Name _____ **Class: 13S**_____ **Reg Number:** _____

MERIDIAN JUNIOR COLLEGE
JC 2 Preliminary Examination
Higher 2

Chemistry 9647/03

Paper 3 Free Response **17 September 2014**

2 hours

Additional Materials: *Data Booklet*
Writing Paper

INSTRUCTIONS TO CANDIDATES

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

Answer 4 out of 5 questions in this paper.

Begin each question on a fresh page of writing paper.

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

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

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

INFORMATION FOR CANDIDATES

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

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

Answer any 4 out of 5 questions in this paper.
*Begin each question on a **fresh sheet** of writing paper.*

1 The following tables show some standard enthalpies change of solution, $\Delta H^{\ominus}_{sol}$, regarding some Group I chlorides and Group II carbonates, as well as their corresponding solubility in water under standard conditions.

Group I chlorides	NaCl	KCl	RbCl
$\Delta H^{\ominus}_{sol}$ / kJ mol^{-1}	+3.9	+17.2	+16.7
Solubility / mol per 100 cm^3 of water	0.615	0.481	0.781

Group II carbonates	$MgCO_3$	$CaCO_3$	$SrCO_3$
$\Delta H^{\ominus}_{sol}$ / kJ mol^{-1}	–25.3	–12.3	–3.4
Solubility / mol per 100 cm^3 of water	1.26×10^{-4}	1.30×10^{-5}	7.45×10^{-6}

Use relevant data from the tables above, if applicable, to answer the following questions.

(a) It is a well-known fact that the solubility of Group II carbonates decreases down the group.

(i) Using the $\Delta H^{\ominus}_{sol}$ data from **both** tables, comment on whether $\Delta H^{\ominus}_{sol}$ is a good predictor for the solubilities of salts in water.

Group II carbonates have negative / exothermic $\Delta H^{\ominus}_{soln}$ even though they are insoluble, On the other hand, $\Delta H^{\ominus}_{soln}$ of soluble Group I chlorides are positive / endothermic. Hence, $\Delta H^{\ominus}_{soln}$ is not a good predictor of solubility.

(ii) Calculate the solubility product of calcium carbonate, stating its units.

[3]

Solubility of $CaCO_3 = 1.30 \times 10^{-5} \times 10 = 1.30 \times 10^{-4}$ mol dm^{-3}

K_{sp} of $CaCO_3$ $= [Ca^{2+}] [CO_3^{2-}]$
$= (1.30 \times 10^{-4})^2$
$= 1.69 \times 10^{-8}$ mol^2 dm^{-6}

(b) (i) Assuming a 100% efficient system, calculate the maximum temperature change that could take place when potassium chloride is dissolved in 100 cm^3 of water. State clearly whether the temperature increases or decreases.

0.481 mol of KCl dissolves in 100 cm^3 water to give a saturated solution.

Quantity of heat evolved by solution = 0.481 x 17.2
= 8.273 kJ = mcΔT

Maximum temperature decrease, $\Delta T = \dfrac{8.273 \times 10^3}{100 \times 4.18}$

$= 19.8\ ^{o}C / K$

(ii) The enthalpy change of solution assumes that an infinitely dilute solution is formed when one mole of ionic compound dissolves in water. Based on this assumption, suggest a reason to account for the maximum temperature change not being achieved in practice other than the system is not 100% efficient.

[3]

A very concentrated solution results in ions being in close proximity in the solution allowing repulsive and attractive forces to exist.

(c) The standard entropy change of solution, $\Delta S^{\ominus}_{sol}$, of sodium chloride is $+42.6\ J\ mol^{-1}\ K^{-1}$.

(i) Calculate the standard Gibbs free energy change of solution, $\Delta G^{\ominus}_{sol}$, of sodium chloride, explaining why sodium chloride is soluble.

$\Delta G^{\ominus}_{sol} = \Delta H^{\ominus}_{sol} - T\Delta S^{\ominus}_{sol}$

$= +3.9 - 298\left(\dfrac{+42.6}{1000}\right)$

$= -8.79\ kJ\ mol^{-1} < 0,$

hence reaction is (energetically) feasible and salt dissolves.

(ii) The standard Gibbs free energy change of solution, $\Delta G^{\ominus}_{sol}$, of magnesium chloride is $-126.3\ kJ\ mol^{-1}$. Some standard enthalpy change of formation, $\Delta H^{\ominus}_{f}$, related to magnesium chloride are provided below.

Substances	$MgCl_2(s)$	$Mg^{2+}(aq)$	$Cl^-(aq)$
$\Delta H^{\ominus}_f$ / kJ mol^{-1}	–641.6	–462.0	–167.5

Calculate the $\Delta S^{\ominus}_{sol}$ of magnesium chloride. Hence, explain with reasoning, whether the sign of $\Delta S^{\ominus}_{sol}$ obtained is as expected.

[5]

$\Delta H^{\ominus}_{soln}(MgCl_2) = \Delta H^{\ominus}_f(Mg^{2+}(aq)) + 2\Delta H^{\ominus}_f(Cl^-(aq)) - \Delta H^{\ominus}_f(MgCl_2(s))$

$= -462.0 + 2(-167.5) - (-641.6)$

$= -155.4\ kJ\ mol^{-1}$

$\Delta G^{\ominus}_{soln} = \Delta H^{\ominus}_{soln} - T\Delta S^{\ominus}_{soln}$

$\Delta S^{\ominus}_{soln} = \dfrac{-155.4 - (-126.3)}{298}$

$= -0.0977\ kJ\ mol^{-1}\ K^{-1}$

$= -97.7\ J\ mol^{-1}\ K^{-1}$

The negative sign is unexpected.

When solid $MgCl_2$ is dissolved, aqueous ions are formed which caused entropy to increase and system is supposed to be more disordered.

(d) The melting point of $CaCO_3$ is 825 ^oC and its thermal decomposition temperature is 837 ^oC.

(i) The melting point of $BeCO_3$ is 54 ^oC. Briefly explain why the melting point of $BeCO_3$ is much lower than that of $CaCO_3$.

- $BeCO_3$ is a simple molecular compound with weak van der Waals' forces between molecules. $CaCO_3$ is a giant ionic lattice compound with strong electrostatic forces of attraction between oppositely charged ions of Ca^{2+} and CO_3^{2-}.

(ii) By quoting data from the *Data Booklet*, predict whether the thermal decomposition temperature of $SrCO_3$ would be higher or lower than that of $CaCO_3$.

[5]

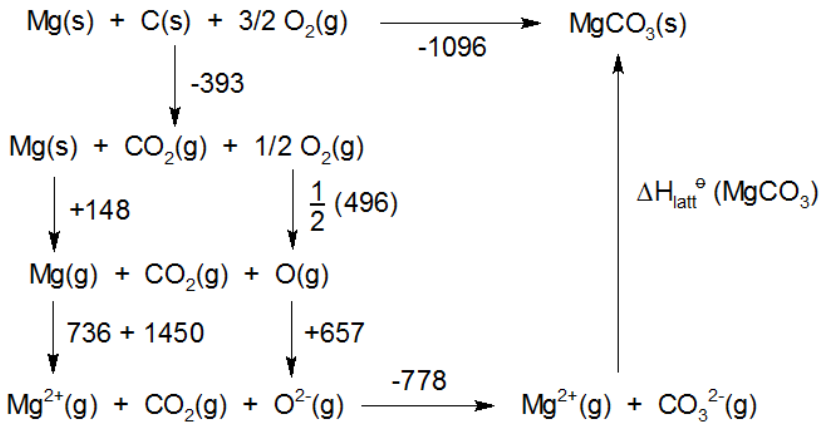
- ionic radius of Ca^{2+} = 0.099 nm, ionic radius of Sr^{2+} = 0.113 nm.
- ionic radius: $Sr^{2+} > Ca^{2+}$
- charge density and polarising power: $Sr^{2+} < Ca^{2+}$
- ease of cation to polarise CO_3^{2-} anion and break C–O bond: $Sr^{2+} < Ca^{2+}$
- energy required to break C–O bond and decompose compound: $SrCO_3 > CaCO_3$
- thermal stability: $SrCO_3 > CaCO_3$
- thermal decomposition temperature: $SrCO_3 > CaCO_3$

(e) Using relevant data from the *Data Booklet* and information given below, construct an energy cycle to calculate the lattice energy of $MgCO_3$.

enthalpy change of formation of magnesium carbonate	= –1096 kJ mol^{-1}
enthalpy change of formation of CO_2 (g)	= –393 kJ mol^{-1}
enthalpy change of atomisation of magnesium	= +148 kJ mol^{-1}
sum of first and second electron affinities of oxygen	= +657 kJ mol^{-1}
CO_2 (g) + O^{2-} (g) $\longrightarrow$ CO_3^{2-} (g) ;	ΔH_1 = –778 kJ mol^{-1}

[4]

[Total: 20]



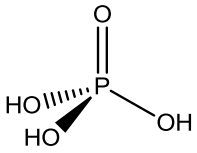
By Hess' Law,

$\Delta H_{latt}^{\ominus}(MgCO_3) = -1096 - (-393) - 148 - \frac{1}{2}(496) - 736 - 1450 - 657 - (-778)$

$= -3164 \text{ kJ mol}^{-1}$

2 This question is about phosphoric acid.

(a) Phosphoric acid, H_3PO_4, is a triprotic acid and its structure is given below.



phosphoric acid

The pK_a values of the two successive dissociations of H_3PO_4 at 25 ^{o}C are as shown.

	pK_{a1}	pK_{a2}
Phosphoric acid	2.1	7.2

Small quantities of H_3PO_4 are used to impart the sour taste to many soft drinks. A typical can of soft drink with density of 1.00 g cm^{-3} contains 0.05 % by mass of H_3PO_4.

(i) Briefly explain why the pK_{a2} of phosphoric acid is higher than its pK_{a1}.

$H_2PO_4^-$ is a weaker acid than H_3PO_4.

It is more difficult to dissociate H^+ from a negatively charge species / ion.

(ii) Calculate the concentration, in mol dm^{-3}, of phosphoric acid in the soft drink.

No. of moles of H_3PO_4 in 1 cm^3 of soft drink = $\frac{0.05}{100} \times \frac{1}{98.0} = 5.10 \times 10^{-6}$

$[H_3PO_4] = 5.10 \times 10^{-3}$ mol dm^{-3}

(iii) Hence, by considering only the first dissociation of H_3PO_4, determine the pH of this soft drink. Assume that the acidity of the soft drink arises only from H_3PO_4.

$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$ $\quad K_a = 10^{-2.1}$ mol dm^{-3}

$[H^+] = \sqrt{10^{-2.1} \times 5.10 \times 10^{-3}}$

$= 6.36 \times 10^{-3}$ mol dm^{-3}

$pH = -\log [H^+] = -\log (6.36 \times 10^{-3})$

$= 2.20$

(iv) Suggest, with reasoning, a suitable indicator that can be used to detect the first end point of the titration between H_3PO_4 and sodium hydroxide. [5]

Methyl orange.
The pH transition range (of its colour change) lies within the sharp pH change over the equivalence point.

(b) A buffer solution was prepared by mixing 50 cm^3 of 1.00 mol dm^{-3} Na_2HPO_4 and 50 cm^3 NaH_2PO_4 of unknown concentration. When 5.00×10^{-3} moles of sodium hydroxide was added to the buffer solution, the pH increased to 7.38.

Determine the unknown concentration of NaH_2PO_4 used to prepare the buffer. [2]

Let the original concentration of NaH_2PO_4 be y mol dm^{-3}.

When 5.00×10^{-3} mole of NaOH added,

$H_2PO_4^- + OH^- \rightarrow HPO_4^{2-} + H_2O$

Number of mole of $H_2PO_4^- = \frac{50}{1000}(y) - 0.005 = 0.05y - 0.005$

Number of mole of $HPO_4^{2-} = \frac{50}{1000} \times 1 + 0.005 = 0.055$

$pH = pK_{a1} + \lg \frac{[HPO_4^{2-}]}{[H_2PO_4^-]}$

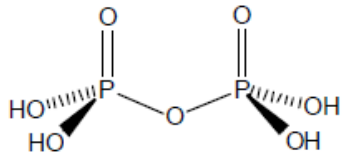
$7.38 = 7.2 + \lg \frac{0.055}{0.05y - 0.005}$

$y = 0.827$ mol dm^{-3}

(c) When pure H_3PO_4 undergoes dehydration, another phosphorus-containing acid **Y** is produced. The addition of calcium hydroxide to **Y** produces a white precipitate, $Ca_2P_2O_7$.

Draw the structure, clearly indicating the shape of **Y**. [1]

Y is $H_4P_2O_7$.



(d) Porous ceramics containing calcium phosphate, $Ca_3(PO_4)_2$, are commonly used in the manufacture of artificial teeth.

Given: K_{sp} of $Ca_3(PO_4)_2 = 1.21 \times 10^{-26}$ mol^5 dm^{-15}.

(i) Calculate the solubility of calcium phosphate in water.

$Ca_3(PO_4)_2\ (s) \rightleftharpoons 3Ca^{2+}\ (aq) + 2PO_4^{3-}\ (aq)$

Let the solubility of $Ca_3(PO_4)_2$ be x mol dm^{-3}.

$[Ca^{2+}]^3\ [PO_4^{3-}]^2 = 1.21 \times 10^{-26}$

$(3x)^3(2x)^2 = 1.21 \times 10^{-26}$

$x = 2.57 \times 10^{-6}$ mol dm^{-3}

(ii) Some calcium phosphate is dissolved into a solution of 0.50 g dm^{-3} calcium hydroxide, $Ca(OH)_2$, to produce a saturated solution. Calculate the solubility of $Ca_3(PO_4)_2$ in the saturated solution.

$[Ca(OH)_2] = [Ca^{2+}] = \dfrac{0.50}{74.1} = 6.748 \times 10^{-3}$ mol dm^{-3}

Assumes z mol of $Ca_3(PO_4)_2$ is dissolved in 1 dm^3 of 6.748×10^{-3} mol dm^{-3} $Ca(OH)_2$ to produce a saturated solution.

K_{sp} of $Ca_3(PO_4)_2 = [Ca^{2+}]^3\ [PO_4^{3-}]^2$
$1.21 \times 10^{-26} = (6.748 \times 10^{-3} + 3z)^3\ (2z)^2$
$z = 9.92 \times 10^{-11}$ mol dm^{-3}

(iii) Comment on the difference in the solubility values of calcium phosphate in **(d)(i)** and **(d)(ii)**.

[6]

$Ca_3(PO_4)_2$ (s) $\rightleftharpoons$ $3Ca^{2+}$ (aq) + $2PO_4^{3-}$ (aq) ---------- (1)

$Ca(OH)_2$ (aq) $\rightarrow$ Ca^{2+} (aq) + $2OH^-$ (aq) ---------- (2)

This is due to common ion effect due to the presence of common ion, Ca^{2+}.

By Le Chatelier's Principle, the equilibrium position in (1) will shift left to reduce $[Ca^{2+}]$.

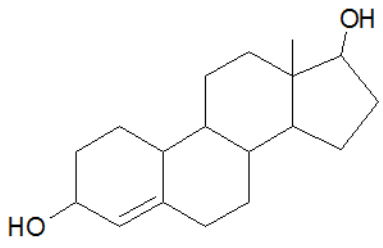
Solubility of $Ca_3(PO_4)_2$ in $Ca(OH)_2$ will be lower than that in water.

(e) When concentrated phosphoric acid and concentrated sulfuric acid are reacted separately with solid potassium bromide, different bromine-containing substances **A** and **B** are formed respectively.

When concentrated sulfuric acid is reacted with solid potassium chloride, the product formed reacted with manganese(II) oxide to give a chlorine-containing substance **C**. Substances **C** and **B** are structurally similar.

For the following questions, you need to use the actual identity of A, B and C in your answers.

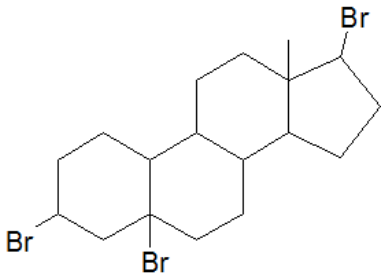
(i) Bolandiol is a banned synthetic anabolic steroid.



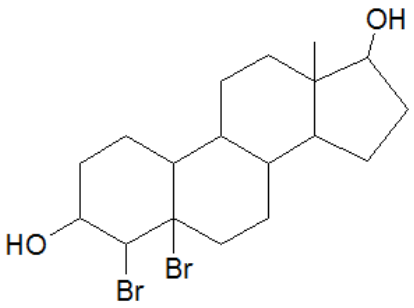
bolandiol

Draw the structural formulae of the organic products formed when bolandiol is heated with:

1. A.



2. B.



(ii) Write the equation when **C** is reacted with hot concentrated NaOH.

$3Cl_2 + 6NaOH \rightarrow 5NaCl + NaClO_3 + 3H_2O$

(iii) By considering the reactions of **C** and I_2 with thiosulfate, $S_2O_3^{2-}$, explain the difference in the oxidising strength of **C** and I_2 in terms of their oxidation numbers. Include any relevant equations in your answers.

[6]

[Total: 20]

$4Cl_2 + Na_2S_2O_3 + 5H_2O \rightarrow 2NaHSO_4 + 8HCl$

$I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI$

Chlorine, being the stronger oxidising agent can oxidise thiosulfate to sulfate (change in oxidation no. of S: from +2 to +6).

Iodine, being the weaker oxidising agent can only oxidise thiosulfate to tetrathionate (change in oxidation no. of S: from +2 to +2.5).

3 In mammals including humans, nitrogen monoxide NO is an important cellular signaling molecule. It acts as a powerful vasodilator.

(a) Although elements in the same group can be said to have similar chemical properties, there are variations, e.g. in reactivity or products formed in a reaction.

For example, nitrogen is the only element in Group V that does not readily produce an oxide when burnt in oxygen or air. Nitrogen monoxide is produced only when temperatures typically found in fuel engines are reached.

Down Group V, there is also an increased tendency for the element to possess metallic properties. This is due to the changes in ionisation energies and electronegativity down the group.

(i) Suggest a reason why nitrogen monoxide is formed only when temperatures in fuel engines are reached.

A high temperature is needed to overcome the large activation energy to break the very strong NΞN bond.

(ii) State and explain how the first ionisation energy of the element changes down the group.

Down the group, 1st ionisation energy decreases.
Atomic radius increases due to increasing number of quantum shells of electrons. Valence electrons are further away from the nucleus and better shielded by the inner quantum shells of electrons. Hence, there is a weaker electrostatic attraction between the nucleus and valence electrons.

(iii) How does the changes in ionisation energies and electronegativity down the group account for the increasing metallic behaviour of the Group V elements? [4]

The decrease in ionisation energy, and decrease in electronegativity means that down the group, the elements are less likely to share electrons, and more likely to lose electrons.

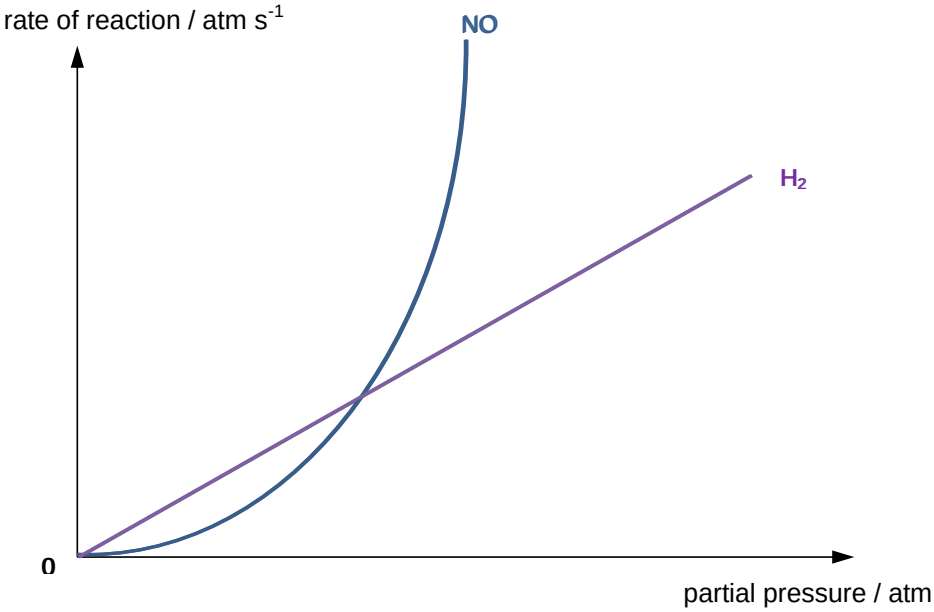
(b) At 800 K, nitrogen monoxide reacts with hydrogen as shown below:

$$2H_2(g) + 2NO(g) \longrightarrow 2H_2O(g) + N_2(g)$$

In a series of experiments, the initial rate of the above reaction was investigated with varying partial pressures of the reactants. The following data was obtained:

Experiment	$p(H_2)$ / atm	p(NO) / atm	initial rate / atm s^{-1}
1	0.64	1.60	1.50×10^{-7}
2	0.64	0.80	3.75×10^{-8}
3	0.32	1.60	7.50×10^{-8}

(i) On the same axes, sketch suitable graphs to illustrate clearly how the rate of reaction would vary with increasing partial pressures of H_2 and NO respectively.



(ii) Write down the rate equation in terms of the partial pressures, indicating clearly the units of the rate constant.

Rate = $k\ (p_{H2})\ (p_{NO})^2$
Units of k: $atm^{-2}\ s^{-1}$

(iii) Based on the rate equation, the following mechanism was proposed for this reaction.

Step 1 $\quad 2NO \longrightarrow N_2O + O$

Step 2 $\quad H_2 + O \longrightarrow H_2O$

Step 3 $\quad H_2 + N_2O \longrightarrow H_2O + N_2$

Suggest which of the steps in the mechanism is therefore the rate determining step.

[4]

Step 3

(c) The following reduction potentials regarding nitrogen monoxide and its related compounds are relevant in this question.

	$E^{\ominus}$ / V
$NO_3^- + 3H^+ + 2e \rightleftharpoons HNO_2 + H_2O$	+0.93
$HNO_2 + H^+ + e \rightleftharpoons NO + H_2O$	+0.99
$2NO + 2H^+ + 2e \rightleftharpoons N_2O + H_2O$	+1.59
$N_2O + 2H^+ + 2e \rightleftharpoons N_2 + H_2O$	+1.77

(i) An excess of iron(II) sulfate was added to a solution of nitric(V) acid. Using the information provided, state which nitrogen-containing product would be produced.

N_2 is expected to be produced.

(ii) Instead of the predicted product in **(c)(i)**, a dark brown iron(II) octahedral complex is formed in the reaction, whereby one molecule of nitrogen monoxide is involved in each unit of the cation. Suggest the formula of this compound.

$[Fe(H_2O)_5(NO)]^{2+}SO_4^{2-}$

(iii) Hence, by considering the structure of nitrogen monoxide, relative to the other possible nitrogen compounds, suggest a reason why the reaction stops at the production of nitrogen monoxide.

[3]

Compared to the other possible nitrogen compounds, NO is the only radical species (or NO has an odd number of electrons.) Hence it is highly reactive, and forms a complex via dative bonding.

(d) Compound **F**, C_4H_5NO, is a neutral compound to form a series of compounds investigated for their possible vasodilation properties. By heating **F** in dilute H_2SO_4, compound **G** $C_4H_6O_3$ is obtained. In a separate one-step reaction, **F** is able to form **H** $C_4H_{11}NO$.
Compared to their solubility in water, compound **G** is more soluble in sodium hydroxide, whereas compound **H** is more soluble in dilute acid. When **G** reacts with PCl_5 and subsequently added to **H** in a 1:1 ratio, two possible isomers **J** and **K**, with a formula $C_8H_{15}NO_3$, are produced. Of the two, **J** is a neutral compound whereas **K** is not.

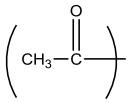
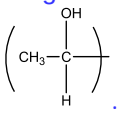
All the compounds **F**, **G**, **H**, **J** and **K**, produce a yellow precipitate with alkaline aqueous iodine.

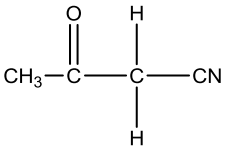
Deduce the structures of **F**, **G**, **H**, **J** and **K**, clearly stating your reasoning. Include in your answer, the possible reagents and conditions needed to convert **F** to **H**.

[9]

[Total: 20]

Since F is neutral, it cannot contain an amine group.

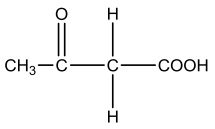
Since like G, H, J and K, it undergoes mild oxidation with alkaline aqueous iodine, it would contain  or  .

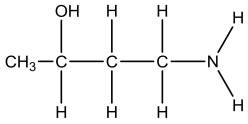


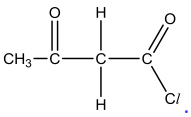
- From its formula, it is likely to be .

F likely undergoes hydrolysis in H_2SO_4 to give G.
G is also likely to be acidic since it dissolves better in NaOH.

Conversely H is likely to be basic (or contains $–NH_2$) since it dissolves better in acid.

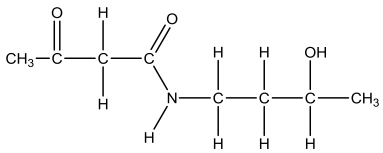
G is likely to be  .

H is likely to be  .

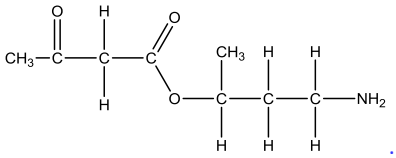
G likely undergoes nucleophilic substitution with PCl_5, giving  .

The resulting compound undergoes nucleophilic substitution (or esterification) with H to give J an amide group, or K an ester group (since K with $–NH_2$ group is not neutral).

J and K are therefore likely to be



and



.

To obtain H from F, the reagents and conditions needed are
LiA*l*H_4 in dry ether, r.t.p.

4 (a) (i) Describe the reactions that occur when separate samples of sodium and phosphorous are heated in excess chlorine.

Na reacts very vigorously with excess chlorine to form NaC*l*.
P reacts slowly with excess chlorine to PCl_5.

(ii) Describe the reaction of each of the resulting chloride with excess water, stating the approximate pH of the solution formed, and writing a balanced equation with state symbols for any reaction that takes place. [4]

NaC*l* undergoes hydration to form neutral solution with pH 7.

PCl_5 undergoes complete hydrolysis to form strongly acidic solution with pH 2.

PCl_5 (s) + $4H_2O$ (*l*) $\longrightarrow$ H_3PO_4 (aq) + 5HC*l* (aq)

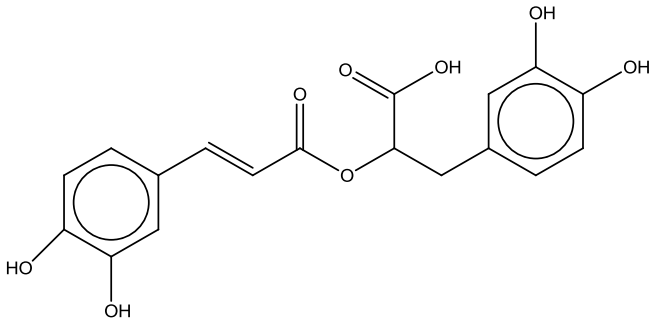
(b) Sulfur and chlorine can react together to form S_2Cl_2. When 1.35 g of this sulfur chloride reacted with water, a yellow solid was formed, together with a solution containing sulfurous acid and hydrochloric acid. The resulting solution required 20.00 cm^3 of 1.00 mol dm^{-3} silver nitrate for complete reaction.

Use the data above to deduce the equation for the reaction between S_2Cl_2 and water, and suggest the type of reaction. [2]

$2S_2Cl_2$ + $3H_2O$ $\rightarrow$ 3S + H_2SO_3 + 4HC*l*

Disproportionation

(c) Rosmarinic acid occurs in culinary herbs such as rosemary, sage and thyme

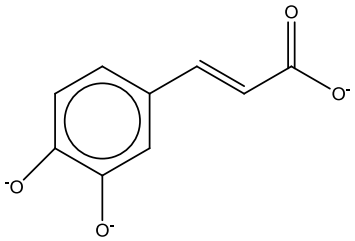


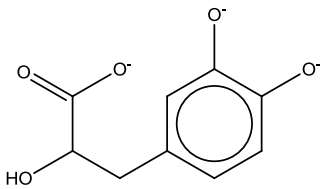
rosmarinic acid

(i) State the number of moles of HC*l* that will be formed when excess PCl_5 is added to one mole of rosmarinic acid.

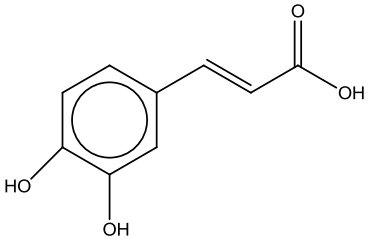
1

(ii) Draw the structural formulae of the organic products produced when rosmarinic acid is reacted with hot KOH(aq).

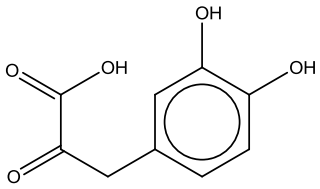




(iii) Draw the structural formulae of the two compounds produced when rosmarinic acid is heated under reflux with acidified $Na_2Cr_2O_7$(aq). Suggest one test (stating reagents, conditions and observations) that would enable the two compounds to be distinguished from each other.



product D



product E

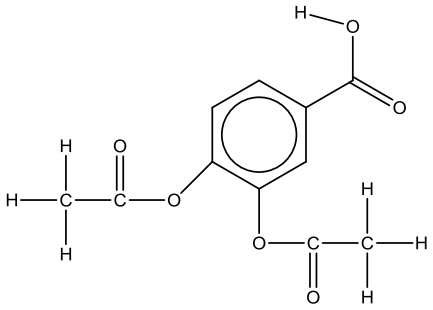
Add 2,4-DNPH to each compound/product separately and warm/heat.
For product D, no ppt is seen.
For product E, orange ppt is seen.

[Turn Over

(iv) Rosmarinic acid produced an aromatic compound and a carbon-containing inorganic compound when heated under reflux with alkaline $KMnO_4(aq)$ followed by dilute HC*l*.

Draw the displayed formula of the compound formed when the aromatic compound is treated with excess ethanoyl chloride.

[7]



(d) Rosmarinic acid contains two organic groups with pK_a values lower than that of alcohol. Compare and explain the relative pK_a values of these three organic groups.

[3]

Relative acidity: carboxylic acid > phenol > alcohol
pK_a: carboxylic acid < phenol < alcohol

For phenol:
The phenoxide ion is stabilised by charge delocalisation.
The lone pair of electrons on the oxygen atom of the phenoxide ion is delocalised into the benzene ring.
This reduces the intensity of the negative charge on the oxygen atom of the phenoxide ion.
$\Rightarrow$ Hence stabilising the phenoxide ion relative to the alkoxide ion.

For alcohol:
The electron-donating alkyl group increases the intensity of the negative charge on the oxygen atom.
$\Rightarrow$ Hence destabilising the alkoxide ion (relative to the phenoxide ion).

For carboxylic acid:
The carboxylate anion is resonance stabilised by the delocalisation of the negative charge over the C atom and both oxygen atoms.
$\Rightarrow$ Hence carboxylate anion is more stable than phenoxide ion.

Hence stability of conjugate base: carboxylate > phenoxide > alkoxide
Relative acidity: carboxylic acid > phenol > alcohol

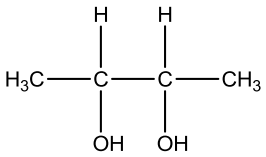
(e) 1 mol of diol **P**, $C_4H_{10}O_2$, undergoes oxidation to produce 2 mol of yellow solid. **P** produces a mixture of 4 different products when heated with concentrated sulfuric acid. Three of the products, **W**, **X** and **Y** with the formula C_4H_6 are unsaturated compounds while product **Z** with formula $C_8H_{16}O_2$ is a saturated compound.

(i) State the reagents and conditions used for the oxidation reaction.

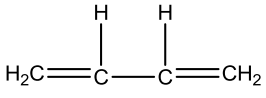
NaOH(aq), I_2, warm

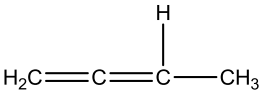
(ii) Suggest the structural formulae of **P**, **W**, **X**, **Y** and **Z**.

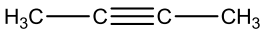
[4]



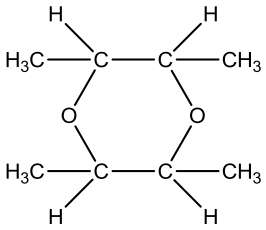
P







X, Y, Z



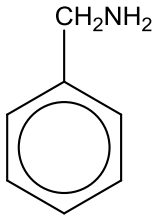
Z

[Total: 20]

[Turn Over

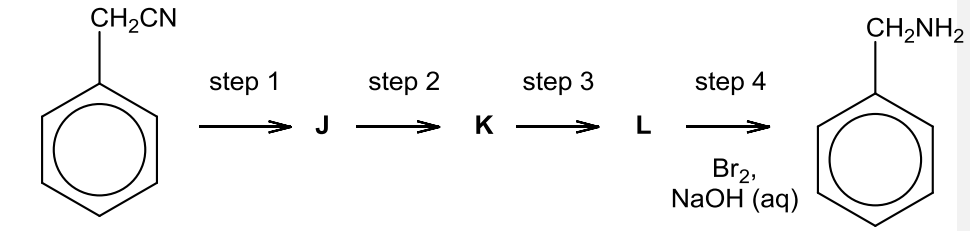
5 (a) An amine may be derived from an amide following a reaction known as the Hofmann rearrangement. In this reaction, a primary amide is treated with Br_2 and aqueous NaOH to yield the corresponding amine and CO_2 as a by-product.

(i) Benzylamine is a compound used in topical creams and antifungal solutions.



benzylamine

Suggest reagents and conditions you would use in a four-step synthesis of benzylamine from phenylacetonitrile, using the Hofmann rearrangement as the final step. Identify the intermediates **J**, **K** and **L**.

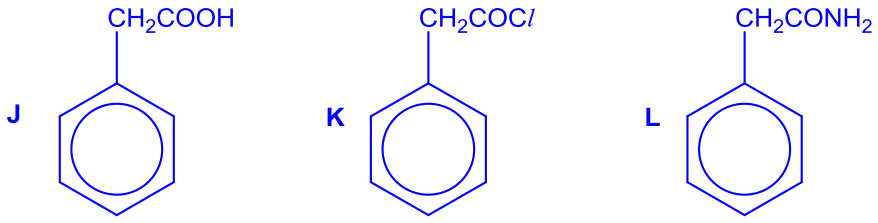


phenylacetonitrile

step 1 - HC*l* (aq) *or* H_2SO_4 (aq), heat

step 2 - PCl_5, r.t.p. *or* $SOCl_2$, r.t.p.

step 3 - Excess NH_3, r.t.p.



(ii) In a laboratory experiment of the synthesis in **(a)(i)**, the carbon dioxide gas produced in step 4 was collected. Calculate the volume of gas collected at standard conditions when 0.468 g of phenylacetonitrile was used in the experiment.

[6]

M_r of $C_6H_5CH_2CN = 117$

No. of mol of $C_6H_5CH_2CN = \frac{0.468}{117}$
$= 0.00400$

$C_6H_5CH_2CN \equiv CO_2$
Volume of $CO_2 = 0.00400 \times 24.0$
$= 0.0960\ dm^3$ *or* $96.0\ cm^3$

(b) In the human body, carbon dioxide is dissolved in the bloodstream as carbonic acid, H_2CO_3. The carbonic acid is in equilibrium with hydrogen carbonate, HCO_3^-, which allows the blood to maintain the pH of the body at 7.4.

(i) Briefly describe how hydrogen carbonate, HCO_3^-, maintained relatively constant pH when the acid concentration in the bloodstream increases and decreases. Write any equations necessary to account for the observations.

When excess H^+ is present in the bloodstream,
$H^+ + HCO_3^- \rightarrow H_2CO_3$
$H_2CO_3 \rightarrow CO_2 + H_2O$

Excess acid in the blood (which stimulates deep breathing) is removed by reacting with HCO_3^- to form H_2CO_3, which is then decomposed into H_2O and CO_2 (which can be exhaled); pH of blood is thus kept fairly constant.

When a decrease in H^+ occurs,
$H_2CO_3\,(aq) \rightleftharpoons H^+\,(aq) + HCO_3^-\,(aq)$

By Le Chatelier's Principle, the equilibrium position shifts right hence causing an increase in H^+ concentration to counteract the change; pH of blood is thus kept fairly constant.

(ii) Suggest another example of buffer in biological system.

[3]

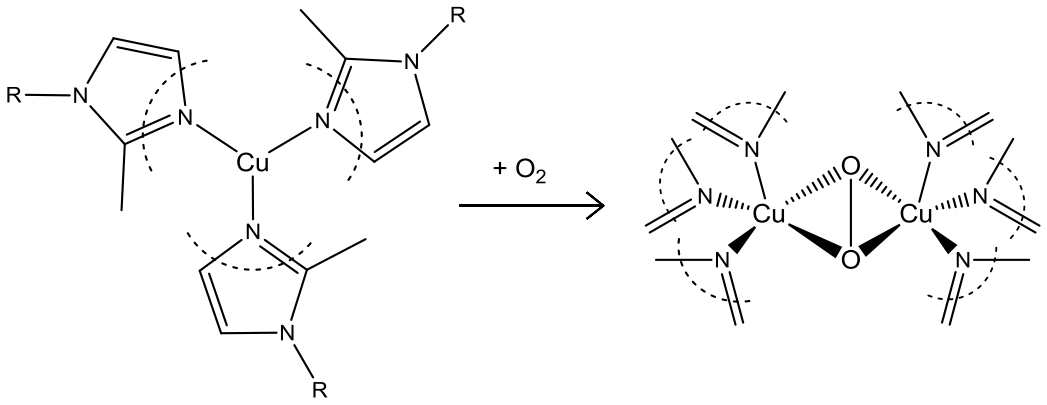
Amino acids as buffers.

Or

Phosphoric acid-phosphate (H_3PO_4 / $H_2PO_4^{2-}$) buffer in cells

(c) In the human bloodstream, the oxygen-carrying haemoglobin protein is red in colour due to iron being present. In certain crustaceans such as crabs, the oxygen-carrying protein is haemocyanin, where copper is involved.

Deoxyhaemocyanin is colourless. When it combines with oxygen as oxyhaemocyanin, the protein turns blue, giving crab's blood its characteristic blue colour.



deoxyhaemocyanin - colourless oxyhaemocyanin - blue

Suggest the oxidation states of copper in deoxyhaemocyanin and oxyhaemocyanin, and explain why oxyhaemocyanin is blue in colour whereas deoxyhaemocyanin is colourless. [4]

Deoxyhaemocyanin: Cu in +1 oxidation state / Cu(I)
Oxyhaemocyanin: Cu in +2 oxidation state / Cu(II)

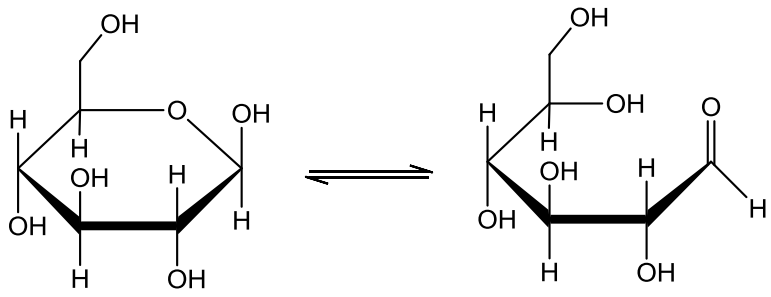
In the copper complexes, the d orbitals to be split split into different energy levels in the presence of ligands. (d orbitals splitting).

In oxyhaemocyanin where Cu(II) has $[Ar]3d^9$ electron configuration, a lower energy d electron undergoes d-d transition and is promoted to a higher energy partially filled d orbital.

During the transition, the d electron absorbs orange / longer wavelength(s) of light from the visible region of the electromagnetic spectrum and the remaining wavelengths are not absorbed, hence oxyhaemocyanin appears blue.

In deoxyhaemocyanin where Cu(I) has $[Ar]3d^{10}$ electron configuration, the d orbitals are all filled, so no d-d transition is possible, hence deoxyhaemocyanin is colourless.

(d) Copper ions are present in Fehling's solution and can be used to test for "reducing sugars". Glucose, a basic form of sugar, has the following structure.



cyclic form of glucose

open-chain form of glucose

Glucose gives a positive test with Fehling's solution.

(i) Identify the functional group involved in the reaction and describe what is observed when Fehling's solution is added to glucose with heating.

Aldehyde

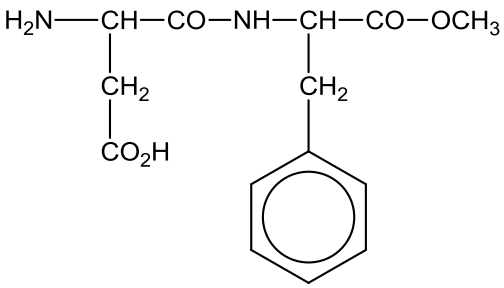
Brick-red ppt of Cu_2O formed.

(ii) Explain why glucose is classified as a "reducing sugar".

[2]

Cu^{2+} (Cu in oxidation state +2) in Fehling's solution is reduced by glucose to Cu(I) oxide (Cu in oxidation state +1).

(e) *Aspartame* is a simple synthetic dipeptide used as a sweetening agent which is often sold under the trade names of *Nutrasweet* or *Equal*. It is 180 times as sweet as sugar. It is often used to sweeten soft drinks due to its relatively good solubility in water.



Aspartame

(i) Apart from the phenyl ring, name **four** different functional groups in the *aspartame* molecule.

1° amine, carboxylic acid, amide, ester

(ii) Identify a functional group in *aspartame* which contributes to its solubility in water. Give a reason for your answer.

Carboxylic acid *or* amine

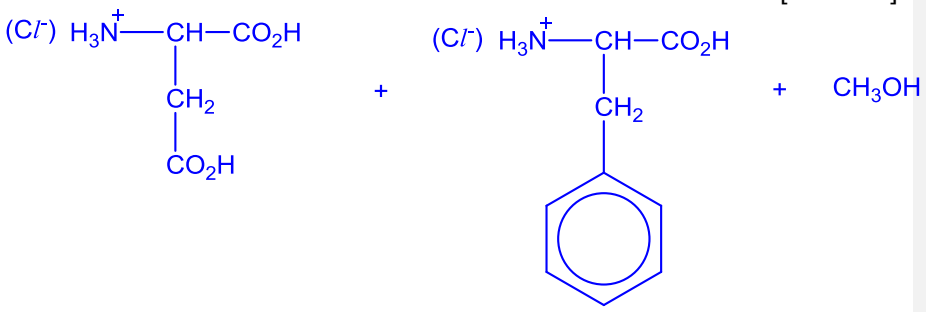
Hydrogen bonding can form between the functional groups and water molecules. *(accept ion-dipole from zwitterion)*

(iii) Aspartame is also not stable under low pH conditions. Draw the products formed when *aspartame* is reacted with hot aqueous hydrochloric acid.

Comment [M1]: Change to low pH since you are using hot acid for reaction.

[5]

[Total: 20]



End of Paper 3