Cambridge Pre-U

Cambridge International Examinations
Cambridge Pre-U Certificate

CANDIDATE NAME	
CENTRE NUMBER	
CANDIDATE NUMBER	

1736351697

CHEMISTRY (PRINCIPAL) **9791/02**

Paper 2 Part A Written **May/June 2018**

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, if you do not use appropriate units or if you do not give your answer to appropriate significant figures.
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	

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

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

CAMBRIDGE International Examinations

1 This question is about atomic structure.

(a) (i) What is the relationship between the principal shell number, *n*, and the number of subshells within the principal shell?

.....[1]

(ii) Explain why, in a multi-electron atom, the 2p subshell has higher energy than the 2s subshell.

.....

.....[1]

(iii) The angular wavefunction describes the shapes of orbitals.

Draw the approximate shape of an s orbital and of a p orbital.

s orbital p orbital

[2]

(iv) Give the order, in increasing energy, of the subshells in the fourth principal shell.

.....[1]

(b) (i) What is the difference between two electrons in the same orbital?

.....[1]

(ii) Use electron-in-box notation to show the most stable arrangement of electrons in the p^4 configuration.

[1]

(c) Complete the electronic configuration of a Cu^{2+} ion.

Cu^{2+} $1s^2$ ..... [1]

(d) (i) The electronic emission spectrum of sodium is dominated by a characteristic yellow line. This transition corresponds to the movement of an electron from its first excited state to its ground state.

The electron moves between subshells during this emission. State the subshells involved in this electron movement.

from subshell ..... to subshell ..... [1]

(ii) The yellow light in the emission spectrum of sodium has a wavelength of 589 nm (1 nm = 10^{-9} m). Use a suitable equation from the *Data Booklet* to calculate the energy change of this transition in kJ mol^{-1}.

Frequency, f, wavelength, λ, and the speed of light, c, are related by the equation $c = f\lambda$.

energy change = ... kJ mol^{-1} [3]

(e) The emission spectrum of hydrogen atoms, like all atoms, is caused by the movement of one electron during a transition.

(i) What is different about the relative energies of the subshells within each shell of a hydrogen atom compared to other atoms?

.....

.....[1]

(ii) State the effect this has on the emission spectrum of hydrogen compared to the emission spectra of other atoms.

.....

.....[1]

[Total: 14]

2 Some properties of SCl_2, S_2Cl_2, S_8 and Cl_2 are shown in the table.

property	SCl_2	S_2Cl_2	S_8	Cl_2
density / g cm^{-3}	1.62	1.69	2.07	0.00290
melting point / °C	–78	–80	115	–102
boiling point / °C	decomposes at 59	137	445	–34
$\Delta_f H^{\ominus}$ (298 K) / kJ mol^{-1}	–49.8	–59.4		

(a) SCl_2 and S_2Cl_2 can both be made by direct combination of sulfur, S_8, and chlorine gas, Cl_2.

(i) Write the equation that represents the standard enthalpy change of formation of S_2Cl_2 at 298 K. Include state symbols.

.....[2]

(ii) A chemist wishes to prepare 10.0 cm^3 of S_2Cl_2 from its elements. Use the data in the table to calculate the mass of sulfur required to produce this volume of S_2Cl_2.

Give your answer to 3 significant figures.

mass of sulfur = ... g [3]

(iii) Preparation of S_2Cl_2 from its elements may result in an equilibrium mixture containing SCl_2 as well as sulfur and chlorine.

Name the technique most suitable for separating pure S_2Cl_2 from the reaction mixture.

.....[1]

(b) S_2Cl_2 can also be formed when SCl_2 decomposes.

$$2SCl_2 \rightarrow S_2Cl_2 + Cl_2$$

Use data in the table to calculate the standard enthalpy change, $\Delta_r H^{\ominus}$ (298 K), for this reaction.

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

(c) **(i)** S_2Cl_2 undergoes hydrolysis with water.

$$S_2Cl_2 + 2H_2O \rightarrow SO_2 + H_2S + 2HCl$$

State and explain the type of redox reaction taking place.

type of redox reaction .....

explanation .....

.....

[2]

(ii) The SO_2 and H_2S formed in the hydrolysis of S_2Cl_2 react to form S_8.

Write an equation for this reaction.

.....[2]

(d) Predict and explain the Cl–S–S bond angle in Cl–S–S–Cl.

bond angle .....

explanation .....

.....

.....

[3]

(e) The presence of sulfur chlorides can be confirmed by mass spectrometry.

(i) Chlorine-containing compounds are particularly well suited to identification by mass spectrometry because of chlorine's isotopic signature.

What is chlorine's isotopic signature?

.....

.....[1]

(ii) The mass spectrum of S_2Cl_2 shows signals at m/z = 134, 136 and 138 (to the nearest whole number). Identify the species responsible for the signals at m/z = 136 and 138.

m/z = 136 ..... m/z = 138 ..... [2]

(iii) The mass spectrum of S_xCl_y shows signals at m/z = 198, 200 and 202 (to the nearest whole number).

Write the formula of S_xCl_y. Suggest its structure, showing all of the bonds.

formula .....

structure

[2]

[Total: 20]

3 Chloramine, NH_2Cl, is now often used instead of chlorine in the disinfection of water.

The main advantage of chloramine over chlorine is that it is less likely to form chloroalkanes such as trichloromethane, $CHCl_3$, in polluted water.

(a) $CHCl_3$ is a carcinogen. It can be safely destroyed by hydrolysis.

(i) Name the functional group level of the carbon atom in $CHCl_3$.

..... [1]

(ii) Predict the organic product of the complete hydrolysis of $CHCl_3$ under acidic conditions.

..... [1]

(iii) Suggest the equation for the complete hydrolysis of $CHCl_3$ using aqueous sodium hydroxide.

.....[2]

(b) Chloramine is prepared by adding aqueous ammonia to aqueous chlorine.

$$Cl_2(aq) + NH_3(aq) \rightarrow NH_2Cl(aq) + HCl(aq)$$

(i) Draw the 3D structure of the ammonia molecule and name its shape.

structure

shape ..... [2]

(ii) Chlorine and ammonia both dissolve in water.

- Suggest the pH of the solution formed when ammonia dissolves in water.
- Write the equation for the reaction of ammonia with water.
- Write the equation for the reaction of chlorine with water.

pH of $NH_3(aq)$ .....

ammonia equation .....

chlorine equation .....
[4]

(iii) The rate of reaction between aqueous ammonia and aqueous chlorine is pH-dependent. Suggest why this reaction is relatively slow in acidic conditions.

.....

.....[1]

(c) **(i)** State the intermolecular forces between:

- H_2O molecules in water
- CCl_4 molecules in tetrachloromethane.

H_2O .....

CCl_4 .....
[2]

(ii) Suggest why NH_2Cl is more soluble in water than it is in tetrachloromethane.

.....

.....[1]

(d) Chlorine can react with chloramine to form nitrogen trichloride, NCl_3, which is an explosive liquid.

(i) Suggest an equation for the reaction between chlorine and chloramine to form nitrogen trichloride.

.....[1]

(ii) Nitrogen trichloride decomposes to form gaseous products.

$$2NCl_3(l) \longrightarrow N_2(g) + 3Cl_2(g)$$

Calculate the volume of gas, in cm^3, produced at r.t.p. when 1.00 g of nitrogen trichloride decomposes.

volume of gas = ... cm^3 [3]

(e) When NH_2Cl reacts with NH_3 it forms compound **A** with an acidic by-product, **B**. Compound **A** contains 87.5% nitrogen and 12.5% hydrogen by mass.

Calculate the empirical formula of **A** and suggest its structure. Suggest the formula of **B**.

empirical formula of **A** .....

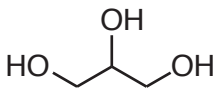
formula of **B** .....

structure of **A**

[3]

[Total: 21]

4 The modern production of biodiesel from natural fats and oils generates a large amount of glycerol as a by-product. The systematic name of glycerol is propane-1,2,3-triol. Efforts are being made to use glycerol as a chemical feedstock.



glycerol

(a) (i) What is the molecular formula of glycerol?

..... [1]

(ii) When glycerol is heated to 280 °C it decomposes into acrolein, which gives burnt fat its acrid smell.

Acrolein:

- has three carbon atoms
- decolourises bromine water
- gives a silver mirror when warmed with Tollens' reagent.

Suggest the structure for acrolein and state its systematic name.

systematic name ..... [3]

(iii) Glycerol can be dichlorinated with hydrogen chloride. **Two** of the OH groups are substituted by C*l*.

Draw the structures and state the systematic names of all the possible dichlorinated products from this reaction. Ignore any stereoisomers.

[3]

(iv) The dichlorinated products from **(iii)** eliminate HC*l* when treated with aqueous sodium hydroxide to form the same molecule, **C**.

C contains a three-membered ring and has the formula C_3H_5OCl. Suggest its structure.

[1]

(v) A more efficient way to produce the dichlorinated products in **(iii)** is from the reaction between chloric(I) acid, HOC*l*, and 3-chloropropene C_3H_5Cl.

By considering the molecular formulae of the reactants and products, deduce what type of reaction takes place.

.....[1]

(b) 3-chloropropene, C_3H_5Cl, can be made by reacting propen-3-ol with phosphorus trichloride.

Write an equation for this reaction using **molecular** formulae.

.....[2]

(c) 3-chloropropene reacts with ethanolic ammonia to produce 3-aminopropene.

(i) Suggest why ethanol is a good choice of solvent and why water would be a poor choice of solvent for this reaction.

.....

.....

.....[2]

(ii) The 3-aminopropene produced in this reaction may react with unreacted 3-chloropropene to form a secondary amine.

Suggest the structure of this secondary amine.

[1]

(iii) Suggest one practical way to maximise the yield of 3-aminopropene over the secondary amine in the reaction between 3-chloropropene and ethanolic ammonia.

Explain your answer.

.....

.....

.....[2]

(d) 3-aminopropene can undergo addition polymerisation to form poly(3-aminopropene).

Use the displayed formula of the repeat unit of poly(3-aminopropene) to show the structure of the polymer.

[2]

[Total: 18]

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5 Mass spectrometry can distinguish natural variations in isotopic ratios. Samples of elements from different sites may have different relative atomic masses.

(a) (i) Complete the table to show the number of protons, neutrons and electrons in a $^{13}C^{+}$ ion.

	number of protons	number of neutrons	number of electrons
$^{13}C^{+}$			

[1]

(ii) Define *relative atomic mass*.

.....

.....

.....[2]

(iii) Accurate mass spectrometry data give the following information about carbon isotopes from Pee Dee Belemnite, PDB, a marine fossil.

isotope	relative isotopic mass	percentage abundance
carbon-12	12.000000	98.88877
carbon-13	13.003355	1.11123
carbon-14	14.003241	negligible

Calculate the relative atomic mass of carbon in PDB. Give your answer to 5 decimal places.

relative atomic mass = ... [2]

(b) In time-of-flight mass spectrometry, an ion of mass m and charge z travels along a tube to a detector. In a given spectrometer, the square of the time t to pass along the tube is proportional to m/z:

$$t^2 \propto \frac{m}{z}$$

A mass spectrum can be complicated by a molecular ion having a 2+ charge.

(i) The molecular ion of methane, CH_4^+, has an m/z value of 16 (to the nearest whole number). What is the m/z value of its 2+ molecular ion, CH_4^{2+}?

..... [1]

(ii) In a particular mass spectrometer, the CH_4^+ molecular ion takes a time of 3.5×10^{-6} s to pass along the tube.

What is the time taken for the CH_4^{2+} molecular ion to pass along the tube?

time = ... s [1]

(c) All carbon-containing substances have a particular $^{13}C/^{12}C$ ratio. It is quoted as a δ value comparing it to Pee Dee Belemnite, PDB, in parts per thousand.

$$\delta = \left(\frac{\left(\frac{^{13}C}{^{12}C}\right)_{sample}}{\left(\frac{^{13}C}{^{12}C}\right)_{PDB}} - 1 \right) \times 1000$$

(i) The δ values for most other carbon-containing materials are negative.

Suggest and explain how the proportion of ^{13}C in PDB compares to most other carbon-containing materials.

.....

.....[1]

(ii) Synthetic testosterone is a performance-enhancing drug produced from plants. It can only be distinguished from natural testosterone by its δ value. The δ value for synthetic testosterone is between –24 and –33. The δ values found for natural testosterone are less negative.

The testosterone from an athlete was analysed. The proportion of ^{13}C carbon atoms in the athlete's testosterone was 1.10000%.

The $^{13}C/^{12}C$ ratio in PDB is 0.011237.

Calculate the δ value for the athlete's testosterone and state whether or not the athlete used synthetic testosterone.

δ .....

.....[2]

[Total: 10]

6 Arsenic in ground water is a public health issue in many countries around the world. A method for determining the concentration of arsenic in ground water is given.

step 1 Measure out a known mass of hydrated sodium thiosulfate.
step 2 Make a standard solution of sodium thiosulfate from this solid.
step 3 Transfer a 100.0 cm^3 sample of the arsenic-containing water into a large conical flask. This is solution **X**.
step 4 Add concentrated HC*l*(aq) to solution **X** to make solution **Y**.
step 5 Add $NaHCO_3$ and then excess KI to solution **Y**, and leave to stand for 5 minutes to make solution **Z**.
step 6 Titrate the iodine produced in solution **Z** with the standard solution of sodium thiosulfate.

(a) When solution **X** is strongly acidified in step 4, the dissolved arsenic is converted to arsenic acid, H_3AsO_4. Arsenic acid is a tribasic acid.

Give the oxidation number of arsenic in H_3AsO_4 and suggest its structure. Show all of the bonds.

oxidation number .....

structure

[2]

(b) A standard solution of sodium thiosulfate of concentration 1.00×10^{-3} mol dm^{-3} is prepared in a 500 cm^3 volumetric flask.

(i) Calculate the required mass of hydrated sodium thiosulfate to be measured out in step 1. Assume the hydrated sodium thiosulfate has a molar mass of 248 g mol^{-1}.

Give your answer to 3 decimal places.

mass = ... g [1]

(ii) Describe how you would carry out step 2 to prepare the standard solution of sodium thiosulfate.

.....

.....

.....

.....

.....[4]

(c) 100.0 cm^3 of the arsenic-containing water is transferred to a large conical flask (step 3) for the titration. This is solution **X**.

The concentration of HCl(aq) in solution **Y** needs to be 4.0 mol dm^{-3}.

What volume, in cm^3, of 11.65 mol dm^{-3} concentrated hydrochloric acid must be added to solution **X** in step 4 to make the concentration of HCl 4.0 mol dm^{-3} in solution **Y**?

volume = ... cm^3 [1]

(d) The equilibrium shown occurs in solution **Z**.

$$H_3AsO_4 + 2H^+ + 2I^- \rightleftharpoons H_3AsO_3 + I_2 + H_2O$$

(i) Suggest why solution **Z** must contain a large excess of hydrochloric acid.

.....

.....[1]

(ii) Before the KI is added in step 5, a small quantity of sodium hydrogencarbonate, $NaHCO_3$, is added.

The $NaHCO_3$ reacts with some of the hydrochloric acid, producing carbon dioxide which displaces air from the flask.

Suggest the reason for displacing air from the flask.

.....

.....

.....[1]

(iii) The concentration of H_3AsO_4 is determined by titration of the iodine present in solution **Z**.

Why is the mixture in step 5 left to stand for 5 minutes?

.....

.....[1]

(e) The concentration of iodine in solution **Z** is determined by titration with sodium thiosulfate in step 6 using a suitable indicator.

(i) Write the equation for the reaction of iodine with sodium thiosulfate.

.....[1]

(ii) Name a suitable indicator for this titration and state the colour change seen at the end-point.

indicator .....

colour change from ..... to ..... [2]

(iii) It has been suggested that a sample of water near a mine has an arsenic concentration of 6.65×10^{-5} mol dm^{-3}.

Calculate the volume in cm^3 of sodium thiosulfate solution required if the concentration of arsenic in the 100 cm^3 sample of ground water is 6.65×10^{-5} mol dm^{-3}.

volume = ... cm^3 [3]

[Total: 17]

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