrofoam cup which is held in a 250 cm^3 glass beaker to prevent it tipping over.
3. Stir the solution in the cup with the thermometer and measure its temperature. Record this temperature in your table in **(a)(i)** (this is the temperature at t = 0 min) and start the stop-watch. Repeat this measurement each minute for 3 minutes and record each temperature.
4. At the fourth minute, carefully add **FA 3** from the weighing bottle to **FA 5** in the cup. Quickly stir the mixture with the thermometer but **do not measure the temperature**.
5. Continue to stir the mixture. Measure and record the temperature at 4½ minutes, then **every half minute** until the temperature reaches a maximum, and then **every minute** until the tenth minute.
6. Empty and wash the Styrofoam cup. Rinse the cup with deionised water and dry it using a paper towel.

7. Reweigh the emptied weighing bottle and record its mass. Calculate and record the mass of **FA 3** used.

(a) (i) Results

Record the required mass readings in Table 2.1 and in an appropriate format in the space below, record all measurements of time and temperature.

Table 2.1

Mass of weighing bottle with **FA 3** /g	5.382
Mass of empty weighing bottle / g	5.248
Mass of **FA 3** used / g	0.134

Measurements of time and temperature:

Time / min	Temperature / °C
0	29.6
1	29.6
2	29.6
3	29.6
4	-
4½	41.6
5	42.0
5½	41.6
6	41.3
7	40.6
8	40.0
9	39.4
10	38.9

[1] Tabulates all time-temp data in a single table with correct headers and units. If headers have no units, then each reading must have units stated + records all masses consistently to 2/3 d.p. and correctly calculates mass of FA3.

[1] Records all time readings consistently in the same format e.g. "4½" "5" "5½" / "4.5" "5.0" "5.5" / "4 min 30 s" "5 min 0 s" + changes from ½ min to 1 min intervals AFTER maximum temp reached + need to have at least one ½ minute reading after the maximum temp.

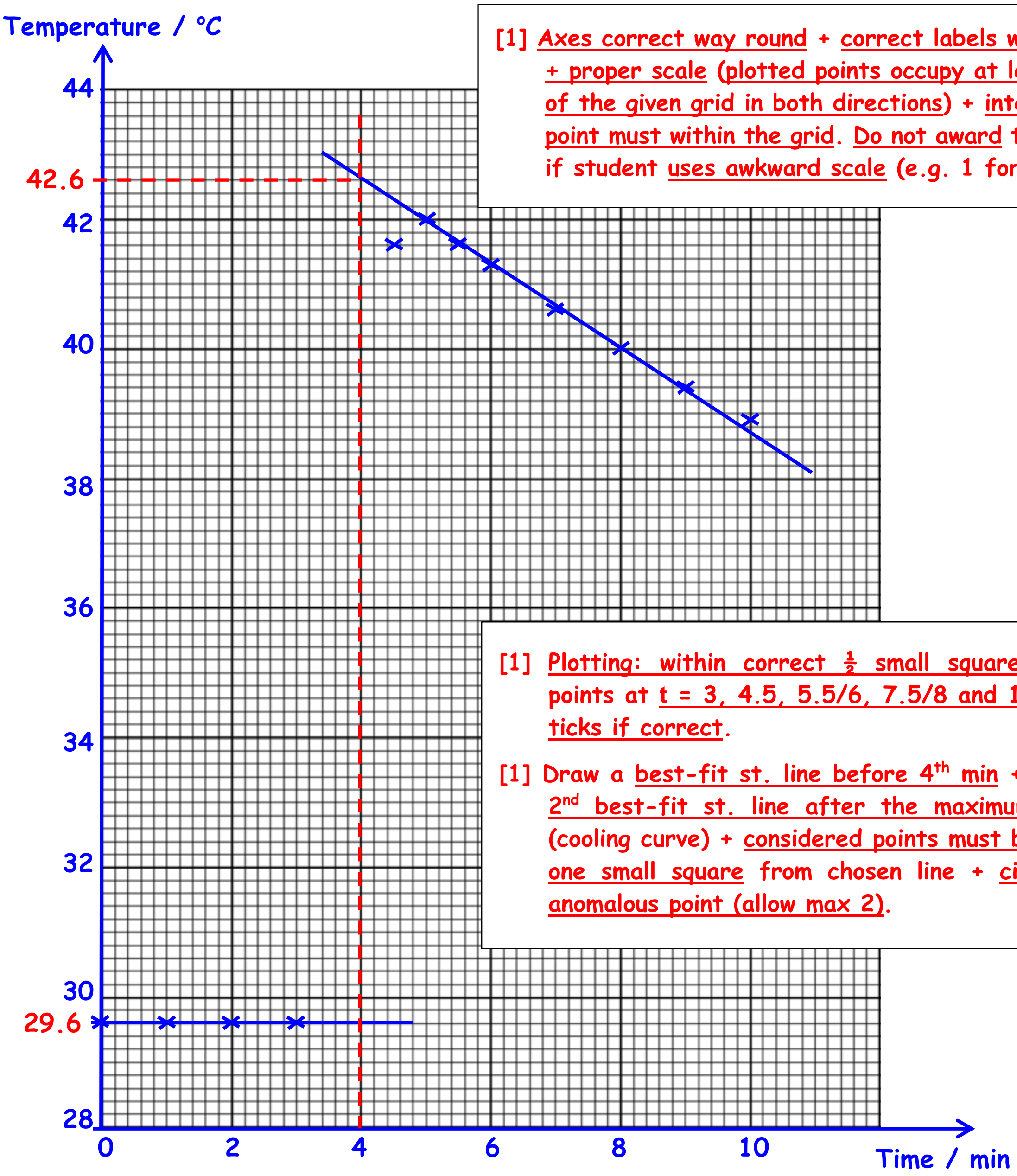
[3]

[1] Records ALL temperature readings to the nearest 0.1 °C (1 d.p.) (using 0.2 °C interval thermometer)

For Examiner's Use

(a) **(ii)** Plot a graph of temperature (y-axis) against time (x-axis) on the grid below. You will use the graph to determine the theoretical temperature change at 4 minutes. The scale for temperature should extend at least 1 °C above your highest recorded temperature.

1. Draw a straight line of best-fit for the points before the fourth minute. Draw a second straight line of best-fit for the points after the fourth minute. Extrapolate both lines to the fourth minute.
2. From your graph, read the minimum and maximum temperature at the fourth minute. Record these values in the spaces below and determine a value for the maximum temperature rise, ΔT, at the fourth minute.



[1] Axes correct way round + correct labels with units + proper scale (plotted points occupy at least half of the given grid in both directions) + intersection point must within the grid. Do not award this mark if student uses awkward scale (e.g. 1 for 3/7)

[1] Plotting: within correct ½ small square. Check points at t = 3, 4.5, 5.5/6, 7.5/8 and 10; place ticks if correct.

[1] Draw a best-fit st. line before 4th min + draw a 2nd best-fit st. line after the maximum temp. (cooling curve) + considered points must be within one small square from chosen line + circle any anomalous point (allow max 2).

Temperature at 4th minute [4]

[1] Extrapolates the both straight lines to intersect the vertical line (line may not be drawn) at 4 min + states min temp, max temp and ΔT correctly to the nearest half square or in 1 d.p. (following the precision of thermometer)

minimum = 29.6 °C

maximum = 42.6 °C

temperature rise, ΔT = 13.0 K

(iii) Use your ΔT from **(a)(ii)** to calculate a value for the molar enthalpy change of **reaction 1** between **FA 3** and **FA 5**, $\Delta H_{\text{rxn 1}}$, in kJ mol^{-1}.
Assume that the specific heat capacity of the final solution is 3.75 J g^{-1} K^{-1} and that its density is 1.05 g cm^{-3}. [A_r: Mg, 24.3]

Heat evolved = q = mcΔT

$= \underline{(50.0 \times 1.05)} \times \underline{3.75} \times \underline{13.0}$ J

= 2559 J = 2.559 kJ [1] (in J or kJ) ignore sign

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g) \quad \Delta H_{\text{rxn 1}}$$

Mg is limiting, HCl is in excess.

$$\Delta H_{\text{rxn 1}} = -\frac{2.559}{\left(\frac{0.134}{24.3}\right)} = -464 \text{ kJ mol}^{-1}$$ [1] with –ve sign

$\Delta H_{\text{rxn 1}}$ = -464 kJ mol^{-1} [2]

(b) **Determining the enthalpy change of reaction 2 between FA 4 and FA 5.**

A student carried out an experiment to determine the enthalpy change of **reaction 2**, $\Delta H_{rxn\,2}$, using a known mass of **FA 4** that reacts with excess **FA 5**.

The student was provided with five pre-weighed samples of **FA 4**, labelled **v**, **w**, **x**, **y** and **z**, and carried out the experiment according to the following instructions.

Method 2

1. Use a 50 cm^3 measuring cylinder to transfer 50.0 cm^3 of **FA 5** into a Styrofoam cup. Place this cup inside a second Styrofoam cup which is held in a 250 cm^3 glass beaker to prevent it tipping over.
2. Stir the solution in the cup with the thermometer. Read and record its temperature. This is the initial temperature of **FA 4**, $T_{initial}$.
3. Carefully add sample **v** to the **FA 5** in the cup.
4. Using the thermometer, stir the mixture continuously until it reaches its maximum temperature. Record the maximum temperature reached, T_{max}.
5. Wash and carefully dry the Styrofoam cup.
6. Repeat steps 1 to 5 with the remaining samples **w**, **x**, **y** and **z**.

The student recorded all masses and temperatures in Table 2.2 below.

Table 2.2

	expt **v**	expt **w**	expt **x**	expt **y**	expt **z**
Mass of **FA 4** added to the cup, **m** / g	0.507	0.503	0.487	0.506	0.476
$T_{initial}$ / °C	31.2	31.2	31.0	31.1	31.3
T_{max} / °C	38.7	38.6	38.2	38.2	38.3
Temperature change, ΔT / °C	7.5	7.4	7.2	7.1	7.0
$\dfrac{\Delta T}{m}$ / °C g^{-1}	14.8	14.7	14.8	14.0	14.7

(i) Complete Table 2.2 by calculating values for ΔT and ΔT/**m**. Leave values for ΔT/**m** to 3 significant figures.

[1] correctly computes <u>ΔT to 1 d.p.</u> and <u>'ΔT/m' to 3 s.f.</u>

(ii) Based on the calculated ΔT/**m** values in Table 2.2, determine an appropriate mean maximum temperature change, ΔT_{ave}, and mean mass of **FA 4**, m_{ave}.

$$\Delta T_{ave} = \frac{7.5 + 7.4 + 7.2 + 7.0}{4} = 7.3 \text{ (1 d.p.)}$$

$$m_{ave} = \frac{0.507 + 0.503 + 0.487 + 0.476}{4} = 0.493 \text{ (3 d.p.)}$$

[1] correctly calculates <u>both ΔT_{ave} (in 1 d.p.) and m_{ave} (in 3 d.p.)</u> based on <u>4 consistent values</u> (excludes one anomalous result)

ΔT_{ave} = <u>7.3</u> °C m_{ave} = <u>0.493</u> g [2]

(iii) Use your results in **(b)(ii)** to calculate a value for the molar enthalpy change of **reaction 2** between **FA 4** and **FA 5**, $\Delta H_{rxn\,2}$, in kJ mol^{-1}.
Assume that the specific heat capacity of the final solution is 3.75 J g^{-1} K^{-1} and that its density is 1.05 g cm^{-3}. [A_r: Mg, 24.3; O, 16.0]

Heat evolved = $q = mc\Delta T_{ave}$

$= \underline{(50.0 \times 1.05) \times 3.75 \times 7.3}$ J

$= 1437$ J $= 1.437$ kJ [1] (in J or kJ) ignore sign!

$MgO(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2O(g)$ $\Delta H_{rxn\,2}$

MgO is limiting, HCl is in excess.

$$\Delta H_{rxn\,2} = -\frac{1.437}{\left(\frac{0.493}{40.3}\right)} = \underline{-117} \text{ kJ mol}^{-1}$$ [1] with -ve sign

$\Delta H_{rxn\,2}$ = $\underline{-117}$ kJ mol^{-1} [2]

(c) Use your values for $\Delta H_{rxn\,1}$ and $\Delta H_{rxn\,2}$, together with the enthalpy change of formation of water, $\Delta H_f(H_2O)$, to calculate a value for the enthalpy change of formation of magnesium oxide, $\Delta H_f(MgO)$.

$H_2(g) + ½\,O_2(g) \rightarrow H_2O(l)$ $\Delta H_f(H_2O) = -286$ kJ mol^{-1}

Note: If you were unable to calculate the enthalpy changes, assume that the value of $\Delta H_{rxn\,1}$ is –457 kJ mol^{-1} and the value $\Delta H_{rxn\,2}$ is –141 kJ mol^{-1}.

$$\begin{tikzcd}
Mg(s) + \tfrac{1}{2}O_2(g) \arrow[r, "\Delta H_f(MgO)"] \arrow[d, "\Delta H_{rxn\,1}"', "+2HCl(aq)"] & MgO(s) \arrow[d, "\Delta H_{rxn\,2}"', "+2HCl(aq)"] \\
MgCl_2(aq) + H_2(g) + \tfrac{1}{2}O_2(g) \arrow[r, "\Delta H_f(H_2O)"] & MgCl_2(aq) + H_2O(l)
\end{tikzcd}$$

[1] correct working (simultaneous eqns or energy cycle)

By Hess's law,
$\underline{\Delta H_f(MgO) = \Delta H_{rxn\,1} + (-286) - (\Delta H_{rxn\,2})}$
$= -464 + (-286) - (-117)$ (or $-457 + (-286) - (-141)$)
$= \underline{-633}$ (or $\underline{-602}$) kJ mol^{-1} [1] with sign

$\Delta H_f(MgO)$ = $\underline{-633}$ (3 s.f. or exact value) kJ mol^{-1} [2]

(d) Two methods, **Method 1** and **Method 2**, have been used to determine the maximum temperature change, ΔT, of an exothermic reaction. Which method would give a more accurate ΔT ? Explain your answer.

ΔT obtained by <u>Method 1</u> is more accurate as a <u>cooling correction has been done</u> by the extrapolating the cooling curve to the time of mixing <u>to compensate/account for the heat loss to the surroundings</u>. [1]

[1]

[Total: 16]

Bonus [1]: <u>shows workings in all calculations</u> + <u>gives all final answers to 3 s.f.</u> in 1(c), 1(d), 2(a)(iii), 2(b)(iii) and 2(c).

3 Planning

The solubility of calcium iodate(V), $Ca(IO_3)_2$, at 20 °C, is approximately 2.4 g dm^{-3}.

When solid calcium iodate(V) is added to water, a small amount dissolves to form a saturated solution, establishing an equilibrium between the undissolved salt and its aqueous ions.

$$Ca(IO_3)_2\,(s) \ll Ca^{2+}\,(aq) + 2IO_3^{-}\,(aq)$$

The equilibrium constant for the above solubility equilibrium, K_{sp}, is also known as the solubility product of calcium iodate.

$$K_{sp} = [Ca^{2+}(aq)]\,[IO_3^{-}(aq)]^2$$

This solubility product can be found by determining the equilibrium concentration of IO_3^- ions in a saturated solution of calcium iodate.

The exact concentration of IO_3^- ions is determined by titration. Excess aqueous KI and aqueous H^+ is first added to a sample of saturated calcium iodate solution to liberate iodine.

$$IO_3^-\,(aq) + 5I^-\,(aq) + 6H^+\,(aq) \rightarrow 3I_2\,(aq) + 3H_2O\,(l)$$

The iodine liberated in the resulting mixture is then titrated with sodium thiosulfate, $Na_2S_2O_3$ of known concentration.

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

(a) Using the information given above, you are required to write a plan to determine the solubility product, K_{sp}, of calcium iodate, $Ca(IO_3)_2$, at 20 °C.

You may assume that you are provided with:

- solid sodium thiosulfate crystals, $Na_2S_2O_3.5H_2O$ (M_r = 248.2)
- solid calcium iodate, $Ca(IO_3)_2$
- aqueous potassium iodide, KI, of about 0.2 mol dm^{-3}
- aqueous hydrochloric acid, HC*l*, of about 1 mol dm^{-3}
- starch indicator
- any other required apparatus normally found in a college laboratory.

Your plan should include details of, including quantities:

- the preparation of 250.0 cm^3 of 0.075 mol dm^{-3} aqueous $Na_2S_2O_3$;
- the preparation of about 100 cm^3 of a saturated solution of calcium iodate, $Ca(IO_3)_2$ at 20 °C;
- the essential details of the titration process;
- an outline of how you would use your mean titre value to determine the solubility product of $Ca(IO_3)_2$.

In your calculations, you should let **V** cm^3 be your mean titre and express your final mathematical expression in terms of **V**.

To prepare 250.0 cm^3 of 0.075 mol dm^{-3} $Na_2S_2O_3(aq)$:

Mass of $Na_2S_2O_3.5H_2O$ required = $\frac{250}{1000} \times 0.075 \times 248.2$ = *4.65 g

1. Weigh accurately *4.65 g of solid $Na_2S_2O_3.5H_2O$ into a weighing bottle using an electronic weighing balance.

[1] weigh correct mass of solid used in 2-3 d.p. (accept a range)

2. Transfer all the weighed solid into a small beaker and dissolve the solid completely with about 50 cm^3 deionised water.
3. Using a filter funnel, carefully transfer the solution and all washings into a 250.0 cm^3 graduated flask. Make up to the graduated mark with deionised water. Stopper and shake the flask well to obtain a homogeneous solution.

[1] accurately prepares 250 cm^3 of standard soln with complete transfer (no loss of $S_2O_3^{2-}$)

To prepare 100 cm^3 of $Ca(IO_3)_2$ saturated solution at 20 °C:

1. Use a 100 cm^3 measuring cylinder to transfer 100 cm^3 of deionised water into a 250 cm^3 conical flask.
2. Using a spatula, add a few tips of solid $Ca(IO_3)_2$ into the conical flask. Stopper the flask and shake the flask for a few minutes. Keep adding more solid $Ca(IO_3)_2$, with shaking after each addition, until some $Ca(IO_3)_2$ solids are left undissolved.

   To ensure that the solution is saturated, shake the flask at intervals and leave the conical flask in a *thermostat controlled water bath set at 20 °C for some time. There must be some solids left undissolved.

[1] correctly prepares a saturated soln of $Ca(IO_3)_2$ at 20 °C (with *)

(allow stirring or swirling in place of shaking)

3. To remove undissolved solids, filter the saturated solution into a clean, dry conical flask using a dry filter funnel and a piece of dry filter paper. [1] dry filtration

Titration procedure:

1. Fill a burette with 0.075 mol dm^{-3} $Na_2S_2O_3(aq)$.
2. Pipette 25.0 cm^3 of the saturated solution into a conical flask.
3. Use a 10 cm^3 measuring cylinder to add to the flask 5 cm^3 of $HCl(aq)$ and 10 cm^3 of $KI(aq)$.

[1] accurately prepares titrant and analyte with min 10 cm^3 of KI & 5 cm^3 of H^+

4. Titrate the liberated I_2 in the mixture with $Na_2S_2O_3(aq)$ from the burette until the solution turns pale yellow. Then add about 1 cm^3 of starch indicator and continue the titration until the dark blue-black colour just disappears/turns colourless at the end-point.
5. Repeat the titration to obtain two consistent titres within 0.10 cm^3 in difference.

[1] correct titration procedure using starch (allow a few drops)

To calculate K_{sp} of $Ca(IO_3)_2$:

Amount of $S_2O_3^{2-}$ required $= \frac{V}{1000} \times 0.075 = 7.5 \times 10^{-5}$ V mol

Amount of IO_3^- in 25.0 cm^3 saturated solution

$= \frac{1}{6} \times 7.5 \times 10^{-5}$ V $= 1.25 \times 10^{-5}$ V mol

IO_3^-	:	I_2	:	$S_2O_3^{2-}$
1	:	3	:	6

$[IO_3^-]$ in saturated solution $= 1.25\times10^{-5}$ V $\times \frac{1000}{25.0} = \underline{5 \times 10^{-4}\ V}$ mol dm^{-3} [1]

$$Ca(IO_3)_2\,(s) \ll Ca^{2+}\,(aq) + 2IO_3^-\,(aq)$$

	$Ca(IO_3)_2$ (s)	Ca^{2+} (aq)	$2IO_3^-$ (aq)
eqm conc.	-	2.5×10^{-4} V	5×10^{-4} V

K_{sp} $(Ca(IO_3)_2) = [Ca^{2+}(aq)]\,[IO_3^-(aq)]^2$

$= (2.5\times10^{-4}\ V)(5\times10^{-4}\ V)^2$

$= \underline{6.25 \times 10^{-11}\ V^3}$ mol^3 dm^{-9} [1]

[8]

(b) The solubility of calcium iodate(V), $Ca(IO_3)_2$, at 20 °C, is approximately 2.4 g dm^{-3}. Justify, with calculations, that the chosen concentration, 0.075 mol dm^{-3}, of aqueous $Na_2S_2O_3$ solution is appropriate. [M_r of $Ca(IO_3)_2$ = 389.9]

Expected $[IO_3^-]$ in the saturated solution $= \frac{2.4}{389.9} \times 2 = 0.0123$ mol dm^{-3} [1]

Amount of IO_3^- in 25.0 cm^3 $= \frac{25.0}{1000} \times 0.0123 = 3.08 \times 10^{-4}$ mol

Amount of $S_2O_3^{2-}$ required $= 3.08 \times 10^{-4} \times 6 = 1.85 \times 10^{-3}$ mol

Expected titre when 0.075 mol dm^{-3} $Na_2S_2O_3$ is used

$= \frac{1.85 \times 10^{-3}}{0.075} = 0.0246$ dm^3

$= 24.6$ cm^3 which is within the capacity of a burette. [1]

[2]

(c) The experiment described in your plan in **(a)** is repeated using 0.1 mol dm^{-3} aqueous $Ca(NO_3)_2$ solution, instead of deionised water, to prepare a saturated solution of calcium iodate(V).

State and explain how, if at all, the titre values and calculated K_{sp} would be expected to differ from that obtained in **(a)**.

[Assume that both the experiments were carried out under the same conditions.]

$$\underline{Ca(IO_3)_2\,(s) \ll Ca^{2+}\,(aq) + 2IO_3^-\,(aq)}\text{---(1)}$$

Presence of <u>common ion Ca^{2+}</u> from $Ca(NO_3)_2$ <u>causes the position of equilibrium (1) to shift left</u> (or the <u>solubility</u> of $Ca(NO_3)_2$ in 0.10 mol dm^{-3} $Ca(NO_3)_2$ <u>is lower</u>) and hence the <u>titre values will be smaller due to lower $[IO_3^-]$</u> in saturated solution. [1]

However, since the <u>temperature is kept constant</u>, the <u>calculated K_{sp} value would remain the same/unchanged</u>. [1]

Award [1] for correct conclusions: smaller titre <u>and</u> constant K_{sp} value

[2]

[Total: 12]

4 Qualitative Analysis

(a) You are provided with solid **FA 6** which contains $S_2O_8^{2-}$ anion and one cation from the ions listed in the *Qualitative Analysis Notes*.

You are to perform the tests described in Table 4.1 to deduce the nature of **FA 6** and to identify the cation present in **FA 6**.

Record your observations in Table 4.1. Your answers should include

- details of colour changes and precipitates formed,
- the identity of any gases evolved, and details of the test used to identify each one.

You should indicate clearly at what stage in a test a change occurs.
Marks are not given for chemical equations.
No additional or confirmatory tests for ions present should be attempted.

Table 4.1

Tests	Observations
(i) To a spatula measure of **FA 6** in a boiling tube, add 1-2 cm depth of dilute hydrochloric acid and heat cautiously. Retain the solution for **test (ii)**.	• Pungent, yellowish green Cl_2 gas (✓) • bleaches a damp blue litmus paper (✓) • pale yellow solution obtained. {FA 8 oxidises Cl^- to Cl_2}
(ii) To the resulting solution from **test (i)**, add barium nitrate(V) solution.	• White ppt. (✓) insoluble in H^+ {$BaSO_4$ ppt.⇒ SO_4^{2-} formed}
(iii) To a spatula measure of **FA 6** in a test tube, add 1-2 cm depth of freshly prepared solution of iron(II) sulfate solution and warm.	• Pale green Fe^{2+} solution turns yellow • Upon warming, solution turns brown/red-brown/orange-brown/orange. (✓) {FA 8 oxidises Fe^{2+} to Fe^{3+}}
(iv) Place a spatula measure of **FA 6** in a boiling tube and add dilute nitric acid to dissolve the solid. Then add 1 cm depth of manganese(II) sulfate solution and 4 drops of silver nitrate(V) solution to act as a catalyst. Heat cautiously to bring the mixture to boiling.	• Upon heating, pale pink Mn^{2+} solution turns brown (✓) then to a black ppt./purple solution/black suspension. (✓) {FA 8 oxidises Mn^{2+} to Mn^{3+} then to MnO_2/MnO_4^-}
(v) To a spatula measure of **FA 6** in a boiling tube, add 1 cm depth of aqueous sodium hydroxide. Heat cautiously.	• No ppt. (✓) • Upon heating, colourless, pungent NH_3 gas (✓) • turns damp red litmus paper blue (✓) {NH_4^+ present}

[5]

8-9(✓) [5], 6-7(✓) [4], 4-5(✓) [3], 2-3(✓) [2], 1(✓) [1]

(b) **(i)** State, with supporting evidence, the nature of **FA 6**.

nature of **FA 6**: oxidising agent [1]

evidence: FA 6 oxidises Fe^{2+} in test (iii) to Fe^{3+} (or Cl^- in test (i) to Cl_2 or Mn^{2+} in test (iv) to $Mn^{3+}/MnO_2/MnO_4^-$) [1]

(ii) Identify the cation in **FA 6**.

cation: NH_4^+ [1]

(iii) Write the ionic equation, including state symbols, for the reaction that occurs in **test (i)**.

$S_2O_8^{2-}$ (aq) or (s) + $2Cl^-$(aq) → Cl_2(g) + $2SO_4^{2-}$(aq) [1]

[4]

(c) You are provided with an organic solution **FA 7** which contains one functional group.

Care: FA 7 is flammable. Do not use Bunsen burner for heating.
Use the hot water provided.

FA 7 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 7**.

Carry out the tests and record details of the tests performed and observations made in Table 4.2.

Table 4.2

Confirmatory Tests	*Observations*
To 1 cm depth of FA 7 in a test-tube, add 1-2 cm depth of dilute H_2SO_4(aq) and 1-2 drop of $KMnO_4$(aq). Heat in hot water-bath. [1]	Purple $KMnO_4$ decolourised. [1]
To 1 cm depth of FA 7 in a test-tube, add 1 cm depth of Fehling's solution. Heat in hot water-bath. [1]	Red-brown / brick-red ppt. formed. [1]

Functional group present in **FA 7**: aliphatic aldehyde [1]

[5]

[Total: 14]

Qualitative Analysis Notes
[ppt. = precipitate]

(a) Reactions of aqueous cations

cation	***reaction with***	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white ppt. with high [Ca^{2+}(aq)]	no. ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt., turning brown on contact with air insoluble in excess	green ppt., turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt., rapidly turning brown on contact with air insoluble in excess	off-white ppt., rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

anion	***reaction***
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, Cl^-(aq)	gives white ppt. with Ag^+(aq) (soluble in NH_3(aq))
bromide, Br^-(aq)	gives pale cream ppt. with Ag^+(aq) (partially soluble in NH_3(aq))
iodide, I^-(aq)	gives yellow ppt. with Ag^+(aq) (insoluble in NH_3(aq))
nitrate, NO_3^-(aq)	NH_3 liberated on heating with OH^-(aq) and A*l* foil
nitrite, NO_2^-(aq)	NH_3 liberated on heating with OH^-(aq) and A*l* foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, SO_4^{2-}(aq)	gives white ppt. with Ba^{2+}(aq) (insoluble in excess dilute strong acids)
sulfite, SO_3^{2-}(aq)	SO_2 liberated with dilute acids; gives white ppt. with Ba^{2+}(aq) (soluble in excess dilute strong acids)

(c) Tests for gases

gas	***test and test results***
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	“pops” with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	***colour of element***	***colour in aqueous solution***	***colour in hexane***
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

2018 Prelim Exam Paper 4 Chemical list:

Label	Identity	Preparation	per candidate
FA 1	0.1 mol dm^{-3} hydrochloric acid	Dilute 50 cm^3 of 2.0 mol dm^{-3} HC*l* to 1 dm^3 with deionised water.	200 cm^3
FA 2	0.1 mol dm^{-3} sodium hydroxide	Dissolve 4.00g of NaOH **[C]** in each dm^3 of solution.	200 cm^3
FA 3	Mg ribbon	0.11 – 0.13 g of Mg ribbon supplied in a stoppered weighing bottle (*cannot exceed 0.135 g) Note: sand Mg ribbons and cut into ≈ 1.5 - 2 cm length before weighing	1 bottle
FA 5	2 mol dm^{-3} hydrochloric acid	Dilute 170 cm^3 of concentrated (35-37%; ≈ 11 mol dm^{-3}) hydrochloric acid **[C]** to 1 dm^3 with deionised water	150 cm^3
FA 6	solid ammonium persulfate, $(NH_4)_2S_2O_8$	About 3 g of solid $(NH_4)_2S_2O_8$ supplied in a stoppered weighing bottle	1 bottle
FA 7	Ethanal	10% (v/v) aqueous solution of ethanal (acetaldehyde) To reduce the possibility of the presence of acid, a fresh batch of ethanal should be used.	1 bottle (8-10 cm^3)
Methyl orange indicator			1 bottle

Central Supplies:

aqueous iron(II) sulfate, $FeSO_4$ (freshly prepared)	0.5 mol dm^{-3} $FeSO_4$(aq) Dissolve 140 g of $FeSO_4.7H_2O$ in 1 dm^3 of water containing 7 cm^3 of concentrated H_2SO_4.	2 bottles per lab (about 5 cm^3 per student)
aqueous manganese(II) sulfate, $MnSO_4$	0.1 mol dm^{-3} $MnSO_4$(aq) Dissolve 16.9 g of $MnSO_4.H_2O$ in 1 dm^3 of water	2 bottles per lab (about 5 cm^3 per student)
Fehling's solution		2 bottles per lab (about 5 cm^3 per student)
Hot water		200 cm^3 per student
Small white labels (Teacher's bench)		
Electronic Weighing balance		**4 per lab**

Student's QA reagents:

aq. potassium manganate(VII), $KMnO_4$	Standard QA reagents concentrations	1 bottle
aq. silver nitrate(V), $AgNO_3$		1 bottle
aq. barium nitrate(V), $Ba(NO_3)_2$		1 bottle
aq. sodium hydroxide, $NaOH$		1 bottle
dilute hydrochloric acid, HCl		1 bottle
dilute sulfuric acid, H_2SO_4		1 bottle
dilute nitric acid, HNO_3		1 bottle
aqueous ammonia, NH_3		1 bottle
limewater (freshly prepared)		1 bottle
Red litmus paper		4 pieces
Blue litmus paper		4 pieces
Filter paper strip		2 pieces
Wooden splint		2 pieces

Student's apparatus:		**per candidate**
1	50.00 cm^3 burette	1
2	Burette stand and clamp	1
3	25.0 cm^3 pipette	1
4	Pipette filler	1
5	250 cm^3 conical flask	2
6	Filter funnel	1
7	White tile	1
8	50 cm^3 measuring cylinder	1
9	Styrofoam cup	2 (supported in a big beaker)
10	Thermometer (–5 °C to +50 °C) 0.2 °C interval	1
11	Stop-watch	1
12	Plastic dropper	2
13	100 cm^3 beaker	1 (for burette waste)
14	200 cm^3 beaker	1 (for hot water bath)
15	Wash bottle with deionised water	1
16	Test-tube rack	1
17	Test-tube	6 } inside a Ziploc bag
18	Boiling tube	2
19	Bunsen Burner	1
20	Test-tube holder	1
21	Glass rod	1
22	Test-tube brush	1
23	Delivery tube (for test-tube)	1
24	Delivery tube (for boiling tube)	1
25	Plastic spatula (small measure)	1
26	Paper Towel	2 pieces