Name:		Centre/Index Number:		Class:	

DUNMAN HIGH SCHOOL
Preliminary Examination
Year 6

H2 CHEMISTRY

9729/03

Paper 3 Free Response Questions

22 September 2021
2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your centre number, index number, name and class at the top of this page.
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.

Answer **all** questions in the spaces provided on the Question Paper. If additional space is required, you should use the pages at the end of this booklet. The question number must be clearly shown.

Section A
Answer **all** questions.

Section B
Answer **one** question.

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.

For Examiner's Use	
Section A	
1	/20
2	/20
3	/20
Section B	
4 / 5	/20
Total	/80

This document consists of **28** printed pages.

Section A

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

1 (a) Aqueous sodium hydroxide reacts with halogens, such as chlorine, under different conditions, to form NaC*l*O and NaC*l*O_3.

At 10 °C, aqueous sodium hydroxide reacts with chlorine to produce NaC*l* and NaC*l*O.

(i) State the change(s) in oxidation state of chlorine when chlorine is reacted with aqueous sodium hydroxide at 10 °C. Hence, name the type of reaction that occurred. [1]

(ii) Write the balanced equation for the reaction occurring in **(a)(i)**. [1]

(iii) Draw the structure of C*l*O_3^- ion, stating its shape and bond angle. [2]

(iv) Explain why fluorine does not undergo a similar reaction with aqueous sodium hydroxide to produce $NaFO_3$. [1]

(v) Describe and explain the relative volatility of Cl_2 and I_2. [2]

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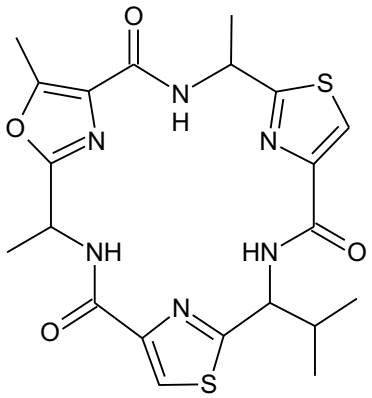
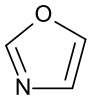
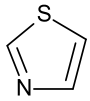
(b) Venturamide A is a cyclic peptide with anti-malarial activity. It has the following structure.



Suggest reagents and conditions for the basic hydrolysis of Venturamide A and draw the structures of the organic products.

Assume that the 2 rings,  and  , are inert in the reaction. [3]

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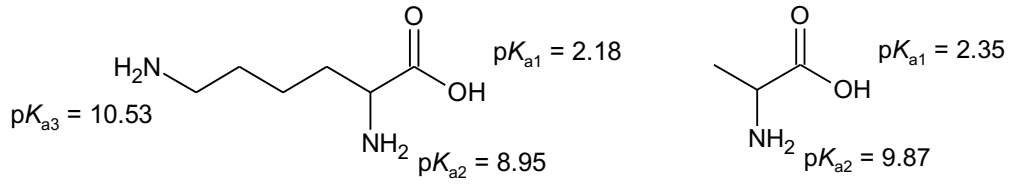
(c) Lysine and alanine are naturally–occurring amino acids.



Lysine Alanine

(i) Write an equation to show how the zwitterionic form of lysine can remove small amounts of H^+. [2]

(ii) Draw the structures of the major species present in a solution of the lys–ala dipeptide at **each** of the following pH values at room temperature.

- pH 1
- pH 10 [2]

(iii) Briefly explain why the α–NH_2 group of lysine is less basic than its side–chain –NH_2 group. [1]

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(d) Compound **X**, $C_8H_{16}Cl_2$, is a symmetrical molecule which has two chiral carbon centres.

When compound **X** is heated under reflux with excess aqueous sodium hydroxide, compound **Y**, $C_8H_{18}O_2$, is formed. The reaction kinetics follows the rate equation, rate = k[**X**].

Upon heating **Y** with acidified potassium manganate(VII), no decolourisation is observed. When compound **X** is heated in a sealed tube in excess ammonia gas, compound **Z** with the molecular formula $C_8H_{20}N_2$ is produced.

Deduce the structures of compounds **X** to **Z**, giving your reasoning. [5]

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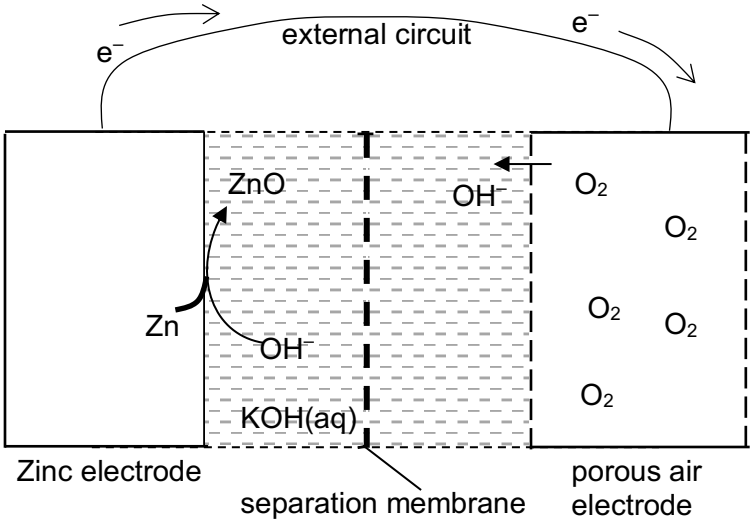
2 (a) Zinc–air batteries have received revived interest recently due to its higher energy density, larger storage capacity and lower production cost as compared to the commonly–used conventional lithium–ion batteries.

A zinc-air battery comprises zinc electrode, porous carbon–containing air electrode, an electrolyte and a separation membrane. The electrolyte used is aqueous potassium hydroxide.

The zinc–air battery has a standard cell potential of +1.59 V.



During discharging, zinc is oxidised to zinc oxide, ZnO, at the zinc electrode according to the following reaction:

$$Zn + 2OH^- \rightarrow ZnO + H_2O + 2e^-$$

(i) Write the half-equation for the reaction that occurred at the air electrode during discharging. [1]

(ii) Using suitable data from the *Data Booklet,* calculate the $E^{\ominus}$ value for the ZnO / Zn electrode. [1]

(iii) With reference to your answer in **(a)(i),** predict how the operating cell potential of the zinc–air batteries will be affected when the atmospheric pressure is lowered. [1]

(iv) A polymer in the porous air electrode controls the passage of carbon dioxide into the electrolyte.

Given that the separation membrane allows Zn^{2+} ions to pass through, suggest a reason why there is a need to control the passage of carbon dioxide into the electrolyte. [1]

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(b) An organic polymer, which is used as the separation membrane in the zinc–air battery, can be synthesised from compound **X**.

Compound **X** has molecular formula C_3H_3N. On heating with dilute sulfuric acid, **X** forms compound **Y**, $C_3H_4O_2$. Both **X** and **Y** decolourise aqueous bromine but only **Y** reacts with sodium carbonate to form a gas which forms white precipitate in $Ca(OH)_2(aq)$.

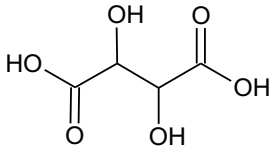
(i) Suggest structures for compounds **X** and **Y**, giving reasons for your answers. [3]

(ii) Compound **Z** is a constitutional isomer of **Y**. They can be distinguished using Fehling's solution or alkaline aqueous iodine.

Draw the displayed formula for **Z**. [1]

Fehling's solution is made by adding equal volumes of aqueous copper(II) sulfate and potassium sodium tartrate in sodium hydroxide.

Potassium sodium tartrate is a double salt of tartaric acid.



Tartaric acid

Table 2.1 below lists some properties of three stereoisomers of tartaric acid.

Table 2.1

Isomer	Effect on plane–polarised light	Melting point/ °C
A	Rotate to the right	170
B	Rotate to the left	170
C	No effect	140

(iii) Explain why isomers **A** and **B** behave differently towards plane–polarised light. [1]

(iv) Draw the structural formula of isomer **C**. Explain why
- it has a lower melting point from **A** and **B**
- it does not rotate plane–polarised light. [3]

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(c) Mazak is an alloy of magnesium, aluminium, zinc and copper which is widely used to make die–cast toys.

Magnesium and aluminium are adjacent elements in the third Period of the Periodic Table; copper and zinc are next to each other in the first row of transition elements.

The densities of the four metals present in Mazak, in ascending numerical order, are given below.

	metal 1	metal 2	metal 3	metal 4
density/ g cm^{-3}	1.74	2.70	7.13	8.94

Suggest which two of the metals, Mg, A*l*, Zn and Cu are metals 1 and 2. Explain your answer. [2]

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(d) A solution contains 4.40×10^{-3} mol dm^{-3} of Al^{3+}(aq) and 1.00 mol dm^{-3} of Cu^{2+}(aq).

Aqueous NaOH was then added slowly to 1 cm depth of the solution in a test–tube.

(i) Using numerical values of K_{sp} given below, show that the addition of NaOH will **not** allow for the separation of the Al^{3+} and Cu^{2+} metal cation in the above solution.

compound	K_{sp}
$Cu(OH)_2$	2.20×10^{-20}
$Al(OH)_3$	4.60×10^{-33}

[3]

(ii) Suggest how the separation of the two aqueous ions can be effectively carried out. Use *Le Chatelier's Principle* to explain your observations and include relevant equations in your answer. [3]

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3 (a) Concentrated sulfuric acid reacts with solid sodium chloride to produce hydrogen chloride according to the equation shown.

$$H_2SO_4 + NaCl \rightarrow HCl + NaHSO_4$$

(i) Explain what is meant by the term *Brønsted-Lowry acid*. [1]

(ii) Identify the two different conjugate acid-base pairs in the reaction, stating clearly which is the acid and base in each pair. [1]

When mixed with water, sulfuric acid dissociates in two steps.

equation 1	$H_2SO_4 + H_2O \rightleftharpoons HSO_4^- + H_3O^+$	$K_{a_1} = 10^3$ at 25 °C
equation 2	$HSO_4^- + H_2O \rightleftharpoons SO_4^{2-} + H_3O^+$	$K_{a_2} = 10^{-1.9}$ at 25 °C

(iii) Explain the difference in the K_a values. [1]

(iv) Use equations 1 and 2 to write expressions for the acid dissociation constants, K_{a_1} and K_{a_2}. [1]

(v) A sample of dilute sulfuric acid at 25 °C was found to have a pH value of 1.2. Use your answer in **(a)(iv)** to calculate the $[SO_4^{2-}]/[H_2SO_4]$ ratio and hence show that the amount of H_2SO_4 in the sample is negligible. [2]

(vi) 10 cm^3 of 0.500 mol dm^{-3} sulfuric acid is diluted to 100 cm^3 with deionised water. Calculate the pH of the diluted solution. [1]

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(b) Concentrated sulfuric acid also reacts with solid sodium bromide to produce hydrogen bromide.

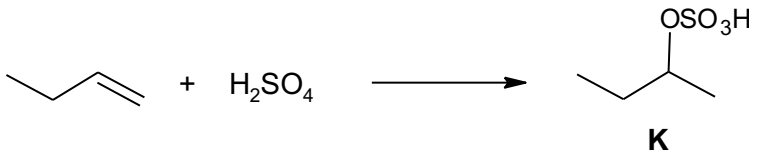
$$H_2SO_4 + NaBr \rightarrow HBr + NaHSO_4$$

In addition, the hydrogen bromide produced further reacts with concentrated sulfuric acid to give a reddish brown gas.

(i) Suggest the identity of the reddish brown gas and use relevant data from the *Data Booklet* to explain why HBr further reacts with H_2SO_4 whereas HC*l* does not. [2]

(ii) Explain the difference in thermal stability of HBr and HC*l*. [2]

(c) But-1-ene reacts with cold concentrated sulfuric acid to produce an alkyl hydrogen sulfate, **K**.



K

(i) Suggest a mechanism for the formation of **K** from but-1-ene. Show the displayed formula of the sulfuric acid molecule, the structure of the intermediate and the movement of electron pairs by using curly arrows. [3]

(ii) State the type of stereoisomerism shown by compound **K** and draw its stereoisomers. [1]

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(d) Silver chloride exists in equilibrium with its ions.

$$AgCl(s) \rightleftharpoons Ag^{+}(aq) + Cl^{-}(aq)$$

(i) Using relevant data from the *Data Booklet* together with the following data, construct a fully labelled energy cycle to calculate the enthalpy change for the dissociation of silver chloride in water.

standard enthalpy change of formation of $AgCl(s)$	$= -127$ kJ mol^{-1}
first electron affinity of chlorine	$= -349$ kJ mol^{-1}
standard enthalpy change of hydration of chloride ion	$= -378$ kJ mol^{-1}
standard enthalpy change of reaction of $Ag(s) \rightarrow Ag^{+}(aq) + e^{-}$	$= +543$ kJ mol^{-1}

[3]

(ii) State and explain the effect of adding concentrated hydrochloric acid on the solubility of silver chloride. [2]

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Section B

Answer **one** question from this section.

4 (a) A saltwater chlorine generator (SWG) is an alternative method of disinfecting swimming pools as opposed to the direct addition of hypochlorite salts into water.

The SWG uses electrolysis to produce chlorine gas.

(i) The working principle of a SWG can be understood by the electrolysis of concentrated aqueous NaC*l* using inert titanium electrodes.

Write equations to illustrate the reactions taking place at each electrode in the SWG. [2]

(ii) With reference to relevant half-equations and their $E^{\ominus}$ values from the *Data Booklet*, explain the reaction occurring at the anode. [2]

(iii) A current of 2.08 A was passed through a SWG prototype for 4 h 30 min. Calculate the volume of chlorine gas that is expected to be liberated at room temperature and pressure. [2]

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(b) The distinctive smell of swimming pool water is attributed to a by-product known as chloramines.

Ammonia, which originates from bodily sources such as perspiration and urine, reacts with hypochlorous acid, HC*l*O, to produce various types of chloramines, namely NH_2Cl, $NHCl_2$ and NCl_3.

(i) At a temperature of 70 °C and a pressure of 1.2 atm, 0.400 g of a gaseous mixture containing NH_2Cl, $NHCl_2$ and NCl_3 takes up a volume of 150 cm^3.

Calculate the average M_r of the sample. [2]

(ii) NCl_3 gas behaves less ideally than NH_3 gas. Explain this observation. [1]

(iii) NCl_3 can be removed by channelling swimming pool water through an Ultraviolet (UV) disinfection system, producing chlorine gas as shown by the equation below.

$$2NCl_3(l) \rightarrow N_2(g) + 3Cl_2(g) \qquad \Delta H^{\ominus} = +184 \text{ kJ mol}^{-1}$$

Predict, with reasoning, the sign of the entropy change. [1]

(iv) Using your answer in **(b)(iii)**, suggest whether the removal of NCl_3 in swimming pool water is easier on a hotter or colder day. Explain your answer. [2]

(v) A student determined $\Delta G^{\ominus}$ of the reaction in **(b)(iii)** to be −154 kJ mol^{-1}.

State a limitation of this value in predicting the spontaneity of this reaction. [1]

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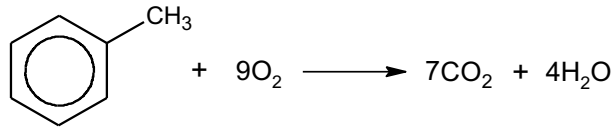
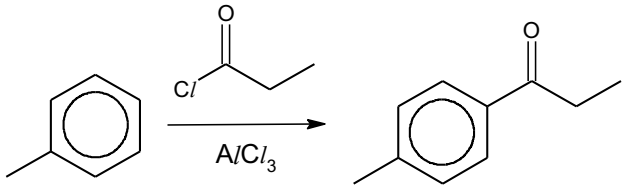
(c) Methylbenzene can be used as an additive in unleaded petrol. It has a boiling point of 111°C. The combustion of methylbenzene is shown below.



(i) Using bond energy data from the *Data Booklet*, calculate the standard enthalpy change of combustion, ΔH_c, of methylbenzene. [2]

(ii) The ΔH_c calculated in **(c)(i)** is more exothermic than its experimental value. Other than the use of average bond energy values in the calculation, suggest a reason for the discrepancy between the two values. [1]

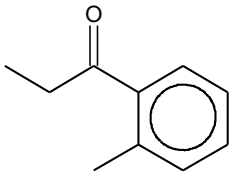
Methylbenzene undergoes a reaction with propanoyl chloride as shown below.



J

(iii) Write an equation to show the generation of the electrophile. [1]

(iv) Compound **K** is another possible product of the reaction.



K

Suggest why **K** is likely to be formed in smaller quantities compared to **J**. [1]

(v) Compound **J** is reacted with bromine gas in the presence of UV light.

Draw all possible monobrominated products formed and suggest their relative ratios. [2]

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5 Addition and substitution reactions are common reactions in organic chemistry.

(a) Alkenes and carbonyl compounds can undergo addition reactions. However, carbonyl compounds undergo nucleophilic addition reactions while alkenes do not.

Explain why alkenes do not undergo nucleophilic addition reactions. [1]

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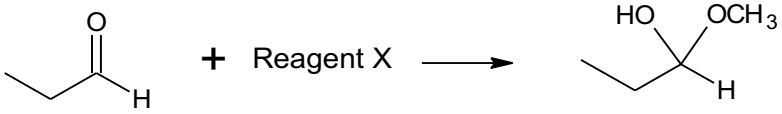
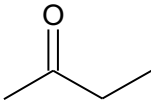
(b) One example of a nucleophilic addition reaction that carbonyl compounds can undergo is the conversion of the carbonyl group to a hemiacetal. An example involving propanal is shown below.



Propanal Hemiacetal

(i) Suggest the identity of reagent X. [1]

Butanone can undergo the same nucleophilic addition reaction using the reagent X.



Butanone

Observations were made about the reactions as shown in Table 5.1.

Table 5.1

	Reaction between propanal and reagent X	Reaction between butanone and reagent X
Relative Rate	Faster	Slower
Optical activity of product	Optically inactive	Optically inactive

(ii) Suggest the structure of the product formed when butanone reacts with reagent X, and explain the observations made about the two reactions in Table 5.1. [4]

(iii) Describe two chemical tests that would be able to distinguish propanal and butanone.

The two tests must include:
Test 1 that gives a positive test with propanal but not butanone
Test 2 that gives a positive test with butanone but not propanal

You should include the positive observation of each test in your answer. [3]

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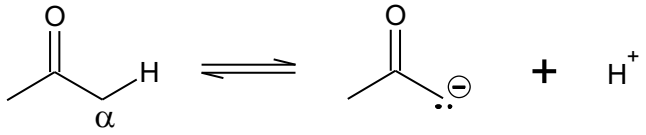
(c) Ketones can undergo electrophilic substitution because the hydrogen atom on the alpha (α) carbon of a ketone is considered to be weakly acidic. The alpha carbon is the carbon atom that is next to the carbonyl group.

The deprotonation of ketones at the alpha carbon results in the formation of a resonance–stabilised conjugate base, which can then react with electrophiles.



(i) Suggest why the conjugate base of the ketone is resonance–stabilised. [1]

(ii) Suggest why ketones are much less acidic than carboxylic acids. [2]

(iii) Suggest the structure of the organic product formed when the conjugate base of propanone reacts with a molecule of iodine. [1]

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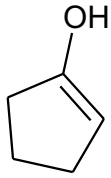
(d) Phosphorus trichloride, PCl_3, and phosphorus pentachloride, PCl_5, are commonly used in the substitution reactions involving carboxylic acids and alcohols.

(i) Cyclopenten–1–ol does not undergo substitution with PCl_3 or PCl_5. Suggest a reason for this.



Cyclopenten–1–ol [1]

Phosphorus pentachloride, silicon chloride and magnesium chloride were added separately to three beakers of water. A few drops of universal indicator were added to each beaker and the colour of the solution in each beaker was recorded in Table 5.2.

Table 5.2

Beaker	Colour of solution
A	Red
B	Red
C (to which $MgCl_2$ was added)	Yellow

(ii) With the aid of a chemical equation, account for the colour of the solution observed in beaker C. [2]

(iii) A precipitate was observed in beaker A.

State the identity of this precipitate. [1]

(iv) Write an equation that describes the reaction that happens when phosphorus pentachloride dissolves in excess water. [1]

(v) A unknown mass of phosphorus pentachloride was completely dissolved in 500 cm^3 of water. A 10 cm^3 aliquot of the resultant solution required 16.00 cm^3 of 0.2 mol dm^{-3} aqueous KOH for complete neutralisation.

Calculate the mass of phosphorus pentachloride that was dissolved in 500 cm^3 of water. [2]

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Additional answer space

If you use the following pages to complete the answer to any question, the question number must be clearly shown.