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.

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.

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....

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....

.... [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 $\dfrac{\text{rate at pH 1.0}}{\text{rate at pH 2.0}}$.

$\dfrac{\text{rate at pH 1.0}}{\text{rate at pH 2.0}}$ = ……………………………..[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: $Fe^{3+} + I^{-} \rightleftharpoons FeI^{2+}$

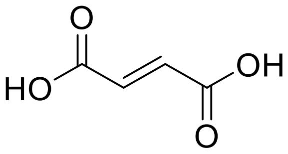
step 2: ……………………………………………………………………………………………..

step 3: ……………………………………………………………………………………………..

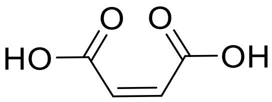
rate-determining step: …………………

[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.

....

....

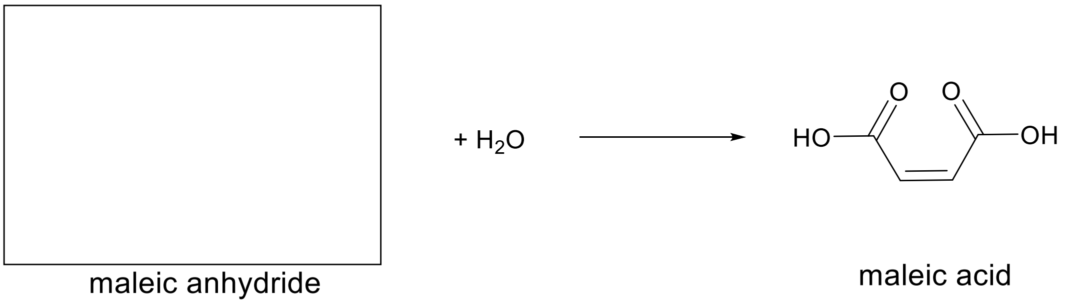
....

....

....[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.



[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 $C_4H_{10} + 3\tfrac{1}{2}\,O_2 \rightarrow C_4H_2O_3 + 4H_2O$

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

(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]

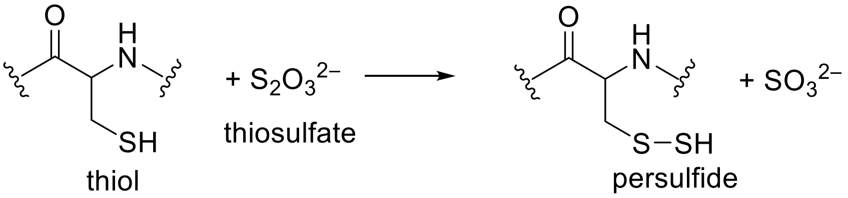
(iii) Suggest whether 2-hydroxy-2-methylpropanenitrile produced through this reaction will rotate plane-polarised light.

....

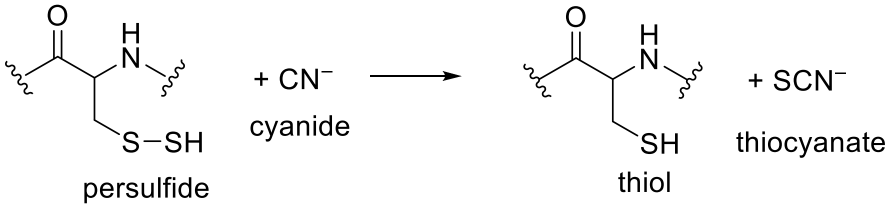
.... [1]

(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.

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.... [1]

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

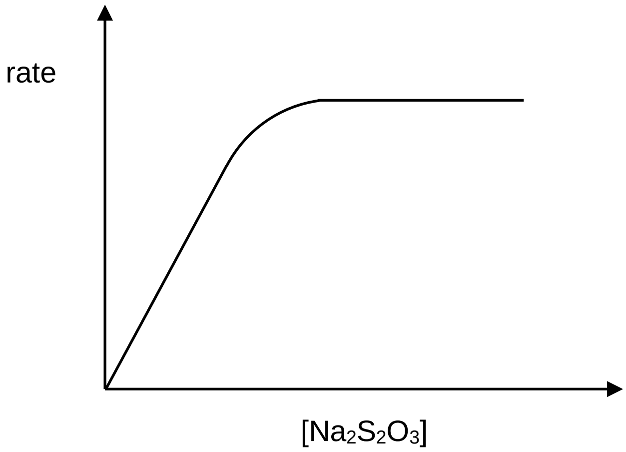

Fig. 2.1

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.

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....

....[1]

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

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....

....

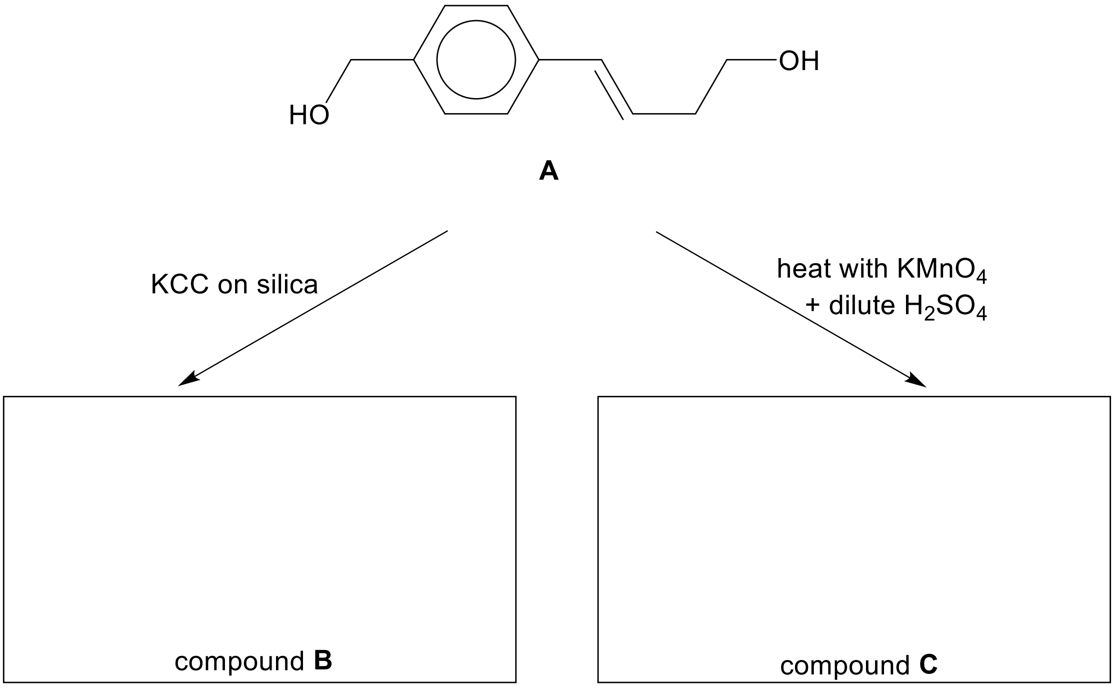
....[1]

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**.



A

[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.

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....

.... [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 J mol^{-1} 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.

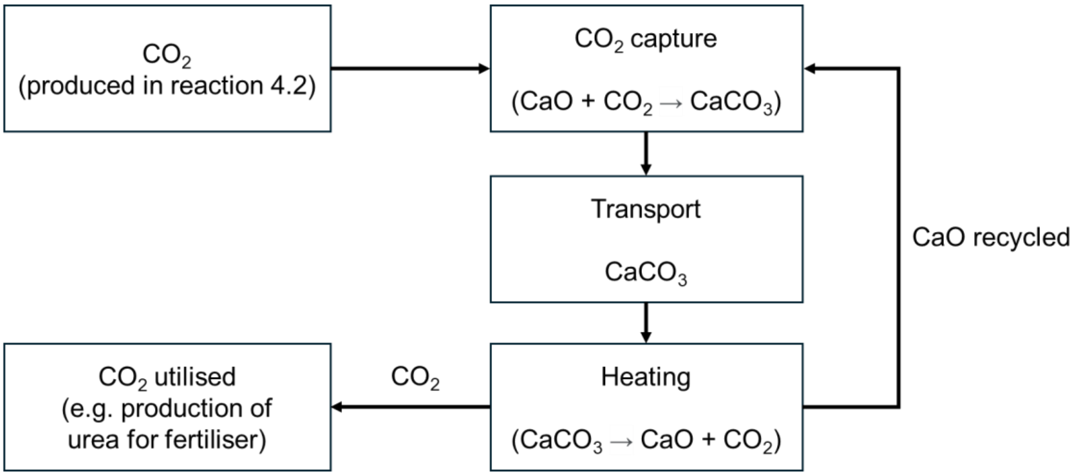

Fig. 4.1

(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.

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…………………………………………………………………………………………………...

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………………………………………………………………………………………………[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.

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……………………………………………………………………………………………

……………………………………………………………………………………………[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.

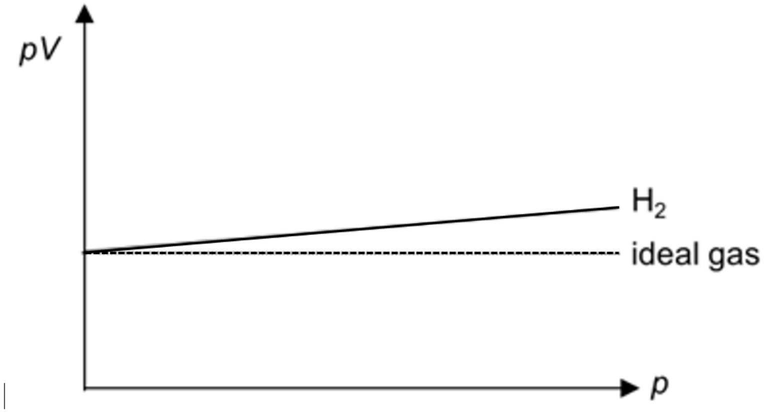


Fig. 4.2

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 $[Ce(NO_3)_6]^{2-}$.

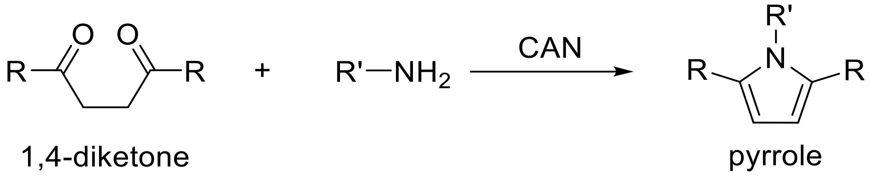
……………………………………………………………………………………………………[1]

(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**.

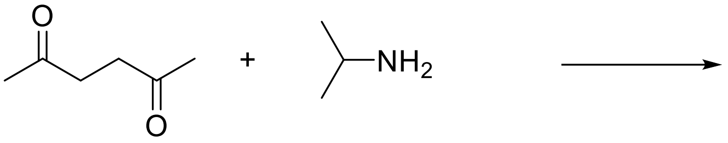
[3]

(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.

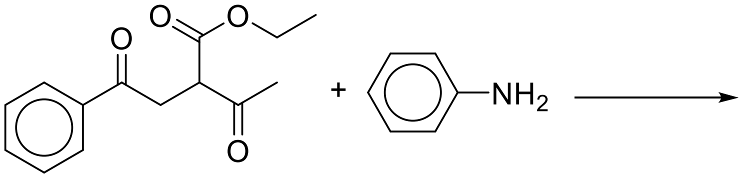


where R and R’ are alkyl or aryl groups.

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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