



**ANDERSON JUNIOR COLLEGE**  
**2016 JC2 PRELIMINARY EXAMINATIONS**

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**CHEMISTRY**

**9647/03**

**Higher 2**

**21 September 2016**

**Paper 3 Free Response**

**2 hours**

Candidates answer on separate paper.

Additional Materials:      Writing Paper  
                                         Data Booklet  
                                         Graph Paper

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**READ THESE INSTRUCTIONS FIRST**

Write your name, PDG and register number on all the work you hand in.

Write in dark blue or black pen on both sides of the paper.

You may use a pencil for any diagrams or graphs.

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

Answer any **four** questions.

**Start each question on a fresh sheet of paper.**

A Data Booklet is provided.

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

You are reminded of the need for good English and clear presentation in your answers.

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.

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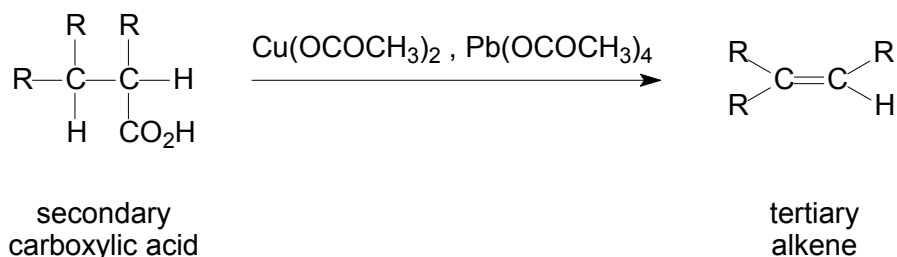
This document consists of **12** printed pages.

- 1 (a) Transition elements show typical properties that distinguish them from s-block elements such as calcium. The following table gives data about some physical properties of the elements calcium, iron and copper.

property	calcium	iron	copper
relative atomic mass	40.1	55.8	63.5
atomic radius (metallic) / nm	0.197	0.126	0.128
ionic radius (2+) / nm	0.099	0.076	0.069
melting point / °C	839	1535	1085
density / g cm <sup>-3</sup>	1.54	7.86	8.92
electrical conductivity / x 10 <sup>6</sup> S cm <sup>-1</sup>	0.298	0.100	0.596

- (i) Explain why the atomic radii of iron and copper are similar to each other. [2]
- (ii) The melting point of iron is significantly higher than that of calcium. Explain this in terms of the type and strength of bonding in each metal. [3]
- (iii) Using relevant data from the table, explain why the densities of iron and copper are significantly greater than that of calcium. (No calculations are required.) [2]
- (b) Cu(I) ions are unstable and readily undergo disproportionation in aqueous solution.
- Write an ionic equation showing the disproportionation of Cu<sup>+</sup>(aq) ions, and choose relevant  $E^\ominus$  values from the *Data Booklet* to calculate  $E_{\text{cell}}^\ominus$  for the reaction. [2]
- (c) Cu(I) is stable in insoluble salts and in some complexes. Complexes of Cu(I) are colourless whereas complexes of Cu(II) are coloured. Use these facts to explain the following observations, writing equations for all reactions.
- (i) The addition of KI(aq) to CuSO<sub>4</sub>(aq) produces a white precipitate, CuI, and a brown solution. The brown solution turns colourless when aqueous sodium thiosulfate, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, is added, and the white precipitate remains. [2]
- (ii) On boiling with copper foil, the colour of a solution of CuCl<sub>2</sub> in concentrated hydrochloric acid changes from blue to colourless. The colourless solution contains a linear complex ion of copper and chlorine.
- After filtering off the excess copper metal and diluting the solution with water, a white precipitate is formed, which contains 35.9 % of chlorine by mass. [3]

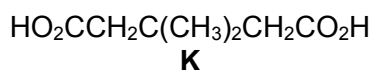
- (d) Some copper compounds have found a use as reagents for unusual organic reactions. An example is the use of a mixture of copper(II) ethanoate and lead(IV) ethanoate for the conversion of carboxylic acids into alkenes containing one less carbon atom. This reaction is known as oxidative decarboxylation.



When a secondary carboxylic acid **G**,  $\text{C}_9\text{H}_{16}\text{O}_2$ , was treated in this way, alkene **H**,  $\text{C}_8\text{H}_{14}$ , was formed. On treatment with hot acidified concentrated  $\text{KMnO}_4$ , **H** produced a single compound **J**,  $\text{C}_8\text{H}_{14}\text{O}_3$ .

Compound **J** evolved  $\text{CO}_2$  with  $\text{Na}_2\text{CO}_3(\text{aq})$ , gave an orange precipitate with 2,4-dinitrophenylhydrazine reagent, and gave a yellow precipitate with alkaline aqueous iodine.

When the yellow precipitate had been filtered off, acidification of the aqueous solution produced 3,3-dimethylpentan-1,5-dioic acid, **K**.

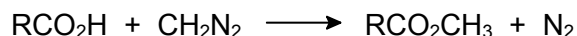


Use the information above to deduce the structures for compounds **G**, **H** and **J**, explaining all the reactions involved.

[6]

[Total: 20]

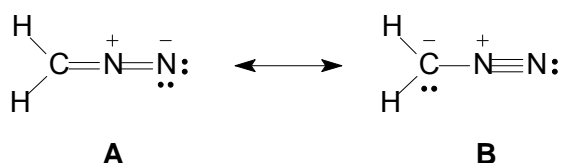
- 2 (a) One frequently used method for preparing methyl esters is by reaction of carboxylic acids with diazomethane,  $\text{CH}_2\text{N}_2$ .



The reaction of a carboxylic acid with diazomethane occurs via a two-step mechanism.

- Protonation of diazomethane by the carboxylic acid to yield methyldiazonium ion,  $\text{CH}_3\text{N}_2^+$ , and carboxylate ion in the first step.
- Reaction of the carboxylate ion with  $\text{CH}_3\text{N}_2^+$  to form  $\text{N}_2$  in the second step.

- (i) **A** and **B** are two possible resonance structures of diazomethane,  $\text{CH}_2\text{N}_2$ .



Suggest which resonance structure of diazomethane, **A** or **B**, is likely to be involved in the first step of the mechanism.

[1]

- (ii) Using your answer from (a)(i), suggest the mechanism for the reaction between  $\text{RCO}_2\text{H}$  and diazomethane. Show any relevant lone pairs, dipoles and charges, and indicate the movement of electron pairs with curly arrows.

[3]

- (b) (i) Write an equation for the complete combustion of methyl ethanoate,  $\text{CH}_3\text{CO}_2\text{CH}_3$ .

[1]

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

[2]

- (iii) Use the standard enthalpy changes of combustion,  $\Delta H_c^\ominus$  in **Table 2.1** to calculate the standard enthalpy change of formation of methyl ethanoate.

**Table 2.1**

	$\Delta H_c^\ominus / \text{kJ mol}^{-1}$
carbon	−393.5
hydrogen	−285.8
methyl ethanoate	−1592.1

[3]

(c) Describe one simple chemical test to distinguish between  $\text{HCO}_2\text{CH}_2\text{CH}_3$  and  $\text{CH}_3\text{CO}_2\text{CH}_3$ . State clearly how each compound behaves in the test. [3]

(d) Consecutive elements **W**, **X**, **Y** and **Z** are in the third period of the Periodic Table. Element **Y** has the highest first ionisation energy and the lowest melting point of these four elements.

(i) Describe what you would see when elements **W** and **Z** are separately burned in air or oxygen. [2]

(ii) The oxides of elements **X** and **Y** can be obtained when the elements are burned in excess oxygen. The oxides of **X** and **Y** have melting points of  $1720^\circ\text{C}$  and  $580^\circ\text{C}$  respectively.

Briefly relate these melting points to the structure of and bonding in each of these oxides. [2]

(iii) Describe the reactions, if any, of the oxides of elements **X** and **Y** with water. Include the approximate pH value of any resulting solutions, and write equations for any reactions that occur. [3]

[Total: 20]

- 3 (a) Nickel–metal hydride (Ni–MH) batteries are the most common rechargeable batteries used for devices that require large amounts of energy such as digital cameras and MP3 players. Most Ni–MH batteries use an alloy containing mainly lanthanum and nickel.

In one such battery, one of the electrodes is  $\text{LaNi}_5\text{H}_6$  and the other is  $\text{NiO}(\text{OH})$ . The electrolyte is aqueous  $\text{KOH}$ . During discharge, an electrochemical reaction takes place to produce  $\text{LaNi}_5(\text{s})$  and  $\text{Ni}(\text{OH})_2(\text{s})$  and releases electrical energy.

- (i) Construct the two half–equations for the reactions that take place at each electrode during **discharge**. Indicate the polarity of the electrodes in your answer. [2]

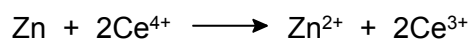
- (ii) During **recharge**, an electrical potential is applied across the electrodes to reverse the electrochemical reaction.

Using your answer in (a)(i), write the overall equation for the reaction that occurs during **recharge**. [1]

- (iii) Overcharging the Ni–MH battery may result in the electrolyte being discharged at the electrodes. A safety vent is thus incorporated in the battery to release the excess pressure.

With reference to the *Data Booklet*, suggest a relevant half–equation for the formation of one product at the electrode of the Ni–MH battery. [1]

- (b) Zinc–cerium battery is another type of rechargeable battery using a two–electrolyte system. The overall equation for the discharging process is given below.



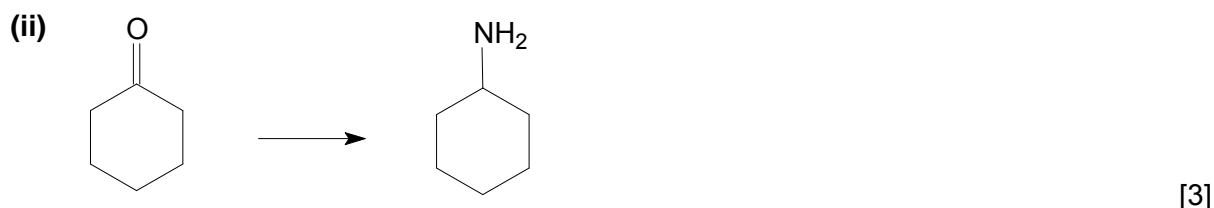
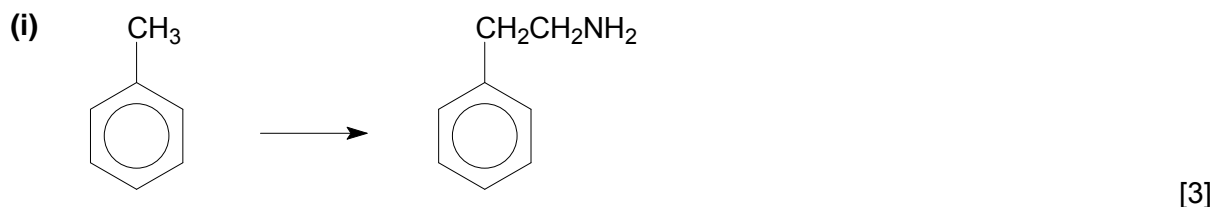
- (i) Given that the typical cell voltage for the cell is 2.2 V, calculate the standard electrode potential of the cerium half–cell, using relevant data from the *Data Booklet*. [1]

- (ii) Using relevant data from the *Data Booklet*, deduce if the  $\text{Ce}^{4+}/\text{Ce}^{3+}$  half–cell can be replaced with  $\text{Br}_2/\text{Br}^-$  half–cell. [1]

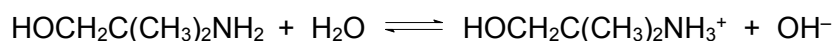
- (c) Amines can be made from a variety of compounds.

Suggest, **in no more than three steps**, how each of the following transformations can be achieved.

For each transformation, draw the structures of the intermediate compounds and indicate reagents and conditions for each of the steps.



- (d) The buffer of 2-amino-2-methylpropan-1-ol (AMP) has been shown to be well suited for the determination of the activity of enzymes like alkaline phosphatase and lactate dehydrogenase. It hydrolyses in water with a  $pK_b$  value of 4.3.



- (i) A  $100 \text{ cm}^3$  solution containing  $0.500 \text{ mol dm}^{-3}$  of  $\text{HOCH}_2\text{C}(\text{CH}_3)_2\text{NH}_2$  is mixed with a  $100 \text{ cm}^3$  solution containing  $0.800 \text{ mol dm}^{-3}$   $\text{HOCH}_2\text{C}(\text{CH}_3)_2\text{NH}_3^+$ .

Calculate the pH of the buffer solution formed.

[2]

- (ii) State the ratio of  $\frac{[\text{HOCH}_2\text{C}(\text{CH}_3)_2\text{NH}_2]}{[\text{HOCH}_2\text{C}(\text{CH}_3)_2\text{NH}_3^+]}$  when the pH of the buffer solution is 9.7.

Hence calculate the mass of solid NaOH to be added to the buffer solution in (d)(i) to achieve this ratio.

[2]

- (e) Proteins are long-chain molecules made by linking together amino acids.

Myoglobin is one such protein that stores and releases oxygen in vertebrate muscle cells. The table below shows some of the amino acids in a molecule of myoglobin.

amino acid	aspartic acid	serine	alanine	lysine
abbreviation	asp	ser	ala	lys
formula of side chain	$-\text{CH}_2\text{CO}_2\text{H}$	$-\text{CH}_2\text{OH}$	$-\text{CH}_3$	$-(\text{CH}_2)_4\text{NH}_2$

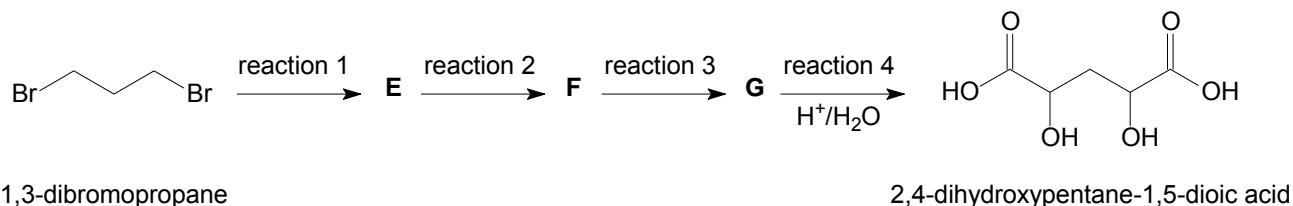
- (i) Given that asp–lys–ala is a particular **section** of the protein chain of myoglobin, draw the displayed formula for this **section** at pH 7. [1]
- (ii) Describe **two** types of side-chain interaction that would occur between the amino acids residues of myoglobin. Illustrate your answer with suitable pairs of amino acids from the table above. [2]
- (iii) Casein is the predominant protein found in milk. The conversion of milk to cheese is a denaturation process involving the addition of the *Lactobacillus* bacterium which produces lactic acid.

Explain this phenomenon by considering the types of side-chain interaction that are affected during the denaturation of casein. [1]

[Total: 20]



- 4 (a) 1,3-dibromopropane is the starting material 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  $C_3H_4O_2$ . On treatment with Tollens' reagent, it gives a silver mirror.

- (i) Draw the structures of **E** and **F**. [2]

- (ii) When preparing compound **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]

- (iii) In an experiment, 9.0 g of 1,3-dibromopropane was converted into compound **F** with an overall yield of 67 %. Calculate the mass of **F** that was obtained.

[2]

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

[1]

- (b) The oxides of Group I and II metals have many uses. Beryllium oxide,  $BeO$ , is used in many high-performance semiconductor parts for applications such as radio equipment, while sodium oxide,  $Na_2O$ , is a significant component of glasses and windows.

- (i) Using the given data and other relevant data from the *Data Booklet*, construct an energy level diagram and use it to calculate the lattice energy of beryllium oxide. Label each energy level in your diagram and draw arrows representing the energy terms involved. Use symbols or numbers to represent these energy terms.

enthalpy change of formation of beryllium oxide	$-609 \text{ kJ mol}^{-1}$
enthalpy change of atomisation of beryllium	$+324 \text{ kJ mol}^{-1}$
first electron affinity of oxygen	$-141 \text{ kJ mol}^{-1}$
second electron affinity of oxygen	$+798 \text{ kJ mol}^{-1}$

[3]

- (ii) The theoretical lattice energy of beryllium oxide is  $-4293 \text{ kJ mol}^{-1}$ . Suggest a reason why this value is different from your answer in (b)(i).

[1]

- (iii) Explain how you would expect the numerical magnitude of the lattice energy of beryllium oxide to compare with that of sodium oxide.

[2]

- (iv) Explain the reaction(s) that occur(s) when chlorine gas is bubbled into a flask containing water, at room temperature, to which sodium oxide has been added. Write equation(s) where appropriate.

[2]

- (c) Soluble chromates(VI) in the soil are toxic at low concentrations for plants.

In water treatment to remove the chromate(VI) ions,  $\text{CrO}_4^{2-}(\text{aq})$ , from a sample of soil water, aqueous acidified iron(II) sulfate is first added to the water sample to convert the chromate(VI) ions to chromium(III) ions,  $\text{Cr}^{3+}(\text{aq})$ . This is followed by adding aqueous sodium carbonate to the resultant solution to produce effervescence and an insoluble compound.

- (i) Construct an equation for the reaction between aqueous acidified iron(II) sulfate and chromate(VI) ions.

[1]

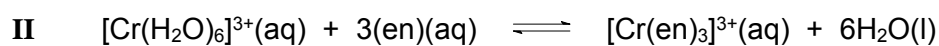
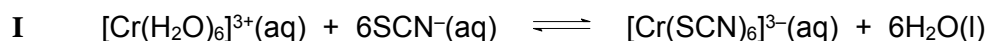
- (ii) Identify the insoluble compound formed upon adding aqueous sodium carbonate.

With the aid of an appropriate ionic equation, explain its formation.

[2]

- (d) Chromium(III) ions coordinate with both monodentate and polydentate ligands.

Consider the following complex formation reactions with thiocyanate,  $\text{SCN}^-$ , and ethylenediamine,  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ , ligands:



where (en) is ethylenediamine

- (i) Explain what is meant by *entropy*.

[1]

- (ii) Explain how you would expect the entropy change,  $\Delta S_r^\ominus$ , for reaction **II** to compare with that for reaction **I**.

[2]

[Total: 20]

- 5 Nitrogen forms numerous oxides, two of which are dinitrogen monoxide,  $\text{N}_2\text{O}$ , and dinitrogen tetroxide,  $\text{N}_2\text{O}_4$ .

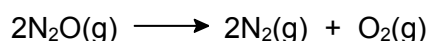
- (a) Dinitrogen monoxide,  $\text{N}_2\text{O}$ , is a non-toxic gas that is used commercially as the propellant in cans of whipped cream.

Given that  $\text{N}_2\text{O}$  is a linear molecule, draw a 'dot-and-cross' diagram showing the electrons (outer shells only) in  $\text{N}_2\text{O}$ .

You should distinguish carefully between electrons originating from each of the nitrogen atoms.

[1]

- (b) At 1200 K and in the presence of a gold wire,  $\text{N}_2\text{O}$  decomposes as follows.



The kinetics of this reaction can be followed by measuring the total pressure,  $P$ , as it changes with time,  $t$ . In one such experiment, the total pressure changes as follows.

total pressure, $P$ / kPa	25.0	27.5	30.0	32.5	34.0	35.0
time, $t$ / s	0	1030	2360	4230	5870	7420
partial pressure, $p$ , of $\text{N}_2\text{O}$ / kPa	25.0					

- (i) What is the total pressure when the reaction is complete? [1]

- (ii) Show that the partial pressure of  $\text{N}_2\text{O}$  at any time,  $t$ , is equal to  $(75.0 - 2P)$  kPa. [2]

- (iii) Hence calculate the partial pressures of  $\text{N}_2\text{O}$  after 1030 s, 2360 s, 4230 s, 5870 s and 7420 s. [1]

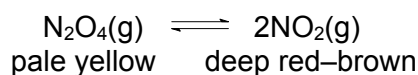
- (iv) Using your answers from (b)(iii) and the data above, plot these data on suitable axes and use your graph to determine the order of reaction with respect to  $\text{N}_2\text{O}$ .

You should show all your working and draw clearly any construction lines on your graph.

[3]

- (v) The rate of reaction is expressed in  $\text{kPa s}^{-1}$ . Write the rate equation for the reaction, and calculate a value for the rate constant. Include units in your answer. [3]

At a temperature of 27 °C, gaseous N<sub>2</sub>O<sub>4</sub> and NO<sub>2</sub> are in dynamic equilibrium according to the following equation.



- (c) When 4.60 g of N<sub>2</sub>O<sub>4</sub> is placed in an evacuated 1.48 dm<sup>3</sup> flask at 27 °C, the equilibrium pressure is 1.00 atm (101 kPa).
- (i) Calculate the number of moles of N<sub>2</sub>O<sub>4</sub> at the start. [1]
  - (ii) Calculate the number of moles of gas at equilibrium, assuming the gases behave ideally. [1]
  - (iii) Hence calculate the percentage of the N<sub>2</sub>O<sub>4</sub> that has been dissociated. [2]
  - (iv) Write an expression for the equilibrium constant,  $K_p$ , for the reaction and show it has a value of 0.17 atm at 27 °C. [3]
- (d) When the equilibrium mixture from (c) at 27 °C is suddenly compressed in a gas syringe, the mixture immediately darkens and then slowly becomes paler. Suggest why the mixture behaves in this way. [2]

[Total: 20]