Class	Adm No

Candidate Name: ____________________

2024 Preliminary Examination
Pre-University 3

H2 CHEMISTRY **9729/02**

Paper 2 Structured Questions

10 September 2024

2 hours

Candidates answer on the Question paper.

Additional materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not turn over this question paper until you are told to do so

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

Write in dark blue or black pen.

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

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

Answer **all** questions.

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.

Question	1	2	3	4	5	Total
Marks	15	17	15	13	15	75

1 **(a)** Table salt can be fortified with iodine to supplement the diet. Common iodine chemicals used to fortify salt are sodium or potassium iodate(V).

Aqueous acidified iodate(V) ions, IO_3^-, react with iodide ions, as shown.

$$IO_3^- + 6H^+ + 5I^- \rightarrow 3I_2 + 3H_2O$$

The initial rate of this reaction is investigated. Table 1.1 shows the results obtained.

Table 1.1

Expt	$[IO_3^-]$ / mol dm^{-3}	$[H^+]$ / mol dm^{-3}	$[I^-]$ / mol dm^{-3}	initial rate / mol dm^{-3} min^{-1}
1	0.0400	0.0150	0.0250	4.20×10^{-2}
2	0.0200	0.0150	0.0250	2.10×10^{-2}
3	0.0200	0.0150	0.0500	8.40×10^{-2}

It is known that the reaction is second order with respect to hydrogen ions.

(i) Determine the order of the reaction with respect to IO_3^- and I^- ions. Explain your reasoning.

....

....

....

....

....

....

....

.... [2]

(ii) Hence, write the rate equation for the reaction.

.... [1]

The reaction is then repeated at the same temperature but at different pH.

Table 1.2 lists the concentrations of IO_3^-, I^- and the pH at which the experiments are carried out.

Table 1.2

Expt	$[IO_3^-]$ / mol dm^{-3}	$[I^-]$ / mol dm^{-3}	pH	$[H^+]$ / mol dm^{-3}
4	0.0400	0.0250	1.0	
5	0.0400	0.0250	2.0	

(iii) Complete Table 1.2 with the concentrations of H^+ ions in experiments 4 and 5. [1]

(iv) Calculate the value of $\frac{\text{rate at pH 1.0}}{\text{rate at pH 2.0}}$.

$\frac{\text{rate at pH 1.0}}{\text{rate at pH 2.0}}$ = ...[1]

(b) In an aqueous solution, iron(III) ions react with iodide ions as shown.

$$2Fe^{3+} + 2I^{-} \rightarrow 2Fe^{2+} + I_2$$

The kinetics of this reaction were investigated and below are some information about the reaction

- The reaction is first order with respect to Fe^{3+} and second order with respect to I^{-}.
- The mechanism for this reaction has three steps.
- Each step involves only two ions reacting together.

The first step of the mechanism has been written for you.

Suggest equations for the remaining two steps of this mechanism and identify the rate-determining step.

step 1: $Fe^{3+} + I^{-} \rightleftharpoons FeI^{2+}$

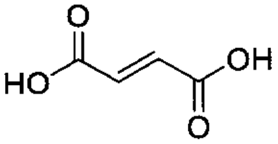
step 2: ....

step 3: ....

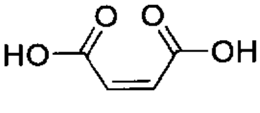
rate-determining step: ....

[3]

(c) Fumaric acid is a white solid that occurs widely in nature and has a fruit-like taste and hence used as a food additive. Maleic acid is a stereoisomer of fumaric acid.



fumaric acid



maleic acid

(i) State the type of isomerism that fumaric acid and maleic acid shows.

.... [1]

(ii) Fumaric acid has a melting point of 286 °C while maleic acid has a melting point of 131 °C.

With the aid of a suitable diagram, suggest why maleic acid has a lower melting point than fumaric acid.

....

....

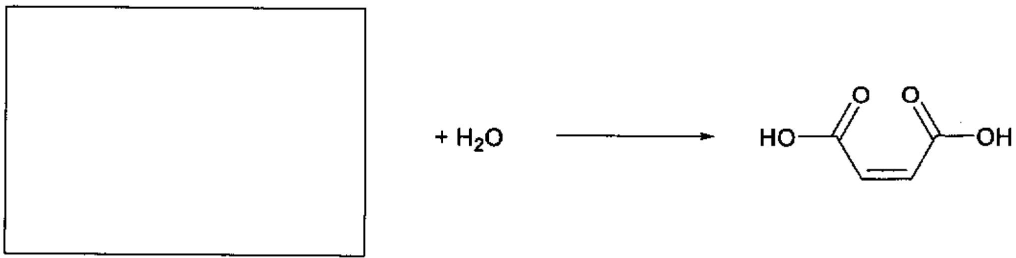
....

....

....[2]

(iii) In the industry, maleic acid is obtained by reacting maleic anhydride, $C_4H_2O_3$, with water.

Suggest a possible structure of maleic anhydride.



maleic anhydride

maleic acid

[1]

The atom economy of a reaction is a measure of the amount of starting materials that end up as useful products. It is important for sustainable development and for economic reasons to use reactions with high atom economy.

The percentage atom economy of a reaction is calculated with the following equation.

$$\text{atom economy} = \frac{\text{mass of desired product}}{\text{total mass of products}} \times 100\%$$

Maleic anhydride can be obtained industrially by the oxidation of butane (reaction 1.1) or benzene (reaction 1.2).

reaction 1.1 $C_4H_{10} + 3\frac{1}{2}\,O_2 \rightarrow C_4H_2O_3 + 4H_2O$

reaction 1.2 $C_6H_6 + 4\frac{1}{2}\,O_2 \rightarrow C_4H_2O_3 + 2H_2O + 2CO_2$

(iv) Calculate the atom economy for each reaction and suggest which reaction is preferred.

[2]

(v) Suggest another reason why the reaction you selected in **(iv)** is preferred.

....

....

....[1]

[Total: 15]

2 The Andrussow process involves heating a mixture of methane, ammonia and oxygen over a platinum catalyst at 1200 °C to generate hydrogen cyanide.

$$2CH_4 + 2NH_3 + 3O_2 \rightarrow 2HCN + 6H_2O$$

(a) **(i)** Draw a dot-and-cross diagram of HCN and state its shape.

shape = ...

[2]

(ii) Given that the oxidation number of hydrogen remains at +1 throughout the reaction, complete Table 2.1 with the oxidation numbers of carbon, nitrogen and oxygen in the reactants and products.

Table 2.1

	carbon	nitrogen	oxygen
oxidation number of element in reactant			
oxidation number of element in product			

[2]

(b) Hydrogen cyanide is a weak acid in aqueous solution.

(i) State what is meant by the term *weak acid*.

....

....[1]

(ii) The pH of a solution of 0.10 mol dm^{-3} HCN is 5.10.

Calculate the acid dissociation constant, K_a, of HCN.

[2]

(c) The reaction between propanone and HCN produces 2-hydroxy-2-methylpropanenitrile.

$$(CH_3)_2CO + HCN \rightarrow (CH_3)_2C(OH)CN$$

(i) Describe the mechanism for this reaction between propanone and HCN.

Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows.

[3]

(ii) State the hybridisation state of the carbonyl carbon in propanone.

.... [1]

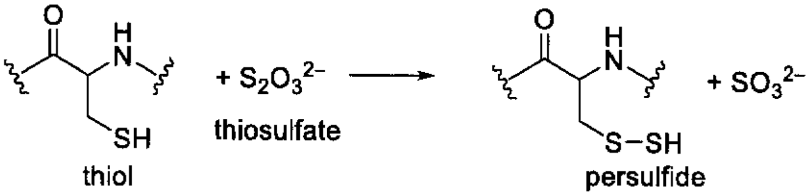
(iii) Suggest whether 2-hydroxy-2-methylpropanenitrile produced through this reaction will rotate plane-polarised light.

....

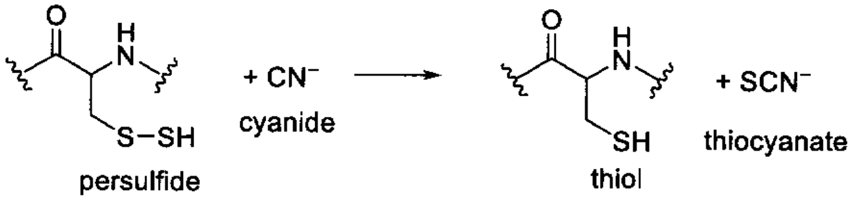
.... [1]

(d) Sodium thiosulfate, $Na_2S_2O_3$, is administered as a treatment of cyanide poisoning. It converts the cyanide ion to the less toxic thiocyanate ion. This process is facilitated by the enzyme rhodanese found in the kidney and liver via a two-step process.

In the first step, thiosulfate is reduced by the thiol group present on cysteine-247 of rhodanese to form a persulfide.



In the second step, the persulfide reacts with cyanide to produce thiocyanate.



(i) Explain why the reaction between thiosulfate and cyanide ions occurs slowly in the absence of rhodanese.

....

....

.... [1]

(ii) Fig. 2.1 shows how the rate of the reaction varies with increasing concentrations of sodium thiosulfate.

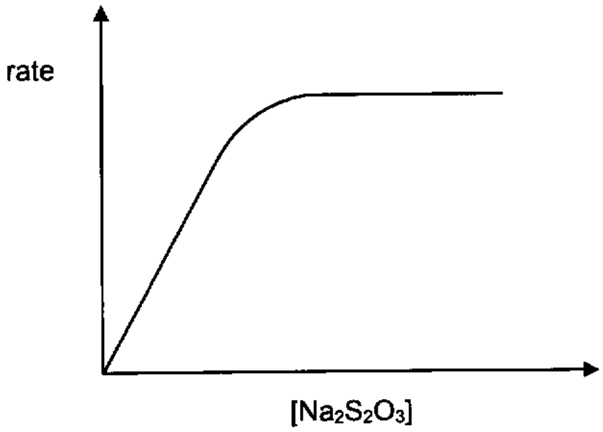


Fig. 2.1

Explain why the graph in Fig. 2.1 levels off at high concentrations of sodium thiosulfate.

....

....

....[1]

(e) Hydrogen cyanide can be oxidised to form cyanogen, a highly toxic gas.

Cyanogen is composed of 46.2% carbon and 53.8% nitrogen by mass.

(i) Determine the empirical formula for cyanogen.

[1]

(ii) At 25 °C and 101 kPa, 1.05 g of cyanogen occupies 0.500 dm^3.

Calculate the relative molecular mass of cyanogen, and hence deduce its molecular formula.

[2]

[Total: 17]

3 (a) The following is a procedure for the preparation of potassium chlorochromate (KCC), $KCrO_3Cl$, also called Péligot's salt in recognition of the French chemist who discovered it.

> Place 6.0 g of potassium dichromate(VI) in a 100 cm^3 beaker. Slowly add 8.0 g of concentrated hydrochloric acid and 1.0 cm^3 water and warm the mixture gently. If this is done carefully, the dichromate(VI) will dissolve without the evolution of chlorine. On cooling the beaker in an ice bath, orange-red crystals of Péligot's salt will be deposited.

However, the procedure suggests that strong heating may cause chlorine gas to be formed.

(i) Write an overall **ionic** equation for the production of chlorine gas from the reaction between $K_2Cr_2O_7$ and HCl.

....[1]

(ii) Calculate the standard cell potential, $E^\ominus_{cell}$, for the reaction in **a(i)**.

[1]

(iii) Using dilute $HCl(aq)$ in the above process will prevent the production of chlorine gas. Suggest why this is so.

....

....

....[1]

(iv) Predict if it is possible to prepare the bromine equivalent of Péligot's salt by using HBr in place of HCl.

....

....

....

....

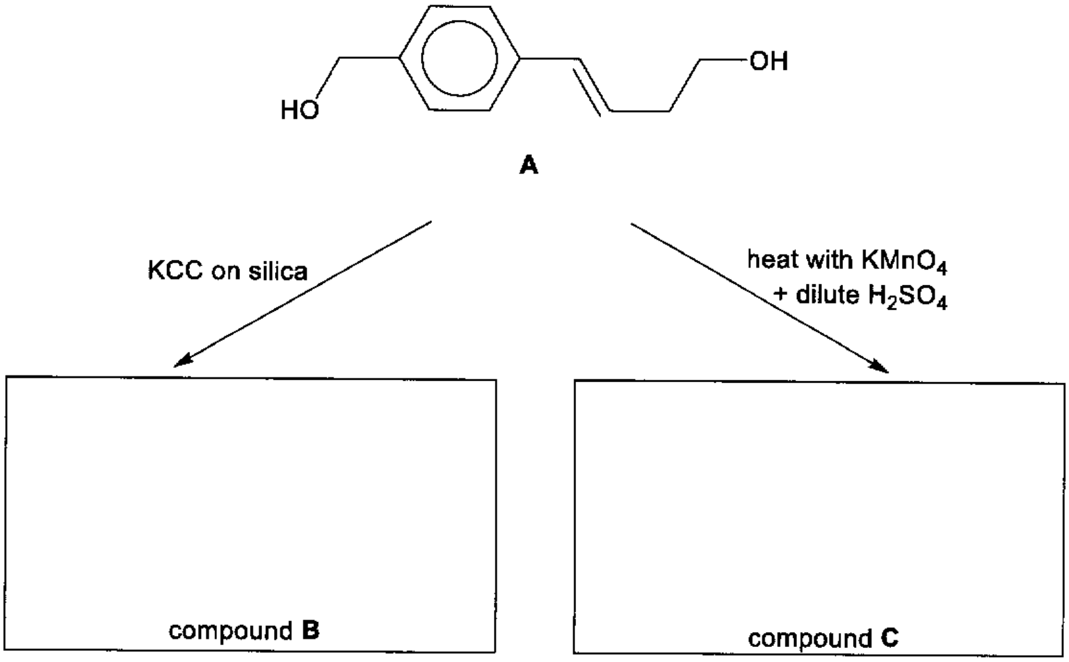
....[1]

KCC supported on silica gel is used to selectively oxidise alcohols to their carbonyl compounds without further oxidation to carboxylic acids.

(v) Compound **A** can undergo oxidation with KCC on silica and acidified potassium(VII) manganate but the organic product formed in each reaction is different.

Compound **B** has the molecular formula $C_{11}H_{10}O_2$ and compound **C** has the molecular formula $C_8H_6O_4$.

Deduce the structures of **B** and **C**.



[2]

(b) Phosphorus is an element in Group 15. It forms two chlorides, PCl_3 and PCl_5 which are commonly used in qualitative analysis to test for specific organic functional groups.

(i) With the aid of a relevant equation, describe what would be observed when PCl_5 is added to a beaker of water containing a few drops of methyl orange.

....

....

....

....[2]

An organic compound, **D**, $C_nH_{2n+2}O$, was vapourised and 10 cm^3 of the vapour was burnt in excess oxygen and cooled to room temperature and pressure. A contraction of 20 cm^3 in volume was observed as the reaction mixture was shaken with sodium hydroxide. White fumes are produced when **D** reacted with PCl_5.

(ii) State the identity of compound **D**.

....[1]

(iii) Hence write a balanced equation for the reaction between PCl_5 and **D.**

....[1]

Phosphoramides are compounds in which one or more of the OH groups of phosphoric acid, H_3PO_4, have been replaced with an amino or substituted amino group. A common example is phosphoric triamides, $PO(NR_2)_3$, where R represents an alkyl group.

(iv) Explain why the nitrogen equivalent of phosphoric triamides, $NO(NR_2)_3$, does not exist.

....

....

....

....[1]

(v) Explain why phosphoric triamides, $PO(NR_2)_3$, cannot be produced by reacting phosphoric acid with an amine.

....

....

....[1]

(c) Silver nitrate is commonly used to test for the presence of halides. In the presence of halides, a precipitate of sparingly soluble silver halide would be formed.

A mixture of water and solid silver chloride is shaken and left to equilibrate at 25 °C. The resulting mixture was then filtered to obtain a saturated solution of silver chloride.

(i) Write an expression for the solubility product, K_{sp}, of Ag*Cl*.

.... [1]

(ii) Given that the concentration of the saturated solution is 1.33×10^{-5} mol dm^{-3} at 25 °C, calculate the value of K_{sp} for Ag*Cl* at 25 °C and state its units.

[2]

[Total: 15]

4 Hydrogen is considered a clean fuel because it only produces water upon combustion.

The current method of large-scale production of hydrogen is through steam methane reforming followed by the water-gas shift reaction.

Methane, the main component of natural gas, is first reacted with steam (reaction 4.1).

reaction 4.1 $CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$ $\Delta H = +206\ \text{kJ mol}^{-1}$

The carbon monoxide generated is then reacted with more steam in the water-gas shift reaction (reaction 4.2).

reaction 4.2 $CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$

(a) State the total amount of hydrogen that can be obtained per mole of methane through this entire process.

....[1]

(b) **(i)** Explain what is meant by the term *entropy*.

....

....[1]

(ii) The value of ΔS for reaction 4.1 is $+111\ \text{J mol}^{-1}\ \text{K}^{-1}$.

Explain why the sign of ΔS for reaction 4.1 is positive.

....

....[1]

(iii) Calculate the Gibbs Free Energy, ΔG for reaction 4.1 at 298 K and explain the significance of its sign.

....

....[2]

Hydrogen that is produced by the method described in reactions 4.1 and 4.2 is referred to as "grey" hydrogen as carbon dioxide is released during production. However, if the carbon dioxide can be significantly removed, it is then referred to as "blue" hydrogen.

Fig. 4.1 shows how calcium oxide is used to capture carbon dioxide to be utilised in the industry and how the calcium oxide can be reused.

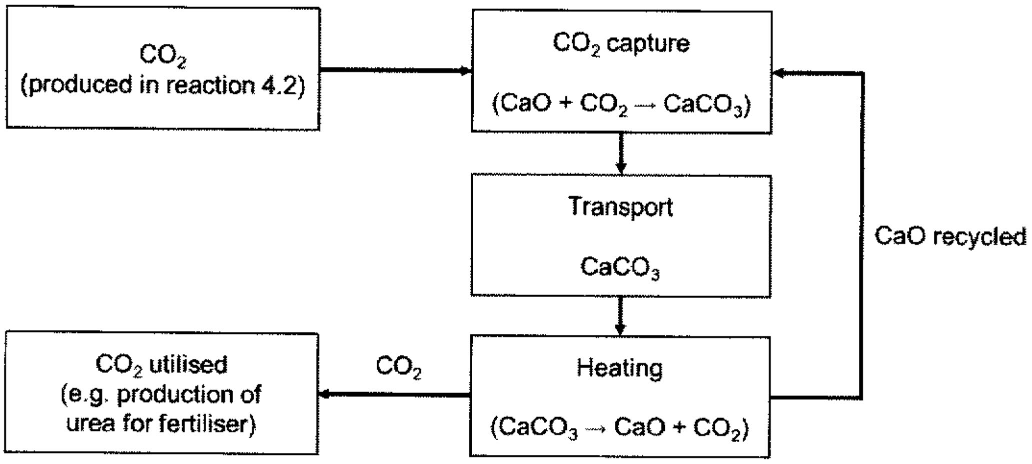


Fig. 4.1

(c) By considering the carbon dioxide capturing process above, suggest if magnesium oxide should be used instead of calcium oxide. Explain your answer.

You may assume that both magnesium oxide and calcium oxide react in the same way with carbon dioxide.

....

....

....

....[2]

In the search for alternatives to hydrogen, ammonia emerged as a promising substitute. Ammonia combusts to form nitrogen gas and water.

In March 2024, Fortescue successfully conducted trials involving the use of ammonia, in combination with diesel, as a marine fuel onboard the Singapore-flagged Fortescue Green Pioneer.

(d) State one advantage of using a combination of ammonia and diesel as fuel.

....[1]

(e) State one disadvantage of using ammonia as a fuel.

....[1]

Ammonia can also be used directly in fuel cells.

Solid oxide fuel cells (SOFCs) employ a solid oxide material as the electrolyte to transport oxide ions from the cathode to the anode. Oxygen is fed through the cathode while the chosen fuel is fed through the anode. SOFCs typically operate at high temperatures ranging from 800 to 1000 °C.

In SOFCs that utilise ammonia, the ammonia supplied is first thermally decomposed over a catalyst to form nitrogen and hydrogen.

$$2NH_3 \rightarrow 3H_2 + N_2$$

The hydrogen produced from the decomposition of ammonia is then oxidised to form water.

(f) Write the equations for the reactions at the cathode and anode.

cathode: ....

anode: ....[2]

(g) One advantage of ammonia over hydrogen as a fuel in SOFCs is that it can be easily liquefied by applying pressure at room temperature making transportation much easier.

(i) Suggest why ammonia can be easily liquefied at room temperature by compressing it under pressure.

....

....

....[1]

(ii) The values of pV are plotted against p for an ideal gas and H_2 on Fig. 4.2, where p is the pressure of the gas and V is the volume occupied by the gas.

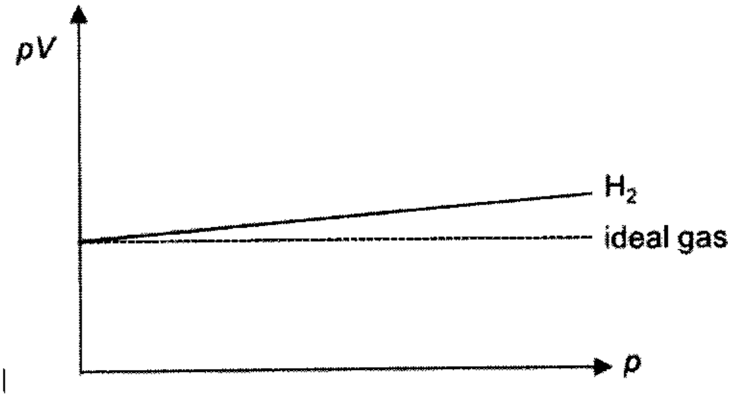


Fig. 4.2

Sketch a graph on Fig. 4.2, to illustrate how the pV of NH_3 changes with p. [1]

[Total: 13]

5 The lanthanoids (Ln) form a series in the Periodic Table comprising the elements from lanthanum to lutetium. They play a vital role in the manufacturing of smartphones, be it in the phone circuitry or speakers. The vivid red, blue and green colours on the screens can also be attributed to these metals. In fact, the vibration unit of the phone utilises neodymium, terbium and dysprosium. These elements have some similar properties as d–block elements.

- Many of the lanthanoid elements are obtained through heating their trichlorides or trifluorides with calcium at 1000 °C.
- The electronic configuration of the atoms of lanthanoid elements consists of the electronic configuration of xenon followed by electrons in the 4f and 6s orbitals and sometimes the 5d orbitals.
- There are a total of 7 orbitals in the 4f subshell. As the 4f orbitals are very diffused, the shielding effect from electrons in these orbitals is negligible.
- All lanthanoids are known to form Ln^{3+} ions and form complex ions such as $[Sm(H_2O)_9]^{3+}$ and $[Yb(H_2O)_8]^{3+}$.
- While some lanthanoids can occasionally exist in the +4 oxidation state, these are rare and typically unstable. Cerium, however, is notable for its stable +4 oxidation state, which exists even in aqueous solution.
- Many of the complex ions formed from the elements in the lanthanoid series are coloured and this colour can be attributed to f–f transitions.

Table 5.1 lists the electronic configurations and ionic radii of eight lanthanoids.

Table 5.1

element	atomic number	electronic configuration	ionic radius, Ln^{3+}/nm
Lanthanum, La	57	[Xe] $5d^1$ $6s^2$	0.115
Cerium, Ce	58	[Xe] $4f^2$ $6s^2$	0.111
Gadolinium, Gd	64	[Xe] $4f^7$ $5d^1$ $6s^2$	0.102
Terbium, Tb	65	[Xe] $4f^9$ $6s^2$	0.100
Holmium, Ho	67	[Xe] $4f^{10}$ $6s^2$	0.097
Thulium, Tm	69	[Xe] $4f^{13}$ $6s^2$	0.095
Ytterbium, Yb	70	[Xe] $4f^{14}$ $6s^2$	0.094
Lutetium, Lu	71	[Xe] $4f^{14}$ $5d^1$ $6s^2$	0.093

The electronic configuration of xenon is $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^{10}$ $4s^2$ $4p^6$ $4d^{10}$ $5s^2$ $5p^6$.

(a) The lanthanoids can be described as being in a 'block' of the Periodic Table.

State the name of this block.

....[1]

(b) Write a balanced equation for the reduction of holmium(III) fluoride, HoF_3, by calcium.

....[1]

(c) **(i)** State the electronic configuration of a La^{3+} ion.

La^{3+} : ....[1]

(ii) Hence, suggest why solutions containing $[La(H_2O)_9]^{3+}$ are colourless.

....

....[1]

(iii) Suggest a reason why gadolinium has the electronic configuration [Xe] $4f^7\ 5d^1\ 6s^2$ rather than [Xe] $4f^8\ 6s^2$.

....

....

....[1]

(iv) State and explain the trend observed for the ionic radii of the Ln^{3+} ions.

....

....

....

....

....[2]

(d) Suggest why the complex ions of the lanthanoids can contain more ligands than those of transition metals.

....

....

....[1]

(e) Cerium(IV) oxide in catalytic converters helps decrease harmful gas emissions by oxidising carbon monoxide to carbon dioxide and reducing nitrogen monoxide to oxygen and nitrogen.

State a chemical property exhibited by cerium which allows it to behave as a catalyst.

....

....[1]

(f) Cerium ammonium nitrate (CAN) is used in organic chemistry as a test for alcohol functional groups as it forms a red complex in the presence of alcohols.

$$(NH_4)_2[Ce(NO_3)_6] + 3ROH \rightarrow \underset{\text{red complex}}{[Ce(NO_3)_4(ROH)_3]} + 2NH_4NO_3$$

(i) Given that the nitrate ions act as bidentate ligands, calculate the coordination number of Ce in $[Ce(NO_3)_6]^{2-}$.

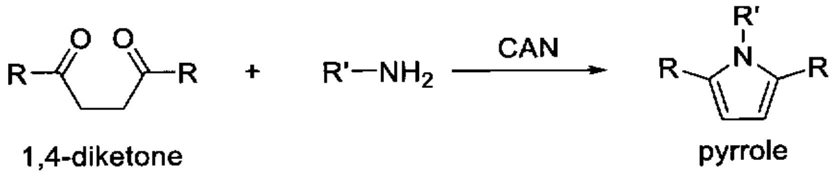
....[1]

(ii) An organic compound, **E**, with the molecular formula $C_7H_{16}O$ did not react with acidified potassium dichromate(VI) solution but gave a red colour with CAN. **E** exists as a pair of enantiomers.

Deduce a possible structure of **E**.

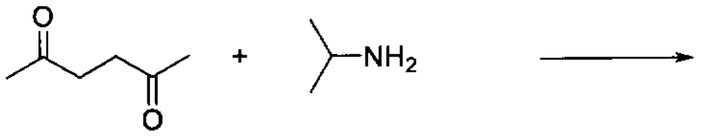
[3]

(g) The Paal-Knorr reaction involves the reaction of a 1,4-diketone with an amine to form a pyrrole and CAN is used as a catalyst.

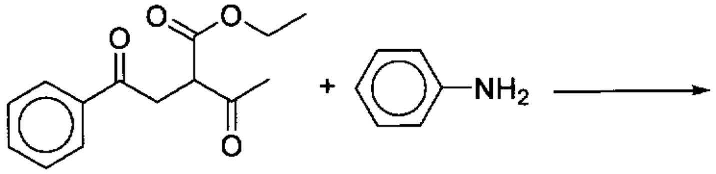


where R and R' are alkyl or aryl groups.

Predict the structures of the pyrroles **F** and **G** formed when the following reactants undergo the Paal-Knorr reaction.



F



G

F

G

[2]

[Total: 15]

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Class	Adm No

Candidate Name: ____________________

millennia institute

2024 Preliminary Examination
Pre-University 3

H2 CHEMISTRY **9729/02**

Paper 2 Structured Questions

10 September 2024

2 hours

Candidates answer on the Question paper.

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Answer **all** questions.

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

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

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Question	1	2	3	4	5	Total
Marks	/ 15	/ 17	/ 15	/ 13	/ 15	/ 75

1 **(a)** Table salt can be fortified with iodine to supplement the diet. Common iodine chemicals used to fortify salt are sodium or potassium iodate(V).

Aqueous acidified iodate(V) ions, IO_3^-, react with iodide ions, as shown.

$$IO_3^- + 6H^+ + 5I^- \rightarrow 3I_2 + 3H_2O$$

The initial rate of this reaction is investigated. Table 1.1 shows the results obtained.

Table 1.1

Expt	$[IO_3^-]$ / mol dm^{-3}	$[H^+]$ / mol dm^{-3}	$[I^-]$ / mol dm^{-3}	initial rate / mol dm^{-3} min^{-1}
1	0.0400	0.0150	0.0250	4.20×10^{-2}
2	0.0200	0.0150	0.0250	2.10×10^{-2}
3	0.0200	0.0150	0.0500	8.40×10^{-2}

It is known that the reaction is second order with respect to hydrogen ions.

(i) Determine the order of the reaction with respect to IO_3^- and I^- ions. Explain your reasoning. [2]

Using Expt 1 and 2, where $[H^+]$ and $[I^-]$ are kept constant,
When $[IO_3^-]$ doubles, the initial rate doubles.
Hence the reaction is 1st order with respect to IO_3^-. [1]

Using Expt 2 and 3, where $[H^+]$ and $[IO_3^-]$ are kept constant,
When $[I^-]$ doubles, the initial rate quadruples.
Hence the reaction is 2nd order with respect to I^-. [1]

Examiners' Comments:

- Majority of students were able to solve this question, with most using the easier "by observation" method. Students using this method are advised to use 'increases' (e.g. doubled / 2 times) instead of 'decreases' (e.g. halved / ½ times) as it becomes confusing when the ratio is not a nice 2x or 4x.
- Students who did not make reference to relevant experiments were penalised.

(ii) Hence, write the rate equation for the reaction. [1]

rate = k $[IO_3^-][H^+]^2[I^-]^2$ [1]

Examiners' Comments:

- Majority of students were able to solve this question. The most common mistake was omitting H^+ from the equation due to not recognising the significance of it being in Table 1.1, and also not reading the question properly.

The reaction is then repeated at the same temperature but at different pH.

Table 1.2 lists the concentrations of IO_3^-, I^- and the pH at which the experiments are carried out.

Table 1.2

Expt	$[IO_3^-]$ / mol dm^{-3}	$[I^-]$ / mol dm^{-3}	pH	$[H^+]$ / mol dm^{-3}
4	0.0400	0.0250	1.0	0.100
5	0.0400	0.0250	2.0	0.0100

(iii) Complete Table 1.2 with the concentrations of H^+ ions in experiments 4 and 5. [1]

(iv) Calculate the value of $\frac{\text{rate at pH 1.0}}{\text{rate at pH 2.0}}$. [1]

$$\frac{\text{rate at pH 1.0}}{\text{rate at pH 2.0}} = \frac{(0.100)^2}{(0.0100)^2} = 100$$ [1] with working, ecf from (iii)

Examiners' Comments:

- Majority of students were able to solve this question. Some students however, went through the unnecessarily longer method of determining the rate via a ratio method using Expt 1, not recognising that the other values would all cancel out using Expts 4 & 5.

(b) In an aqueous solution, iron(III) ions react with iodide ions as shown.

$$2Fe^{3+} + 2I^{-} \rightarrow 2Fe^{2+} + I_2$$

The kinetics of this reaction were investigated and below are some information about the reaction

- The reaction is first order with respect to Fe^{3+} and second order with respect to I^{-}.
- The mechanism for this reaction has three steps.
- Each step involves only two ions reacting together.

The first step of the mechanism has been written for you.

Suggest equations for the remaining two steps of this mechanism and identify the rate-determining step. [3]

step 1: $Fe^{3+} + I^{-} \rightleftharpoons FeI^{2+}$

step 2: $FeI^{2+} + I^{-} \rightarrow Fe^{2+} + I_2^{-}$ OR $FeI^{2+} + I^{-} \rightarrow FeI_2^{+}$ [1]

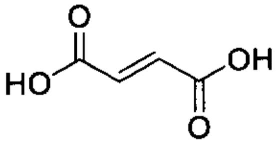
step 3: $Fe^{3+} + I_2^{-} \rightarrow Fe^{2+} + I_2$ OR $Fe^{3+} + FeI_2^{+} \rightarrow 2Fe^{2+} + I_2$ [1]

rate-determining step: 2 [1]

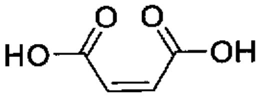
Examiners' Comments:

- Majority of students were unable to solve this question, with many failing to utilise the information that "each step involves only two ions reacting together". Many students also did not ensure that their atoms and charges for each step were balanced, and that their overall reaction equation matched the one given in the question stem.

(c) Fumaric acid is a white solid that occurs widely in nature and has a fruit-like taste and hence used as a food additive. Maleic acid is a stereoisomer of fumaric acid.



fumaric acid



maleic acid

(i) State the type of isomerism that fumaric acid and maleic acid shows. [1]

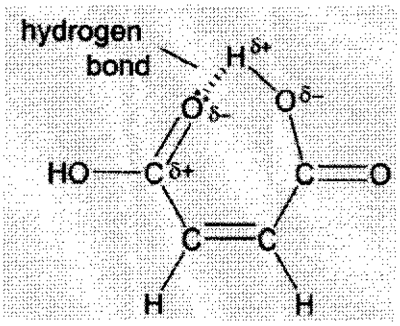
cis-trans isomerism [1]

Examiners' Comments:

- Question was well done.

(ii) Fumaric acid has a melting point of 286 °C while maleic acid has a melting point of 131 °C.

With the aid of a suitable diagram, suggest why maleic acid has a lower melting point than fumaric acid. [2]



Intramolecular hydrogen bonds form between the two COOH groups due their proximity to each other. [1] diagram + explanation

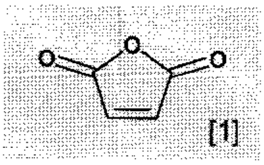
This results in less extensive intermolecular hydrogen bonds forming and hence maleic acid has a lower melting point. [1]

Examiners' Comments:

- Majority of students were unable to recognise that intramolecular hydrogen bonding was the reason for the huge difference in melting point.
- The weakest students explained using reasons that resulted in fumaric acid having a lower melting point instead.

(iii) In the industry, maleic acid is obtained by reacting maleic anhydride, $C_4H_2O_3$, with water.

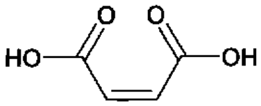
Suggest a possible structure of maleic anhydride.



[1]

maleic anhydride

$+ H_2O \longrightarrow$



maleic acid

[1]

Examiners' Comments:

- Majority of students were unable to obtain the correct structure, with many having structures with more H atoms than in the given molecular formula. Many students also had a charged structure, which is incorrect.
- For the students who attempted to draw a structure with the correct molecular formula, many did not consider if the reaction was viable based on their knowledge of OC reactions. This reaction is the hydrolysis of ester, adding "H_2O" to the anhydride's molecular formula.

The atom economy of a reaction is a measure of the amount of starting materials that end up as useful products. It is important for sustainable development and for economic reasons to use reactions with high atom economy.

The percentage atom economy of a reaction is calculated with the following equation.

$$\text{atom economy} = \frac{\text{mass of desired product}}{\text{total mass of products}} \times 100\%$$

Maleic anhydride can be obtained industrially by the oxidation of butane (reaction 1.1) or benzene (reaction 1.2).

reaction 1.1 $C_4H_{10} + 3\frac{1}{2}\,O_2 \rightarrow C_4H_2O_3 + 4H_2O$

reaction 1.2 $C_6H_6 + 4\frac{1}{2}\,O_2 \rightarrow C_4H_2O_3 + 2H_2O + 2CO_2$

(iv) Calculate the atom economy for each reaction and suggest which reaction is preferred. [2]

for reaction 1.1:
atom economy
$= (4\times12 + 2\times1 + 3\times16) / (4\times12 + 2\times1 + 3\times16 + 4\times18.0) \times 100\%$
$= 98/170$
$= 57.6\%$

for reaction 1.2:
atom economy
$= (4\times12 + 2\times1 + 3\times16) / (4\times12 + 2\times1 + 3\times16 + 2\times18.0 + 2\times44.0) \times 100\%$
$= 98/222$
$= 44.1\%$ [1] both values

Reaction 1.1 should be used because it has the larger atom economy. [1]

Examiners' Comments:
- Majority of students were able to perform the calculations correctly.
- Students are reminded to always explain their answers fully where it is not immediately obvious.

(v) Suggest another reason why the reaction you selected in **(iv)** is preferred. [1]

Benzene in reaction 1.2 is toxic OR
Reaction 1.1 does not generate CO_2 which is a greenhouse gas. [1]

ecf from (iv): butane is more flammable than benzene, etc.

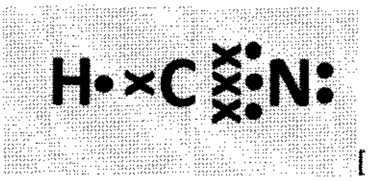
Examiners' Comments:
- Atom economy already comprises the element of cost, so that should not be the focus.
- For students who talked about CO_2, an explanation of the relevant property (i.e. it is a greenhouse gas) must be given. Students should also not jump straight to the final effect of 'global warming'.

[Total: 15]

2 The Andrussow process involves heating a mixture of methane, ammonia and oxygen over a platinum catalyst at 1200 °C to generate hydrogen cyanide.

$$2CH_4 + 2NH_3 + 3O_2 \rightarrow 2HCN + 6H_2O$$

(a) **(i)** Draw a dot-and-cross diagram of HCN and state its shape. [2]



[1]

linear [1]

(ii) Given that the oxidation number of hydrogen remains at +1 throughout the reaction, complete Table 2.1 with the oxidation numbers of carbon, nitrogen and oxygen in the reactants and products.

Table 2.1

	carbon	nitrogen	oxygen
oxidation number of element in reactant	–4	–3	0
oxidation number of element in product	+2	–3	–2

[2]

[2] for all 6 values
[1] for 3-5 correct values

Examiners' Comments:

- Few students were able to obtain the full 2marks (due to HCN), reflecting a fundamental lack of understanding of the term "oxidation state". The oxidation state of an element is the charge that it would have, if it were an ion (note that there need not actually be ions present). A consideration of the electrons gained/lost by the element would enable determination of the corresponding oxidation state.

(b) Hydrogen cyanide is a weak acid in aqueous solution.

(i) State what is meant by the term *weak acid.* [1]

Weak acids are acids that partially dissociate / ionise in aqueous solution to give H^+.

Examiners' Comments:

- The most common mistake was omitting "H^+" to explain for the term "acid".

(ii) The pH of a solution of 0.10 mol dm^{-3} HCN is 5.10.

Calculate the acid dissociation constant, K_a, of HCN. [2]

$[H^+] = 10^{-5.1}$

$= 7.943\times10^{-6}$ mol dm^{-3} [1]

$$K_a = \frac{[H^+][CN^-]}{[HCN]}$$

$$= \frac{(7.943\times10^{-6})^2}{0.10 - 7.943\times10^{-6}}$$

$= 6.31\times10^{-10}$ mol dm^{-3} [1]

since the "change" is known, mark not awarded if assumption is made that degree of dissocation is small, such that $[HCN]_{eqm} = [HCN]_{initial}$ (although final answer is same)

(c) The reaction between propanone and HCN produces 2-hydroxy-2-methylpropanenitrile.

$$(CH_3)_2CO + HCN \rightarrow (CH_3)_2C(OH)CN$$

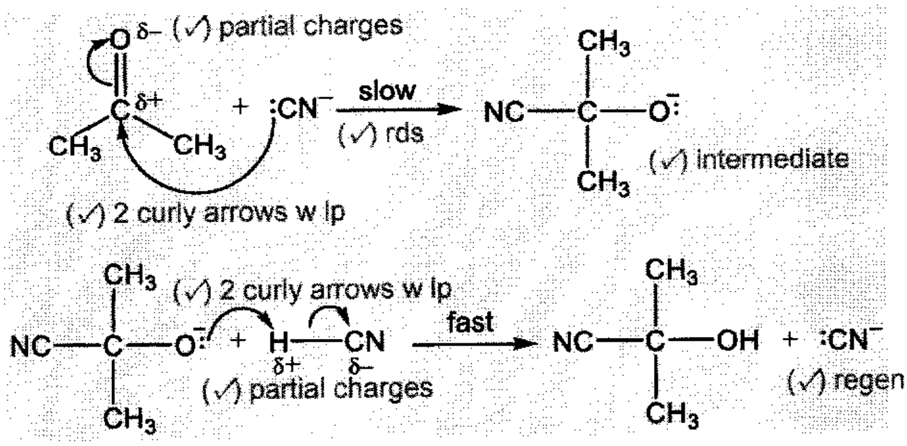
(i) Describe the mechanism for this reaction between propanone and HCN.

Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows. [3]

Nucleophilic Addition (✓)

$HCN \rightleftharpoons H^+ + CN^-$

$NaCN \rightarrow Na^+ + CN^-$ OR $NaOH + HCN \rightarrow Na^+ + CN^- + H_2O$ (✓) both



[3] – all 9 (✓) [2] – any 5 (✓) [1] – any 3 (✓)

Examiners' Comments:

- Despite this being a recall question, a significant number of students were unable to get at least 2m.
- Many students omitted the 'generation of nucleophile' step; had misconceptions on the direction of curly arrows; used HCN instead of CN$^-$ for the first step.

(ii) State the hybridisation state of the carbonyl carbon in propanone. [1]

sp^2 [1]

Examiners' Comments:
- Question was well done.

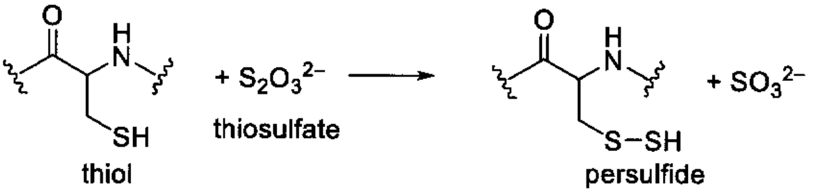
(iii) Suggest whether 2-hydroxy-2-methylpropanenitrile produced through this reaction will rotate plane-polarised light. [1]

No, as 2-hydroxy-2-methylpropanenitrile is not chiral.

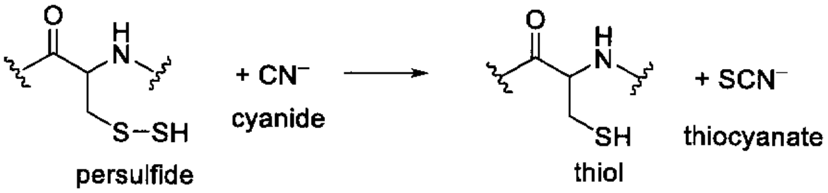
"reaction produces a racemic mixture" not accepted (product is not even chiral to begin with)

(d) Sodium thiosulfate, $Na_2S_2O_3$, is administered as a treatment of cyanide poisoning. It converts the cyanide ion to the less toxic thiocyanate ion. This process is facilitated by the enzyme rhodanese found in the kidney and liver via a two-step process.

In the first step, thiosulfate is reduced by the thiol group present on cysteine-247 of rhodanese to form a persulfide.



In the second step, the persulfide reacts with cyanide to produce thiocyanate.



(i) Explain why the reaction between thiosulfate and cyanide ions occurs slowly in the absence of rhodanese. [1]

The electrostatic repulsion between similarly charged ions / anions $S_2O_3^{2-}$ and CN^- leads to a high activation energy for the reaction. [1]

Examiners' Comments:
- Many students only explained what the catalyst does, instead of why this specific reaction had a low rate

(ii) Fig. 2.1 shows how the rate of the reaction varies with increasing concentrations of sodium thiosulfate.

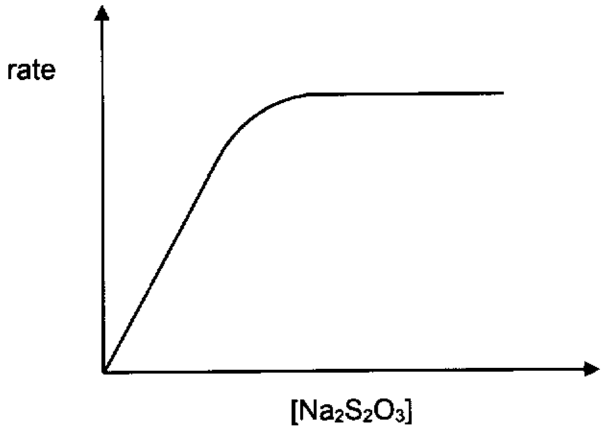


Fig. 2.1

Explain why the graph in Fig. 2.1 levels off at high concentrations of sodium thiosulfate. [1]

At high concentrations of sodium thiosulfate, the active sites on rhodanese are fully occupied / saturated, hence increasing the concentration of sodium thiosulfate will not increase the rate of reaction. [1]

Examiners' Comments:
- Question is generally well done.

(e) Hydrogen cyanide can be oxidised to form cyanogen, a highly toxic gas.

Cyanogen is composed of 46.2% carbon and 53.8% nitrogen by mass.

(i) Determine the empirical formula for cyanogen. [1]

	C	N
% by mass	46.2	53.8
% by mass / A_r	46.2/12 = 3.85	53.8/14 = 3.84
Simplest mole ratio	1	1

empirical formula is CN [1] with working

Examiners' Comments:
- Question is generally well done. Students should work on their presentation of answers for this standard question.

(ii) At 25 °C and 101 kPa, 1.05 g of cyanogen occupies 0.500 dm^3.

Calculate the relative molecular mass of cyanogen, and hence deduce its molecular formula. **[2]**

Using pV = nRT,
$101\times10^3\times0.500\times10^{-3} = \frac{1.05}{M_r}\times8.31\times298$
M_r of cyanogen = 51.5 (1dp) [1]

Check for conversion of units for pressure to Pa and volume to m^3.

Let molecular formula of cyanogen be $(CN)_n$
$(CN)_n = 51.5$
$n = 51.5\div(12 + 14)$
$n = 2$
Molecular formula of cyanogen is C_2N_2 [1]

Examiners' Comments:

- Question is generally well done. Weaker students still struggle with unit conversions involving the ideal gas equation.

[Total: 17]

3 (a) The following is a procedure for the preparation of potassium chlorochromate (KCC), $KCrO_3Cl$, also called Péligot's salt in recognition of the French chemist who discovered it.

> Place 6.0 g of potassium dichromate(VI) in a 100 cm^3 beaker. Slowly add 8.0 g of concentrated hydrochloric acid and 1.0 cm^3 water and warm the mixture gently. If this is done carefully, the dichromate(VI) will dissolve without the evolution of chlorine. On cooling the beaker in an ice bath, orange-red crystals of Péligot's salt will be deposited.

However, the procedure suggests that strong heating may cause chlorine gas to be formed.

(i) Write an overall ionic equation for the production of chlorine gas from the reaction between $K_2Cr_2O_7$ and HCl. [1]

$Cr_2O_7^{2-} + 14H^+ + 6Cl^- \rightarrow 2Cr^{3+} + 7H_2O + 3Cl_2$ [1]

Examiners' Comments:

- Not as well done as expected. Most common mistake was not balancing the electrons as required for a redox reaction.

(ii) Calculate the standard cell potential, E°_{cell}, for the reaction in **a(i)**. [1]

$E^\circ_{cell} = +1.33 - (+1.36)$
$= -0.03$ V [1]

Examiners' Comments:

- Not as well done as expected. Most common mistake was flipping the values in order to obtain a positive E°_{cell}, neglecting consideration of the actual reactions and question context, which is that the halogen is **not** a desired product.
- Similarly to ΔH, the sign is also always required, even if positive.

(iii) Using dilute HCl(aq) in the above process will prevent the production of chlorine gas. Suggest why this is so. [1]

$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ $E^\circ_{red} = +1.36$V

When dilute HCl is used, $[Cl^-]$ is lowered and the resultant E_{cell} will be more negative and hence Cl_2 will not be produced.

OR

$Cr_2O_7^{2-} + 14H^+ 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$ $E^\circ_{red} = +1.33$V

When dilute HCl is used, $[H^+]$ is lowered and the resultant E_{cell} will be more negative and hence Cl_2 will not be produced.

[1] either case to show the decrease in concentration leading to E_{cell} is more negative

Examiners' Comments:

- A significant number of students were unable to see that the concentration change would shift POE of the redox reactions due to LCP.
- A handful of students raised the possibility of H_2O reacting with dichromate instead since $E^\circ_{cell} > 0$. However, we frequently use $K_2Cr_2O_7$(aq) (not in this question), and although the reaction with H_2O is spontaneous, it takes place at a very low rate.

(iv) Predict if it is possible to prepare the bromine equivalent of Péligot's salt by using HBr in place of HC*l*. [1]

$E^\ominus_{cell}$ = +1.33 – (+1.07)
= +0.26V insufficient to just say $E^\ominus_{Br_2/Br^-} < E^\ominus_{Cl_2/Cl^-}$
> 0 (spontaneous)

<u>No, as HBr will be oxidised to Br_2</u>. [1] with working

Examiners' Comments:

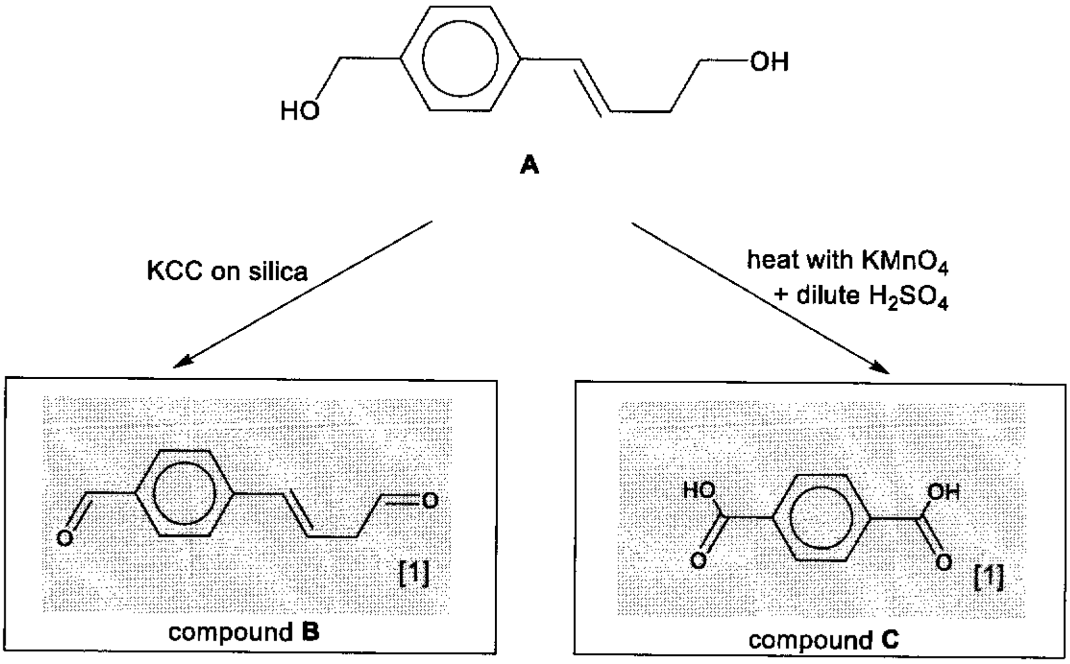
- Refer to comments in **(ii)**. The halogen is **not** a desired product as it means that there is less dichromate and HX for the actual reaction to produce the salt.

KCC supported on silica gel is used to selectively oxidise alcohols to their carbonyl compounds without further oxidation to carboxylic acids.

(v) Compound **A** can undergo oxidation with KCC on silica and acidified potassium(VII) manganate but the organic product formed in each reaction is different.

Compound **B** has the molecular formula $C_{11}H_{10}O_2$ and compound **C** has the molecular formula $C_8H_6O_4$.

Deduce the structures of **B** and **C**.



[2]

Examiners' Comments:

- Question was generally well done.
- Most common mistake was for **C**, where students did not oxidise the entire side-chain on the right side of the benzene ring to –COOH (H on C_α present).

(b) Phosphorus is an element in Group 15. It forms two chlorides, PCl_3 and PCl_5 which are commonly used in qualitative analysis to test for specific organic functional groups.

(i) With the aid of a relevant equation, describe what would be observed when PCl_5 is added to a beaker of water containing a few drops of methyl orange. [2]

$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$ [1]

The solution will turn **red** due to the formation of a strongly acidic solution. [1]

Examiners' Comments:
A number of students gave $POCl_3$ as the product instead of H_3PO_3.

An organic compound, **D**, $C_nH_{2n+2}O$, was vapourised and 10 cm^3 of the vapour was burnt in excess oxygen and cooled to room temperature and pressure. A contraction of 20 cm^3 in volume was observed as the reaction mixture was shaken with sodium hydroxide. White fumes are produced when **D** reacted with PCl_5.

(ii) State the identity of compound **D**. [1]

Ethanol or CH_3CH_2OH [1]

Examiners' Comments:
Majority of students did not give the identity of D although they identified the correct molecular formula.

(iii) Hence write a balanced equation for the reaction between PCl_5 and **D**. [1]

$CH_3CH_2OH + PCl_5 \rightarrow CH_3CH_2Cl + POCl_3 + HCl$ [1]

Examiners' Comments:
Majority of students were unable to do this question. Some of the students who attempted gave H_3PO_4 as the product instead of $POCl_3$.

Phosphoramides are compounds in which one or more of the OH groups of phosphoric acid, H_3PO_4, have been replaced with an amino or substituted amino group. A common example is phosphoric triamides, $PO(NR_2)_3$, where R represents an alkyl group.

(iv) Explain why the nitrogen equivalent of phosphoric triamides, $NO(NR_2)_3$, does not exist. [1]

The central N atom does not have low-lying vacant orbitals to expand octet.
OR
N atom is smaller than P atom and the bulky $-NR_2$ groups around the N atom results in too much steric hindrance. [1]

Examiners' Comments:
Some students gave the correct concept but did not include keywords like "low-lying" or "energetically accessible".

(v) Explain why phosphoric triamides, $PO(NR_2)_3$, cannot be produced by reacting phosphoric acid with an amine. [1]

An acid-base reaction would take place instead. [1]

Examiners' Comments:
This question was generally well-done.

(c) Silver nitrate is commonly used to test for the presence of halides. In the presence of halides, a precipitate of sparingly soluble silver halide would be formed.

A mixture of water and solid silver chloride is shaken and left to equilibrate at 25 °C. The resulting mixture was then filtered to obtain a saturated solution of silver chloride.

(i) Write an expression for the solubility product, K_{sp}, of $AgCl$. [1]

$K_{sp} = [Ag^+][Cl^-]$ [1]

Examiners' Comments:
This question was generally well-done. Most common error was the inclusion of $[AgCl]$

(ii) Given that the concentration of the saturated solution is 1.33×10^{-5} mol dm^{-3} at 25 °C, calculate the value of K_{sp} for $AgCl$ at 25 °C and state its units. [2]

$[AgCl] = [Ag^+] = [Cl^-] = 1.33 \times 10^{-5}$ mol dm^{-3}

$K_{sp} = (1.33 \times 10^{-5})^2 = 1.77 \times 10^{-10}$ mol^2 dm^{-6}

[1] for value
[1] for units

Examiners' Comments:
This question was generally well-done.

[Total: 15]

4 Hydrogen is considered a clean fuel because it only produces water upon combustion.

The current method of large-scale production of hydrogen is through steam methane reforming followed by the water-gas shift reaction.

Methane, the main component of natural gas, is first reacted with steam (reaction 4.1).

reaction 4.1 $CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$ $\Delta H = +206 \text{ kJ mol}^{-1}$

The carbon monoxide generated is then reacted with more steam in the water-gas shift reaction (reaction 4.2).

reaction 4.2 $CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$

(a) State the total amount of hydrogen that can be obtained per mole of methane through this entire process. [1]

4 mol [1]

Examiners' Comments:
This question was generally well-done.

(b) **(i)** Explain what is meant by the term *entropy.* [1]

Entropy is a measure of the disorderliness of a system. It gives a measure of the extent to which particles and energy are distributed within the system. [1]

Examiners' Comments:
This question was not done well as students missed out on the keywords required.

(ii) The value of ΔS for reaction 4.1 is $+111 \text{ J mol}^{-1} \text{ K}^{-1}$.

Explain why the sign of ΔS for reaction 4.1 is positive. [1]

As the amount of gaseous product is more than the amount of gaseous reactants (4 >2), this results in more ways to arrange the particles and distribute the energy and hence the change in entropy is positive. [1]

Examiners' Comments:
Many students did not state "more ways to arrange the particles and distribute the energy" in the answer.
Most common error include the omission of "gaseous" in the answer.

(iii) Calculate the Gibbs Free Energy, ΔG for reaction 4.1 at 298 K and explain the significance of its sign. [2]

$\Delta G = \Delta H - T\Delta S$

$\Delta G = +206 - 298(\frac{+111}{1000}) = +173 \text{ kJ mol}^{-1}$ [1]

Since $\Delta G > 0$, reaction is **<u>not spontaneous</u>** at 298 K. [1]

ecf significance based on sign of calculated value

Examiners' Comments:
This question was generally well-done.
Common errors include not converting the units of ΔS, and omitting the sign for ΔG.

Hydrogen that is produced by the method described in reactions 4.1 and 4.2 is referred to as "grey" hydrogen as carbon dioxide is released during production. However, if the carbon dioxide can be significantly removed, it is then referred to as "blue" hydrogen.

Fig. 4.1 shows how calcium oxide is used to capture carbon dioxide to be utilised in the industry and how the calcium oxide can be reused.

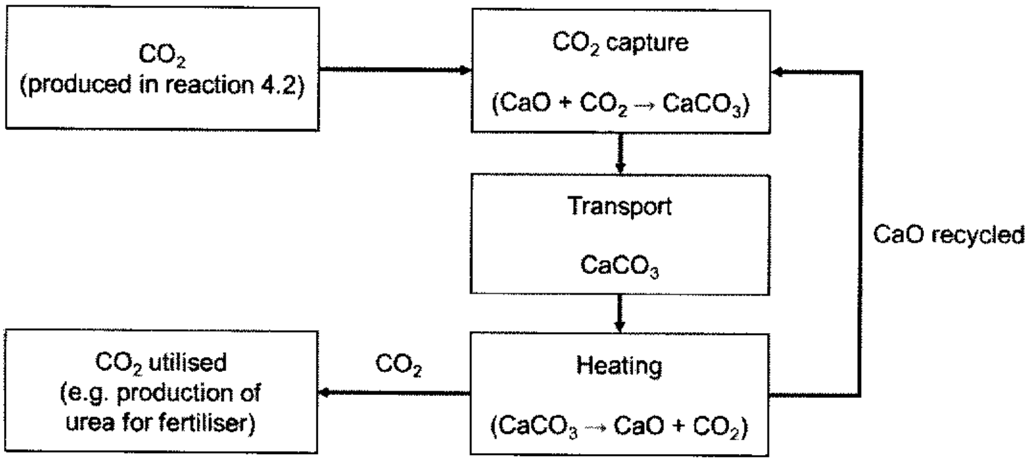


Fig. 4.1

(c) By considering the carbon dioxide capturing process above, suggest if magnesium oxide should be used instead of calcium oxide. Explain your answer.

You may assume that both magnesium oxide and calcium oxide react in the same way with carbon dioxide. [2]

Yes. MgO should be used instead because $MgCO_3$ has a <u>lower thermal decomposition temperature</u> [1] than $CaCO_3$, hence <u>lesser energy would be required to release the CO_2</u> [1] and regenerate MgO for subsequent use.

Examiners' Comments:
Many students did not use the correct concept to answer this question and did not give all the required keywords. Some students linked lower thermal decomposition to rate of reaction instead of the energy required to decompose the metal carbonate.

In the search for alternatives to hydrogen, ammonia emerged as a promising substitute. Ammonia combusts to form nitrogen gas and water.

In March 2024, Fortescue successfully conducted trials involving the use of ammonia, in combination with diesel, as a marine fuel onboard the Singapore-flagged Fortescue Green Pioneer.

(d) State one advantage of using a combination of ammonia and diesel as fuel. [1]

Lesser carbon dioxide will be emitted because burning ammonia does not produce carbon dioxide. [1]

Examiners' Comments:
Some students gave ambiguous answers like "produces less harmful gas", "environmentally friendly"

(e) State one disadvantage of using ammonia as a fuel. [1]

Ammonia is toxic.

OR

High chance of forming oxides of nitrogen at high temperatures. [1]

Examiners' Comments:
Majority of the students are unable to answer this question, with some restating the information given in the question stem (i.e., formation of nitrogen gas).

Ammonia can also be used directly in fuel cells.

Solid oxide fuel cells (SOFCs) employ a solid oxide material as the electrolyte to transport oxide ions from the cathode to the anode. Oxygen is fed through the cathode while the chosen fuel is fed through the anode. SOFCs typically operate at high temperatures ranging from 800 to 1000 °C.

In SOFCs that utilise ammonia, the ammonia supplied is first thermally decomposed over a catalyst to form nitrogen and hydrogen.

$$2NH_3 \rightarrow 3H_2 + N_2$$

The hydrogen produced from the decomposition of ammonia is then oxidised to form water.

(f) Write the equations for the reactions at the cathode and anode. [2]

cathode: $\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-}$ [1]

anode: $H_2 + O^{2-} \rightarrow H_2O + 2e^-$ [1]

Examiners' Comments:
Majority of the students find this question demanding. Many did not read the question carefully to know the reactions that happen at the respective electrode.

(g) One advantage of ammonia over hydrogen as a fuel in SOFCs is that it can be easily liquefied by applying pressure at room temperature making transportation much easier.

(i) Suggest why ammonia can be easily liquefied at room temperature by compressing it under pressure. [1]

When compressed, the ammonia molecules are close enough for the strong hydrogen bonds to become significant, causing ammonia to be liquefied. [1]

Intermolecular forces of attraction acceptable here

Examiners' Comments:
Many students did not link to the question on "compressing" the gas.

(ii) The values of pV are plotted against p for an ideal gas and H_2 on Fig. 4.2, where p is the pressure of the gas and V is the volume occupied by the gas.

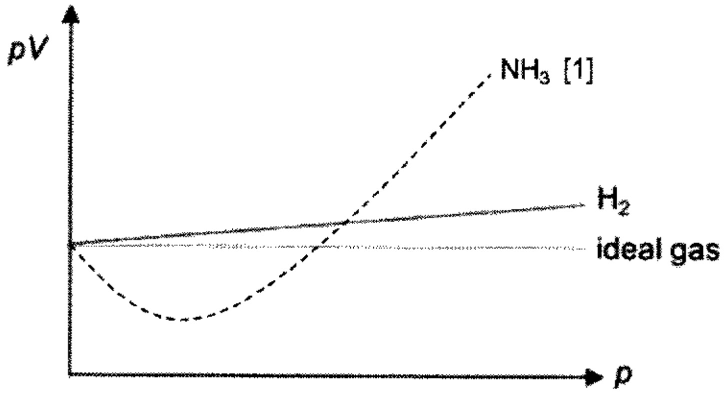


Fig. 4.2

Sketch a graph on Fig. 4.2, to illustrate how the pV of NH_3 changes with p. [1]

Examiners' Comments:
This question was badly done.

[Total: 13]

5 The lanthanoids (Ln) form a series in the Periodic Table comprising the elements from lanthanum to lutetium. They play a vital role in the manufacturing of smartphones, be it in the phone circuitry or speakers. The vivid red, blue and green colours on the screens can also be attributed to these metals. In fact, the vibration unit of the phone utilises neodymium, terbium and dysprosium. These elements have some similar properties as d–block elements.

- Many of the lanthanoid elements are obtained through heating their trichlorides or trifluorides with calcium at 1000 °C.
- The electronic configuration of the atoms of lanthanoid elements consists of the electronic configuration of xenon followed by electrons in the 4f and 6s orbitals and sometimes the 5d orbitals.
- There are a total of 7 orbitals in the 4f subshell. As the 4f orbitals are very diffused, the shielding effect from electrons in these orbitals is negligible.
- All lanthanoids are known to form Ln^{3+} ions and form complex ions such as $[Sm(H_2O)_9]^{3+}$ and $[Yb(H_2O)_8]^{3+}$.
- While some lanthanoids can occasionally exist in the +4 oxidation state, these are rare and typically unstable. Cerium, however, is notable for its stable +4 oxidation state, which exists even in aqueous solution.
- Many of the complex ions formed from the elements in the lanthanoid series are coloured and this colour can be attributed to f–f transitions.

Table 5.1 lists the electronic configurations and ionic radii of eight lanthanoids.

Table 5.1

element	atomic number	electronic configuration	ionic radius, Ln^{3+}/nm
Lanthanum, La	57	[Xe] $5d^1$ $6s^2$	0.115
Cerium, Ce	58	[Xe] $4f^2$ $6s^2$	0.111
Gadolinium, Gd	64	[Xe] $4f^7$ $5d^1$ $6s^2$	0.102
Terbium, Tb	65	[Xe] $4f^9$ $6s^2$	0.100
Holmium, Ho	67	[Xe] $4f^{10}$ $6s^2$	0.097
Thulium, Tm	69	[Xe] $4f^{13}$ $6s^2$	0.095
Ytterbium, Yb	70	[Xe] $4f^{14}$ $6s^2$	0.094
Lutetium, Lu	71	[Xe] $4f^{14}$ $5d^1$ $6s^2$	0.093

The electronic configuration of xenon is $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^{10}$ $4s^2$ $4p^6$ $4d^{10}$ $5s^2$ $5p^6$.

(a) The lanthanoids can be described as being in a 'block' of the Periodic Table.

State the name of this block. [1]

f block [1]

Examiners' Comments:
A number of students wrongly identified this block as Transition metals or d-block.

(b) Write a balanced equation for the reduction of holmium(III) fluoride, HoF_3, by calcium. [1]

$2HoF_3 + 3Ca \rightarrow 2Ho + 3CaF_2$ [1]

Examiners' Comments:
Many students did not attempt this question or gave a wrong equation.

(c) **(i)** State the electronic configuration of a La^{3+} ion. [1]

La^{3+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6$ [1]

(essentially [Xe])

Examiners' Comments:
This question was generally well done.

(ii) Hence, suggest why solutions containing $[La(H_2O)_9]^{3+}$ are colourless. [1]

La^{3+} has no electrons in the 4f orbitals and no f–f transitions can take place [1]. Hence solutions appears colourless.

Examiners' Comments:
Majority of the students found this question challenging. Weaker responses use d-d transition to explain.

(iii) Suggest a reason why gadolinium has the electronic configuration [Xe] $4f^7\ 5d^1\ 6s^2$ rather than [Xe] $4f^8\ 6s^2$. [1]

There is extra stability associated with a half filled 4f subshell.

OR

To reduce interelectronic repulsion between paired electrons in the 4f orbital. [1]

Examiners' Comments:
This question was generally well done. Weaker response used "partially filled" instead of "half filled".

(iv) State and explain the trend observed for the ionic radii of the Ln^{3+} ions. [2]

Across the period, nuclear charge increases but shielding effect is the same as electrons are added to the 4f orbitals which have negligible shielding effect, hence the effective nuclear charge increases. [1]
There is greater nuclear attraction on the valence electrons resulting in a smaller ionic radius. [1]

Examiners' Comments:
Many applied the correct concept but lack keywords.

(d) Suggest why the complex ions of the lanthanoids can contain more ligands than those of transition metals. [1]

The lanthanoid ions are larger than the transition metal ions hence there is space for more ligands.

OR

There are more orbitals available to accept lone pairs of electrons from ligands. [1]

Examiners' Comments:
Students must mention "more orbitals" or "larger" to explain in order to show the comparison with transition metals. Weaker responses stated "more d orbitals than transition metals".

(e) Cerium(IV) oxide in catalytic converters helps decrease harmful gas emissions by oxidising carbon monoxide to carbon dioxide and reducing nitrogen monoxide to oxygen and nitrogen.

State a chemical property exhibited by cerium which allows it to behave as a catalyst. [1]

Cerium has energetically accessible vacant orbitals that can be used to form weak bonds with the reactant particles. [1]

OR

Cerium is able to exist in multiple oxidation states. [1]

Examiners' Comments:
This question was generally well done.

(f) Cerium ammonium nitrate (CAN) is used in organic chemistry as a test for alcohol functional groups as it forms a red complex in the presence of alcohols.

$$(NH_4)_2[Ce(NO_3)_6] + 3ROH \rightarrow \underset{\text{red complex}}{[Ce(NO_3)_4(ROH)_3]} + 2NH_4NO_3$$

(i) Given that the nitrate ions act as bidentate ligands, calculate the coordination number of Ce in $[Ce(NO_3)_6]^{2-}$. [1]

6 x 2 = 12 [1]

Examiners' Comments:
A number of students were unable to correctly calculate the coordination number.

(ii) An organic compound, **E**, with the molecular formula $C_7H_{16}O$ did not react with acidified potassium dichromate(VI) solution but gave a red colour with CAN. **E** exists as a pair of enantiomers.

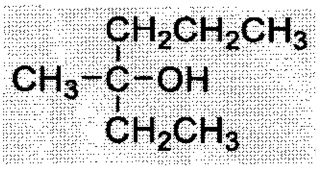
Deduce a possible structure of **E**. [3]

E is alcohol based on the red colour with cerium(IV) ammonium nitrate.

E is a tertiary alcohol since it was not oxidised by acidified dichromate.

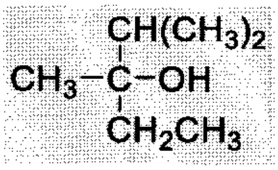
E has a chiral centre/ has a carbon bonded to four different groups

[2] – 3 points
[1] – 2 points



$$\begin{array}{l} \qquad\;\; \mathrm{CH_2CH_2CH_3} \\ \qquad\;\; | \\ \mathrm{CH_3-C-OH} \\ \qquad\;\; | \\ \qquad\;\; \mathrm{CH_2CH_3} \end{array}$$

or

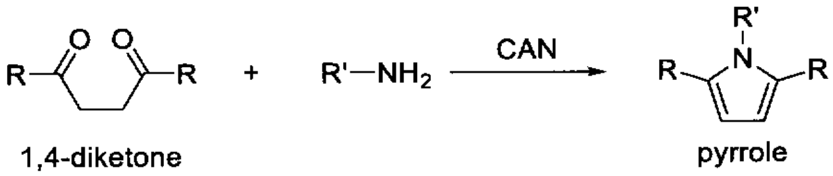


$$\begin{array}{l} \qquad\;\; \mathrm{CH(CH_3)_2} \\ \qquad\;\; | \\ \mathrm{CH_3-C-OH} \\ \qquad\;\; | \\ \qquad\;\; \mathrm{CH_2CH_3} \end{array}$$

[1]

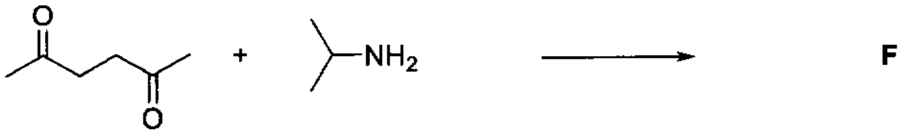
Examiners' Comments:
This questions was demanding for the students and majority of the students did not include deductions in their answers.

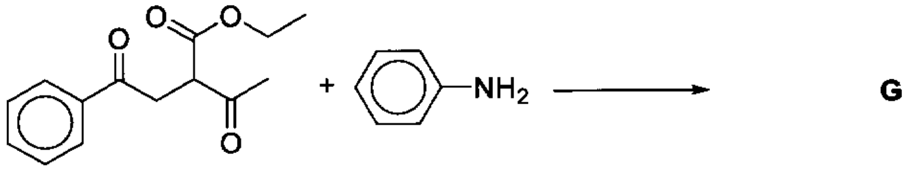
(g) The Paal-Knorr reaction involves the reaction of a 1,4-diketone with an amine to form a pyrrole and CAN is used as a catalyst.



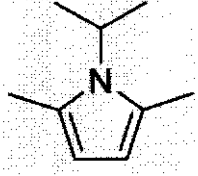
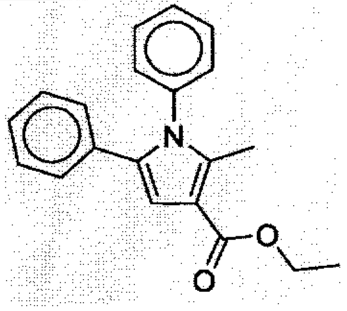
where R and R' are alkyl or aryl groups.

Predict the structures of the pyrroles **F** and **G** formed when the following reactants undergo the Paal-Knorr reaction.





[2]

F	 [1]
G	 [1]

Examiners' Comments:
Students found it challenging to predict structure G.

[Total: 15]