

ANDERSON SERANGOON JUNIOR COLLEGE

2025 JC 2 PRELIMINARY EXAMINATION PAPER 3 SOLUTIONS

Section A

1 (a) Transition elements have characteristic physical and chemical properties.

(i) Explain what is meant by the term *transition element*.

[1]

A transition element is a d block element that can form one or more stable ions with partially filled d subshells. [1]

(ii) Explain why the melting point and density of nickel is higher than that of calcium.

[3]

- [A] In Ni, both the 3d and 4s electrons are available for metallic bonds since the energy level difference between the 3d and 4s orbitals is small. In Ca, only two 3s electrons are available for metallic bonding.
- [B] The greater number of 3d and 4s delocalised electrons available for metallic bonding in Ni results [A or B - 1m]
- in stronger electrostatic attraction between the cations and the 'sea' of delocalised electrons. More energy is required to overcome the stronger metallic bonds in transition elements as compared to Ca. [1m]
- Ni has smaller atomic radii and higher atomic mass compared to Ca.
- Also, Ni has more closely packed [1m] structure due to their stronger metallic bonding.
- Thus, transition elements are denser than Ca.

(b) (i) A solution containing the $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ complex ion is green.

When 1,2-diaminoethane, *en*, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, is added, the colour of the solution changes to purple. This is due to the formation of the $[\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$ complex ion.

Explain why the two solutions are coloured, and why the colours are different.

[3]

In the presence of the ligands, the partially filled 3d orbitals of Ni^{2+} are split into two levels with a small energy gap, ΔE (*d orbital splitting*).

When a 3d electron absorbs energy from the visible light region corresponding to ΔE , this electron is promoted from the d orbital of a lower energy level to a d orbital of a higher energy level (*d-d transition*).

The colour observed is the complementary of the colour absorbed.

The colours are different as different ligands split the partially filled 3d orbitals to different extents with different ΔE . Red is absorbed for $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ complex and yellow is absorbed for $[\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$ complex.

[1]: presence of ligand; partially filled 3d-orbital for $\text{Fe}^{2+}(\text{aq})$; small energy gap

[1]: d-d transition explanation; colour is the complement of the colour absorbed

[1]: different ligands, different ΔE

- (ii) $[\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$ complex ion can exist in three different forms where the ions differ in the spatial arrangement of the ligands around the central metal ion.

Fig. 1.1 shows one of the isomers.

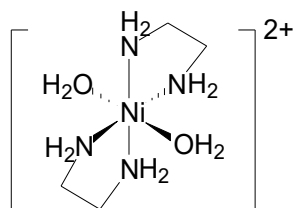
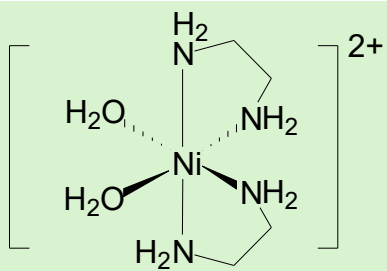


Fig. 1.1

Draw another isomer and state the type of isomerism.

[2]



[1]

cis-trans isomerism [1]

- (c) When a sample of aqueous copper(II) sulfate was added to a small amount of aqueous ammonia, a blue precipitate **A** was formed. Upon adding excess aqueous ammonia, **A** dissolved, and a deep blue solution containing a complex ion, **B**, was formed.

When another sample of aqueous copper(II) sulfate was added to concentrated hydrochloric acid, a yellow-green solution was formed.

- (i) Identify **A** and **B** and explain their formation. Include relevant equations. [4]

[1] correct ID of **A** and **B**

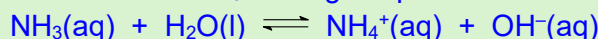
A is $\text{Cu}(\text{OH})_2(\text{H}_2\text{O})_4$ [accept $\text{Cu}(\text{OH})_2$] and **B** is $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$.

To explain formation of A

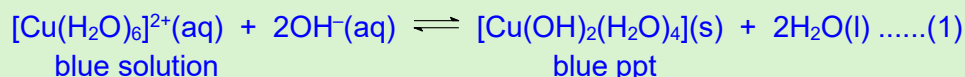
[1] for mention of acid-base reaction with correct relevant equation

Either

In aqueous solution, the weak base NH_3 undergoes partial ionisation, producing OH^- ions.



When a small amount of $\text{NH}_3(\text{aq})$ is added, the $\text{OH}^-(\text{aq})$ undergoes acid-base reaction with $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$ to produce a blue precipitate of $\text{Cu}(\text{OH})_2$.



OR

Acid-base reaction occurs



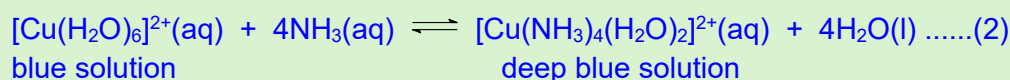
To explain formation of B

[1] for mention of ligand exchange reaction with correct relevant equation

[1] explanation for ppt dissolving

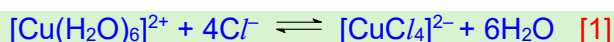
The increasing addition of $\text{NH}_3(\text{aq})$ shifts the position of equilibrium (2) to the right, forming a deep blue solution of $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}(\text{aq})$. As the concentration of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$ decreases, the position of equilibrium (1) shifts left, causing the blue precipitate of $\text{Cu}(\text{OH})_2$ to dissolve.

When excess $\text{NH}_3(\text{aq})$ is added, ligand exchange reaction occurs and the $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ ion is formed.



- (ii) Write an equation to explain the observation of the yellow-green solution.

[1]



- (d) Ruthenium can form complexes with ligands like $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ (represented as *en*) and NH_3 .

Three half equations involving rubidium complex ions are shown in Table 1.1.

Table 1.1

half-cell	half equation
A	$[\text{Ru}(\text{H}_2\text{O})_6]^{3+} + \text{e}^- \rightleftharpoons [\text{Ru}(\text{H}_2\text{O})_6]^{2+}$
B	$[\text{Ru}(\text{NH}_3)_6]^{3+} + \text{e}^- \rightleftharpoons [\text{Ru}(\text{NH}_3)_6]^{2+}$
C	$[\text{Ru}(\text{en})_3]^{3+} + \text{e}^- \rightleftharpoons [\text{Ru}(\text{en})_3]^{2+}$

- (i) Two electrochemical cells are set up to compare the standard electrode potential, E^\ominus , of the three half-cells. Fig 1.2 shows the relative potential of each electrode.

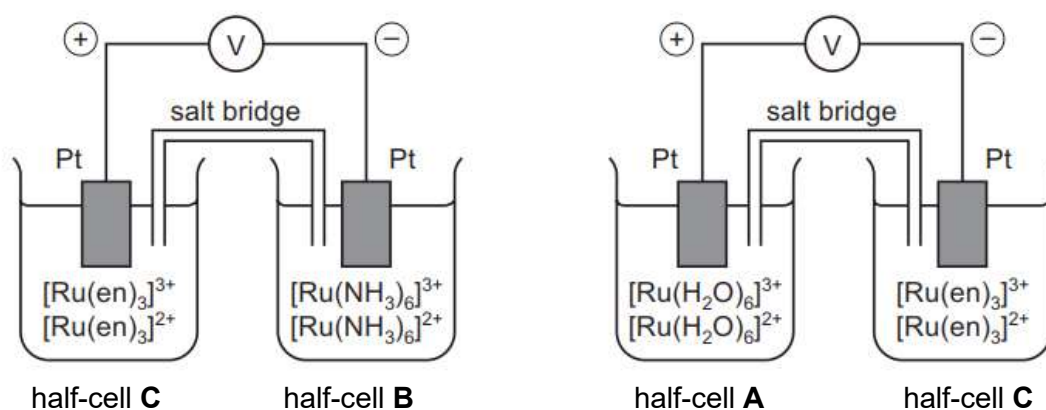


Fig 1.2

Using this information, state and explain the order of standard reduction potential, E^\ominus , for the three half-cells from the least negative to the most negative.

[2]

In the first electrochemical cell, half-cell **C** has a positive electrode (cathode) and half-cell **B** has a negative electrode (anode). Hence, reduction take place in half-cell C and oxidation take place in half-cell B. Therefore half-cell **C** will have a less negative E^\ominus than half-cell **B**.

In the second electrochemical cell, half-cell **A** has a positive electrode (cathode) and half-cell **C** has a negative electrode (anode). Hence, reduction take place in half-cell A and oxidation take place in half-cell C. Therefore half-cell **A** will have a less negative E^\ominus than half-cell **C**. [1]

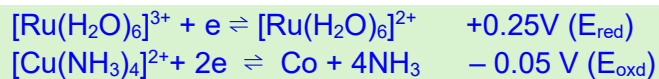
Hence, from the order of E^\ominus from the least negative to the most negative is **A, C, B**. [1]

- (ii) The standard electrode potential of the half-cell **A** is +0.25 V.

An electrochemical cell was set up using half-cell **A** and a $[\text{Cu}(\text{NH}_3)_4]^{2+}/\text{Cu}$ half cell.

Use data from the *Data Booklet* to calculate the E° cell for this cell

[1]

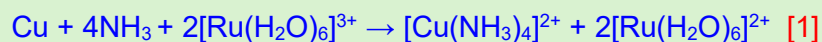
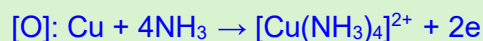
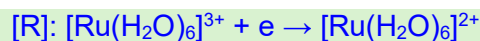


$$E^\circ_{\text{cell}} = 0.25 - (-0.05) = +0.30\text{V} \quad [1]$$

- (iii) Write the overall equation for the reaction that occurs in the cell in (d)(ii).

Using the E°_{cell} you have calculated in (d)(ii), calculate a value of ΔG° for the cell reaction represented by your overall equation.

[2]



$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

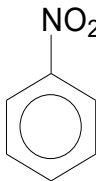
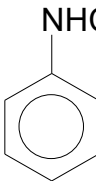
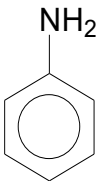
The no. of electrons exchanged in the overall balanced equation is 2. Hence, $n = 2$.

$$\Delta G^\circ = -2 \times 96500 \times (+0.300) = -57900 \text{ J mol}^{-1} \text{ or } -57.9 \text{ kJ mol}^{-1} \quad [1]$$

[Total: 19]

- 2 (a) The reactivity of three nitrogen-containing compounds with aqueous bromine is shown in the Table 2.1.

Table 2.1

	 nitrobenzene	 acetanilide	 phenylamine
reactivity with Br ₂ (aq) at room temperature	no reaction	mono-substitution of benzene ring	tri-substitution of benzene ring

- (i) Explain the difference in the reactivity of the three compounds with Br₂(aq). [3]

Phenylamine is the most reactive as the lone pair of electrons on N can delocalise into the benzene ring due to overlap between p orbital of N and π electron cloud of benzene. This increases the electron density of the benzene ring greatly, making it most susceptible to electrophilic attack. [1]

Acetanilide is less reactive than phenylamine because delocalisation of the lone pair of electrons on N into the C=O reduces the extent of delocalisation of the lone pair into the benzene ring. Hence, the benzene ring is less electron-rich than phenylamine. [1]

Nitrobenzene is the least reactive as the -NO₂ withdraw electrons from the benzene ring. This decreases the electron density of the ring and electrophiles are less attracted to the benzene ring slowing down the rate the electrophilic substitution greatly. [1]

- (ii) State the reagents and conditions to form acetanilide from nitrobenzene. [2]

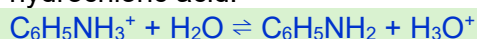
Step 1: Sn, conc HCl, heat followed by NaOH [1]

Step 2: CH₃COC/ [1] r.t.p.

- (iii) Explain why acetanilide is effectively neutral. [1]

The orbital of the lone pair of electrons on the N atom overlaps with the π -electron cloud of the adjacent C=O group and the lone pair of electrons is delocalised and thus not available for dative bond with a proton. [1]

- (iv) Phenylamine can react with hydrochloric acid to form phenylammonium chloride. Given the pK_b of phenylamine at 25 °C is 9.38, calculate the pH of the resultant mixture when 25 cm³ of 0.25 mol dm⁻³ phenylamine is titrated with 25 cm³ of 0.25 mol dm⁻³ of hydrochloric acid. [2]



$$[\text{H}^+] = \sqrt{K_a \times [\text{phenylammonium ion}]}$$

$$\text{Amt of C}_6\text{H}_5\text{NH}_3^+ = \frac{25}{1000} \times 0.25 = 0.00625 \text{ mol}$$

$$[\text{H}^+] = \sqrt{\frac{K_w}{K_b} \times [\text{phenylammonium ion}]}$$

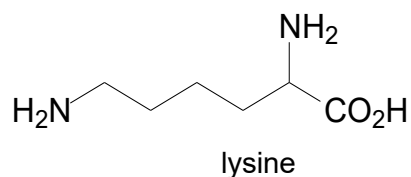
$$\text{Total volume} = 50 \text{ cm}^3$$

$$[\text{C}_6\text{H}_5\text{NH}_3^+] = \frac{0.00625}{50/1000} = 0.125 \text{ mol dm}^{-3} \text{ [1]}$$

$$[\text{H}^+] = \sqrt{\frac{10^{-14}}{10^{-9.38}} \times 0.125} = 0.001732 \text{ mol dm}^{-3}$$

$$\text{pH} = -\lg 0.001732 = 2.76 \text{ [1]}$$

- (b) Lysine is an α -amino acid that is used in the biosynthesis of proteins.



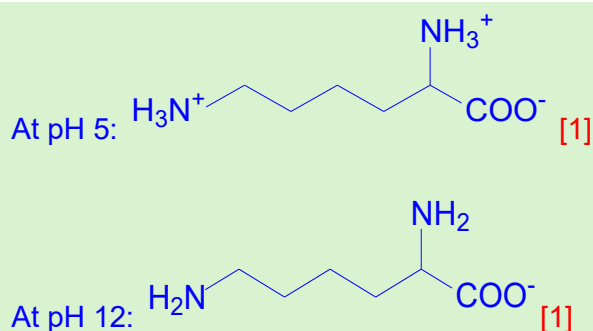
The pK_a values of lysine are given Table 2.2.

Table 2.2

functional group on lysine	pK_a value
α -carboxyl group	2.2
α -amino group	9.0
side chain	10.5

- (i) Draw the structures of the major species present in solution of lysine at pH 5 and pH 12.

[2]



- (ii) Suggest a reason why the α -amino group of protonated lysine has a lower pK_a than the amino group on the side chain.

[1]

Due to its closer proximity to the electron-withdrawing α -COOH group.

This decreases the availability of the lone pair of electron on N atom in the amine on α -amino group of lysine to accept a proton, resulting in a lower pK_a [1]

- (c) When a 10.0 cm^3 sample of the fully protonated lysine is titrated against $0.100 \text{ mol dm}^{-3} \text{ NaOH}$, the following titration curve is obtained.

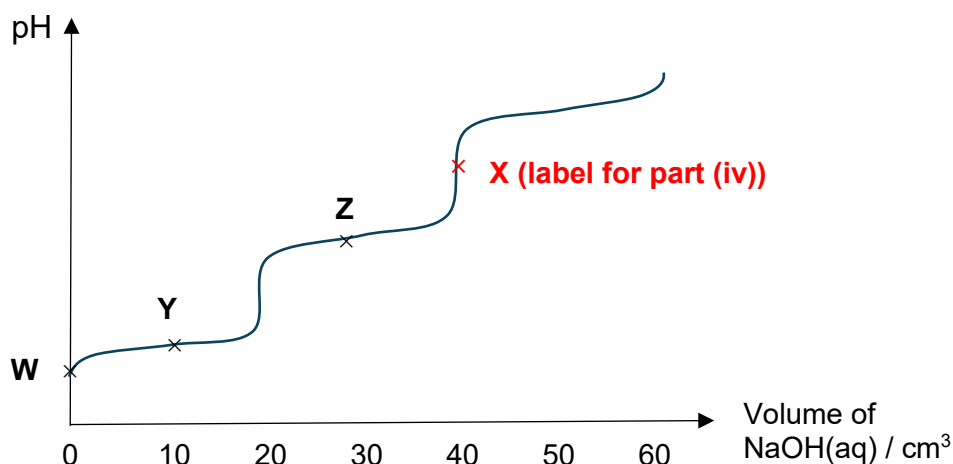


Figure 2.1

- (i) Calculate the concentration of lysine in the 10.0 cm^3 sample. Hence, calculate the pH of the solution at point **W** (ignore the effects of the second and third acid dissociations on the pH). [3]

Concentration of lysine = $0.100 \times 20 \div 10 = 0.200 \text{ mol dm}^{-3}$ [1]

$$\begin{aligned} [\text{H}^+] &= \sqrt{K_a \times [\text{acid}]} \\ &= \sqrt{10^{-2.2} \times [0.100]} \\ &= 0.0251 \text{ mol dm}^{-3} \quad [1] \end{aligned}$$

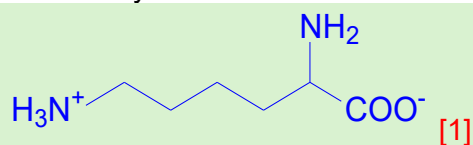
$$\begin{aligned} \text{pH} &= -\lg(0.0251) \\ &= 1.6 \quad [1] \end{aligned}$$

Calculate $[\text{H}^+]$ correctly [1] allow ecf from (c)(i)
Calculate pH correctly [1] allow ecf from $[\text{H}^+]$ calculated

- (ii) Determine the pH at point **Y** and **Z** [2]

pt Y = 2.2 (since $\text{pH} = \text{p}K_{a1}$), [1] pt Z = 9.0 (since $\text{pH} = \text{p}K_{a2}$) [1]

- (iii) Suggest the structure of the zwitterion of lysine and indicate the point of the titration curve where only the zwitterion is found. Mark it with an "X". [2]



[1] for labelling on graph.

[Total: 18]

- 3 (a) (i) Describe and explain the trend in the thermal stability of HCl, HBr and HI. [2]

Down the group from Cl to I

- **Valence orbital** of halogen used in bonding with hydrogen is **bigger** and **more** diffused
- **Overlap of orbitals between the H atom and halogen atom** is **less** effective
- **Bond energy**: $\text{H-Cl} > \text{H-Br} > \text{H-I}$
- **Thermal stability**: $\text{HCl} > \text{HBr} > \text{HI}$

2 points for [1] must include the last point

4 points for [2]

- (ii) Explain why the volatility of Group 17 hydrides decreases from HCl, HBr and HI. [2]

Hydrogen halides have simple molecular structures

The volatility of Group 17 hydrides decreases from HCl, HBr and HI, volatility inversely proportional to boiling point [1]

[1] for **HCl to HBr to HI** explanation

- **From HCl to HBr to HI**, the **number of electrons** in the hydrogen halide molecules **increases**
- **Strength of instantaneous dipole-induced dipole attractions** between the hydrogen halide molecules **increases**
- **Larger amount of energy** is required to overcome the **stronger** instantaneous dipole-induced dipole attractions between the hydrogen halide molecules.

- (iii) Predict the colour of the solutions that would be observed when the following pairs of solution are mixed. Give equations for any reactions that occurs.

- $\text{Br}_2(\text{aq})$ and $\text{KI}(\text{aq})$
- $\text{I}_2(\text{aq})$ and $\text{KBr}(\text{aq})$

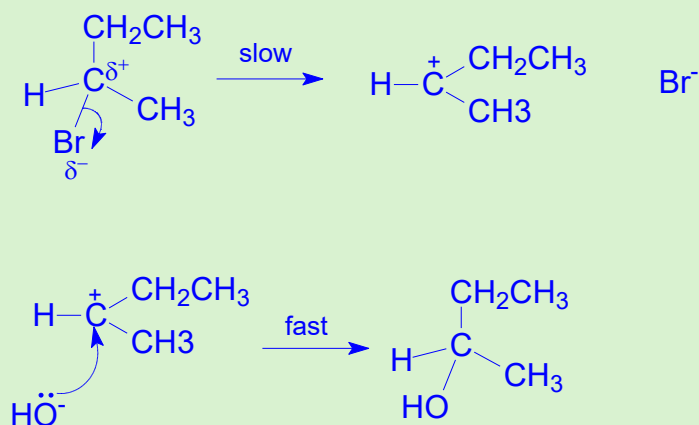
[2]

Equation	colour of solution
$\text{Br}_2 + 2\text{I}^- \rightarrow 2\text{Br}^- + \text{I}_2$ ✓	brown ✓
$\text{I}_2 + 2\text{Br}^- \rightarrow$ no reaction ✓ Or didn't write equations for this reaction	brown ✓

4✓ → [2]; 2✓ → [1]

(b) S_N1 and S_N2 are two different mechanisms for the nucleophilic substitution of halogenoalkanes.

- (i) Draw a mechanism for the reaction between 2-bromobutane and OH^- via S_N1 . Show relevant lone pairs of electrons, dipoles and use curly arrows to indicate the movement of electron pairs. [2]



[1] for lone pairs, dipoles, slow and fast

[1] for carbocation and arrows

- (ii) Write the rate equation for the reaction in (b)(i). Suggest if the value of the rate constant, k , will change when concentration of 2-bromobutane is doubled. [2]

Rate = $k[2\text{-bromobutane}]$ [1]

Rate constant, k , will not change as it is only dependent on activation energy and temperature. [1] (do not accept if mention independent of [reactant])

- (iii) An investigation of the kinetics of the nucleophilic substitution of 2-bromobutane with OH^- is carried out. The overall rate equation of this nucleophilic substitution is found to be:

$$\text{rate} = y [\text{2-bromobutane}] + z [\text{2-bromobutane}][\text{OH}^-]$$

where y and z are rate constants.

The results of two such experiments are recorded in Table 3.2

Table 3.2

Experiment	[2-bromobutane]/ mol dm^{-3}	$[\text{OH}^-]/$ mol dm^{-3}	Initial rate / $\text{mol dm}^{-3} \text{ s}^{-1}$
1	0.20	0.20	8.0×10^{-7}
2	0.20	0.40	1.4×10^{-6}

Use the results to calculate the values of y and z for the rate equation shown, stating their units. [3]

$$\text{rate} = y [\text{2-bromobutane}] + z [\text{2-bromobutane}][\text{OH}^-]$$

From experiment 1,

$$8.0 \times 10^{-7} = y(0.2) + z(0.2)(0.2)$$

From experiment 2,

$$1.4 \times 10^{-6} = y(0.2) + z(0.2)(0.4)$$

Both equations – [1]

$$y = 1.00 \times 10^{-6}$$

$$\text{units of } y = \text{s}^{-1}$$

$$z = 1.50 \times 10^{-5}$$

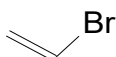
$$\text{units of } z = \text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$$

Both units – [1]

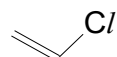
Both value – [1]

Can add in the explanation of mixed order in the mark scheme for further reading.

- 3 (c) Vinyl bromide and vinyl chloride are common monomers used in manufacture of addition polymers.



Vinyl bromide



Vinyl chloride

In order to differentiate vinyl bromide and vinyl chloride, the following steps are observed.

Step 1: $\text{H}_2(\text{g})$ in the presence of solid platinum was introduced into the respective vinyl halides.

Step 2: Hot aqueous sodium hydroxide is added followed by nitric acid. The samples are then cooled before silver nitrate is added. Precipitate will be observed.

Step 3: To confirm the identity of the precipitate, dilute $\text{NH}_3(\text{aq})$ was added to fresh sample of the precipitate.

- (i) Complete Table 3.3 by stating the relevant observations for each step.

Table 3.3

compound	Name of organic substance after step 1	Colour of ppt after step 2	Solubility of precipitate	
			In dil. $\text{NH}_3(\text{aq})$	In conc $\text{NH}_3(\text{aq})$
Vinyl bromide	bromoethane	Cream ppt	Insoluble	Soluble
Vinyl chloride	chloroethane	White ppt	Soluble	Soluble

[2]

All correct [2]

At least 2 correct [1]

- (ii) Step 1 is conducted before step 2 as vinyl halides do not undergo nucleophilic substitution. Explain the unreactivity of vinyl halides towards nucleophiles. [1]

- In the halogenoalkene the p orbital of the halogen atom interact with the pi electron cloud of the $\text{C}=\text{C}$.
- This strengthen the C-X bond which make nucleophilic substitution not possible. [1]
- By reducing the vinyl halides into halogenoalkane, nucleophilic substitution can then occur.

- (iii) Explain why it is necessary to add nitric acid in step 2. [1]

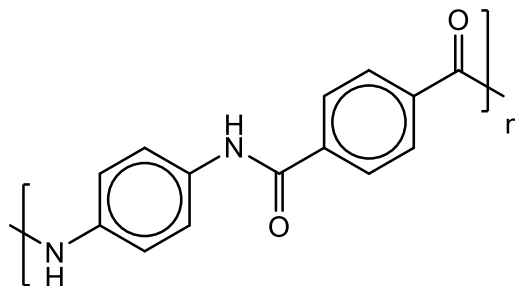
To react with excess acid and prevent the formation of ppt between Ag^+ and OH^- , affecting the results. [1]

- (iv) H_2 gas with platinum can be used to reduce C=C bond in an alkene and C=O bond in an aldehyde.

Explain why the C=C bond in an alkene is weaker than the C=O bond in an aldehyde. [2]

- oxygen is more electronegative than carbon creating a polar C=O bond which increases the electrostatic attraction between atoms, making the bond stronger. [1]
- The C=C bond in propene is non-polar and lacks the additional electrostatic attraction between atoms due to partial charges. [1]

- 3 (d) Kevlar is a lightweight and strong material, used to make tyres and bulletproof vests. Its structure is given below.



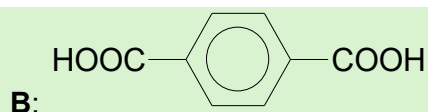
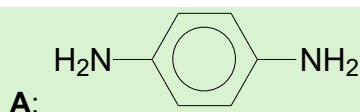
Kevlar

Upon undergoing hydrolysis, two monomers **A** and **B** are formed.

monomer A	$C_6H_8N_2$
monomer B	$C_8H_6O_4$

- (i) Draw the structures of **A** and **B**.

[1]



[1] for both

- (ii) Suggest reagents and conditions required to differentiate the monomers **A** and **B**.

[2]

Add anhydrous PCl_3 / $SOCl_2$ / PCl_5 room temperature to **A** and **B**.
White fume will be observed for **B** but not for **A**.

Or

Add $Br_2(aq)$ to **A** and **B**
Orange $Br_2(aq)$ decolourised and white ppt will be observed for **A** but not for **B**.

Or

Add Na_2CO_3 / $NaHCO_3$ to **A** and **B**
Effervescence will be observed for **B** but not for **A**.

[1] for test [1] for correct observation

- (iii) Kevlar can withstand a large amount of pulling force before breaking. Explain why Kevlar has such property

[1]

Presence of extensive **H-bonding** and instantaneous dipole-instantaneous dipole between the polymer chain require great amount of energy to overcome thus leading to high tensile strength.

[1]

[Total: 23]

Section B

- 4 (a) (i) Sodium, magnesium and phosphorous are elements from Period 3.

Describe what you would observe when water is added to separate samples of the chlorides of these three elements.

Suggest the pH of the resulting solutions, and write equations where appropriate. [3]

NaCl undergoes hydration in water to form a neutral solution of pH 7. [1]

Hydration: $\text{NaCl(s)} \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$

MgCl_2 undergoes hydration and slight hydrolysis in water to form a slightly acidic solution of pH 6.5. [1] with equation

$\text{MgCl}_2(\text{s}) + 6\text{H}_2\text{O(l)} \rightarrow [\text{Mg}(\text{H}_2\text{O})_6]^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq})$

$[\text{Mg}(\text{H}_2\text{O})_6]^{2+}(\text{aq}) \rightleftharpoons [\text{Mg}(\text{H}_2\text{O})_5(\text{OH})]^+(\text{aq}) + \text{H}^+(\text{aq})$

PCl_5 undergoes complete hydrolysis (vigorous hydrolysis) in water to form a strongly acidic solution of pH 1. [1] with equation

$\text{PCl}_5(\text{s}) + 4\text{H}_2\text{O(l)} \rightarrow \text{H}_3\text{PO}_4(\text{aq}) + 5\text{HCl(aq)}$

- (ii) Carbon tetrachloride, CCl_4 , and silicon tetrachloride, SiCl_4 , are both tetrachlorides of Group 14 elements. Explain why CCl_4 does not hydrolyse in water but SiCl_4 does. [2]

CCl_4 does not undergo hydrolysis in water because of the much smaller size of the C atom relative to the large Cl atoms which hinders the approach of the water molecules. [1]

In addition, C does not have available and energetically accessible 3d orbitals to accommodate the lone pair of electrons from water unlike Si. [1]
(accept explanation in terms of Si)

- (iii) NC_3 and PCl_3 are both chlorides of Group 15 elements. Predict and explain the difference in bond angles between NC_3 and PCl_3 . [2]

Bond angle of NC_3 (107°) is larger than PCl_3 (100°). [1]

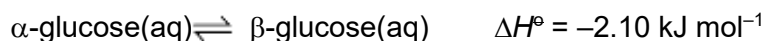
Explanation [1]

N is more electronegative than P. Hence,

- bonding electrons in N–Cl bond is drawn more towards the N atom
- more crowding of electron density around N atom
- more inter-electronic repulsion between the electron pairs around the N atom
- larger bond angle in NC_3

- (b) D-glucose exists in two forms. The α -form has an optical rotation of $+113.4^\circ$ and the β -form which has an optical rotation of $+19.0^\circ$.

The following equilibrium exists in aqueous solution.



If an aqueous solution of either form is allowed to stand, the optical rotation changes until it reaches $+52.2^\circ$.

- (i) Show that the equilibrium mixture contains 35.2% of the α -form. [1]

Let the proportion of α -glucose be x and that of β -glucose be $1 - x$.
 $x[\alpha\text{-glucose}] + (1-x)[\beta\text{-glucose}] = [\text{glucose}]_{\text{eqm}}$
 $113.4x + (1-x)19 = 52.2$
 $x = 0.352$
 \therefore % of α -form in equilibrium mixture $\approx 35.2\%$ (shown) [1] with correct working

- (ii) Calculate the K_c value at 298 K. [1]

$$\begin{aligned} K_c &= \frac{[\beta\text{-glucose}]}{[\alpha\text{-glucose}]} \\ &= \frac{100 - 35.2}{35.2} \\ &= 1.84 \text{ [1]} \end{aligned}$$

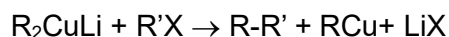
- (iii) Given that $\Delta G^\circ = -RT \ln K_c$, using your answer from (b)(ii), calculate the value of ΔG° and ΔS° at 298 K. [2]

$$\begin{aligned} \Delta G^\circ &= -RT \ln K_c \\ &= -(8.31)(298) \ln(1.84) \\ &= -1510 \text{ J mol}^{-1} \text{ [1]} \end{aligned}$$

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ \Delta S^\circ &= \frac{\Delta H^\circ - \Delta G^\circ}{T} \\ &= -1.98 \text{ J mol}^{-1} \text{ K}^{-1} \text{ [1]} \end{aligned}$$

- (c) The Corey–House reaction is an organic reaction that involves the reaction of a lithium dialkyl cuprate, R_2CuLi , with a halogenoalkane, $R'X$, to form a new alkane, an organocopper compound and a lithium halide.

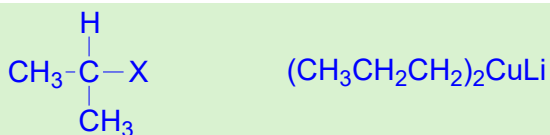
The reaction is as shown.



(X = Cl, Br or I)

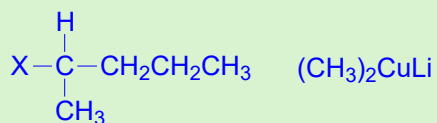
- (i) Suggest the lithium dialkyl cuprate and a secondary halogenoalkane to form $CH_3CH(CH_3)CH_2CH_2CH_3$.

[1]

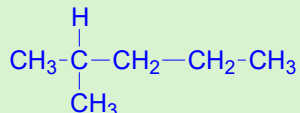


[1] for both structures

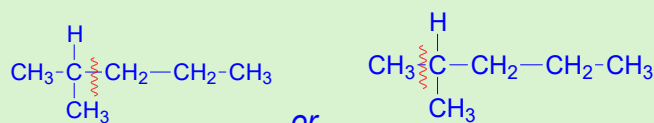
OR



Thinking process:



Given , as stated by question, you need a secondary halogenoalkane, the only way to get is by “cutting” the structure as shown.



halogenoalkane.

all other sites will result in primary

- (ii) Suggest the type of reaction for the Corey–House reaction.

[1]

Nucleophilic substitution [1]

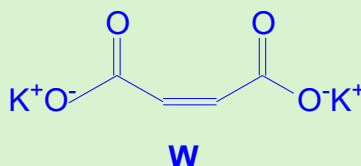
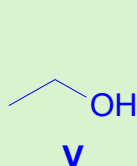
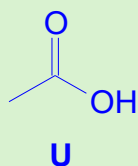
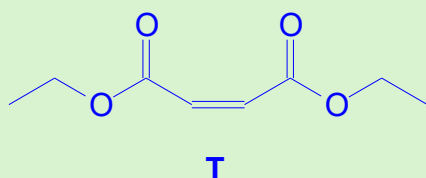
- (d) Compound **T**, $C_8H_{12}O_4$, is a neutral, sweet-smelling liquid. It does not give any orange precipitate with 2,4-DNPH. One mole of compound **T** decolourised one mole of liquid Br_2 .

Samples of compound **T** are reacted separately with

- hot aqueous KOH to form organic compound **V**, C_2H_6O , and salt **W**, $C_4O_4H_2K_2$.
- hot acidic $KMnO_4$ to form **U**, $C_2H_4O_2$, as the only organic product

Compound **V** gives a yellow precipitate with alkaline aqueous iodine.

Suggest possible structures for **T**, **U**, **V** and **W**. For each reaction, state the type of reaction described and explain what the information tells you about the functional group present in each compound. [7]



[1] for each correct structure

	Deduction
Compound T , $C_8H_{12}O_4$, is a neutral, sweet-smelling oil	Ester is present in T ✓
does not give any orange precipitate with 2,4-DNPH	No condensation ✓, no carbonyl compound ✓
compound T decolourised one mole of liquid Br_2	Electrophilic addition ✓, presence of alkene ✓
compound T reacts with hot aqueous KOH	Basic hydrolysis ✓, ester in T
compound T reacts with hot acidic $KMnO_4$ forming U , $C_2H_4O_2$, as the only organic product	Acidic hydrolysis of ester ✓; Oxidation of alkene ✓
Compound V gives a yellow precipitate with alkaline aqueous iodine	Oxidation ✓, <div style="text-align: center;"> $\begin{array}{c} CH_3 \\ \\ R-C-OH \\ \\ H \end{array}$ </div> presence of ✓

8 to 9 ✓ → [3]

6 to 7 ✓ → [2]

4 to 5 ✓ → [1]

[Total: 20]

5 In aqueous solution, chlorine dioxide, ClO_2 , reacts with hydroxide ions as shown.



- (a) (i) Suggest how the shape and bond angle of a ClO_3^- ion is different from those of ClO_2^- ion. [2]

In ClO_3^- , there are also three bond electron pairs and one lone pair around the central Cl atom.

In ClO_2^- , there are also two bond electron pairs and two lone pair around the central Cl atom.

Lone pair-lone pair repulsion in ClO_2^- is stronger than lone pair-bond pair repulsion in ClO_3^- . [1]

Hence, shape changes from trigonal pyramidal in ClO_3^- to bent in ClO_2^- . Bond angle in ClO_2^- is smaller than in ClO_3^- . [1]

- (ii) Determine the oxidation number of chlorine in ClO_2 , ClO_3^- and ClO_2^- . Hence, suggest what is special about this reaction. [2]

ON of Cl in ClO_2 : +4

ON of Cl in ClO_3^- : +5

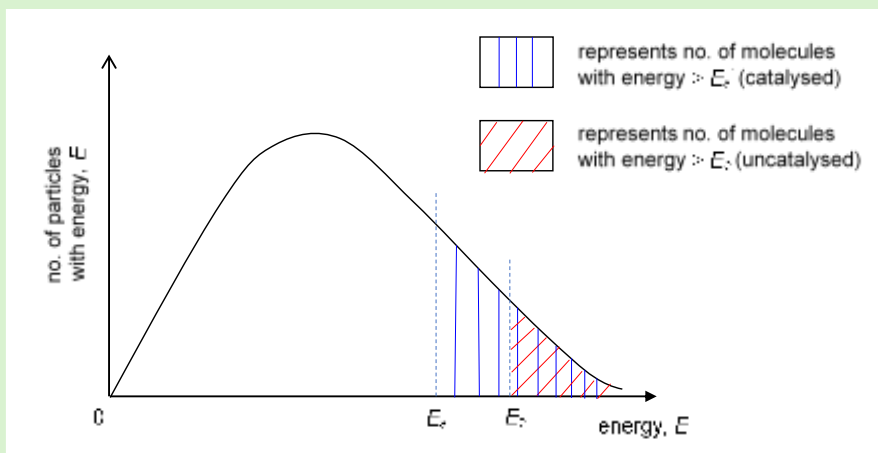
ON of Cl in ClO_2^- : +3

ON all correct :[1]

This is a disproportionation reaction [1] as chlorine undergo reduction and oxidation at the same time.

- (b) The reaction between chlorine dioxide and hydroxide ions can be influenced by the presence of $\text{Fe}^{2+}(\text{aq})$ catalyst.

Explain, with the aid of a labelled Boltzmann distribution diagram, the effect of the use of $\text{Fe}^{2+}(\text{aq})$ on the rate constant. [3]



[1]

- In the presence of a Fe^{2+} catalyst at a certain temperature T , the reaction proceeds via an alternative pathway which has lower activation energy ($E_a' < E_a$).
- As shown on the diagram, more molecules have energies greater than or equal to the lowered activation energy E_a' . [1]
- This results in an increase in the frequency of effective collisions.
- The rate constant, k , increases. [1]

(c) **R**, **S** and **T** are oxides of Period 3 elements which are solids at room temperature.

R, **S**, and **T** are added to excess cold water, HCl(aq) and NaOH(aq) separately at room temperature. Table 5.1 shows the observation and reactions.

Table 5.1

	Observation on addition to water	Reaction with HCl(aq)	Reaction with NaOH(aq)
R	White solid did not dissolve.	Reacts to form salt.	Reacts to form complex ions.
S	Some white solid remain undissolved.	Reacts to form salt.	No reaction.
T	All white solid dissolved.	No salt formed.	Reacts to form salt.

Using Table 5.1, identify **R**, **S** and **T**. State the pH of the solution when each of the oxide is added to water. [3]

	Observations on addition of sample to water	Reaction with HCl	Reaction with NaOH	pH of solution	Identity of sample
R	White solid did not dissolve at all.	Reacts to form salt.	Reacts to form complex ions.	7 ✓	Al_2O_3 ✓
S	Some white solid remain undissolved.	Reacts to form salt.	No reaction.	10 ✓	MgO ✓
T	All of the white solid dissolved.	No salt formed.	Reacts to form salt.	2 ✓	P_4O_{10} ✓

6 ✓ → [3] 4 to 5 ✓ → [2] 2 to 3 ✓ → [1] 0 to 1 ✓ → No marks

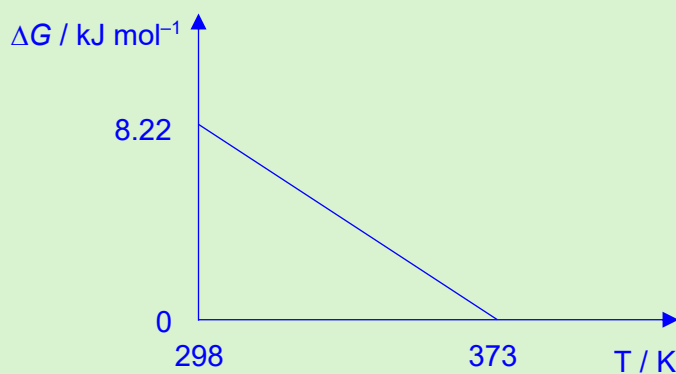
- (d) The evaporation of one mole of pure water has a standard entropy change of $\Delta S^\ominus = +110 \text{ J mol}^{-1}$ at 298 K.

- (i) Given that the standard enthalpy change for the evaporation of one mole of pure water, $\Delta H^\ominus = +41.0 \text{ kJ mol}^{-1}$, calculate the ΔG^\ominus in kJ mol^{-1} at 298 K. [1]

$$\begin{aligned}\Delta G^\ominus &= \Delta H^\ominus - T\Delta S^\ominus \\ \Delta G^\ominus &= +41.0 - 298\left(\frac{+110}{1000}\right) \\ &= \underline{+8.22 \text{ kJ mol}^{-1}} \quad [1]\end{aligned}$$

- (ii) State the ΔG of water at 373 K and sketch a clearly labelled graph of ΔG , on the y-axis, against temperature measured in Kelvin, on the x-axis, to show how ΔG changes for the evaporation process when temperature increases from 298 K to 373 K. [1]

Water boils at 373 K $\therefore \underline{\Delta G = 0 \text{ kJ mol}^{-1}}$ as an equilibrium is established between liquid water and gaseous water vapour.



[1]: well labelled sketch showing a decreasing straight line with constant gradient (from 298 K to 373 K)

- (iii) Comment on the gradient of your graph and explain how temperature affects the spontaneity of the evaporation process. [2]

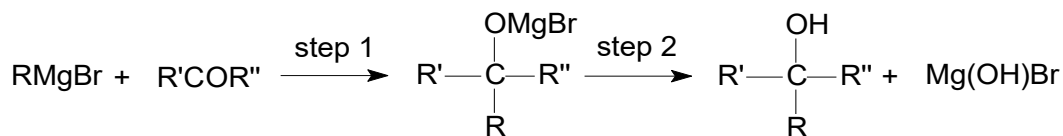
As observed from the sketch,

- gradient is negative because $\text{gradient} = -\Delta S$ and ΔS for evaporation is positive (as number of ways to arrange the particles increases during a phase change from liquid to gas).
- ΔG becomes more negative / less positive as the temperature increases. Hence, the evaporation process becomes more spontaneous.

[1]: recognise that the gradient is negative ($\text{gradient} = -\Delta S$) and infer the positive ΔS to the increase in entropy as liquid water is converted to water vapour at 373 K

[1]: use the sketch or sign of ΔH and ΔS to conclude the effect of changing T on ΔG and hence spontaneity of the process

- (e) Grignard reagents, RMgBr , are excellent carbon-based nucleophiles as well as strong bases. They can add to aldehydes and ketones to form alcohols. A typical example of the use of Grignard reagent is the two-step reaction of RMgBr with a carbonyl compound to form an alcohol.



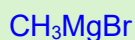
where R = alkyl, R' and R'' = alkyl group or H .

- (i) State the type of reaction in step 1. [1]

Nucleophilic addition [1]

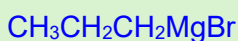
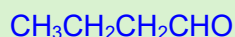
- (ii) Suggest the identity of the Grignard reagent and aldehyde that is needed to form pentan-2-ol. [1]

Grignard reagent

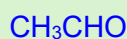


&

aldehyde



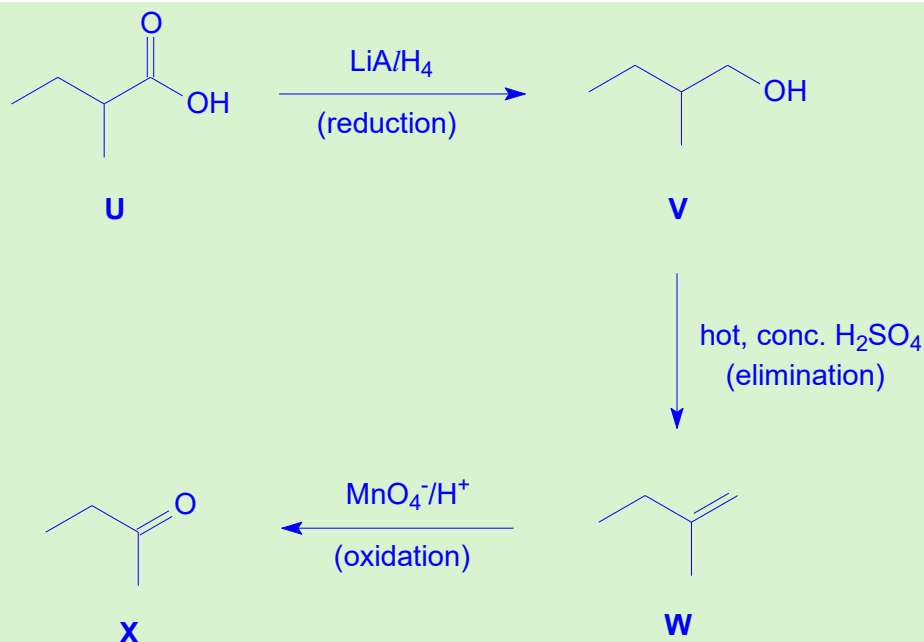
&



[1] for either pair of Grignard reagent and aldehyde

- (iii) The Grignard reagent $\text{C}_2\text{H}_5\text{CH}(\text{CH}_3)\text{MgBr}$ can be converted into carboxylic acid **U** by using carbon dioxide. When **U** reacted with LiAlH_4 , **V** is produced. **W** is produced when **V** is reacted with hot concentrated sulfuric acid. When hot acidified potassium manganate(VII) is added, **X** is formed. **X** forms a yellow precipitate when reacted with alkaline aqueous iodine.

Suggest the structural formulae of **U**, **V**, **W** and **X**. [4]



[1] each structure

[Total: 20]