ST ANDREW'S JUNIOR COLLEGE

JC2 Preliminary Examinations

Higher 2

CANDIDATE NAME	
CLASS	**1 9 S**

CHEMISTRY

9729/03

Paper 3 Free Response

16 September 2020

2 hours

Candidate answer on the Question Paper.
Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.

Write in dark blue or black pen.

You may use a HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper. If additional space is required, you should use the pages at the end of this booklet. The question number must be clearly shown.

Section A

Answer **all** the questions.

Section B

Answer **one** question.

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

A Data Booklet is provided.

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

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

For Examiner's Use		
Q1		**19**
Q2		**19**
Q3		**22**
Q4/5		**20**
Total		**80**

Section A

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

1 Elements in Group 17 are known as halogens. The term “halogen” means “salt-former” in Greek because these elements will readily react with alkali metal and alkaline earth metals to form important halide salts such as sodium chloride.

(a) Describe and explain how the volatilities of the halogens vary down Group 17. [2]

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(b) The table below shows the results of experiments in which the halogens, $\mathbf{X}_2$, $\mathbf{Y}_2$ and $\mathbf{Z}_2$ were added to separate aqueous solutions containing $\mathbf{X}^-$, $\mathbf{Y}^-$ and $\mathbf{Z}^-$ ions. The possible identities of the halogens are chlorine, bromine and iodine.

	$\mathbf{X}^-$ (aq)	$\mathbf{Y}^-$ (aq)	$\mathbf{Z}^-$ (aq)
$\mathbf{X}_2$	-	no reaction	$\mathbf{Z}_2$ formed
$\mathbf{Y}_2$	$\mathbf{X}_2$ formed	-	$\mathbf{Z}_2$ formed
$\mathbf{Z}_2$	no reaction	no reaction	-

(i) Based on the results in the given table, identify $\mathbf{X}_2$, $\mathbf{Y}_2$ and $\mathbf{Z}_2$. Explain your answer. [1]

(ii) Describe and explain how the solubility of the solid silver halides, AgC*l*, AgBr and AgI, is affected by adding concentrated NH_3. [3]

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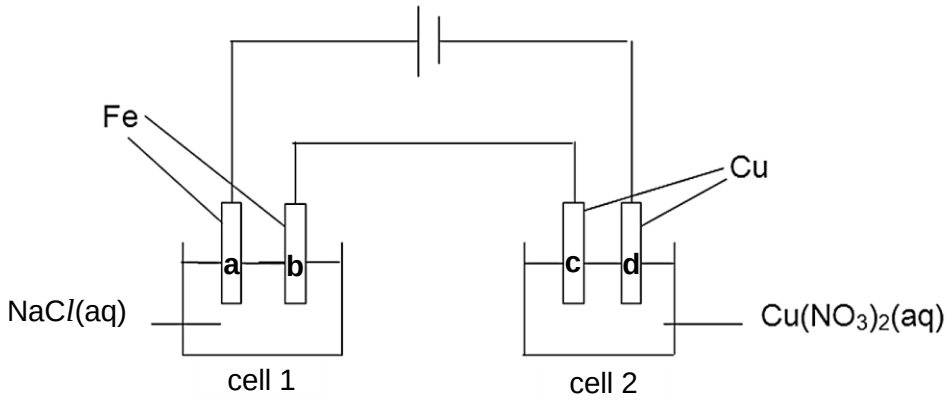
(c) A student was presented the following set-up, which involved sodium chloride solution in one half-cell.



The student predicted the following:

- Hydrogen is produced at the cathode of cell 1 when concentrated or dilute sodium chloride solution is used.
- The anode of cell 2 would increase in mass.

(i) State which electrode, **a** to **d**, is the cathode of cell 1 and which is the anode of cell 2. [1]

(ii) Do you agree with **each** of his prediction? Explain your answer.
You should use relevant $E^{\ominus}$ values from the *Data Booklet* for cell 1. [3]

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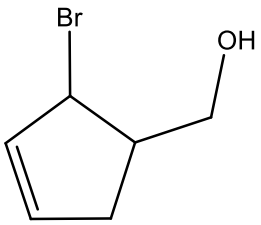
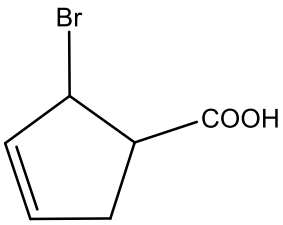
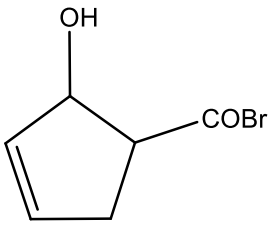
(d) Organohalogens are organic compounds that contain halogen atoms. The following compounds are examples of organohalogens.



A



B



C

(i) Suggest and explain how the acidity of compound **A** might compare with that of compound **B**. [2]

(ii) Describe and explain the relative reactivity of compounds **A** and **C** with respect to hydrolysis. [2]

(iii) Suggest a simple chemical test to distinguish compounds **B** and **C**. State the observation and write equation(s) to explain the reactions that happened. [3]

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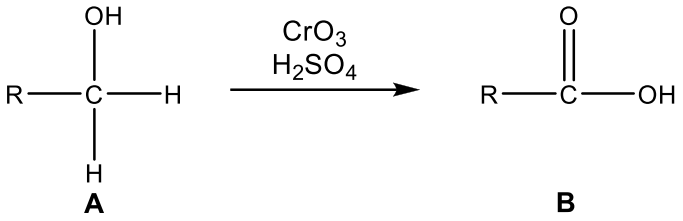
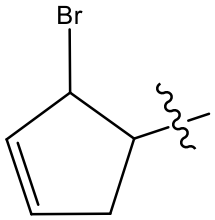
Jones oxidation can be used to oxidise compound **A** to compound **B**. Jones reagent uses chromium trioxide dissolved in sulfuric acid, to form chromic (VI) acid, $HCrO_4^-$. During the reaction, $HCrO_4^-$ is reduced to Cr^{3+}.



A **B**

where R is 

(iv) Determine the change in oxidation number for the carbon atom that is directly bonded to oxygen atom in compounds **A** and **B**. [1]

(v) Hence, using oxidation numbers, construct a balanced equation for this reaction. You should use RCH_2OH and RCO_2H to represent compounds **A** and **B** respectively. [1]

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[Total: 19]

2 Ozone, O_3, is a powerful oxidising agent that can destroy viruses and bacteria. Ozone is used to disinfect water and sterilise food.

(a) To generate ozone for industrial use, electricity is passed briefly through oxygen gas. Some oxygen molecules decompose to form oxygen atoms, which collide with more oxygen gas to form ozone, until an equilibrium is reached.

$$3O_2\,(g) \rightleftharpoons 2O_3\,(g)$$

(i) Draw a dot-and-cross diagram to show the bonding present within an ozone molecule and suggest a value for its bond angle. [2]

(ii) Write an expression for K_p for this equilibrium. [1]

(iii) The value of K_p under a particular set of industrial conditions is 5×10^{-8}. Deduce the sign and magnitude for ΔG at these conditions. [2]

(iv) Predict and explain the effect of compressing the volume of the reaction mixture on the yield of ozone. [2]

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(b) The concentration of ozone in a sample of disinfectant can be determined by its reaction with alkaline potassium iodide.

$$O_3 + 2I^- + H_2O \rightarrow I_2 + 2OH^- + O_2$$

The iodine formed can be estimated by its reaction with sodium thiosulfate.

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

- 5 cm^3 of disinfectant concentrate was diluted with water to make 1 dm^3 of diluted disinfectant solution.
- 25.0 cm^3 of the diluted disinfectant solution was reacted with excess potassium iodide.
- The resultant mixture was titrated with 0.0100 mol dm^{-3} sodium thiosulfate. 22.40 cm^3 of sodium thiosulfate was required to reach end-point.

Calculate the concentration of ozone in the 5 cm^3 disinfectant concentrate. [3]

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(c) Besides ozone, another active ingredient of ozone-based disinfectants is phosphorous pentachloride, PCl_5. PCl_5 is added to prolong the shelf life of the disinfectant.

Write an equation for the reaction of PCl_5 with water. Hence, explain why PCl_5 undergoes hydrolysis readily with water. [2]

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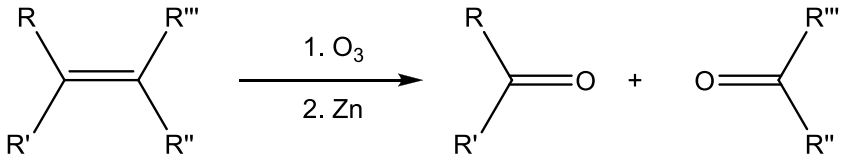
(d) Carbonyl compounds can be formed from alkenes through a reaction with ozone and zinc. This is known as ozonolysis.



R, R', R'' and R''' = H or alkyl or aryl

(i) Ozonolysis of alkene **D** produces ethanal as the only organic product.
Draw and label the stereoisomers of alkene **D**. [1]

(ii) Compound **E**, $C_{10}H_{10}$, has a benzene ring and undergoes ozonolysis with ozone and zinc to form compound **F**, $C_{10}H_{10}O_2$.

F gives a yellow precipitate when reacted with alkaline aqueous iodine. **F** forms a silver mirror with Tollens' reagent, but does not react with Fehling's solution.

When **E** and **F** is heated with acidified potassium (VII) manganate, the same compound **G** is produced.

Deduce the structures of compounds **E** and **F**.
Write a balanced equation for the reaction of **E** to form **G**. [6]

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3 (a) Amines are Lewis bases.

Explain what is meant by this statement. Illustrate your answer with an equation for a suitable reaction of an amine of your choice. [2]

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(b) In an experiment, 50.0 cm^3 of 1.00 mol dm^{-3} hydrochloric acid is added to 50.0 cm^3 of 2.00 mol dm^{-3} ethylamine. The temperature increased from 26.0°C to 31.5°C.

The heat transfer for this reaction is 85% efficient.

(i) Calculate ΔH_r for the reaction.
Assume that the specific heat capacity of the solution is 4.2 J g^{-1} K^{-1} and that the density of the solution is 1.0 g cm^{-3}. [2]

(ii) Suggest and explain how the enthalpy change of reaction in **(b)(i)** would differ when hexylamine is used in place of ethylamine. [1]

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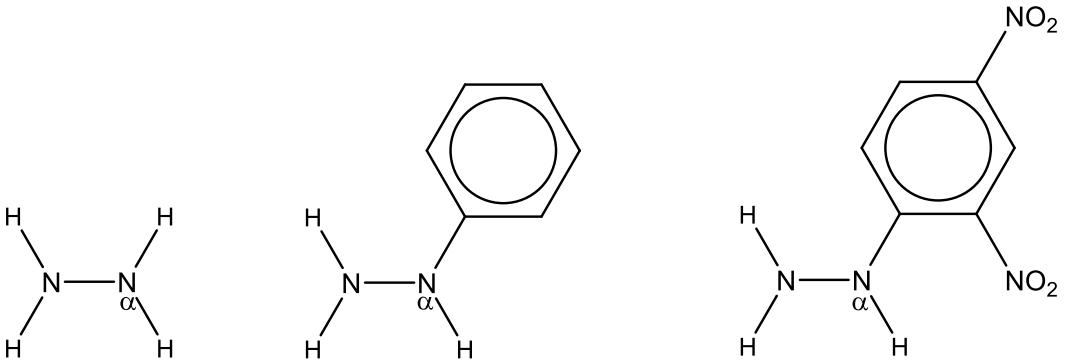
(c) Hydrazine is a key building block for the preparation of many heterocyclic compounds via condensation. It is also a precursor to several pharmaceuticals including phenylhydrazine and 2,4-dinitrophenylhydrazine.



hydrazine phenylhydrazine 2,4-dinitrophenylhydrazine

(i) Describe and explain the relative basicities of the α-labelled nitrogen atom for hydrazine, phenylhydrazine and 2,4-dinitrophenylhydrazine in the gas phase. [3]

(ii) Two moles of ethanal react with 1 mole of hydrazine to form compound **H**.

Draw the **skeletal** formula for **H**. [1]

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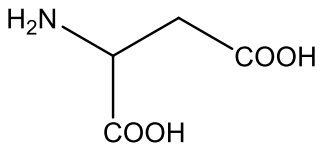
(d) Amino acids is another class of compounds that possess the amine functional group. Research has suggested that supplements containing essential amino acids can help reduce inflammation in patients suffering from liver disease. An example of an essential amino acid is aspartic acid.



aspartic acid

(i) Crystals of aspartic acid has a melting point of 270°C.

Explain why the melting point of aspartic acid is much higher than that of 4-hydroxybutanoic acid (48°C). [2]

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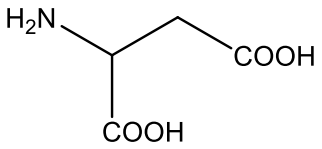

aspartic acid

There are three pK_a values associated with aspartic acid:

pK_{a1}	pK_{a2}	pK_{a3}
1.88	3.65	9.60

(ii) Make use of these pK_a values to suggest the major species present in solutions of aspartic acid with the following pH values.

- pH 1
- pH 13 [2]

(iii) Draw a diagram showing the intramolecular hydrogen bond formed in aspartic acid. [1]

(iv) Use pK_{a1} to calculate the pH of a 0.200 mol dm^{-3} solution of aspartic acid. [1]

(v) Write equations to show how the zwitterion of aspartic acid maintains the pH of a solution. [2]

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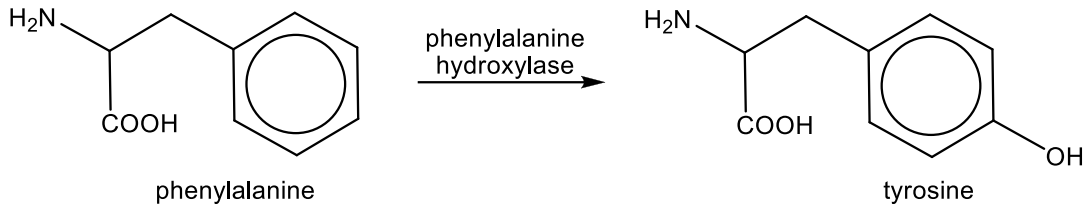
(e) Phenylalanine is another essential amino acid. It is broken down into tyrosine by an enzyme, phenylalanine hydroxylase, in the liver. Tyrosine aids in reduction of body fat.



phenylalanine tyrosine

(i) Suggest a simple chemical test to detect the presence of tyrosine. State the observation you would expect. [1]

The breakdown of phenylalanine by liver cells is a first-order reaction.

(ii) Sketch the graph of rate against concentration of phenylalanine. [1]

(iii) Using your answer in **(e)(i)**, outline a suitable experiment for obtaining the graph in **(e)(ii)**.

You may find it useful to use $\frac{\mathbf{1}}{\mathbf{time}}$ to represent the reaction rate. [3]

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Section B

Answer **one** question from this section.

4 Coronavirus disease 2019 (COVID-19) is an infectious disease that has spread globally. One of the most common symptoms developed by people affected with COVID-19 is difficulty in breathing.

(a) During breathing, the lungs take in oxygen gas and remove carbon dioxide gas. During inhalation, the volume of the lungs increases, causing air to flow into the lungs. During exhalation, the volume of the lungs decreases, causing air to flow out of the lungs.

Fig. 4.1 shows the volume of the lungs during inhalation (V_{in}) and exhalation (V_{ex}) at 30°C. The volume of gas taken in for each breath can be determined from the difference in volume of the lungs during inhalation and exhalation.

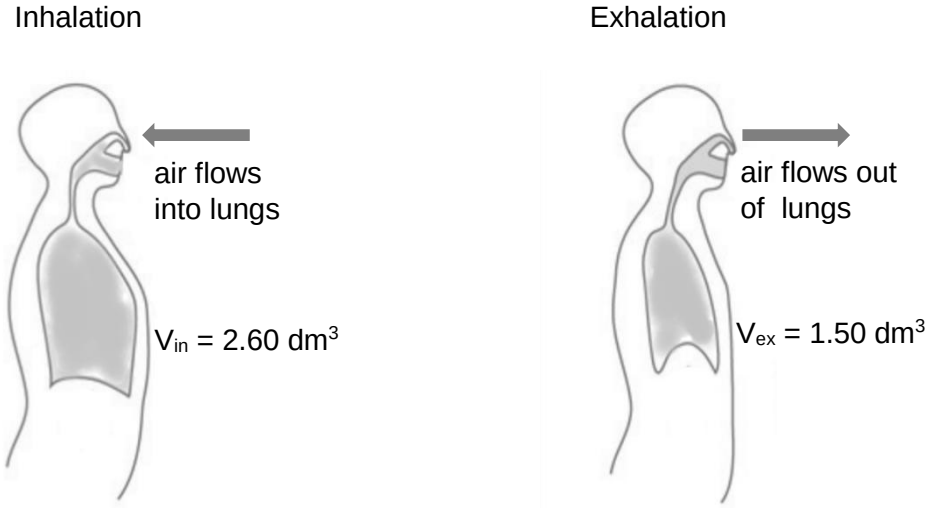

Fig. 4.1

Image taken from https://courses.lumenlearning.com/boundless-biology/chapter/breathing/

(i) Calculate the amount, in moles, of oxygen gas taken in for each breath at 1 atm and 30°C, given that the percentage by volume of atmospheric oxygen is 21%. [2]

(ii) The pressure in the lungs during inhalation was found to be 758 Torr at 30°C (1 Torr = 133 Pa).

Assuming that the amount of gas inhaled and exhaled is the same, calculate the pressure in the lungs during exhalation at 30°C. [1]

(iii) Explain the relative deviations from ideal gas behaviour of oxygen gas and carbon dioxide gas. [1]

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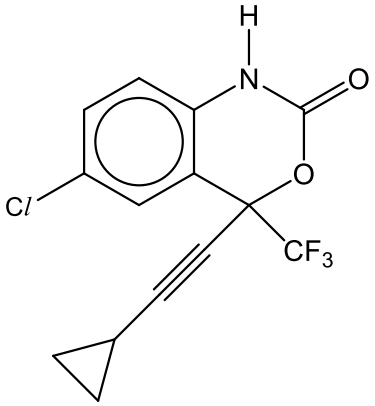
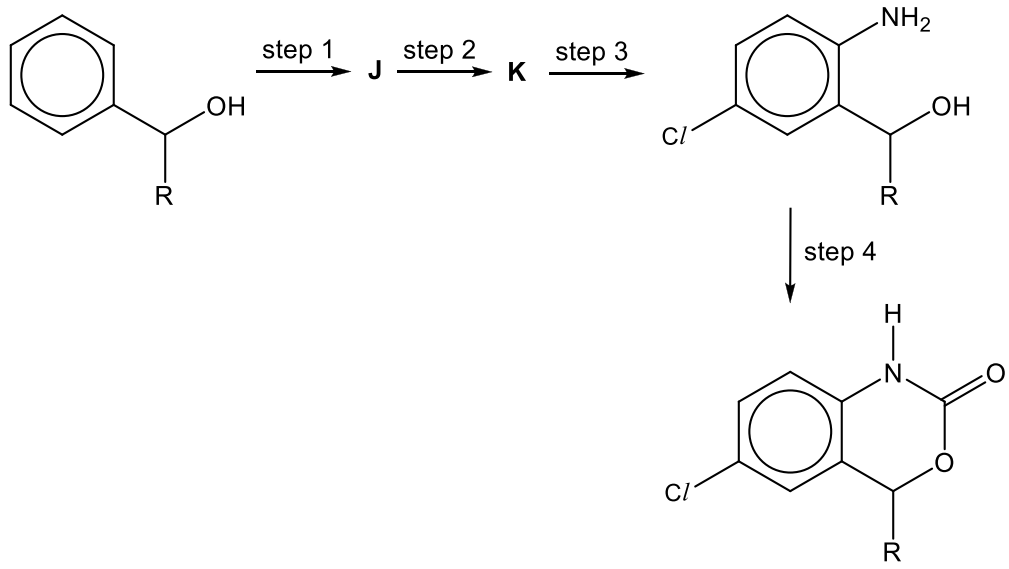
(b) Anti-HIV drugs were used in the early treatment of COVID-19. One such anti-HIV drug is efavirenz.



efavirenz

(i) Besides benzene ring, alkyne (C≡C) and fluoroalkane, name three other functional groups in efavirenz. [1]

(ii) Efavirenz can be made using appropriate reagents by the following 4-step synthesis.



efavirenz

Suggest the structures of compounds **J** and **K** and the reagents and conditions for the four steps. [5]

(iii) It was found that the nitrogen atom in efavirenz is sp^2 hybridised.

Explain why this hybridisation results in partial double bond character in the C-N bond in efavirenz. Hence, use the *Data Booklet* to predict the bond energy of the C-N bond in efavirenz. [3]

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(c) Lignans are a class of natural products widely produced by various plant species. They are widely researched in their anti-viral activities. One such lignan is styron, $C_9H_{10}O$.

Styron decolourises bromine water to give a compound with molecular formula $C_9H_{11}O_2Br$. When treated with hot acidified $K_2Cr_2O_7$, styron forms compound **L**. **L** liberates CO_2 from Na_2CO_3(aq). When treated with hot acidified $KMnO_4$, styron forms compound **M**, $C_7H_6O_2$, which is a white precipitate.

N is a constitutional isomer of styron. It does not decolourise bromine water. When treated with hot $K_2Cr_2O_7$, **N** forms compound **P**, C_9H_8O. **P** gives an orange precipitate with 2,4-DNPH.

Deduce the structures of compounds **L**, **M**, **N**, **P** and styron, explaining the reactions described. [7]

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5 Iron and platinum are used in several inorganic and organic reactions.

(a) The reaction between $S_2O_8^{2-}$ and I^- ions is very slow. When a small amount of $Fe^{2+}(aq)$ is added to the mixture, the rate of reaction increases.

With reference to relevant $E^\ominus$ values, describe the catalytic role of Fe^{2+} in the I^- / $S_2O_8^{2-}$ reaction. [4]

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(b) **(i)** $Fe^{3+}(aq)$ can be represented as its aqua complex, $[Fe(H_2O)_6]^{3+}$. In this aqua complex, the five 3d orbitals are no longer degenerate. They split into two energy levels. The $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals are in the higher energy level.

Draw a fully labelled diagram of a 3d orbital from the **lower** energy level. [1]

(ii) Both solutions of $Al^{3+}(aq)$ and $Fe^{3+}(aq)$ are acidic.

With the aid of an equation, explain why $Fe^{3+}(aq)$ solution is acidic. [2]

(iii) Describe how the reaction of $Al^{3+}(aq)$ with excess NaOH(aq) differs from that of $Fe^{3+}(aq)$ with excess NaOH(aq). Write equations for any reactions that occur. [2]

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(c) **(i)** Alkenes can be reduced to alkanes by hydrogen with a platinum catalyst.

Outline the mode of action of the catalyst in this reduction reaction. [3]

(ii) Platinum complexes have been researched extensively due to its anti-cancer properties. One such platinum complex is *cis*-platin, which can be synthesised from $PtCl_4$.

The central atom, platinum, in $PtCl_4$ is surrounded by six pairs of electrons arranged in an octahedral shape. An octahedral arrangement is shown in Fig. 5.1.

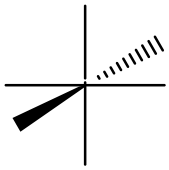

Fig. 5.1

Two different molecular arrangements of $PtCl_4$ are possible.

Draw clear diagrams of these two arrangements. Hence, apply the principles of the VSEPR theory to discuss the relative stabilities of these two possible arrangements. [3]

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(iii) Platinum compounds are also commonly used in cross-coupling reactions, where two different compounds come together through the formation of carbon-carbon bonds.

One such cross-coupling reaction between an amine and a nitro compound is shown in Fig. 5.2.

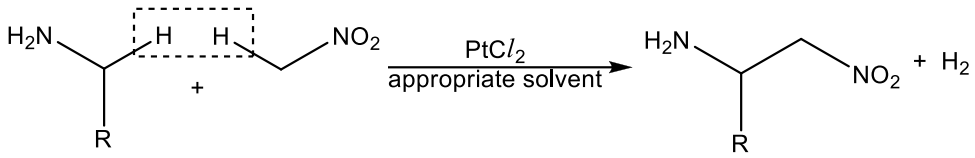
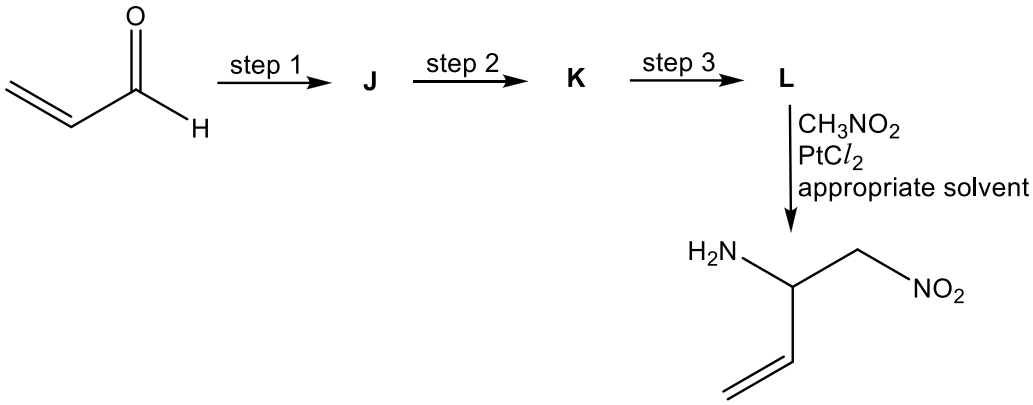


Fig. 5.2

The cross-coupling reaction in Fig. 5.2 is used in the following 4-step synthesis.



Suggest the structures of compounds **J** to **L** and the reagents and conditions for steps 1 to 3. [5]

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Additional Answer Space

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