NAME		Class	

ST ANDREW'S JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION

Chemistry (9729) **11 September 2017**

Paper 2 Structured Questions **2 hours**

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS:

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

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

Answer **all** questions in the spaces provided on the Question Paper.

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

A Data Booklet is provided.

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.

For Examiner's use:

Question	1	2	3	4	5	6	Total
Marks	17	5	10	16	6	21	75

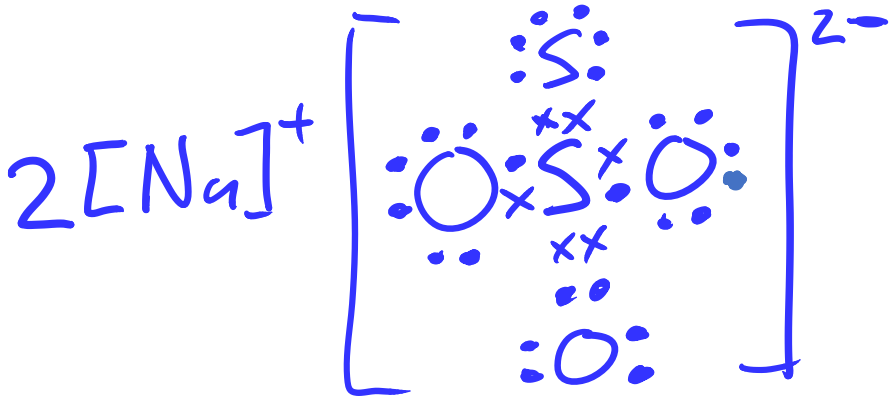
This document consists of **XX** printed pages (including this page).

Turn Over

Answer **all** the questions

1 Sulfur is a common element on Earth that forms many important chemical compounds. One of these compounds is sodium thiosulfate, $Na_2S_2O_3$, an ionic compound used to treat several medical conditions, such as cyanide poisoning and fungal growths.

(a) (i) Draw a dot-and-cross diagram for sodium thiosulfate, $Na_2S_2O_3$. State the shape and bond angle in the thiosulfate ion. [2]



shape around sulfur – tetrahedral

bond angle - 109°

1 mark for correct dot-cross diagram

1 mark for both shape and bond angle

Double bond between S-S atoms is accepted

Additional electrons can be shown as either dot or cross. Triangle/square/circle/any other shape cannot accept.

(ii) Below are the melting points of sodium thiosulfate and sulfur.

Compound	**Melting point / °C**
Sodium thiosulfate	49
Sulfur, S_8	115

Explain why sulfur has a higher melting point than sodium thiosulfate. [3]

Sodium thiosulfate has a giant ionic lattice structure with electrostatic forces of attraction between Na^+ and $S_2O_3^{2-}$ ions. [1]

Sulfur/S_8 is a simple non-polar covalent molecules with instantaneous-dipole-induced-dipole (id-id) interactions between its molecules.[1]

The large number of electrons in each sulfur molecule leads to strong id-id interactions, which require more energy to overcome compared to the ionic bonds in sodium thiosulfate, hence it has a higher melting point than sodium thiosulfate[1]

(b) Another important sulfur compound is sulfuric acid, H_2SO_4. Before the Contact Process was discovered, concentrated sulfuric acid for industrial purposes was produced by the following method.

The mineral pyrite, FeS_2, was first heated in air and oxidised to solid $Fe_2(SO_4)_3$ and sulfur dioxide gas.

$Fe_2(SO_4)_3$ decomposes at 480 °C to form iron(III) oxide and sulfur trioxide gas. The sulfur trioxide gas could be mixed with any volume of water to produce sulfuric acid of the desired concentration. However, this process was expensive and not efficient.

(i) Write a balanced equation, with state symbols for the reaction between pyrite, FeS_2, and oxygen to form $Fe_2(SO_4)_3$. [1]

$2FeS_2(s) + 7O_2(g) \rightarrow Fe_2(SO_4)_3(s) + SO_2(g)$ [1]

(ii) With the aid of an equation, define the term standard enthalpy change of formation of gaseous sulfur trioxide, SO_3. [2]

Standard enthalpy of formation of gaseous SO_3 is the energy released or required when 1 mole of gaseous SO_3 is formed from its constituent elements under standard conditions of 298 K and 1 bar. [1]

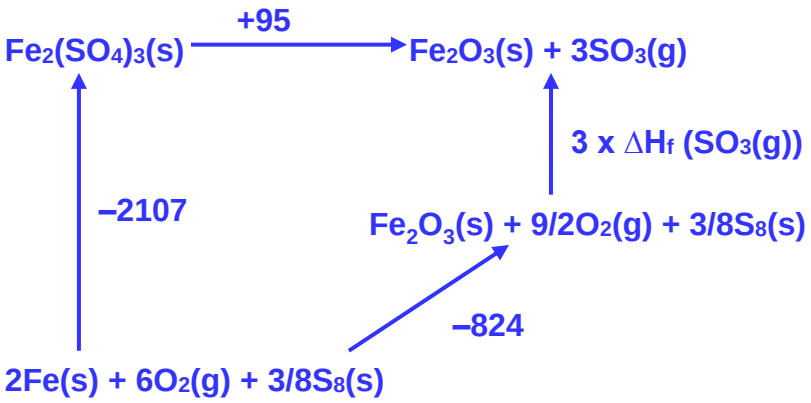
$1/8\ S_8(s) + 3/2\ O_2(g) \rightarrow SO_3(g)$ [1]

(iii) Given the following information, determine the enthalpy change of formation of gaseous sulfur trioxide SO_3.

$Fe_2(SO_4)_3(s) \rightarrow Fe_2O_3(s) + 3SO_3(g) \qquad \Delta H_{rxn} = +95\ kJ\ mol^{-1}$

Substance	ΔH_f / kJ mol^{-1}
$Fe_2(SO_4)_3(s)$	–2107
$Fe_2O_3(s)$	–824

[3]



2 marks for energy cycle

3 x ΔH_f ($SO_3(g)$) + (–824) = –2107 + 95

3 x ΔH_f ($SO_3(g)$) = –1188

ΔH_f ($SO_3(g)$) = –396 kJ mol^{-1} [1]

OR

ΔH_{rxn} = ΔH_f(products) – ΔH_f(reactants) = +95 [1]

–824 – (–2107 + 3ΔH_f($SO_3(g)$) = +95

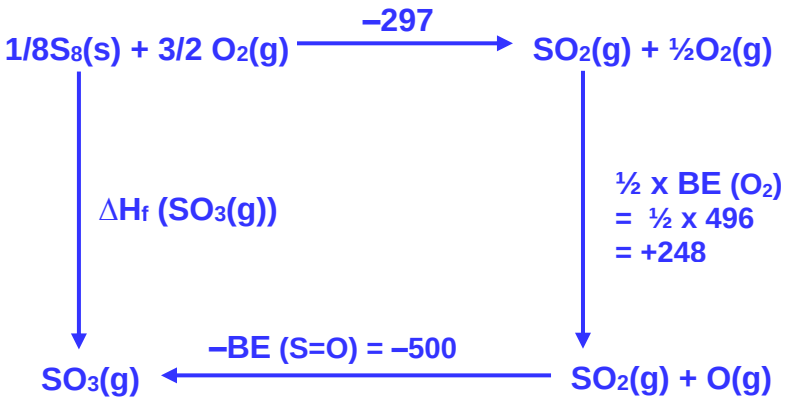
[1 mark for correct substitution of values]

3ΔH_f($SO_3(g)$) = –1188

ΔH_f ($SO_3(g)$) = –396 kJ mol^{-1} [1]

(iv) Use the appropriate bond energies given in the *Data Booklet* and the data below to calculate another value for the standard enthalpy change of formation of gaseous sulfur trioxide SO_3.

$\frac{1}{8}S_8(s) + O_2(g) \rightarrow SO_2(g)$ $\Delta H_f = -297$ kJ mol^{-1} [3]



ΔH_f (SO_3(g)) = –549 kJ mol^{-1}

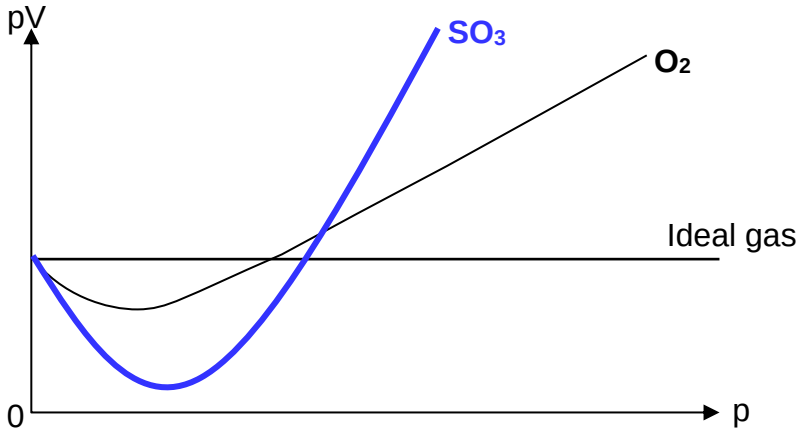
2 marks for energy cycle, ½ mark for each correct arrow with reactants and products

1 mark for calculation

(v) Suggest a reason for the discrepancy between the values in **(b)(iii)** and **(b)(iv)**. [1]

The bond energy data from the data booklet are only average values and would not apply exactly to particular compounds.[1]

(c) The value of pV is plotted against p for 1 mol of oxygen O_2, where p is the pressure and V is the volume of the gas at 300 K.



(i) On the diagram above, draw and label the graph of pV against p for SO_3 at 300 K. [1]

Can cut the ideal gas line at any point, but negative and positive deviation must be more than O_2.

(ii) Explain the difference between the graph of SO_3 and the graph of O_2. [1]

SO_3 has more electrons than O_2, hence it has stronger instantaneous-dipole-induced-dipole interactions and has greater deviation from ideality. [1]

OR

SO_3 has a larger size, hence the volume of SO_3 compared to the total volume occupied by the gas is more significant. [1]

[Total: 17]

2 Transition elements show typical properties that distinguish them from s-block elements, such as calcium. These include variable oxidation states in their compounds, and the formation of coloured complex ions.

(a) An ion of manganese has 3 electrons in its 3d subshell. Suggest the oxidation state of this manganese ion. [1]

+4 [1]

(b) The following table gives data about some physical properties of the elements calcium, chromium, and manganese.

Property	**Ca**	**Cr**	**Mn**
Atomic radius (metallic) / nm	0.197	0.129	0.132
Ionic radius (2+) / nm	0.099	0.073	0.083
Melting point / K	1112	1907	1246
Density / g cm^{-3}	1.54	7.19	7.43
Electrical conductivity / x 10^6 S cm^{-1}	0.298	0.0774	0.00695

(i) Explain why the atomic radii of chromium and manganese are similar to each other. [2]

Mn has more proton and hence greater nuclear charge. However, the two paired electrons in the 4s subshell of Mn also experience interelectronic repulsion.[1] The effect on the radius due to nuclear charge is counteracted by the interelectronic repulsion between the two paired electrons in the 4s subshell.[1]

Accept

Proton number increases and hence nuclear charge increases from Cr to Mn. Shielding effect increases because the electrons are added to the inner 3d subshell. [1] The effect on the radius due to nuclear charge is counteracted by the effect on the radius due to the shielding effect / effective nuclear charge is approximately constant/similar. [1]

(ii) Explain why the density of manganese is significantly greater than that of calcium, using relevant data from the table and the Data Booklet. (No calculations are required.) [2]

Density = mass / volume

Manganese has atomic mass of 54.9, which is greater than the atomic mass of calcium, 40.1. [1]

Manganese has atomic radius of 0.132 nm, which is less than the atomic radius of calcium, 0.197 nm. [1] Or

Manganese has ionic radius of 0.083 nm or 0.058 nm, which is less than the ionic radius of calcium, 0.099 nm. [1]

[Total: 5]

3 A student investigated the thermal decomposition of two carbonates, calcium carbonate and barium carbonate in the following way to determine its exact composition. He used the same amount, in moles, of each carbonate.

MCO_3 (s) → MO(s) + CO_2 (g) ***M*** is Ca or Ba

He heated the carbonates separately for 5 minutes. The solid obtained after heating was then shaken with distilled water to form an alkaline solution. A portion of the solid remained insoluble and was filtered. A sample of the alkaline filtrate was titrated with hydrochloric acid. No effervescence was observed during the titration.

(a) (i) Suggest which carbonate is less likely to decompose completely. Explain your answer. [2]

$BaCO_3$ is more thermally stable and not decomposed completely.
Ionic radius of Ba^{2+} > Ca^{2+} Hence charge density(charge/volume ≈ charge/ionic radius)of Ba^{2+} smaller than Ca^{2+}. [1] Polarising power of Ba^{2+} weaken, less able to polarise the electron cloud of carbonate, less weakening of the C-O bond in the carbonate. Hence the carbonate is less likely to decompose.[1]

(ii) It was observed that the volume of acid used in the titration was smaller for the carbonate which did not decompose completely.

Explain how the incomplete decomposition can result in a lower volume of acid used in the titration. [2]

Incomplete decomposition of $BaCO_3$ will result in smaller amount of BaO being formed [1] BaO is a basic oxide and will dissolve in water to give an

alkaline solution and hence less $Ba(OH)_2$ being produced hence requiring lower volume of HCl for titration.[1]

$BaO + H_2O \rightarrow Ba(OH)_2$

$Ba(OH)_2 + 2HCl \rightarrow BaCl_2 + 2H_2O$

(b) Explain the difference between the magnitude of the lattice energies of calcium carbonate and calcium oxide. [2]

LE $\alpha \left| \frac{q_+ \times q_-}{r_+ + r_-} \right|$

r^+, q^+ and q^- same for both compound. CO_3^{2-} has a larger ionic radius than O^{2-}.[1]

Thus magnitude of LE of $CaCO_3$ is smaller than that of CaO.[1]

(c) Given that the decomposition of calcium carbonate is an endothermic reaction.

$$\Delta H = +178 \text{ kJ mol}^{-1} \text{ and } \Delta S = +159 \text{ J K}^{-1} \text{ mol}^{-1}$$

Calculate the minimum temperature at which this reaction becomes spontaneous. [2]

$\Delta G = \Delta H - T\Delta S < 0$

$T > 178000/159$ [1]

$T > 1120K$

Minimum temperature is 1120 K. [1]

(d) Beryllium oxide can react with sodium hydroxide.

$$BeO + 2NaOH \rightarrow Na_2BeO_2 + H_2O$$

Explain this behaviour despite Be being a Group 2 element. [2]

Due to the high charge density of Be^{2+}[1], BeO shows a degree of covalent character / amphoteric [1] and thus able to react with a base.

[Total: 10]

4 Gaseous phosphorus(V) chloride dissociates according to the following equation.

$$PCl_5\ (g) \rightleftharpoons PCl_3\ (g) + Cl_2\ (g)$$

Different amounts of the three gases were placed in a closed container and allowed to come to equilibrium at 200 °C. The experiment was repeated at 425 °C.
The equilibrium partial pressure of the three gases at each temperature are given in the table below.

	Partial pressure / 10^{-3} N m^{-2}		
temperature/°C	PCl_5	PCl_3	Cl_2
200	1.46	11.8	2.77
425	7.61	0.211	0.368

(a) (i) Write the expression for the equilibrium constant, K_p, for this reaction. Give the units. [2]

$K_p = \frac{P_{PCl3}P_{Cl2}}{P_{PCl5}}$ [1]

Units: N m^{-2} [1]

(ii) Calculate the value of K_p at each of the temperatures given. [2]

At 200°C

$K_p = (11.8 \times 10^{-3})\ (2.77 \times 10^{-3}) / (1.46 \times 10^{-3})$

$= 0.0224$ N m^{-2} [1]

At 425°C

$K_p = (0.211 \times 10^{-3})\ (0.368 \times 10^{-3}) / (7.61 \times 10^{-3})$

$= 1.02 \times 10^{-5}$ N m^{-2} [1]

(iii) Is the forward reaction exothermic or endothermic? Explain your answer. [2]

According to Le Chatelier's Principle, when temperature is increased, endothermic reaction is favoured to "absorb" the additional heat. Since the positon of equilibrium shifts to the left (as evident from the higher partial pressure of PCl_5) at higher temperature, this suggests that the backward reaction is endothermic and hence the forward reaction is exothermic.[1]

Or

Since $K_p = \frac{k_f}{k_b}$, a drop in K_p as temperature increases implies that the rate of backward reaction increases to a greater extent [1]than rate of the forward reaction. This suggests that the backward reaction is endothermic and hence the forward reaction is exothermic.[1]

(b) What will be the effect on the equilibrium partial pressure of PCl_5 when the following changes are carried out on this new equilibrium? Explain your answers clearly.

(i) The pressure of the system is halved at constant temperature. [2]

When pressure is halved, position of equilibrium will shift right [1] as there are more moles of gaseous products to increase the number of moles of gases [1] to increase the pressure. Less PCl_5.

(ii) Helium gas is added at constant volume and temperature. [2]

Individual partial pressures for each gas did not change.[1]

No change in position of equilibrium. [1]

Chloroethane can be made by reacting PCl_3 with ethanol, via nucleophilic substitution mechanism.

$$PCl_3 + CH_3CH_2OH \rightarrow CH_3CH_2Cl + HOPCl_2$$

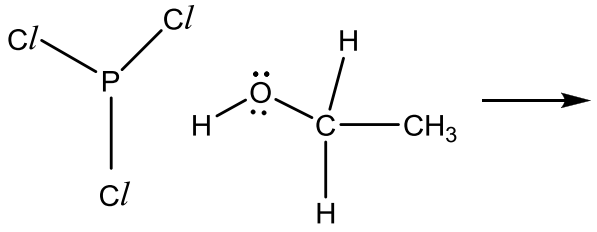
(c) Outline a simple chemical test that can be carried out to see if chloroethane is produced in the mixture after reacting with PCl_3. [2]

Heat chloroethane with aq NaOH. Cool, acidify with nitric acid, then add dilute $AgNO_3$ to sample. [1] A white precipitate should be obtained. [1]

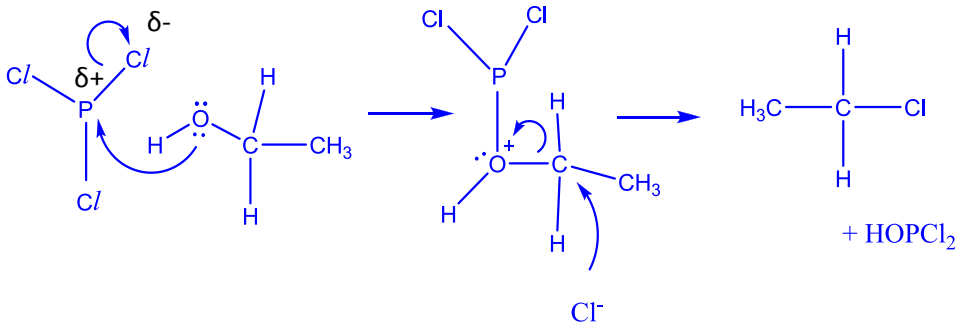
(d) The mechanism is thought to involve these steps.

- The first step is where P-C*l* bond breaks. P is electron deficient and reacts with alcoholic O to form a protonated oxygen intermediate.
- The C-O bond is broken. Cl^- act as a nucleophile.

Complete the diagram to suggest a mechanism to show how chloroethane is formed. Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows.



[3]



Nucleophilic Substitution

2marks for both sets of arrows

1 mark for intermediate

dipoles

Lone pair on Cl during intermediate step

No penalty for slow/fast

(e) Explain why chlorobenzene cannot be made in the same way using phenol and PCl_3. [1]

The **lone pair of electrons on O can delocalise into the benzene ring** and resulting in **strengthening of the C-O bond**. [1] Hence the bond does not break easily for NS to take place.

[Total: 16]

5 Bromine reacts with organic compounds in different ways.

(a) When butane reacts with gaseous bromine in the presence of ultraviolet light, the major product was 2-bromobutane instead of 1-bromobutane. Using the stability of the intermediates, explain the observation. [3]

The reaction of gaseous bromine and butane is **free radical substitution**, where the **ultraviolet light splits the bromine-bromine sigma bond in the bromine molecule homolytically** to form 2 bromine radicals / atoms. **[1 mark for either stating FRS or the formation of bromine radical]**

The bromine radical formed reacts with the butane molecule to form the following 2 different radicals.

radical **A** radical **B** **[1]**

can describe in words – 2 alkyl groups vs 1 alkyl group / lone electron on 1st vs 2nd carbon / primary vs secondary radical

Radical **A** is formed in a larger proportion than radical **B** because the carbon with the radical in radical **A** has **1 additional electron donating alkyl group** than in radical **B**. This **stabilises the radical to a greater extent** and hence lead to the higher

proportion of 2-bromobutane formed despite having a smaller number of hydrogen atoms to be substituted.**[1]**

(b) A solution of 2-bromobut-2-ene, upon heating with ethanolic silver nitrate solution, does not form a cream precipitate.

Upon addition of concentrated sulfuric acid in the cold and followed by heating with ethanolic silver nitrate, 2-bromobut-2-ene formed a cream precipitate.

Explain the above observations. [3]

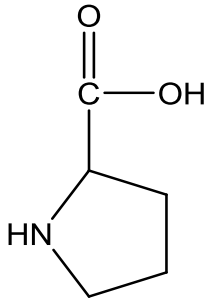
The bromine atom's lone pair of electrons would **delocalise into the alkene functional group, forming a partial double bond**. This partial double bond is **very strong** and hence would not break upon heating and thus no cream-white precipitate was formed. **[1]**

Upon addition of sulfuric acid, the pi-bond in the alkene would **undergo electrophilic addition and hence break**. **[1]** Therefore the bromine atom no longer delocalises its electrons and the carbon-bromine single bond remains. Upon heating with silver nitrate solution, **nucleophilic substitution occurs / the carbon-bromine single bond would break heterolytically, forming the bromide ion. [1]** Upon addition of aqueous silver nitrate, would result in the formation of silver bromide, the cream precipitate.

[Total: 6]

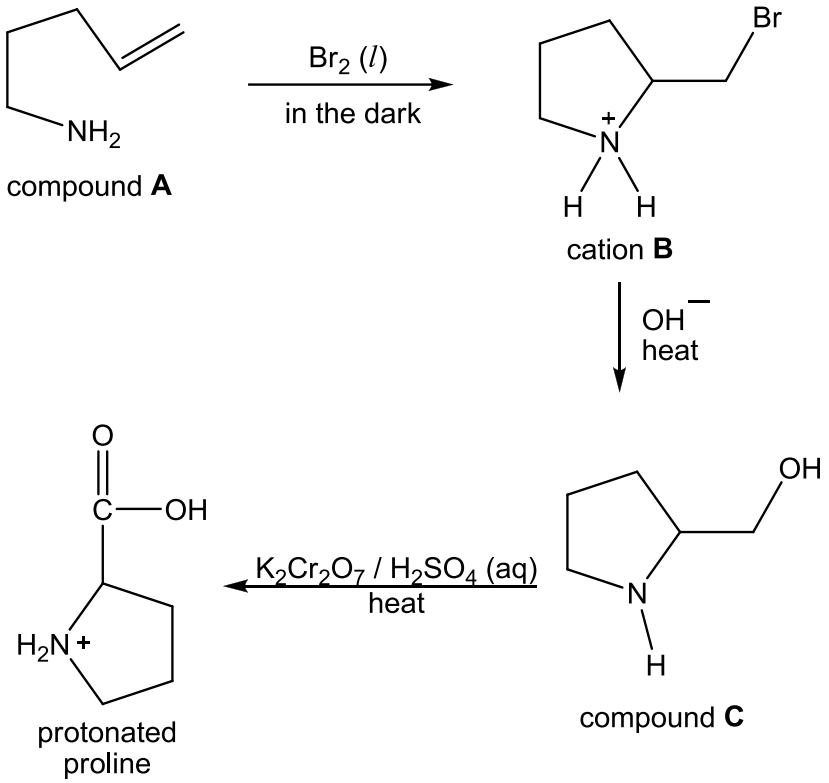
6 Proteins, found within the human body, are formed by amino acids. These amino acids are classified as either essential (cannot be synthesised by the human body) or non-essential (can be synthesised by the human body) amino acids.

(a)



Proline

Proline, one of the non-essential amino acids, is associated with the production of collagen which promotes healthy skin and heart muscle. Protonated proline can potentially be synthesised in the following manner.

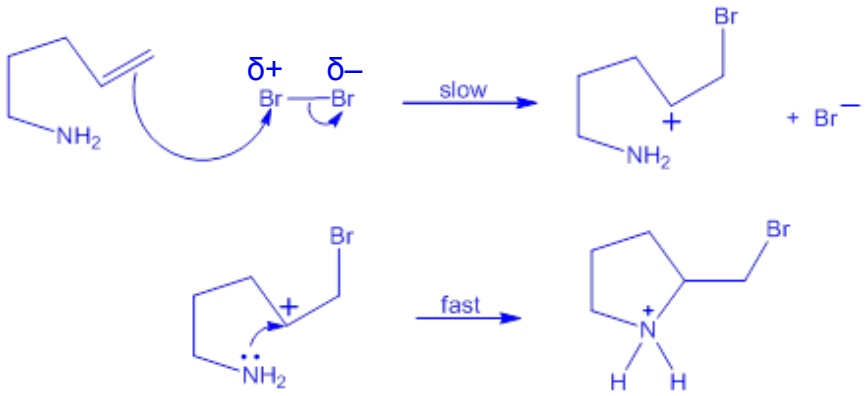


The reaction of compound **A** with liquid bromine occurs via a two-step mechanism.

- compound **A** reacts with bromine to form a carbocation intermediate in the first step.
- the ammonium ion is formed in the second step.

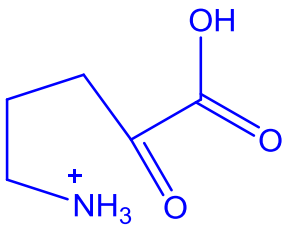
(i) Name and suggest the mechanism for this reaction. Show any relevant lone pairs, dipoles and charges, and indicate the movement of electron pairs with curly arrows. [3]

Electrophilic addition **[1]**



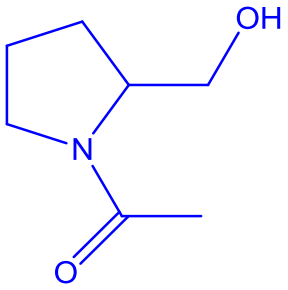
[1] – for each equation (inclusive of dipoles, lone pairs, slow/fast, etc.)

(ii) This synthesis also produces another organic compound (molecular formula $C_5H_{10}NO_3Br$). Suggest the skeletal formula of the cation. [1]



[1]

(iii) Compound **C** was extracted and reacted with 1 mole of ethanoyl chloride to form a neutral compound **D** with molecular formula $C_7H_{13}NO_2$. Draw the structure of compound **D**. Explain why this product is formed. [2]



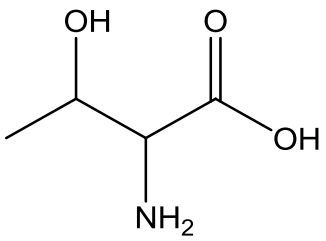
[1]

The amine functional group reacts with ethanoyl chloride as it is a stronger nucleophile as the lone pair of electrons on the nitrogen atom are **more available / likely to attack** the electron-deficient carbon on ethanoyl chloride than the oxygen atom in the alcohol functional group. [1 – availability of lone pair of electrons]

OR

N is less electronegative than O, hence l.p more available to attack. [to be confirmed as answer]

(b)



Threonine

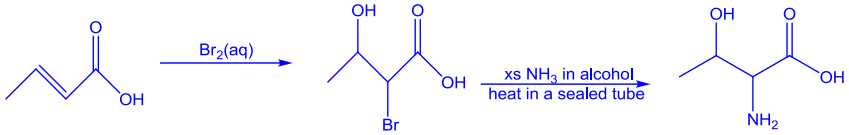
Threonine, one of the essential amino acids, maintains protein balance within the human body and supports the cardiovascular, liver, central nervous and immune system functions.

In the laboratory, threonine could be synthesised from but-2-enoic acid.

(i) State the type of isomerism exhibited by but-2-enoic acid. [1]

cis-trans isomerism

(ii) Suggest a 2-step synthesis for the formation of threonine from but-2-enoic acid, showing the intermediate clearly in your answer. [3]



reagents and conditions **[1]** for each step

intermediate **[1]**

(iii) By considering the stereoisomers of threonine, suggest why only 25% of the synthesised threonine could be used in the human body. [2]

Threonine exhibits **enantiomerism** due to the **presence of 2 chiral carbons**. **[1]** There is a total of **4 possible enantiomers** and **only one of which** matches the threonine within the human body. **[1]**

Accept optical isomers / isomerism

(c) **(i)** Suggest whether threonine or proline has the more basic amine group. Explain your answer. [2]

Proline's amine functional group is **more basic** than that of threonine's.**[1]**
Proline's amine functional group is a secondary amine whereas threonine's amine functional group is a primary amine. The **lone pars are more available for protonation due to two/more electron-donating groups** in the secondary amine, hence proline is more basic. **[1]**
OR
On top of which threonine has **an additional secondary alcohol functional group**, which **causes the availability of the lone pair of electrons on the nitrogen atom in the amine to be less available to be donated to a proton**.[1]

(ii) Explain, in terms of their structures, the higher solubility of threonine in water as compared to benzoic acid in water. [2]

Threonine exist as **a zwitterion [1]** in water whereas benzoic acid exist as a simple covalent molecule in water.

Threonine would form **ion-dipole interactions with water molecules** and **releases significantly more energy** as compared to the **hydrogen bonds** formed between benzoic acid molecules with water molecules. Thus threonine is more soluble in water as compared to benzoic acid.**[1]**

(d) According to dieticians, a teenager requires approximately 1.00 g of calcium each day. This particular mineral is found predominantly in milk, cheeses and yogurts, which most individuals consume in the morning.

(i) Procedure to extract calcium ions is stated as follows :

1. A cup of milk (300 ml) was first filtered to remove impurities before excess amounts of sodium carbonate was added to form $CaCO_3$.

2. The mixture was then refiltered and the white residue (assumed to be solely calcium carbonate) was washed once again with deionised water and filtered again.
3. The white residue was then dissolved in 0.500 dm^3 of 0.160 mol dm^{-3} hydrochloric acid. 25.0 cm^3 of this resulting solution was then titrated against 0.125 mol dm^{-3} sodium hydroxide. The titre volume was found to be 26.45 cm^3.

What is the recommended number of cups of milk each day a teenager should consume to meet the daily requirements? [3]

amount of sodium hydroxide used = 0.00330 mol

amount of excess hydrochloric acid present in 0.500 dm^3 of resulting solution = 0.0661 mol **[1]**

amount of hydrochloric acid used to dissolve the white precipitate ($CaCO_3$) = 0.0138 mol

amount of calcium carbonate = 0.00693 mol **[1]**

mass of calcium ions in 1 cup of milk = 0.278 g

no. of cups needed = 1 / 0.278 = 3.60

hence the teenager should drink about 4 cups of milk a day. **[1]**

3.6 cups also accepted as answer

(ii)

Compound	Amount per serving
Vitamin A	5000 IU
Vitamin C	300 mg
Vitamin D	600 IU
Vitamin E	30 IU
Vitamin K	80 mcg
Thiamin (Vitamin B-1)	50 mcg
Riboflavin (Vitamin B-2)	50 mg
Folic Acid	600 mcg
Vitamin B-12 (as Cyanocobalamin)	50 mcg
Calcium (as in calcium carbonate)	200 mg

Iodine (as Potassium iodide)	150 mcg
Magnesium (as magnesium oxide)	50 mg
Zinc (as zinc oxide)	25 mg
Selenium (as L-Selenomethionate)	200 mcg
Molybdenum (as sodium molybdate)	75 mcg

A typical multivitamin dietary supplement tablet would have the above composition. Given that the teenager does not consume any form of dairy products, how many tablets would a teenager need to take to achieve the daily requirement of calcium? [1]

No. of tablets = 1.0 g / 0.2 g = 5 **[1]**

(iii) A student wants to test the validity of the composition of calcium in this tablet and decided to follow the steps mentioned in **(d)(i)**.

State 1 possible problem that the student would face. [1]

1. The calcium carbonate precipitate would be formed along with copper carbonate, magnesium carbonate, etc.

   OR

2. The tablet would have to be treated initially to dissolve it completely.

[1 mark for any point]

[Total: 21]

~ END OF PAPER ~