NATIONAL JUNIOR COLLEGE
SH2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME			
SUBJECT CLASS		REGISTRATION NUMBER	

CHEMISTRY

9729/02
Paper 2 Structured Questions
23 August 2024
2 hours

Candidates answer on Question Paper.
Additional Materials: Data Booklet

READ THE INSTRUCTIONS FIRST

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

Answers **all** questions.

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

For Examiner's Use	
1	/9
2	/22
3	/6
4	/7
5	/14
6	/17
Paper 2 Total	/75

	Marks	Weightings
Paper 1	/30	**15%**
Paper 2	/75	**30%**
Paper 3	/80	**35%**
Paper 4	/55	**20%**

Overall Percentage	
Grade	

This document consists of **19** printed pages and **1** blank page.

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

1 (a) Element **A** is from Period 4 of the Periodic Table. The first eight ionisation energies of element **A**, in kJ mol^{-1}, are

947 1798 2735 4837 6043 12310 14300 16800

(i) Identify element **A** and explain your answer.

Element A is Arsenic. There is a large difference between the 5th and 6th ionisation energies of A. The 6th electron is from an inner electronic shell. A has 5 valence electrons, hence it is from Group 15.

[2]

(ii) Explain the difference between the first ionisation energy of element **A** compared to the element to its right on the Periodic Table.

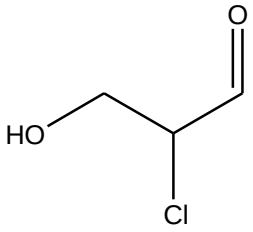
The element to the right is Selenium. 1st ionisation energy of Se involves the removal of paired 4p electrons which experiences inter-electronic repulsion. Less energy is needed to remove the electron from Se than the unpaired 4p electron in A. Hence, the IE of Se is lower.

[2]

(b) In organic chemistry, an aldol is a structure consisting of a hydroxy group (-OH) two carbons away from either an aldehyde or a ketone.

Aldols are the product of a carbon-carbon bond-formation reaction, giving them wide applicability as a precursor for a variety of other compounds.

(i) Give the IUPAC name of the structure below:



IUPAC name: 2-chloro-3-hydroxypropanal [1]

[1]

(ii) The compound above undergoes elimination to form the following product: CH(OH)CHCHO.

Give the reagents and conditions for the reaction.

Ethanolic KOH and heat [1]

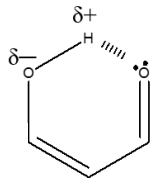
[1]

(iii) State the isomerism which the product displays.

Cis-trans isomerism [1]

[1]

(iv) With the use of a diagram, explain why the cis isomer is formed preferentially.



[1]

The cis isomer is favoured due to the intra-molecular hydrogen bonding that stabilises the cis isomer. [1]

[2]

[Total:9]

2 (a) Some information about NO_3^- and NO_2^- are provided in Table 2.1 and Table 2.2

Table 2.1

Electron arrangement around N in NO_3^-	3 bond pairs & 0 lone pair
Electron arrangement around N in NO_2^-	2 bond pairs & 1 lone pair

Table 2.2

Nitrogen−oxygen bond in NO_3^-	0.124 nm
Theoretical N−O bond length	0.136nm
Theoretical N=O bond length	0.115nm

Fig. 2.1 shows a possible structure of NO_3^-.

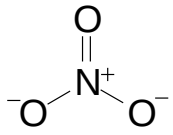


Fig.2.1

(i) Use relevant information from the above tables to explain why Fig. 2.1 does not represent an accurate model for the bonding in NO_3^-.

If the model is correct, there should be 1 shorter bond (N=O) and 2 longer bonds (N-O) in NO_3^-. However, there is only one N−O bond length in NO_3^- in table 2.2.

[1]

(ii) Nitrogen atoms undergo the same type of hybridisation as carbon atoms do. Suggest the mixing and overlap of atomic orbitals which accounts for the N−O bond length in NO_3^-.

One s and 2p orbitals mixed to give 3 degenerate sp^2 orbitals in N. The **sp^2 hybridised orbital of N** undergo **head on overlap** with the **p/sp^2 orbitals of each O** to form the **sigma bond**. The **p orbitals of N** undergo **continuous p orbital sideway overlap** with the the O atoms, resulting in delocalisation of pi electrons / a resonance structure with a **partial N-O double bond.**

Mixing of correct orbitals [1]
Correct orbitals identified for head on **[½]**
Correct orbitals identified for side on **[½]**
Correct overlap leading to sigma bond **[½]**
Correct explanation on equal bond length **[½]**

[3]

(iii) The bond angle around nitrogen in NO_3^- and NO_2^- are different.

Use VSEPR theory to explain how the bond angle in NO_3^- is different from that in NO_2^-.

VSEPR states that electron pair **arrange themselves as far apart as possible to minimise interelectronic repulsion**. However, since **lone-pair bond-pair repulsion is stronger than bond-pair bond-pair repulsion**, the bond angle in NO_2^- is smaller than that in NO_3^-. (NO_3^- has an angle of 120º while NO_2^- has an angle of 118º)

[2]

(b) When solid magnesium nitrate is heated, it decomposes to give magnesium oxide, oxygen and nitrogen dioxide gas.

(i) Write an equation for the decomposition of solid magnesium nitrate.

$2Mg(NO_3)_2(s) \rightarrow 2MgO(s) + O_2(g) + 4NO_2(g)$

[1]

(ii) Zinc nitrate decomposes in the same way as magnesium nitrate when it is heated.

Use data from the Data Booklet to explain the difference in decomposition temperature between zinc nitrate and magnesium nitrate.

Zn^{2+}: 0.074nm

Mg^{2+}: 0.065nm

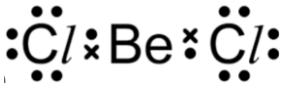
Mg^{2+} has higher $\frac{charge}{size}$ ratio and has higher polarising power. It can polarise and weaken the N–O bond in NO_3^- to a greater extent. [1] As such, $MgNO_3$ is less thermally stable and require a lower decomposition temperature [1] as compared to $ZnNO_3$.

Quote data : [1]

[3]

(c) Magnesium and beryllium are Group 2 elements, but beryllium behaves differently from that of magnesium. There is said to be a 'diagonal relationship' between beryllium and aluminium as they show similar chemical behaviour due to their similarities in electronegativity and charge density.

(i) Draw the dot-and-cross diagram to show the bonding in $BeCl_2$.



Similar to $AlCl_3$, $BeCl_2$ is a covalent molecule

[1]

(ii) When a few drops of water are added to solid beryllium chloride, steamy white fumes are evolved and a white solid remains, which is insoluble in water.

Write a balanced equation for this reaction.

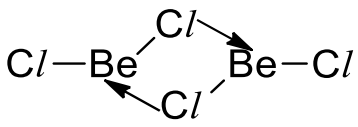
$BeCl_2(s) + 2H_2O(l) \rightarrow Be(OH)_2(s) + 2HCl(g)$

Similar to reaction of $AlCl_3$ with limited water.

[1]

(iii) At 750 °C, the relative molecular mass of gaseous beryllium chloride corresponds to the formula $BeCl_2$. At 550 °C, gaseous beryllium chloride exists as a mixture of $BeCl_2$ and **Y** (relative molecular mass of **Y** is 160)**.**

(I) Suggest the structure of **Y**, showing any dative bonding.



[1]

[1]

(II) Determine the relative ratio of $BeCl_2$ and **Y** in a gaseous sample at 550 °C which has a relative molecular mass of 100.

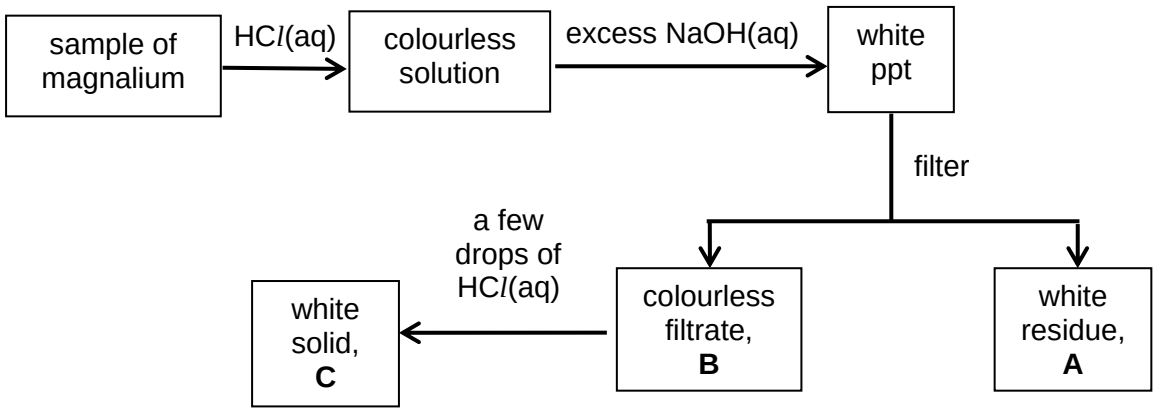
$100 = 80x + 160(1-x)$

$x = 0.75$ and $1-x = 0.25$

Composition is 75% $BeCl_2$ and 25% Y [1]

[1]

(d) Magnalium is an alloy of aluminium and magnesium which is used in boat-building. The diagram below shows some reactions of magnalium.



Identify **A**, **B** and **C.**

A: ……

B: ……

C: ……

A : $Mg(OH)_2$

B : $[Al(OH)_4]^-$

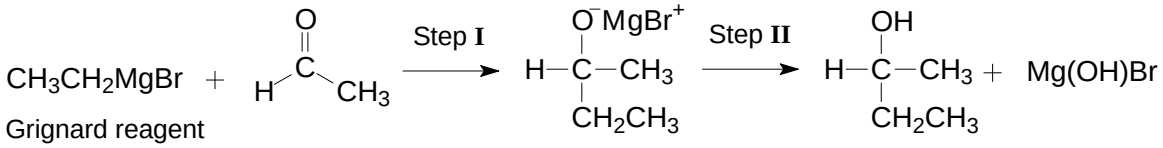
C : $Al(OH)_3$

3 correct- [2], 2 correct[1], 1 correct [½]

[2]

(e) Grignard reagents, RMgX, can be prepared by the reaction of magnesium with halogenoalkane, RX, using dry ether as the solvent.

A Grignard reaction occurs when a Grignard reagent is reacted with a carbonyl compound to prepare alcohols in a two-step reaction. An example of a Grignard reaction is shown below.



(i) What type of reaction takes place in steps **I and II**?

Step **I**: Nucleophilic addition

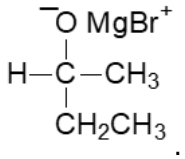
Step **II**: Hydrolysis or Acid–base reaction

[2]

(ii) Step **I** of the above Grignard reaction is known to proceed via the following two stages:

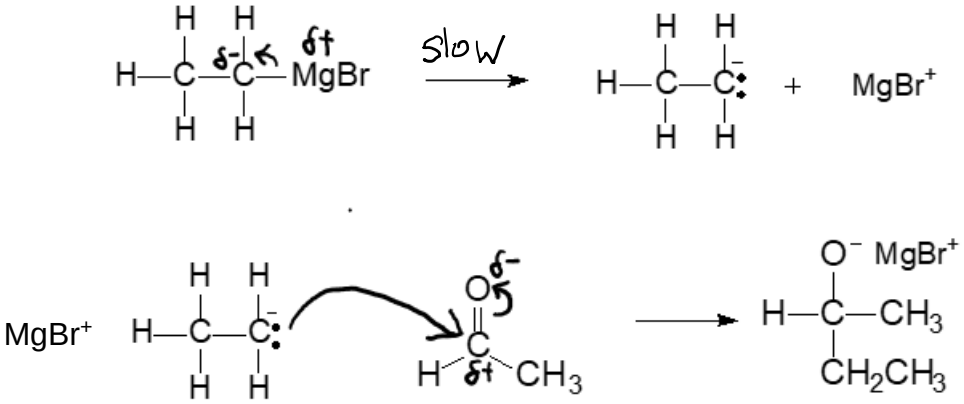
Stage 1: The covalent bond C−Mg in CH_3CH_2MgBr break to give $^-CH_2CH_3$ and $MgBr^+$.

Stage 2: $^-CH_2CH_3$ attack the carbonyl carbon in CH_3CHO to give the intermediate



.

Using the information given above, draw the mechanism to describe step **I** of the Grignard reaction, showing dipoles, lone pairs, and curly arrows.



[2]

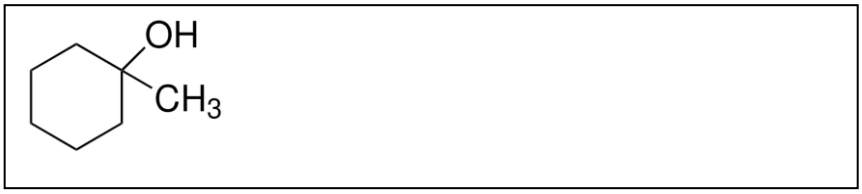
(iii) Suggest and explain whether a single enantiomer or a racemic mixture of the organic product is formed in the above Grignard reaction.

The nucleophile -CH_2CH_3 can attack the trigonal planar ethanal from the top and bottom of the plane in step I with equal probability, resulting in a racemic mixture.

[1]

(iv) $CH_3CO(CH_2)_5MgBr$ undergo the Grignard reaction to give a product with molecular formula of $C_7H_{14}O$.

Draw the structural formula of the product.



[1]

[Total: 21]

3 (a) Ethyne, C_2H_2, can be produced from methane, as shown in the equation below.

$$2CH_4(g) \rightleftharpoons C_2H_2(g) + 3H_2(g) \qquad \Delta H > 0$$

At a constant pressure of 4.0×10^6 Pa, 1.20 mol of CH_4 in a sealed vessel is allowed to reach equilibrium. At equilibrium, 70% of the original sample of CH_4 has reacted.

(i) Write the K_p expression for the reaction.

$$K_p = \frac{(P_{H2})^3(P_{C2H2})}{(P_{CH4})^2}$$

[1]

(i) Calculate K_p for the reaction, stating the units.

	$2CH_4$	$\rightleftharpoons$	C_2H_2	$+3H_2$
I /mol	1.2		0	0
C /mol	-0.84		+(0.5)(0.84)	+(1.5)(0.84)
E /mol	0.36		0.42	1.26

Total amount of gas = 0.36 + 0.42 + 1.26 = 2.04 mol

$P_{CH4} = \frac{0.36}{2.04}(4.0 \times 10^6) = 0.706 \times 10^6\ Pa$

$P_{C2H2} = \frac{0.42}{2.04}(4.0 \times 10^6) = 0.8235 \times 10^6\ Pa$

$P_{H2} = \frac{1.26}{2.04}(4.0 \times 10^6) = 2.471 \times 10^6\ Pa$

$$K_p = \frac{(2.471 \times 10^6)^3(0.8235 \times 10^6)}{(0.706 \times 10^6)^2} = 2.492 \times 10^{13} Pa^2$$

[1] for ICE in mol
[1] for partial pressure of each gas correctly calculated
[1] for correct K_p

[3]

(ii) Suggest why the reaction becomes spontaneous at high temperature.

Since $\Delta H>0$ and $\Delta S>0$ (increased number of mol of gas), for $\Delta G<0$, T has to be high for $|T\Delta S| > |\Delta H|$

1m for explanation

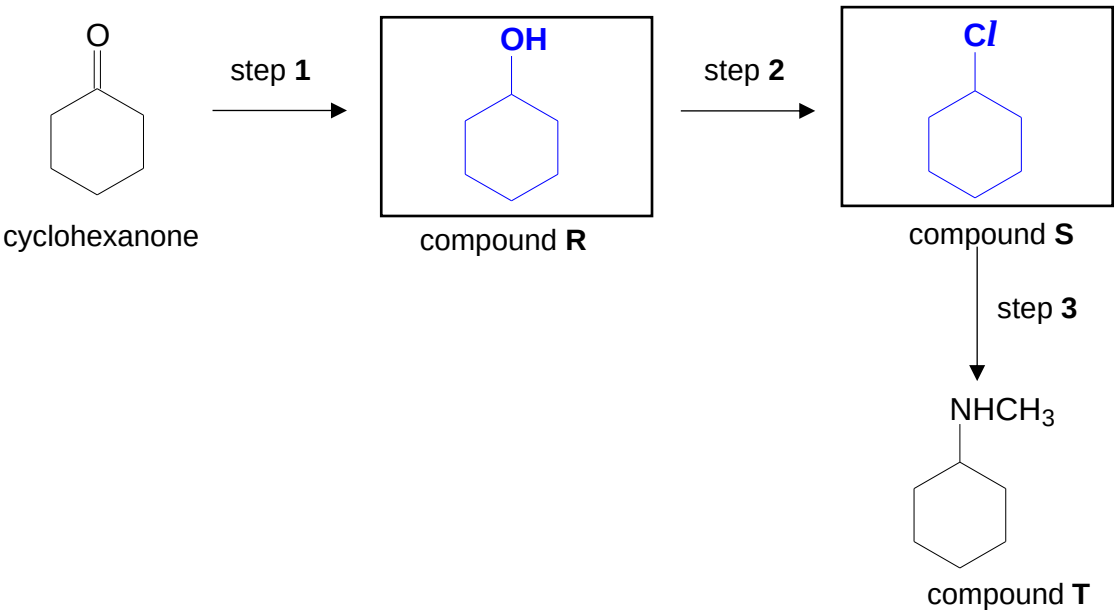
1m for correct T(high)

[2]

[Total: 6]

4 (a) Cyclohexanone can be converted to compound **T** in 3 steps.

Suggest the reagents and conditions for steps **1** to **3** and draw the structure of the compounds **R** to **S** in the synthetic scheme below.

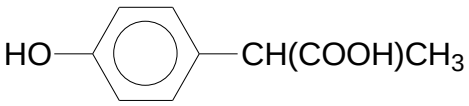


step	reagents and conditions
1	**1: H_2, Ni, heat / H_2, Pt, rt / LiA/H_4 in dry ether [1]**
2	**2: Anhydrous PCl_3, PCl_5 / SOCl_2 [1]**
3	**3: Excess CH_3NH_2 heat in a seal tube [1]**

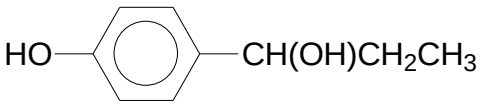
[1] for each compound R and S.

[5]

(b) Suggest a simple chemical test that could be used to distinguish between compounds **X** and **Y**. You should state what you would observe for each compound.



compound **X**



compound **Y**

Reagent and condition: **Na_2CO_3 (aq) [1] / $K_2Cr_2O_7$ dil H_2SO_4, heat**

Observation:

[1] for both correct observation

compound **X**: **Effervescence** / **Orange solution remains**

compound **Y**: **No effervescence** /**Orange solution turns green**

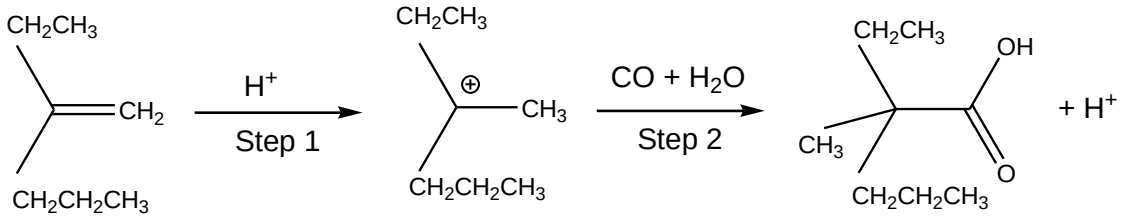
Note: Hot acidified $KMnO_4$ will lead to side chain oxidation for both

[2]

[Total: 7]

5 The Koch reaction is an organic reaction for the synthesis of carboxylic acids from alkenes. The reaction is a strongly acid-catalysed carbonylation using carbon monoxide, and typically occurs at harsh conditions.

The mechanism for the formation of **K** from 2-ethylpent-1-ene is shown below.



K

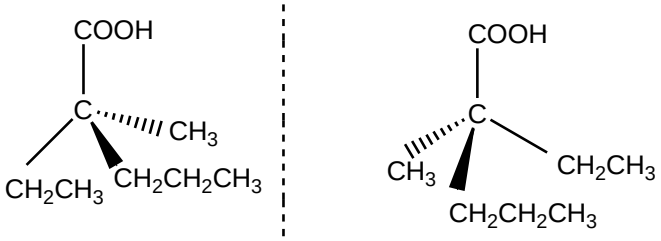
(a) (i) State the role of H^+ in Step 1.

Electrophile/ Lewis Acid [1]
Catalyst not accepted as looking only at Step 1.

[1]

(iii) State the type of isomerism **K** displays and draw the isomers.

Optical isomerism/Enantiomerism [1]

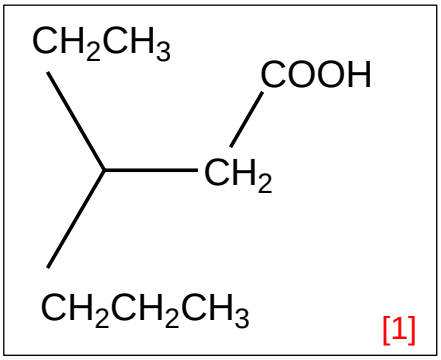


[1 for both isomers]

[2]

(b) (i) **L**, a structural isomer of **K,** is a minor product formed from 2-ethylpent-1-ene in the Koch reaction.

Suggest the structure of **L**.



[1]

[1]

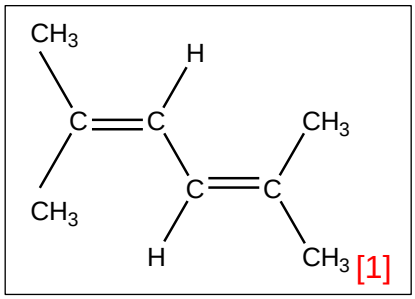
(ii) Explain why **K** is formed preferentially over **L**.

K is formed through a **tertiary carbocation** [½] which has **more electron donating alkyl groups** [½] than the primary carbocation intermediate of **L**. Hence, **the positive charge is dispersed to a larger extent for the tertiary carbocation** [½] and is **formed preferentially** [½].

[2]

(c) 1 mole of compound **M**, C_8H_{14}, was heated with H_2SO_4(aq) and $KMnO_4$. 2 moles of propanone and 2 moles of CO_2 were produced in the reaction.

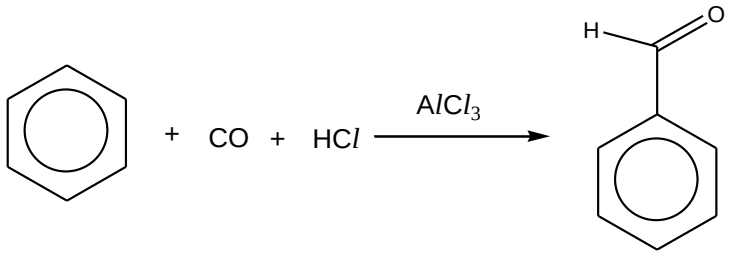
Suggest the structure of compound **M**.



[1]

[1]

(d) A variation of the Koch reaction is the Gattermann Koch Reaction, which converts a benzene into benzaldehyde as shown in the equation below.



(i) Suggest the type of reaction of the Gattermann Koch Reaction.

Electrophilic Substitution.[1]

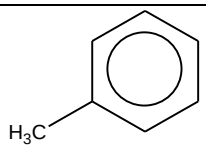
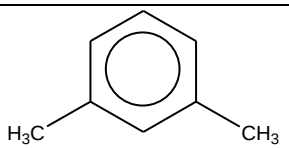
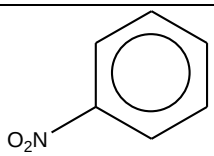
[1]

(ii) By considering the role of $AlCl_3$, explain why the above reaction can only occur under anhydrous condition.

Water contains lone pair of electrons that will **react /destroy the $AlCl_3$ catalyst**. [1]

[1]

(iii) The Gattermann Koch Reaction was repeated with the following compounds:

A	B	C
		

Arrange the compounds according in increasing order of reactivity. Explain your answer.

Order: **C,A,B [1]**

B has one more electron-donating alkyl group than **A**. The **electron density** in the benzene ring is **increased to a larger extent** in **B** than in **A**, making it more reactive towards an electrophile. [1]

C has a **electron-withdrawing nitro group** which **reduces electron density** on the benzene ring, making it less reactive towards an electrophile. [1]

[3]

(e) At 450 °C, 5.00 g of the hydrocarbon **X** was found to exert a pressure of 50 kPa in a 4.0×10^3 cm^3 vessel.

(i) Prove that the molar mass of **X** is 150.2 g mol^{-1}.

$4.0 \times 10^3\ cm^3 = 4.0 \times 10^{-3}\ m^3$

$pV = nRT = \frac{m}{M} RT$

$M = \frac{mRT}{pV} = \frac{5.00\ x\ 8.31\ x\ (450+273)}{50x10^3 x\ 4.0\ x\ 10^{-3}}$ **[1]**

$= 150.2\ g\ mol^{-1}$

[1]

(ii) The actual molar mass of **X** is 144.0 g mol^{-1}. Explain why the experimental value calculated in **(e)(i)** is higher than the actual value.

This is due to the significant instantaneous dipole- induced dipole between the molecules that causes the p value to be smaller than expected, leading to a larger calculated molar mass.

[1]

[Total:14]

6 (a) Gilding metal is a type of brass alloy that consists of copper and a small amount of zinc, ranging from 5 % to 11 % by mass. . Copper is very malleable and is hardened by the addition of zinc.

The proportions of copper and zinc determine the exact properties of the gilding metal and can be determined by chemical analysis.

2.72 g of brass **A** was dissolved in 30 cm^3 of excess concentrated nitric acid, forming a blue solution **B**, containing both copper and zinc ions.

When solution **B** was heated with ammonium thiocyanate, NH_4SCN, precipitate **C** and a gas were produced. The precipitate **C** was found to have a mass of 4.69 g.

(i) Precipitate **C** has the following composition by mass.

Cu, 52.2%; S, 26.4%; C, 9.9%; N, 11.5%

Calculate the empirical formula of precipitate **C**.

Element	Cu	S	C	N
Composition by mass	52.2	26.4	9.9	11.6
A_r	63.5	32.1	12.0	14.0
Mole	0.8220	0.8224	0.825	0.829
Mole ratio	1	1	1	1

Empirical formula = CuSCN **[1]**

[1]

(ii) Use the information provided and your answer from **(a)(i)**, calculate the percentage by mass of zinc in brass **A**. Hence, suggest if brass **A** is a gilding metal.

Molar mass of CuSCN = 63.5 + 32.1 +12.0 + 14.0 = 121.6 g mol^{-1}

Amt of copper in brass = amount of Cu^+ in CuSCN

$$= \frac{4.69}{121.6}$$

$$= 3.857 \times 10^{-2} \text{ mol}$$

Mass of copper in brass = $3.857 \times 10^{-2} \times 63.5$

= 2.449g **[1]**

Percentage by mass of copper in brass = $\left(\frac{2.449}{2.72}\right) \times 100\%$

= 90.0%

Percentage by mass of zinc in brass = 100 – 90.0 = 10.0%. **[1]**

Since percentage by mass of zinc in brass is between 5% to 11%, the brass is a gilding metal. **[1] with ecf**

[3]

(iii) Explain why precipitate **C** is white.

In **C**, copper has a +1 oxidation state **[½]**. Cu^+ : $[Ar]3d^{10}$

Since 3d subshell is fully occupied **[½]**, no d-d transition **[½]** can take place.

Wavelength of light from the visible light spectrum is not absorbed **[½]**,

thus **C** appears white.

[2]

(iv) When sulfur dioxide, SO_2, was bubbled into blue solution **B**, the solution turned colourless and no solid was formed.

(I) Construct a balanced equation for the reaction between solution **B** and SO_2.
(II) By selecting appropriate $E^{\ominus}$ values from the Data Booklet, explain why it would be expected that this redox reaction would **not** occur.

$2Cu^{2+}(aq) + SO_2(g) + 2H_2O(l) \rightarrow 2Cu^+(aq) + SO_4^{2-}(aq) + 4H^+(aq)$ **[1]**

[O] $SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^-$ $E^{\theta}(SO_4^{2-}/SO_2) = +0.17$ V

[R] $Cu^{2+} + e^- \rightarrow Cu^+ + e^-$ $E^{\theta}(Cu^{2+}/Cu^+) = +0.15$ V

$E^{\theta}_{cell} = +0.15 - 0.17 = -0.02$ V **[1]**

Since E^{θ}_{cell} <0, reaction is non spontaneous and hence does not take place [1]- for both calculation and explanation of sign of E^{θ}_{cell}.

[2]

(v) With reference to your answer from **a(ii)**, prove that the concentration of copper ion in solution **B** is 1.29 mol dm^{-3}. Hence, explain why the reaction between solution **B** and SO_2 does in fact occur.

Mass of Cu in brass A = 2.72 × 0.90 = 2.448 g

$[Cu^{2+}]$ in solution **B** $= \left(\frac{2.448}{63.5}\right) \div \left(\frac{30}{1000}\right) = 1.29$ mol dm^{-3}. **[½]**

Eqn 1 : $Cu^{2+} + e^- \rightarrow Cu^+ + e^-$ $E^{\theta}(Cu^{2+}/Cu^+) = +0.15$ V

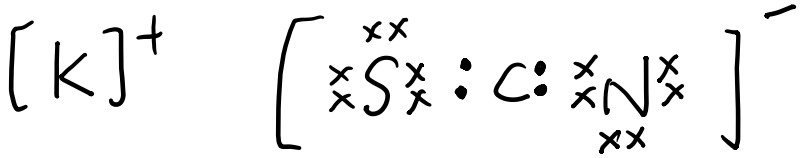
As $[Cu^{2+}(aq)]$ is above 1 mol dm^{-3}, the position of equilibrium in eqn 1 shift to the right **[½]**, favoring reduction and $E(Cu^{2+}/Cu^+)$ becomes more positive than +0.15V. **[½]**

Since $E_{cell} = E(Cu^{2+}/Cu^+) - E^{\ominus}(SO_4^{2-}/SO_2)$, E_{cell} becomes positive and reaction is spontaneous. **[½]**

[2]

(b) When excess potassium thiocyanate, KSCN, were added to a yellow solution, containing iron(III) ions, a blood red solution containing $[Fe(SCN)(H_2O)_5]^{2+}(aq)$ was formed.

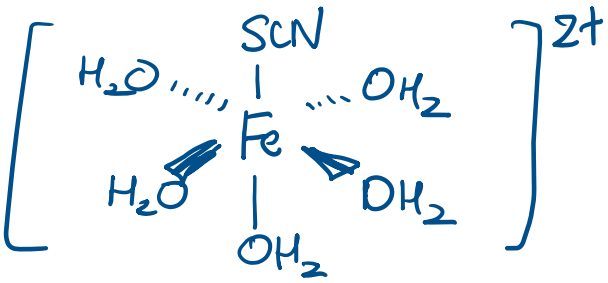
(i) Draw the dot-and-cross diagram to show the bonding in KSCN.



1m for ionic
1m for correct dot-cross in SCN^-

[2]

(ii) Draw a diagram of the structure of $[Fe(SCN)(H_2O)_5]^{2+}$, showing the 3-dimensional arrangement around the Fe(III) ion.



1m for correct orientation and correct shape.

(iii) State the type of reaction taking place and write a balanced equation, with state symbols, for the reaction.

Type of reaction: Ligand exchange reaction **[1]**

Equation: $[Fe(H_2O)_6]^{3+}(aq) + SCN^-(aq) \rightleftharpoons [Fe(SCN)(H_2O)_5]^{2+}(aq) + H_2O(l)$ **[1]**

[2]

(iii) Explain why the colours of the aqueous ions, Fe^{3+} and $[Fe(SCN)(H_2O)_5]^{2+}$, are different.

Different ligands attached to the Fe^{3+} ion cause different degrees of repulsion between the lone pair electrons of the ligands and the electrons in the 3d orbitals **[½]**, splitting the degenerate 3d orbitals into two energy levels differently, giving rise to different energy gaps. **[½]** This results in light of different wavelengths, with energy equal to the energy gap **[½]**, is absorbed, and hence, a different complementary colour **[½]** is observed.

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[2]

[Total: 17]

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