Answer **all** the questions.

1 Research is being conducted into chemical reactions that can be used on other planets such as Mars.

One reaction being studied is shown below.

$$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g) \qquad \Delta H = +40\,kJ\,mol^{-1} \qquad \textbf{equation 1.1}$$

The atmosphere of Mars consists mainly of carbon dioxide. Hydrogen is initially brought from Earth.

(a) Suggest, with reasons, what effect increasing temperature and pressure would have on the **equilibrium yield** of carbon monoxide and water in **equation 1.1**.

In your answer you should use appropriate technical terms, spelled correctly.

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..... **[4]**

(b) A catalyst of iron and chromium is used.

State why a catalyst is used, giving its effect on K_c.

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..... **[2]**

$$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g) \qquad \Delta H = +40\,kJ\,mol^{-1} \qquad \textbf{equation 1.1}$$

(c) At 500 K, the equilibrium constant for **equation 1.1** is 7.76×10^{-3}.

In an equilibrium mixture at 500 K, the concentrations of hydrogen and carbon dioxide are:

$[H_2] = 1.00 \times 10^{-5}\,mol\,dm^{-3}$

$[CO_2] = 3.46 \times 10^{-5}\,mol\,dm^{-3}$

Calculate the equilibrium concentrations of H_2O and CO at 500 K.

Assume the H_2O and CO come solely from this reaction.

Give your answers to an **appropriate** number of significant figures.

$[H_2O(g)]$ = ... $mol\,dm^{-3}$ $[CO(g)]$ = ... $mol\,dm^{-3}$ **[4]**

(d) The water is electrolysed to regenerate the hydrogen.

(i) Suggest a source of the energy needed to electrolyse water.

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..... **[1]**

(ii) Suggest a reason why the electrolysis of water is beneficial to sustaining life on Mars.

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..... **[1]**

Turn over

$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$ $\Delta H = +40\,kJ\,mol^{-1}$ **equation 1.1**

(e) The entropies of the gases involved in **equation 1.1** are:

Gas	**Entropy, *S* / J mol^{-1} K^{-1}**
CO	+198
CO_2	+214
H_2O	+189
H_2	+131

(i) Calculate the entropy change, ΔS_{sys}, of the forward reaction in **equation 1.1**.

ΔS_{sys} = ... J mol^{-1} K^{-1} **[1]**

(ii) Calculate the temperature at which $\Delta S_{tot} = 0$, giving the units.

T = ... units ..... **[3]**

(iii) What can you conclude about the equilibrium when $\Delta S_{tot} = 0$?

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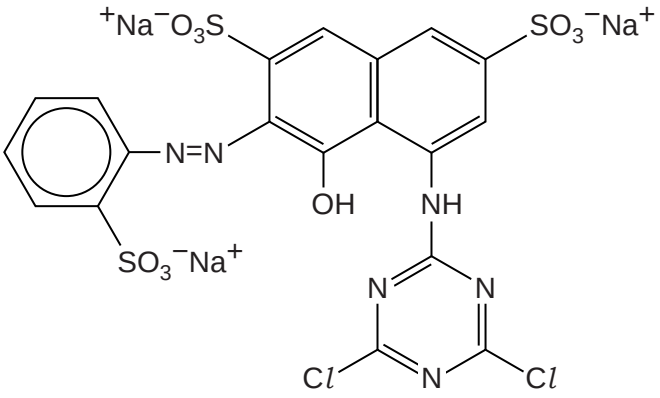
..... **[1]**

[Total: 17]

2 Procion Brilliant Red 2BS, shown below, is a 'fibre reactive' dye that attaches itself to wool by covalent bonds.



Procion Brilliant Red 2BS

(a) Suggest the formula of **one** functional group on the dye that makes it more soluble in water.

Explain why your suggested group does this.

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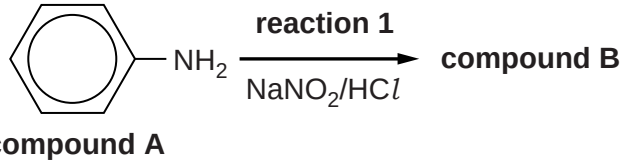
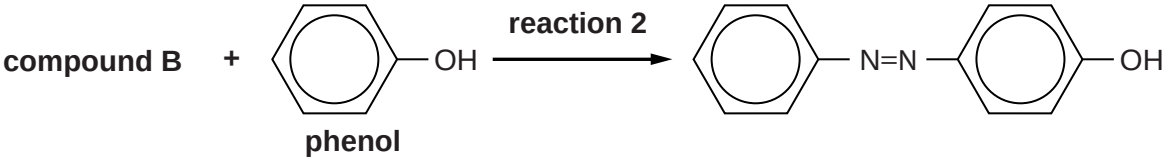
..... **[2]**

(b) A reaction scheme for the formation of a simple azo dye is shown below.





(i) Name the functional group in compound **A** other than the benzene ring.

..... **[1]**

(ii) **Name** compound **B**.

..... **[1]**

(iii) Give the name that describes **reaction 2** in the context of dye formation.

..... **[1]**

(iv) Phenol is acidic in solution. Carboxylic acids are also acidic but react in a way that phenols do not.

Give details of this acidic reaction of carboxylic acids.

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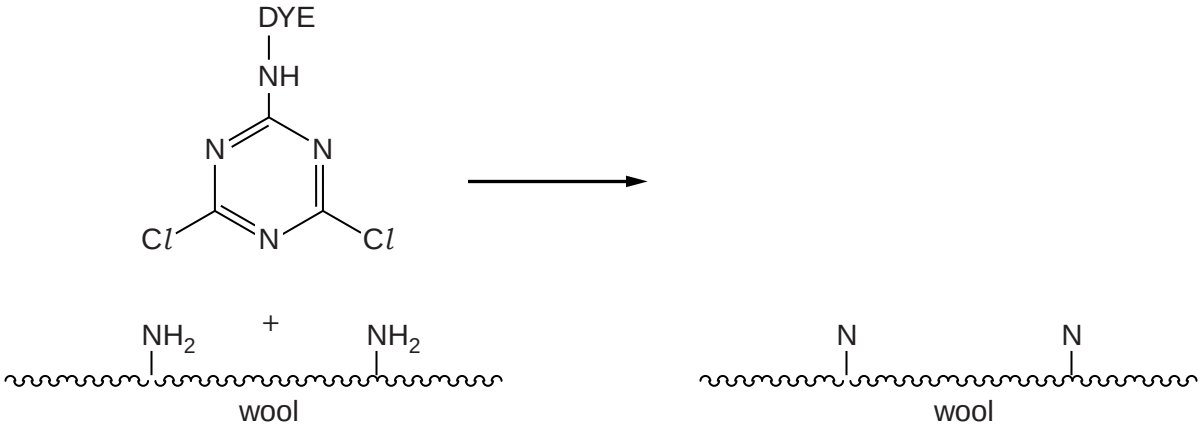
..... **[2]**

(c) Procion Brilliant Red 2BS reacts with the side-groups in wool in a condensation reaction.

(i) Give **both** products of the reaction below.



[2]

(ii) It is often necessary to wash wool that has been dyed.

Give an advantage of a dye that is attached to wool by covalent bonds compared with a dye that is attached to wool by hydrogen bonds.

Explain why it has this advantage.

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..... **[3]**

Turn over

(d) Explain, in terms of chromophores and electron energy levels, why different dyes have different colours.

In your answer you should make it clear how your points link together.

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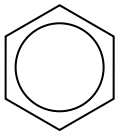
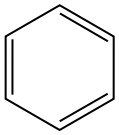
..... **[5]**

(e) C_6H_6 can be represented as either structure **C**, which is benzene, or structure **D**, which contains three separate double bonds.



structure C



structure D

(i) Predict the reactions of structures **C** and **D** with bromine.

Give the **type** of reaction and the **skeletal formula** of the organic product you would expect in each case.

	Structure C	**Structure D**
Type of reaction		
Skeletal formula of organic product		

[4]

(ii) What would structure **D** suggest about the bond lengths between carbon atoms in the ring? Explain your answer.

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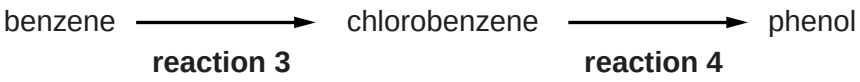
..... **[2]**

(f) Hydroxyl groups can be substituted on to aromatic rings by a reaction sequence, such as that shown below.



(i) Write an equation for reaction **3**, giving the formula of a suitable catalyst over the reaction arrow.

[2]

(ii) Suggest a reagent for reaction **4**.

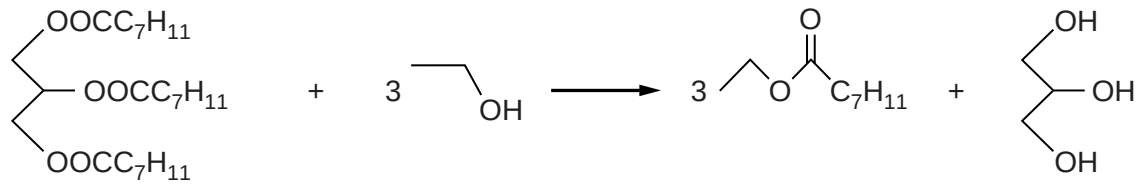
..... **[1]**

[Total: 26]

Turn over

3 Trans-esterification reactions are used to make esters from vegetable oils. These esters are suitable for use as biofuels, such as biodiesel.

One trans-esterification reaction is shown below.



ester E **compound F** **ester G** **compound H**

(a) **(i)** Give the systematic name for compound **F**.

..... **[1]**

(ii) Give the systematic name for compound **H**.

..... **[1]**

(b) Ester **G** is unsaturated.

Give the number of double bonds in the C_7H_{11} group.

..... **[1]**

(c) One type of intermolecular bonding in esters **E** and **G** is instantaneous dipole–induced dipole.

(i) Give another type of intermolecular bond that exists between molecules of **E** and also between molecules of **G**.

..... **[1]**

(ii) Ester **G** is more suitable as 'biodiesel' than ester **E** as it has a lower boiling point.

Explain the difference in boiling points in terms of intermolecular bonding.

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..... **[3]**

(d) An alkaline catalyst is used in the process of trans-esterification.

The catalyst removes a proton from the alcohol, ROH, to form an RO^- ion.
The RO^- ion then attacks ester **E**.

The intermediate rearranges to eliminate one molecule of ester **G**.

(i) Complete the mechanism for this reaction by adding the intermediate and the curly arrows showing the electron movements in **step 1** and **step 2**.

ester E **step 1 addition** **intermediate** **step 2 elimination** **ester G**

[3]

(ii) What is the role of RO^- in the mechanism in **step 1**?

..... **[1]**

(e) **(i)** A chemist makes ester **G** in the laboratory by reacting the appropriate acid and the alcohol ROH.

Write an equation for the equilibrium reaction, using structural formulae.

[2]

(ii) The chemist uses concentrated sulfuric acid in carrying out the esterification.

Suggest **two** functions of the sulfuric acid in the esterification process.

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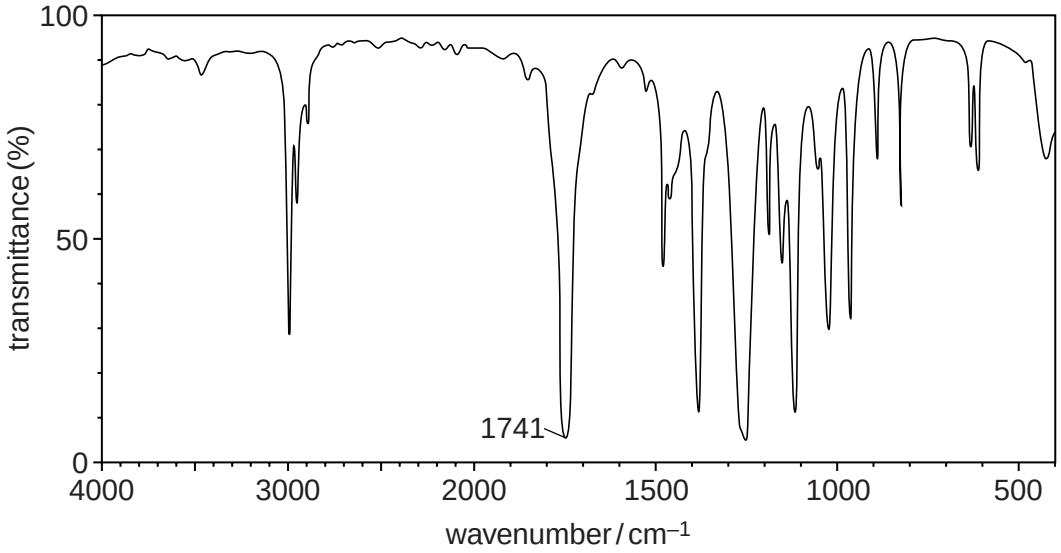
..... **[2]**

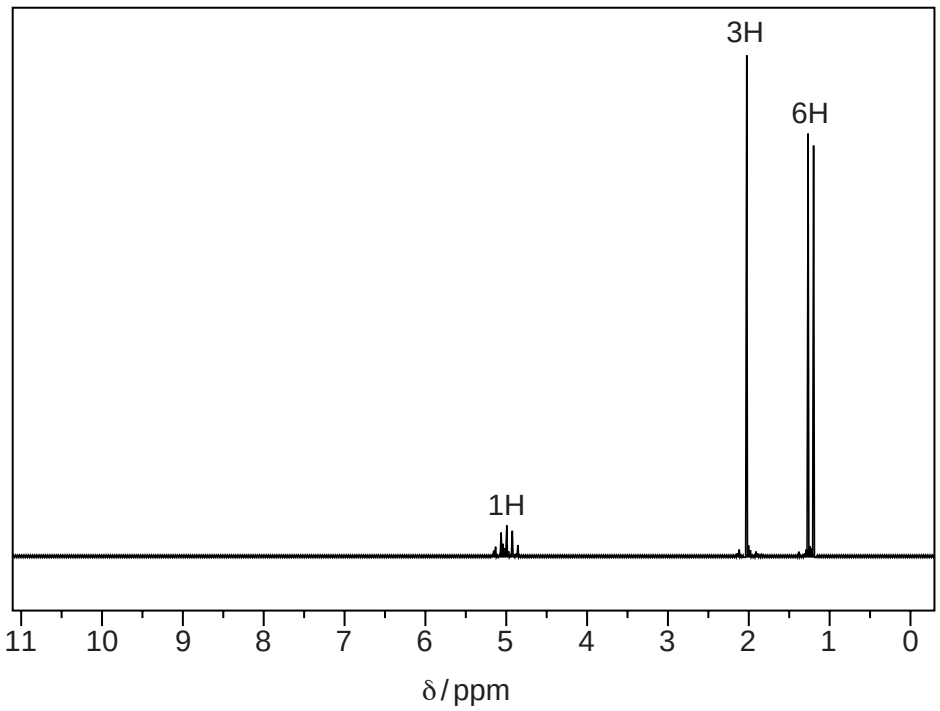
Turn over

(f) Another ester **J** has the molecular formula $C_5H_{10}O_2$. The infrared and proton NMR spectra for ester **J** are given below.

infrared spectrum



proton NMR spectrum



You may use this page for working but all answers must be transferred to the lines on page 13 opposite.

13

(i) $C_5H_{10}O_2$ has isomers that are acids.
One of these acids has a chiral centre.

Give the structure of this isomer, circling the chiral centre.

[2]

(ii) Explain, using the infrared spectrum, why compound **J** cannot be an acid and is an **ester**.

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..... **[2]**

(iii) Use the NMR spectrum to work out the structure of ester **J**, $C_5H_{10}O_2$.

Give your reasoning.

Include in your answer an explanation of the doublet at a chemical shift of 1.2 ppm.

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..... **[5]**

[Total: 24]

Turn over

4 Scientists involved in the conservation of old leather books are concerned about the presence of acidic ammonium sulfate rotting the surface of the leather. This ammonium sulfate is formed by sulfuric acid from polluted air reacting with proteins in the leather.

(a) Proteins contain $-CONH_2$ groups that react with aqueous sulfuric acid.

(i) Name the $-CONH_2$ group.

..... **[1]**

(ii) Complete and balance the equation below to show the reaction of this group with aqueous sulfuric acid to form ammonium sulfate, $(NH_4)_2SO_4$ and an organic product.

$$RCONH_2 \quad + \quad H_2SO_4 \quad + \quad H_2O \longrightarrow$$

[2]

(iii) Classify this reaction by circling one word from the list below.

addition condensation elimination hydrolysis substitution

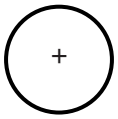
[1]

(b) The dissolving of ammonium sulfate in water is an endothermic process.

(i) The circle below represents an ammonium ion.

Complete the diagram to show how this ion is hydrated in aqueous solution and name the bonds formed between water and the ion.

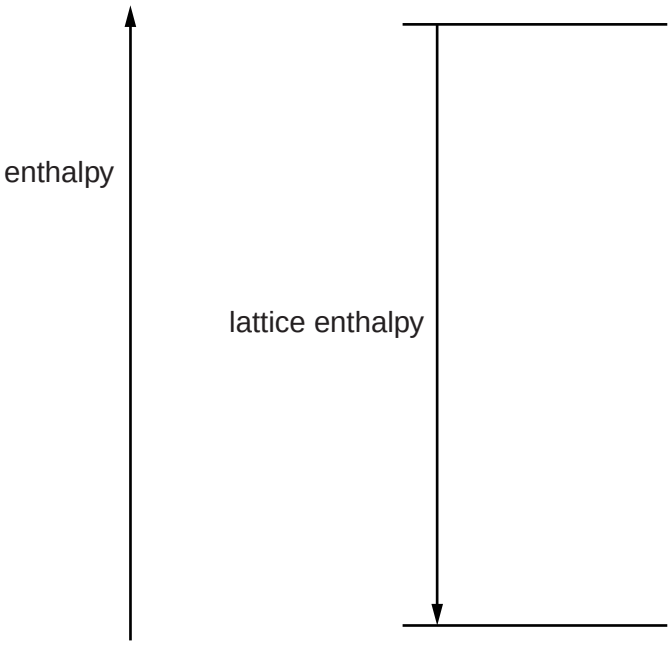
Include any relevant partial charges.



name of bonds .....

[3]

(ii) Part of the relevant enthalpy level diagram for the endothermic dissolving of ammonium sulfate, $(NH_4)_2SO_4$, is shown below.



- Complete the enthalpy level diagram to show the level for ammonium sulfate solution.
- Label the levels with the correct species including state symbols.
- Label the other enthalpy changes.

[5]

Question 4 continues on page 16

16

(c) The following equilibrium exists in an aqueous solution of ammonium ions.

$$NH_4^+ \rightleftharpoons NH_3 + H^+$$

(i) Indicate an acid–base pair on the equation above, labelling which is the acid and which the base. **[1]**

(ii) Write the expression for K_a for the ammonium ion.

K_a =

[1]

(iii) The pH of a 0.10 mol dm^{-3} solution of ammonium ions is 5.13.

Calculate the value of K_a for the ammonium ion and give its units.

K_a = ... units ..... **[3]**

(iv) Ammonia is a weak base and it has an 'ionisation constant', K_b, given by:

$$K_b = \frac{[NH_4^+]\,[OH^-]}{[NH_3]}$$

Use the expressions for K_a, K_b and K_w and your value for K_a to calculate a value for K_b.

$K_w = 1.0 \times 10^{-14}$ mol^2 dm^{-6}

K_b = ... mol dm^{-3} **[2]**

(d) A buffer solution based on 'lactic acid' is sometimes used to buffer the acidic effects of the ammonium sulfate. Lactic acid is a weak acid and its ionisation can be represented by the equation below.

$$HA \rightleftharpoons H^+ + A^-$$

Explain, using the equation above, how a solution containing HA and A^- ions acts as a buffer solution when a small amount of acid is added.

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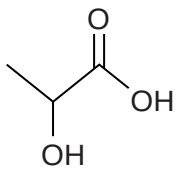
..... **[4]**

(e) The skeletal structure of lactic acid is shown below.



lactic acid

When left standing over concentrated sulfuric acid, lactic acid, $C_3H_6O_3$, forms a cyclic ester with molecular formula $C_6H_8O_4$.

Suggest how the cyclic ester is formed from lactic acid.

Give the structure of the cyclic ester.

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[2]

[Total: 25]

Turn over

5 In the volcanic crater at Solfatara, near Naples, the air smells of sulfur dioxide. Crystals of sulfur can be seen on the ground, together with orange ammonium sulfide.

(a) Sulfur dioxide can be represented as a sulfur atom with double bonds to each of two oxygen atoms.

(i) Draw a '*dot-and-cross*' diagram for this structure.

[2]

(ii) Explain why this molecule is 'V-shaped'.

Predict the bond angle.

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..... **[3]**

(iii) Ozone has a similar **shape** to sulfur dioxide, with an oxygen atom replacing the sulfur atom. Oxygen, however, can only have a maximum of eight electrons in its outer shell.

Suggest a possible '*dot-and-cross*' diagram for ozone.

[2]

(iv) Sulfur dioxide gives rise to 'acid rain' in the atmosphere.

Write an equation that shows how sulfur dioxide forms aqueous hydrogen ions in the atmosphere.

Show state symbols.

[2]

(b) (i) The element sulfur can be formed by the reaction of hydrogen sulfide with sulfur dioxide, as shown in the equation below.

Write the oxidation states of sulfur on the dotted lines below the equation.

$$SO_2 + 2H_2S \rightarrow 3S + 2H_2O$$

....

[3]

(ii) 44.3 g of SO_2 are mixed with 44.3 g of H_2S.

Calculate the maximum mass of sulfur that could be formed.

Show your working.

mass of S = ... g **[3]**

(iii) The element sulfur has a simple molecular structure.
Predict **two** physical properties of sulfur, apart from solubility and boiling point, and explain how these are related to the structure.

In your answer, you should make it clear how your points link together.

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..... **[4]**

Turn over

(c) Hydrogen sulfide and water are both Group 6 hydrides. The two hydrides have different states at room temperature.

(i) Explain what is meant by a 'Group 6 hydride'.

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..... **[2]**

(ii) Water is a liquid at room temperature whereas hydrogen sulfide is a gas. This is because the intermolecular bonding is much stronger in water.

Explain this difference in strength of intermolecular bonds in terms of the differences between sulfur and oxygen atoms.

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..... **[2]**

(iii) Another unusual property of water is the density change when it freezes.

Describe and explain this change.

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..... **[2]**

(d) Ammonium sulfide crystals, $(NH_4)_2S$, are also found in the volcanic crater.

(i) Write the electron configuration (in terms of s and p sub-shells) for a sulfide ion, S^{2-}.

[1]

(ii) Ammonium sulfide, $(NH_4)_2S$, reacts with sodium hydroxide to form sodium sulfide.

Suggest an equation for this reaction.

[2]

[Total: 28]

END OF QUESTION PAPER