CATHOLIC JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATIONS
Higher 2

CANDIDATE NAME

CLASS 2T

CHEMISTRY

9647/02

Paper 2 Structured Questions

Monday 1 September 2014
2 hours

Candidates answer on the Question Paper
Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class in the spaces provided above.
Write in dark blue or black pen in the spaces provided, on the Question 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 all questions.
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 of the question.

	For Examiner's Use		
Paper 1			40
Paper 2	Q 1	12	
	Q 2	15	
	Q 3	15	
	Q 4	15	
	Q 5	15	72
Paper 3	Q 1	20	
	Q 2	20	
	Q 3	20	
	Q 4	20	
	Q 5	20	80
Total			192

Answers

[Turn over

Planning (P)

1 ***FA1*** is a solution of 1.00 mol dm^{-3} sodium hydroxide, NaOH.

FA2 is a solution of 1.00 mol dm^{-3} acid which is either a ***monobasic*** with the formula HA, or ***dibasic*** with the formula H_2A.

You are required to determine the ***basicity*** of an acid (either ***monobasic*** or ***dibasic***), based on the information given below and the planning of the procedure you have to undertake.

Three separate experiments were carried out. Varying volumes of ***FA1*** were measured and then added to different volumes of ***FA2*** and the rise in temperatures, as a result of the mixing were recorded. The relevant measurements and results are tabulated below.

	Experiment 1	Experiment 2	Experiment 3
Volume of ***FA1*** / cm^3	25	25	50
Volume of ***FA2*** / cm^3	25	50	25
Temperature rise, ΔT / °C	6.9	4.6	9.1

(a) **(i)** Write a balanced equation for the reaction between ***FA1*** and ***FA2*** if the acid is ***monobasic***. Do not omit spectator ions.

$HA(aq) + NaOH(aq) \rightarrow NaA(aq) + H_2O(l)$

(ii) Write a balanced equation for the reaction between ***FA1*** and ***FA2*** if the acid is ***dibasic***. Do not omit spectator ions.

$H_2A(aq) + 2NaOH(aq) \rightarrow Na_2A(aq) + 2H_2O(l)$

[2]

(b) You are provided with the following apparatus and materials:

1 thermometer
1 styrofoam cup
Two 50 cm^3 measuring cylinders
Sufficient ***FA1*** solution
Sufficient ***FA2*** solution

Plan a simple procedure by describing the steps you would carry out for ***Experiment 1*** given above so as to make the relevant measurements and recordings. You are to use ***only*** the apparatus and materials listed above.

1. **Using a measuring cylinder, pour *25 cm^3 of FA1* into a styrofoam cup.**
2. **Read and record the initial temperature with a thermometer.**
3. **Using another measuring cylinder, measure *25 cm^3 of FA2* and carefully add *FA2* to *FA1*, contained in the styrofoam cup.**
4. **Stir/swirl gently with the thermometer and read and record the highest temperature reached.**

[4]

(c) Use the results of the relevant experiments given in the table above, explain clearly how the ***basicity*** of the acid is determined. Hence, state the ***basicity*** of the acid.

Need to compare experiments 2 & 3 as the total volume of the mixture is the same at 75 cm^3.

	$HA(aq)$ +	**$NaOH(aq) \rightarrow$**	**$NaA(aq)$ +**	**$H_2O(l)$**	**$H_2A(aq)$ +**	**$2NaOH(aq) \rightarrow$**	**$Na_2A(aq)$ +**	**$2H_2O(l)$**
Exp 2:	0.025 mol	0.025 mol		0.025 mol	0.0125 mol	0.025 mol		0.025 mol
Exp 3:	0.025 mol	0.025 mol		0.025 mol	0.025 mol	0.050 mol		0.050 mol

Since the rise in temperature is *doubled* in Exp 3 compared to that of Exp 2, *FA2* is a *dibasic acid*, H_2A.

If the acid is *monobasic*, then the rise in temperature in Exp 2 and 3 should be the *same*.

The acid is *dibasic*.

[2]

(d) **(i)** Hence, calculate the amount of heat evolved in ***Experiment 1***. In your calculations, you are to assume that the specific heat capacity of the reaction mixture is 4.18 J g^{-1} K^{-1} and the density of the reaction mixture is 1 g cm^{-3}.

Heat evolved = m c ΔT
= (25+25) x 4.18 x 6.9 J
= 1.44 x 10^3 J

(ii) Using your answers to **(d)(i)** and the relevant equation in **(a)**, calculate the enthalpy change of neutralisation, ΔH_{neu}.

$H_2A(aq)$	**+**	**$2NaOH(aq) \rightarrow$**	**$Na_2A(aq)$**	**+**	**$2H_2O(l)$**
0.0125 mol		**0.025 mol**			**0.025 mol**

$$\Delta H_{neu} = -\frac{1.44 \times 10^3}{0.025} \text{ J mol}^{-1}$$

$$= -57.7 \text{ kJ mol}^{-1}$$ **(with correct units & negative sign)**

[2]

(e) From your calculated ΔH_{neu} value, state whether the acid is strong or weak.

Strong acid as the value is approximately – 57.3 kJ mol^{-1}.

[1]

(f) Identify one source of error in your procedure and explain how you would minimise the error.

Heat loss to the surrounding. Perform the experiment in a draught free environment or provide a lid to cover the styrofoam cup or provide lagging to the styrofoam cup.

Measuring cylinders are not precise enough to measure volumes of *FA1* and *FA2*. Use of burette to measure their volumes more accurately.

Measure the initial temperatures of *FA1* and *FA2* separately before mixing. The initial temperature of the mixture can then be calculated by the taking the mean/average of the initial temperatures.

[1]

[Turn over

[Total: 12]

2 Scuba diving is a form of underwater diving, in which a diver uses a self-contained underwater breathing apparatus (scuba) to breathe underwater. Scuba diving is an exhilarating sport, and thanks in part to the gas laws, it is also a safe activity for trained individuals who are in good health.

A typical dive might be 12 to 19 m, but dives to 27 m are not uncommon. As seawater has a slightly higher density than fresh water, the pressure exerted by a column of 10 m of seawater is equivalent to a pressure of 1 atm. Pressure increases with increasing depth, so at a depth of 20 m, the pressure of the water will be 2 atm, and so on. The **total** pressure exerted on the diver is the **sum** of the atmospheric pressure and the pressure due to the column of water.

(a) Consider a diver rising to the surface of the water from a depth of 6 m without breathing.

(i) Calculate the total pressure exerted on a diver at 6 m.

pressure of water at 6 m = $\frac{6}{10}$ **x 1 = 0.6 atm**

total pressure = atm pressure + pressure exerted by water

= 1 + 0.6

= 1.6 atm

(ii) Show that, when the diver rises to the surface of the water, the volume of air trapped in the diver's lungs would be increased by 1.6 times.

At the surface of water, pressure = atm pressure of 1 atm

Let the volume of air trapped in the lungs be V_2**,**

Using Boyle's Law, $P_1V_1 = P_2V_2$

$$\frac{V_2}{V_1} = \frac{P_1}{P_2}$$

$$\frac{V_2}{V_1} = \frac{1.6}{1} = 1.6$$

The most important rule in scuba diving is to breathe continuously, especially when ascending, and to avoid holding breath underwater. This is to avoid barotrauma where physical damage to body tissues is caused by a difference in pressure between a gas space inside, or in contact with the body, and the surrounding waters. The sudden expansion of air can fatally rupture the membranes of the lungs. This is different in free diving, which relies on the diver's ability to hold his or her breath until resurfacing, rather than on the use of a breathing apparatus.

(iii) By considering the volume of air in the diver's lungs, explain why barotrauma is not experienced for a free diver ascending at a depth of 6 m.

This is because the free diver has inhaled the air at atmospheric pressure. When he surfaces, the pressure of the air in his lungs reverts to the atmospheric pressure, hence there is no difference in pressure.

[5]

[Turn over

A scuba set is a breathing set that is carried entirely by an underwater diver and provides the diver with breathing gas at the ambient pressure. A breathing gas is usually a mixture of oxygen and nitrogen used for respiration. For instance, air is the most common and only natural breathing gas. Our bodies function best when oxygen gas has a partial pressure of 0.20 atm, as in the air we breathe. When a diver is submerged, a special valve automatically adjusts the pressure of the air breathed from the scuba tank to ensure that the air pressure equals the water pressure at all times.

Although nitrogen gas may seem to be the obvious choice to mix with oxygen gas for use in the scuba tank, there is a serious problem associated with it. When the partial pressure of nitrogen gas exceeds 1 atm, enough of the gas dissolves in the blood to cause *nitrogen narcosis*. The effects on the diver resemble those associated with nitrous oxide ("laughing gas") inhalation. For this reason, helium is often used to dilute oxygen gas.

(b) **(i)** Show that the oxygen present in air has a partial pressure of 0.20 atm.

Composition of air - O_2: 20 %; N_2: 80 % by volume

Using Dalton's Law,

$$P_{O2} = \frac{n_{O2}}{n_{O2} + n_{N2}} \times P_{total}$$

Since volume is directly proportional to number of moles,

$$P_{O2} = \frac{V_{O2}}{V_{O2} + V_{N2}} \times P_{total}$$

$$= \frac{20}{20+80} \times 1$$

$$= 0.20 \text{ atm}$$

(ii) Consider a diver submerged at a depth of 6 m.
Using your answer in **(a)(i)**, calculate the mole fraction of oxygen that is needed to maintain the partial pressure of 0.20 atm.

Total pressure = 1.6 atm

Since the partial pressure of O_2 needs to be maintained at 0.20 atm,

$$P_{O2} = \chi_{O2} \times P_{total} \quad (\chi_{O2} \text{ is the mole fraction of O2})$$

$$0.20 = \chi_{O2} \times 1.6$$

$$\chi_{O2} = 0.125$$

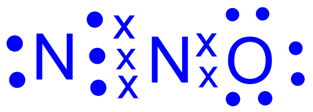
(iii) Suggest a reason why helium can be used in place of nitrogen gas.

Helium is less soluble in water/blood. OR Helium produces no narcotic effect. OR Helium is inert

[4]

Nitrous oxide (N_2O) commonly known as laughing gas, is a colourless and non-flammable gas, with a slightly sweet odour and taste. It is used in surgery and dentistry for its anaesthetic and analgesic effects. It is known as “laughing gas” due to the euphoric effects of inhaling it, a property that has led to its recreational use as a dissociative anaesthetic.

(c) **(i)** Draw the dot-and-cross diagram of N_2O, given that N is the central atom, and state its shape.



Shape: Linear

Nitrous oxide decomposes into oxygen and nitrogen according to the following equilibrium:

$$2\,N_2O(g) \rightleftharpoons O_2(g) + 2\,N_2(g)$$

At 25 °C, K_c is 7.30×10^{34} mol dm^{-3}.

(ii) Suggest how N_2O can be stored to prevent decomposition.

High pressure

(iii) Suggest the significance of the value of K_c in the reaction.

From the high value of K_c (of 7.30×10^{34}), nitrous oxide has a high tendency to decompose into oxygen and nitrogen at 25 °C. OR position of equilibrium lies largely to the right OR the reaction tends to completion OR composition of O_2 and N_2 is high.

(iv) The value of K_p is related to K_c according to the following formula:

$$K_p = K_c(RT)^{\Delta n}$$

where Δn = no. of moles of gaseous products – no. of moles of gaseous reactants

Using the given formula, calculate the value of K_p for the reaction at 25 ^oC, indicating clearly its units.

$K_p = (7.30 \times 10^{34})(8.31)(25 + 273)^{(3-2)}$ $(\text{mol dm}^{-3})(\text{J K}^{-1}\ \text{mol}^{-1})(\text{K})$

$= 1.81 \times 10^{38}$ J dm^{-3}

[6]

[Total: 15]

3 Nickel is a silvery-white metal and shows significant chemical activity with oxygen in powdered form but larger pieces of the metal are slow to react with air at ambient conditions due to the formation of a protective oxide layer.

Cadmium is a soft, bluish-white metal chemically similar to zinc and also displays properties similar to heavy metals. Cadmium occurs as a minor component in zinc ores and is a by-product of zinc manufacture.

Both nickel and cadmium are used in applications such as batteries and electroplating for corrosion resistance.

	nickel	cadmium
melting point / °C	1455	321
density / g cm^{-3}	8.91	8.65

(a) Complete the electronic configuration of nickel(II) and cadmium(II) ions.

$_{28}Ni^{2+}$ $1s^2\ 2s^2\ 2p^6$ **$3s^2\ 3p^6\ 3d^8$**……………………………………..

$_{48}Cd^{2+}$ $1s^2\ 2s^2\ 2p^6$ **$3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}$**………………………..

[2]

(b) Briefly account for the difference in melting points between nickel and cadmium.

There are fewer number of unpaired valence d electrons available for delocalisation in Cd compared to Ni (alternative ans: Cd^{2+} has a larger ionic size and thus lower charge density). Hence, the metallic bond strength is relatively weaker in Cd as compared to Ni. Hence less energy is required to break the electrostatic forces of attraction during the melting process. [2]

(c) The nickel–cadmium battery (NiCad battery) is a type of rechargeable battery using nickel oxide hydroxide and metallic cadmium as electrodes.

(i) During electrical discharge, the overall chemical reaction is as shown:

$$2NiO(OH) + Cd + 2H_2O \rightarrow 2Ni(OH)_2 + Cd(OH)_2$$

Cadmium reacts with an alkaline electrolyte at one of the electrodes. Write the equations for reactions that take place at the anode and the cathode.

Anode: **$Cd + 2OH^- \rightarrow Cd(OH)_2 + 2e^-$**……………………………………

Cathode: **$NiO(OH) + H_2O + e^- \rightarrow Ni(OH)_2 + OH^-$**……………………………………

[Turn over

(ii) If the cell produces 1.8 A of current, and if the mass of nickel oxide hydroxide contained in a typical NiCad battery is 9.15 g, how long can the battery operate before it stops discharging electrical power?

No. moles of NiO(OH) = 9.15 / 91.7 = 0.0998 mol

No. moles of electrons discharged = 0.0998 mol

Charge Q = 0.0998 x 96500 = 9629C

Q = I x t

t = 9629 / 1.8 = 5349 s (or 89.2 min)

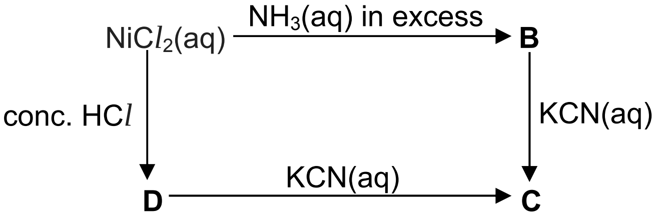
(iii) List one advantage and one disadvantage of the NiCad battery over the conventional alkaline dry cell battery.

Advantage: **rechargeable**

Disadvantage: **cadmium is toxic or higher cost**

[6]

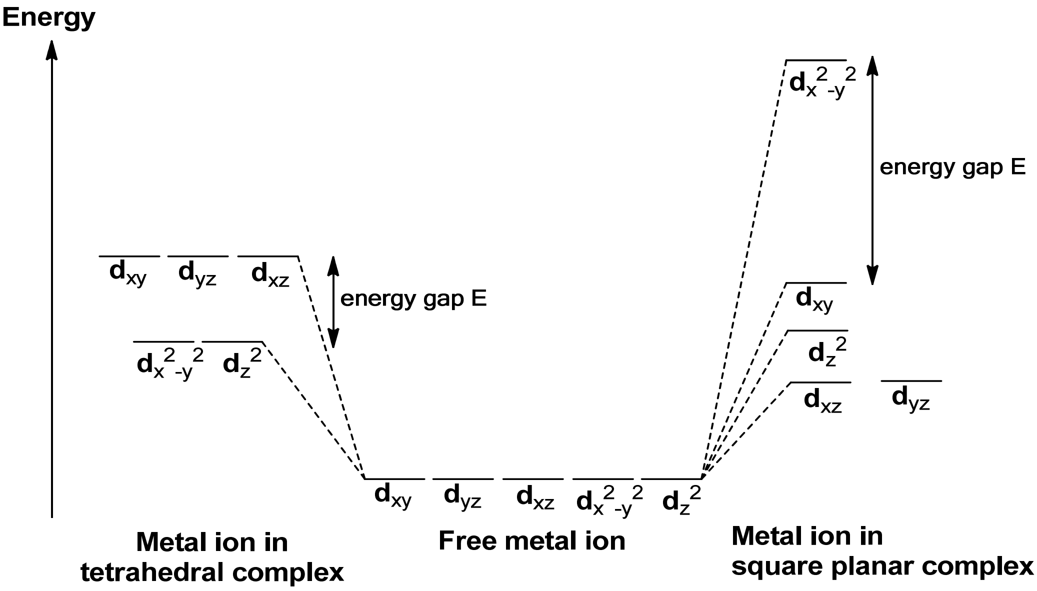
(d) Aqueous nickel(II) chloride, $NiCl_2$, is a green solution which undergoes the following reactions:



(i) State the formula of compound **B** given that the coordination number of the cation in **B** is the same as that found in the cation present in $NiCl_2(aq)$.

$[Ni(NH_3)_6]Cl_2$

(ii) The following diagram shows how the d-orbitals of a metal ion are split in a tetrahedral and square planar complex.

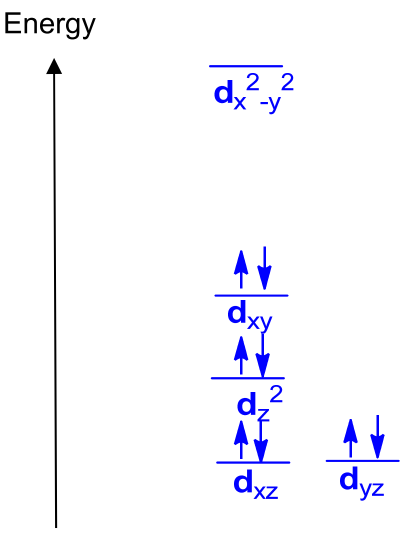


Both **C** and **D** contain complexes with cations having coordination number of 4. When Cl^- ligands in **D** is changed to CN^- ligands in **C**, the Ni^{2+} ion changes its geometry and electronic configuration from a 'high spin' state with lower energy gap to a 'low spin' state with higher energy gap.

In a 'high spin' state, the electrons occupy all the d-orbitals singly, before starting to pair up in the lower energy d-orbitals.

In a 'low spin' state, the lower energy d-orbitals are filled first, by pairing up if necessary, before the higher energy d-orbitals are used.

Complete the diagrams showing the electrons distribution of Ni^{2+} ion in **C** and in **D** and hence predict the number of unpaired electrons in each complex.

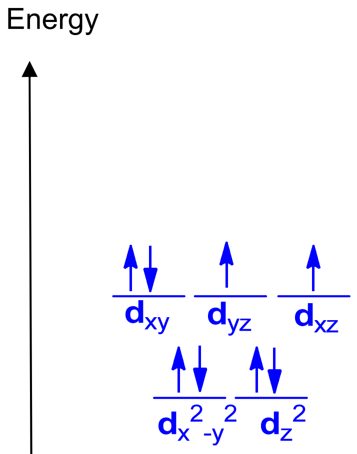


d-orbitals of Ni^{2+} in **C**

0

[Turn over

Number of unpaired electrons: ……………



d-orbitals of Ni^{2+} in **D**

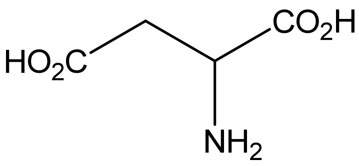
Number of unpaired electrons: ….2…………

[5]

[Total: 15]

4 Amino acids are critical to life and they serve as the building blocks of proteins.

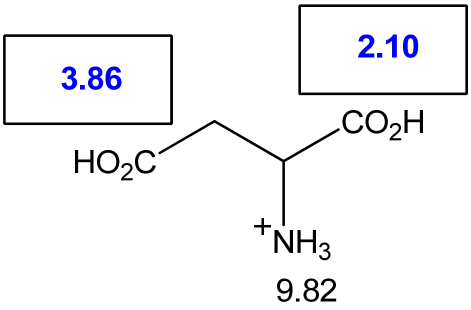
(a) Aspartic acid plays a role in the neuroendocrine system, as a regulator in the synthesis and release of hormones. It also plays an important role in the conversion of carbohydrates into energy. Proper levels of aspartic acid are necessary for the synthesis of other biochemicals.



aspartic acid

The three pK_a values associated with aspartic acid are 2.10, 3.86 and 9.82. The isoelectric point is 2.77.

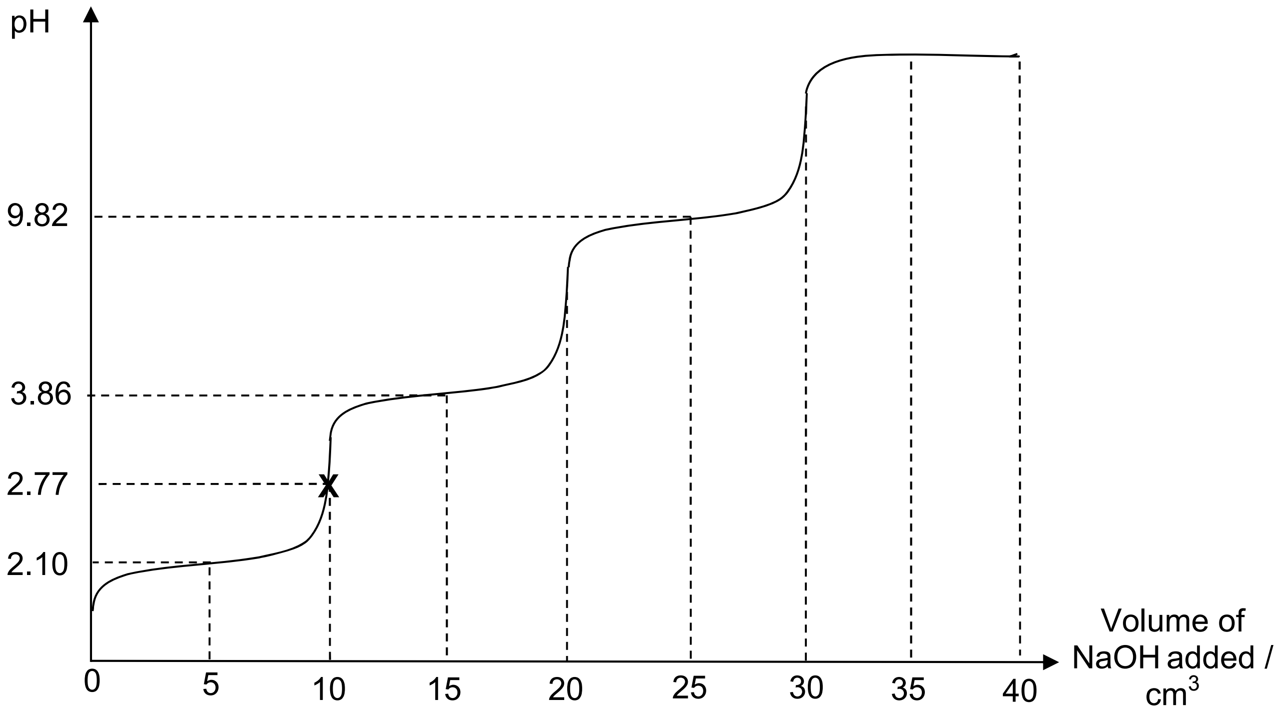
(i) In the boxes provided, assign the pK_a values for each carboxylic acid group. Suggest, with explanations, the pK_a values associated with these groups.



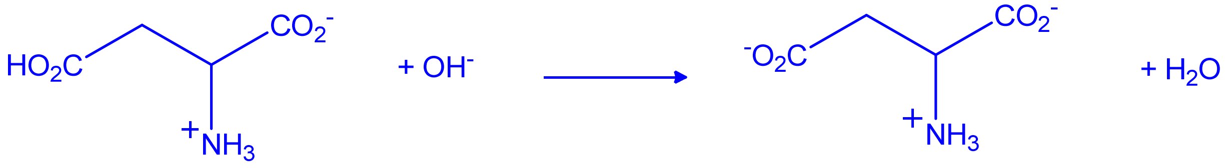
The –CO_2H nearer to –NH_2 has the smaller pKa and is the stronger acid as the O-H bond is more polarised and weaker due to its close proximity to the electronegative N atom.

[Turn over

(ii) Sketch the pH-volume added curve you would expect to obtain when 40 cm^3 of 0.10 mol dm^{-3} NaOH is added to 10 cm^3 of 0.10 mol dm^{-3} of the **protonated** form of aspartic acid. Show clearly on your curve where the three pK_a values occur and the isoelectric point.



(iii) Write an equation to show how aspartic acid can act as a buffer when a small amount of OH^- is added at a pH of 3.86.



(iv) Calculate the pH of the resulting solution when 40 cm^3 of NaOH has been added.

Amount of excess NaOH = (40 – 30) / 1000 × 0.10 = <u>1 × 10^{-3} mol</u>

Final volume of resultant solution = 40 + 10 = 50 cm^3

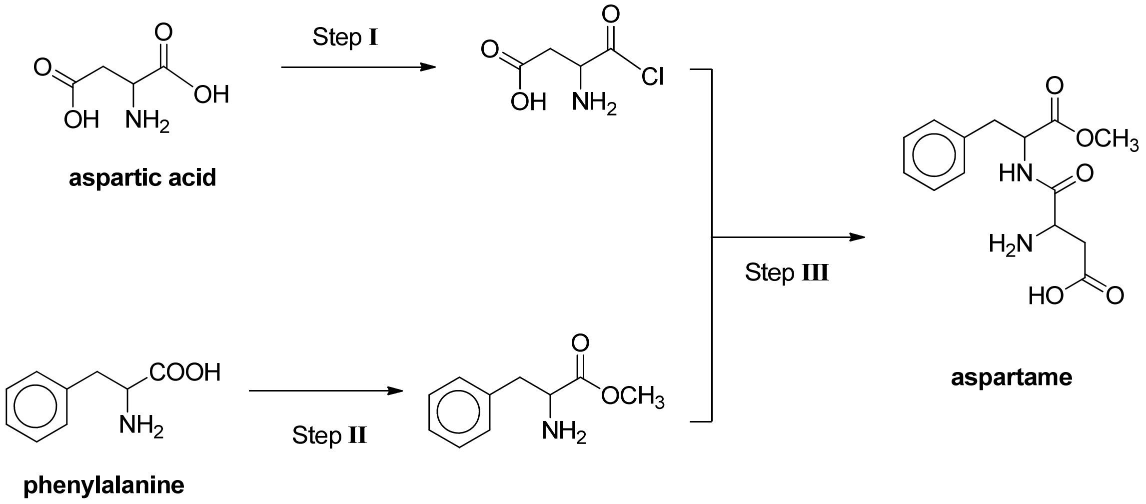
[NaOH] = 1 × 10^{-3} / (50/1000) = 0.02 mol dm^{-3}

pH = 14 – (-lg 0.02)

= <u>12.3</u>

[8]

(b) Phenylalanine, together with aspartic acid, is also used to make aspartame, an artificial sweetener. The main synthesis steps are shown below.



(i) State the reagents and conditions required for Step **II**.

Methanol, concentrated H_2SO_4, heat under reflux

(ii) Identify the type of reaction in Step **III**.

Condensation / Addition-elimination

[2]

(c) Hair is made mostly of a protein called keratin, which is also present in nails. The table below shows the R groups of some of the α-amino acids which make up keratin.

Acid	**R group**
Lys	$-CH_2CH_2CH_2CH_2NH_2$
Ser	$-CH_2OH$
Glu	$-CH_2CH_2CO_2H$
Cys	$-CH_2SH$
Met	$-CH_2CH_2SCH_3$

Hair can be curly because of the covalent disulfide bonds that can be formed between the amino acid residues. This is brought about by an oxidation process.

(i) Write a chemical equation to show how the cysteine amino acid residues in the keratin molecule can form disulfide bridges.

$-CH_2-S-H + H-S-CH_2- + [O] \rightarrow -CH_2-S-S-CH_2- + H_2O$

OR $-CH_2-S-H + H-S-CH_2- \rightarrow -CH_2-S-S-CH_2- + H_2$

[Turn over

In order to straighten curly hair permanently, using a heating iron is insufficient. Instead, one will need to go to the hairdresser for rebonding, a chemical hair treatment that makes his or her hair straight.

Ammonium thioglycolate ($HSCH_2CO_2NH_4$) is a chemical which is used to straighten hair. It can reverse the reaction in **(i)** and break the disulfide bridges in hair.

$$\text{Keratin-S-S-keratin} + 2\ \text{HS-}CH_2CO_2NH_4 \rightarrow 2\ \text{HS-keratin} + HO_2C\text{-}CH_2S\text{-}SCH_2CO_2H + 2\ NH_3$$

(ii) Suggest the role of ammonium thioglycolate in the above reaction.

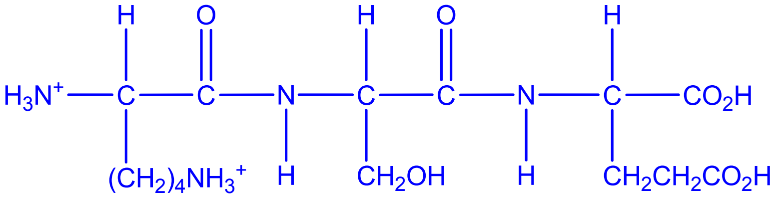
Ammonium thioglycolate acts as a reducing agent and breaks the covalent disulfide bond between two cysteine residues.

(iii) What aspect of keratin's protein structure is altered during the process of rebonding?

As the R-group interactions (covalent disulfide bonds) are being destroyed, tertiary (and quaternary) structures will be affected.

[3]

(d) Upon acidic hydrolysis of keratin, a tripeptide, lys-ser-glu is obtained. Draw the structure of the tripeptide formed.



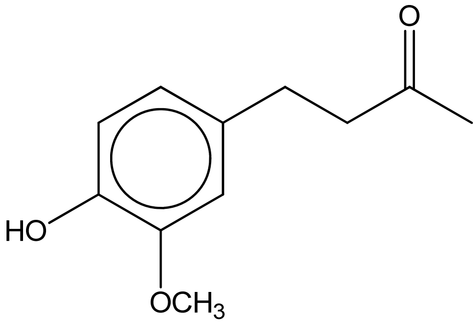
$$H_3N^+\text{—}CH((CH_2)_4NH_3^+)\text{—}C(=O)\text{—}NH\text{—}CH(CH_2OH)\text{—}C(=O)\text{—}NH\text{—}CH(CH_2CH_2CO_2H)\text{—}CO_2H$$

[2]

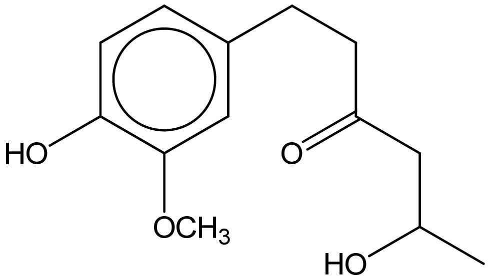
[Total: 15]

5 Spices of the ginger family such as ginger and turmeric have a long history of culinary and medical use.

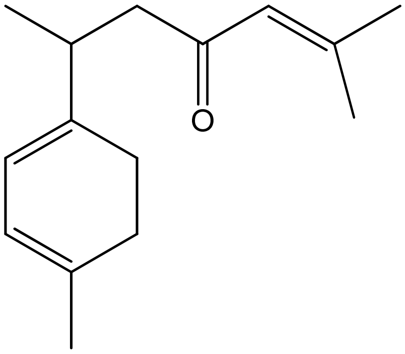
The following three compounds present in either ginger or turmeric are medically important:



zingerone



gingerol



tumerone

The group –OCH_3 which is present in zingerone and gingerol can be regarded as inert.

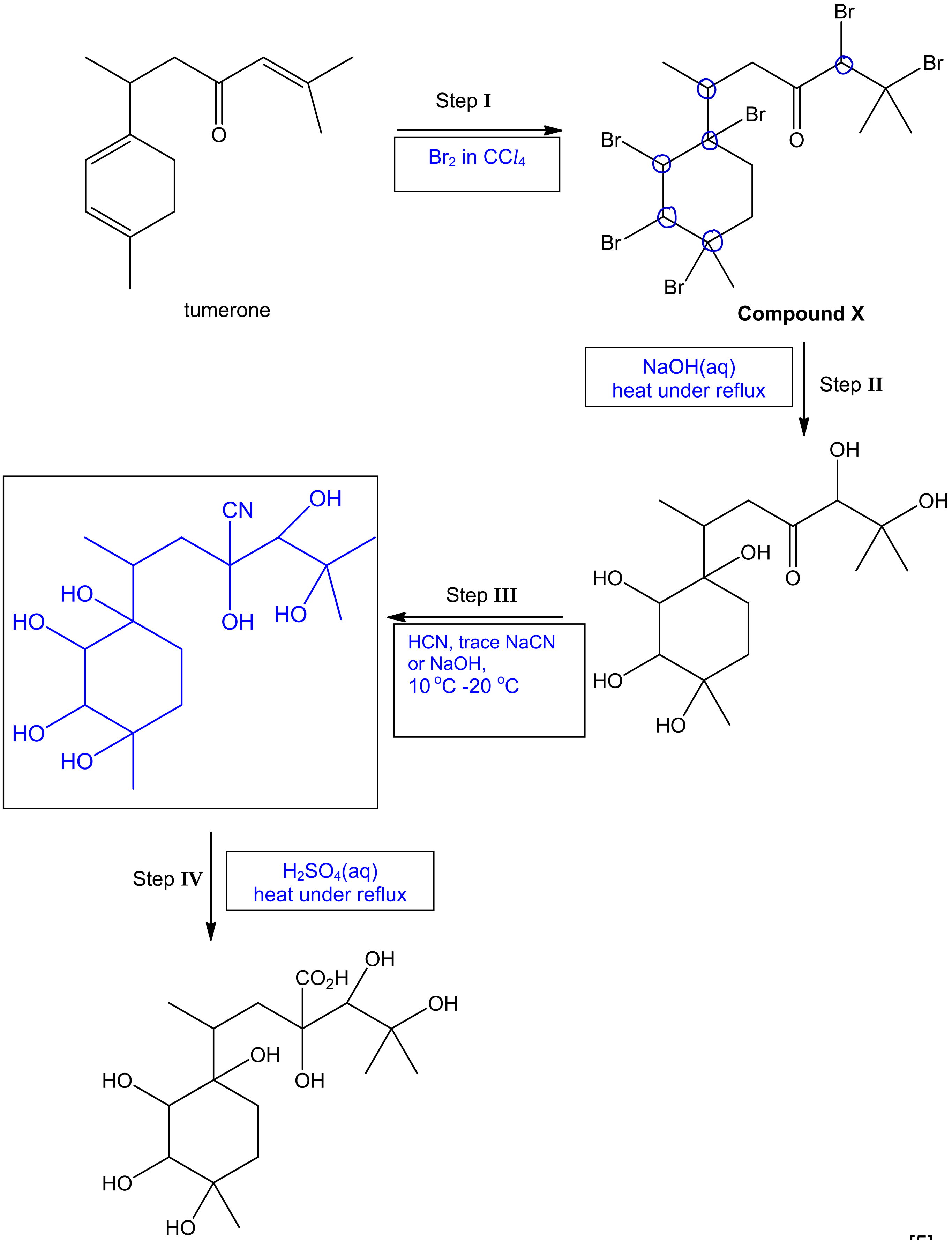
(a) In the boxes below, name **one** of the three compounds above that will react with **each** of the following reagents. In each case, give the observations for the reaction undergone. Each compound may only be used **once**.

Reagent	Name of compound	Observations
Neutral $FeCl_3$(aq)	zingerone	Violet colouration seen
2, 4-DNPH	tumerone	Orange precipitate (crystals) seen
PCl_5	gingerol	Steamy (steamy white/white) fumes of HC*l* seen

[6]

[Turn over

(b) Complete the following diagram with the reagents and conditions required for Steps **I- IV**, and draw the structure of the product formed from Step **III** in the box provided.



[5]

(c) **Compound X** exhibits two types of stereoisomerism.

(i) Circle all chiral centres in the molecule of **Compound X** given in **(b)**.

(ii) While there are no C=C bonds in **Compound X**, it exhibits cis-trans isomerism. Explain why this is the case.

Four carbon atoms in the ring are bonded to two different groups each, and there is restricted rotation about the C-C bonds due to the ring.

(iii) The total number of stereoisomers for a compound is given by 2^n, where

n = number of chiral centres + number of pairs of cis-trans isomers

Suggest why, when determining the total number of stereoisomers for **Compound X**, the above statement is not valid.

The spatial arrangement of groups about the chiral centres in the ring will determine both the optical and geometric isomers involving these centres, hence to avoid double counting, the geometric isomers should not be counted.

[4]

[Total: 15]

[Turn over