



UNIVERSITY OF CAMBRIDGE INTERNATIONAL EXAMINATIONS
General Certificate of Education Advanced Level

CANDIDATE
NAME

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CENTRE
NUMBER

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CHEMISTRY

9701/41

Paper 4 Structured Questions

May/June 2012

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, candidate number and name on all the work you hand in.

Write in dark blue or black pen.

You may use a soft pencil for any diagrams, graphs or rough working.

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

DO **NOT** WRITE IN ANY BARCODES.

Section A

Answer **all** questions.

Section B

Answer **all** questions.

You may lose marks if you do not show your working or if you do not use appropriate units.

A Data Booklet is provided.

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

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

For Examiner's Use

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8	
Total	

This document consists of **17** printed pages and **3** blank pages.



Section A

For
Examiner's
UseAnswer **all** the questions in the spaces provided.

- 1 (a) (i) What is meant by the term *lattice energy*?

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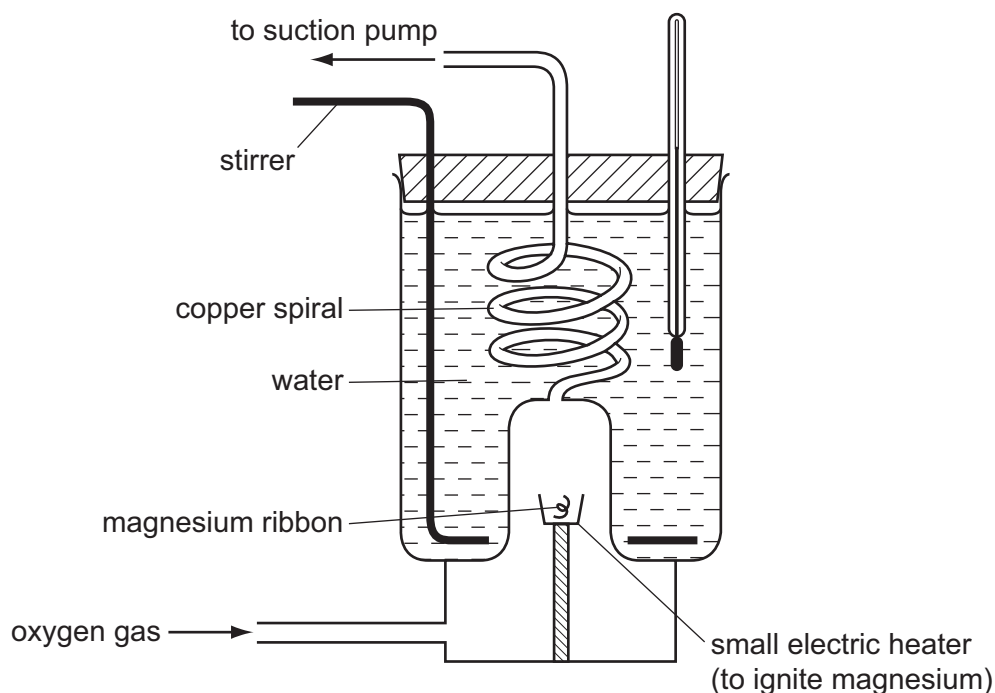
.....

- (ii) Write an equation to represent the lattice energy of MgO.

.....

[3]

- (b) The apparatus shown in the diagram can be used to measure the enthalpy change of formation of magnesium oxide, $\Delta H_f^\ominus(\text{MgO})$.



List the measurements you would need to make using this apparatus in order to calculate $\Delta H_f^\ominus(\text{MgO})$.

.....

.....

.....

.....

[3]

- (c) Use the following data, together with appropriate data from the *Data Booklet*, to calculate a value of $\Delta H_f^\circ(\text{MgO})$.

lattice energy of MgO(s)	=	$-3791 \text{ kJ mol}^{-1}$
enthalpy change of atomisation of Mg	=	$+148 \text{ kJ mol}^{-1}$
electron affinity of the oxygen atom	=	-141 kJ mol^{-1}
electron affinity of the oxygen anion, O^-	=	$+798 \text{ kJ mol}^{-1}$

$$\Delta H_f^\circ(\text{MgO}) = \dots\dots\dots \text{kJ mol}^{-1}$$

[3]

- (d) Write equations, including state symbols, for the reactions, if any, of the following two oxides with water. Suggest values for the pH of the resulting solutions.

oxide	equation	pH of resulting solution
Na_2O		
MgO		

[3]

[Total: 12]

- 2 Nitrogen monoxide, NO, is formed in a reversible reaction when air is heated to the temperature of a car engine.

(a) (i) Suggest a 'dot-and-cross' electronic structure for nitrogen monoxide.

- (ii) The enthalpy change of formation of nitrogen monoxide is $+90 \text{ kJ mol}^{-1}$. What is the enthalpy change for the following reaction?



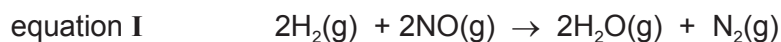
- (iii) Explain why nitrogen monoxide is formed in the car engine.

.....

- (iv) Using bond enthalpy values from the *Data Booklet* and your answer in (ii) above, calculate a value for the bond energy of nitrogen monoxide.

bond energy = ... kJ mol^{-1}
[5]

- (b) At 800 K, nitrogen monoxide reacts with hydrogen according to the following equation.



The following table shows how the initial rate of this reaction depends on the partial pressures of the reagents.

experiment	$p(\text{H}_2)/\text{atm}$	$p(\text{NO})/\text{atm}$	initial rate / atm s^{-1}
1	0.64	1.60	1.50×10^{-7}
2	0.64	0.80	3.75×10^{-8}
3	0.32	1.60	7.50×10^{-8}

- (i) Find the order of the reaction with respect to each reactant, explaining how you arrive at your answer.

.....

.....

.....

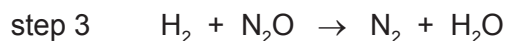
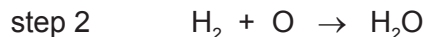
.....

.....

- (ii) Write down the rate equation and the units of the rate constant.

.....

The following mechanism has been put forward for this reaction.



- (iii) Show how the overall stoichiometric equation **I** can be derived from the three equations for the individual steps given above.

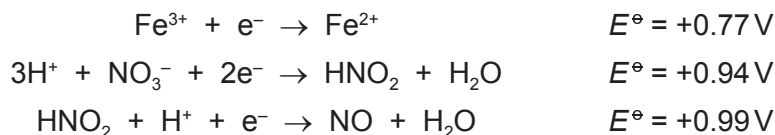
- (iv) Suggest which of the three reactions in the mechanism is the rate determining step. Explain your answer.

.....

.....

[8]

- (c) The following information on half-reactions relates to the reaction between HNO_3 and an excess of FeSO_4 .



- (i) Suggest the formula of the nitrogen-containing final product of this reaction.

.....

- (ii) Write an equation for the formation of this nitrogen-containing product.

- (iii) Nitrogen monoxide forms a dark brown complex with an excess of $\text{FeSO}_4(\text{aq})$. What kind of bonding is involved in the complex formation?

.....

- (iv) Suggest a formula for this complex.

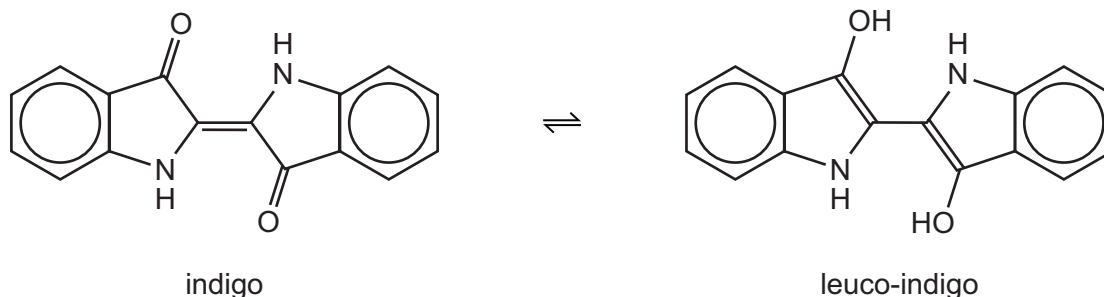
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[4]

[Total: 17]

- 3 Indigo is the dye used in blue jeans. Although originally extracted from plants of the type *indigofera*, it is now almost entirely made artificially.

Indigo is insoluble in water but this disadvantage can be overcome by converting it into the water-soluble colourless leuco-indigo. If cloth soaked in a solution of leuco-indigo is left to dry in the air, the leuco-indigo is converted into the insoluble blue indigo, which is precipitated out onto the fibres of the cloth.



- (a) (i) Give the molecular formula of indigo.

.....

- (ii) Name **three** functional groups in indigo.

.....

[3]

- (b) (i) What *type of reaction* is the conversion of indigo into leuco-indigo?

.....

- (ii) Suggest a laboratory reagent for this reaction.

.....

[2]

- (c) Suggest **two** chemical tests that could be used to distinguish between indigo and leuco-indigo. Write your answers in the following table.

test	reagents and conditions	observation with indigo	observation with leuco-indigo
1			
2			

[5]

(d) When indigo is heated with hydrogen and a nickel catalyst, compound **A**, $C_{16}H_{28}N_2O_2$, is formed.

(i) Suggest a structure for **A**.

(ii) Calculate the volume of hydrogen, measured at room temperature and pressure, that would have been absorbed if 2.50 g of indigo had undergone this reaction.

volume = ...dm³
[3]

(e) Suggest the structure of the product formed when indigo reacts with an excess of $Br_2(aq)$.

[3]

[Total: 16]

- 4 (a) (i) Describe and explain the trend in the volatilities of the Group IV chlorides CCl_4 , GeCl_4 and PbCl_4 .

.....

.....

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.....

.....

.....

- (ii) Describe and explain the reactions, if any, of these chlorides with water. Write equations for any reactions that occur.

.....

.....

.....

.....

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.....

.....

[7]

(b) SnO_2 and PbO_2 react with acids in different ways.

- SnO_2 reacts with concentrated sulfuric acid to form a colourless solution with no evolution of gas.
- PbO_2 reacts with concentrated sulfuric acid to give a white solid, **B**, and oxygen gas.
- PbO_2 reacts with cold concentrated hydrochloric acid to give a yellow solution containing the $[\text{PbCl}_6]^{2-}$ ion, with no evolution of gas.
- Warming this yellow solution causes the evolution of Cl_2 gas, leaving a colourless solution which on cooling in ice precipitates a white solid, **C**.

(i) Identify the two white solids, **B** and **C**, mentioned above.

B

C

(ii) Suggest an equation for **each** of the four reactions described above.

.....

.....

.....

.....

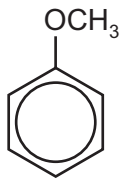
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[4]

[Total: 11]

- 5 (a) Methoxybenzene reacts with $\text{Br}_2(\text{aq})$ in a similar manner to phenol.



methoxybenzene

- (i) Draw the structural formula of the product of the reaction between methoxybenzene and an excess of bromine.

- (ii) Suggest a chemical reaction you could use to distinguish between methoxybenzene and phenol. State the reagent, describe the observations you would make, and give an equation for the reaction.

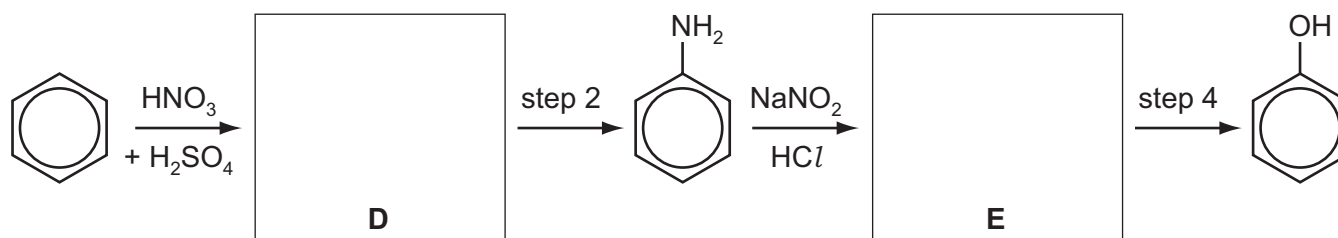
reagent

observation

equation

[4]

- (b) Phenol can be synthesised from benzene by the following route.



- (i) Suggest structures for compounds **D** and **E** and draw them in the boxes above.
- (ii) Suggest reagents and conditions for

step 2, ...

step 4.

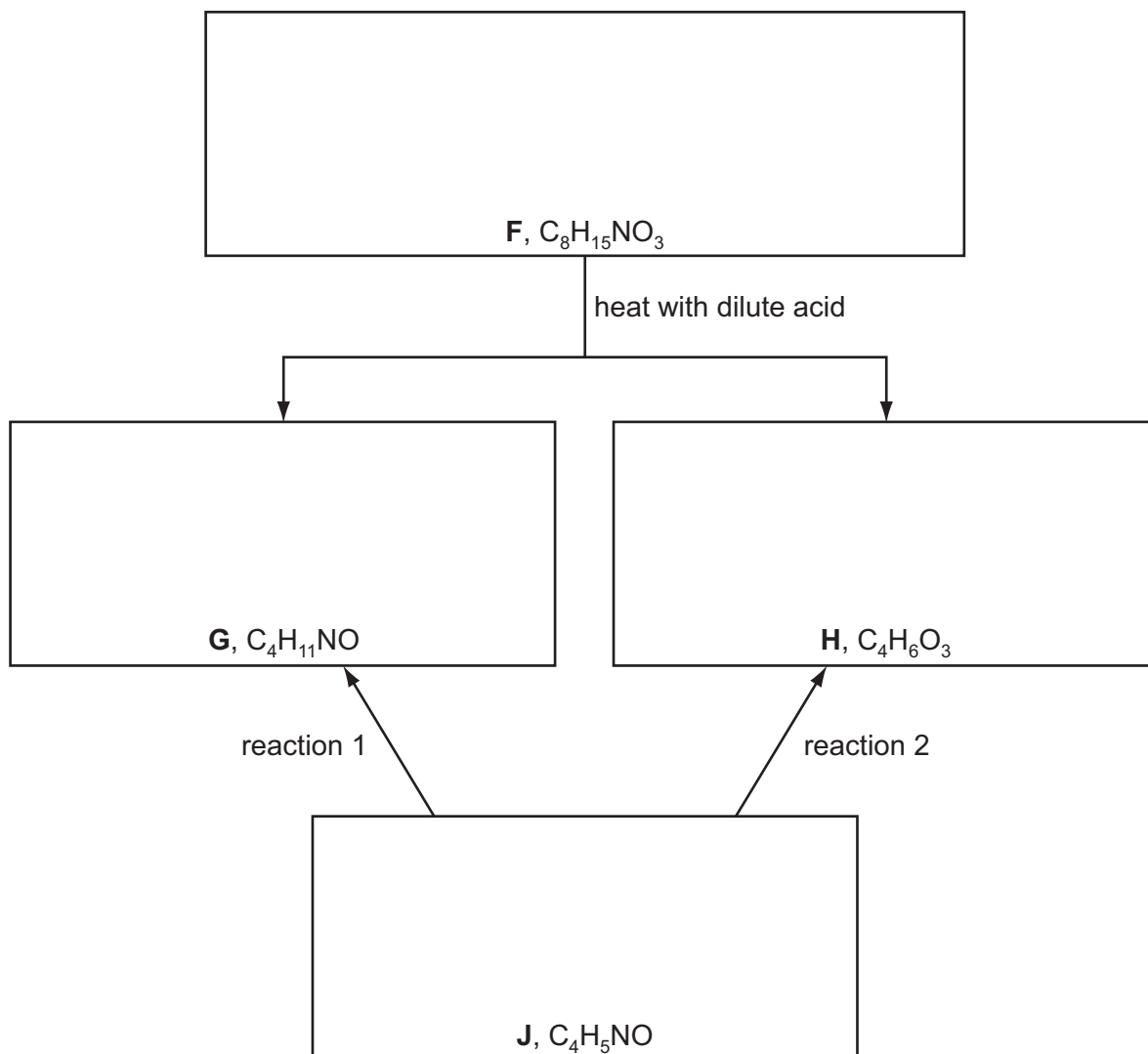
[4]

(c) The following chart shows some reactions of compound **F** which is a neutral compound.

G forms a salt with dilute H_2SO_4 , whereas **H** forms a salt with NaOH(aq) .

Both **G** and **H** can be obtained from compound **J** by separate one-step reactions (reaction 1 and reaction 2 below).

All four compounds **F**, **G**, **H** and **J** form a yellow precipitate with alkaline aqueous iodine.



(i) Suggest structures for **F**, **G**, **H** and **J**, and draw them in the boxes above.

(ii) Suggest reactants and conditions for

reaction 1, ...

reaction 2.

[6]

[Total: 14]

Section B

For
Examiner's
UseAnswer **all** the questions in the spaces provided.

- 6 In key reactions responsible for growth and repair in the human body, amino acids react together to form polymers known as proteins.

(a) (i) What *type of reaction* is this polymerisation?

.....

- (ii) From stocks of glycine and alanine, it is possible to make the dipeptide gly-ala. Using the same three-letter abbreviations for the amino acids, give the structures of all other possible dipeptides that can be made from these stocks of amino acids.

[3]

- (b) (i) DNA consists of a double helix formed by two strands held together by hydrogen bonds between base pairs.

Sketch a section of DNA showing **two** base pairs, using blocks for the various components. You should label all of the components.

- (ii) Suggest what the effect on DNA replication would be if the hydrogen bonds between the strands were replaced by stronger bonds, e.g. covalent bonds.

.....

.....

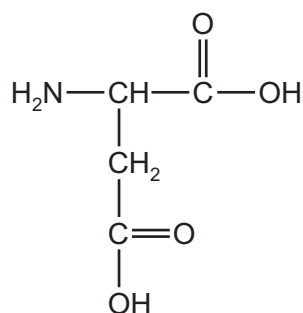
[4]

(c) Some diseases, such as sickle-cell anaemia, are caused by mutation resulting in a change in the triplet code.

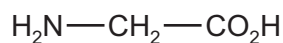
- (i) Explain why some changes in the triplet code do **not** result in a change in the primary structure of a protein.

.....

- (ii) Suggest what change in the tertiary structure of a protein would result from a mutation that replaced aspartic acid with glycine.



aspartic acid



glycine

.....

- (iii) Sometimes a mutation can result in the *deletion* of a single base in DNA (or RNA). Explain why this is likely to have more serious consequences for the protein than the *replacement* of one base by another.

.....

[3]

[Total: 10]

- 7 The analysis of a protein may be carried out by breaking it down into its amino acids. These can then be separated by a process called electrophoresis.

(a) The structures of glycine, lysine and glutamic acid at pH 7 are shown.

glycine



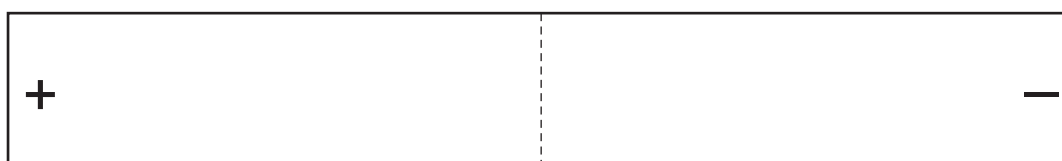
lysine



glutamic acid



Draw and label three circles on the chart below to indicate the likely position of each of these amino acids after electrophoresis of a solution containing these amino acids in a buffer at pH 7.



start point

[3]

- (b) Some organic compounds have very different solubilities in water and in organic solvents such as hexane. They may be extracted from an aqueous reaction mixture by shaking the mixture with portions of hexane and separating the two layers. The process of distribution of a compound between two solvents is called *partition*.

(i) State what is meant by the term *partition coefficient*.

.....

.....

.....

- (ii) One of the concerns about organic pollutants, such as pesticide residues, is that they can enter the food chain and become concentrated in human breast milk. Explain how this can happen.

.....

.....

.....

.....

[3]

- (c) Propene was treated with bromine in the presence of chloride ions and the product analysed using mass spectrometry.

A group of peaks was found in the range m/e 156–160 with the following relative heights.

m/e	relative height
156	3
158	4
160	1

- (i) Identify the species responsible for each of these peaks.

156

158

160

A large peak was present in the spectrum with a m/e value of less than 20.

- (ii) Suggest the m/e value for the peak and the species that produced it.

m/e

species

[4]

[Total: 10]

- 8 Some of the most commonly used polymers are formed by the polymerisation of ethene, C_2H_4 . The presence of side-chains affects the bulk properties of an addition polymer. Unbranched polymers pack closer together than polymers with several side-chains.

Poly(ethene) exists in two different forms LDPE (low density poly(ethene)) which has lots of side-chains, and HDPE (high density poly(ethene)) in which there are fewer and shorter side-chains.

- (a) Explain with the aid of sketches why the presence of side-chains causes a difference in density in poly(ethene).

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

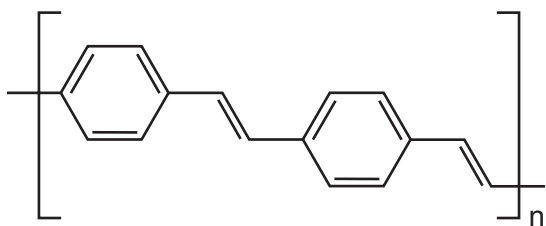
- (b) By reference to the type of bonding between the poly(ethene) chains, explain why LDPE has a lower melting point than HDPE.

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

- (c) Polymerisation can take place by two different methods depending on the monomers involved. The two methods are addition and condensation.
Give **two** differences between the methods.

1.
.....
2.
.....
[2]

- (d) There has been a great deal of commercial interest in the development of polymers that can conduct electricity and/or emit light. A length of one such polymer is shown.



- (i) Suggest how this polymer conducts electricity.

.....

- (ii) Suggest the molecular geometry required for this molecule to conduct.

Explain your answer.

.....

.....

- (iii) What is the empirical formula of this polymer?

.....

[4]

[Total: 10]

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9701/42

May/June 2012

2 hours

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

DO **NOT** WRITE IN ANY BARCODES.

Answer **all** questions.

Answer **all** questions.

A Data Booklet is provided.

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

For Examiner's Use	
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This document consists of **17** printed pages and **3** blank pages.

Section A

For
Examiner's
UseAnswer **all** the questions in the spaces provided.

- 1 (a) (i) What is meant by the term *enthalpy change of hydration*, $\Delta H_{\text{hyd}}^{\ominus}$?

.....

.....

- (ii) Write an equation that represents the $\Delta H_{\text{hyd}}^{\ominus}$ of the Mg^{2+} ion.

.....

- (iii) Suggest a reason why $\Delta H_{\text{hyd}}^{\ominus}$ of the Mg^{2+} ion is greater than $\Delta H_{\text{hyd}}^{\ominus}$ of the Ca^{2+} ion.

.....

.....

- (iv) Suggest why it is impossible to determine the enthalpy change of hydration of the oxide ion, O^{2-} .

.....

.....

[5]

- (b) The enthalpy change of solution for MgCl_2 , $\Delta H_{\text{sol}}^{\ominus}(\text{MgCl}_2(\text{s}))$, is represented by the following equation.



Describe the simple apparatus you could use, and the measurements you would make, in order to determine a value for $\Delta H_{\text{sol}}^{\ominus}(\text{MgCl}_2(\text{s}))$ in the laboratory.

.....

.....

.....

.....

.....

.....

..... [4]

(c) The table below lists data relevant to the formation of $\text{MgCl}_2(\text{aq})$.

enthalpy change	value / kJ mol^{-1}
$\Delta H_f^\ominus(\text{MgCl}_2(\text{s}))$	-641
$\Delta H_f^\ominus(\text{MgCl}_2(\text{aq}))$	-801
lattice energy of $\text{MgCl}_2(\text{s})$	-2526
$\Delta H_{\text{hyd}}^\ominus(\text{Mg}^{2+}(\text{g}))$	-1890

By constructing relevant thermochemical cycles, use the above data to calculate a value for

(i) $\Delta H_{\text{sol}}^\ominus(\text{MgCl}_2(\text{s}))$,

$$\Delta H_{\text{sol}}^\ominus = \dots\dots\dots \text{kJ mol}^{-1}$$

(ii) $\Delta H_{\text{hyd}}^\ominus(\text{Cl}^-(\text{g}))$.

$$\Delta H_{\text{hyd}}^\ominus = \dots\dots\dots \text{kJ mol}^{-1}$$

[3]

(d) Describe and explain how the solubility of magnesium sulfate compares to that of barium sulfate.

.....

.....

.....

.....

..... [4]

[Total: 16]

2 Carbon monoxide, CO, occurs in the exhaust gases of internal combustion engines.

(a) (i) Suggest a dot-and-cross diagram for CO.

(ii) Suggest **one** reason why CO is produced in addition to CO₂ in some internal combustion engines.

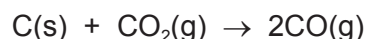
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(iii) Carbon monoxide can be removed from the exhaust gases by a catalytic converter. Write an equation for a reaction that occurs in a catalytic converter that removes CO.

.....
 [3]

(b) The standard enthalpy change of formation, $\Delta H_f^\ominus$, of CO is -111 kJ mol^{-1} , and that of CO₂ is -394 kJ mol^{-1} .

Calculate the standard enthalpy change of the following reaction.



$\Delta H^\ominus = \dots\dots\dots \text{ kJ mol}^{-1}$
 [2]

(c) Carbon monoxide reacts with a ruthenium(II) chloride complex according to the equation



(i) Describe the *type of reaction* that is occurring here.

.....

(ii) During the reaction, the colour of the solution changes from deep blue to green. Explain the origin of colour in transition element complexes, and why different complexes often have different colours.

.....

The following table shows how the initial rate of this reaction varies with different concentrations of reactants.

$[\text{Ru}(\text{H}_2\text{O})_2\text{Cl}_4]^{2-} / \text{mol dm}^{-3}$	$[\text{CO}] / \text{mol dm}^{-3}$	rate / $\text{mol dm}^{-3} \text{s}^{-1}$
1.1×10^{-2}	1.7×10^{-3}	1.6×10^{-7}
1.6×10^{-2}	3.6×10^{-3}	2.3×10^{-7}
2.2×10^{-2}	2.7×10^{-3}	3.2×10^{-7}

- (iii) Use these data to determine the order of reaction with respect to each reagent, and write the rate equation for the reaction.

.....

.....

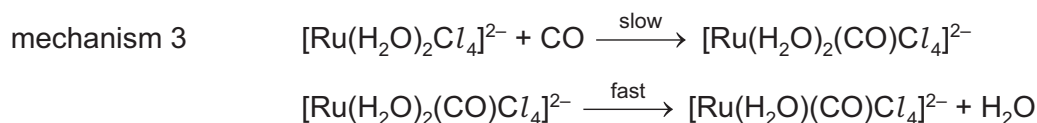
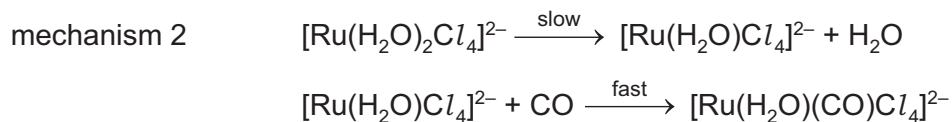
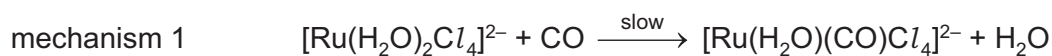
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There are three possible mechanisms for this reaction, which are described below.



- (iv) Deduce which of these three mechanisms is consistent with the rate equation you suggested in part (iii). Explain your answer.

.....

.....

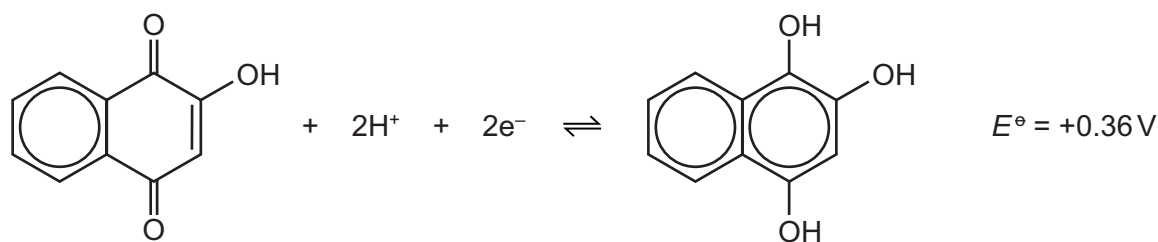
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[10]

[Total: 15]

- 3 Lawsone is the dye that is extracted from the henna plant, *Lawsonia inermis*. Although its natural colour is yellow, lawsone reacts with the proteins in hair and skin to produce the characteristic brown henna colour.

Lawsone can readily be reduced to 1,2,4-trihydroxynaphthalene, compound **A**.



lawsone

1,2,4-trihydroxynaphthalene, **A**

- (a) (i) Name **three** functional groups in lawsone.

.....

- (ii) Describe a reaction (reagent with conditions) that you could use to distinguish lawsone from compound **A**.

Describe the observations you would make with **both** compounds.

.....

- (iii) Suggest a reagent that could be used to convert lawsone into compound **A** in the laboratory.

.....

- (iv) Draw the structural formula of the compound formed when lawsone is reacted with $\text{Br}_2(\text{aq})$.

[6]

(b) Compound **A** can be oxidised to lawsone by acidified $\text{K}_2\text{Cr}_2\text{O}_7$.

(i) Use the *Data Booklet* to calculate the $E^\ominus_{\text{cell}}$ for this reaction.

.....

(ii) Construct an equation for this reaction. Use the molecular formulae of lawsone, $\text{C}_{10}\text{H}_6\text{O}_3$, and compound **A**, $\text{C}_{10}\text{H}_8\text{O}_3$, in your equation.

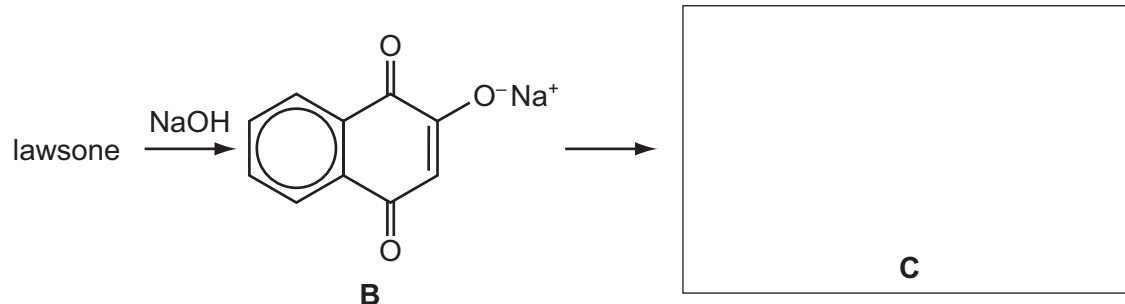
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(iii) When 20.0 cm^3 of a solution of compound **A** was acidified and titrated with $0.0500 \text{ mol dm}^{-3} \text{ K}_2\text{Cr}_2\text{O}_7$, 7.50 cm^3 of the $\text{K}_2\text{Cr}_2\text{O}_7$ solution was needed to reach the end-point.

Calculate [**A**] in the solution.

[**A**] = ... mol dm^{-3}
[5]

(c) When lawsone is reacted with NaOH(aq), compound **B** is produced.



Reacting **B** with ethanoyl chloride, CH_3COCl , produces compound **C**, with the molecular formula $\text{C}_{12}\text{H}_8\text{O}_4$.

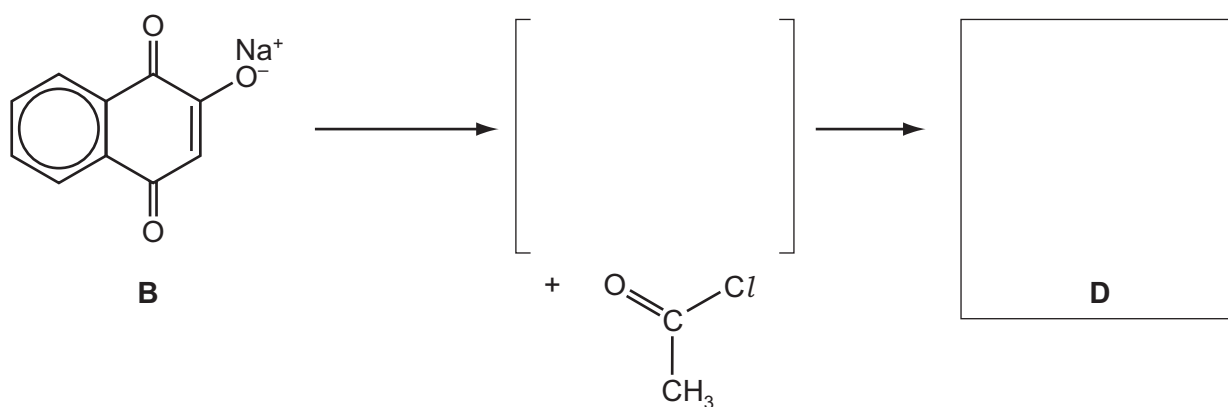
(i) Suggest the identity of compound **C**, and draw its structure in the box above.

Another compound, **D**, in addition to **C**, is produced in the above reaction. **D** is an isomer of **C** which contains the same functional groups as **C**, but in different positions.

(ii) Suggest a possible structure for **D**.



(iii) Suggest a mechanism for the formation of **D** from **B** and ethanoyl chloride by drawing relevant structures and curly arrows in the following scheme.



[3]

[Total: 14]

- 4 (a) Describe and explain the trend in the volatilities of the halogens Cl_2 , Br_2 and I_2 .

.....

.....

.....

..... [3]

- (b) For each of the following pairs of compounds, predict which compound has the higher boiling point, and explain the reasons behind your choice.
Use diagrams in your answers where appropriate.

(i) H_2O and H_2S

(ii) $\text{CH}_3-\text{CH}_2-\text{CH}_3$ and $\text{CH}_3-\text{O}-\text{CH}_3$

[4]

- (c) Briefly explain the shape of the SF_6 molecule, drawing a diagram to illustrate your answer.

[2]

[Total: 9]

- 5 (a) Describe and explain how the acidities of $\text{CHCl}_2\text{CO}_2\text{H}$ and $\text{CH}_2\text{ClCO}_2\text{H}$ compare to each other, and to the acidity of ethanoic acid.

.....

.....

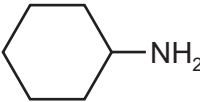
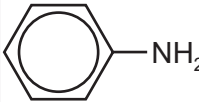
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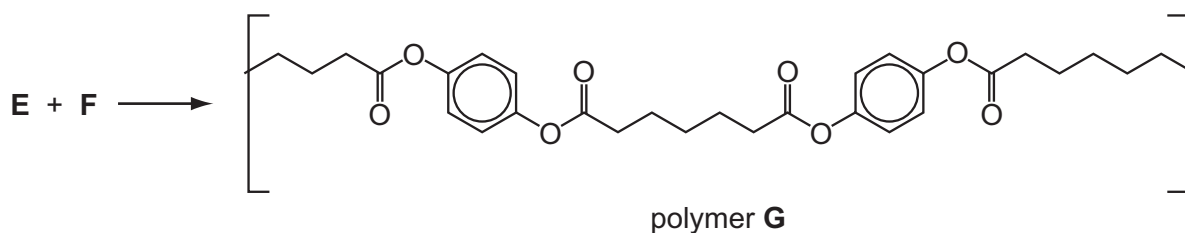
[3]

- (b) For each of the following pairs of compounds, suggest one chemical test (reagents and conditions) that would distinguish between them.
State the observations you would make with each compound, writing 'none' if appropriate.

first compound	second compound	test (reagents and conditions)	observation with first compound	observation with second compound
				
$\text{CH}_3\text{CH}_2\text{COCl}$	$\text{CH}_3\text{COCH}_2\text{Cl}$			
$\text{CH}_3\text{CH}_2\text{CHO}$	CH_3COCH_3			

[7]

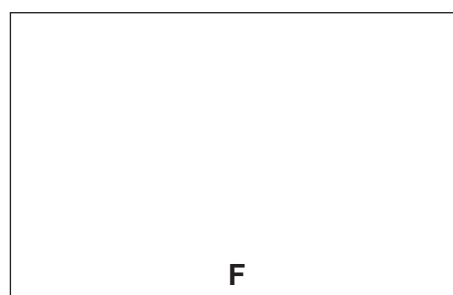
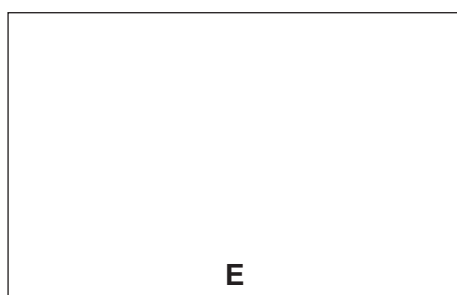
- (c) The following diagram shows a section (not a repeat unit) of a polymer, **G**, that can be made from the two monomers **E** and **F**.



- (i) What *type of polymerisation* made this polymer?

.....

- (ii) Draw the structures of the two monomers **E** and **F**.



- (iii) Suggest the conditions needed to make polymer **G** from **E** and **F** in the laboratory.

.....

.....

.....

- (iv) One of the monomers, **E** or **F**, could be changed to make a more rigid polymer of a similar chemical type to **G**.
Suggest which of your two monomers could be changed, and suggest a structure for the new monomer.

Monomer to be changed (**E** or **F**)

Structural formula of the new monomer

[6]

[Total: 16]

Section B

For
Examiner's
UseAnswer **all** the questions in the spaces provided.

- 6 (a) The table shows the structures of four amino acids found in proteins in the human body. Complete the table by indicating the type of tertiary interaction each side-chain is most likely to have when its amino acid is present in a protein chain.

amino acid	structure	type of interaction
alanine	$\text{H}_2\text{NCH}(\text{CH}_3)\text{CO}_2\text{H}$	
cysteine	$\text{H}_2\text{NCH}(\text{CH}_2\text{SH})\text{CO}_2\text{H}$	
lysine	$\text{H}_2\text{NCH}((\text{CH}_2)_4\text{NH}_2)\text{CO}_2\text{H}$	
serine	$\text{H}_2\text{NCH}(\text{CH}_2\text{OH})\text{CO}_2\text{H}$	

[3]

- (b) Metal ions play an important role in the biochemistry of the human body. For each of the following metal ions, outline one of the places in the body it can be found and its main role there.

iron

.....

.....

potassium

.....

.....

zinc

.....

.....

[3]

(c) Many chemical reactions at a cellular level require energy in order to take place. This energy is largely provided by the breakdown of one particular compound.

(i) Write an equation showing the breakdown of this compound.

.....

(ii) What type of chemical reaction is this?

.....

[2]

(d) Cystic fibrosis is a genetic disease caused by a mutation in the DNA sequence resulting in the production of a faulty version of an important protein which acts as an ion pump in the cell membrane. This pump controls the flow of ions into and out of cells. People with the faulty protein show two major symptoms.

- water is retained in cells in the lungs resulting in the formation of a thick, sticky mucous outside the cells;
- their sweat is very salty.

Based on the information given for people with cystic fibrosis,

(i) suggest which ions are involved in the ion flow,

.....

.....

(ii) suggest and explain what type of bonding might result in thick or sticky mucous.

.....

.....

[2]

[Total: 10]

- 7 NMR and X-ray crystallography are two important analytical techniques which can be used to study the structure and function of molecules.

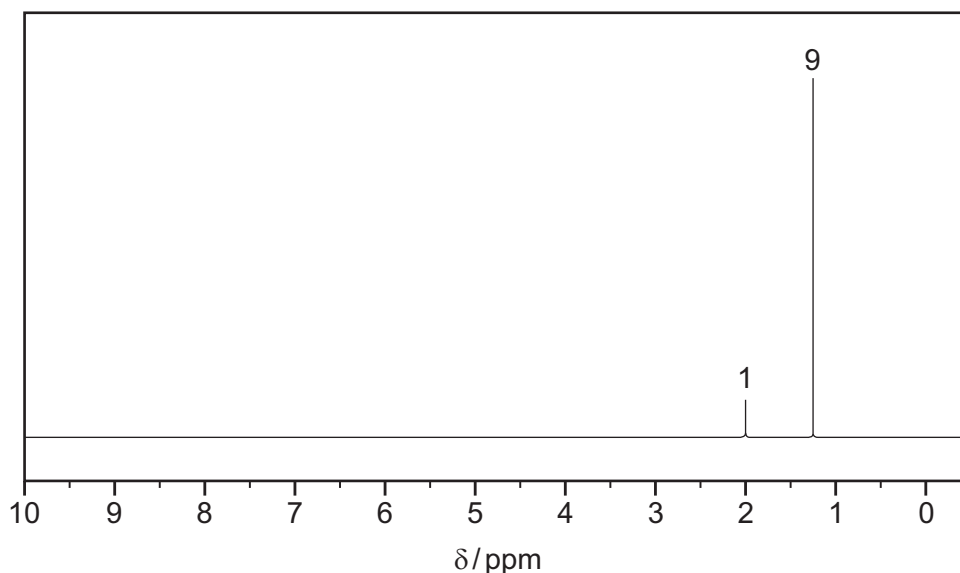
(a) Nuclear magnetic resonance, NMR, arises because protons possess spin which generates a small magnetic moment. When an external magnetic field is applied the protons can align with or against the external field. If they are given a small amount of energy in the radio frequency range each can be 'promoted' so that their magnetic moment opposes the external field.

Two factors can influence the energy required for this promotion. What are they?

(i)

(ii) [2]

(b) A compound, **J**, has the formula $C_4H_{10}O$. The NMR spectrum of **J** is shown.



(i) Indicate the groups responsible for each peak and hence deduce the structure of **J**.

peak at 1.26δ peak at 2.0δ

structure of **J**

- (ii) There are three other isomers of **J** containing the same functional group as **J**. Draw the structures of two of these three isomers and indicate how many different chemical shifts each would show in its NMR spectrum.

isomer 1

isomer 2

number of groups of peaks number of groups of peaks
[6]

- (c) X-ray crystallography can be useful in gathering information about the structure of large organic molecules, such as nucleic acids.

- (i) Which element will show up most strongly in the X-ray crystallography of a nucleic acid? Explain your answer.

.....
.....

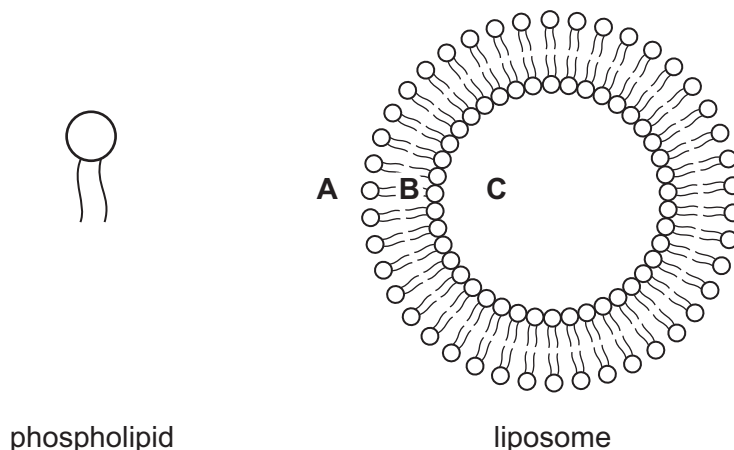
- (ii) X-ray crystallography will **not** detect hydrogen atoms. Explain why this is so.

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

[Total: 10]

- 8 The developments in nanotechnology and drug delivery over the past 20 years have been wide-ranging.

- (a) One of the most widespread developments for delivering a range of pharmaceutical products has been the use of liposomes. These are artificially created spheres made from phospholipids which have an ionic phosphate 'head' and two hydrocarbon 'tails'.



Liposomes have also been used to carry pharmaceuticals such as vitamins and moisturisers used in cosmetic anti-ageing creams. Otherwise these pharmaceuticals may be oxidised or dehydrated if exposed to air.

- (i) State in which area of the liposome, **A**, **B** or **C**, each of the following types of molecule would be carried.

a hydrophilic moisturiser

a fat-soluble vitamin

- (ii) For one of the areas, **A**, **B** or **C**, suggest why this would **not** be an appropriate place to carry either molecule.

.....

[3]

- (b) When liposomes are used to carry drugs, their main purpose is to prevent the drug molecules from being broken down on passage through the digestive system.

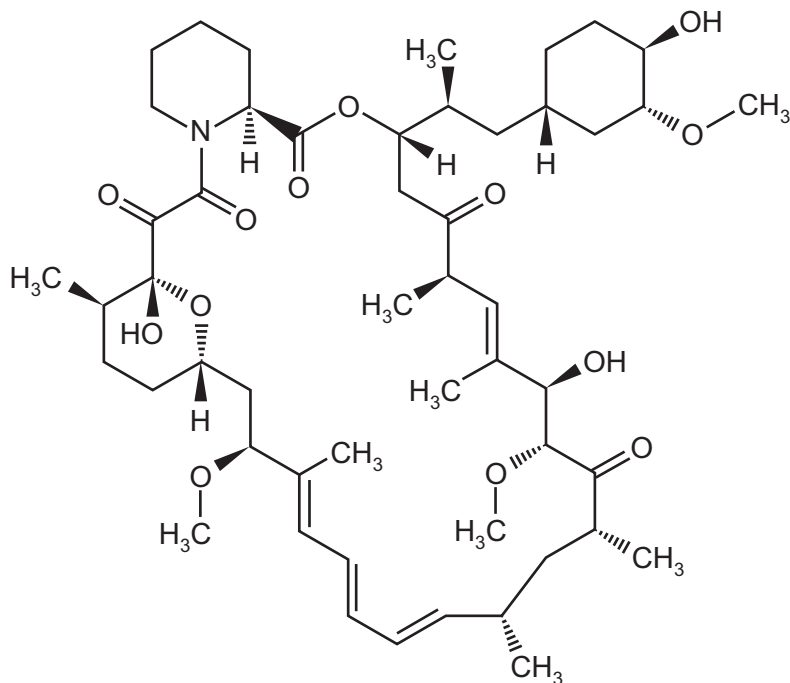
- (i) Name a functional group present in drug molecules that might be broken down by acid in the stomach.

.....

- (ii) Name the *type of reaction* that would cause such a breakdown.

.....

- (iii) The drug *Sirolimus* is used to suppress possible rejection by the body after kidney transplants.

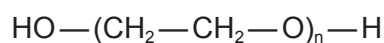


Sirolimus

Circle **two bonds**, each in a **different** functional group that could be broken down in the digestive system.

[4]

- (c) *Sirolimus* is not very soluble in water, greatly reducing its effectiveness when given by mouth or by injection. To increase its effectiveness when taken by mouth nano-sized crystals of the drug combined with poly(ethylene glycol) or PEG (shown below) are produced.



- (i) Suggest what is meant by the term *nano-sized*.

.....

- (ii) Suggest where on the molecule of PEG the drug would be attached.

.....

- (iii) Why would bonding the drug to a PEG molecule improve its solubility in water?

.....

[3]

[Total: 10]

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CHEMISTRY

9701/43

Paper 4 Structured Questions

May/June 2012

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, candidate number and name on all the work you hand in.

Write in dark blue or black pen.

You may use a soft pencil for any diagrams, graphs or rough working.

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

DO **NOT** WRITE IN ANY BARCODES.

Section A

Answer **all** questions.

Section B

Answer **all** questions.

You may lose marks if you do not show your working or if you do not use appropriate units.

A Data Booklet is provided.

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

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

For Examiner's Use

1	
2	
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7	
8	
Total	

This document consists of **17** printed pages and **3** blank pages.



Section A

For
Examiner's
UseAnswer **all** the questions in the spaces provided.

- 1 (a) (i) What is meant by the term *lattice energy*?

.....

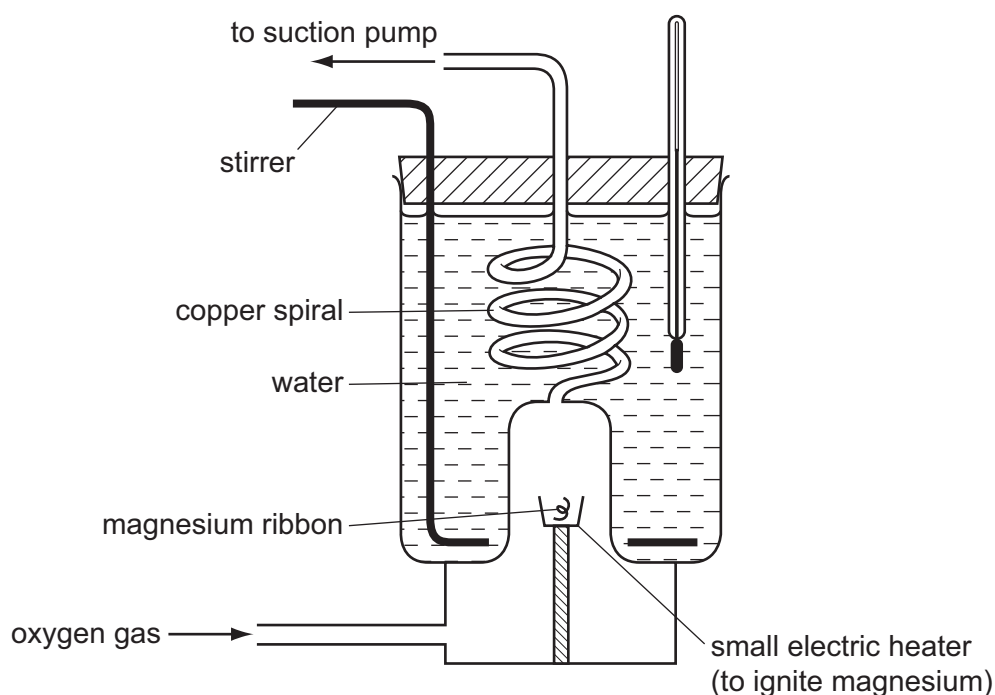
.....

- (ii) Write an equation to represent the lattice energy of MgO.

.....

[3]

- (b) The apparatus shown in the diagram can be used to measure the enthalpy change of formation of magnesium oxide, $\Delta H_f^\circ(\text{MgO})$.



List the measurements you would need to make using this apparatus in order to calculate $\Delta H_f^\circ(\text{MgO})$.

.....

.....

.....

.....

[3]

- (c) Use the following data, together with appropriate data from the *Data Booklet*, to calculate a value of $\Delta H_f^\circ(\text{MgO})$.

lattice energy of MgO(s)	=	$-3791 \text{ kJ mol}^{-1}$
enthalpy change of atomisation of Mg	=	$+148 \text{ kJ mol}^{-1}$
electron affinity of the oxygen atom	=	-141 kJ mol^{-1}
electron affinity of the oxygen anion, O^-	=	$+798 \text{ kJ mol}^{-1}$

$$\Delta H_f^\circ(\text{MgO}) = \dots\dots\dots \text{kJ mol}^{-1}$$

[3]

- (d) Write equations, including state symbols, for the reactions, if any, of the following two oxides with water. Suggest values for the pH of the resulting solutions.

oxide	equation	pH of resulting solution
Na_2O		
MgO		

[3]

[Total: 12]

- 2 Nitrogen monoxide, NO, is formed in a reversible reaction when air is heated to the temperature of a car engine.

(a) (i) Suggest a 'dot-and-cross' electronic structure for nitrogen monoxide.

- (ii) The enthalpy change of formation of nitrogen monoxide is $+90 \text{ kJ mol}^{-1}$. What is the enthalpy change for the following reaction?



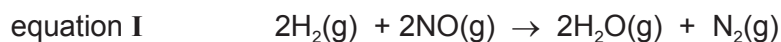
- (iii) Explain why nitrogen monoxide is formed in the car engine.

.....

- (iv) Using bond enthalpy values from the *Data Booklet* and your answer in (iii) above, calculate a value for the bond energy of nitrogen monoxide.

bond energy = ... kJ mol^{-1}
[5]

- (b) At 800 K, nitrogen monoxide reacts with hydrogen according to the following equation.



The following table shows how the initial rate of this reaction depends on the partial pressures of the reagents.

experiment	$p(\text{H}_2)/\text{atm}$	$p(\text{NO})/\text{atm}$	initial rate / atm s^{-1}
1	0.64	1.60	1.50×10^{-7}
2	0.64	0.80	3.75×10^{-8}
3	0.32	1.60	7.50×10^{-8}

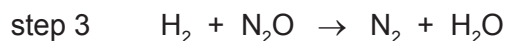
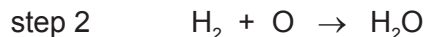
- (i) Find the order of the reaction with respect to each reactant, explaining how you arrive at your answer.

.....
.....
.....
.....
.....

- (ii) Write down the rate equation and the units of the rate constant.

.....

The following mechanism has been put forward for this reaction.



- (iii) Show how the overall stoichiometric equation **I** can be derived from the three equations for the individual steps given above.

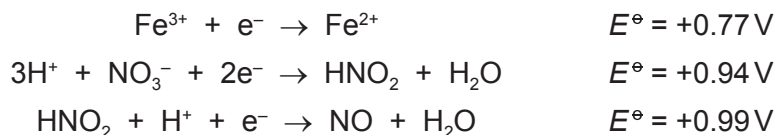
- (iv) Suggest which of the three reactions in the mechanism is the rate determining step. Explain your answer.

.....

.....

[8]

- (c) The following information on half-reactions relates to the reaction between HNO_3 and an excess of FeSO_4 .



- (i) Suggest the formula of the nitrogen-containing final product of this reaction.

.....

- (ii) Write an equation for the formation of this nitrogen-containing product.

- (iii) Nitrogen monoxide forms a dark brown complex with an excess of $\text{FeSO}_4(\text{aq})$. What kind of bonding is involved in the complex formation?

.....

- (iv) Suggest a formula for this complex.

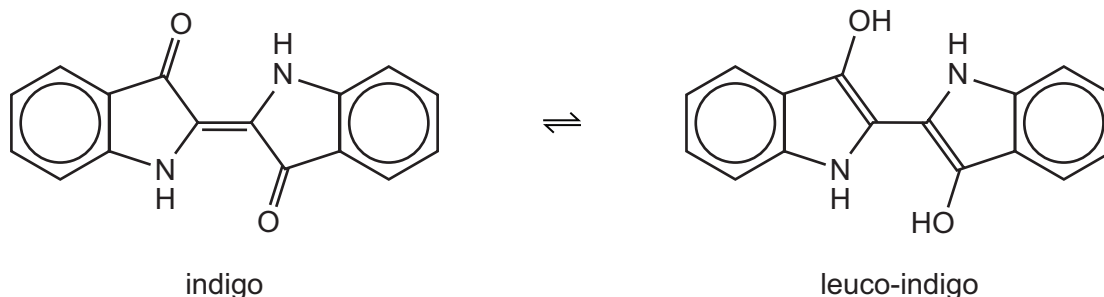
.....

[4]

[Total: 17]

- 3 Indigo is the dye used in blue jeans. Although originally extracted from plants of the type *indigofera*, it is now almost entirely made artificially.

Indigo is insoluble in water but this disadvantage can be overcome by converting it into the water-soluble colourless leuco-indigo. If cloth soaked in a solution of leuco-indigo is left to dry in the air, the leuco-indigo is converted into the insoluble blue indigo, which is precipitated out onto the fibres of the cloth.



- (a) (i) Give the molecular formula of indigo.

.....

- (ii) Name **three** functional groups in indigo.

.....

[3]

- (b) (i) What *type of reaction* is the conversion of indigo into leuco-indigo?

.....

- (ii) Suggest a laboratory reagent for this reaction.

.....

[2]

- (c) Suggest **two** chemical tests that could be used to distinguish between indigo and leuco-indigo. Write your answers in the following table.

test	reagents and conditions	observation with indigo	observation with leuco-indigo
1			
2			

[5]

(d) When indigo is heated with hydrogen and a nickel catalyst, compound **A**, $\text{C}_{16}\text{H}_{28}\text{N}_2\text{O}_2$, is formed.

(i) Suggest a structure for **A**.

(ii) Calculate the volume of hydrogen, measured at room temperature and pressure, that would have been absorbed if 2.50 g of indigo had undergone this reaction.

volume = ...dm³
[3]

(e) Suggest the structure of the product formed when indigo reacts with an excess of $\text{Br}_2(\text{aq})$.

[3]

[Total: 16]

- 4 (a) (i) Describe and explain the trend in the volatilities of the Group IV chlorides CCl_4 , GeCl_4 and PbCl_4 .

.....

.....

.....

.....

.....

.....

- (ii) Describe and explain the reactions, if any, of these chlorides with water. Write equations for any reactions that occur.

.....

.....

.....

.....

.....

.....

.....

[7]

(b) SnO_2 and PbO_2 react with acids in different ways.

- SnO_2 reacts with concentrated sulfuric acid to form a colourless solution with no evolution of gas.
- PbO_2 reacts with concentrated sulfuric acid to give a white solid, **B**, and oxygen gas.
- PbO_2 reacts with cold concentrated hydrochloric acid to give a yellow solution containing the $[\text{PbCl}_6]^{2-}$ ion, with no evolution of gas.
- Warming this yellow solution causes the evolution of Cl_2 gas, leaving a colourless solution which on cooling in ice precipitates a white solid, **C**.

(i) Identify the two white solids, **B** and **C**, mentioned above.

B

C

(ii) Suggest an equation for **each** of the four reactions described above.

.....

.....

.....

.....

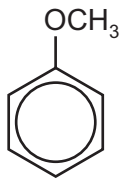
.....

.....

[4]

[Total: 11]

- 5 (a) Methoxybenzene reacts with $\text{Br}_2(\text{aq})$ in a similar manner to phenol.



methoxybenzene

- (i) Draw the structural formula of the product of the reaction between methoxybenzene and an excess of bromine.

- (ii) Suggest a chemical reaction you could use to distinguish between methoxybenzene and phenol. State the reagent, describe the observations you would make, and give an equation for the reaction.

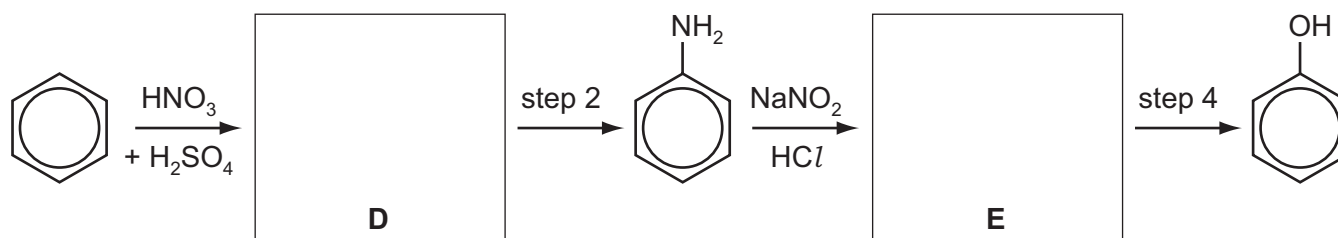
reagent

observation

equation

[4]

- (b) Phenol can be synthesised from benzene by the following route.



- (i) Suggest structures for compounds **D** and **E** and draw them in the boxes above.
- (ii) Suggest reagents and conditions for

step 2, ...

step 4.

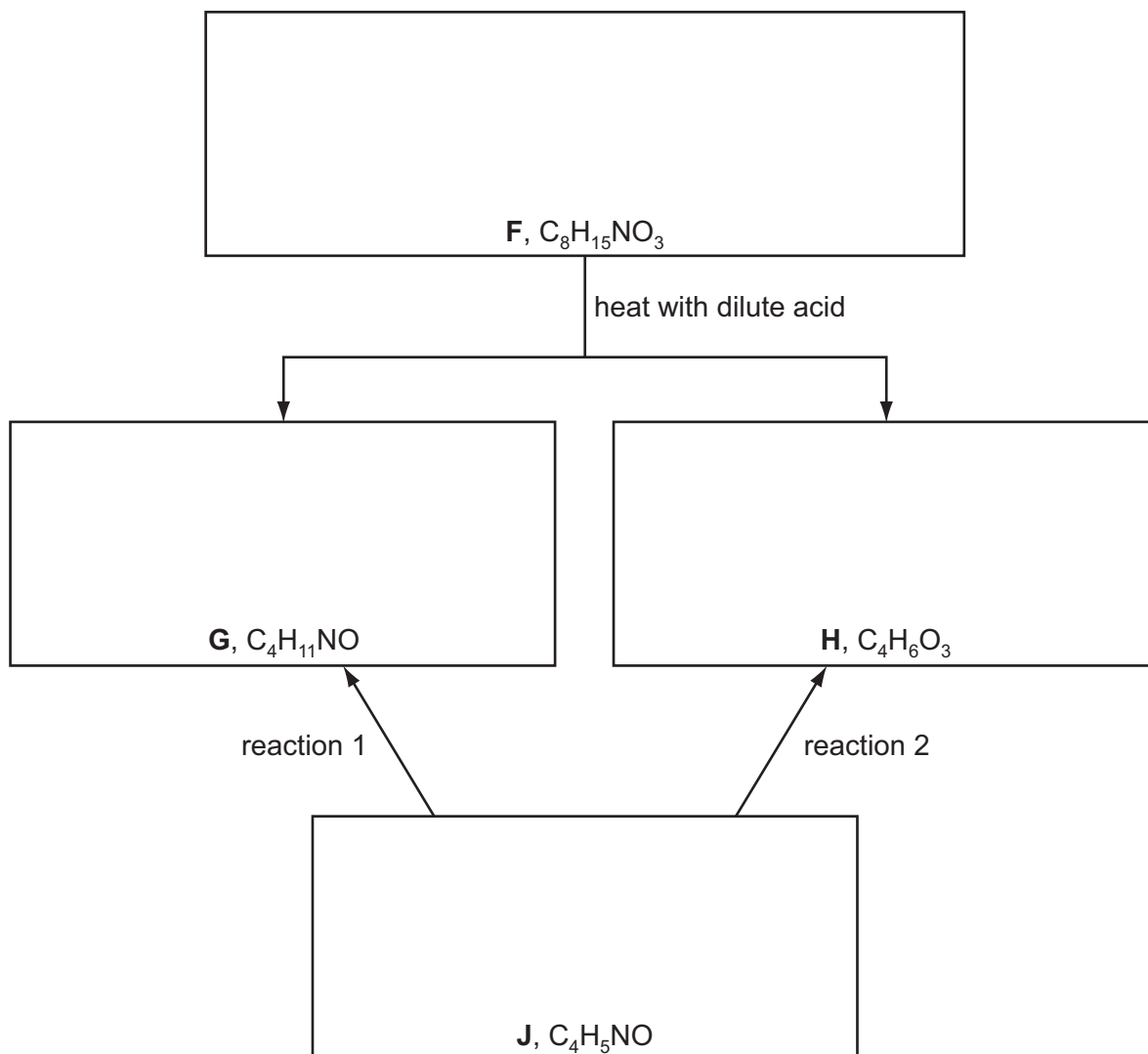
[4]

(c) The following chart shows some reactions of compound **F** which is a neutral compound.

G forms a salt with dilute H_2SO_4 , whereas **H** forms a salt with $\text{NaOH}(\text{aq})$.

Both **G** and **H** can be obtained from compound **J** by separate one-step reactions (reaction 1 and reaction 2 below).

All four compounds **F**, **G**, **H** and **J** form a yellow precipitate with alkaline aqueous iodine.



(i) Suggest structures for **F**, **G**, **H** and **J**, and draw them in the boxes above.

(ii) Suggest reactants and conditions for

reaction 1, ...

reaction 2.

[6]

[Total: 14]

Section B

For
Examiner's
UseAnswer **all** the questions in the spaces provided.

- 6 In key reactions responsible for growth and repair in the human body, amino acids react together to form polymers known as proteins.

(a) (i) What *type of reaction* is this polymerisation?

.....

- (ii) From stocks of glycine and alanine, it is possible to make the dipeptide gly-ala. Using the same three-letter abbreviations for the amino acids, give the structures of all other possible dipeptides that can be made from these stocks of amino acids.

[3]

- (b) (i) DNA consists of a double helix formed by two strands held together by hydrogen bonds between base pairs.

Sketch a section of DNA showing **two** base pairs, using blocks for the various components. You should label all of the components.

- (ii) Suggest what the effect on DNA replication would be if the hydrogen bonds between the strands were replaced by stronger bonds, e.g. covalent bonds.

.....

.....

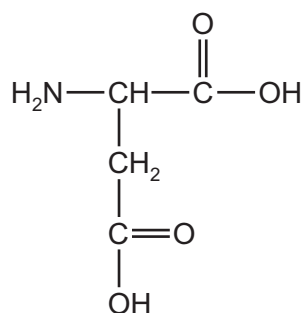
[4]

(c) Some diseases, such as sickle-cell anaemia, are caused by mutation resulting in a change in the triplet code.

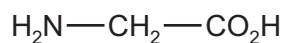
- (i) Explain why some changes in the triplet code do **not** result in a change in the primary structure of a protein.

.....

- (ii) Suggest what change in the tertiary structure of a protein would result from a mutation that replaced aspartic acid with glycine.



aspartic acid



glycine

.....

- (iii) Sometimes a mutation can result in the *deletion* of a single base in DNA (or RNA). Explain why this is likely to have more serious consequences for the protein than the *replacement* of one base by another.

.....

[3]

[Total: 10]

- 7 The analysis of a protein may be carried out by breaking it down into its amino acids. These can then be separated by a process called electrophoresis.

(a) The structures of glycine, lysine and glutamic acid at pH 7 are shown.

glycine



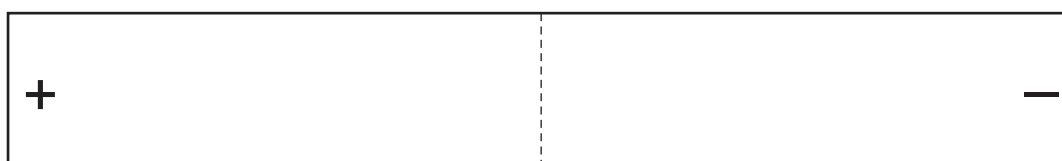
lysine



glutamic acid



Draw and label three circles on the chart below to indicate the likely position of each of these amino acids after electrophoresis of a solution containing these amino acids in a buffer at pH 7.



start point

[3]

- (b) Some organic compounds have very different solubilities in water and in organic solvents such as hexane. They may be extracted from an aqueous reaction mixture by shaking the mixture with portions of hexane and separating the two layers. The process of distribution of a compound between two solvents is called *partition*.

(i) State what is meant by the term *partition coefficient*.

.....

.....

.....

- (ii) One of the concerns about organic pollutants, such as pesticide residues, is that they can enter the food chain and become concentrated in human breast milk. Explain how this can happen.

.....

.....

.....

.....

[3]

- (c) Propene was treated with bromine in the presence of chloride ions and the product analysed using mass spectrometry.

A group of peaks was found in the range m/e 156–160 with the following relative heights.

m/e	relative height
156	3
158	4
160	1

- (i) Identify the species responsible for each of these peaks.

156

158

160

A large peak was present in the spectrum with a m/e value of less than 20.

- (ii) Suggest the m/e value for the peak and the species that produced it.

m/e

species

[4]

[Total: 10]

- 8 Some of the most commonly used polymers are formed by the polymerisation of ethene, C_2H_4 . The presence of side-chains affects the bulk properties of an addition polymer. Unbranched polymers pack closer together than polymers with several side-chains.

Poly(ethene) exists in two different forms LDPE (low density poly(ethene)) which has lots of side-chains, and HDPE (high density poly(ethene)) in which there are fewer and shorter side-chains.

- (a) Explain with the aid of sketches why the presence of side-chains causes a difference in density in poly(ethene).

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

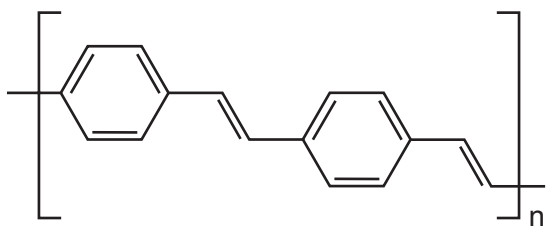
- (b) By reference to the type of bonding between the poly(ethene) chains, explain why LDPE has a lower melting point than HDPE.

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

- (c) Polymerisation can take place by two different methods depending on the monomers involved. The two methods are addition and condensation.
Give **two** differences between the methods.

1.
.....
2.
.....
[2]

- (d) There has been a great deal of commercial interest in the development of polymers that can conduct electricity and/or emit light. A length of one such polymer is shown.



- (i) Suggest how this polymer conducts electricity.

.....

- (ii) Suggest the molecular geometry required for this molecule to conduct.

Explain your answer.

.....

.....

- (iii) What is the empirical formula of this polymer?

.....

[4]

[Total: 10]

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