

Answer Scheme Paper 3

Section A

- 1 Nitrogen, a Period 2 element, forms a wide variety of compounds with diverse structures, oxidation states, and properties. These include ammonia, ammonium salts, amines, and nitrates, all of which play important roles in industry, agriculture, and the environment.

(a) The enthalpy changes involved in the formation of ionic and covalent compounds vary across the period.

- (i) Explain why the first ionisation energy of nitrogen is more endothermic than that of carbon and oxygen. [2]



Comparing C and N:

N has a higher nuclear charge, while the shielding effect caused by inner shell electrons remains approximately constant. Therefore, it has a smaller atomic radius, and valence electrons experience a stronger nuclear attraction. Consequently, N has a higher first ionisation energy compared to C.

Comparing N and O:

Less energy is required to remove one of the paired 3p electrons in oxygen due to the larger interelectronic repulsion. Thus, O has a lower first ionisation energy than N.

- (ii) Some Period 3 elements can react with chlorine to produce chlorides, for example, NaCl and SiCl₄.

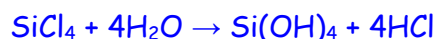
Describe and explain what happens when NaCl and SiCl₄ are separately added to excess water. State the pH of the resultant mixtures and give relevant equations. [3]

NaCl is an ionic chloride and will dissolve/hydrate in water to form a solution of pH 7.



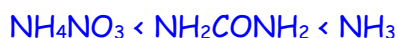
SiCl₄ is a covalent chloride and has energetically accessible vacant 3d orbitals that allow the water molecule to form dative bonds.

Thus SiCl₄ hydrolyse in water to form an acidic solution of pH 1-2.



- 1 (b) Ammonia (NH_3), ammonium nitrate (NH_4NO_3), and ethanamide (CH_3CONH_2) are important compounds that can be used as fertilisers due to their high nitrogen content.

Arrange these three compounds in order of increasing pH value of their aqueous solution. Explain your answer. [3]



NH_4NO_3 will dissociate into NH_4^+ and NO_3^- ions in solution. NH_4^+ will undergo hydrolysis to produce H^+ ions, forming an acidic solution. Thus, the pH value of NH_4NO_3 solution is less than 7.

NH_3 will be basic due to the availability of lone pair electrons on N for protonation. Thus, the pH value of the solutions will be higher than 7.

CH_3CONH_2 will be neutral due to the delocalisation of the lone pair of electrons on N into the neighbouring π electron cloud of the electron-withdrawing C=O group, the lone pair of electrons in urea is not available for protonation than NH_3 . Thus, it is a weaker base compared to NH_3 , hence, lower pH value.

- (c) Aqueous iron(III) nitrate, $\text{Fe}(\text{NO}_3)_3(\text{aq})$, is yellow in colour.

- (i) Explain why the solution of iron(III) nitrate is yellow in colour. [3]

The presence of ligands cause the d orbitals to split into 2 different energy levels with a small energy gap, ΔE , that corresponds to the visible light region of the electromagnetic spectrum.

Visible light is absorbed when an electron transits from a lower energy d orbital to a higher energy d orbital which is unfilled or partially filled.

Hence, the colour observed is the complement of the colours absorbed.

- (ii) Using data from the *Data Booklet*, predict what will be observed when aqueous iron(III) nitrate is added to potassium iodide, KI, giving a balanced equation for the reaction that occurs. [3]

From Data Booklet:



$$\begin{aligned} E_{\text{cell}}^{\ominus} &= (+0.77) - (+0.54) \\ &= +0.23 \text{ V} > 0 \text{ (reaction is energetically feasible)} \end{aligned}$$

Obs: Yellow solution of Fe^{3+} turn pale green and brown solution of I_2 formed



- (iii) A sample of $\text{Fe}(\text{NO}_3)_3(\text{aq})$ was added to aqueous sodium hydroxide. A red-brown precipitate formed immediately and remained unchanged upon standing.

When a solution of $\text{SCN}^-(\text{aq})$ is added to the resulting precipitate, the precipitate dissolves and blood red solution of $[\text{Fe}(\text{SCN})(\text{H}_2\text{O})_5]^{2+}$ complex is formed. The formation of the blood red complex is non-reversible.

Explain the above observations and include relevant equations.

[3]

Fe^{3+} reacts with OH^- to form red-brown precipitate of $\text{Fe}(\text{OH})_3$



When SCN^- is added, a ligand exchange reaction occurs. The stronger SCN^- ligand replaces the weaker H_2O ligand to form a stronger dative bond and a more stable complex.



The precipitate in the solution is sparingly soluble.

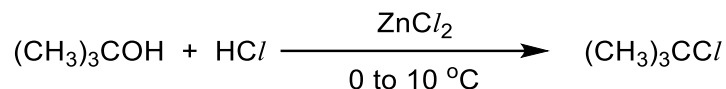


This decreases concentration of Fe^{3+} in the solution, causing position of equilibrium (1) to shift left and thus precipitate dissolves.

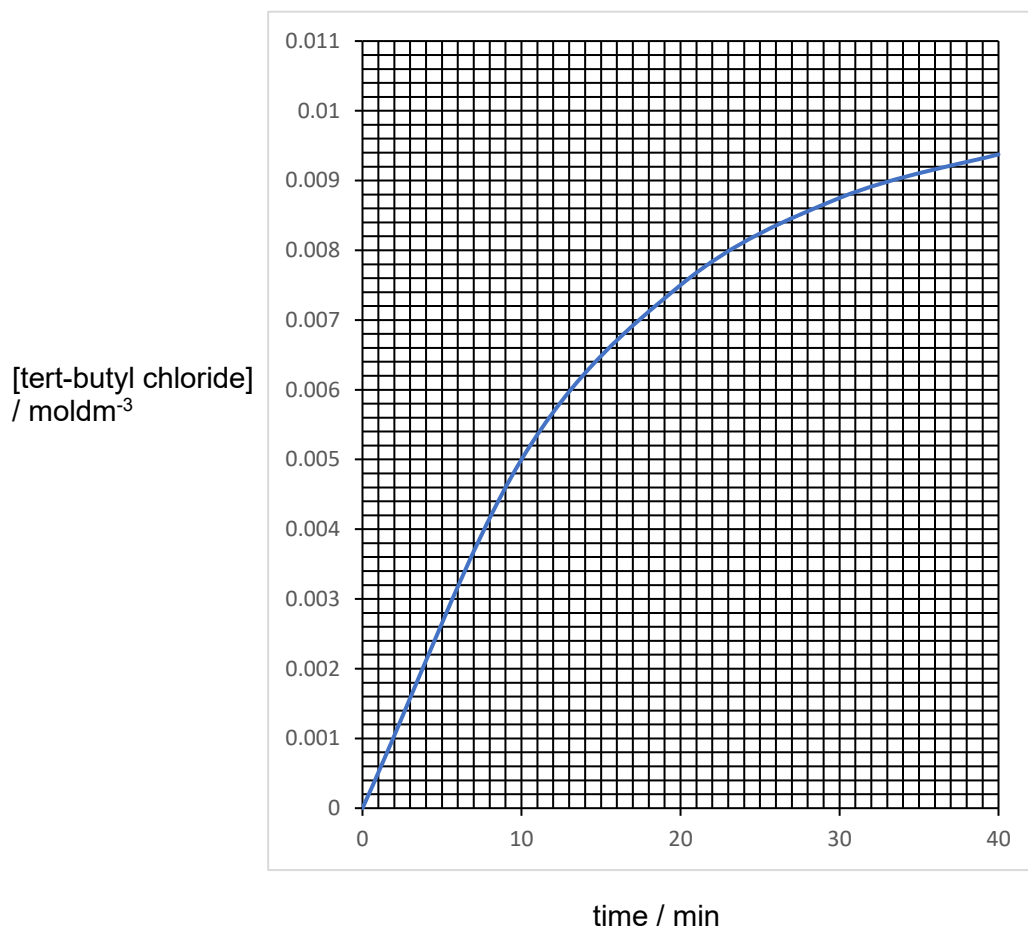
[Total: 17]

- 2 Lucas Test, named after an American chemist, Howard Luca, is a simple qualitative test, using concentrated HCl in the presence of ZnCl_2 , to classify alcohols by observing the rate of turbidity, indicating the formation of insoluble alkyl halides.

(a) The rate of the Lucas Test is investigated, using tert-butanol, $(\text{CH}_3)_3\text{COH}$.



When 1 dm^3 of 0.0100 mol of tert-butanol is reacted with 5.00 mol of HCl in the presence of ZnCl_2 , the concentration of tert-butyl chloride, $(\text{CH}_3)_3\text{CCl}$, formed over time is shown in the graph below.



- (a) (i) Define the term *order of reaction*.

[1]

order of reaction with respect to a reactant is the power to which the concentration of the reactant is raised to in the rate equation

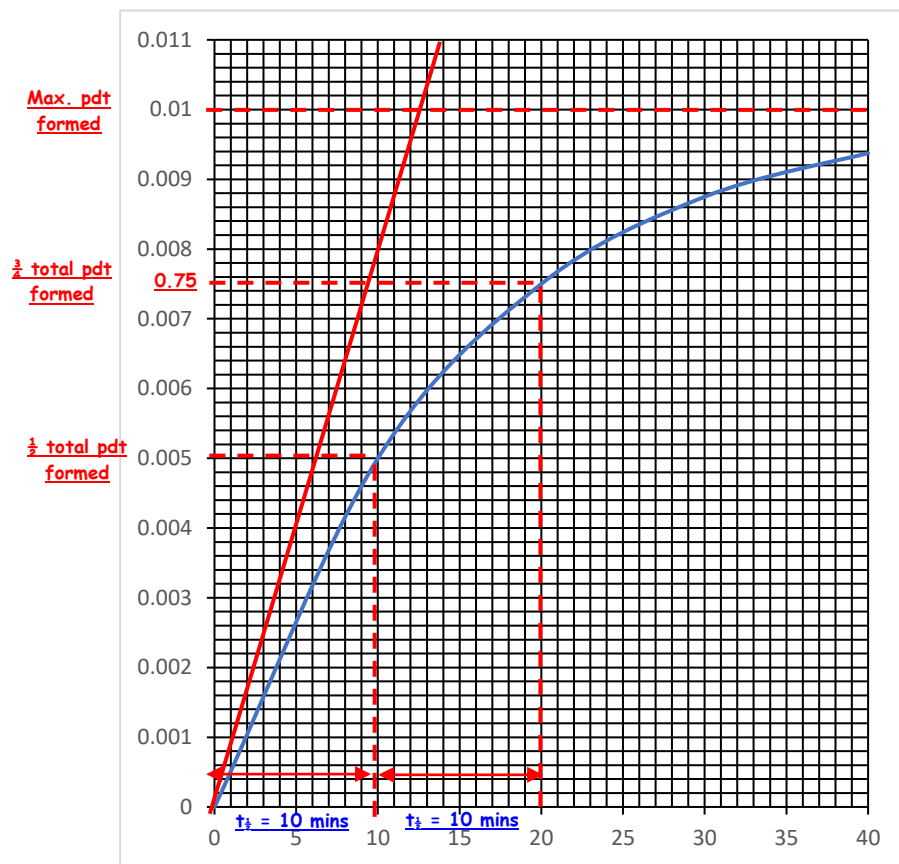
OR

In an experimentally determined rate equation: $\text{rate} = k[\text{A}]^m[\text{B}]^n$ where A and B are the reactants, the orders of reaction with respect to [A] and [B] are m and n respectively

- (ii) The same graph was obtained when the test was repeated with 7.5 mol of HCl.

Using the information provided and the graph, deduce the orders with respect to $(\text{CH}_3)_3\text{COH}$ and HCl. Show clearly your working and any construction lines on the graph.

[3]



Since $1^{\text{st}} t_{\frac{1}{2}} = 2^{\text{nd}} t_{\frac{1}{2}} = 10$ mins, the half life of the reaction is (approximately) constant. The reaction is 1^{st} order w.r.t $(\text{CH}_3)_3\text{COH}$ and When concentration of HCl is increased by 1.5 times/changed, the rate of reaction remains the same, thus, the reaction is 0 order w.r.t HCl.

- (iii) Hence, write the rate equation for the Lucas Test, and calculate a value for the rate constant. Include units in your answer.

[3]

$$\text{Rate} = k[(\text{CH}_3)_3\text{COH}]$$

Since it is a overall first order reaction

$$k = \ln 2 / t_{\frac{1}{2}} = \ln 2 / 10 = \underline{0.0693 \text{ min}^{-1}}$$

OR

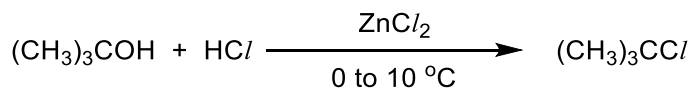
Initial rate method:

y-intercept at 16 mins

$$\text{Initial rate} = 0.011 / 16 = 0.000688 \text{ mol dm}^{-3} \text{ min}^{-1}$$

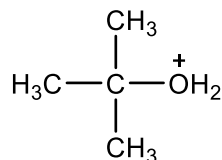
$$K = 0.000688 / 0.01 \\ = \underline{0.0688 \text{ min}^{-1}}$$

2 (b)



The Lucas Test, as shown above, follows a nucleophilic substitution reaction mechanism as follows:

- Tert-butanol reacts with HCl to generate the following reaction intermediate in the first step.



- This intermediate subsequently loses water to form a carbocation, which reacts further to form the product, tert-butyl chloride.
- HCl is acting as a Lewis acid in the first step and as a source for *nucleophile* in the subsequent steps.

(i) Define the term, *nucleophile*.

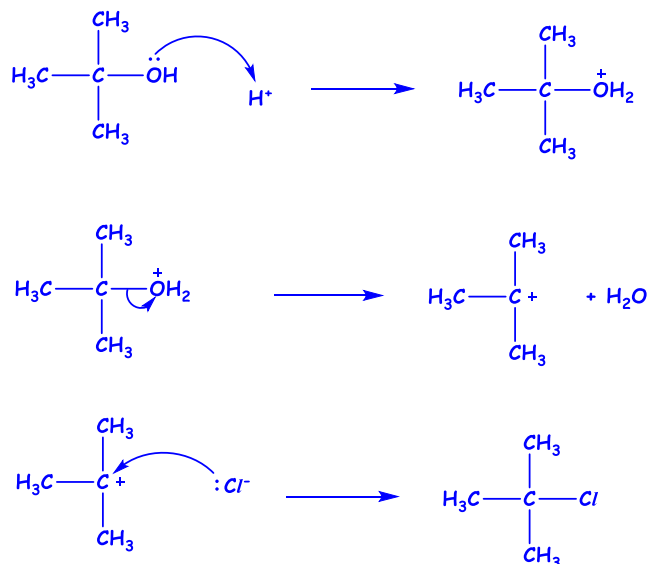
[1]

Nucleophile is defined as electron-rich species that can donate an electron pair.

(ii) Use the data and information given above, draw the mechanism for the Lucas Test.

Show all relevant curly arrows, charges and structure of the intermediates. Include an equation for the formation of the reaction intermediate.

[3]



(iii) Suggest two reasons why the reaction between $(\text{CH}_3)_3\text{COH}$ and concentrated HCl follows a $\text{S}_{\text{N}}1$ mechanism rather than a $\text{S}_{\text{N}}2$ mechanism.

[2]

- $\text{S}_{\text{N}}1$ is preferred because the tertiary carbocation intermediate, $(\text{CH}_3)_3\text{C}^+$ formed has three electron-donating alkyl groups that disperse the positive charge to a larger extent and stabilise it.
- $\text{S}_{\text{N}}2$ is not preferred because the presence of 3 bulky alkyl groups prevents the backside approach of the nucleophile, resulting in steric hindrance.

(c) ZnCl_2 is a *Lewis acid* and functions as a catalyst for the Lucas Test.

FeCl_3 is a stronger *Lewis acid* compared to ZnCl_2 . However, it causes multiple side reactions to occur and is thus not preferred.

(i) Define the term *Lewis acid*.

[1]

A *Lewis acid* is an electron pair acceptor.

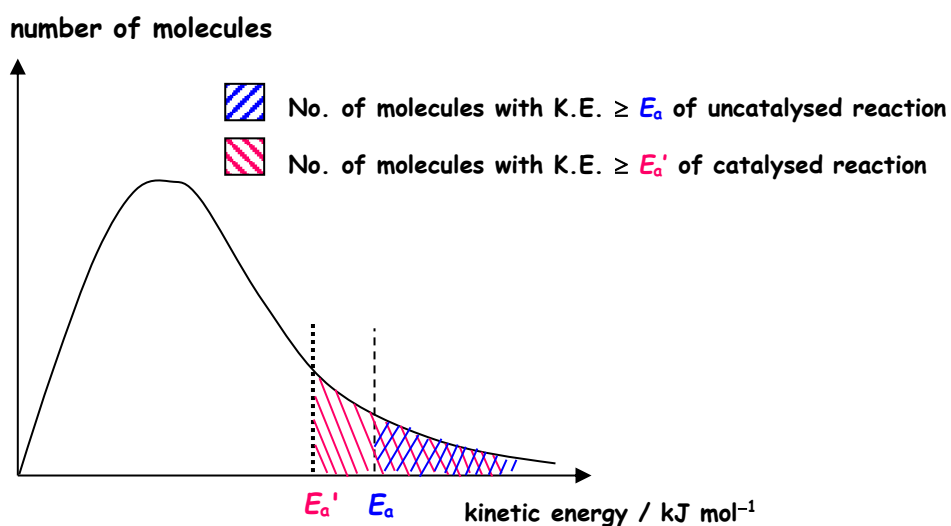
(ii) By considering the electronic configuration of Zn^{2+} and Fe^{3+} , suggest two reasons why FeCl_3 is a stronger *Lewis acid* compared to ZnCl_2 .

[2]

- Fe^{3+} ions have a higher charge and a smaller radius compared to Zn^{2+} ions. As such, the Fe^{3+} ion is more likely to attract an electron pair and behaves as a stronger *Lewis acid*.
- Fe^{3+} ion has available low-lying 3d orbitals which easier to accept an electron pair. Zn^{2+} ion has fully filled 3d orbitals. The next available orbital is 4s, which has a higher energy level and is less accessible.

(iii) Explain, with the aid of an appropriate diagram, how ZnCl_2 increases the rate of the Lucas Test.

[3]



A catalyst provides an alternative reaction pathway with lowered activation energy.

When catalyst is used, the proportion of molecules possessing energy greater or equal to the lowered activation energy increases.

Frequency of effective collision increases, rate increases.

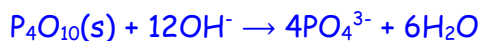
[Total: 19]

- 3 (a) Describe the variation in the acid-base behaviour of Al_2O_3 and P_4O_{10} by reference to their reactions with H_2SO_4 and NaOH respectively.

Write equations for any reactions described.

[3]

Both Al_2O_3 and P_4O_{10} can act as acidic oxide and react with NaOH .

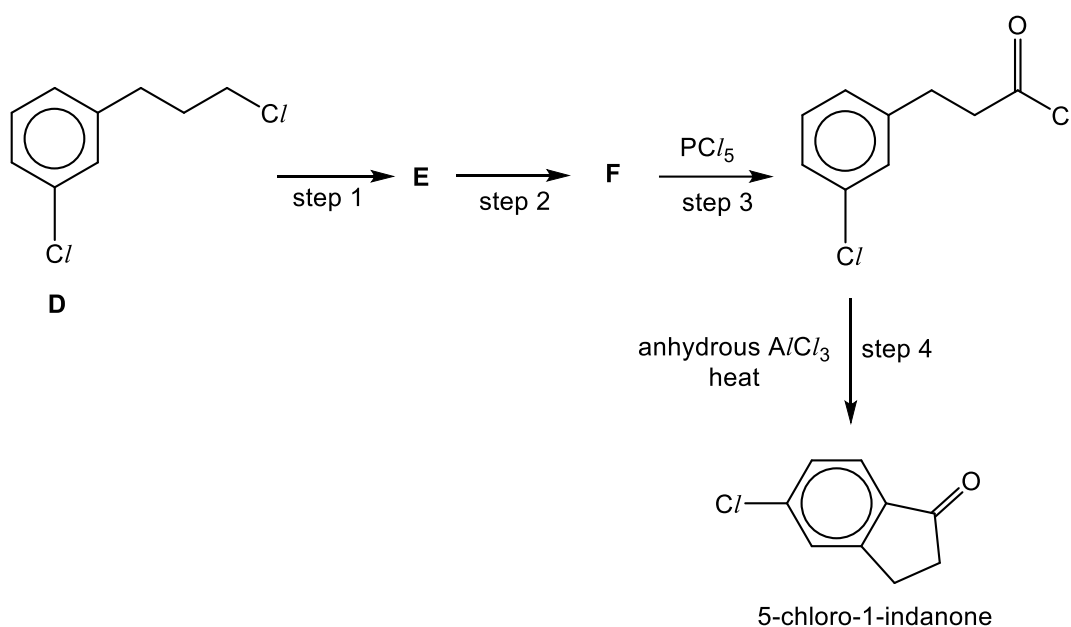


However, only Al_2O_3 can act as basic oxide to react with H_2SO_4 , but P_4O_{10} cannot.



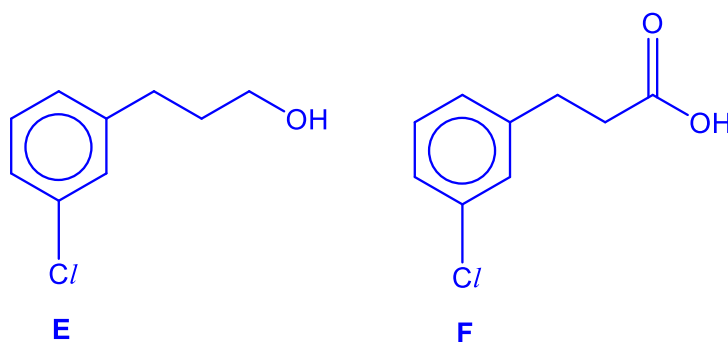
- (b) 5-chloro-1-indanone is mainly used as a chemical intermediate in pharmaceuticals, agrochemicals, and material sciences. It serves as a building block for drugs, pesticides like indoxacarb, and advanced materials such as fluorescent dyes.

5-chloro-1-indanone can be synthesised from compound D as shown below.



- (i) Deduce the structures of organic product **E** and **F**.

[2]



- (ii) Suggest reagents for step 1 and for step 2.

[2]

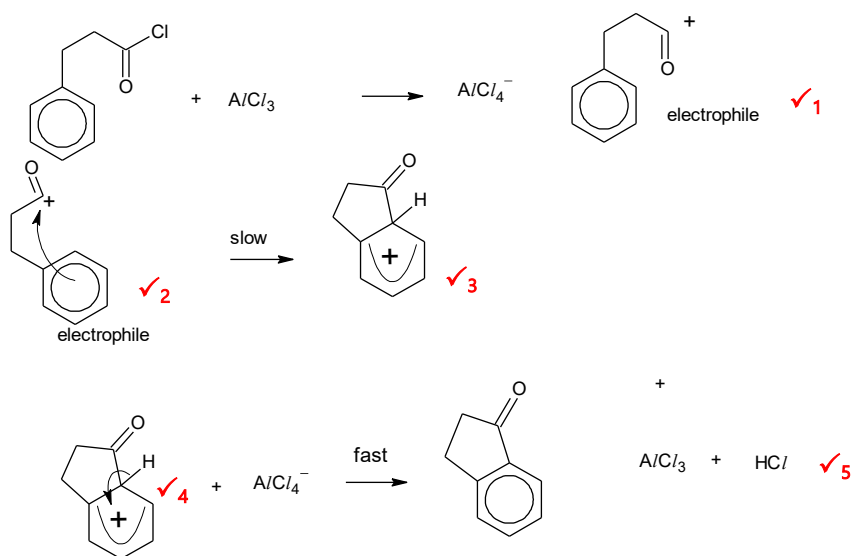
Step 1: $\text{NaOH}(\text{aq})$, heat

Step 2: acidified $\text{K}_2\text{Cr}_2\text{O}_7$, heat

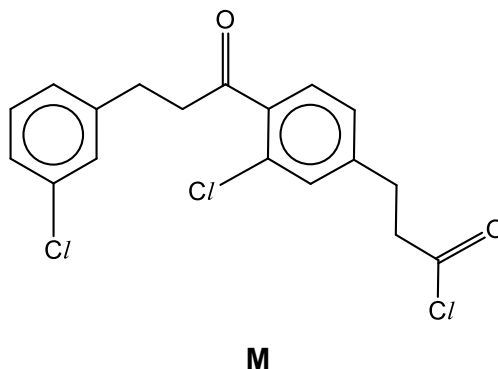
(iii) Name and describe the reaction mechanism for Step 4.

[3]

Electrophilic substitution [1]



(iv) In step 4, another by-product **M** can be formed.



By considering the structure of the starting reactant and the overall entropy change of the reaction, explain **two** reasons why the formation of 5-chloro-1-indanone is preferred over **M**.

[2]

1. Intramolecular reaction is faster and favoured due to the close proximity of the acyl chloride and aromatic ring.
2. Intramolecular reaction increases the number of molecules ($\Delta S > 0$), whereas intermolecular reaction does not, making the former more favoured.

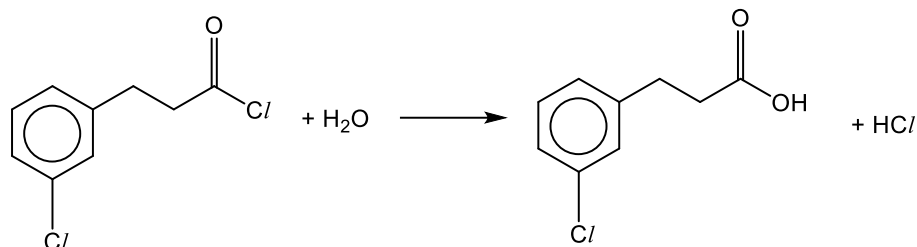
(v) In Step 4, anhydrous AlCl_3 must be used, and no water can be introduced. With the aid of appropriate equations, explain why this is so.

[1]

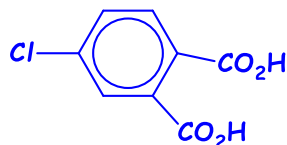
The catalyst AlCl_3 will hydrolyse in water, and cannot generate the +ve charged electrophile for the reaction.



OR Acyl chloride will hydrolyse in water to form carboxylic acid, thus, no longer can form the +ve charged electrophile for the reaction.



- (vi) When 5-chloro-1-indanone is oxidised with acidified KMnO_4 , CO_2 is evolved as a side product. Suggest the structure of the organic product formed. [1]



- (c) Compound **G**, $\text{C}_5\text{H}_9\text{NO}_3$, is a neutral compound that contains 2 chiral centres.

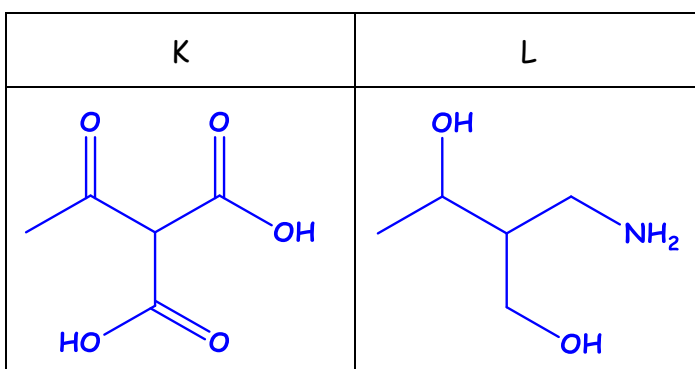
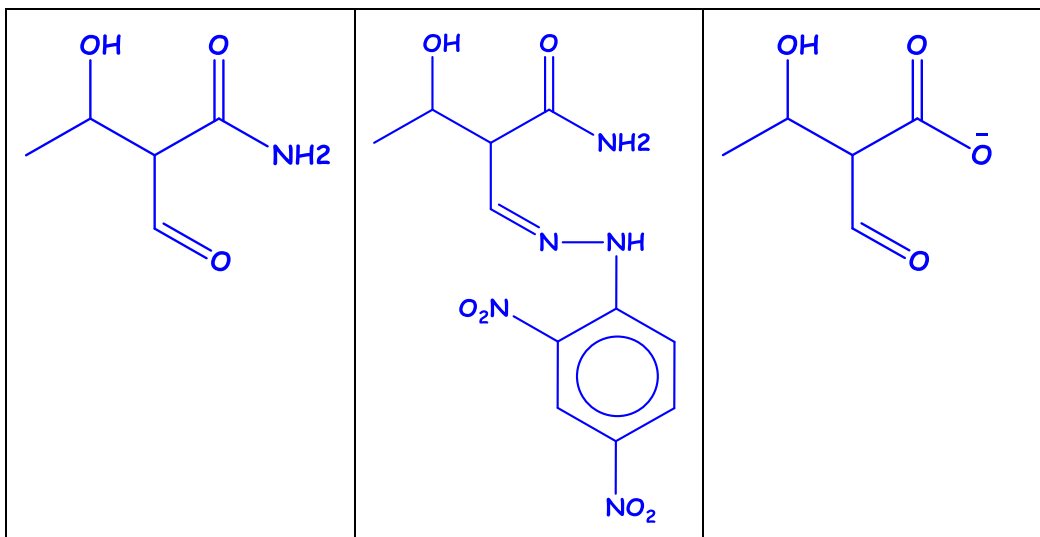
Samples of compound **G** are reacted separately with

- NaOH(aq) and heat to form product **H** and a pungent gas
- 2,4-DNPH forming an orange precipitate **J**, $\text{C}_{11}\text{H}_{13}\text{N}_5\text{O}_6$
- Fehling's reagent to form a brick red precipitate
- Alkaline aqueous iodine and heat forming a yellow precipitate
- $\text{K}_2\text{Cr}_2\text{O}_7$ in the presence of sulfuric acid and heat to form an organic compound, **K**, $\text{C}_5\text{H}_6\text{O}_5$.
- An excess of LiAlH_4 forming an organic compound **L**, $\text{C}_5\text{H}_{13}\text{NO}_2$

Deduce the structures for **G**, **H**, **J**, **K** and **L**, explaining the reactions described. [10]

Observation	Type of reaction	FGs
G is neutral	-	G contains amide
G + $\text{NaOH(aq)} \rightarrow \text{H}$ and pungent gas	Alkaline hydrolysis	G contains primary amide
G + 2,4-DNPH \rightarrow orange ppt J	Condensation	G contains aldehyde or ketone
G + alkaline $\text{I}_2\text{(aq)} \rightarrow$	Oxidation / positive iodoform test	G contains either
G + Fehling reagent \rightarrow brick red ppt	Oxidation	G contains aliphatic aldehyde
G + $\text{K}_2\text{Cr}_2\text{O}_7 \rightarrow \text{K}$	Oxidation Acid hydrolysis	K contains carboxylic acid G contains aldehyde G contains alcohol
G + $\text{LiAlH}_4 \rightarrow \text{L}$	Reduction	L contains amine G contains amide

G	J	H
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[Total: 24]

Answer one question from this section.

- 4 Aluminium-air batteries are used as back-up power supplies in many telephone exchanges. The structure of one such battery is shown in **Fig 4.1** below.

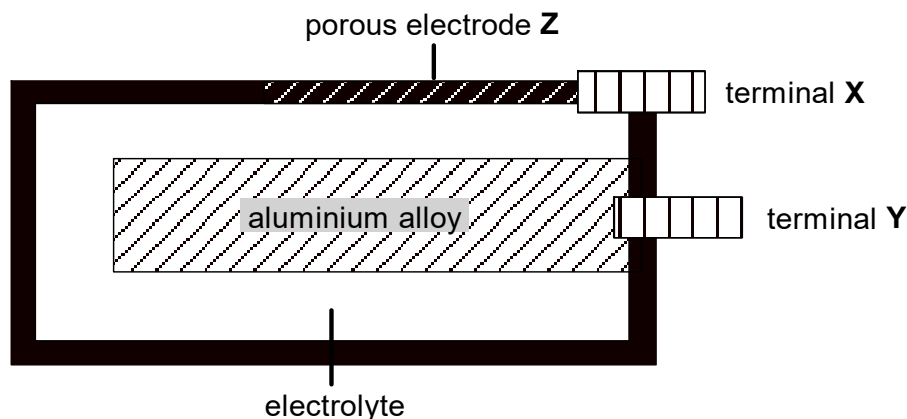
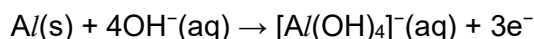


Fig 4.1

The electrolyte used is aqueous potassium hydroxide. During discharge, oxygen in air is reduced while aluminium is oxidised as shown by the following equation:

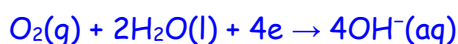


- (a) (i) State, with a reason, the polarity of terminal Y. [1]

Terminal Y is connected to the aluminium alloy and electrons are being produced when aluminium is oxidised.

Hence, terminal Y is negative.

- (ii) Write a balanced equation with state symbols for the reaction that takes place at the porous electrode Z. [1]



- (iii) State why electrode Z must be porous. [1]

To allow $\text{O}_2(\text{g})$ to diffuse through and interact with the electrolyte to be reduced.

- (iv) In this battery, aluminium may be replaced by zinc.

Using data from the *Data Booklet*, suggest an advantage of using aluminium rather than zinc. [1]

- $E(\text{Al}^{3+}/\text{Al})$ is more negative than $E(\text{Zn}^{2+}/\text{Zn})$ so the operating voltage of the battery is higher. OR
- Al produces more electrons per mol of metal, so more electrons/electricity can be produced for the same mass of metal used.

- 4 (a) (v) When aqueous potassium hydroxide is replaced by aqueous sodium chloride, it is noticed that white $\text{Al}(\text{OH})_3$ solid is formed around the aluminium electrode instead.

Explain why it is formed.

[1]

There is insufficient hydroxide ions formed from the reduction of oxygen to form the soluble complex ion.

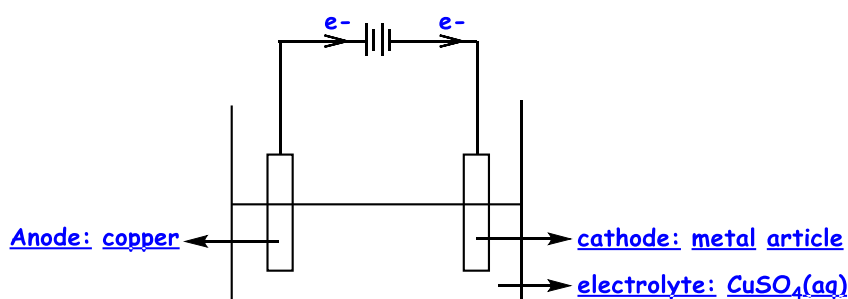
- (b) The aluminium-air battery was used as an electrical source to electroplate an article with copper.

- (i) Draw a labelled diagram of an electrolytic cell setup to show how an article can be electroplated with copper.

In your diagram, state clearly the choice of anode, cathode, electrolyte to be used and the direction of electron flow.

You may use the standard battery symbol $\text{---}||\text{---}$ to represent the aluminium-air battery in your diagram.

[2]



- (ii) If the mass of aluminium electrode in the aluminium-air battery as described earlier in (a) decreased by 5.4 g, calculate the mass of copper that was deposited on the article.

[2]

$$\text{amount of Al reacted} = \frac{5.4}{27.0} = 0.200 \text{ mol}$$

$$\text{amount of electrons formed} = 3 \times 0.200 = 0.600 \text{ mol}$$

Since $\text{Cu} \equiv 2e$

$$\text{amount of Cu formed} = \frac{1}{2} \times 0.600 = 0.300 \text{ mol}$$

$$\therefore \text{mass of Cu formed} = 0.300 \times 63.5 = 19.1 \text{ g}$$

- (iii) The electroplating process took 468 min.

Calculate the current delivered by the aluminium-air battery.

[1]

Using $Q = It = nF$

$$I(468 \times 60) = (0.600)(96500)$$

$$I = 2.06 \text{ A}$$

- (iv) In some batteries, graphite can be used as electrodes.

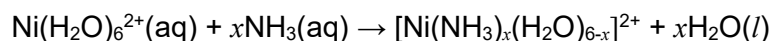
Describe and explain, in terms of structure and bonding, how graphite can serve this role.

[2]

Graphite has a giant covalent structure, with each C atom is covalently bonded to 3 other atoms with delocalised electrons along/within the layers over the structure.

Graphite can conduct electricity due to the presence of mobile delocalised electrons.

- (c) A ligand exchange reaction occurs when aqueous ammonia is added to a solution of green $\text{Ni}^{2+}(\text{aq})$.



The formula of a nickel-ammonia complex that is blue in colour can be found using a colorimeter.

Eleven tubes containing 20 cm^3 of 0.05 mol dm^{-3} of $\text{Ni}^{2+}(\text{aq})$ had 0.4 mol dm^{-3} aqueous ammonia added. The first tube has 2 cm^3 of aqueous ammonia added, the second tube 4 cm^3 and so on. Distilled water was added to bring the total volume to 50 cm^3 .

Each tube was then placed in a calorimeter and the absorbance recorded. The absorbance intensity is proportional to the concentration of the complex.

The results are shown in Fig 4.1 below.

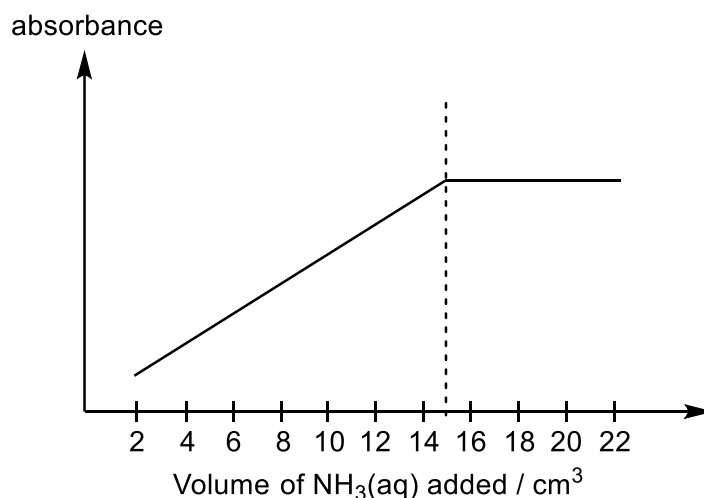


Fig 4.2

- (i) Explain why the absorbance value in **Fig 4.2** remains constant after 15 cm^3 of $\text{NH}_3(\text{aq})$ is added.

[1]

All the $\text{Ni}^{2+}(\text{aq})$ present in the sample has been completely reacted and thus no more complex will be formed. As such, amount/concentration of the complex remains a constant and thus the graph shows no change in absorbance.

- (ii) Deduce the formula of the complex based on the stoichiometry information that could be inferred from the graph. [2]

$$\begin{aligned}\text{amount of Ni}^{2+} \text{ in each test tube} &= \frac{20}{1000} \times 0.05 \\ &= 1.00 \times 10^{-3} \text{ mol}\end{aligned}$$

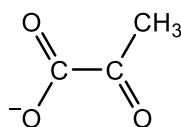
$$\begin{aligned}\text{amount of NH}_3 \text{ at } 15 \text{ cm}^3 &= \frac{15}{1000} \times 0.4 \\ &= 6.00 \times 10^{-3} \text{ mol}\end{aligned}$$

$$\text{mol ratio of Ni}^{2+} \text{ to NH}_3 = 1.00 \times 10^{-3} : 6.00 \times 10^{-3} = 1 : 6$$

$$\therefore x = 6$$

Formula of the complex is $[\text{Ni}(\text{NH}_3)_6]^{2+}$

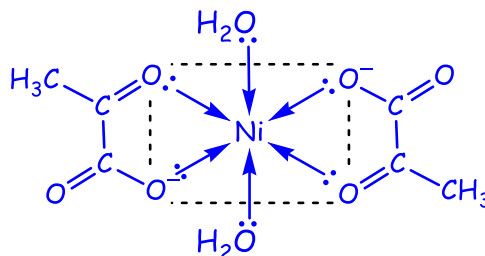
- (iii)



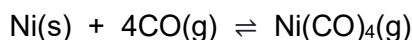
ligand **Z**

Z is a bidentate ligand, and experiments show that two mole of **Z** react with each mole of $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ to form an octahedral complex.

Given that the complex has no dipole moment, draw the structure of the complex formed, showing the 3-dimensional arrangement around the nickel ion. Indicate the overall charge, if any, on this complex. [2]



- (d) Nickel (Ni) readily forms a tetracarbonyl complex, $\text{Ni}(\text{CO})_4$, where four carbon monoxide (CO) molecules act as ligands.



- (i) State two physical properties of nickel, apart from the colour of the metal, in which it differs from calcium. Explain the reasons for those differences. [2]

The melting point of Ni is higher compared to that of Ca. As compared to Ca, more energy is required to overcome the stronger metallic bonds between the Ni^{2+} ions and the sea of delocalised electrons, since both 3d and 4s electrons are involved in the metallic bonding.

The density of Ni is higher compared to that of Ca, because Ni has a smaller atomic radius (or cationic radius) and a larger A_r than Ca. Since density is the mass per unit volume, assuming that the atoms are spherical in shape, Ni will have a higher density as compared to

Ca. In addition, having a smaller atomic radius also means that its structure is more closely packed.

- (ii) Explain why carbon monoxide, CO, is poisonous. [1]

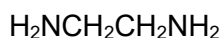
Stronger CO ligand displaces the weaker O₂ ligand by forming a stronger dative bond with Fe²⁺ in the haem group of haemoglobin to give a more stable complex.

This results in the inability of haemoglobin to transport oxygen to the cells and thus accounts for the toxic nature of CO.

[Total: 20]

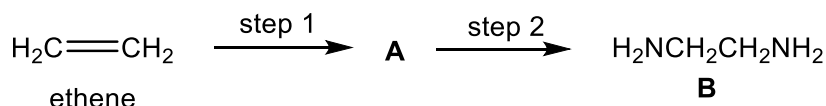
- 5 Cobalt is a brittle and hard transition metal with magnetic properties similar to those of iron. One of the characteristic properties of transition metals is their ability to form complexes.

- (a) The compound **B** can act as a *bidentate ligand* can form a complex with Co^{3+} ions in the mole ratio 3:1.



B

Compound B can be made using ethene and appropriate inorganic reagents by the following 2-step synthesis.



- (i) What can be understood by the term *bidentate ligand*? [1]

Bidentate ligand is a ligand that contain two groups that have a lone pair of electrons each that can form two dative bonds to the central metal cation.

- (ii) Suggest the structure of compound L and the reagents and conditions for Step 1 and 2. [3]

Structure of L: $\text{BrCH}_2\text{CH}_2\text{Br}$

Step 1: $\text{Br}_2(\text{l})$

Step 2: excess NH_3 , ethanol, heat in sealed tube

- (iii) State the coordination number of the cobalt(III) complex. [1]

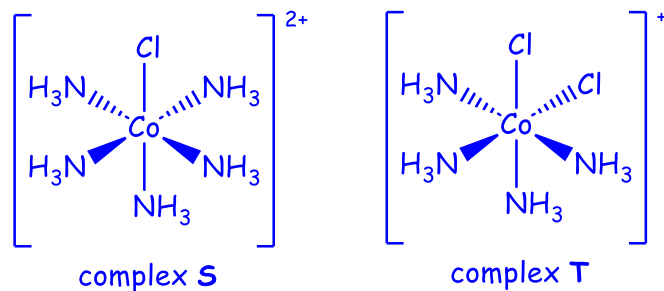
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- (b) Two different complexes can be obtained by reacting aqueous cobalt(III) chloride with ammonia under various conditions.

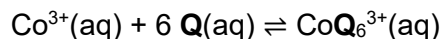
Different proportions of chloride are precipitated when each of the complexes is treated with aqueous silver nitrate.

complex	empirical formula	No. of moles of AgCl precipitated per mole of complex	Does the complex have a dipole moment?
S	$\text{CoCl}_3(\text{NH}_3)_5$	2	yes
T	$\text{CoCl}_3(\text{NH}_3)_4$	1	yes

Suggest the structures of complexes S and T, showing clearly the three dimensional arrangement of the ligands around the metal ion center. [2]



- (c) When an aqueous solution of the ligand **Q** is mixed with an aqueous solution of cobalt salt, the following equilibrium is set up:



A similar equilibrium occurs with the ligand **R**, forming $\text{CoR}_6^{3+}(\text{aq})$.

Solutions **X**, **Y** and **Z** were made by mixing 0.1 mol dm^{-3} solutions of Co^{3+} , **Q** and **R**. The table below gives the volumes of each used.

Solution	Volumes of 0.1 mol dm^{-3} solution / cm^3		
	$\text{Co}^{3+}(\text{aq})$	Q (aq)	R (aq)
X	4	96	0
Y	4	0	96
Z	4	48	48

The visible absorption spectra of the three solutions **X**, **Y** and **Z** are shown below:

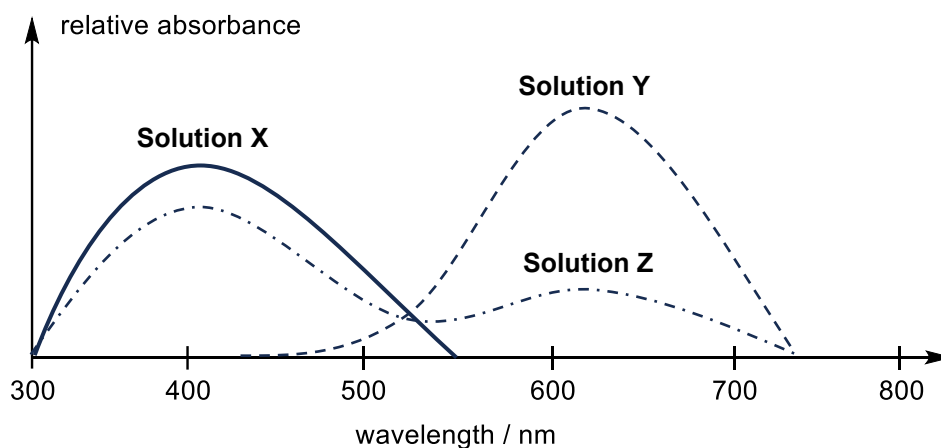


Fig 5.1

The wavelength at which the maximum absorbance is observed is inversely proportional to the energy gap between the two sets of d orbitals in an octahedral complex.

- (i) The spectra show that the peak in the curve for solution **Y** is at a longer wavelength than is the peak in the curve for solution **X**.

What deduction can be made from this fact about the size of the d-orbital splitting in the two complexes?

[1]

The size of the d-orbital splitting in $\text{CoQ}_6^{3+}(\text{aq})$ is larger than that in CoR_6^{2+} .

- 5 (c) (ii) The absorbance of a solution at a particular wavelength is proportional to the concentration of the ion responsible for the absorption.

Use this information and the given absorption spectra in **Fig 5.1** to suggest and explain which ligand, Q or R, forms the stronger bond with Co^{3+} .

[2]

From the spectrum of solution **Z**, when there are equal proportions of ligands **Q** and **R**, the relative absorbance of CoQ_6^{3+} is higher, and hence the proportion of CoQ_6^{3+} in the mixture is higher.

Hence, the stability of CoQ_6^{3+} in the mixture is higher, thus **Q** forms a stronger bond with Co^{3+} .

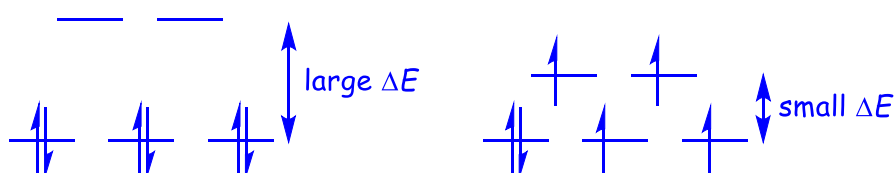
- (iii) The energy gap between the two levels of d orbitals in an octahedral complex depends on the strength of the ligand. The energy gap in turn affects how electrons occupy the d subshell in the complex. Electrons in the d subshell may occupy all the orbitals singly before pairing up or they may fill up the d orbitals in the lower energy level before filling up the d orbitals in the higher energy level.

Paramagnetic materials have one or more unpaired electrons in their electron configuration. These unpaired electrons spin and create a magnetic dipole moment, making the molecule magnetic.

By considering the electronic configuration of Co^{3+} and your answers in (c)(ii), suggest and explain which of the two complexes, CoQ_6^{3+} or CoR_6^{3+} , have the higher tendency to be paramagnetic.

[2]

The electron arrangement due to the size of the d orbital splitting:



From (c)(ii), since **Q** forms a stronger dative with the metal ion center, it is the stronger ligand. As such, the energy gap between the two sets of d orbitals is larger.

There is a higher probability of the electrons filling up the d orbitals in the lower energy level first. This will result in the complex to not have any unpaired electrons.

Hence CoQ_6^{3+} have a higher tendency to not be paramagnetic / CoR_6^{3+} have a higher tendency to be paramagnetic.

- 5 (d) Many transition metals and their compounds are useful catalysts.

An aqueous solution of Co^{2+} can catalyse the reaction between iodide and peroxodisulfate, $\text{S}_2\text{O}_8^{2-}$ whereas Ca^{2+} cannot.

- (i) Why is it necessary to catalyse the reaction between iodide and peroxodisulfate? [1]

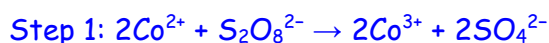
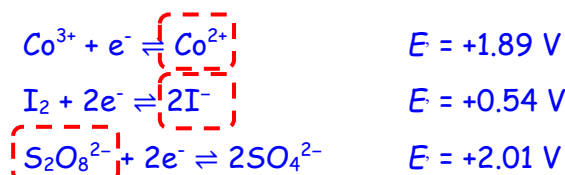
Both ions are negatively charged and the electronic repulsion increases the activation energy thus the reaction is very slow.

- (ii) Explain why Ca^{2+} is not suitable as a catalyst. [1]

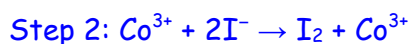
Co^{2+} has variable oxidation states and can function as homogenous catalyst while Ca^{2+} only has one oxidation state.

- (iii) With reference to the *Data Booklet*, show how Co^{2+} can catalyse the above reaction. [2]

From Data Booklet



$$\begin{aligned} E_{\text{cell}}^{\ominus} &= (+2.01) - (+1.89) \\ &= +0.12 \text{ V} > 0 \text{ (reaction is energetically feasible)} \end{aligned}$$



$$\begin{aligned} E_{\text{cell}}^{\ominus} &= (+1.89) - (+0.54) \\ &= +1.35 \text{ V} > 0 \text{ (reaction is energetically feasible)} \end{aligned}$$

- 5 (e) Stellite alloys are cobalt–chromium alloys prized for their hardness, wear, and corrosion resistance. The corrosion resistance is largely due to the chromium content, which forms a stable, protective Cr_2O_3 oxide layer. In contrast, cobalt does not form a stable protective oxide and therefore reacts more readily in acidic environments.

A 5.00 g sample of the cobalt–chromium alloy is being analysed to determine its cobalt content. The sample is dissolved in excess dilute sulfuric acid, forming a pink solution containing Co^{2+} ions while chromium remains as green insoluble Cr_2O_3 sludge.

The resulting solution was made up to 100 cm^3 and a 25.0 cm^3 aliquot of this solution is titrated with $0.120 \text{ mol dm}^{-3} \text{ KMnO}_4$ in acidic solution. The volume of KMnO_4 required for complete reaction is 22.0 cm^3 .

Calculate the percentage by mass of Co in the alloy.

[4]

$$\text{amount of MnO}_4^- \text{ reacted} = \frac{22.0}{1000} \times 0.120 = 2.64 \times 10^{-3} \text{ mol}$$



Since 1 $\text{MnO}_4^- \equiv 5 \text{Co}^{2+}$

$$\text{amount of Co}^{2+} \text{ reacted} = \frac{5 \times 2.64 \times 10^{-3}}{1} = 1.32 \times 10^{-2} \text{ mol}$$

$$\text{amount of Co}^{2+} \text{ in original solution} = \frac{1.32 \times 10^{-2} \times \frac{100}{25}}{1} = 5.28 \times 10^{-2} \text{ mol}$$

$$\text{mass of Co} = \frac{5.28 \times 10^{-2} \times 58.9}{1} = 3.11 \text{ g}$$

$$\text{percentage by mass of Co} = \frac{3.11}{5} \times 100\% = 62.2\%$$

[Total: 20]

This image shows a full page of white paper with horizontal dotted lines. The lines are evenly spaced and run across the width of the page, providing a guide for handwriting practice. There are no margins, text, or other markings on the page.

