

CANDIDATE NAME	CT GROUP	17S
CENTRE NUMBER	INDEX NUMBER	
CHEMISTRY		9729/03

18 September 2018

2 hours

Paper 3 Free Response

Candidates answer on separate paper. Additional Materials: Answer Paper

Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, CT group, centre number and index number clearly in the spaces above.

Write in dark blue or black pen.

You may use a HB pencil for any diagrams or graphs.

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

Section A

Answer all questions.

Section B

Answer one question.

Begin each question on a <u>new</u> sheet of writing paper.

A Data Booklet is provided.

The use of an approved scientific calculator is expected, where appropriate.

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.

<u>Circle</u> the question number for the question that you have attempted for Section B on the cover page provided.

Section A

Answer **all** the questions in this section.

1 (a) Aluminium is a major component used in the manufacture of various parts of airplanes.

With the aid of a labelled diagram, describe the structure and bonding in aluminium. [3]

(b) Pure aluminium is too soft to be used directly for aircraft applications. An alloy of aluminium is used instead to improve its tensile strength and corrosion resistance. One such alloy is aluminium bronze, which contains aluminium, copper and iron.

To determine the percentage by mass of copper in the alloy, an experiment is performed with the following procedure:

- step 1: Concentrated HNO_3 is added to a 1.20 g sample of the alloy. The mixture is then heated until all the solid dissolves. The resulting solution, which contains Cu^{2+} , Fe^{2+} and Al^{3+} ions, is cooled and diluted.
- step 2: $H_2O_2(aq)$ is added dropwise until no further change is observed.
- step 3: Excess concentrated NH_3 is added to the solution. The resulting mixture is filtered and a dark blue solution is obtained as filtrate.
- step 4: HNO₃(aq) is added to the filtrate until no more traces of precipitate is observed in the solution.
- step 5: Excess KI(aq) is added to the resulting solution. The reaction produces brown iodine and a white precipitate of copper(I) iodide, CuI.

$$2Cu^{2+}(aq) + 4I^{-}(aq) \rightarrow I_2(aq) + 2CuI(s)$$

A filtration is performed again, and the filtrate is made up to 250 cm³ in a volumetric flask.

step 6: 25.0 cm³ of this solution is titrated with aqueous sodium thiosulfate, $Na_2S_2O_3(aq)$, in the presence of starch indicator.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^{-}(aq) + S_4O_6^{2-}(aq)$$

[1]

- (i) State the chemical role of $H_2O_2(aq)$ in step 2.
- (ii) It is found that 17.50 cm³ of 0.100 mol dm⁻³ Na₂S₂O₃(aq) is required for complete reaction in step 6.

Calculate the percentage by mass of copper in the alloy. [3]

(iii) Suggest how the volume of Na₂S₂O₃(aq) needed in step 6 would be affected if step 3 was not carried out in the procedure. Explain your answer. [2]

- (c) When an airplane flies at very high altitude, the atmospheric pressure outside the airplane becomes very low. For the comfort of passengers, the airplane cabin is typically pressurised to 81.0 kPa and the temperature is maintained at 23.0 C at cruising altitude.
 - (i) A passenger brought a balloon filled with 1500 cm³ of carbon dioxide gas on board the airplane at sea level, which has an atmospheric pressure of 101 kPa, and a temperature of 30.0 C.

Assuming that carbon dioxide gas behaves ideally, calculate the final volume of the balloon when the airplane is at cruising altitude. [1]

- (ii) Would the actual volume of the balloon at cruising altitude be larger or smaller than the volume you calculated in (c)(i)? Justify your answer. [1]
- (d) Swift Enterprises, a chemical company, has proposed 2-methylbutane as a fuel for light airplanes. Its structure is shown in Fig. 1.1.



Fig. 1.1

2-methylbutane can react with chlorine in the presence of UV light to give substitution products. The following table shows the relative reactivity of different types of hydrogen for this reaction.

types of hydrogen	relative reactivity
primary	1
secondary	3.5
tertiary	5

- (i) Draw the structures of all the monochlorinated products for 2-methylbutane (ignoring stereoisomers), and give the relative proportions of all the products obtained using the data in Table 1.1.
 [3]
- (ii) With an appropriate sketch of the Boltzmann distribution, explain how an increase in temperature affects the rate of reaction between 2-methylbutane and chlorine.
- (iii) The monochlorinated products serve as raw materials in the manufacture of chlorofluoroalkanes (CFCs), which have been banned in a number of countries due to their effect on the ozone layer in the upper atmosphere.

Explain how CFCs destroy ozone.

[1]

[Total: 18]

2 Olympicene, first synthesised to celebrate the 2012 London Olympics, is made up of five rings like the Olympic logo.

The scheme in Fig. 2.1 shows a synthesis of olympicene.

(a) In stage I, A is formed from 1-pyrenecarboxaldehyde via a Wittig reaction. In a Wittig reaction, an aldehyde or ketone reacts with a triphenyl phosphonium ylide to give an alkene and triphenylphosphine oxide, as shown in Fig. 2.2.



- (i) Suggest a reason why Wittig reaction is useful in organic synthesis. [1]
- (ii) By considering the structure of **A**, suggest the structure of the triphenyl phosphonium ylide used in stage I. [1]
- (b) State the *types of reaction* that occur during each of the three steps in stage II. [3]
- (c) The formation of C from B in stage III follows a three-step mechanism:

- 1. Cl on **B** is first abstracted by $AlCl_3$ catalyst to form a carbocation and $[AlCl_4]^-$.
- 2. Electrons from a neighbouring π bond attack the carbocation to form a second carbocation which has five rings.
- 3. [A/Cl₄]⁻ deprotonates the second carbocation, producing **C** and a by-product, and regenerating the catalyst.

Outline this mechanism, showing clearly any intermediates that are formed and use curly arrows to indicate the movement of electron pairs. You may represent **B** as shown below.



[3]

- (d) Draw the structure of the organic product formed when **C** reacts with 2,4-dinitrophenylhydrazine and state the *type of reaction* that occurs. [2]
- (e) Suggest a 2-step synthesis of **D** from **C** in stage IV.

You should state the reagents and conditions needed for each step, and show clearly the structure of the intermediate compound. [3]

- (f) State the isomeric relationship between **D** and olympicene. [1]
- (g) (i) Deduce whether olympicene is a planar molecule. [1]
 - (ii) State the number of π electrons in one molecule of olympicene. [1]
 - (iii) Explain why olympicene has a higher boiling point than benzene. [2]
- (h) Under suitable conditions, olympicene can also be formed from E, along with another by-product, F.



State the type of reaction shown above.

[1]

[Total: 19]

3 (a) Magnesium oxide, MgO, can be obtained from sea water which contains significant amounts of Mg²⁺ and Ca²⁺ ions. The steps involved are shown in Fig. 3.1.





The numerical values of the relevant solubility products are given below.

Table 3.1

compound	solubility product
MgCO ₃	1.0 × 10 ^{−5}
CaCO ₃	8.7 × 10 ⁻⁹
Mg(OH) ₂	1.1 × 10 ^{−11}
Ca(OH) ₂	5.5 × 10 ⁻⁶

- (i) Calculate the solubility of $MgCO_3$ and $Mg(OH)_2$ respectively in mol dm⁻³. [2]
- (ii) If the concentration of Mg^{2+} ions in the filtrate is 3.0×10^{-5} mol dm⁻³, calculate the concentration of OH^- ions present in the filtrate when the first trace of solid $Mg(OH)_2$ appears. [1]
- (iii) Explain why CO₃²⁻ ions is added to the sea water before the addition of OH⁻ ions, and why this must be controlled.
 [2]
- (iv) With the aid of an equation, suggest how Mg(OH)₂ can be converted to MgO in the final step in Fig. 3.1.
- **(b)** Magnesium and aluminium are period 3 elements with different physical and chemical properties.
 - (i) With the aid of electronic configurations, explain why the first ionisation energy of aluminium is lower than that of magnesium. [2]
 - (ii) Both magnesium and aluminium react with chlorine to form their respective chlorides.

Describe and explain the reactions, if any, of each of these chlorides with water, suggesting the pH of the resulting solutions and writing balanced equations where appropriate. [3]

- (c) Calcium metal is produced mainly by the electrolysis of molten calcium chloride at 800 °C.
 - (i) Determine the mass of calcium metal that can be obtained when 200 A of current is passed through an electrolytic cell for 3 hours. [1]

- (ii) Using relevant data from the *Data Booklet*, explain why calcium metal cannot be obtained by the electrolysis of aqueous calcium chloride. [2]
- (d) Compound I can be formed from compound G via a two-step synthesis as shown in Fig. 3.2.



Fig. 3.2

- (i) Suggest the structure of intermediate **H** in this synthesis. [1]
- (ii) Name the mechanism of the reaction in step 2, and suggest the reagents and conditions used in this step. [2]

In step 3, I is heated with aqueous potassium hydroxide and the resulting mixture is then distilled. J is collected as the distillate and K is a salt obtained in the distillation flask.

In step 4, dilute sulfuric acid and potassium manganate(VII) solution is added to **K** and compound **L** is formed.

- (iii) Suggest the structures of compounds J, K and L.
- (iv) Describe one simple chemical test to distinguish compounds J and L.

You should state the reagents and conditions required and how each compound behaves in the test. Write a balanced equation for the reaction involved. [3]

[Total: 23]

[3]

Section B

Answer **one** question from this section.

4 Amino acids are commonly found in coffee and tea.

Theanine is an amino acid found in green tea and is known to produce a calming effect. Glutamic acid can be found in coffee and it helps with neurotransmission in the brain.

The structures of theanine and glutamic acid are shown below.



theanine

glutamic acid



- (a) Compare the basicity of the nitrogen-containing groups –CONH and –NH₂ in theanine.
 Explain your answer. [2]
- (b) There are three pK_a values associated with glutamic acid: 2.19, 4.25 and 9.67.
 - (i) Calculate the pH of 0.100 mol dm^{-3} of glutamic acid in its fully protonated form. [2]
 - (ii) Sketch the titration curve when 10.0 cm³ of the *fully protonated* form of glutamic acid is being titrated with NaOH(aq) of the same concentration, until 40.00 cm³ of NaOH(aq) has been added.
 - (iii) Draw the structures of the major species obtained at the first and second equivalence points of the titration described in (b)(ii). [2]
 - (iv) The isoelectric point is the pH at which there is no net charge on a particular amino acid.

Estimate a value for the isoelectric point of glutamic acid. [1]

- (c) 0.0400 g of NaOH(s) was added to a 100 cm³ portion of 0.100 mol dm⁻³ glutamic acid at pH 4.25.
 - (i) Write an equation to illustrate why the pH of the solution remains relatively unchanged. Show the structure of glutamic acid clearly in your equation. [1]
 - (ii) Calculate the final pH of the solution.

[2]

(d) M is a neutral compound with molecular formula C₁₄H₁₈NOC*l*. When M is heated with aqueous sodium hydroxide, it forms the salt of compound N, as well as compound P. N has molecular formula C₉H₁₀O₃, and it contains a chiral carbon. When heated with a few drops of concentrated sulfuric acid, N forms Q which has molecular formula C₉H₈O₂. When P is heated with acidified potassium manganate(VII), ⁺H₃NCH₂CO₂H and (CH₃)₂CO are obtained.

Deduce the structures of compounds M, N, P and Q. Explain the chemistry of the reactions described. [8]

[Total: 20]

- **5 (a) (i)** State the electronic configuration of the manganese atom. [1]
 - (ii) Explain why manganese can exhibit a number of different oxidation states in its compounds. [1]

- (b) (i) Draw a dot-and-cross diagram to illustrate the bonding in the manganate(VII) oxyanion, MnO₄⁻, showing only the electrons in the outer shells of the atoms involved. [1]
 - (ii) Suggest a value for the bond angle in MnO_4^- . [1]
- (c) Using relevant data from the *Data Booklet*, describe and explain what you would see when acidified potassium manganate(VII), KMnO₄, is added slowly to aqueous potassium iodide. Write a balanced equation for any reaction that occurs. [3]
- (d) The Latimer diagrams for manganese and iodine in alkaline and neutral solutions are given in Fig. 5.1.

In a Latimer diagram, the most highly oxidised form of an element is shown on the left, with successively lower oxidation states to the right. The species are connected by arrows, and the numerical value of the standard electrode potential, in volts, is written above each arrow. For example, $E^{\ominus}(MnO_4^- / Mn(OH)_2) = +0.34$ V.





(i) When potassium iodide reacts with KMnO₄ in an alkaline solution, the MnO₄⁻ oxyanion is reduced to manganese dioxide, MnO₂.

Use the Latimer diagrams in Fig. 5.1 to predict the final oxidation state of iodine in this reaction, explaining how you arrive at your answer. [2]

(ii) In an experiment, it is found that 100 cm³ of 0.020 mol dm⁻³ KMnO₄ is needed to react completely with 10.0 cm³ of 0.10 mol dm⁻³ potassium iodide under alkaline conditions.

Use this result to deduce the final oxidation state of iodine. [1]

- (iii) R is a green compound containing potassium, manganese and oxygen. Aqueous solutions of R are only stable at high pH. At neutral pH, it slowly converts into a purple solution S and a black solid T. State what reaction has occurred and identify R, S and T.
- (e) KMnO₄ is commonly used as an oxidising agent in organic chemistry.

A compound **U** has the molecular formula $C_{10}H_{12}$. When treated with HBr, **U** yields the compound **V** which contains a chiral carbon.

With cold, alkaline KMnO₄, **U** is first oxidised to **W**; warming this mixture then gives **X**, which gives a positive tri-iodomethane test. Both **W** and **X**, on boiling with alkaline KMnO₄ followed by acidification, each gives benzene-1,2-dicarboxylic acid.

- (i) Deduce the structures of **U** to **X**. Explain the chemistry of the reactions described. [6]
- (ii) Explain why the solution containing **V** is optically inactive.

[Total:20]

[2]

END OF PAPER