

CANDIDATE NAME	CT GROUP	18S
CENTRE NUMBER	INDEX NUMBER	
CHEMISTRY		9729/03
Paper 3 Free Response	20 \$	September 2019
		2 hours
Candidates answer on separate answer booklet.		

Additional Materials: 12-Page Answer Booklet

Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, CT group, centre number and index number on all the work you hand in.

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 page of writing paper</u>.

A Data Booklet is provided.

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

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

At the end of the paper, submit only the 12-Page Answer Booklet and any additional booklets you have used.

Section A

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

- **1 (a) (i)** Write an equation for the thermal decomposition of MgCO₃. [1]
 - (ii) Explain how the magnitude of the lattice energy of MgCO₃ differs from that of the solid product formed in (a)(i). [2]
 - (iii) The thermal decomposition of MgCO₃ is an endothermic process. Explain whether the decomposition of MgCO₃ is spontaneous at high or low temperature. [2]
 - (iv) State whether MgCO₃ or BaCO₃ has the lower decomposition temperature. Explain your answer. [3]
 - (b) The Strecker synthesis is a method used to prepare amino acids. Alanine, 2-aminopropanoic acid, can be prepared from ethanal via Strecker synthesis as shown below.

$$\begin{array}{c} O \\ II \\ CH_{3} \end{array} \xrightarrow{C} H \end{array} \xrightarrow{NH_{3}} \begin{array}{c} OH \\ I \\ CH_{3} \end{array} \xrightarrow{L} H \\ H \end{array} \xrightarrow{NH_{2}} \begin{array}{c} OH \\ I \\ CH_{3} \end{array} \xrightarrow{H} \begin{array}{c} HCN \\ I \\ CH_{3} \end{array} \xrightarrow{H} \begin{array}{c} HCN \\ I \\ Step 3 \end{array} \xrightarrow{E} \begin{array}{c} OH \\ I \\ Step 4 \end{array} \xrightarrow{NH_{2}} O \\ I \\ H \end{array} \xrightarrow{NH_{2}} O \\ I \\ OH \end{array}$$

- (i) Suggest the type of reaction occurring in steps 1 and 2. [2]
- (ii) Draw the fully displayed structure of compound E.
- (iii) Suggest why step 3 produces an equimolar mixture of two stereoisomers. [2]
- (iv) Another amino acid, isoleucine, can be prepared from aldehyde F via Strecker synthesis.



Draw the structure of aldehyde F.

[1]

[1]

(c) In the Petasis reaction, carbonyl compounds, amines and suitable boronic acids can react to form substituted amines.

The general structure of a boronic acid is $B(OH)_2R$ where R is an alkyl or aryl group.

An example of the Petasis reaction is given below.



Consider the following Petasis reaction:



- (i) Draw the structure of compound G.
- (ii) The Petasis reaction can be used in step 4 of the following synthesis of compound **K** from butanal.



Suggest reagents and conditions for steps 1 to 4, and the structure of compound **J**. [5]

[Total: 20]

[1]

2 When an onion is cut, the damaged tissues release the lachrymatory factor molecule, LF, that makes eyes water. The diagram below shows how LF is produced in the cut onion, starting from compound P.



(a) In the first step, **P** reacts with a water molecule, in the presence of the enzyme *alliinase*, to give **Q**, **R** and ammonia.

(i`	i) Find the molecular formula of compound R .	[1]
v		[']

(ii) Compound **R** reacts in a 1:1 ratio with PC*l*₅ and gives a yellow precipitate with alkaline aqueous iodine. Draw the structure of compound **R**. [1]

[1]

- (b) State the isomeric relationship between Q and LF.
- (c) LF is very soluble in water. Explain why LF dissolves well in water. [1]
- (d) LF is also volatile. For years, the conversion of Q to LF was thought to be direct, but in 2002, scientists discovered the pathway requires an enzyme *LF synthase*.

Two methods, found on the internet, claim to prevent eyes from watering while cutting onions. Suggest how **each** of these methods could work, considering the volatility of **LF**, and the pathway that produces **LF**.

(i)	"Cool the onion before cutting it."	[1]

- (ii) "Heat the onion before cutting it." [1]
- (e) In 2016, scientists developed "tearless" onions by irradiating seeds with heavy-ion beams to reduce *LF synthase* levels. This mutation causes increased thiosulfinate production from Q via the alternate pathway above.
 - (i) In this alternate pathway, two molecules of Q react to form thiosulfinate, losing a water molecule. Name the type of reaction that occurs.



The percentage of sulfur in an organic compound, such as cepaene, can be determined via the elemental analysis set-up in Fig. 2.1:





The organic sample is first combusted in a gas mixture of 40% O_2 and 60% He, to form CO_2 , H_2O and oxides of sulfur: SO_2 and SO_3 .

The resultant gases then flow over a vessel containing heated copper metal to convert any SO_3 into SO_2 . The heated copper also removes any unreacted O_2 .

 CO_2 , H_2O and SO_2 gases are cooled in a separating tube immersed in liquid nitrogen at -196 °C, and then released one by one, by increasing the temperature, to the detector.

In one analysis, 5.0 mg of cepaene ($C_9H_{16}OS_3$, $M_r = 236.3$) is introduced into the combustion zone.

- (ii) Write an equation for the combustion of cepaene in the combustion zone to form CO_2 , H_2O and SO_3 only. [1]
- (iii) Hence, calculate the minimum volume of the O₂/He gas mixture at r.t.p. (in cm³) required for the combustion of 5.0 mg of cepaene. [2]
- (iv) State the role of the heated copper metal, and hence write an equation to show how the unreacted O₂ is removed by the heated copper. [2]
- (v) If the temperature of the heated copper metal is not high enough or insufficient copper is used, a sulfur-containing compound could be formed in the vessel as blue crystals. Identify the blue crystals and suggest how they may be formed.
- (vi) Predict the sequence in which the three compounds in the separating tube are released to the detector. Explain your answer fully. [3]

[Total: 16]

- **3** Cobalt is a *transition element* that can be found in the blue pigments used for jewellery and paints.
 - (a) Explain what is meant by the term *transition element*. [1]
 - (b) A cobalt-chrome alloy is a metal alloy of cobalt and chromium.

A sample of this alloy was dissolved in dilute HC*l* to form a solution containing 1.23×10^{-2} mol dm⁻³ of Cr³⁺(aq) and 5.77×10^{-3} mol dm⁻³ of Co²⁺(aq).

Aqueous NaOH was then added slowly to 1 cm³ of the solution.

(i) Using the K_{sp} information below, show that the addition of NaOH will **not** allow for the separation of the Cr³⁺ and Co²⁺ metal cation ions in the above solution.

compound	$K_{ m sp}$
Cr(OH) ₃	1.60 × 10 ⁻²⁰
Co(OH) ₂	5.92 × 10 ⁻¹⁵

[3]

(ii) A better way to separate the two aqueous ions is to add excess NaOH into the solution as Cr(OH)₃ dissolves.

With the aid of equations, explain why the precipitate of Cr(OH)₃ dissolves in excess NaOH using *Le Chatelier's Principle*. [3]

- (c) When cobalt(II) chloride is dissolved in water, it forms a pink solution. Upon addition of excess aqueous potassium thiocyanate, KSCN, the solution turns blue.
 - (i) Draw a fully labelled diagram to account for the splitting of the degenerate d orbitals into two energy levels in an octahedral ligand field.

Explain how you arrived at your answer, taking into account the shape and the orientation of the d orbitals. [2]

- (ii) Using your diagram in (c)(i), account for the pink colour of the solution when cobalt(II) chloride is dissolved in water. [2]
- (iii) Identify the type of reaction responsible for the colour change from pink to blue. [1]
- (iv) Different proportions of 0.1 mol dm⁻³ Co²⁺(aq) and 0.2 mol dm⁻³ SCN⁻(aq) were mixed. The intensity of the blue colour of the resultant solution was measured using a colorimeter. The maximum colour intensity was observed when 2 cm³ of SCN⁻(aq) was added to 1 cm³ of Co²⁺(aq). Deduce the identity of the species responsible for the blue solution.

- (d) When cobalt(II) chloride is dissolved in aqueous ammonia, it forms [Co(NH₃)₆]²⁺ which is oxidised by air to the +3 oxidation state.
 - (i) Explain why cobalt shows variable oxidation states as compared to a main group element like calcium. [2]
 - (ii) With the aid of the *Data Booklet* and the information below, calculate the E^{e}_{cell} for the oxidation of $[Co(NH_3)_6]^{2+}$ by atmospheric oxygen.

$$[Co(NH_3)_6]^{3+} + e^- \ll [Co(NH_3)_6]^{2+} \qquad E = +0.17 V$$

[1]

(e) **S** and **T** are ionic compounds which contain six-coordinate cobalt(III) complex ions, whose ligands are either NH_3 or Cl^- .

When excess aqueous AgNO₃ is added to 1 mole of **S** and 1 mole of **T** separately, 2 moles of a white precipitate is formed from **S** while 1 mole of the same white precipitate is formed from **T**.

- (i) Identify the white precipitate and explain why different amounts of the white precipitate are formed from **S** and **T**. [2]
- (ii) Draw the cobalt(III) complex ion in **S**, showing clearly how the ligands are bonded to the central metal ion. [1]
- (iii) The cobalt(III) complex ion in **T** exhibits *cis-trans* isomerism. Suggest the structure of the *trans* isomer. [1]
- (f) Cobalt is used as a heterogeneous catalyst in the synthesis of aldehydes from carbon monoxide and water.

Describe the mode of action of the cobalt catalyst in the reaction. [3]

[Total: 24]

Section B

Answer **one** question from this section.

4 (a) The world's first implantable cardiac pacemaker is powered by zinc and platinum electrodes which are placed directly within the body tissues.

These electrodes in the body fluid at a pH of 7.4 form a 'biogalvanic' cell in which zinc is oxidised to zinc hydroxide and oxygen is reduced.

- (i) State the polarities of the zinc and platinum electrodes and write a half-equation for the reaction that occurs at each electrode.
 [3]
- (ii) Given that the value of ΔG^{e} at 298 K for the reaction in the biogalvanic cell is -637 kJ per mole of oxygen reduced, calculate a value for $E^{\text{e}}_{\text{cell}}$.

Hence, determine the value of the standard reduction potential of zinc hydroxide. [2]

- (iii) A pacemaker operates at an average current of 8.0 × 10⁻⁴ A. Calculate how long the pacemaker will last when 5.0 g of zinc electrode is used before it needs to be replaced. Give your answer to the nearest day.
- (b) Zinc and silver are often present as impurities in crude copper obtained from minerals.

Explain, in terms of electrode reactions, how zinc and silver are removed in the industrial process of the purification of copper, using relevant data from the *Data Booklet*. Illustrate your answer with a labelled diagram. [4]

(c) Zinc oxide is used as a catalyst in the condensation of ethylene glycol and urea. One of the products formed is ethylene urea ($M_r = 87.0$),



- (i) The reaction between ethylene glycol and urea also produces two other molecules, **X** $(M_r = 86.0)$ and **Y** $(M_r = 88.0)$. Suggest the structures of **X** and **Y**. [2]
- (ii) Suggest the products formed when ethylene urea is heated with aqueous sodium hydroxide. [2]

(d) Zinc chloride may be used in the free radical substitution of but-1-ene as shown below. N-bromosuccinimide (NBS) is the source of molecular bromine, Br₂.



In the initiation step below, ZnCl₂ (initiator•) reacts with Br₂ to form Br• radicals:

initiator• + Br–Br \rightarrow initiator–Br + Br•

- Draw curly arrows to show the movement of electrons in the initiation step shown above. [1]
- (ii) Write equations for the propagation steps in the mechanism for reaction 1, starting from the Br• radical. The use of curly arrows is **not** required.
 [2]
- (iii) NBS is a preferred source of Br₂ as it maintains a low concentration of Br₂ in this reaction. Suggest why liquid bromine is not directly added to but-1-ene instead. [1]

[Total: 20]

- 5 (a) Describe and explain the trend and variations in first ionisation energies of the Period 3 elements from sodium to chlorine. [3]
 - (b) The halogens can form many interhalogen compounds. Most interhalogen compounds contain two halogens and have the general formula XY_n where n = 1, 3, 5 or 7.

ClF₃ is an interhalogen compound which exists as a colourless gas.

(i) C_lF_3 and C_{l_2} react to form another interhalogen compound. No other product is formed in the reaction.

State the oxidation numbers of chlorine in ClF_3 and Cl_2 and write an equation for the reaction between ClF_3 and Cl_2 . [2]

The standard enthalpy change of formation, ΔH^{e}_{f} , of C/F₃(g) is -163 kJ mol⁻¹.

- (ii) What can you infer about the stability of ClF₃ from its standard enthalpy change of formation?
- (iii) Use the standard enthalpy change of formation, ΔH^{e}_{f} , of $ClF_{3}(g)$ and data from the *Data Booklet* to determine a value for the bond energy of the Cl-F bond. [2]

Another interhalogen compound is ICl_3 . In the solid state, ICl_3 exists as a dimer, I_2Cl_6 , which consists of two bridging Cl atoms. The shape around each iodine atom is square planar.

(iv) Draw the structure of the I_2Cl_6 dimer including its co-ordinate (dative covalent) bonds. [2]

Cyclic esters are called lactones. One of the most effective ways to synthesise lactones is iodolactonisation, which involves the addition of an oxygen and iodine across a carbon-carbon double bond. An example using 4-pentenoic acid is shown below.



- (c) (i) Draw the structure of the organic product formed when 4-pentenoic acid reacts with NaHCO₃. [1]
 - (ii) Hence, suggest a mechanism for the formation of compound **A** from your product in (c)(i).

Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows. [2]

(d) Compound **B** contains only carbon, hydrogen and oxygen and exhibits stereoisomerism. 1 mole of **B** produces 4 moles of carbon dioxide gas when heated with acidified potassium manganate(VII). No other carbon-containing product is formed in the reaction with potassium manganate(VII).1 mole of **B** also reacts with 2 moles of aqueous NaOH.

Deduce the structure of **B**, giving your reasoning.

(e) Both non-cyclic esters and lactones undergo hydrolysis reactions.



- (i) State the reagents and conditions needed to carry out the hydrolysis. [1]
- (ii) State and explain whether the ΔH for the two reactions would be similar or different. [1]
- (iii) The ΔS for reaction 1 is more positive than the ΔS for reaction 2. Use this information, and your answer to (e)(ii), to compare the ΔG for both reactions and hence the magnitudes of the equilibrium constants, K_1 and K_2 . [2]

[Total: 20]

[3]

END OF PAPER