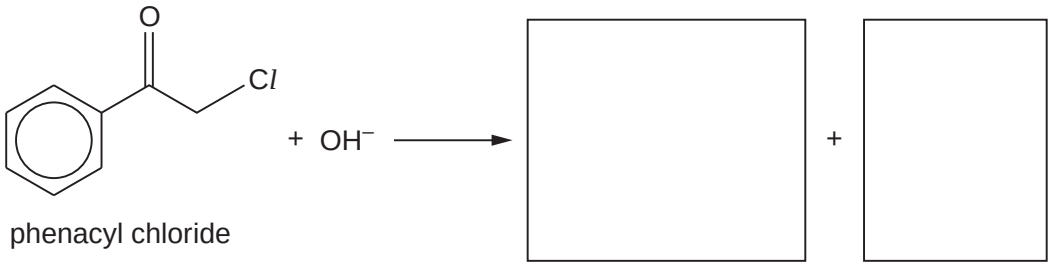
## Section A

For Examiner's Use

Answer **all** questions in the spaces provided.

**1** Phenacyl chloride has been used as a component of some tear gases. Its lachrymatory and irritant properties are due to it reacting with water inside body tissues to produce hydrochloric acid.

It undergoes a nucleophilic substitution reaction with NaOH(aq).




phenacyl chloride

**(a)** Write the formulae of the products of this reaction in the two boxes above. [2]

When the rate of this reaction was measured at various concentrations of the two reagents, the following results were obtained.

| experiment number | [phenacyl chloride] | [NaOH] | relative rate |
|---|---|---|---|
| 1 | 0.020 | 0.10 | 1.0 |
| 2 | 0.030 | 0.10 | 1.5 |
| 3 | 0.025 | 0.20 | 2.5 |

**(b) (i)** What is meant by the term *order of reaction*?

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**(ii)** Use the above data to deduce the order with respect to each reactant. Explain your reasoning.

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**(iii)** Write the overall rate equation for the reaction.

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**(iv)** Describe the mechanism for this reaction that is consistent with your overall rate equation.
You should show all intermediates and/or transition states and partial charges, and you should represent the movements of electron pairs by curly arrows.

*For Examiner's Use*

[7]

**(c) (i)** Describe an experiment that would show that $CH_3COCl$ reacts with water at a much faster rate than phenacyl chloride. Include the reagents you would use, and the observations you would make with each chloride.

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**(ii)** Suggest an explanation for this difference in reactivity.

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[4]

[Total: 13]

**2** **(a)** Describe and explain how the solubilities of the sulfates of the Group II elements vary down the group.

*For Examiner's Use*

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..... [3]

**(b)** The following table lists some enthalpy changes for magnesium and strontium compounds.

| enthalpy change | value for magnesium / kJ mol$^{-1}$ | value for strontium / kJ mol$^{-1}$ |
|---|---|---|
| lattice enthalpy of $\boldsymbol{M}(OH)_2$ | –2993 | –2467 |
| enthalpy change of hydration of $\boldsymbol{M}^{2+}(g)$ | –1890 | –1414 |
| enthalpy change of hydration of $OH^-(g)$ | –550 | –550 |

**(i)** Use the above data to calculate values of $\Delta H^{\ominus}_{solution}$ for $Mg(OH)_2$ and for $Sr(OH)_2$.

$Mg(OH)_2$ .....

.....

$\Delta H^{\ominus}_{solution}$ = ..... kJ mol$^{-1}$

$Sr(OH)_2$ .....

.....

$\Delta H^{\ominus}_{solution}$ = ..... kJ mol$^{-1}$

**(ii)** Use your results in **(i)** to suggest whether $Sr(OH)_2$ is more or less soluble in water than is $Mg(OH)_2$. State any assumptions you make.

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**(iii)** Suggest whether $Sr(OH)_2$ would be more or less soluble in hot water than in cold. Explain your reasoning.

.....

..... [5]

**(c)** Calcium hydroxide, $Ca(OH)_2$, is slightly soluble in water.

*For Examiner's Use*

**(i)** Write an expression for $K_{sp}$ for calcium hydroxide, and state its units.

$K_{sp}$ = units .....

**(ii)** 25.0 $cm^3$ of a saturated solution of $Ca(OH)_2$ required 21.0 $cm^3$ of 0.0500 $mol\,dm^{-3}$ $HCl$ for complete neutralisation.

Calculate the $[OH^-(aq)]$ and the $[Ca^{2+}(aq)]$ in the saturated solution, and hence calculate a value for $K_{sp}$.

$[OH^-(aq)]$ = .....

$[Ca^{2+}(aq)]$ = .....

$K_{sp}$ = .....

**(iii)** How would the solubility of $Ca(OH)_2$ in 0.1 $mol\,dm^{-3}$ NaOH compare with that in water?
Explain your answer.

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[6]

[Total: 14]

**3** **(a)** Fluorine is much more electronegative than both silicon and sulfur, but whereas the molecule of $SF_4$ has an overall dipole, that of $SiF_4$ has none.

*For Examiner's Use*

Suggest a reason for this difference.

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..... [1]

**(b)** Predict whether or not the following molecules will have an overall dipole. Place a tick in the appropriate column.

| compound | molecule has an overall dipole | molecule does not have an overall dipole |
|---|---|---|
| $BCl_3$ | | |
| $PCl_3$ | | |
| $CCl_4$ | | |
| $SF_6$ | | |

[2]

**(c)** Boron and silicon are two elements adjacent to carbon in the periodic table. $CCl_4$ does not react with water, whereas $BCl_3$ and $SiCl_4$ do react.

**(i)** Suggest a reason for this difference in reactivity.

.....

.....

**(ii)** Construct equations showing the reaction of these two chlorides with an excess of water.

$BCl_3$ .....

$SiCl_4$ .....

[3]

**(d)** When reacted with a small quantity of water, $SiCl_4$ produces an oxychloride **X**, $Si_xCl_yO_z$. The mass spectrum of **X** shows peaks at mass numbers of 133, 149, 247, 263 and 396. (You should assume that the species responsible for all these peaks contain the $^{16}O$, the $^{35}Cl$ and the $^{28}Si$ isotopes only.)

*For Examiner's Use*

**(i)** Use these data to deduce the molecular formula of **X**.

molecular formula .....

**(ii)** Suggest the structures of the fragments responsible for the peaks at the following mass numbers.

| mass number | structure |
|---|---|
| 133 | |
| 247 | |
| 263 | |

**(iii)** Hence suggest the displayed formula of **X**.

[5]

[Total: 11]

**4** **(a)** Complete the electronic structures of the $Cr^{3+}$ and $Mn^{2+}$ ions.

*For Examiner's Use*

$Cr^{3+}$ $1s^2 2s^2 2p^6$ .....

$Mn^{2+}$ $1s^2 2s^2 2p^6$ .....

[2]

**(b)** **(i)** Describe what observations you would make when dilute $KMnO_4(aq)$ is added slowly and with shaking to an acidified solution of $FeSO_4(aq)$ until the $KMnO_4$ is in a large excess.

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**(ii)** Construct an ionic equation for the reaction that occurs.

.....

[4]

**(c)** By selecting relevant $E^{\ominus}$ data from the *Data Booklet* explain why acidified solutions of $Fe^{2+}(aq)$ are relatively stable to oxidation by air, whereas a freshly prepared precipitate of $Fe(OH)_2$ is readily oxidised to $Fe(OH)_3$ under alkaline conditions.

relevant $E^{\ominus}$ values and half equations

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.....

explanation

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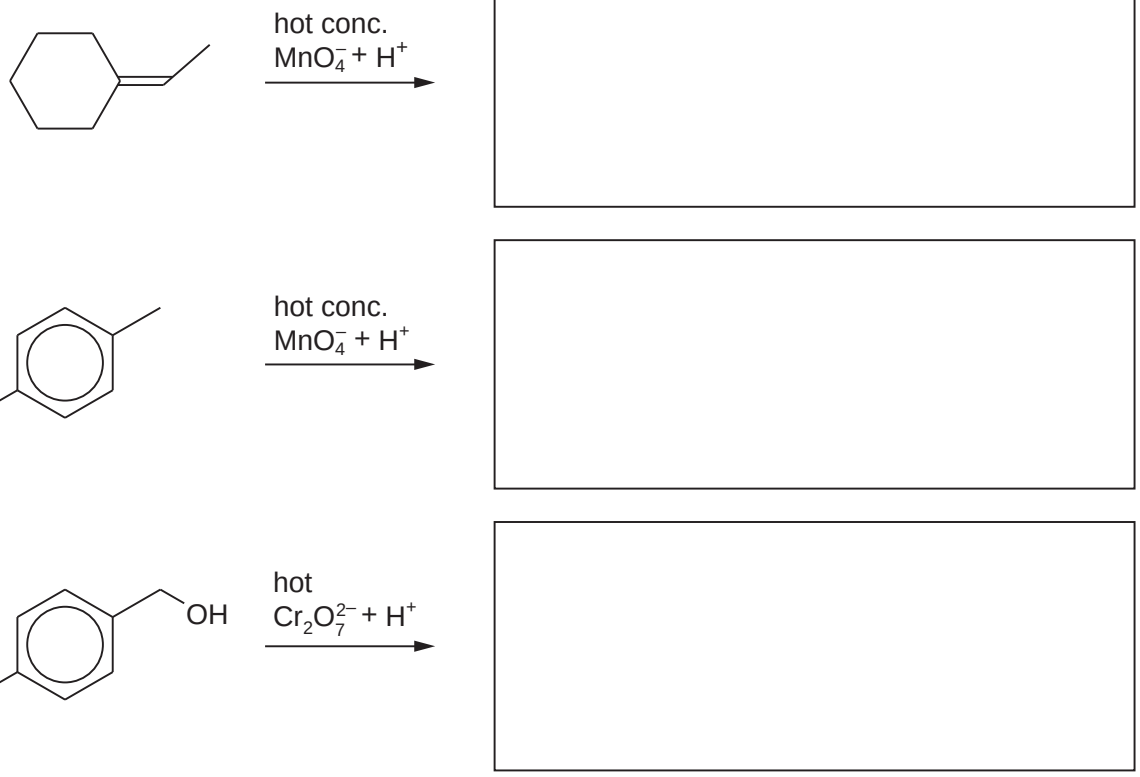
[4]

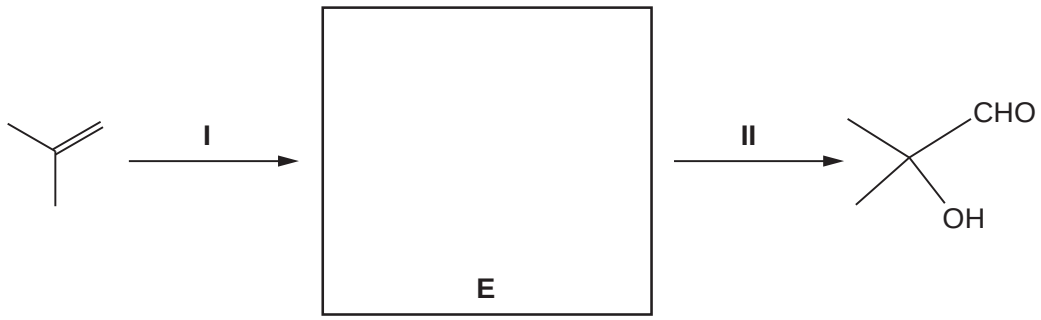
**(d)** Predict the organic products of the following reactions and draw their structures in the boxes below. You may use structural or skeletal formulae as you wish.

*For Examiner's Use*




[4]

**(e)** $KMnO_4$ and $K_2Cr_2O_7$ are the reagents that can be used to carry out the following transformation.




**(i)** Draw the structure of intermediate **E** in the box above.

**(ii)** Suggest reagents and conditions for the following.

reaction **I** .....

reaction **II** .....

[3]

[Total: 17]

**5** **(a)** **(i)** Briefly explain why the benzene molecule is planar.

*For Examiner's Use*

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**(ii)** Briefly explain why all the carbon-carbon bonds in benzene are the same length.

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.....

[2]

**(b)** Benzene can be nitrated by warming it with a mixture of concentrated sulfuric and nitric acids.

**(i)** By means of an equation, illustrate the initial role of the sulfuric acid in this reaction.

.....

**(ii)** Name the type of reaction and describe the mechanism for the nitration reaction, including curly arrows showing the movement of electrons and all charges.

type of reaction .....

mechanism

[4]

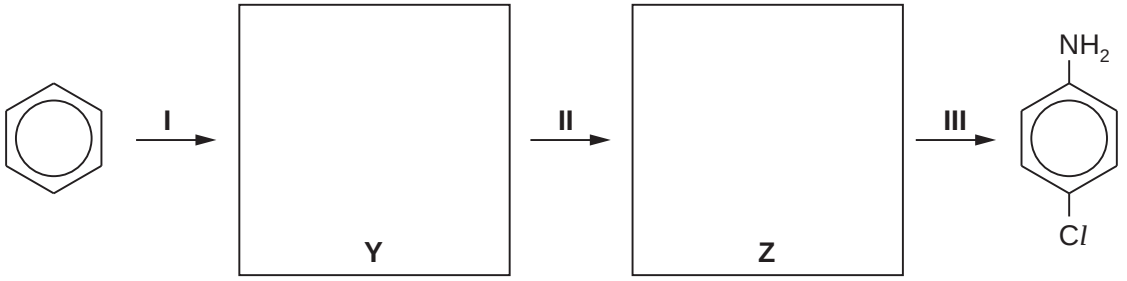
**(c)** State the reagents and conditions needed to convert benzene into chlorobenzene.

.....[1]

**(d)** Nitrobenzene undergoes further substitution considerably more slowly than chlorobenzene. In nitrobenzene the incoming group joins to the benzene ring in the 3-position, whereas in chlorobenzene the incoming group joins to the benzene ring in the 4-position.

*For Examiner's Use*

**(i)** Use these ideas to suggest the structures of the intermediate compounds **Y** and **Z** in the following synthesis of 4-chlorophenylamine.




**(ii)** Suggest the reagents and conditions needed for reaction **III** in the above synthesis.

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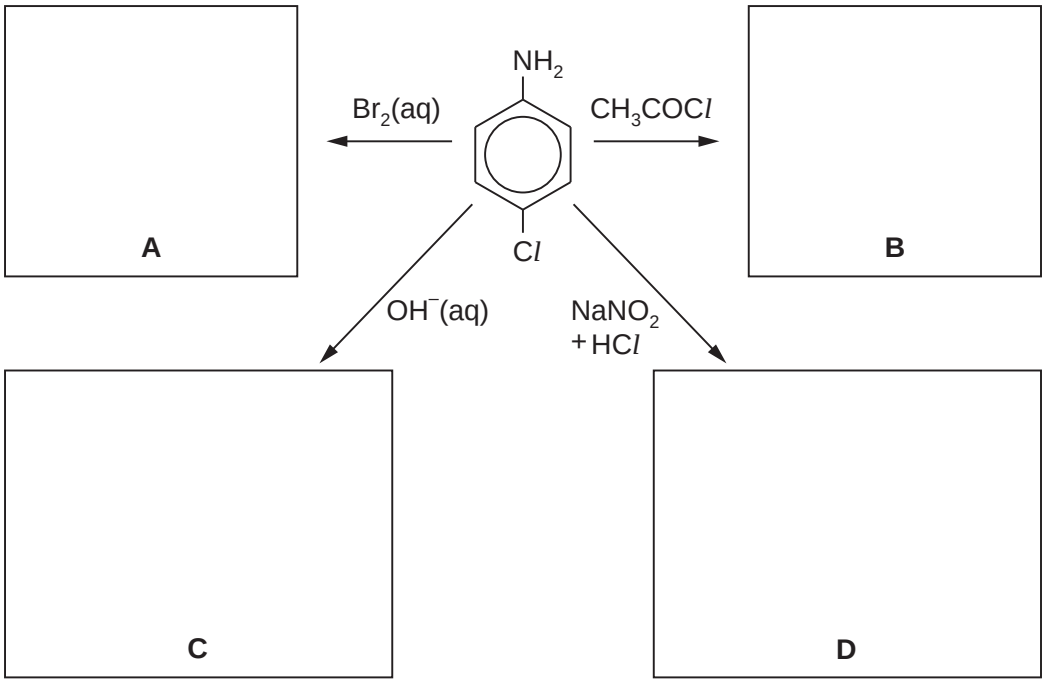
**(iii)** Suggest the structural formulae of the products **A**, **B**, **C** and **D** of the following reactions. If no reaction occurs write "no reaction" in the relevant box.




[8]

[Total: 15]

## Section B

For Examiner's Use

Answer **all** questions in the spaces provided.

**6** Human hair and silk both consist of proteins. Proteins are described as having three major levels of structure: primary, secondary and tertiary.

**(a)** Outline what is meant by the terms *primary structure* and *tertiary structure* of a protein.

primary structure .....

.....

.....

tertiary structure .....

.....

.....

[2]

**(b)** In hair, the secondary structure consists of α-helices which are cross-linked by disulfide bonds. The amino acid responsible for this cross-linking is cysteine, $H_2NCH(CH_2SH)CO_2H$.

**(i)** Show by means of a diagram how the disulfide cross-links are formed.

**(ii)** What type of reaction is this?

.....

**(iii)** State **three** other interactions that stabilise the tertiary structure of proteins.

*For Examiner's Use*

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.....

.....

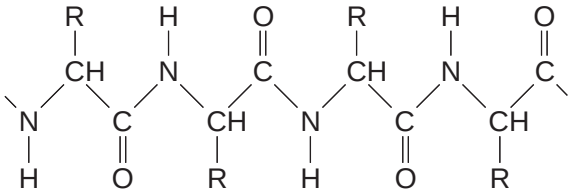
[4]

**(c)** The β-pleated sheet is a different form of secondary structure found in proteins, such as those in silk.

**(i)** What type of bonding is responsible for stabilising the β-pleated sheet in silk?

.....

**(ii)** On the diagram below, draw a second polypeptide strand and show how bonds would be formed that stabilise this β-pleated sheet.




[3]

**(d)** The cysteine-containing protein in hair is called α-keratin. A similar sequence of amino acids can produce β-keratin proteins found in the scales, claws and shells of reptiles such as tortoises. In β-keratin the secondary structure of the protein is in the form of a β-pleated sheet.

Suggest what makes the β-pleated sheet in β-keratin so much less flexible than the β-pleated sheet in silk.

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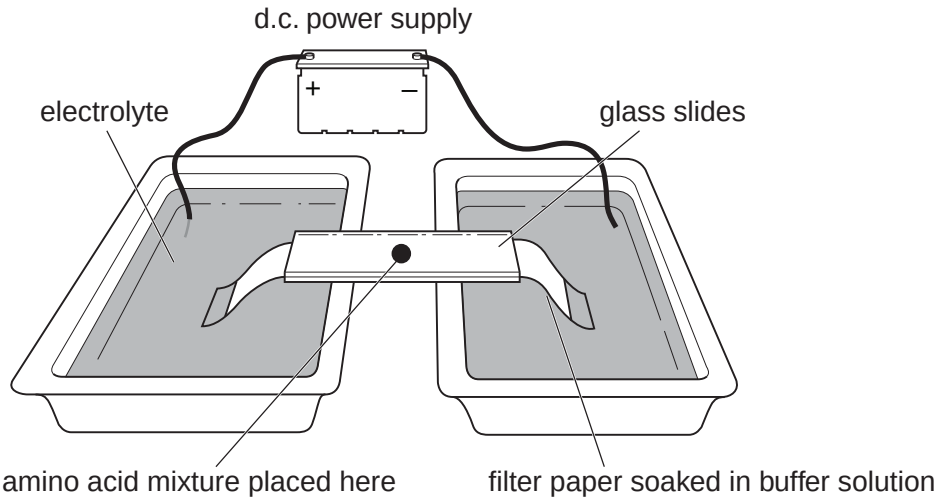
.....[1]

[Total: 10]

**7** A mixture of amino acids may be separated using electrophoresis. A typical practical set-up is shown in the diagram.

*For Examiner's Use*




**(a)** When the power supply is switched on, some amino acids may **not** move, but remain stationary. Suggest an explanation for this observation.

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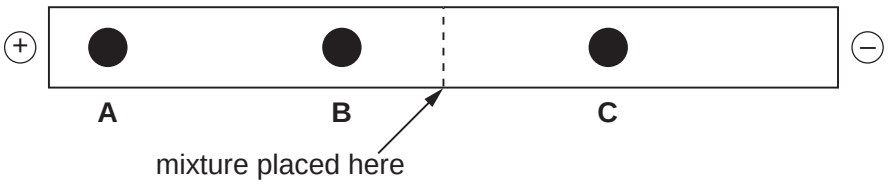
.....

..... [2]

**(b)** The amino acid glycine has the formula $H_2NCH_2CO_2H$. Identify the species formed on the filter paper if glycine moves to the left (positive) end of the filter paper.

..... [1]

**(c)** The following result was obtained from another electrophoresis. What can be deduced about the relative sizes of, and charges on, the amino acid species **A**, **B** and **C**?




| amino acid | relative size | charge |
|---|---|---|
| **A** | | |
| **B** | | |
| **C** | | |

[3]

**(d)** The sequence of amino acids in a polypeptide may be determined by partial hydrolysis of the chain into smaller pieces, often tripeptides.

*For Examiner's Use*

**(i)** Following such a partial hydrolysis, the following tripeptides were obtained from a given polypeptide.

ala-gly-asp gly-ala-gly lys-val-ser ser-ala-gly val-ser-ala

Given that the N-terminal amino acid is lysine (lys) suggest the amino acid sequence of the **shortest** polypeptide that would give the above tripeptides.

.....

The structural formulae of the amino acids in the polypeptide are given below.

| abbreviation | amino acid | structural formula |
|---|---|---|
| ala | alanine | $H_2NCH(CH_3)CO_2H$ |
| asp | aspartic acid | $H_2NCH(CH_2CO_2H)CO_2H$ |
| gly | glycine | $H_2NCH_2CO_2H$ |
| lys | lysine | $H_2NCH(CH_2CH_2CH_2CH_2NH_2)CO_2H$ |
| ser | serine | $H_2NCH(CH_2OH)CO_2H$ |
| val | valine | $H_2NCH(CH(CH_3)_2)CO_2H$ |

**(ii)** Which of the tripeptides in **(i)** has the lowest $M_r$?

.....

**(iii)** Select **one** amino acid **from those listed in the table** which contains an ionic side-chain at pH 8.

.....

[4]

[Total: 10]

**8** The design and development of batteries has been a major research area in recent years.

*For Examiner's Use*

**(a)** Lead-acid batteries, used in cars, are made up of a number of rechargeable cells in series, and were first developed in 1860. They have the disadvantage of a relatively high mass compared to the energy stored. During discharge, the electrode reactions in the cells of these batteries are as follows.

**I** $Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^-$

**II** $PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$

State which of these reactions occurs at the positive electrode in a lead-acid cell during discharge, explaining your answer.

.....

.....[1]

**(b)** Use the *Data Booklet* and the equations **I** and **II** above to calculate the voltage produced by a lead-acid cell under standard conditions.

[2]

**(c)** Nickel-metal hydride batteries were developed in the 1980s and have become increasingly common particularly for small devices such as mobile phones and digital cameras that need near-constant sources of electrical energy. These cells use nickel oxohydroxide (NiO(OH)) as one electrode and a hydrogen-absorbing alloy such as $LiNi_5$ as the other electrode.

One reaction that takes place in these batteries is

$$NiO(OH) + H_2O + e^- \rightleftharpoons Ni(OH)_2 + OH^-$$

**(i)** State the oxidation state of nickel in NiO(OH). .....

**(ii)** Suggest a likely advantage of these batteries compared with lead-acid batteries.

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[2]

**(d)** Hydrogen fuel cells have been suggested as the next major advance in electrically powered vehicles. In these fuel cells hydrogen is oxidized to produce water, using a catalyst and inert electrodes.

*For Examiner's Use*

**(i)** Suggest a material for the electrodes.

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**(ii)** Use your knowledge of hydrogen to suggest a disadvantage of these fuel cells in powering vehicles.

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[2]

**(e)** Many of the world's countries are developing ways of recycling materials which are valuable or which require large amounts of energy to produce.

For each of the following recyclable materials, state whether recycling of this material is important in saving energy or in saving resources. Use your knowledge of chemistry to explain each choice.

glass .....

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steel .....

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plastics .....

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[3]

[Total: 10]

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