**CATHOLIC JUNIOR COLLEGE**
**JC2 PRELIMINARY EXAMINATIONS**
**Higher 2**

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# CHEMISTRY

**9647/03**

**Paper 3 Free Response**

**Thursday 29 August 2013**
**2 hours**

Additional Materials: Data Booklet
Answer Paper

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## READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark blue or black pen on both sides of the paper. **[PILOT FRIXION ERASABLE PENS ARE NOT ALLOWED]**
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. Write your answers on the answer paper provided.

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

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

At the end of the examination, fasten all your work securely together.

This document consists of **13** printed pages and **1** blank page.

**[Turn over**

Answer any **four** questions.

**1.** *Use of the Data Booklet is relevant to this question*.

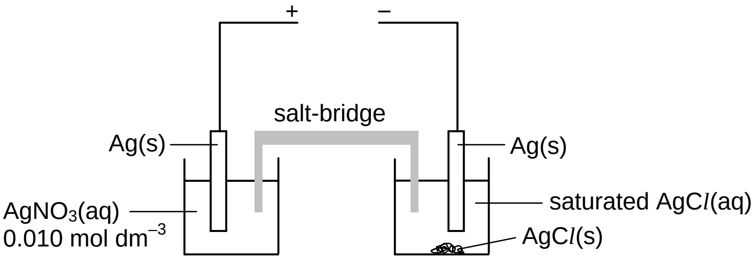
**(a)** **(i)** Define the term *standard electrode potential*, $E^\ominus$.

**(ii)** For the element $M$ (where $M$ is Co or Ni), suggest an explanation for the difference in the $E^\ominus$ values between

$$M^{2+} + 2e^- \rightleftharpoons M \qquad \text{and} \qquad [M(NH_3)_6]^{2+} + 2e^- \rightleftharpoons M + 6NH_3$$

**[4]**

**(b)** A student set up the following electrochemical cell.



**(i)** What device is used to measure the e.m.f. of the cell?

**(ii)** Name a compound that could be used to prepare a workable salt-bridge for this cell and explain how it helps to maintain electrical neutrality.

**(iii)** Amongst other factors, the electrode potential is dependent on the temperature and the concentration of the ions.

At 298 K, the reduction potential, $E$, of $Ag^+(aq)/Ag(s)$ can be obtained from the equation

$$E = E^\ominus + 0.059 \log_{10} [Ag^+(aq)]$$

The student found that the e.m.f. of the cell was +0.17 V at 298 K.

Calculate the reduction potential, $E$, of each half-cell and hence the concentration of $Ag^+(aq)$ ions in the saturated $AgCl(aq)$.

[Given: $E^\ominus$ of $Ag^+(aq)/Ag(s)$ = +0.80 V at 298 K]

**(iv)** State and explain the effect on the cell e.m.f. of adding a small volume of $NH_3(aq)$ to the $Ag^+(aq)/Ag(s)$ half-cell.

**[9]**

**(c)** Putrescine (1,4-diaminobutane) is a foul-smelling compound found in rotting flesh and in "bad breath". It is produced by the breakdown of amino acids in living and dead organisms.

Like ammonia, putrescine is a weak base. While ammonia has a p$K_b$ value of 4.74, putrescine has two p$K_b$ values which are found to be 3.20 (p$K_{b1}$) and 4.65 (p$K_{b2}$) respectively.

**(i)** Explain why putrescine is a stronger base than ammonia.

**(ii)** Write equations to represent $K_{b1}$ and $K_{b2}$ of putrescine. Hence explain why p$K_{b1}$ of putrescine is smaller than p$K_{b2}$.

A chemist proposed the following synthetic routes to synthesise putrescine.

Route **1**:

$$CH_3CH_2CH_2CH_2Cl \xrightarrow{Cl_2\text{, uv light}} ClCH_2CH_2CH_2CH_2Cl$$

Route **2**:

$$ClCH_2CH_2CH_2CH_2Cl \xrightarrow[\text{heat in sealed tube}]{\text{conc. }NH_3\text{ (excess)}} \underset{\textit{putrescine}}{H_2NCH_2CH_2CH_2CH_2NH_2}$$

**(iii)** By considering the type of reaction taking place, comment briefly on the yield of putrescine synthesised via route **1**.

**(iv)** Route **2** is found to give only 10 % yield of putrescine.

Suggest another synthetic route to obtain a higher yield of putrescine, starting from ethene. State clearly the reagents and conditions required.

**[7]**

**[Total: 20]**

**2.** **(a)** Sodium hypochlorite (NaC*l*O) is a chemical commonly found in bleaching agents. It was developed in the 18th century and was initially used to bleach cotton. It became a popular compound for bleaching clothes when it was found that sodium hypochlorite can remove stains from clothes at room temperature. Sodium hypochlorite is also used as a disinfectant in water treatment and in swimming pools. As compared to chlorine which can cause respiratory problems, sodium hypochlorite is a safer choice of disinfectant.

The original method of producing sodium hypochlorite involved passing chlorine gas through a solution of sodium carbonate. The addition of chlorine to water results in the equilibrium shown below.

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^-$$

**(i)** Some chlorine gas was bubbled through 100 $cm^3$ of water at 25 °C and allowed to reach equilibrium. The initial concentration of chlorine was 0.10 mol $dm^{-3}$. At equilibrium, the concentration of chlorine decreased by 30 %.

Write an expression for $K_c$ for the above equilibrium and use the data provided to calculate its value. You may assume that the $[H_2O]$ is 55.5 mol $dm^{-3}$ throughout.

**(ii)** A typical household bleach contains a mixture of sodium hypochlorite, calcium hypochlorite and sodium hydroxide.

Suggest why sodium hydroxide is added to household bleach.

**(iii)** HOC*l* is a weak acid ($pK_a = 7.5$) which partially dissociates at a pH range of 5 to 8, thus giving rise to the equilibrium below.

$$Cl_2 + H_2O \rightleftharpoons 2H^+ + OCl^- + Cl^-$$

Using this information and your answer in **(a)(i)**, calculate the $K_c$ value for this equilibrium. Include its units in your answer.

**(iv)** A more effective method to manufacture sodium hypochlorite is through the reaction of chlorine gas with sodium hydroxide.

Write an equation for this reaction. Explain why the resulting mixture has to be kept at temperatures below 40 °C.

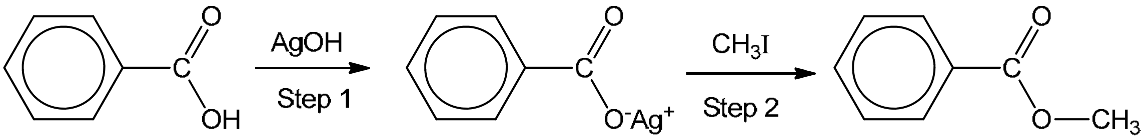
**[9]**

**(b)** Elements ***X***, ***Y*** and ***Z*** are found in periods 2 and 3 of the Periodic Table. The proton numbers of these elements fall within the range of 4 to 15.

- Element ***X*** reacts readily with water. 1 mol of the resulting compound is neutralised by 1 mol of ethanoic acid.
- The oxide of ***Y*** is amphoteric but the chloride of ***Y*** is acidic. 1 mol of the chloride of ***Y*** reacts with 2 mol of ammonia to give a single compound.
- Element ***Z*** forms two chlorides, $\boldsymbol{Z}\mathrm{C}l_{\mathrm{a}}$ and $\boldsymbol{Z}\mathrm{C}l_{\mathrm{b}}$. 1 mol of $\boldsymbol{Z}\mathrm{C}l_{\mathrm{a}}$ reacts with water in the cold to give two chlorine-containing products in the mole ratio of 1: 2.

Identify ***X***, ***Y*** and ***Z***. Explain your reasoning and give relevant equations to support your answer. **[5]**

**(c)** Benzoic acid can react with alkyl halides to form esters.

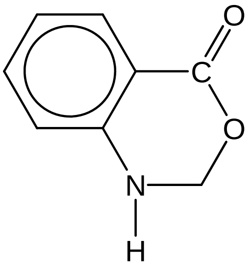


**(i)** Why is it necessary to react benzoic acid with silver(I) hydroxide in Step 1?

**(ii)** What will be observed at the end of step 2?

**(iii)** Describe the mechanism for the reaction that occurred in step 2.

**(iv)** A carboxylic acid reacted with silver(I) hydroxide followed by dibromomethane to give the following product.



Deduce the structure of this carboxylic acid.

**[6]**

**[Total: 20]**

**3.** During any vigorous physical activity**,** sweating is the primary means by which the body maintains its core temperature of 37 °C. However, this will result in the loss of body fluid and electrolytes like chloride, phosphate, calcium, magnesium, sodium and potassium ions. If the levels of electrolytes are not adequately replenished, this can potentially lead to dehydration followed eventually by heat stroke if the percentage bodyweight lost as sweat exceeds 10 % or more.

An isotonic sports drink contains electrolytes, which aid fluid absorption, and carbohydrates that provide the necessary fuel for the body to maintain peak performance and enhance post exercise recovery.

**(a)** Magnesium and calcium ions are found in many isotonic drinks. A student decides to investigate the amount of magnesium ion in a certain brand of isotonic drink by precipitating the ion with aqueous ammonia.

| | **$K_{sp}$ / mol$^3$ dm$^{-9}$** | **Decomposition Temperature / °C** |
|---|---|---|
| $Mg(OH)_2$ | $1.5 \times 10^{-11}$ | 350 |
| $Ca(OH)_2$ | $4.7 \times 10^{-6}$ | 580 |

**(i)** Given that the base dissociation constant, $K_b$, of ammonia is $1.0 \times 10^{-5}$ mol dm$^{-3}$, calculate the [OH$^-$] in $1.0 \times 10^{-3}$ mol dm$^{-3}$ aqueous ammonia.

**(ii)** The student discovered that precipitation occurred when equal volumes of the isotonic drink and $2.0 \times 10^{-3}$ mol dm$^{-3}$ aqueous ammonia were mixed together.

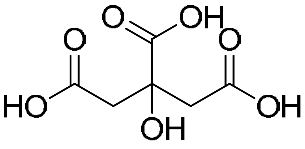
Using your answer in **(a)(i)**, determine the minimum concentration of magnesium ion in the isotonic drink. Hence, find the minimum mass, in milligrams, of magnesium ions in 500 cm$^3$ of the isotonic drink.

**(iii)** Write a balanced equation, with state symbols, for the thermal decomposition of magnesium hydroxide.

The data given in the table above shows that calcium hydroxide has to be heated to a higher temperature before it decomposes. Explain why.

**[7]**

**(b)** Another two key ingredients commonly found in isotonic drinks are citric acid and sodium citrate. The structure of citric acid is given below:



citric acid

**(i)** There are three p$K_a$ values associated with citric acid: 3.1, 4.8 and 6.4. Suggest the major species present in solutions of citric acid at the following pH values.

- pH 2
- pH 4
- pH 6

**(ii)** Write two relevant equations to show how a solution containing citric acid and sodium citrate is able to regulate pH within a very specific range in isotonic drinks. You may use HA to represent citric acid and NaA to represent sodium citrate.

**(iii)** Using the information given in **(b)(i)**, calculate the pH of the resulting solution when 35.0 $cm^3$ of 0.100 mol $dm^{-3}$ of citric acid is added to 25.0 $cm^3$ of 0.100 mol $dm^{-3}$ of sodium hydroxide.

**[7]**

**(c)** Citric acid can be dehydrated to give a mixture of two isomeric compounds **J** and **K** with the molecular formula $C_6H_6O_6$. When one of the isomers is heated gently, a cyclic compound **L**, $C_6H_4O_5$, is formed.

**L** is a 6-membered ring and does not react with 2,4-dinitrophenylhydrazine. **L** decolourises $Br_2(aq)$. 1 mol of **L** reacts with sodium to give ½ mol of hydrogen gas.

**(i)** Draw the displayed formulae of the two isomers **J** and **K**, and state the type of isomerism shown.

**(ii)** Suggest the structure for compound **L** and identify which isomer, **J** or **K**, produces **L**. Write equations for all reactions, and explain the observations.

**[6]**

**[Total: 20]**

**4.** This question is about reactions involving propanone.

**(a)** In an experiment to determine the enthalpy change of combustion of propanone, $\Delta H_c$, the fuel was burned under a copper can containing 250 g of water. It was found that the temperature of the water rose by 23.5 $^oC$ after 1.0 g of propanone had been burned. The heat transfer was known to be 80 % efficient.

**(i)** Define enthalpy change of combustion of propanone, $\Delta H_c$.

**(ii)** Calculate the $\Delta H_c$ of propanone. Ignore the heat capacity of the copper can, and use 4.18 J $g^{-1}$ $K^{-1}$ for the heat capacity of water.

**[4]**

**(b)** The Wacker oxidation is an industrial process where ketones can be synthesised by the palladium-catalysed oxidation of alkene with oxygen. Propanone can be made from propene as shown below.

$$CH_3CH{=}CH_2 + \tfrac{1}{2}O_2 \rightarrow CH_3COCH_3$$

**(i)** Using relevant bond energy data from the *Data Booklet*, calculate the enthalpy change for the reaction.

**(ii)** How would you expect the enthalpy changes of the reaction to differ from that calculated in **(b)(i)** if pent-2-ene was used to synthesise pentanone?

**(iii)** By considering the entropy and enthalpy change during the reaction, explain why the reaction cannot be carried out at very high temperatures.

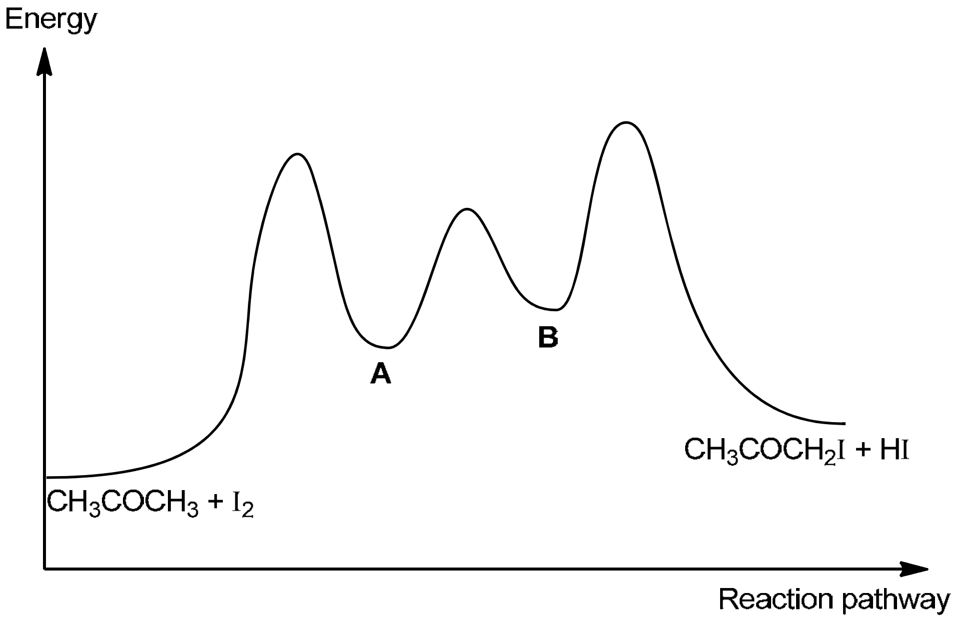
**(iv)** The enthalpy change of formation of water and carbon dioxide are –289 and –394 kJ $mol^{-1}$ respectively. With the aid of an energy cycle, use these values and your answer in **(b)(i)** to calculate the enthalpy change of formation of propene.

**[7]**

**(c)** Propanone and iodine reacts in an acidic medium according to the equation.

$$CH_3COCH_3 + I_2 \xrightarrow{H^+} CH_3COCH_2I + HI$$

The energy profile diagram of the reaction is as shown.



**A** is formed when propanone undergoes a rearrangement reaction without the loss of any atoms. **A** can react with sodium metal but not with 2,4-dinitrophenylhydrazine. **B** is formed when **A** undergoes electrophilic addition with $I_2$.

**(i)** Using the information above, suggest an equation for each step of the mechanism for the reaction between propanone and iodine, showing clearly the structures of compounds **A** and **B**. State which step in the mechanism is the slow step. You are not required to use curly arrows to show movement of electrons.

**(ii)** $H^+$ ions functions as a *homogenous catalyst* in this reaction.

Explain what is meant by *homogenous catalyst.*

**(iii)** Suggest **two** *other* reactions of propanone, one involving a homogeneous catalyst and the other, involving a heterogeneous catalyst. In each case, state clearly the identity of the catalyst and write an equation to represent the reaction.

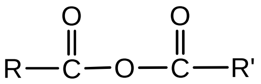
**(iv)** Draw the structures of all organic compounds formed when the reaction between propanone and iodine is carried out in hot aqueous sodium hydroxide instead.

**[9]**

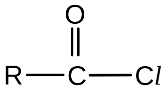
**[Total: 20]**

**5.** This question involves carboxylic acids and its derivatives.

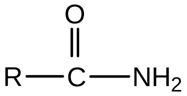
**(a)** Carboxylic acids can be used to form a number of derivatives. For example,


$R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R'$

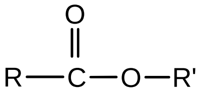
acid anhydride


$R-\overset{\overset{O}{\|}}{C}-Cl$

acyl chloride

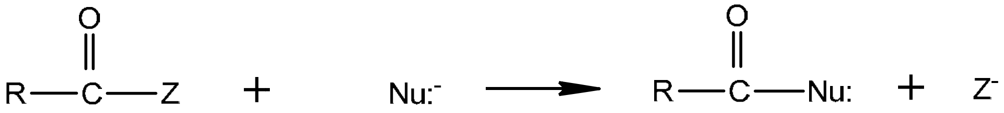

$R-\overset{\overset{O}{\|}}{C}-NH_2$

amide


$R-\overset{\overset{O}{\|}}{C}-O-R'$

ester

Carboxylic acid and its derivatives tend to undergo the following reaction:


$$R-\overset{\overset{O}{\|}}{C}-Z \quad + \quad Nu:^- \longrightarrow R-\overset{\overset{O}{\|}}{C}-Nu: \quad + \quad Z^-$$

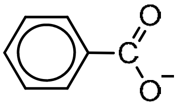
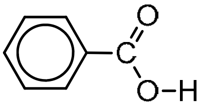
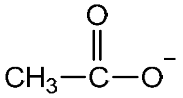
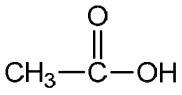
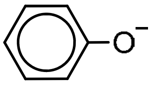
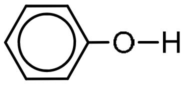
The reaction mechanism consists of two steps. The first step is a slow step. It involves an attack by a nucleophile, $Nu^-$, at the electron-deficient carbonyl carbon, forming an unstable tetrahedral intermediate anion. This is then followed by the loss of $Z^-$ from the intermediate.

**(i)** Based on the description of the mechanism given above, suggest the type of reaction taking place.

**(ii)** Write the rate equation for the above reaction.

The susceptibility of carboxylic acid derivatives, RCOZ, to attacks by nucleophiles can be determined by the relative basicity of the nucleophile and the leaving group, $Z^-$.

The table below gives the p$K_a$ values of some acids.

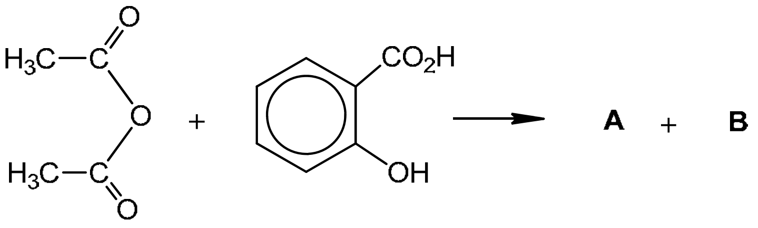
| **Conjugate base** | **Acid** | **p$K_a$** |
|---|---|---|
| $Cl^-$ | H–Cl | - |
|  |  | 4.2 |
|  $CH_3-\overset{\overset{O}{\|}}{C}-O^-$ |  $CH_3-\overset{\overset{O}{\|}}{C}-OH$ | 4.7 |
|  |  | 9.9 |
| $OH^-$ | H–OH | 16 |
| $CH_3O^-$ | H–$OCH_3$ | 17 |
| $NH_2^-$ | H–$NH_2$ | 35 |

**(iii)** State the relationship between the relative strength of an acid and its conjugate base.

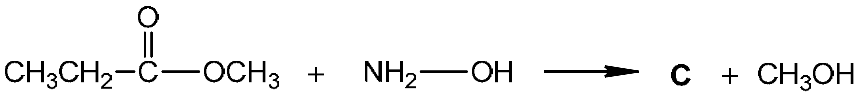
**(iv)** Acyl chloride reacts more readily with $CH_3O^-$ than with $C_6H_5O^-$. By considering the data above and your answer in **(a)(iii)**, explain why this is so.

**(v)** Hence, identify the products **A** to **C** for the following reactions. You may assume that the reactants are in equimolar ratio.

**I**



**II**



$$CH_3CH_2-\overset{O}{\overset{\|}{C}}-OCH_3 + NH_2-OH \longrightarrow \mathbf{C} + CH_3OH$$

**[7]**

**(b)** Fibrous protein has polypeptide chains arranged parallel to one another along a single axis cross-linked to give long fibres (twisted helices) or sheets (pleated sheets). Collagen is a fibrous protein that contains three polypeptide chains wound around one another.

With reference to collagen, describe and explain what is meant by the terms *primary, secondary* and *tertiary* structures of proteins. In each case you should state the type of bonding or interaction involved. **[3]**

**(c)** Gelatin can be derived from collagen.

**(i)** Complete hydrolysis of a protein produces individual amino acids, but partial hydrolysis can break the protein down into dipeptide or tripeptide fragments.

Using the same 3-letter abbreviations as below, write out the amino acid sequence of a portion of the gelatin polypeptide containing nine amino acids that could produce the following fragments on hydrolysis.

gly-pro-arg

pro-gly-pro

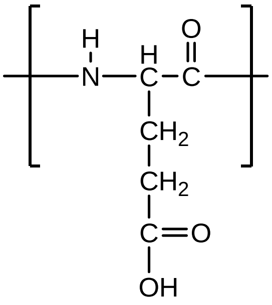
glu-pro-gly

arg-gly-glu

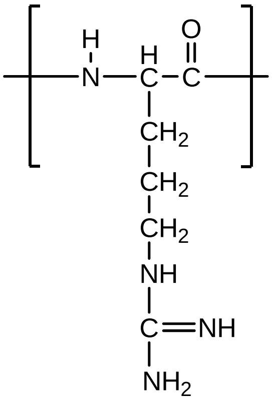
ala-gly-pro

**(ii)** Gelatin is produced by the partial denaturation of collagen. The collagen is treated with either dilute acid or base where the arginine residue or the glutamic acid residue will undergo some changes that lead to denaturation.

The structures of arginine residue and glutamic acid residue are as follows.



glutamic acid residue



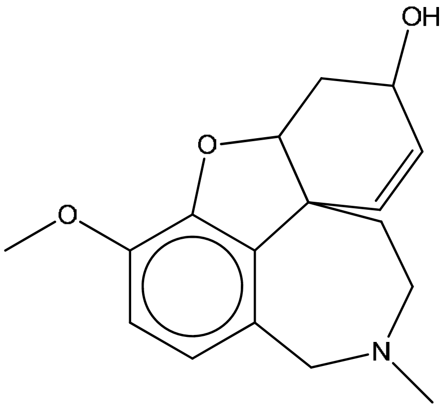
arginine residue

**I** What is meant by the term *denaturation*?

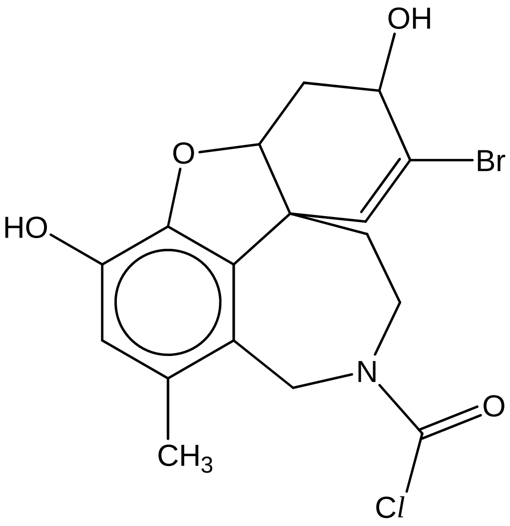
**II** Sketch a diagram to show the interaction between glutamic acid residues and arginine residues in collagen, taking into account the forms that the amino acid residues exist in at pH 7. Hence, suggest how an acid might interact with collagen to bring about denaturation.

**[4]**

**(d)** Galanthamine is a drug used to treat Alzheimer's disease. It can be extracted from snowdrops. The structures of galanthamine and its derivative (**compound A**) are shown below.



Galanthamine



**Compound A**

**(i)** Draw the structures of all products obtained when **compound A** is treated with

**I** hot acidified potassium dichromate(VI)

**II** hot aqueous sodium hydroxide

**(ii)** Suggest a simple chemical test which allows you to distinguish between galanthamine and **compound A**. You should state clearly the reagents and conditions used and the observations you would expect to make.

**[6]**

**[Total: 20]**

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**JC2 PRELIMINARY EXAMINATIONS**
**Higher 2**

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At the end of the examination, fasten all your work securely together.

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This document consists of **26** printed pages and **0** blank page.

Answer any **four** questions.

**1.** *Use of the Data Booklet is relevant to this question*.

**(a)** **(i)** Define the term *standard electrode potential*, $E^{\ominus}$.

***Standard electrode potential*, $E^{\ominus}$, is defined as the potential difference between a standard hydrogen electrode and a metal (the electrode) which is immersed in a solution containing metal ions at 1 mol dm$^{-3}$ concentration at 25 °C and 1 atmospheric pressure.**

[***values of standard conditions should be given***]

**(ii)** For the element *M* (where *M* is Co or Ni), suggest an explanation for the difference in the $E^{\ominus}$ values between

$$M^{2+} + 2e^{-} \rightleftharpoons M \qquad \text{and} \qquad [M(NH_3)_6]^{2+} + 2e^{-} \rightleftharpoons M + 6NH_3$$

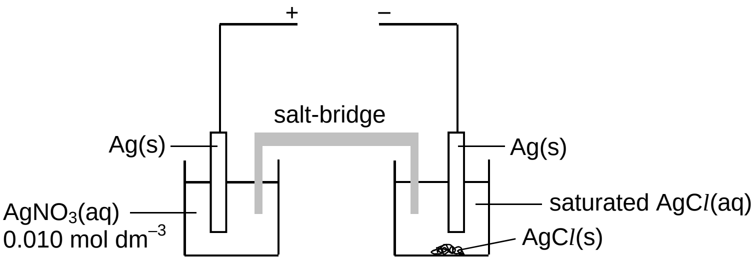
**[4]**

| | | | $E^{\ominus}$/V |
|---|---|---|---|
| | $Co^{2+}(aq) + 2e^{-}$ | $\rightleftharpoons$ Co(s) | –0.28 |
| | $[Co(NH_3)_6]^{2+} + 2e^{-}$ | $\rightleftharpoons$ $Co + 6NH_3$ | –0.43 |
| OR | $Ni^{2+}(aq) + 2e^{-}$ | $\rightleftharpoons$ Ni(s) | –0.25 |
| | $[Ni(NH_3)_6]^{2+} + 2e^{-}$ | $\rightleftharpoons$ $Ni + 6NH_3$ | –0.51 |

**$E^{\ominus}$ of $[M(NH_3)_6]^{2+}/M$ is more negative than that of $[M(H_2O)_6]^{2+}/M$.**

**This is because as $H_2O$ ligands in the aquated ions are replaced by the stronger $NH_3$ ligands, the +2 oxidation state of *M* is stabilised and this makes the metal more reducing, or its ion less oxidising.**

**(b)** A student set up the following electrochemical cell.



**(i)** What device is used to measure the e.m.f. of the cell?

**high-resistance voltmeter.**

**(ii)** Name a compound that could be used to prepare a workable salt-bridge for this cell and explain how it helps to maintain electrical neutrality.

**salt bridge can be prepared by using $KNO_3$(aq) or $NaNO_3$(aq).**

**$K^+$ (or $Na^+$) ions leave the salt bridge into LHS half-cell (where $Ag^+$ is reduced to Ag) to 'balance' the loss of positively charged $Ag^+$ ions;**

**$NO_3^-$ ions leave the salt bridge into RHS half-cell (where Ag is oxidised to $Ag^+$) to 'balance' the increase in positively charged $Ag^+$ ions.**

**(iii)** Amongst other factors, the electrode potential is dependent on the temperature and the concentration of the ions.

At 298 K, the reduction potential, *E*, of $Ag^+$(aq)/Ag(s) can be obtained from the equation

$$E = E^\ominus + 0.059 \log_{10} [Ag^+(aq)]$$

The student found that the e.m.f. of the cell was +0.17 V at 298 K.

Calculate the reduction potential, *E*, of each half-cell and hence the concentration of $Ag^+$(aq) ions in the saturated AgC*l*(aq).

[Given: $E^\ominus$ of $Ag^+$(aq)/Ag(s) = +0.80 V at 298 K]

**$Ag^+$(aq)/Ag(s) half-cell, $E_{red} = E^\ominus + 0.059 \log_{10} [Ag^+(aq)]$**

**$= +0.80 + 0.059 \log_{10} (0.010)$**

**$= +0.682$ V**

**Since e.m.f. of cell = +0.17 V, and $E_{cell} = E_{red} - E_{oxid}$**

**$\therefore\ E_{oxid} = E_{red} - E_{cell}$**

**$= +0.682 - 0.17 = +0.512$ V**

**AgC*l*(aq)/Ag(s) half-cell, $E_{oxid} = E^\ominus + 0.059 \log_{10} [Ag^+(aq)]$**

**$+0.512 = +0.80 + 0.059 \log_{10} [Ag^+(aq)]$**

**$\therefore\ [Ag^+(aq)] = 1.31 \times 10^{-5}$ mol dm$^{-3}$**

**(iv)** State and explain the effect on the cell e.m.f. of adding a small volume of $NH_3$(aq) to the $Ag^+$(aq)/Ag(s) half-cell.

**[9]**

**$Ag^+ + e^- \rightleftharpoons Ag$;  $E = +0.682$ V**
**$Ag^+ + NH_3 + H_2O \rightarrow AgOH(s) + NH_4^+$ or $Ag^+ + 2NH_3 \rightarrow [Ag(NH_3)_2]^+$**

**$NH_3$(aq) reacts with $Ag^+$(aq) to form AgOH ppt (or $[Ag(NH_3)_2]^+$ complex ions). Hence, $[Ag^+]$ decreases which causes the equilibrium position of above equilibrium reaction to shift to LHS and so, electrode potential, $E(Ag^+/Ag)$, becomes less positive; i.e. $E_{red} < +0.682$ V.**

**(c)** Putrescine (1,4-diaminobutane) is a foul-smelling compound found in rotting flesh and in "bad breath". It is produced by the breakdown of amino acids in living and dead organisms.

Like ammonia, putrescine is a weak base. While ammonia has a p$K_b$ value of 4.74, putrescine has two p$K_b$ values which are found to be 3.20 (p$K_{b1}$) and 4.65 (p$K_{b2}$) respectively.

**(i)** Explain why putrescine is a stronger base than ammonia.

**in putrescine - presence of electron-donating alkyl group increases the electron density on the N atom, making the lone pair on the N atom more available to accept protons.**

**(ii)** Write equations to represent $K_{b1}$ and $K_{b2}$ of putrescine. Hence explain why p$K_{b1}$ of putrescine is smaller than p$K_{b2}$.

$$H_2N(CH_2)_4NH_2 + H_2O \overset{K_{b1}}{\rightleftharpoons} H_2N(CH_2)_4NH_3^+ + OH^- \text{ -------- equation 1}$$

$$H_2N(CH_2)_4NH_3^+ + H_2O \overset{K_{b2}}{\rightleftharpoons} H_3\overset{+}{N}(CH_2)_4NH_3^+ + OH^- \text{ -------- equation 2}$$

**Since it is easier to protonate a neutral molecule (equation 1) than to protonate a positively charged ion (equation 2), $K_{b1}$ is larger than $K_{b2}$.**

**Hence, p$K_{b1}$ (= –log$_{10}$ $K_{b1}$) is smaller than p$K_{b2}$.**

A chemist proposed the following synthetic routes to synthesise putrescine.

Route **1**:

$$CH_3CH_2CH_2CH_2Cl \xrightarrow{Cl_2\text{, uv light}} ClCH_2CH_2CH_2CH_2Cl$$

Route **2**:

$$ClCH_2CH_2CH_2CH_2Cl \xrightarrow[\text{sealed tube}]{\text{conc. } NH_3 \text{ (excess)}} \underset{\textit{putrescine}}{H_2NCH_2CH_2CH_2CH_2NH_2}$$

**(iii)** By considering the type of reaction taking place, comment briefly on the yield of putrescine synthesised via route **1**.

**Reaction 1 gives a poor yield since free-radical substitution reaction may occur at any of the C–H bonds and so, many different substitution products are obtained.**

**(iv)** Route **2** is found to give only 10 % yield of putrescine.

Suggest another synthetic route to obtain a higher yield of putrescine, starting from ethene. State clearly the reagents and conditions required.

**[7]**

$$\begin{tikzcd}
CH_2{=}CH_2 \arrow[r, "Cl_2\text{ (in }CCl_4\text{)}", "\text{in the dark}"'] & ClCH_2CH_2Cl \arrow[d, "\text{KCN (ethanol)}", "\text{heat under reflux}"'] \\
 & N{\equiv}CCH_2CH_2C{\equiv}N \arrow[d, "H_2\text{ / Pt}", "\text{heat}"'] \\
 & \underset{\textit{putrescine}}{H_2NCH_2CH_2CH_2CH_2NH_2}
\end{tikzcd}$$

**[Total: 20]**

**2.** **(a)** Sodium hypochlorite (NaC*l*O) is a chemical commonly found in bleaching agents. It was developed in the 18th century and was initially used to bleach cotton. It became a popular compound for bleaching clothes when it was found that sodium hypochlorite can remove stains from clothes at room temperature. Sodium hypochlorite is also used as a disinfectant in water treatment and in swimming pools. As compared to chlorine which can cause respiratory problems, sodium hypochlorite is a safer choice of disinfectant.

The original method of producing sodium hypochlorite involved passing chlorine gas through a solution of sodium carbonate. The addition of chlorine to water results in the equilibrium shown below.

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^-$$

**(i)** Some chlorine gas was bubbled through 100 cm$^3$ of water at 25 °C and allowed to reach equilibrium. The initial concentration of chlorine was 0.10 mol dm$^{-3}$. At equilibrium, the concentration of chlorine decreased by 30 %.

Write an expression for $K_c$ for the above equilibrium and use the data provided to calculate its value. You may assume that the [$H_2O$] is 55.5 mol dm$^{-3}$ throughout.

$$K_c = \frac{[H^+][Cl^-][HOCl]}{[Cl_2][H_2O]}$$

| | $Cl_2$ | $H_2O$ | HOC*l* | $Cl^-$ | $H^+$ |
|---|---|---|---|---|---|
| **Initial conc/ mol dm$^{-3}$** | **0.10** | **55.5** | **0** | **0** | **0** |
| **Change/ mol dm$^{-3}$** | **-(0.3x 0.1)** | **0** | **+0.03** | **+0.03** | **+0.03** |
| **Equilibrium conc/ mol dm$^{-3}$** | **0.07** | **55.5** | **0.03** | **0.03** | **0.03** |

$$K_c = \frac{0.03 \times 0.03 \times 0.03}{0.07 \times 55.5}$$

$$= \underline{6.94 \times 10^{-6}\ \text{mol dm}^{-3}}$$

**(ii)** A typical household bleach contains a mixture of sodium hypochlorite, calcium hypochlorite and sodium hydroxide.

Suggest why sodium hydroxide is added to household bleach.

**When sodium hydroxide is added, this results in a decrease in [H$^+$], the position of equilibrium shifts to the right.**

**This reduces the tendency of OC*l* $^-$ forming chlorine gas which is harmful to humans.**

**(iii)** HOC*l* is a weak acid (p$K_a$ = 7.5) which partially dissociates at a pH range of 5 to 8, thus giving rise to the equilibrium below.

$$Cl_2 + H_2O \rightleftharpoons 2H^+ + OCl^- + Cl^-$$

Using this information and your answer in **(a)(i)**, calculate the $K_c$ value for this equilibrium. Include its units in your answer.

$$K_c = \frac{[H^+]^2[Cl^-][OCl^-]}{[Cl_2][H_2O]}$$

$$HOCl \rightleftharpoons H^+ + OCl^-$$

$$K_a = \frac{[H^+][OCl^-]}{[HOCl]}$$

$$K_c = K_c \text{ (in a(i)) x } K_a$$

$$K_c = 6.94 \text{ x } 10^{-6} \text{ x } 10^{-7.5}$$

$$= 2.20 \text{ x } 10^{-13} \text{ mol}^2 \text{ dm}^{-6}$$

**(iv)** A more effective method to manufacture sodium hypochlorite is through the reaction of chlorine gas with sodium hydroxide.

Write an equation for this reaction. Explain why the resulting mixture has to be kept at temperatures below 40 °C.

$$2NaOH + Cl_2 \rightarrow NaCl + NaClO + H_2O$$

**NaC*l*O undergoes disproportionation at high temperatures to form NaC*l*O$_3$**

**[9]**

**(b)** Elements ***X***, ***Y*** and ***Z*** are found in periods 2 and 3 of the periodic table. The proton numbers of these elements fall within the range of 4 to 15.

- Element ***X*** reacts readily with water. 1 mol of the resulting compound is neutralised by 1 mol of ethanoic acid.
- The oxide of ***Y*** is amphoteric but the chloride of ***Y*** is acidic. 1 mol of the chloride of ***Y*** reacts with 2 mol of ammonia to give a single compound.
- Element ***Z*** forms two chlorides, $\boldsymbol{Z}\mathrm{C}l_{\mathrm{a}}$ and $\boldsymbol{Z}\mathrm{C}l_{\mathrm{b}}$. 1 mol of $\boldsymbol{Z}\mathrm{C}l_{\mathrm{a}}$ reacts with water in the cold to give two chlorine-containing products in the mole ratio of 1: 2.

Identify ***X***, ***Y*** and ***Z***. Explain your reasoning and give relevant equations to support your answer. **[5]**

**X is Na (proton no = 11)**

**(Na reacts readily with water. NaOH formed requires only one mole of acid for neutralisation)**

$\mathbf{2Na + 2H_2O \rightarrow 2NaOH + H_2}$

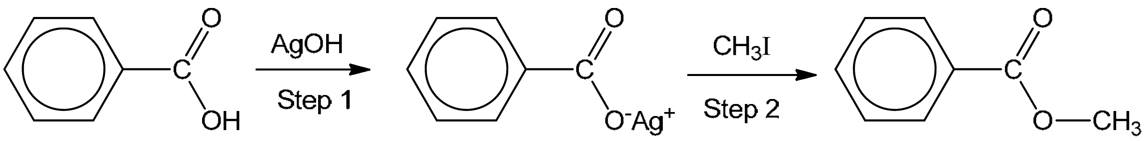
$\mathbf{NaOH + CH_3CO_2H \rightarrow CH_3CO_2^- Na^+ + H_2O}$

**Y is Be (proton no = 4)**
**(Behaviour of Be is similar to A*l*.)**
**Be in BeC*l*$_2$ is electron deficient as it has only 4 electrons. Hence it can form 2 dative covalent bonds with ammonia.**

**Z is P (proton no = 15)**

$\mathbf{PCl_5 + H_2O \rightarrow POCl_3 + 2HCl}$

**(c)** Benzoic acid can react with alkyl halides to form esters.



**(i)** Why is it necessary to react benzoic acid with silver(I) hydroxide in Step 1?

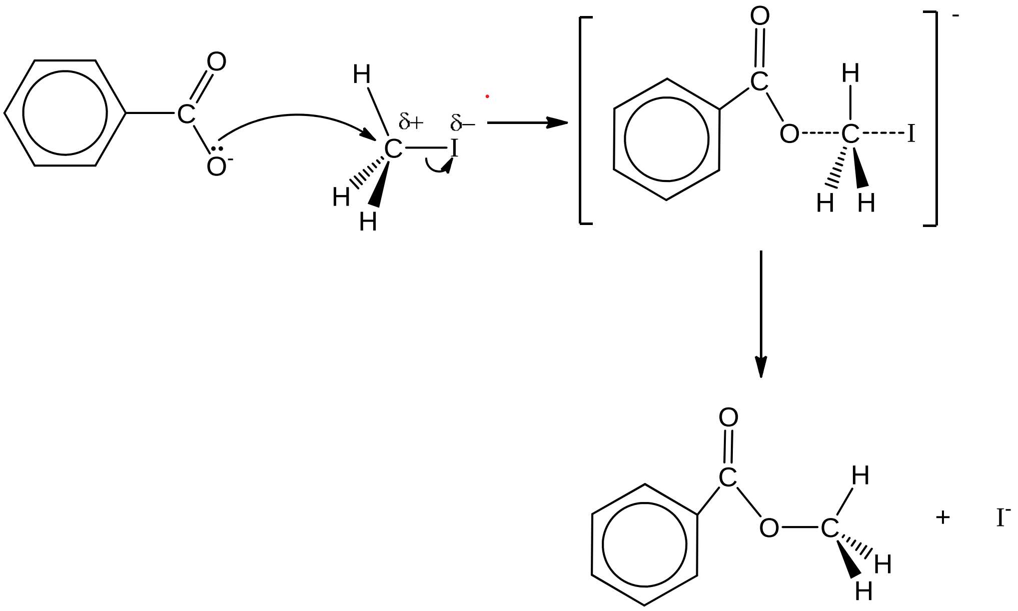
**This to generate the benzoate ion is a <u>stronger nucleophile</u> than benzoic acid for nucleophilic substitution reaction to occur.**

**(ii)** What will be observed at the end of Step 2?

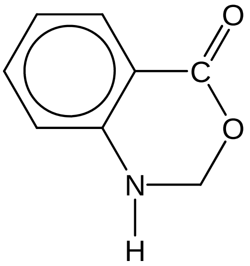
**<u>Yellow ppt of AgI</u> will be observed.**

**(iii)** Describe the mechanism for the reaction in step 2.

**Mechanism: Nucleophilic substitution reaction (S$_N$2)**



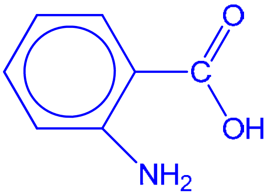
**(iv)** A carboxylic acid reacted with silver(I) hydroxide followed by dibromomethane to give the following product.



Deduce the structure of this carboxylic acid.

**[6]**

**[Total: 20]**



**3.** During any vigorous physical activity**,** sweating is the primary means by which the body maintains its core temperature of 37 °C. However, this will result in the loss of body fluid and electrolytes like chloride, phosphate, calcium, magnesium, sodium and potassium ions. If the levels of electrolytes are not adequately replenished, this can potentially lead to dehydration followed eventually by heat stroke if the percentage bodyweight lost as sweat exceeds 10 % or more.

An isotonic sports drink contains electrolytes, which aid fluid absorption, and carbohydrates that provide the necessary fuel for the body to maintain peak performance and enhance post exercise recovery.

**(a)** Magnesium and calcium ions are found in many isotonic drinks. A student decides to investigate the amount of magnesium ions in a certain brand of isotonic drink by precipitating the ion with aqueous ammonia.

| | **$K_{sp}$ / mol$^3$ dm$^{-9}$** | **Decomposition Temperature / °C** |
|---|---|---|
| $Mg(OH)_2$ | $1.5 \times 10^{-11}$ | 350 |
| $Ca(OH)_2$ | $4.7 \times 10^{-6}$ | 580 |

**(i)** Given that the base dissociation constant, $K_b$, of ammonia is $1.0 \times 10^{-5}$ mol dm$^{-3}$, calculate the $[OH^-]$ in $1.0 \times 10^{-3}$ mol dm$^{-3}$ aqueous ammonia.

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.0 \times 10^{-5}$

**Assume $[NH_3] = 1.0 \times 10^{-3}$ mol dm$^{-3}$ and since $[NH_4^+] = [OH^-]$,**

$1 \times 10^{-5} = \frac{[OH^-]^2}{0.001}$

$[OH^-] = \underline{1 \times 10^{-4}\ \text{mol dm}^{-3}}$

**(ii)** The student discovered that precipitation occurred when equal volumes of the isotonic drink and 2.0 x $10^{-3}$ mol $dm^{-3}$ aqueous ammonia were mixed together. Using your answer in **(a)(i)**, determine the minimum concentration of magnesium ions in the isotonic drink. Hence, find the minimum mass, in milligrams, of magnesium ions in 500 $cm^3$ of the isotonic drink.

**$[NH_3]_{mix}$ = ½ $[NH_3]_{orig}$ (since total volume is doubled)**
**$[NH_3]_{mix} = 1.0 \times 10^{-3}$ mol $dm^{-3}$**
**From (i), $[OH^-]_{mix} = 1 \times 10^{-4}$ mol $dm^{-3}$ when $[NH_3] = 1.0 \times 10^{-3}$ mol $dm^{-3}$**

**For precipitation to occur, $[Mg^{2+}]_{mix}[OH^-]^2_{mix} > 1.5 \times 10^{-11}$**

$$[Mg^{2+}]_{mix} > \frac{1.5\times10^{-11}}{(1.0\times10^{-4})^2}$$

$$> 1.5 \times 10^{-3} \text{ mol dm}^{-3}$$

**$[Mg^{2+}]_{orig} > (2 \times 1.5\times10^{-3})$**
**$>$ $\underline{3.0 \times 10^{-3} \text{ mol dm}^{-3}}$**

**Min. amt of $Mg^{2+}$ in 500 $cm^3$ of isotonic drink = ½ x 3.0 x $10^{-3}$ = 1.5 x $10^{-3}$ mol**
**Min. mass of $Mg^{2+}$ in 500 $cm^3$ of isotonic drink = 1.5 x $10^{-3}$ x 24.3**
**= 0.0365 g**
**= <u>36.5 mg</u>**

**(iii)** Write a balanced equation with state symbols for the thermal decomposition of magnesium hydroxide.

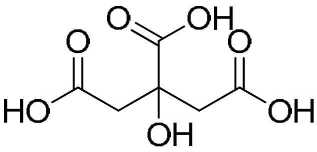
The data given in the table above shows that calcium hydroxide has to be heated to a higher temperature before it decomposes. Explain why.

**$Mg(OH)_2(s) \rightarrow MgO(s) + H_2O(g)$**

**$Ca^{2+}$ has a <u>larger ionic size</u> than $Mg^{2+}$, meaning it has a <u>smaller charge density</u> and hence <u>lower polarising power</u>. The $OH^-$ ion is thus <u>polarised to a smaller extent</u>. $Ca(OH)_2$ is therefore, more stable than $Mg(OH)_2$ and so, decomposes at a higher temperature.**

**[7]**

**(b)** Another two key ingredients commonly found in isotonic drinks are citric acid and sodium citrate. The structure of citric acid is given below:

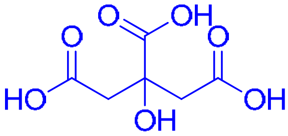


citric acid

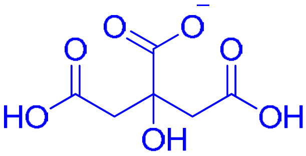
**(i)** There are three p$K_a$ values associated with citric acid: 3.1, 4.8 and 6.4. Suggest the major species present in solutions of citric acid at the following pH values.

- pH 2
- pH 4
- pH 6

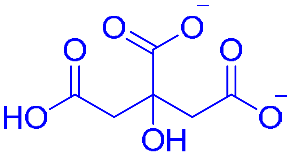
pH 2



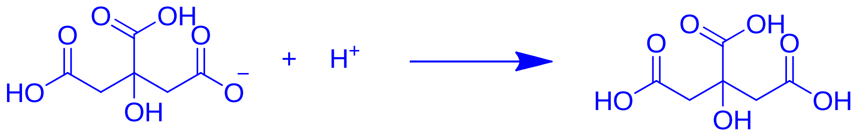
pH 4

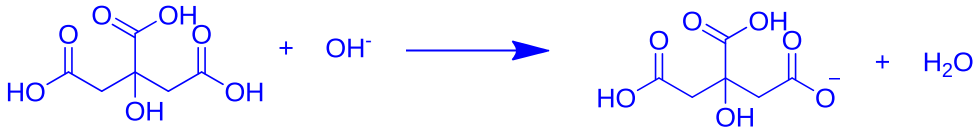


pH 6



**(ii)** Write two relevant equations to show how a solution containing citric acid and sodium citrate is able to regulate pH within a very specific range in isotonic drinks. You may use HA to represent citric acid and NaA to represent sodium citrate.





**[*or* $A^- + H^+ \rightarrow HA$ ; $HA + OH^- \rightarrow A^- + H_2O$]**

**(iii)** Using the information given in **(b)(i)**, calculate the pH of the resulting solution when 35.0 cm$^3$ of 0.100 mol dm$^{-3}$ citric acid is added to 25.0 cm$^3$ of 0.100 mol dm$^{-3}$ sodium hydroxide.

**Upon reaction, weak acid and salt is present – acidic buffer formed.**

| | HA | + NaOH | → | NaA | + | $H_2O$ |
|---|---|---|---|---|---|---|
| **Initial** | 35 cm$^3$ | 25 cm$^3$ | | | | |
| **final** | 10 cm$^3$ | 0 cm$^3$ | | 25 cm$^3$ | | |

$$pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$pH = 3.1 + \log \frac{(25.0 \times 0.100)\,/\,60}{(10.0 \times 0.100)\,/\,60}$$

$$pH = 3.1 + 0.398$$

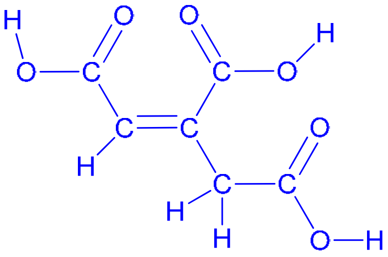
$$= \underline{3.50}$$

**[7]**

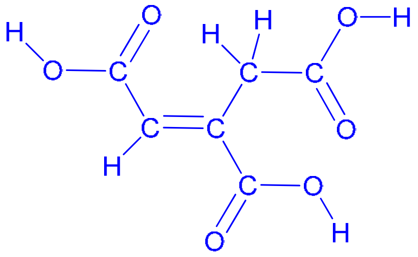
**(c)** Citric acid can be dehydrated to give a mixture of two isomeric compounds **J** and **K** with the molecular formula $C_6H_6O_6$. When one of the isomers is heated gently, a cyclic compound **L**, $C_6H_4O_5$, is formed.

**L** is a 6-membered ring and does not react with 2,4-dinitrophenylhydrazine. **L** decolourises $Br_2$(aq). 1 mol of **L** reacts with sodium to give ½ mol of hydrogen gas.

**(i)** Draw the displayed formulae of the two isomers **J** and **K**, and state the type of isomerism shown.



**J**



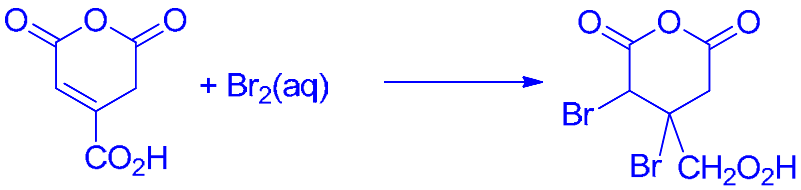
**K**

**Type of isomerism: Geometric isomerism**

**(ii)** Suggest the structure for compound **L** and identify which isomer, **J** or **K**, produces **L**. Write equations for all reactions, and explain the observations.

**L does not react with 2,4-DNPH ⇒ L is not a carbonyl compound**

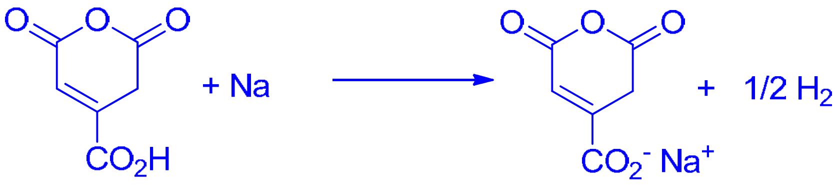
**L decolourises $Br_2$(aq) ⇒ L has C=C bond**



**L**

**1 mol of L reacts with sodium to give ½ mol of hydrogen gas**

**⇒ L has only one –OH group**



**L**

**L is formed from <u>isomer K</u>.**

**[6]**

**[Total: 20]**

**4.** This question is about reactions involving propanone.

**(a)** In an experiment to determine the enthalpy change of combustion of propanone, $\Delta H_c$, the fuel was burned under a copper can containing 250 g of water. It was found that the temperature of the water rose by 23.5 $^{o}$C after 1.0 g of propanone had been burned. The heat transfer was known to be 80 % efficient.

**(i)** Define enthalpy change of combustion of propanone, $\Delta H_c$.

**Enthalpy change (heat or energy change accepted) when 1 mol of propanone is completely burnt in oxygen/ burnt in excess oxygen under the stated conditions.**

**(ii)** Calculate the $\Delta H_c$ of propanone. Ignore the heat capacity of the copper can, and use 4.18 J $g^{-1}$ $K^{-1}$ for the heat capacity of water.

**[4]**

$$Q = mc\Delta T$$

$$= 250 \times 4.18 \times 23.5$$

$$= 24558 \text{ J}$$

$$\Delta H_c = -\frac{100}{80} \times \frac{24558}{1/58}$$

$$= -\ 1780 \text{ kJ mol}^{-1}$$

**(b)** The Wacker oxidation is an industrial process where ketones can be synthesised by the palladium-catalysed oxidation of alkene with oxygen. Propanone can be made from propene as shown.

$$CH_3CH{=}CH_2\ (g)\ +\ \tfrac{1}{2}O_2\ (g) \rightarrow CH_3COCH_3\ (l)$$

**(i)** Using relevant bond energy data from the *Data Booklet*, calculate the enthalpy change for the above reaction.

| | | |
|---|---|---|
| **Bond broken:** | **C=C** | **+610 kJ mol$^{-1}$** |
| | **6 C-H** | **+6(410) kJ mol$^{-1}$** |
| | **1 C-C** | **+350 kJ mol$^{-1}$** |
| | **½ O=O** | **+½(496) kJ mol$^{-1}$** |
| **Bond formed:** | **2 C–C** | **–2(350) kJ mol$^{-1}$** |
| | **6 C-H** | **–6(410) kJ mol$^{-1}$** |
| | **C=O** | **–740 kJ mol$^{-1}$** |

$$\Delta H = +610 + \tfrac{1}{2}(496) - 350 - 740$$

**(ii)** How would you expect the enthalpy changes of the reaction to differ from that calculated in **(b)(i)** if pent-2-ene was used to synthesise pentanone?

**The enthalpy change of reaction would be the same as the net number of bonds broken and formed are the same as the reaction above/ increase in no. of C-C/C-H bonds to be formed and broken cancel out/ reaction involves breaking C=C and ½ O=O bond and forming C=O and C-C only**

**(iii)** By considering the entropy and enthalpy changes during the reaction, explain why the reaction cannot be carried out at very high temperatures.

**Entropy change/ΔS of reaction is negative/ entropy decreases due to the decrease in number of gaseous particles.**

**$\Delta G = \Delta H - T\Delta S$**

**Since $\Delta H$ is negative, at high temperatures, the term $(-T\Delta S)$ becomes more positive than $\Delta H$/ $(-T\Delta S) > \Delta H$ thus causing $\Delta G$ to be positive and the reaction to be non-spontaneous/ not feasible/ does not proceed**

**(iv)** The enthalpy change of formation of water and carbon dioxide are –289 and –394 kJ mol$^{-1}$ respectively. With the aid of an energy cycle, use these values and your answer in **(b)(i)** to calculate the enthalpy change of formation of propene.

**[7]**

$$\begin{tikzcd}
CH_3CH{=}CH_2(g) + \tfrac{1}{2} O_2(g) \arrow[r, "-232"] & CH_3COCH_3(l) \arrow[d, "-1780"] \\
3\,C(s) + 3\,H_2(g) + 4\tfrac{1}{2}\,O_2(g) \arrow[u, "\Delta H_f"] \arrow[r, "3(-289-394)"'] & 3\,CO_2(g) + 3\,H_2O(l)
\end{tikzcd}$$

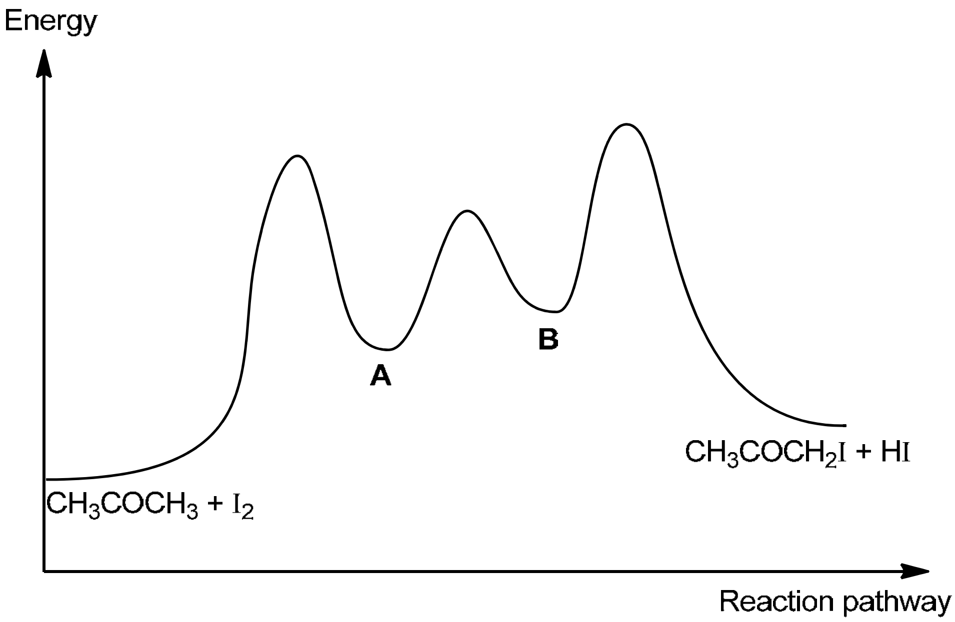
$$\Delta H_f = 3(-289 - 394) + 1780 + 232$$

$$= -37.0 \text{ kJ mol}^{-1}$$

**(c)** Propanone and iodine reacts in an acidic medium according to the equation.

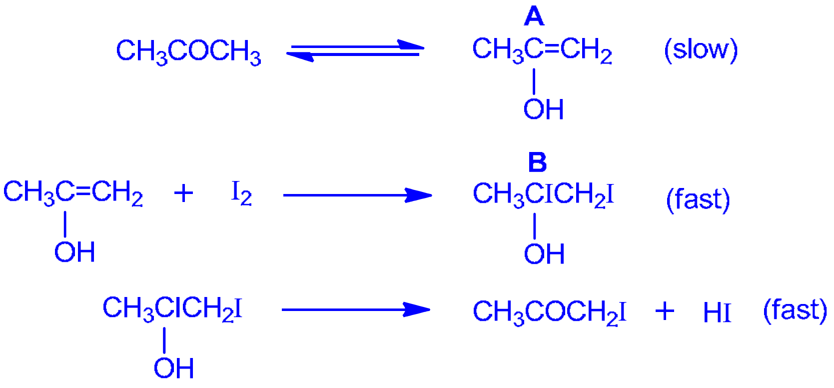
$$CH_3COCH_3 + I_2 \xrightarrow{H^+} CH_3COCH_2I + HI$$

The energy profile diagram of the reaction is as shown.



**A** is formed when propanone undergoes a rearrangement reaction without the loss of any atoms. **A** can react with sodium metal but not with 2,4-dinitrophenylhydrazine. **B** is formed when **A** undergoes electrophilic addition with $I_2$.

**(i)** Using the above information, suggest an equation for each step of the mechanism for the reaction between propanone and iodine, clearly showing the structures of compounds **A** and **B**. State which step in the mechanism is the slow step. You are not required to use curly arrows to show movement of electrons.



$$CH_3COCH_3 \rightleftharpoons \overset{\mathbf{A}}{CH_3\underset{\underset{OH}{|}}{C}=CH_2} \quad \text{(slow)}$$

$$CH_3\underset{\underset{OH}{|}}{C}=CH_2 + I_2 \longrightarrow \overset{\mathbf{B}}{CH_3\underset{\underset{OH}{|}}{CI}CH_2I} \quad \text{(fast)}$$

$$CH_3\underset{\underset{OH}{|}}{CI}CH_2I \longrightarrow CH_3COCH_2I + HI \quad \text{(fast)}$$

**(ii)** $H^+$ ions functions as a *homogenous catalyst* in this reaction.

Explain what is meant by *homogenous catalyst.*

**A homogenous catalyst is one which is in the same phase as the reactants and it alters the rate of the reaction without itself undergoing any permanent chemical change.**

**(iii)** Suggest **two** *other* reactions of propanone, one involving a homogeneous catalyst and the other, involving a heterogeneous catalyst. In each case, state clearly the identity of the catalyst and write an equation to represent the reaction.

**Heterogenous catalyst: Ni**

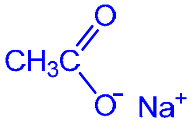
$CH_3COCH_3 + H_2 \rightarrow CH_3CH(OH)CH_3$

**Homogeneous catalyst: $CN^-$**

$CH_3COCH_3 + HCN \rightarrow CH_3C(OH)(CN)CH_3$

**(iv)** Draw the structures of all organic compounds formed when the reaction between propanone and iodine is carried out in hot aqueous sodium hydroxide instead.

**[9]**

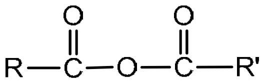


$CHI_3$

**[Total: 20]**

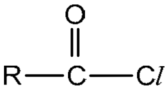
**5.** This question involves carboxylic acids and its derivatives.

**(a)** Carboxylic acids can be used to form a number of derivatives. For example,



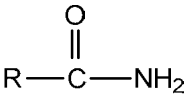
$R{-}C(=O){-}O{-}C(=O){-}R'$

acid anhydride



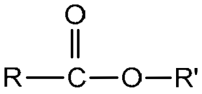
$R{-}C(=O){-}Cl$

acyl chloride



$R{-}C(=O){-}NH_2$

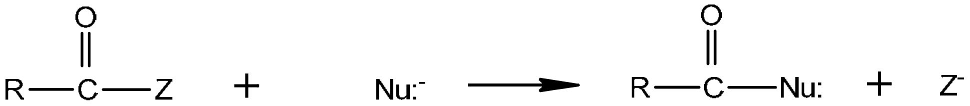
amide



$R{-}C(=O){-}O{-}R'$

ester

Carboxylic acid and its derivatives tend to undergo the following reaction:



$$R{-}C(=O){-}Z + Nu\!:^- \longrightarrow R{-}C(=O){-}Nu\!: + Z^-$$

The reaction mechanism consists of two steps. The first step is a slow step. It involves an attack of a nucleophile, $Nu^-$, at the electron-deficient carbonyl carbon, forming an unstable tetrahedral intermediate anion. This is then followed by the loss of $Z^-$ from the intermediate.

**(i)** Based on the description of the mechanism given above, suggest the type of reaction taking place.

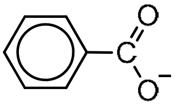
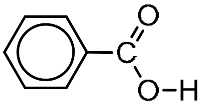
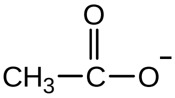
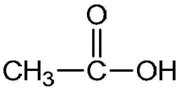
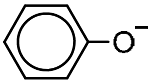
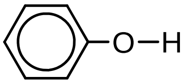
**Addition-elimination reaction**

**(ii)** Write the rate equation for the above reaction.

**Rate = $k$ [RCOZ] [$Nu^-$]**

The susceptibility of carboxylic acid derivatives, RCOZ, to attacks by nucleophiles can be determined by the relative basicity of the nucleophile and the leaving group, $Z^-$.

The table below gives the p$K_a$ values of some acids.

| **Conjugate base** | **Acid** | **p$K_a$** |
|---|---|---|
| $Cl^-$ | $H-Cl$ | - |
|  |  | 4.2 |
|  $CH_3-\overset{O}{\overset{\Vert}{C}}-O^-$ |  $CH_3-\overset{O}{\overset{\Vert}{C}}-OH$ | 4.7 |
|  |  | 9.9 |
| $OH^-$ | $H-OH$ | 16 |
| $CH_3O^-$ | $H-OCH_3$ | 17 |
| $NH_2^-$ | $H-NH_2$ | 35 |

**(iii)** State the relationship between the relative strength of an acid and its conjugate base.

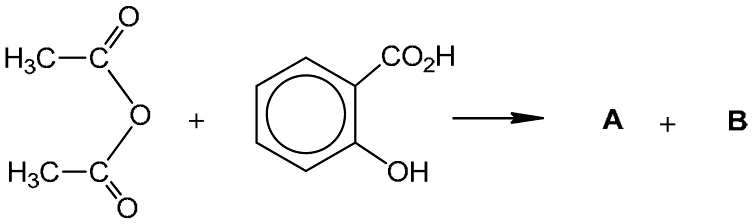
**A stronger acid gives a weaker conjugate base.**

**(iv)** Acyl chloride reacts more readily with $CH_3O^-$ than with $C_6H_5O^-$. By considering the data above and your answer in **(a)(iii)**, explain why this is so.

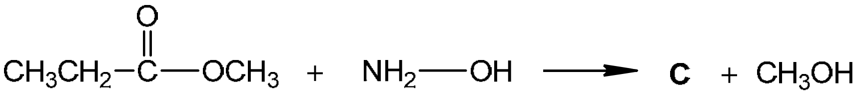
**$CH_3O^-$ is a stronger conjugate base/nucleophile than $C_6H_5O^-$.**

**(v)** Hence, identify the products **A** to **C** for the following reactions. You may assume that the reactants are in equimolar ratio.

**I**

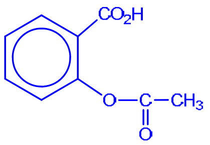


**II**



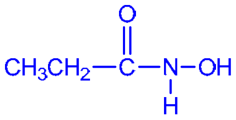
$$CH_3CH_2\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}OCH_3 + NH_2\text{—}OH \longrightarrow \mathbf{C} + CH_3OH$$

**I** **A is**



**B is $CH_3CO_2H$**

**II** **C is**



$$CH_3CH_2\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}\underset{\underset{\displaystyle H}{|}}{N}\text{—}OH$$

**[7]**

**(b)** Fibrous protein has polypeptide chains arranged parallel to one another along a single axis cross-linked to give long fibres (twisted helices) or sheets (pleated sheets). Collagen is a fibrous protein that contains three polypeptide chains wound around one another.

With reference to collagen, describe and explain what is meant by the terms *primary, secondary* and *tertiary* structures of proteins. In each case you should state the type of bonding or interaction involved. **[3]**

**Primary (1$^o$) structure of a protein shows the order (or sequence) of amino acids in a protein chain, and consists of amide/peptide bonds formed between amino acids. The primary structure determines what the protein is, how it folds, and its function.**

**Secondary (2$^o$) structure of proteins refers to the detailed configurations of the chain due to hydrogen bonding. In collagen, most of the secondary structure takes the form of α-helix or β-pleated sheet which is stabilised by large numbers of hydrogen bonds between the C=O and N-H group of peptide/amide linkages.**

**Tertiary (3$^o$) structure refers to the overall 3-dimenional shape of the protein involving folding or coiling of the chains. It shows how protein molecules are arranged in relation to each other due to the various R (residual) group interactions such as ionic bonding between charged groups, hydrogen bonding between polar groups, disulfide linkages containing S-H or S-S groups and van der Waals' between non-polar groups.**

**(c)** Gelatin can be derived from collagen.

**(i)** Complete hydrolysis of a protein produces individual amino acids, but partial hydrolysis can break the protein down into dipeptide or tripeptide fragments.

Using the same 3-letter abbreviations as below, write out the amino acid sequence of a portion of the gelatin polypeptide containing nine amino acids that could produce the following fragments on hydrolysis.

gly-pro-arg

pro-gly-pro

glu-pro-gly

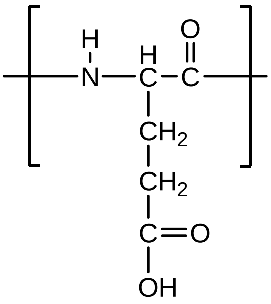
arg-gly-glu

ala-gly-pro

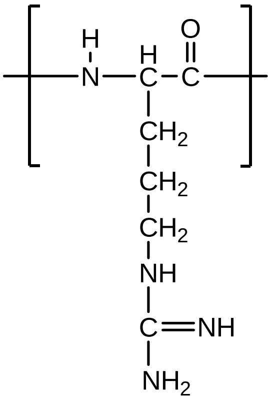
**ala-gly-pro-arg-gly-glu-pro-gly-pro**

**(ii)** Gelatin is produced by the partial denaturation of collagen. The collagen is treated with either dilute acid or base where the arginine residue or the glutamic acid residue will undergo some changes that lead to denaturation.

The structures of arginine residue and glutamic acid residue are as follows.



glutamic acid residue



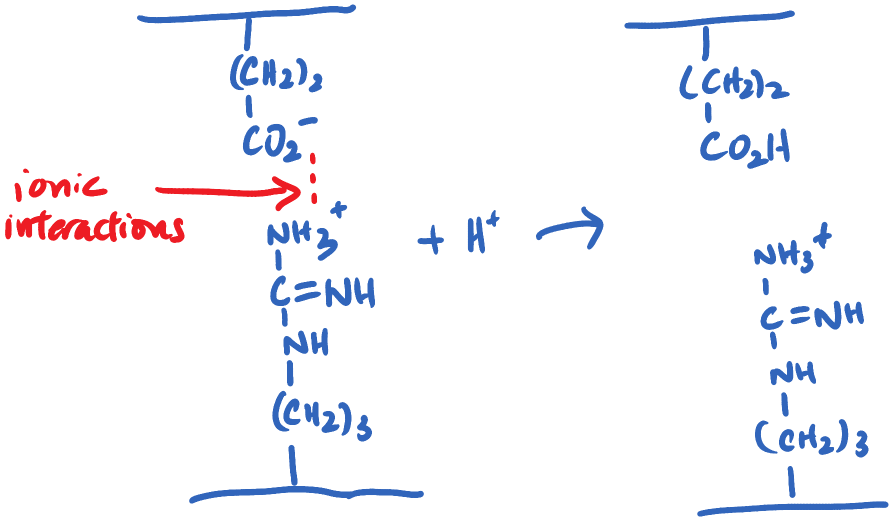
arginine residue

**I** What is meant by the term *denaturation*?

**Denaturation is a process that alters / destroys / disrupts the secondary, tertiary and quaternary structures of proteins.**

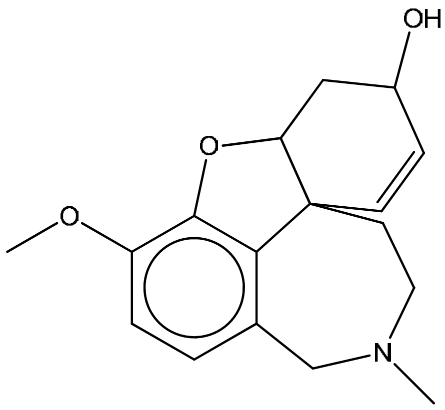
**II** Sketch a diagram to show the interaction between glutamic acid residues and arginine residues in collagen, taking into account the forms that the amino acid residues exist in at pH 7. Hence, suggest how an acid might interact with collagen to bring about denaturation.

**[4]**

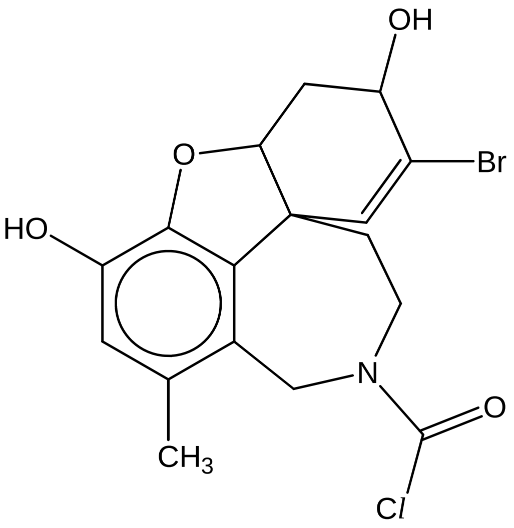


**Negatively charged glutamic residues will be protonated which will disrupt the ionic interactions holding together the tertiary structure of collagen**

**(d)** Galanthamine is a drug used to treat Alzheimer's disease. It can be extracted from snowdrops. The structures of galanthamine and its derivative (**compound A**) are shown below.



Galanthamine



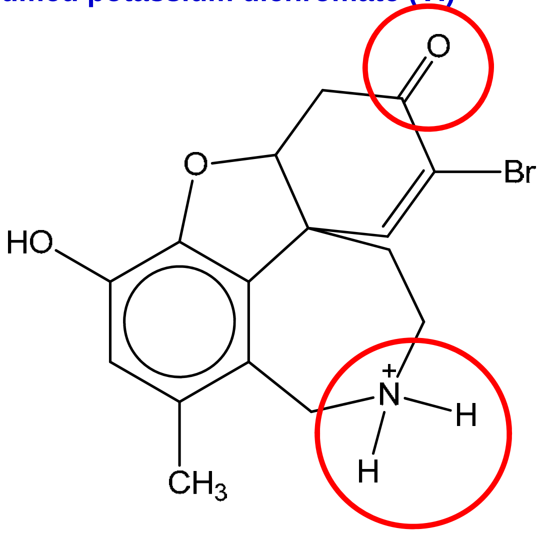
**Compound A**

**(i)** Draw the structures of all products obtained when **compound A** is treated with

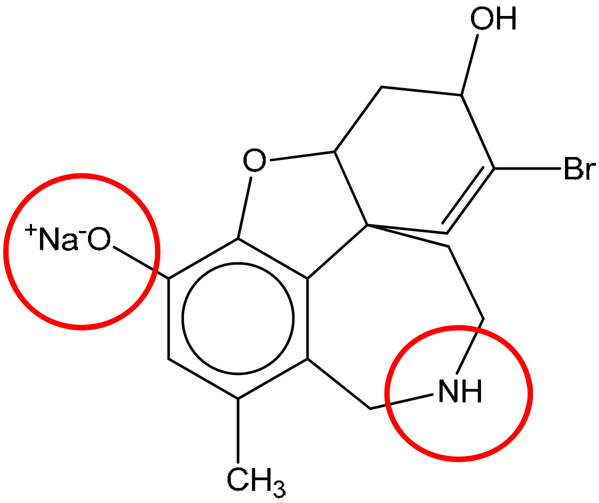
**I** hot acidified potassium dichromate(VI)

**II** hot aqueous sodium hydroxide

**I For hot acidified potassium dichromate (VI)**



**II For hot aqueous sodium hydroxide**



**(ii)** Suggest a simple chemical test which allows you to distinguish between galanthamine and **compound A**. You should state clearly the reagents and conditions used and the observations you would expect to make.

**[6]**

**Add neutral iron (III) chloride to separate samples of compound A and galanthamine.**

**Compound A will give a violet colouration whereas galanthamine will not give any violet colouration.**

**[Total: 20]**