
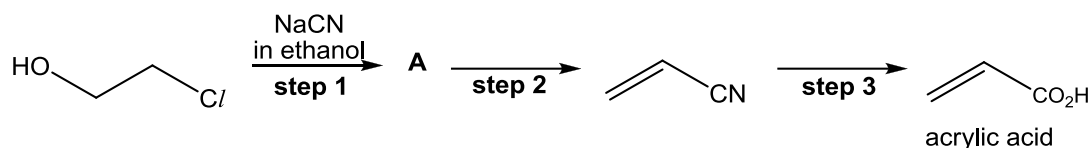


Name:		Class:	
ST ANDREW'S JUNIOR COLLEGE  JC2 Preliminary Examinations			
Chemistry		9647/03	
Higher 2		16 September 2016	
Paper 3		2 hours	
Candidates answer on separate paper. Additional Materials: Writing paper, Data Booklet			
READ THESE INSTRUCTIONS FIRST Write your name and civics group on all the work you hand in. Write in dark blue or black pen. You may use a soft pencil for any diagrams, graphs or rough working. Do not use staples, paper clips, highlighters, glue or correction fluid. Answer any four questions. 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.			
This document consists of 14 printed pages including this page.			

[Turn over

1 Propenoic acid, also commonly known as acrylic acid, is used in the formation of many polymers.

(a) Acrylic acid can be synthesised from 2-chloroethanol in the laboratory by the following route.



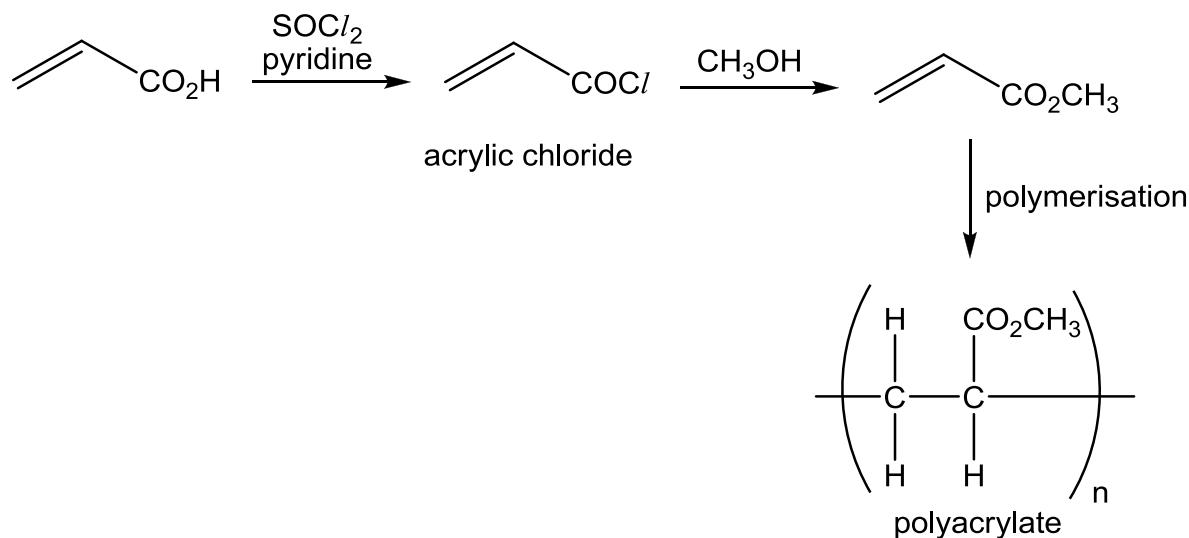
- (i) Suggest the structure for intermediate **A**. [1]
- (ii) Suggest reagents and conditions for **step 2** and for **step 3**. [2]
- (iii) What type of reaction is occurring in **step 2**? [1]

(b) Acrylic acid is manufactured industrially from the reaction of propene and oxygen gas.

- (i) Write a balanced equation for this reaction. [1]
- (ii) Propenal was isolated as an intermediate product in the reaction.
Draw the structure of propenal. [1]

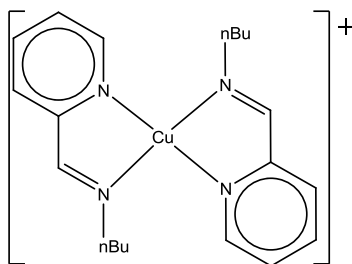
(c) Polyacrylate is used in environmentally-friendly detergents to remove calcium ions and magnesium ions in water.

In the manufacture of polyacrylate, acrylic acid was first converted into acrylic chloride, followed by reaction with an alcohol to form a monomer. Polyacrylate is formed when the monomer undergoes polymerisation.



- (i) Write a balanced equation for the conversion of acrylic acid into acrylic chloride. [1]
- (ii) Suggest the type of reaction occurring in the formation of the monomer from acrylic chloride. [1]
- (iii) Suggest how polyacrylate can remove magnesium ions from water through complex formation. [1]

- 1 (d) In the kinetic studies of polymerisation, *transition element-containing catalysts* were used. A copper(I)-containing catalyst is shown below.



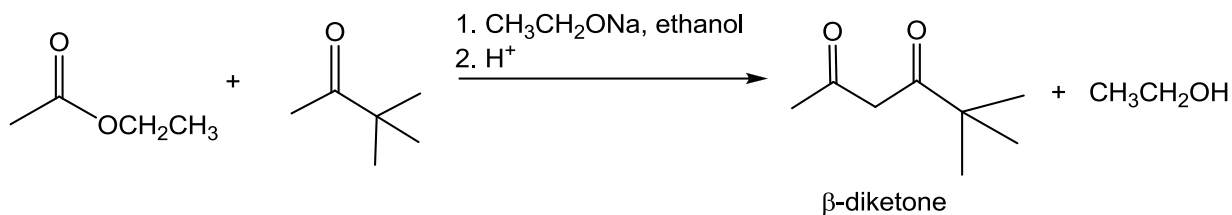
Cu(I)-nBuPCA catalyst

- (i) What is the co-ordination number of copper in the Cu(I)-nBuPCA catalyst? [1]
 - (ii) What is the electronic configuration of copper in Cu(I)-nBuPCA? [1]
 - (iii) Suggest whether copper in Cu(I)-nBuPCA catalyst can be classified as a *transition element*. [1]
- (e) Cu(I) undergoes disproportionation to form Cu and Cu(II).
- (i) Use relevant data from the *Data Booklet* to predict the spontaneity of this disproportionation reaction. [2]
 - (ii) Describe and explain what you would see when aqueous ammonia is added slowly to an aqueous solution of copper(II) chloride, until the aqueous ammonia is in excess. Write equations for any reactions that occur. [4]
 - (iii) Suggest an explanation for the difference in colour between $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{CuCl}_4]^{2-}$. [2]

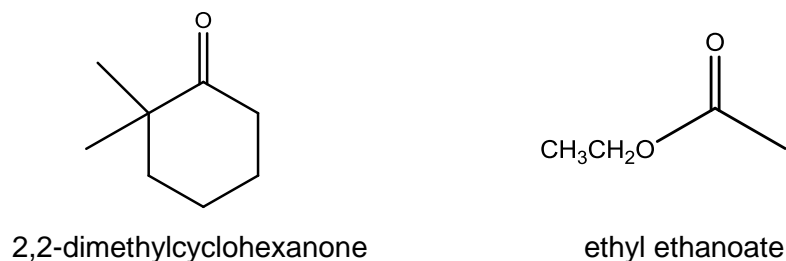
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- 2 In a Mixed Claisen Condensation Reaction, an ester and a ketone react to form a β -diketone.

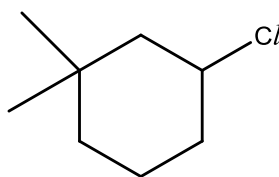


- (a) (i) Draw the β -diketone formed when 2,2-dimethylcyclohexanone reacts with ethyl ethanoate in the Mixed Claisen Condensation Reaction.



[1]

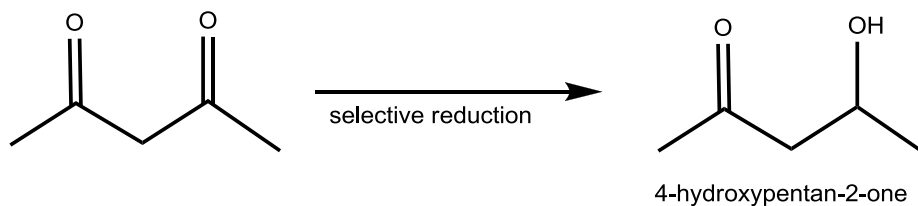
- (ii) In not more than 3 steps, propose the synthesis of 2,2-dimethylcyclohexanone from the following starting material.



[5]

- (b) Due to the presence of two ketone functional groups, β -diketones are a highly valuable substrate in several organic chemistry syntheses.

One of the many examples is selective reduction, in which only one of the ketone reduced.

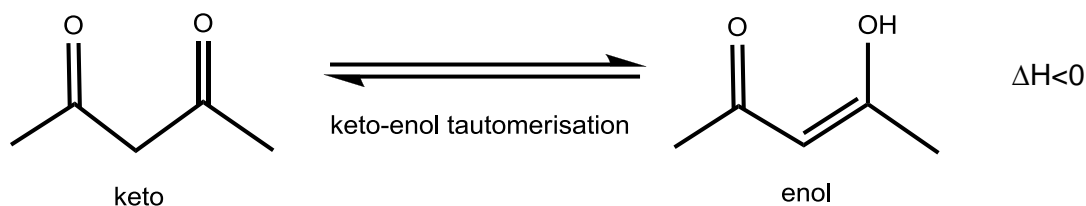


Draw the mechanism for the reaction between 4-hydroxypentan-2-one and HCN.

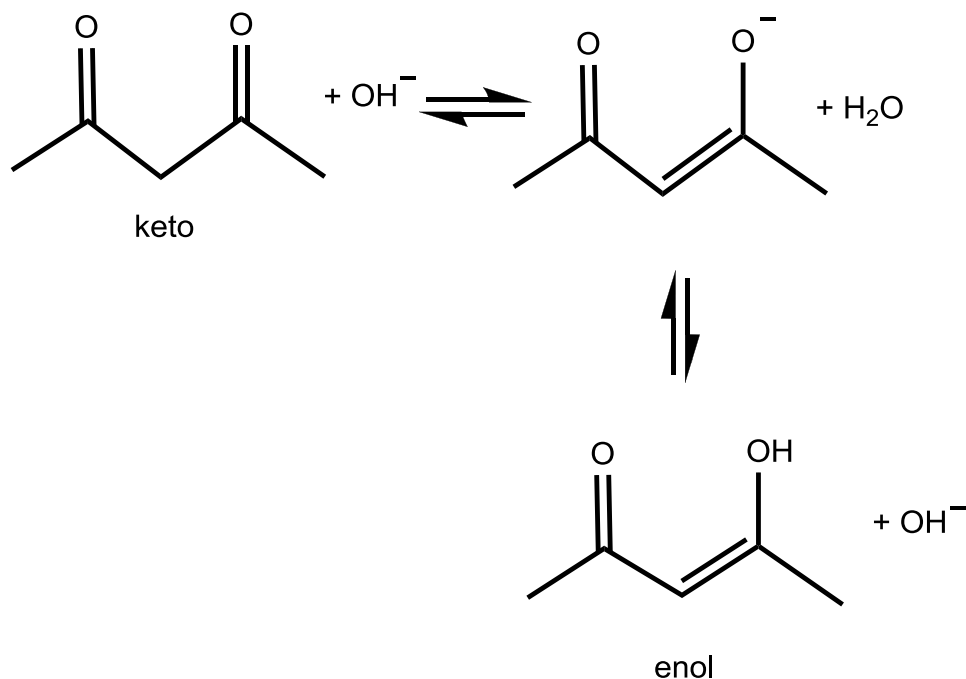
[3]

- 2 (c) β -diketones exist in equilibrium with a tautomeric form, known as an enol.

This is known as keto-enol tautomerisation. The keto-enol tautomerisation of pentan-2,4-dione is shown below.



- (i) Write an expression for K_c for the keto-enol tautomerisation of pentan-2,4-dione. [1]
- (ii) In the case of pentan-2,4-dione, 76% of the mixture exists as an enol at room temperature and pressure. Calculate a value for K_c . [1]
- (iii) Sketch a graph showing how the rates of the forward and reverse reactions change from the time pure keto is added to the time the reaction reaches equilibrium. Label your two lines clearly. [2]
- (d) The keto-enol tautomerisation is catalysed by the presence of an inorganic base, such as NaOH.



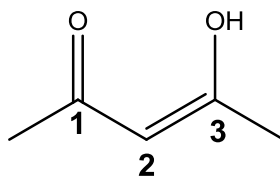
- (i) State how the presence of NaOH would affect the K_c , as calculated in (c)(ii). [1]
- (ii) On the same diagram in (c)(iii), show how the rates of the forward and reverse reactions change for the base catalysed keto-enol tautomerisation. Label your lines clearly. [1]
- (iii) Hence, explain the effect of NaOH on the reaction. [2]

[Turn Over]

- 2 (e) The enol form is more stable than the keto form due to two reasons

Reason I: Intramolecular hydrogen bonding

Reason II: Position of p orbitals



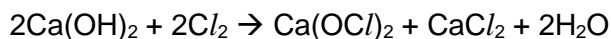
enol

- (i) Draw an appropriate diagram to show how **reason I** contributes to the stability of [1]
the enol form.
- (ii) State the hybridisation of the carbon atoms at positions **1**, **2** and **3**.
Hence, explain how **reason II** contributes to the stability of the enol form. [2]

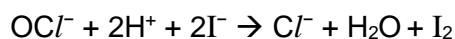
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- 3 (a)** Antiseptics and disinfectants are used to kill bacteria. The difference between antiseptics and disinfectants is that antiseptics are used on living skin and disinfectants are used on surfaces of objects.

Calcium hypochlorite, $\text{Ca}(\text{OCl})_2$, is often used to sanitise public swimming pools. It is produced by treating calcium hydroxide with chlorine gas.



- (i)** Write an equation for the decomposition of calcium hydroxide. [1]
- (ii)** Deduce whether calcium hypochlorite would decompose at a higher or lower temperature than calcium hydroxide. Explain your reasoning. [2]
- (iii)** In order to test the percentage purity of the calcium hypochlorite granules, 1 g of the calcium hypochlorite granules above was dissolved in water and the solution was then reacted with excess iodide in an acidic medium.



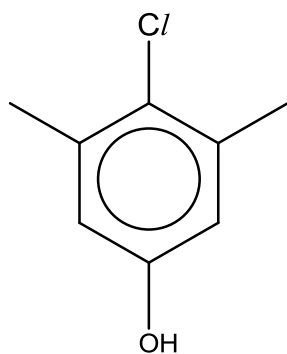
The resulting solution was then titrated with $0.500 \text{ mol dm}^{-3}$ sodium thiosulfate. 22.5 cm^3 of thiosulfate was required to reach the end-point.

Calculate the percentage purity of the granules. [2]

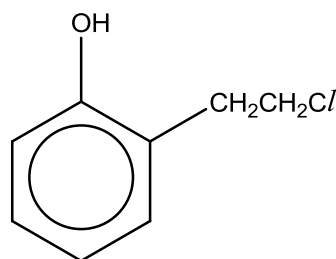
- (iv)** Commercially, calcium hypochlorite is available as granules. Using your answer in **(a)(iii)**, calculate the volume of chlorine gas (measured at room temperature and pressure) required to manufacture 1 kg of calcium hypochlorite granules. [2]

[Turn Over

- 3 (b) Chloroxylenol is commonly used in antibacterial soaps due to its disinfecting and sanitising properties. It is also responsible for the distinctive odour of Dettol. An isomer of chloroxylenol is compound **X**.



chloroxylenol



compound X

When hot ethanolic silver nitrate was added to chloroxylenol and compound **X** separately, the observations were different. State what you would observe for each compound and explain the difference in observations.

[3]

- (c) Compounds **A** and **B** are structural isomers of chloroxylenol. Both **A** and **B** give a violet colouration with neutral FeCl_3 .

A rotates plane-polarised light, but **B** does not. When **B** is treated with hot alcoholic sodium hydroxide, a compound of molecular formula $\text{C}_8\text{H}_8\text{O}$ is formed. When **A** is treated carefully with hot aqueous sodium hydroxide, compound **C**, $\text{C}_8\text{H}_{10}\text{O}_2$, is formed.

C reacts with hot concentrated potassium dichromate(VI) to form compound **D**.

C reacts with hot concentrated potassium manganate(VII) to form compound **E** and carbon dioxide gas.

D gives an orange precipitate with 2,4-dinitrophenylhydrazine, but **E** does not.

Suggest structures for **A** to **E**, and explain the observations described above.

[10]

[Total: 20]

- 4 The table below summarises the different types of acids found in various types of beverages.

Beverage	Acid	Formula	pK_{a1}	pK_{a2}	pK_{a3}
Beer	Carbonic	H_2CO_3	6.37	10.3	–
Fruit Juices	Malic	$HO_2CCH_2CH(OH)CO_2H$	3.46	5.10	–
Soda	Phosphoric	H_3PO_4	2.12	7.21	12.3

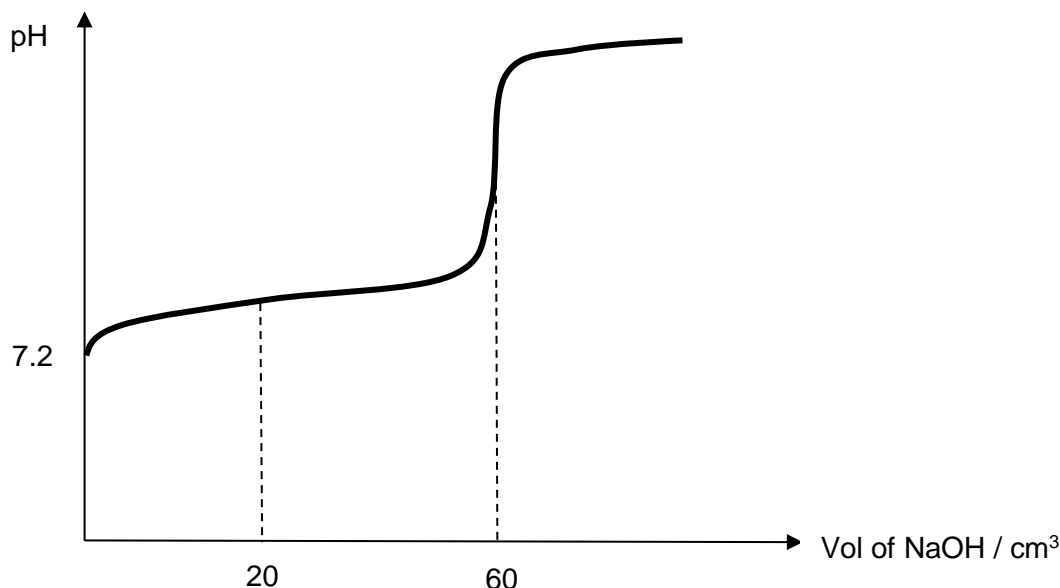
- (a) (i) Explain why the pK_{a1} of malic acid is so much lower than the pK_{a1} of carbonic acid. [2]
- (ii) Explain why the pK_{a3} of phosphoric acid is so much higher than the pK_{a2} of malic acid. [1]
- (b) (i) 50.0 cm^3 of 0.5 mol dm^{-3} aqueous H_3PO_3 was mixed with 30 cm^3 of excess aqueous NaOH. It was found that the temperature of the solution rose by $8.4\text{ }^\circ\text{C}$ after mixing. Calculate the enthalpy change of reaction per mole of $H_3PO_3(\text{aq})$.
- Given: Specific heat capacity of water = $4.18\text{ J g}^{-1}\text{ K}^{-1}$;
Density of water = 1.0 g cm^{-3} . [2]
- (ii) Hence, given that the enthalpy change of neutralisation of $HCl(\text{aq})$ by $NaOH(\text{aq})$ is -57.3 kJ mol^{-1} , suggest the basicity of H_3PO_3 . [1]
- (c) A medical student wanted to investigate the buffer solution in fluids for intravenous injection. He needed to prepare a buffer of pH 7.2. Of the pK_a values given in the table above, suggest a conjugate acid–base pair which is most suitable as the buffer solution. [1]

[Turn Over

- 4 (d) A student titrated 20 cm³ of the buffer sample in (c) containing an acid and its salt, with 0.1 mol dm⁻³ NaOH (aq) and obtained the titration curve below. The maximum buffer capacity is obtained when 20 cm³ of NaOH is added.

The equivalence point of the titration is obtained when 60 cm³ of aqueous sodium hydroxide is added.

[You may use HA and A⁻ to represent the species identified in (c) to answer part (d)].



- (i) Explain why the pH rises only slightly at the start of the titration when a small amount of sodium hydroxide is added. [1]
 - (ii) Determine the total amount of acid in the buffer. Hence, show that the ratio of concentrations of the [HA] and [A⁻] at the start of the titration is 3:1. [2]
 - (iii) Calculate the K_a of the acid at the start of the titration. [1]
- (e) An electrochemical cell is composed of two half-cells, namely the AgBr | Ag and Ag⁺ | Ag half-cells at 298K.



- (i) Using the data booklet and the half-equation of AgBr | Ag above, write the overall equation for the cell reaction and calculate the E^\ominus_{cell} . [2]

- 4 (e) (ii) The Nernst equation is used to calculate the voltage, E_{cell} , generated under non-standard conditions.

$$E_{cell} = E_{cell}^{\ominus} - \frac{RT}{nF} \ln \left(\frac{1}{K_{sp}} \right)$$

where n is the number of moles of electrons transferred per mole of equation, R is the molar gas constant, F is the Faraday constant and K_{sp} is the solubility product of AgBr.

When $E_{cell} = 0$, the system has achieved equilibrium.

Decide on a suitable value of n and hence, use your answer in (e)(i) and the Nernst equation to calculate the solubility product of AgBr at 298 K, stating its units. [3]

- (iii) Predict how the voltage of the cell, E_{cell} , will change when $\text{NH}_3(\text{aq})$ is added to the $\text{Ag}^+|\text{Ag}$ cell. [2]

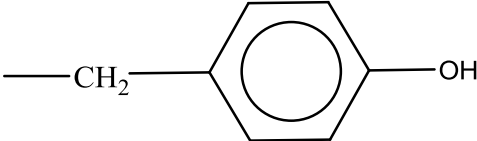
- (iv) Given that silver arsenate, Ag_3AsO_4 has a K_{sp} of 1.40×10^{-22} , show by calculation, if AgBr or Ag_3AsO_4 is the more soluble salt. [2]

[Total: 20]

[Turn Over]

- 5 About 10% of the mass of a chicken egg is made up of proteins. The main protein in egg whites is ovalbumin.

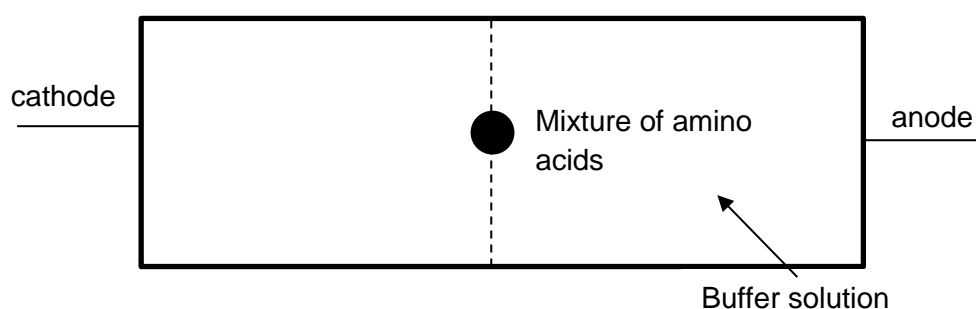
Three of the amino acids obtained from the complete hydrolysis of ovalbumin and their isoelectric points are given in the table below.

Amino acid	Formula of side chain	Isoelectric point
Aspartic acid (asp)	$-\text{CH}_2\text{CO}_2\text{H}$	2.77
Lysine (lys)	$-(\text{CH}_2)_4\text{NH}_2$	9.74
Tyrosine (tyr)		5.66

- (a) State how ovalbumin could be hydrolysed in the laboratory to form the amino acids in the table above. [1]

- (b) (i) Define the term isoelectric point. [1]

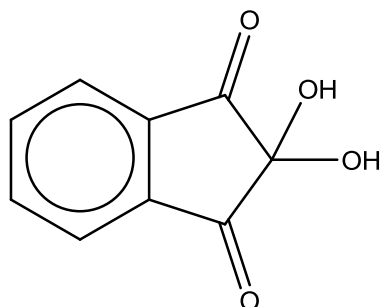
- (ii) Electrophoresis is an electrolytic method used to separate amino acids based on their isoelectric points. A simplified diagram of an electrophoresis set-up is shown below. Depending on the pH of the buffer solution used, the amino acids will move differently. The positions of the amino acids are ascertained by spraying the solution with ninhydrin solution. The colourless amino acid spots will turn blue.



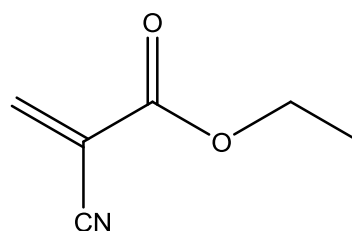
Using data from the table above, explain how electrophoresis can be used to separate and identify the constituent amino acids in a mixture of aspartic acid, lysine and tyrosine in a buffer solution of pH 8. You should include the structural formulae of the three amino acids at pH 8 in your answer. [3]

5 (c) With reference to protein structure, explain why egg white coagulates when cooked. [2]

(d) Besides reacting with amino acids, ninhydrin is also commonly used in fingerprint analysis in criminal investigations. Another method to analyse fingerprints is called cyanoacrylate (Super Glue) fuming. One common cyanoacrylate used for this purpose is ethyl cyanoacrylate. The structures of ninhydrin and cyanoacrylate are given below.



ninhydrin



ethyl cyanoacrylate

Suggest a chemical test that could be used to distinguish ninhydrin and ethyl cyanoacrylate from each other. You should state what you would observe for each compound in the test. [2]

(e) Besides being rich in protein, eggs are also consumed widely as it contains vitamins and minerals needed on a daily basis. An example of a key nutrient that can be obtained from eating eggs is phosphorus, which is as important as calcium in building strong bones in our body.

(i) Describe the reaction of phosphorus(III) oxide, P_4O_6 , with water. Include the pH value of the resulting solution, and write an equation for the reaction that occurs. [2]

(ii) Write an equation to illustrate the acid-base nature of phosphorus(V) oxide, P_4O_{10} . [1]

[Turn Over]

- 5 (f) Eggs are also rich in iodine which is a key component of hormones in the thyroid gland. Iodine deficiency results when we do not consume enough iodine in our diet. In order to combat iodine deficiency, table salt is mixed with various salts of iodine in the production of iodised salts.

Potassium iodate, KIO_3 , is often used in iodised salts. With the aid of an equation, describe how potassium iodate can be prepared using iodine as a starting material. [2]

- (g) Describe what you would see if concentrated sulfuric acid is added to separate samples of solids KBr and KI . Suggest an explanation for the differences in reaction, and write equations for the reactions that occurred. [4]

- (h) Iodine has many isotopes. Only two of its isotopes are used in medicine, such as radiotherapy and imaging. In order to identify the mass of these two isotopes, they were first ionised to form singly-charged ions of +1 charge and passed through an electric field of constant strength. Their angles of deflection, along with a reference sample of helium nucleus, ${}^4_2\text{He}$, were recorded in the table below.

	Angle of deflection
Isotope X	1.07 °
Isotope Y	1.14 °
Helium nucleus, ${}^4_2\text{He}$	70.1 °

Calculate the mass of each isotope, giving your answer to the nearest whole number.

[2]

[Total: 20]

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