Cambridge Pre-U

Cambridge International Examinations
Cambridge Pre-U Certificate

CANDIDATE NAME			
CENTRE NUMBER		CANDIDATE NUMBER	

1824477300

CHEMISTRY **9791/02**

Paper 2 Part A Written **May/June 2014**

2 hours 15 minutes

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 an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.
DO **NOT** WRITE IN ANY BARCODES.

Answer **all** questions.
Electronic calculators may be used.
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	
3	
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6	
Total	

This document consists of **20** printed pages.

DC (NF/SW) 76474/3

CAMBRIDGE International Examinations

[Turn over

1 A goal of chemists is to create a viable process that, like photosynthesis, will convert carbon dioxide into fuel.

(a) A recent development (reported in *Science*, 2010) is to concentrate sunlight onto cerium(IV) oxide, in contact with carbon dioxide and water, to make carbon monoxide, hydrogen and oxygen.

The standard enthalpy changes of formation are given.

substance	$\Delta_f H^\ominus$ (298 K) / kJ mol^{-1}
$CO_2(g)$	–393.5
$H_2O(l)$	–285.8
$CO(g)$	–110.5

(i) Calculate the standard enthalpy change of reaction at 298 K for the reaction between CO_2 and H_2O.

Give your answer to one decimal place and include a sign in your answer.

$$CO_2 + H_2O \rightarrow CO + H_2 + O_2$$

$\Delta_r H^\ominus$ (298 K) = ... kJ mol^{-1} [2]

(ii) Suggest the role of cerium(IV) oxide in this reaction.

.... [1]

(b) A mixture of carbon monoxide and hydrogen is known as synthesis gas. Synthesis gas can be converted to methanol.

$$CO(g) + 2H_2(g) \rightarrow CH_3OH(l) \qquad \Delta_r H^{\ominus} \text{ (298 K)} = -128.6 \text{ kJ mol}^{-1}$$

(i) Define the term *standard enthalpy change of combustion*.

....

....

....

.... [3]

(ii) Use the value of the enthalpy change given and data from **(a)** to find the standard enthalpy change of combustion of methanol.

Give your answer to one decimal place and include a sign in your answer.

$\Delta_c H^{\ominus}$ (298 K) = ... kJ mol^{-1} [2]

(iii) Methanol is a useful fuel; however, synthesis gas is also a fuel in its own right.

Suggest one advantage in converting synthesis gas to methanol.

....

.... [1]

(c) A recent proposal (reported in *Energy & Environmental Science*, 2011) is to obtain the carbon dioxide for the process in part **(a)** by concentrating solar energy on calcium carbonate in order to make it decompose.

(i) Write the equation for this reaction of calcium carbonate.

.... [1]

(ii) State and explain whether more or less solar energy would be required to decompose the same number of moles of magnesium carbonate.

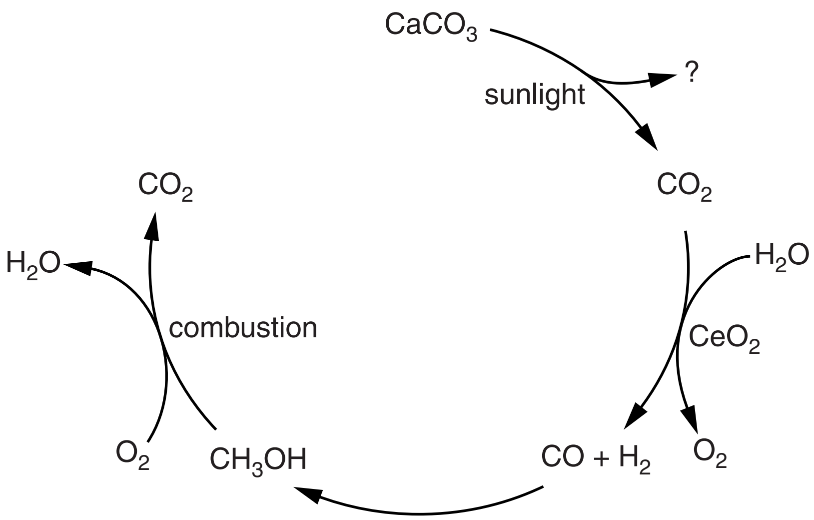
....

....

....

.... [2]

(iii) The flow diagram summarises all the reactions in this question.



Suggest what extra step would complete the cycle and lower the carbon footprint of the overall process.

....

....

.... [1]

[Total: 13]

2 This question is about oxygen and its compounds.

(a) O_2 and O_3 are allotropes of oxygen.

Explain what is meant by the term *allotrope*.

....

.... [1]

(b) A molecule of O_3 contains a dative covalent bond.

(i) What is meant by the term *dative covalent bond*?

....

.... [1]

(ii) Suggest a dot-cross diagram to show the bonding in O_3.

[2]

(c) A recent study (reported in *Proceedings of the National Academy of Sciences, USA*, 2012) has predicted that oxygen under 2 TPa of pressure (1 TPa = 10^{12} Pa = 10^{7} bar) can exist as the long-chain polymer shown.

$$\cdots\!-\!O\!-\!O\!-\!O\!-\!O\!-\!O\!-\!O\!-\!\cdots$$

At room temperature and pressure such a polymer will spontaneously turn into O_2.

(i) What is meant by the term *bond energy*?

....

....

.... [3]

(ii) Calculate the energy change that accompanies the conversion of polymeric oxygen to O_2, per mole of oxygen molecules formed.

$$-\!\!\left[O-O\right]_n\!\!-(g) \longrightarrow nO_2(g)$$

bond	bond energy / kJ mol^{-1}
O–O	144
O=O	498

energy change = ... kJ mol^{-1} [2]

(d) H^+ ions do not exist in isolation in water. They bond to water molecules to form hydronium ions, H_3O^+.

(i) Predict and explain the shape of the hydronium ion.

....

....

.... [2]

(ii) Which molecule with four atoms has the same total number of electrons as the hydronium ion?

.... [1]

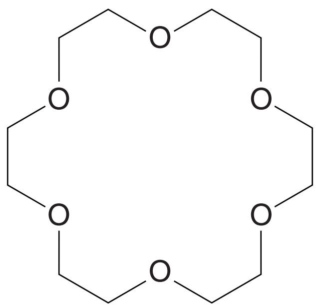
(e) A proton in an H_3O^+ ion can form a hydrogen-bond with a water molecule to form an $H_5O_2^+$ cation.

(i) Draw the $H_5O_2^+$ cation, labelling the hydrogen-bond. Include relevant lone pairs, dipoles and bond angles.

[4]

(ii) The hydronium ion, H_3O^+, may be solvated inside the macrocyclic 18-crown-6 molecule shown.

Draw the hydronium ion inside the macrocycle, showing how it is attached to the ring.



[1]

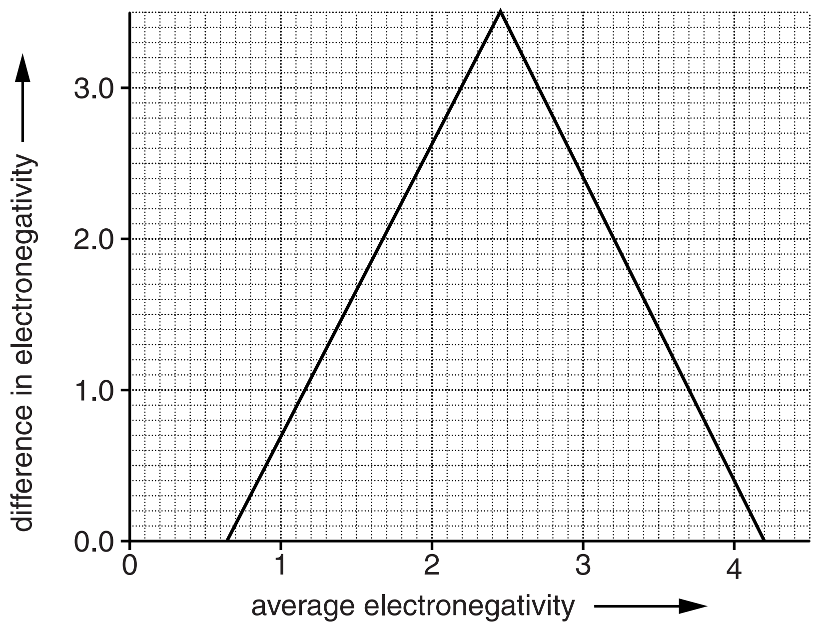
[Total: 17]

3 This question is about compounds of Group 16 elements.

(a) There has been much recent interest in the structural and electronic properties of molybdenum disulfide, MoS_2, and bismuth telluride, Bi_2Te_3. Electronegativity values for their constituent elements are shown.

element	Mo	Bi	Te	S
electronegativity	1.47	2.01	2.16	2.59

(i) Plot and label the points for MoS_2 and Bi_2Te_3 on the van Arkel diagram.



[1]

(ii) Circle the option that **best** describes the bonding in Bi_2Te_3.

intermediate covalent-metallic **intermediate ionic-metallic**

intermediate covalent-ionic **intermediate covalent-ionic-metallic**

[1]

(iii) Circle the option that **best** describes the bonding in MoS_2.

more covalent than Bi_2Te_3 **more ionic than Bi_2Te_3**

less covalent than Bi_2Te_3 **less ionic than Bi_2Te_3**

[1]

(b) **(i)** 'Fool's gold' is iron disulfide, FeS_2. The S atoms exist as an ion containing an S–S covalent bond. The iron ion exhibits an oxidation number of +2.

Draw a dot-cross diagram of the sulfur-containing ion in FeS_2, indicating the charge(s).

[3]

(ii) There are no S–S bonds in MoS_2.

What is the oxidation number of molybdenum in MoS_2?

oxidation number .... [1]

(c) Sulfur can react with hot aqueous sodium sulfide, Na_2S, to form a yellow solution of compound **X**, which has the composition by mass, Na, 26.4%; S, 73.6%.

(i) What is meant by the term *empirical formula*?

....

.... [1]

(ii) Use this information to prove that **X** has an empirical formula of NaS_2.
Show your working.

[2]

(iii) The sulfur-containing ion in compound **X** consists of a chain of sulfur atoms with an overall 2– charge.

Deduce how many sulfur atoms are in the chain of the ion.

.... atoms [1]

(iv) When solid **X** is added to an excess of acid, an oily liquid results that is immiscible with water. Assume that there is only one sulfur-containing product.

Suggest the structure of this product.

[1]

[Total: 12]

4 This question is about halogenoalkanes.

(a) Propane is treated with bromine while irradiated with ultraviolet light, producing isomers of $C_3H_6Br_2$.

(i) Write a chemical equation using molecular formulae for the preparation of $C_3H_6Br_2$ by this reaction.

.... [1]

(ii) Name the type of reaction.

.... [1]

(iii) Draw 3D diagrams to show the optical isomers of 1,2-dibromopropane.

[2]

(iv) State how many different carbon-atom environments there are in

1,2-dibromopropane (considering one enantiomer) .... ,

2,2-dibromopropane .... [2]

(b) 1,2-dibromopropane may be converted to propane-1,2-diol.

State the reagent and solvent used for this reaction.

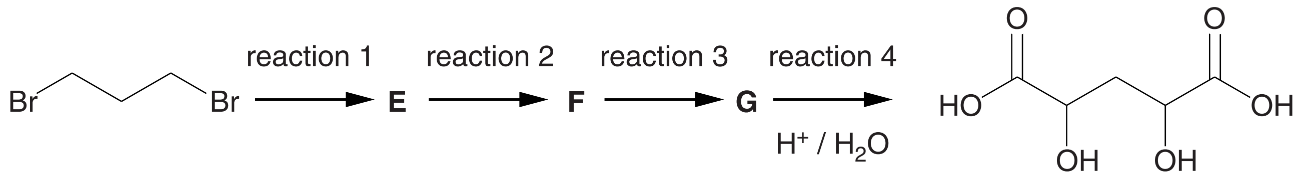
reagent ....

solvent .... [2]

(c) Draw the structure of the product formed when 2,2-dibromopropane is reacted under the same set of conditions as those in part **(b)**.

[1]

(d) 1,3-dibromopropane is the starting point for a four-step reaction sequence which produces 2,4-dihydroxypentane-1,5-dioic acid. The four reactions are shown.



Compound **F** has the molecular formula $C_3H_4O_2$. If it is tested with Tollens' reagent, a silver mirror is produced.

(i) What functional group is present in **F**?

.... [1]

(ii) What change in functional group level did **F** undergo when it reacted with Tollens' reagent?

from functional group level .... to .... [1]

(iii) When preparing **F** from **E** it is important that the product is distilled off rather than continually refluxed.

State which unwanted product is avoided by distilling off compound **F**.

.... [1]

(iv) 9.0 g of 1,3-dibromopropane was used by experimenters who converted it into **F** with an overall yield of 67%. Calculate the mass of **F** that was obtained.

mass of **F** = ... g [2]

(v) Draw the structures of **E** and **F**.

structure of **E**	structure of **F**

[2]

(vi) **G** is converted into the final product by reaction with dilute acid. Suggest the structure of **G**.

[1]

(e) 1,3-dibromopropane can undergo an elimination reaction to form compound **H**.
H has the molecular formula C_3H_4 and is not cyclic.

(i) Suggest the structure of **H**.

[1]

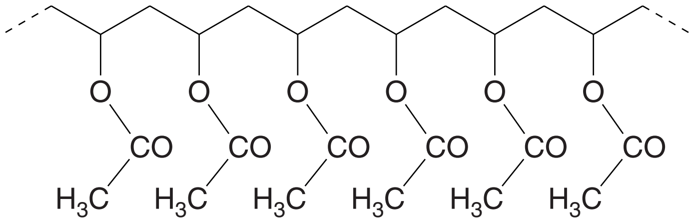
(ii) **H** can isomerise into **I**, which has three different carbon environments.

Draw the structure of **I**.

[1]

[Total: 19]

5 **(a)** Polyvinyl acetate (PVA) is produced on a large scale for use in glues.



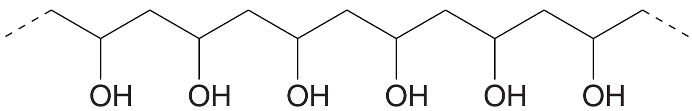
PVA

(i) Circle one repeat unit of the polymer. [1]

(ii) Draw the structure of the monomer used to make PVA.

[1]

(iii) Complete hydrolysis of PVA results in a polymer **Q** and a second product, **R**.



Q

Identify **R**.

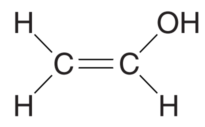
[1]

(iv) Polymer **Q** is unusual in that it dissolves in water. Suggest why it dissolves in water.

....

.... [1]

(v) A logical monomer to make **Q** is shown.



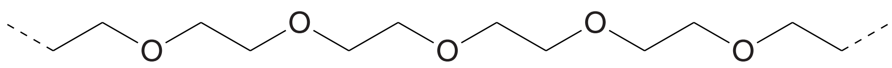
In fact this molecule is not stable. Two isomers of this molecule, **S** and **T**, can be isolated. Draw the structures of **S** and **T**.

structure of **S**

structure of **T**

[2]

(vi) One of the isomers, **S** or **T**, is the monomer for the polymer PEG.



PEG

State the functional group level of the carbon atoms in PEG and explain how this identifies which of the isomers, **S** or **T**, is the monomer for PEG.

functional group level ....

explanation ....

....

.... [2]

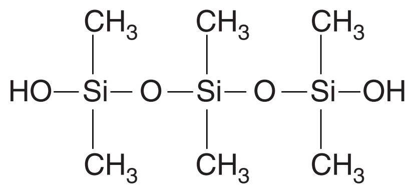
(b) (i) The complete hydrolysis of dimethyldichlorosilane, $(H_3C)_2SiCl_2$ gives two products, **V**, which contains silicon, and **W**, which does not. The Si–C bond is stable towards hydrolysis. **V** has a molar mass of 92 g mol^{-1}.

Draw the structure of **V** and give the formula of **W**.

structure of **V** formula of **W** ....

[2]

(ii) Three molecules of **V** can combine to form the molecule shown.



Five molecules of **V** can combine to form a molecule with a relative molecular mass of 370, where all the silicon atoms are in equivalent environments.

Suggest the structure of this molecule.

[1]

[Total: 11]

6 Cyanide ions are used in the extraction of silver.

(a) The simple silver salt, AgCN, is an insoluble white solid.

(i) Draw a diagram of the cyanide ion, showing all the bonds, lone pairs and the ionic charge.

[2]

(ii) In Tollens' reagent, silver is present as the $Ag(NH_3)_2^+$ ion. Silver(I) also forms a soluble colourless ion with excess cyanide ions, $Ag(CN)_2^-$.

Write **ionic** equations for the precipitation of silver ions by cyanide ions and the subsequent dissolving of the precipitate in excess cyanide.

Include state symbols.

precipitation ....

dissolving .... [2]

(iii) Describe what would be **observed** if a small volume of silver nitrate solution was added to an excess of aqueous sodium cyanide, followed by shaking the mixture.

....

.... [2]

(b) Silver nitrate solutions used in analysis are usually prepared in very dilute acid solution.

(i) Suggest why silver nitrate is **not** prepared in an alkaline solution.

....

.... [1]

(ii) Cyanide ions are normally used in alkaline conditions. Suggest why **acidification** of cyanide ions must be carried out with great care.

....

....

.... [2]

(c) The concentration of cyanide ions in solution can be determined by titration against silver nitrate solution, $AgNO_3(aq)$. Initially $Ag(CN)_2^-(aq)$ is formed until silver ions are in excess, when a white precipitate of $Ag[Ag(CN)_2]$ forms. The appearance of this white precipitate indicates the end-point.

(i) What is the ratio of the number of moles of silver ions needed to reach the end-point to the initial number of moles of cyanide ions present in solution?

Ag^+ **:** CN^- = ... **:** .... [1]

(ii) It is advantageous to carry out the titration in the presence of aqueous ammonia and aqueous iodide ions.

$Ag[Ag(CN)_2]$ dissolves in ammonia, producing soluble $Ag(NH_3)_2^+$ ions. In the presence of aqueous iodide ions, insoluble AgI(s) forms as a precipitate.

The volume of silver nitrate required in the titration is **not** affected, but the end-point precipitate is more distinctive.

What colour is the precipitate at the end-point when aqueous ammonia and iodide ions are present?

.... [1]

(iii) Which fact in the Qualitative Analysis Notes in the *Data Booklet* predicts the production of the precipitate in this titration?

.... [1]

(d) A sample bottle contains 1.00 g of a solid. This solid is thought to contain about 25% cyanide ions by mass. The solid is soluble in water.

You will be asked to plan a titration experiment to determine the exact mass of cyanide ions present in the sample.

Standard laboratory glassware and the following chemicals are available.

0.0500 mol dm^{-3} aqueous silver nitrate
0.2 mol dm^{-3} aqueous sodium iodide
2 mol dm^{-3} aqueous ammonia
deionised water

(i) Plan a titration experiment that would allow a chemist to make an accurate determination of the percentage by mass of cyanide ions in the given solid.

Your plan should include specific quantities that are supported by calculations.

Your plan should allow for repeat titrations.

There is no need to show how you will calculate the percentage by mass from your titration value.

[12]

Question 6 continues on page 20.

(ii) Assuming the 1.00 g sample analysed using your method contained 26.9% cyanide ions by mass, calculate the volume of silver nitrate expected in one of your titrations.

....

....

....

....

....

....

....

....

.... [4]

[Total: 28]