Calculator Model / No.

Name: _____ **Class: 15S**_____ **Reg Number:** _____

MERIDIAN JUNIOR COLLEGE
JC2 Preliminary Examination
Higher 2

Chemistry 9647/03

Paper 3 Free Response **14 September 2016**

2 hours

Additional Materials: *Data Booklet*
Writing Paper

INSTRUCTIONS TO CANDIDATES

Write your name, class and register number in the spaces provided at the top of this page.

Answer 4 out of 5 questions in this paper.

Begin each question on a fresh sheet of writing paper.

Fasten the writing papers behind the given **Cover Page for Questions 1 & 2** and **Cover Page for Questions 3, 4 & 5** respectively.

Hand in Questions **1 & 2** and **3, 4 & 5 separately**.

You are advised to spend about 30 minutes per question only.

INFORMATION FOR CANDIDATES

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

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

This document consists of **18** printed pages.

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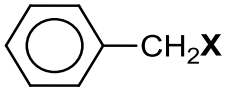
Answer any 4 out of 5 questions in this paper.

*Begin each question on a **fresh sheet** of writing paper.*

1 Benzyl halides are colourless liquids that have been used in chemical warfare due to their ability to cause severe eye, respiratory and skin irritation. Benzyl halides are also used in organic synthesis for the introduction of the benzyl protecting group for alcohols and carboxylic acids.



benzyl halide

(a) Benzyl iodide, $C_6H_5CH_2I$ can be synthesised from benzene in a **four** step pathway involving Friedel–Crafts alkylation. Friedel–Crafts alkylation involves the alkylation of a benzene ring in the presence of a suitable catalyst via electrophilic substitution.

Outline this synthesis route, suggesting relevant reagents, conditions and intermediate products.

[4]

(b) Another method to synthesise benzyl iodide is via the *Finkelstein reaction*, which involves the conversion of benzyl bromide to benzyl iodide using stoichiometric amounts of potassium iodide under reflux conditions.

$$C_6H_5CH_2Br + KI \rightarrow C_6H_5CH_2I + KBr \qquad \textit{Finkelstein reaction}$$

The rate equation is rate = k $[C_6H_5CH_2Br]$.

(i) Draw diagrams to illustrate the mechanism for this reaction. Show relevant lone pairs and dipoles, and use curly arrows to indicate the movement of electron pairs.

[2]

(ii) Suggest a plausible chemical test that can be performed on a sample of the reaction mixture to test whether the reaction is effectively complete.

[2]

(iii) Explain why benzyl bromide undergoes a unimolecular reaction with KI (aq) whereas (2–bromoethyl)benzene, $C_6H_5CH_2CH_2Br$, undergoes a bimolecular reaction with KI (aq).

[1]

(c) The *Finkelstein reaction* proceeds at a faster rate in the presence of polar solvents such as propanone, CH_3COCH_3. The increase in rate lies in the difference in solubility between KI and KBr in propanone.

$C_6H_5CH_2Br + KI \rightarrow C_6H_5CH_2I + KBr$ *Finkelstein reaction*

Potassium halides	Solubility in propanone
KI	Very soluble
KBr	Almost insoluble

(i) Suggest why the *Finkelstein reaction* goes almost to completion.

[1]

(ii) In the solvation process, one potassium ion interacts with six propanone molecules. Draw a diagram to show how this interaction forms an octahedral unit. State clearly the type of interaction involved.

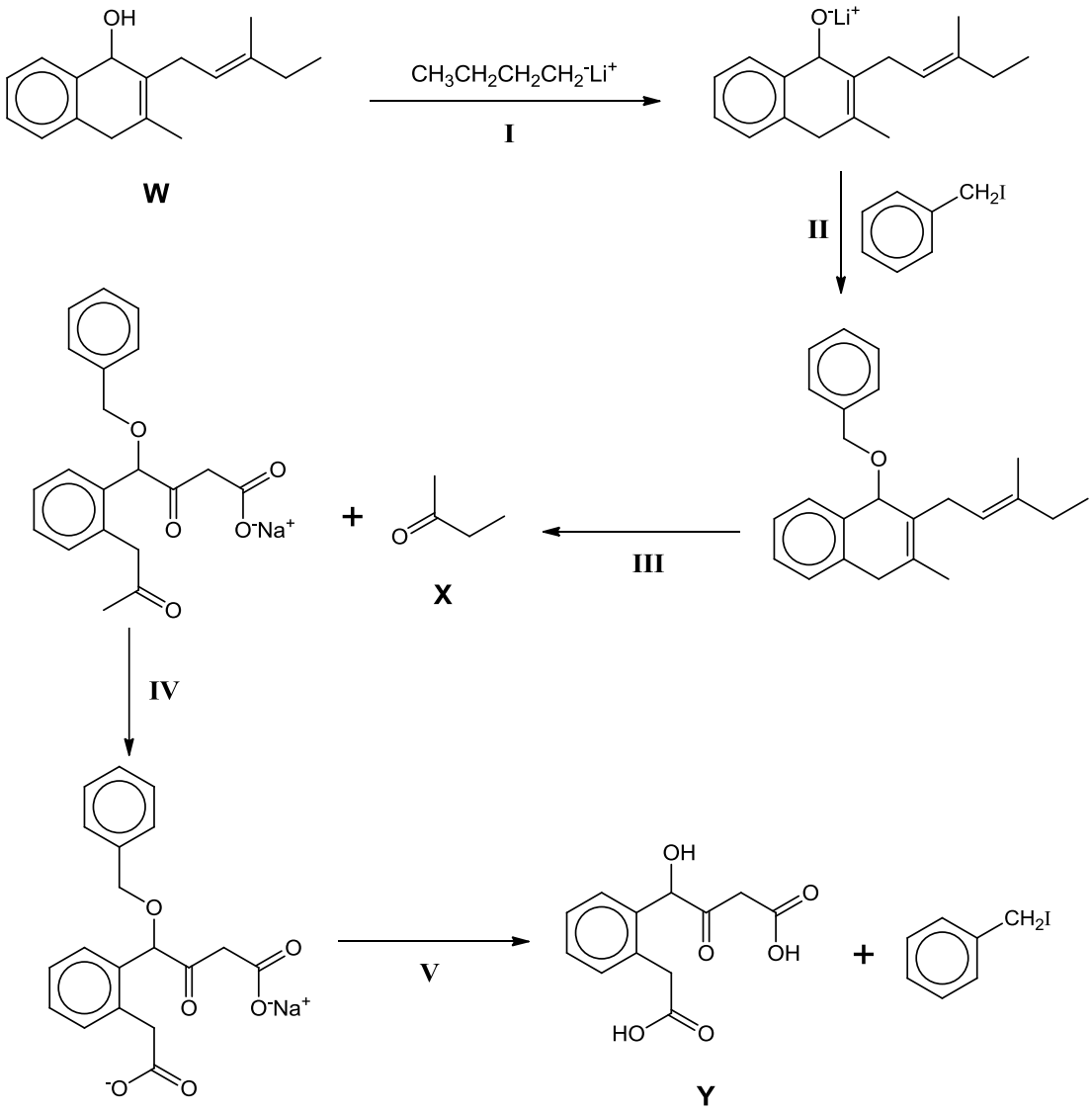
[2]

(iii) Suggest why potassium bromide is less soluble than potassium iodide in propanone by considering the lattice energy of the potassium halides and enthalpy change of solvation of the halides ions.

[1]

(d) Benzyl iodides are widely used in complex organic synthesis to form benzyl ethers ($C_6H_5CH_2$–O–R), which are good blocking groups that protect alcohol functional groups from further reactions. These blocking groups are inert to hydrolysis under normal conditions, but they can be removed at the end of the reaction via the addition of an appropriate hydrogen halide molecule to obtain the original functional group and regenerate the benzyl iodide.

The following illustrates a synthetic scheme from compound **W** in which a benzyl ether is acting as the protecting group.



(i) State the role of $CH_3CH_2CH_2CH_2^-$ Li^+ in step **I**.

[1]

(ii) Predict with reasoning, the relative rate of the reaction in Step **II** when the reactant used is benzyl bromide, $C_6H_5CH_2Br$ instead of benzyl iodide, $C_6H_5CH_2I$. Quote relevant values from the *Data Booklet* to substantiate your answer.

[2]

(iii) State the reagents and conditions needed for steps **III**, **IV** and **V**.

[3]

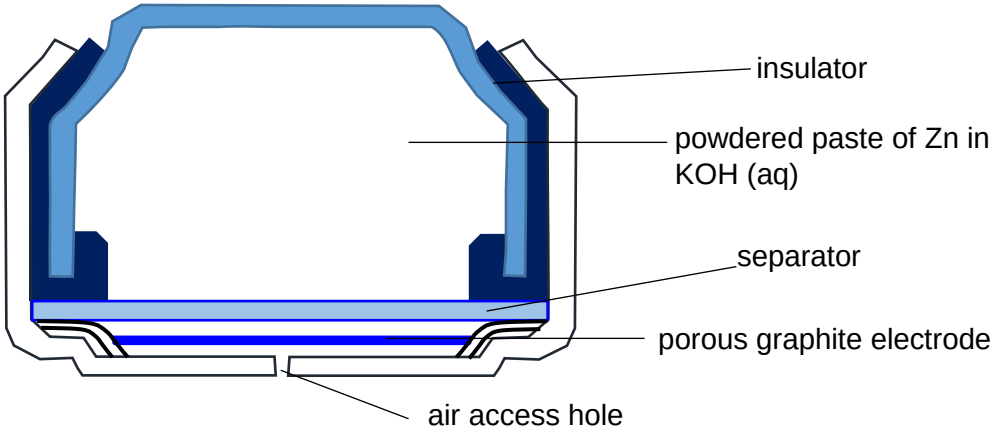
(iv) Write a balanced equation for the reaction between compound **X** and 2,4–dinitrophenylhydrazine.

[1]

[Total: 20]

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.

During discharge, oxygen from the air oxidises zinc to zinc oxide. The electrolyte used in the battery is KOH (aq).The zinc–air battery has a standard cell potential of +1.59 V.



(i) Construct equations for the reactions which occur at the anode and cathode. Hence, construct the overall equation for the cell reaction.

[2]

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

[1]

(iii) Suggest a reason why the air–access hole of these zinc–air batteries must be well–sealed during the packaging of these batteries for storage.

[1]

(iv) With reference to your answer in **(a)(i),** explain fully why the operating cell potential of the zinc–air batteries becomes less positive at high altitudes where the atmospheric pressure is lowered.

[2]

(v) Determine the current output (in amperes) of this zinc–air battery given that the air–access holes allow about 0.20 dm^3 of air exchange in 1 hour at room temperature and pressure. You may assume that the percentage of O_2 present in air is 21.0%.

[2]

(b) Carbon dioxide, when present in sufficient concentration in air, may result in the formation of insoluble zinc carbonate that clogs the porous graphite electrode. This hinders the normal operation of the battery.

(i) Write an equation with state symbols for the thermal decomposition of zinc carbonate.

[1]

(ii) Zinc carbonate and barium carbonate decompose when heated to give similar products.

By quoting appropriate data from the *Data Booklet*, deduce whether zinc carbonate would decompose at a higher or lower temperature than barium carbonate. Explain your answer.

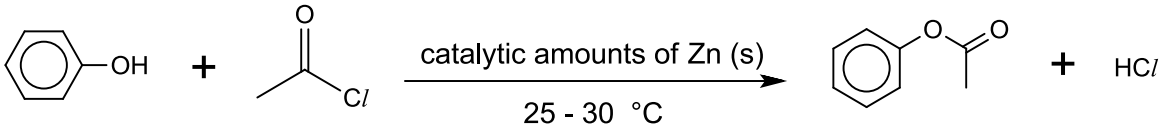
[2]

(iii) Using the following data and relevant data from the *Data Booklet*, construct a Born–Haber cycle to calculate the lattice energy of zinc carbonate.

standard enthalpy change of atomisation of Zn (s) = + 131 kJ mol^{-1}
standard enthalpy change of formation of CO_3^{2-} (g) = − 321 kJ mol^{-1}
standard enthalpy change of formation of $ZnCO_3$ (s) = − 818 kJ mol^{-1}

[3]

(c) Zinc exhibits some properties that are similar to those of a transition element. For example, zinc metal has demonstrated its potential as a *heterogeneous* catalyst for the acylation of a large variety of phenols with acyl chlorides.



Describe fully how zinc functions as a catalyst for this reaction.

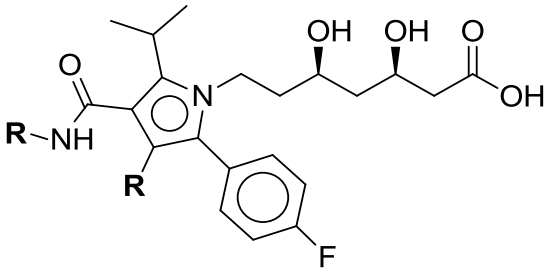
[3]

(d) Similar to aluminium, zinc can be anodised to make it more resistant to corrosion. Draw a fully labelled diagram and with the aid of equation(s), explain how zinc can be anodised.

[3]

[Total: 20]

3 *Atorvastatin* has been a very popular drug since 1996. It is consumed to reduce blood cholesterol level and for prevention of heart diseases.



Atorvastatin

***R** is a hydrocarbon group*

(a) A sample of 1 g of *atorvastatin* was completely burnt in excess oxygen and 103.7 cm^3 of NO_2 gas was produced. All volumes were measured at 80 ^oC and 1 atm.

(i) Calculate the M_r of *atorvastatin*, to the nearest whole number, using the above information.

[2]

(ii) The actual M_r of *atorvastatin* is 558. Explain why there is a discrepancy between the calculated M_r in **(a)(i)** and the actual M_r.

[2]

(b) *Atorvastatin* is sold as the calcium salt in tablet form. Each tablet contains 40 mg of the calcium salt. The maximum dosage is 80 mg per day for an average 65 kg adult.

(i) *Use of information in the photograph above is relevant to this question.*

Calculate the minimum number of bottles of tablets a patient needs to stock up for **a year**, assuming that he adheres strictly to the daily dosage limit and consumes it every day.

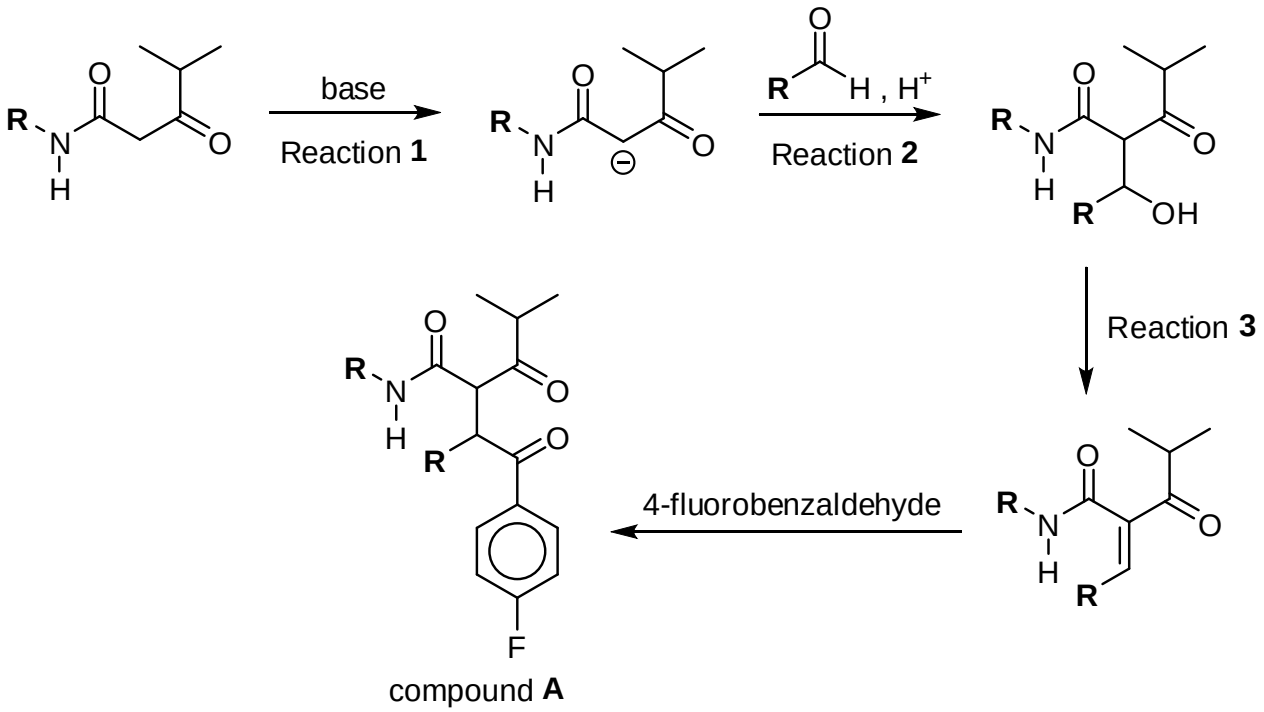
[1]

(ii) Using structure and bonding, explain the differences in solubility of *atorvastatin* and *atorvastatin calcium* in CCl_4.

[2]

In pharmaceutical companies, *atorvastatin* can be synthesised by reacting compound **A** with compound **C.**

(c) Compound **A** is made from smaller molecules. The following reaction scheme shows the synthesis of compound **A.**



compound **A**

Reaction **1**, **2** and **3** are part of an aldol condensation reaction. A brief description of each reaction is given below.

Reaction **1**: The carbonyl α–carbon is deprotonated.

Reaction **2**: Nucleophilic addition takes place on the carbonyl compound.

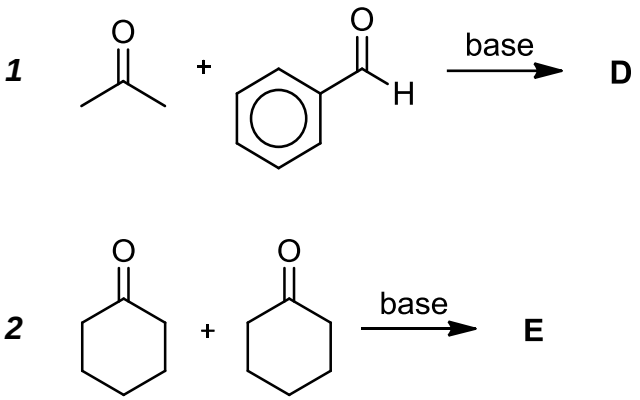
Reaction **3**: Elimination of the alcohol forms an alkene which is conjugated to the ketone.

(i) Outline the mechanism for Reaction **2**. Show relevant lone pairs and dipoles, and use curly arrows to indicate the movement of electron pairs.

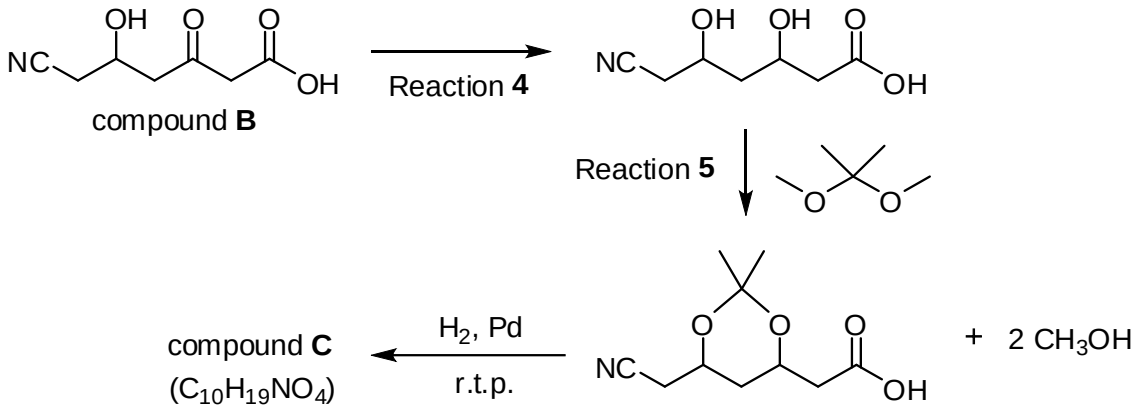
[2]

(ii) Using the information in the reaction scheme given, suggest the products formed, **D** and **E**, when the following carbonyl compounds undergo aldol condensation reaction in the presence of a base.

[2]



(d) The following reaction scheme shows the synthesis of compound **C**.



(i) State the reagent and condition for Reaction **4**.

[1]

(ii) Suggest the type of reaction in Reaction **5**.

[1]

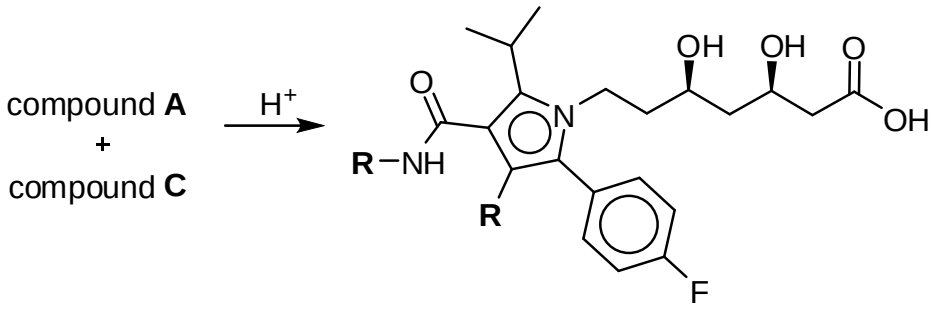
(iii) Draw the structure of compound **C**.

[1]

(iv) Compound **B** forms a cyclic product, with the loss of one water molecule, when it is heated with concentrated sulfuric acid. Suggest the structure of the product formed.

[1]

(e) The following reaction scheme shows the final steps in the production of *atorvastatin*.



Atorvastatin

Atorvastatin contains several functional groups.

(i) It has **two different** acidic functional groups. Name them and explain why one has a higher K_a value than the other.

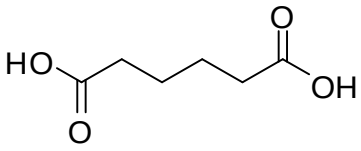
[3]

(ii) The nitrogen atom in the five–membered ring is basic. Draw the structures of the products formed when *atorvastatin* is heated with acidified potassium dichromate(VI).

[2]

[Total: 20]

4 Adipic acid is an organic compound with the formula $(CH_2)_4(COOH)_2$. It is the most important of the dicarboxylic acids from the industrial perspective. Approximately 2.5 billion kilograms of this white crystalline powder are produced annually, predominantly as a precursor for the production of nylon 66.



Adipic acid

(a) One method to synthesis adipic acid is by the carbonylation of gaseous 1,3–butadiene with carbon monoxide and steam.

$$CH_2{=}CHCH{=}CH_2\ (g) + 2CO\ (g) + 2H_2O\ (g) \longrightarrow HOOC(CH_2)_4COOH\ (g)$$

(i) Use relevant bond energy data from the *Data Booklet* to calculate the enthalpy change for this reaction.

(Given that bond energy of C≡O is 1079 kJ mol^{-1})

[2]

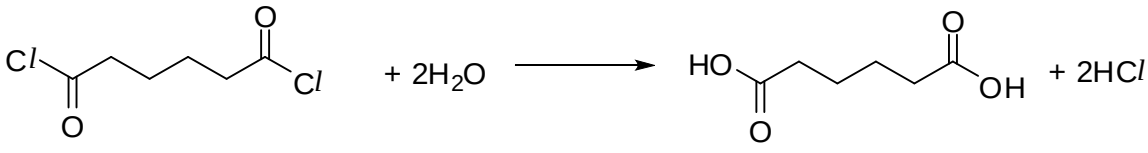
(ii) The enthalpy change for the following reaction to form adipic acid in the solid form is – 248 kJ mol^{-1}.

$$CH_2{=}CHCH{=}CH_2\ (g) + 2CO\ (g) + 2H_2O\ (g) \longrightarrow HOOC(CH_2)_4COOH\ (s)$$

Account for the differences in the values for **(a)(i)** and **(a)(ii)**.

[1]

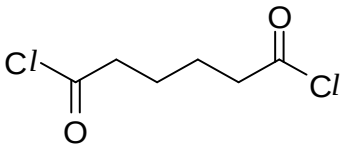
(iii) It is also possible to synthesise adipic acid by reacting adipoyl dichloride through a hydrolysis reaction with water.



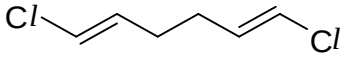
Adipoyl dichloride

Adipic acid

Describe and explain the relative ease of hydrolysis of adipoyl dichloride and compound **A** shown below.



Adipoyl dichloride



Compound **A**

[2]

(b) Adipic acid and its calcium salt are used as a buffer solution to remove sulfur dioxide from exhaust flue gases of fossil–fuel power plants. Calcium sulfate, $CaSO_4$ is formed at the end of the reaction.

(i) Draw the dot–and–cross diagram for the ion, SO_4^{2-}.

[1]

(ii) In principle, $S_2O_8^{2-}$ can be formed from the oxidation of SO_4^{2-}.

Draw the structure of $S_2O_8^{2-}$, given that there are four central atoms and that the ion is symmetrical with an O–O bond.

Account for its shape with respect to **each different** central atom using the VSEPR theory.

[3]

(iii) Adipic acid is a dibasic acid with pK_a values of 4.4 and 5.4.

The optimal buffer pH for the adipic acid–calcium salt mixture is 4.6. Calculate the volume of 0.1 mol dm^{-3} of calcium hydroxide that needs to be added to 500 cm^3 of 0.01 mol dm^{-3} of adipic acid to yield the optimal buffer solution.

[3]

(c) Compound **B** has the same molecular formula, $C_6H_{10}O_4$ as adipic acid. **B** is a neutral molecule but reacts with hot aqueous sulfuric acid to yield two organic compounds **C**, $C_4H_{10}O_2$ and **D** in a 1:1 ratio.

Compound **C** contains 2 chiral carbon atoms. Compound **C** forms no precipitate with 2,4–dinitrophenylhydrazine but reacts with hot aluminium oxide to form only three isomers **E, F** and **G** with the molecular formula of C_4H_8O. **Only** isomer **G** rotates the plane of polarised light.

Compound **D** reacts with hot alkaline Cu^{2+} solution to give a red precipitate. It also reacts with hot acidified $KMnO_4$ to form effervescence of carbon dioxide.

(i) Suggest structures for compounds **B, C, D, E, F** and **G**, showing your reasoning clearly.

[7]

(ii) Write a balanced chemical equation for the reaction between **D** and hot alkaline Cu^{2+} solution.

[1]

[Total: 20]

5 *Hemocyanin* and *chymotrypsin* are proteins used for various functions.

Hemocyanin is a copper–containing oxygen transport protein found in marine invertebrates such as squids. Its mode of transport of oxygen is similar to that of *haemoglobin*. In *hemocyanin,* oxygen is transported in the form of oxyhemocyanin.

(a) Describe what is meant by the *quaternary* structure of *hemocyanin*.

[1]

(b) In squids, one molecule of *hemocyanin* (Hc) binds to one molecule of oxygen via the oxygenation process, according to the following equation:

$$Hc\,(aq) + O_2\,(g) \rightleftharpoons Hc(O_2)\,(aq)$$

(i) In squid *hemocyanin*, when the partial pressure of oxygen gas is 0.13 atm at 25^{o}C, the oxygen–binding sites are 33.0% saturated.

Calculate the equilibrium constant, K_c, at this temperature.

[2]

(ii) The Gibbs free energy change at 25°C when *hemocyanin* interacts with O_2 (g) is related to the equilibrium constant using the following equation.

$$\Delta G = -\,RT \ln K_c$$

Calculate the Gibbs free energy change.

[1]

(iii) It is claimed that *"global warming would harm aquatic organisms such as the squid population"*, through adversely affecting the oxygenation of squid *hemocyanin*.*"*

Verify this claim by considering the signs of the ΔH and ΔS *of* the oxygenation process.

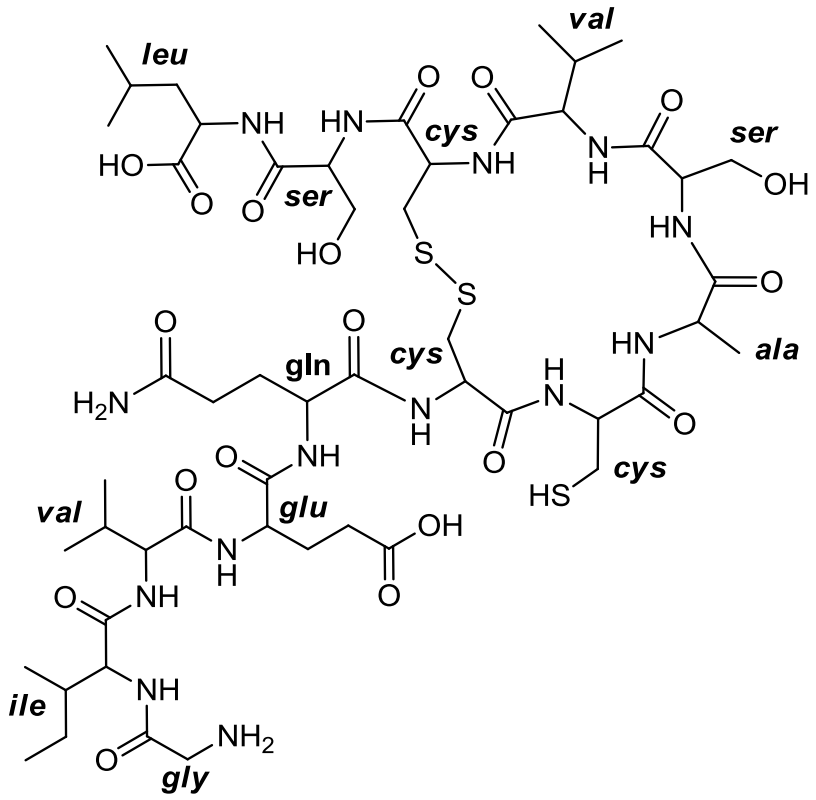
[2]

(iv) The blood of the squid is blue in colour as oxygenation causes a colour change between the colourless Cu(I) deoxygenated form of *hemocyanin* to the blue Cu(II) oxygenated form.

Explain why the oxygenated Cu(II) form of *hemocyanin* is blue in colour.

[3]

Chymotrypsin is an enzyme produced by the pancreas that is responsible for catalysing the hydrolysis of certain proteins in the small intestine during the digestive process. Part of the structure of *chymotrypsin* is given below along with the abbreviated names of its constituent amino acids: **gly**, **leu**, etc.



(c) Use the abbreviated names of the amino acids to state the primary structure of the fragment of *chymotrypsin* given above.

[2]

(d) The biological function of *chymotrypsin* depends on its three–dimensional shape. Describe how the particular amino acids in *chymotrypsin* are likely to be involved in maintaining its three–dimensional shape.

[2]

(e) The activity of *chymotrypsin* is inhibited by prolonged heating with sodium hydroxide.

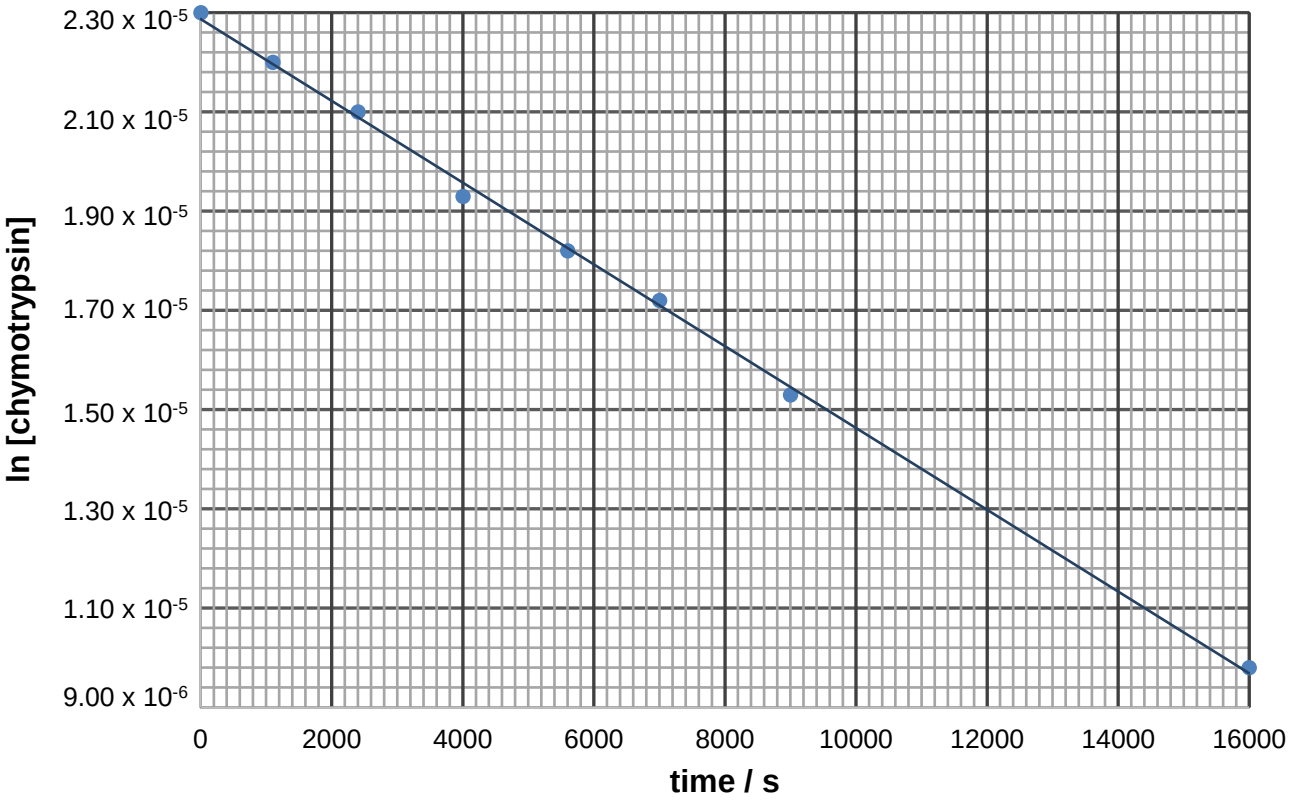
Draw the structure of the tripeptide obtained under these conditions from the part of *chymotrypsin* containing the amino acids: **ile–val–glu**.

[2]

(f) *Chymotrypsin* undergoes denaturation by sodium hydroxide, with the mechanism dependent on pH. At high pH, the reaction is first order with respect to both the *chymotrypsin* and hydroxide ions.

In an experiment, the denaturation of the enzyme was monitored in the presence of excess alkali.

The plot of the time course of the reaction is shown below.



The rate law can be expressed in the form of:

$$\ln[A] = -kt + \ln[A]_0$$

where [A] = concentration of a reactant at time, t
$[A]_0$ = initial concentration of that reactant
t = time since the reaction started
k = rate constant

(i) Explain how the plot of the time course of the reaction confirms that the denaturation is first order with respect to *chymotrypsin* and how the conditions give rise to overall first order kinetics.

[1]

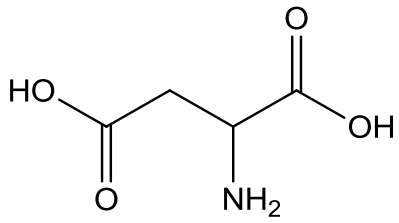
(ii) Using the plot of the time course of the reaction, calculate the value of the experimentally–determined rate constant of this denaturation.

[1]

(iii) Hence, calculate the value of the true rate constant, given that concentration of NaOH used in the experiment was 1.5 mol dm^{-3}.

[1]

(g) One of the amino acids involved in the catalytic activity of *chymotrypsin* is aspartic acid.



Aspartic acid

There are three pK_a values associated with aspartic acid: 2.1, 3.9 and 9.8.

Suggest the predominant species present in solutions of aspartic acid with the following pH values of:

(i) 2.4

(ii) 7.0

[2]

[Total: 20]

END OF PAPER