Cambridge Pre-U

Cambridge International Examinations
Cambridge Pre-U Certificate

CANDIDATE NAME

CENTRE NUMBER

CANDIDATE NUMBER

7970359797

CHEMISTRY (PRINCIPAL) **9791/02**

Paper 2 Part A Written **May/June 2015**

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	
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Total	

The syllabus is approved for use in England, Wales and Northern Ireland as a Cambridge International Level 3 Pre-U Certificate.

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

DC (CW/SW) 90128/5

CAMBRIDGE
International Examinations

1 Many scientists see methane becoming increasingly important as a fuel and as a chemical feedstock. One reason for this is the extraction of methane by fracking.

(a) Methane is combusted to form carbon dioxide when it is used as a fuel. The enthalpy change of combustion can be calculated using enthalpy changes of formation.

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

....

....

....

....[3]

(ii) Use the data below to calculate the standard enthalpy change of combustion of methane.

	$\Delta_f H^{\ominus}$ (298 K) / kJ mol^{-1}
$CH_4(g)$	–74.8
$CO_2(g)$	–393.5
$H_2O(l)$	–285.8

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

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

(b) When methane is being used as a chemical feedstock, it is reacted with steam to form 'synthesis gas'. This is a mixture of carbon monoxide and hydrogen.

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$$

(i) Use the average bond energies given to calculate an approximate value for the enthalpy change of reaction for the forward reaction.

	average bond energy / $kJ\,mol^{-1}$
C–H	435
O–H	464
C≡O	1077
H–H	436

$\Delta_r H^{\ominus}$ = ... $kJ\,mol^{-1}$ [2]

(ii) Explain why a high temperature is required for the industrial production of synthesis gas.

....

....

....

....[2]

(c) Synthesis gas may be converted to a mixture of alkanes and steam using the Fischer-Tropsch process. The alkanes may then be catalytically dehydrogenated to alkenes.

(i) Write a single equation to show the formation of propene from synthesis gas as a result of these two processes taken together.

....[1]

(ii) Tens of millions of tonnes of propene are polymerised annually.

Draw the repeat unit of poly(propene). Show all of the bonds.

[1]

(d) Chemists have recently discovered how to make an alkene directly from methane using sulfur (reported in *Nature Chemistry*, 2013).

(i) Give the formula of a molecule of sulfur in its standard state.

....[1]

(ii) The process occurs at 1000 K, when sulfur exists as S_2(g). With a suitable catalyst a reaction between methane and sulfur takes place, as shown in reaction 1.

reaction 1 $2CH_4(g) + S_2(g) \rightarrow C_2H_4(g) + 2H_2S(g)$

What type of reagent is sulfur in this reaction? Circle the correct option.

acid **base** **oxidising agent** **reducing agent** **catalyst**

[1]

(iii) Use the following information to calculate the enthalpy change of reaction 1.

$CH_4(g) + 2S_2(g) \rightarrow CS_2(g) + 2H_2S(g)$ $\Delta_r H^\ominus = +96\,kJ\,mol^{-1}$

$C_2H_4(g) + 3S_2(g) \rightarrow 2CS_2(g) + 2H_2S(g)$ $\Delta_r H^\ominus = +91\,kJ\,mol^{-1}$

$\Delta_r H^\ominus$ = ... $kJ\,mol^{-1}$ [2]

(iv) Further reaction of hydrocarbons with $S_2(g)$ at 1000 K yields $CS_2(g)$ and $H_2S(g)$.

Suggest the shapes of these molecules.

CS_2 .... H_2S ....[2]

[Total: 17]

2 **(a)** Sodium chloride is an essential part of our diet.

The minimum requirement of sodium ions for a 70 kg adult has been estimated at 0.50 g per day.

(i) Calculate the minimum daily mass of sodium chloride, in g, required by a 70 kg adult, assuming this is the only form of sodium intake.

mass = ... g [1]

(ii) A sample of seawater contains sodium ions at a concentration of 0.50 mol dm^{-3}.

Calculate the volume of seawater, in cm^3, that contains the minimum daily mass of sodium ions.

volume = ... cm^3 [2]

(b) Sodium chloride can be made in the laboratory by the direct combination of sodium and chlorine.

$$2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$$

(i) Calculate the minimum volume at room temperature and pressure, in dm^3, of chlorine required to form exactly 1.5 g of sodium chloride.

Quote your answer to the appropriate number of significant figures.

volume = ... dm^3 [2]

(ii) State the pH of an aqueous solution of sodium chloride.

....[1]

(iii) A chemist prepared sodium chloride from its elements using an insufficient volume of chlorine. At the end of the reaction the solid residue was transferred to a flask of water containing universal indicator solution and shaken.

Predict the colour of the resulting solution and write an equation for any reactions that take place on adding the residue to the water.

colour ....

equation ....[1]

(c) Aluminium chloride can also be prepared directly from its elements. At the end of the reaction with an insufficient volume of chlorine the solid residue was transferred to a flask of water containing universal indicator solution and shaken.

Predict and explain the colour of the resulting solution. Include an equation to support your answer.

colour ....

explanation ....

....

equation ....

[3]

(d) Chlorine and oxygen do not combine directly, but an ion containing a chlorine-oxygen covalent bond results from the reaction between chlorine gas and **cold** sodium hydroxide solution.

(i) Write an equation for this reaction and name the ion that contains the chlorine-oxygen bond.

equation ....

name of ion ....

[2]

(ii) The reaction between chlorine(I) oxide and water produces a single product.

Suggest the equation for the reaction.

....[1]

[Total: 13]

3 Fluorine chemistry is important in the separation of uranium isotopes.

(a) A sample of uranium, atomic number 92, was analysed and gave the following information.

uranium isotope	% natural abundance
^{235}U	0.7
^{238}U	99.3

(i) In the table below, show the number of protons, neutrons and electrons in an atom of ^{235}U.

protons	neutrons	electrons

[1]

(ii) Define the term *relative atomic mass*.

....

....

....[2]

(iii) Calculate the relative atomic mass of the uranium in this sample. Give your answer to **one** decimal place.

relative atomic mass = ...[2]

(b) Uranium hexafluoride is used to separate different isotopes of uranium.

(i) Give the full electronic configuration for an isolated fluorine atom.

....[1]

(ii) Uranium is reacted with fluorine to make its hexafluoride, UF_6.
UF_6 is molecular and octahedral; the U–F bond is polar.
Despite having 146 electrons, UF_6 sublimes at only 57 °C.

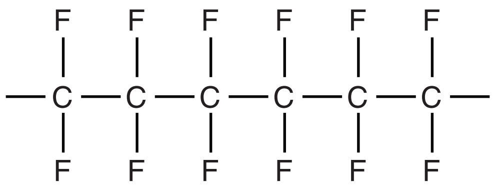
Suggest why the intermolecular forces between UF_6 molecules are so weak.

....

....

....[1]

(iii) UF_6 is highly corrosive and attacks any grease in the isotope-separation apparatus. In place of grease, a newly developed fluorinated polymer was used in the first isotope-separation plants in the 1940s. Part of the structure of this polymer is given.



Draw the monomer for this polymer.

[1]

(c) In some respects the behaviour of fluorine follows a general trend in the halogen group; in other respects it does not.

(i) Suggest an example of a fluorine-containing diatomic molecule that has a boiling point which

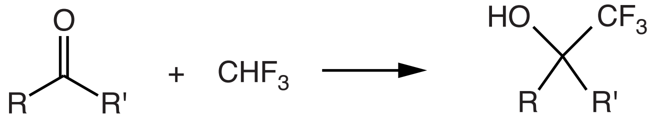
- follows the halogen group trend, ...
- does not follow the halogen group trend. ....[2]

(ii) Give an example of a covalent bond involving fluorine that has a bond strength which

- follows the halogen group trend, ...
- does not follow the halogen group trend. ....[2]

(d) Trifluoromethane, CHF_3, is an unwanted by-product from the chemical industry and a potent greenhouse gas. Recently, chemists have developed methods for converting it into a trifluoromethylating agent (reported in *Science*, 2012).

One of the new methods can be summarised as follows. R and R' represent an alkyl group or a hydrogen atom.



(i) State what type of reaction this is.

....[1]

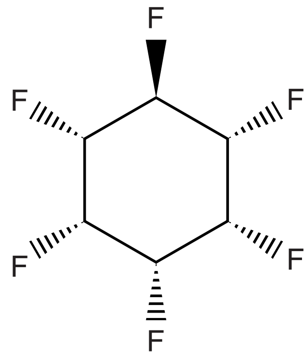
(ii) Identify the molecule that reacts with trifluoromethane to form 1,1,1-trifluorohexan-2-ol.

....[1]

(e) Recent progress has been made by British chemists in the synthesis of isomers of 1,2,3,4,5,6-hexafluorocyclohexane (reported in *Angewandte Chemie International Edition*, 2012).

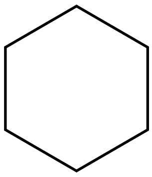
Each fluorine atom may be considered to be pointing in an upwards or downwards direction relative to the ring.

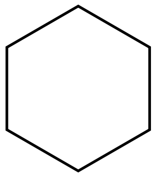
There is only one isomer, shown below, for which a single fluorine atom is pointing in the opposite direction to the other five, due to the symmetry of the molecule.

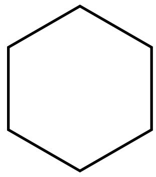


(i) Draw the three isomers of 1,2,3,4,5,6-hexafluorocyclohexane with **two** of the fluorine atoms pointing in the opposite direction to the other four.

Add hashed or wedged bonds to connect the fluorine atoms to the ring.





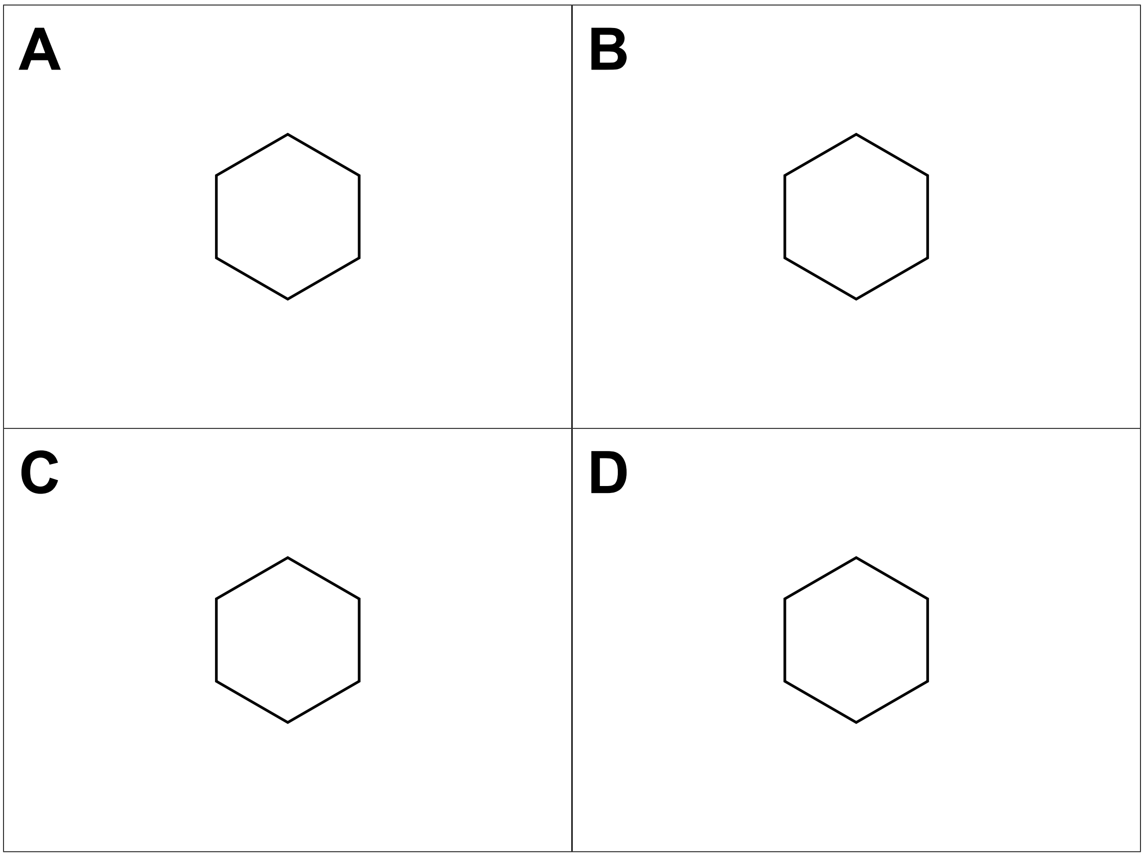


[2]

(ii) Draw the four isomers of 1,2,3,4,5,6-hexafluorocyclohexane with **three** of the fluorine atoms pointing in the opposite direction to the other three.

Add hashed or wedged bonds to connect the fluorine atoms to the ring.

Two of the isomers are enantiomers. Using the capital-letter labels, indicate below which two they are.



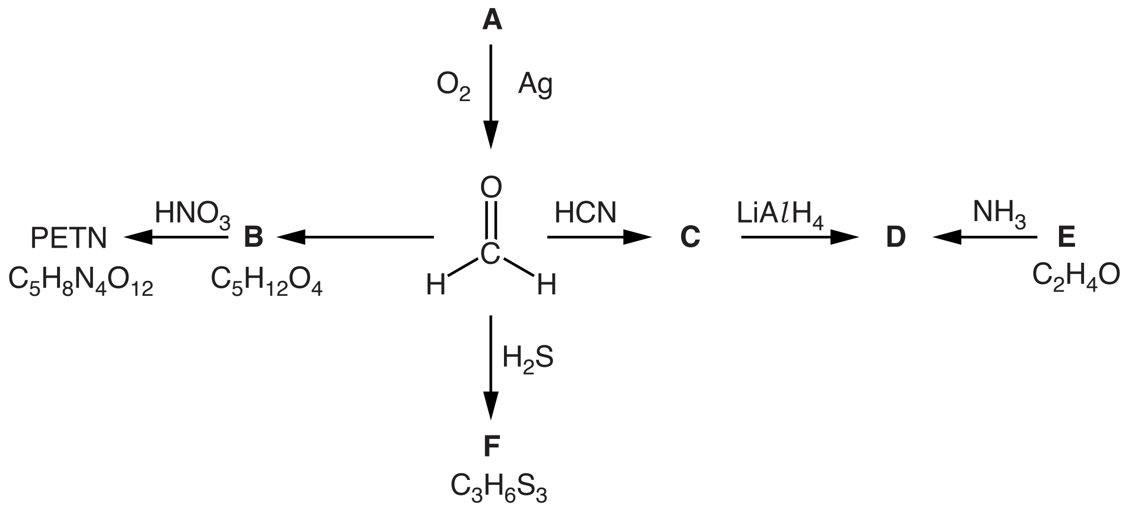
The enantiomers are .... and .... [4]

(iii) Deduce the total number of isomers of 1,2,3,4,5,6-hexafluorocyclohexane.

....[1]

[Total: 21]

4 Millions of tonnes of methanal are produced each year for use as a chemical feedstock. The reaction scheme below shows some reactions based on methanal.



(a) **(i)** Name the functional group level of the carbon atom in methanal.

....[1]

(ii) Suggest the identity of compound **A**.

....[1]

(b) **(i)** Draw the structure of compound **C**.

[1]

(ii) $LiAlH_4$, a source of H^- ions, is a powerful reducing agent.

Draw the structure of compound **D**.

[1]

(c) **(i)** The carbon-13 NMR spectrum of compound **E** contains just one peak.

Draw the structure of **E**.

[1]

(ii) Compound **D** reacts with an excess of **E** to form firstly $C_4H_{11}NO_2$ and subsequently $C_6H_{15}NO_3$. These two additional products, like compound **D**, have just two signals in their carbon-13 NMR spectrum.

Draw the structure of $C_6H_{15}NO_3$.

[1]

(d) Compound **B** is produced from methanal in a series of complex reactions.

Use the following information about compound **B** to deduce its structure.

- It has just two peaks in its carbon-13 NMR spectrum.
- It effervesces when sodium is added.
- It dissolves in water to give a solution with pH 7.

Draw the structure of **B**, $C_5H_{12}O_4$.

[1]

(e) PETN is one of the most powerful high explosives known. It is prepared by adding concentrated nitric acid to compound **B**.

(i) Concentrated nitric acid is used to make many explosives, as it introduces nitro groups, $-NO_2$, into molecules.

Use this information to suggest the structure of PETN, $C_5H_8N_4O_{12}$.

[1]

(ii) Suggest the identity of the other product formed when concentrated nitric acid reacts with **B**.

....[1]

(f) Compound **F**, $C_3H_6S_3$, has only one carbon environment, one hydrogen environment and one sulfur environment.

(i) Write an equation for the reaction between methanal and hydrogen sulfide.

....[1]

(ii) Suggest the structure of compound **F**.

[1]

(g) Devise a series of reactions that will convert methanal to propanal, in which bromoethane is the only other organic reagent. Your scheme should include the formation of a Grignard reagent.

Include equations for the reactions taking place.

Suggest suitable reagents and any essential experimental details.

....

....

....

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....

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....

....

....[7]

[Total: 18]

5 The Fischer titration is used to determine the concentration of water in a non-aqueous solvent.

The Fischer reagent is a methanolic solution of iodine, sulfur dioxide and pyridine (abbreviated as Py). Methanol acts as a reactant as well as being the solvent.

The equations for the reactions that occur in a Fischer titration are shown.

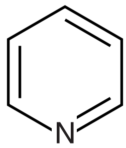
equation 1 $CH_3OH + SO_2 + I_2 + H_2O \rightleftharpoons 2HI + CH_3OSO_3H$

equation 2 $Py + HI \rightarrow PyH^+I^-$

equation 3 $Py + CH_3OSO_3H \rightarrow PyH^+CH_3OSO_3^-$

The Fischer reagent is dark red. In the titration it is added to the non-aqueous solvent containing an unknown quantity of water. The water decolourises the Fischer reagent. The end-point of the titration is when the solution turns pale yellow.

(a) (i) Pyridine is a colourless liquid and has the structure shown.



Give the molecular formula of pyridine.

....[1]

(ii) Draw the structure of CH_3OSO_3H, showing all the bonds.

[1]

(b) (i) How many moles of pyridine react for each mole of water present?

....[1]

(ii) State what type of reaction occurs when pyridine reacts with HI.

....[1]

(iii) Why is the solution pale yellow at the end-point?

....

....[1]

(iv) Explain why it is necessary to add pyridine to the reaction mixture.

....

....[1]

(c) A redox process is involved in equation 1.

State which atoms change oxidation number (ox. no.) and give the oxidation number for each, before and after the redox reaction.

atom being oxidised .... initial ox. no. .... final ox. no. ....

atom being reduced .... initial ox. no. .... final ox. no. .... [3]

(d) A student wanted to determine the value of *x* in hydrated sodium tartrate, $Na_2C_4H_4O_6.xH_2O$, using a Fischer reagent. The materials the student is provided with are shown in the table.

substance	**hazard**
iodine crystals	moderate hazard and hazardous to the aquatic environment
liquid pyridine with a molar volume of 80 cm^3 per mole	highly flammable and moderate hazard
dry methanol,	methanol is acutely toxic and highly flammable (methanol is hygroscopic – absorbs water from the air)
with a sufficiently high concentration of sulfur dioxide dissolved into it	SO_2 is acutely toxic

(i) Describe how the student would make a solution of Fischer reagent that has an iodine concentration of 50.0 $g\,dm^{-3}$. The solution should be prepared in a 250 cm^3 volumetric flask.

In your answer include relevant calculations and details of the apparatus needed. State any safety precautions the student would need to take.

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....

....

.... [8]

(ii) After making the Fischer reagent, the student was left with some unused iodine crystals and methanol solvent. The iodine has to be reacted with another reagent before disposal.

Identify this reagent and suggest how the methanol can be disposed of.

reagent to react with iodine ....

disposal of methanol ....

....

....[2]

(iii) The student made up a 250.0 cm³ solution containing 2.344 g of $Na_2C_4H_4O_6.xH_2O$ dissolved in methanol. The student labelled this solution **Q**.

Describe how the student would carry out a titration experiment between the Fischer reagent and 25.00 cm³ samples of the solution **Q**.

The Fischer reagent is dark red. The end-point of the titration is when the solution turns pale yellow.

Include details of the apparatus needed.

....

....

....

....

....

....

....

....

....

....

....[5]

(iv) A control experiment had to be carried out. In this control experiment the methanol solvent used to make the solution **Q** was titrated with the Fischer reagent. A 25.00 cm³ sample of the methanol solvent exactly reacted with 2.20 cm³ of Fischer reagent.

Explain why the methanol solvent has become contaminated with water.

....

....[1]

(v) The Fischer reagent that the student made has an iodine concentration of 50.0 g dm^{-3}.

Show that 3.54 mg of water react with 1 cm^3 of the Fischer reagent that the student made.

[2]

(vi) The titration of 25.00 cm^3 of the solution of $Na_2C_4H_4O_6.xH_2O$ in methanol required 12.55 cm^3 of the Fischer reagent.

Determine the value of *x*. You must show your working.

The molar mass of anhydrous sodium tartrate is 194.0 g mol^{-1}.

x = ... [4]

[Total: 31]