NATIONAL JUNIOR COLLEGE
PRELIMINARY EXAMINATIONS
Higher 2

CANDIDATE NAME

SUBJECT CLASS | REGISTRATION NUMBER

CHEMISTRY
Paper 3 Free response

9647/03
Wed 17 Sep 2014

2 hours

READ THESE INSTRUCTIONS FIRST

Answer any ***four*** questions.

Start your answer to each question on a fresh piece of paper.

A Data Booklet is 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 behind the cover page.

1 Iodine monochloride, IC*l*, is an interhalogen compound that is formed when chlorine gas is passed through iodine crystals. Generally, interhalogen compounds have chemical properties similar to that of halogens.

(a) **(i)** Predict the physical state of IC*l* at room temperature.
Liquid / solid.
Mr of ICl : 162.5
Mr of Br_2 : 159.8
Strength of td-id expected to be similar to that of Br_2, hence liquid state.
Td-id stronger than Cl_2 but weaker than I_2.

(ii) By considering the partial charges in IC*l*, explain how water reacts with IC*l*.
The lone pair of electrons on the oxygen of H_2O attacks the $\delta+$ I, breaking the I-C*l* bond, forming HOI. The H^+ then combines with the Cl^-.

(iii) Hence construct an equation for the reaction of IC*l* with water.
$ICl + H_2O \rightarrow HOI + HCl$

[3]

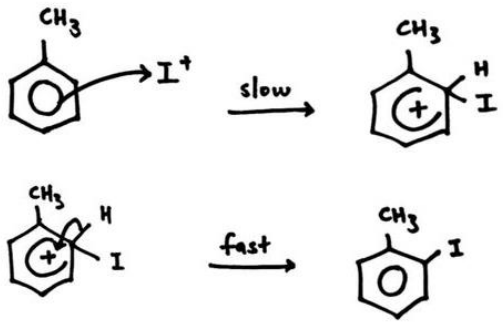
(b) Methylbenzene reacts with IC*l* in the presence of $FeCl_3$ to form compound **A**.

(i) Draw the structure of **A**.
2-iodo methylbenzene

(ii) Describe the mechanism of this reaction, clearly indicating the role of $FeCl_3$.

Electrophilic substitution reaction

$FeCl_3 + ICl \rightarrow [FeCl_4]^- + I^+$



$H^+ + [FeCl_4]^- \rightarrow FeCl_3 + HCl$

[4]

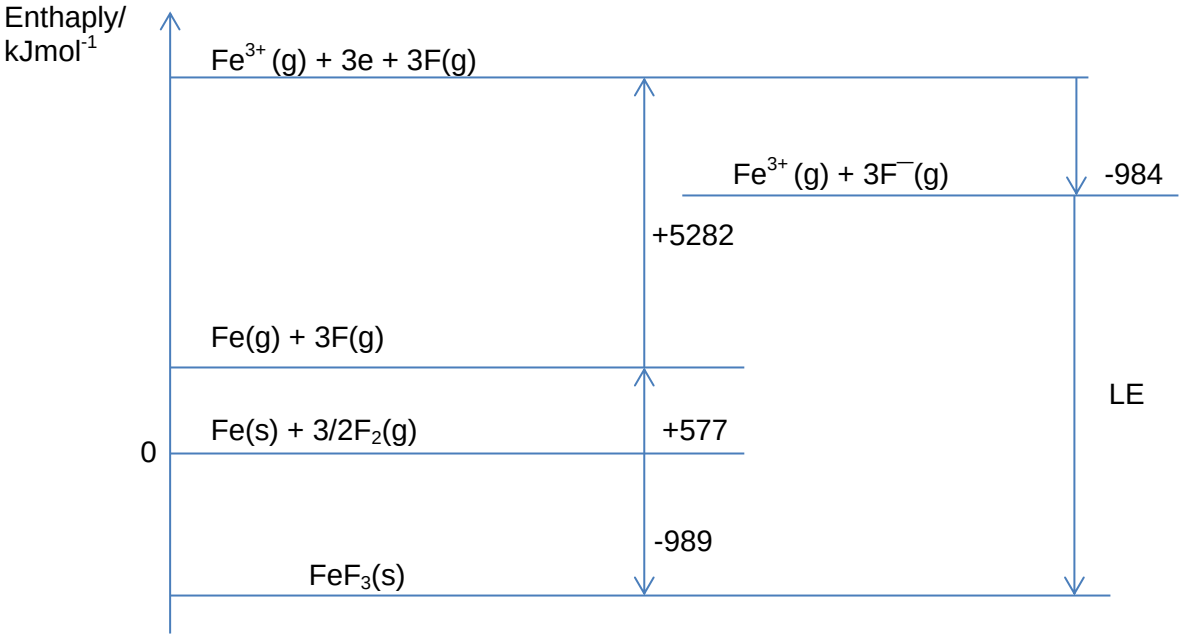
(c) $FeCl_3$ and FeF_3 are both formed from a metal and a non-metal. However, in molten state, only FeF_3 is able to conduct electricity and $FeCl_3$ does not.

(i) Suggest the structures of $FeCl_3$ and FeF_3 and explain why iron forms two different types of compounds when reacted with the different halogens – fluorine and chlorine.

$FeCl_3$: Simple covalent molecules
FeF_3 : Ionic lattice structure
Fe^{3+} has a high charge density and is hence able to polarise the larger electron cloud of the chlorine atoms resulting in more extensive sharing of electrons hence forming a covalent bond.
Fluoride ions due to their small size have low polarisability.

(ii) Using the information given below as well as relevant data from the *Data Booklet*, construct an energy level diagram for the formation of FeF_3 from its elements to determine its lattice energy.

enthalpy change of atomisation of Fe	+340 kJ mol^{-1}
first electron affinity of F	–328 kJ mol^{-1}
standard enthalpy change of formation of FeF_3	–989 kJ mol^{-1}



+340 + 762 + 1560 + 2960 + 3/2 x 158 + 3 x -328 + LE = -989
LE = -5860 kJmol^{-1}

[7]

(d) Iron is a transition metal, a d-block element that varies from s-block metals in terms of physical properties. The table below gives data about some physical properties of the elements – iron and calcium.

Property	calcium	Iron
relative atomic mass	40.1	55.8
atomic radius/ nm	0.197	0.126
density/ g cm^{-3}	1.54	7.86
electrical conductivity	Good	Good

(i) Write down the full electronic configurations of calcium and iron.

Ca : $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
Fe : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$

(ii) Explain why the atomic radius of iron is smaller than that of calcium.

Iron has more protons and hence has a higher nuclear charge than calcium. The additional d electrons in iron are poor shielding electrons and hence the shielding effect is negligible. Iron hence has a higher effective nuclear charge.
The valence electrons in iron are held more tightly resulting in a smaller atomic radius.

(iii) Suggest why iron has a higher density than calcium.

Iron has a larger atomic mass, but a smaller atomic radius that results in a smaller volume than calcium. Since density is mass/volume, iron has a higher density.

(iv) Explain which of the 2 metals would be expected to have a higher electrical conductivity.

Both the 3d and 4s electrons in iron can be delocalised into the sea of electrons as they are of similar energy.
Hence iron is expected to have a higher electrical conductivity due to the larger number of charge carriers.

[6]

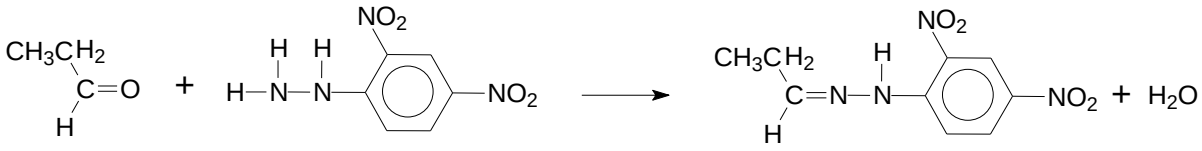
[Total:20]

2 **(a)** In the qualitative analysis of organic compounds, the presence of a carbonyl functional group can be confirmed by using 2,4–dinitrophenylhydrazine.

When 2 cm^3 of 2,4–dinitrophenylhydrazine solution is added to separate test tubes containing 2 cm^3 propanone and 2 cm^3 propanal respectively, a bright orange precipitate is observed in both test tubes.

Write a balanced equation for the reaction of 2,4–dinitrophenylhydrazine with propanal. Hence, identify the type of reaction.

[2]

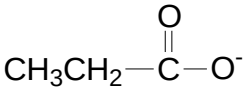


Type of reaction: **Condensation reaction**

(b) Fehling's solution, an alkaline copper(II) tartrate complex, can be used to distinguish between propanal and propanone. A positive test would show the formation of a brick red solid, Cu_2O.

(i) Identify which of the two organic compounds above would give a positive test with the Fehling's solution. Give the structure of the organic product for this reaction.

Propanal will react with Fehling's solution.

Organic product is 

The brick red solid, Cu_2O, is isolated through filtration. It is soluble in excess ammonia to give a colourless solution **B.** When left exposed to air, the colourless solution **B** turns into a deep blue solution, containing the complex ion $[Cu(NH_3)_4]^{2+}$.

(ii) Explain why the solution containing the complex ion $[Cu(NH_3)_4]^{2+}$ is deep blue in colour.

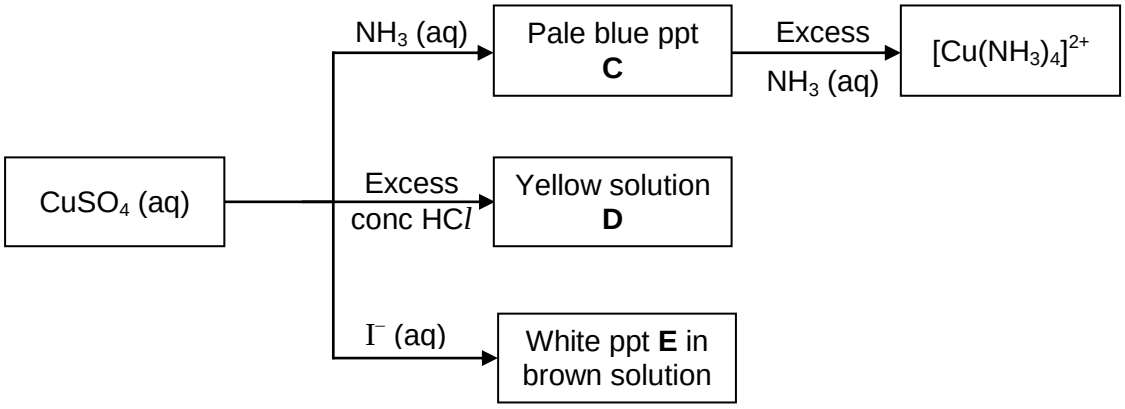
In the presence of NH_3 ligands, the d orbitals of Cu^{2+} split into two different energy levels with an energy gap, ΔE. he **electron** from the lower energy d orbital **can be promoted** to the higher energy d orbital by absorbing wavelength of light with energy corresponding to the energy gap, ΔE. Wavelength of light **not absorbed** will be reflected and **seen as the complementary colour**, deep blue.

(iii) Identify the oxidation state of copper in the copper containing species in the colourless solution **B**, and write its electronic configuration. Hence explain why solution **B** is colourless.

Oxidation state of Cu in **B** = +1
Electronic configuration: [Ar] $3d^{10}$

In Cu^{+} complex, the d orbitals are fully filled. Hence, it is not possible to have d–d transition and all the wavelengths of visible light spectrum are reflected. The solution appears colourless.

(c) $[Cu(NH_3)_4]^{2+}$ can also be prepared by adding excess aqueous NH_3 to aqueous copper(II) sulfate. Three reactions involving aqueous copper(II) sulfate are illustrated below.



(c) **(i)** Explain fully, with the aid of equations, how the pale blue precipitate **C** is formed when NH_3 (aq) is added to $CuSO_4$ (aq).

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$
$Cu^{2+} + 2\ OH^- \rightarrow Cu(OH)_2$

(ii) Write an equation for the formation of the yellow solution **D**. Hence, explain what will be observed when water is added to solution **D**.

$[Cu(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CuCl_4]^{2-} + 6H_2O$
Blue **Yellow**

By Le Chatelier's Principle, when water is added to solution **D**, the above equilibrium will shift to the left, and the yellow solution will turn to blue.

When hexane is added to the brown solution containing the white precipitate **E** and shaken, a purple hexane layer is formed above a colourless aqueous layer containing the white precipitate **E**.

(iii) By referring to the types of intermolecular interactions, explain why the aqueous solution turns from brown to colourless upon mixing of hexane.

Both I_2 and hexane are non-polar and has intermolecular forces of temporary dipole–induced dipole attraction (td-id) between molecules of I_2 and between molecules of hexane. The energy released from forming the solvent-solute interaction (td-id) is sufficient to overcome the solvent-solvent and solute-solute interaction.
I_2 is more soluble in hexane than in H_2O, and thus the hexane layer turns purple, while the aqueous layer turn colourless.

(iv) Construct an ionic equation for the formation of the white precipitate **E** when I^-(aq) is added to $CuSO_4$ (aq).

$$2Cu^{2+} + 4\ I^- \rightarrow 2CuI + I_2$$

[6]

(d) Ethane−1,2−diamine, $NH_2CH_2CH_2NH_2$ (abbreviated as ***en*** when it acts as a ligand), can undergo ligand exchange reaction with $[Cu(NH_3)_4]^{2+}$ to form $[Cu(\textbf{\textit{en}})_2]^{2+}$.

The standard entropy change for this reaction has a value of 88 J mol^{-1} K^{-1}.

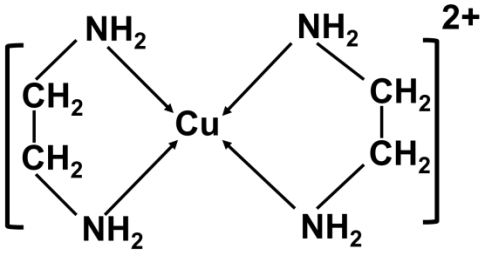
(i) Write an equation for this reaction and hence suggest the sign of the entropy change.

$$[Cu(NH_3)_4]^{2+} + 2\ \textbf{\textit{en}} \rightleftharpoons [Cu(\textbf{\textit{en}})_2]^{2+} + 4\ NH_3$$

There are a greater number of particles in the products of the reaction. Hence the system becomes more disordered after the reaction, thus entropy increases. Entropy change is a positive value.

(ii) Draw the structure of the complex ion $[Cu(\textbf{\textit{en}})_2]^{2+}$ and identify its shape.

Shape is **square planar** or **tetrahedral** (Coordination number = 4)



[4]

(e) Ethane–1,2–diamine, $NH_2CH_2CH_2NH_2$, can be synthesised by reacting 1,2–dichloroethane with ammonia under suitable conditions.

$$ClCH_2CH_2Cl \xrightarrow{NH_3} NH_2CH_2CH_2NH_2$$

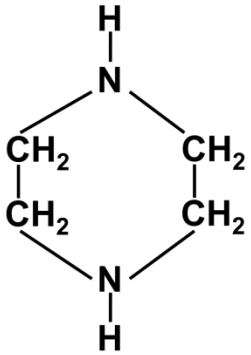
(i) State the type of reaction occurring in the above synthesis.

Nucleophilic substitution

(ii) A student attempted to carry out the above experiment. One of the side products obtained has the molecular formula $C_4H_{10}N_2$.

Suggest the structure of this side product.

Further substitution reaction between $NH_2CH_2CH_2NH_2$ and $ClCH_2CH_2Cl$



[2]

[Total:20]

3 Dental erosion is the irreversible loss of tooth structure due to chemical dissolution by acids. Our dental enamel is composed primarily of hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$.

$$Ca_{10}(PO_4)_6(OH)_2\ (s) + aq \rightleftharpoons 10Ca^{2+}\ (aq) + 6PO_4^{3-}\ (aq) + 2OH^-\ (aq)$$

When a tooth is placed in distilled water of pH 7, a small amount of it will slowly dissolve. In contrast, our saliva fluid contains calcium, phosphate and hydroxide ions that prevent the dissolution of our dental enamel.

Acidic foods and drinks, such as Coca Cola which contains phosphoric acid, may damage our teeth when it is frequently consumed. The solubility of our enamel increases about 10 – fold for each unit decrease in pH.

(a) (i) Phosphoric(V) acid, H_3PO_4, is a triprotic acid. The magnitude of the second acid dissociation, K_{a2}, is much smaller than the first acid dissociation K_{a1}.

Suggest an explanation for this observation using relevant equations.

$$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^- \qquad K_{a_1}$$
$$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{2-} \qquad K_{a_2}$$

Protons are more easily lost from neutral H_3PO_4 molecules than from $H_2PO_4^-$ anions.
OR
The formation of the more stable conjugate base $H_2PO_4^-$, compared to HPO_4^{2-}, favoured the first acid dissociation.

(ii) Identify **two** reasons for the increased solubility of enamel at low pH under constant temperature. Explain your answer.

$Ca_{10}(PO_4)_6(OH)\ (s) + aq \rightleftharpoons 10Ca^{2+}(aq) + 6PO_4^{3-}(aq) + 2OH^-(aq)$ --- eqm (1)

$K_{sp} = [Ca^{2+}]^{10}[PO_4^{3-}]^6[OH^-]^2$

At low pH (high $[H^+]$),
- H^+ reacts with OH^- to form H_2O.
- H^+ reacts with base PO_4^{3-} to form HPO_4^{2-}.

The reduction of $[OH^-]$ and $[PO_4^{3-}]$ results in IP < K_{sp} significantly.
OR
The reduction of $[OH^-]$ and $[PO_4^{3-}]$ favours the forward direction of equilibrium (1).

Thus the enamel dissolves more at low pH.

[5]

(b) One other important function of our saliva is its buffering ability. There are three possible buffer systems in saliva:

- the protein buffer,
- the carbonic acid/ hydrogencarbonate buffer,
- the phosphate buffer.

The carbonic acid/ hydrogencarbonate buffer maintains the oral cavity at about pH 6.3 to reduce the risk of dental erosion.

(i) Write an equation to explain how the carbonic acid/ hydrogencarbonate buffer prevents dental erosion when small amounts of acid are produced from the digestion of sugars.

$$HCO_3^- + H^+ \rightarrow H_2CO_3 \left(\rightleftharpoons CO_2 + H_2O \right)$$

(ii) A solution of 0.5 mol dm^{-3} carbonic acid, H_2CO_3, has a pH of 3.34.

(I) Calculate the acid dissociation constant, K_a, of carbonic acid.

(II) Hence, determine the ratio of $[HCO_3^-]/[H_2CO_3]$ present in the mouth to maintain the pH of the oral cavity at 6.3.

$$pH = 3.34 \Rightarrow [H^+] = 10^{-3.34} = 4.571 \times 10^{-4} \text{ mol dm}^{-3}$$

$$K_a = \frac{[HCO_3^-][H^+]}{[H_2CO_3]}$$

$$K_a = \frac{(10^{-3.34})(10^{-3.34})}{0.5 - 10^{-3.34}}$$

$$= \mathbf{4.18 \times 10^{-7} \text{ mol dm}^{-3}}$$

(II)

$$pH = pK_a + \lg\frac{[HCO_3^-]}{[H_2CO_3]}$$

$$6.3 = 6.379 + \lg\frac{[HCO_3^-]}{[H_2CO_3]}$$

$$\frac{[HCO_3^-]}{[H_2CO_3]} = \mathbf{\underline{0.835}\ or\ \frac{167}{200}}$$

(iii) A student decides to create a phosphate buffer to study its effectiveness in maintaining the pH of the oral cavity in the mouth.

Given that K_a of $KH_2PO_4(aq)$ is 6.23×10^{-8} mol dm^{-3}, what volume of 0.1 mol dm^{-3} NaOH(aq) must be added to 100 cm^3 of 0.1 mol dm^{-3} KH_2PO_4 (aq) to prepare a buffer solution of pH 6.3?

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

pK_a of $KH_2PO_4(aq)$ = 7.206

Let the amount of NaOH to be added be x cm^3.
Amount of HPO_4^{2-} = Amount of NaOH = *x* mol
Amount of $H_2PO_4^-$ = (0.01– *x*)

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

$$6.3 = 7.206 + \lg\frac{[HPO_4^{2-}]}{[H_2PO_4^-]}$$

$$\frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = \underline{\mathbf{0.124}}$$

In the buffer, final total volume is the same, thus:

$$\frac{\text{Amount of } HPO_4^{2-}}{\text{Amount of } H_2PO_4^-} = \underline{\mathbf{0.124}}$$

$$\frac{x}{(0.01-x)} = 0.124$$

$$\underline{\mathbf{x = 0.001106 \text{ mol}}}$$

$$\text{Volume} = \frac{0.001106}{(0.1)} = 0.01106 dm^3 = 11.10 cm^3$$

[7]

(c) Phosphoric(III) acid, H_3PO_3, on heating at 200 °C converts to phosphoric(V) acid, H_3PO_4, and phosphine, PH_3.

(i) Explain, with reference to structure and bonding, the relative boiling points of PCl_3, PH_3 and H_3PO_3.

All three compounds are made up of **simple covalent molecules**.

The **stronger H-bonding** between H_3PO_3 molecules requires **largest amount of energy** to overcome them **compared to the weak temporary dipole – induced dipole interactions** in PCl_3 and PH_3.
Thus H_3PO_3 has the highest boiling point.

PCl_3 molecules, with **greater ease of distortion** of their **larger electron cloud size**, will have **stronger temporary dipole – induced dipole interactions** between each other compare to PH_3 molecules.
So PCl_3 has a higher boiling point than PH_3.

(ii) Describe, with the aid of an equation, how H_3PO_3 can be prepared from PCl_3.
$PCl_3 + 3H_2O \rightarrow 3HCl + H_3PO_3$

PCl_3 undergo hydrolysis to form acidic H_3PO_3.

(iii) When reacted with sulfur at 180 °C, PCl_3 produces a compound **F** with M_r = 169.6. **F** reacts with water readily to form an acidic solution and a colourless gas with a rotten egg smell.

(I) Suggest a formula for **F**, and describe its shape.

$PSCl_3$
Shape: Tetrahedral

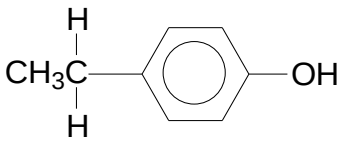
(II) Hence, by considering the partial charges in **F**, write an overall equation for the reaction of **F** with water.

$PSCl_3 + 4H_2O \rightarrow H_3PO_4 + H_2S + 3HCl$

[8]

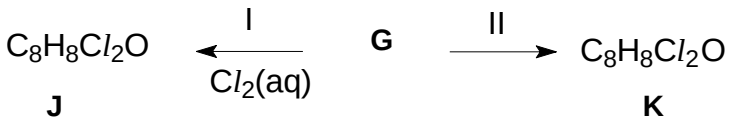
[Total:20]

4 4-ethylphenol, **G**, and its chlorinated products have useful antiseptic properties.



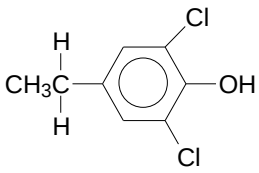
G

Depending on the conditions of the reaction, **G** can react with chlorine in two different ways, giving the two isomers **J** and **K**. In these reactions chlorine reacts in a similar manner to bromine.



J **K**

(a) **(i)** Suggest a structural formula for **J**.



2,6-dichloro-4-ethylphenol

(ii) Explain whether you would expect **J** to be more or less acidic than phenol.

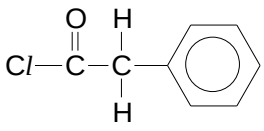
J is a stronger acid. Both conjugate base from **J** and phenol are resonance stabilised but **J** has two electronegative Cl (effect outweigh one electron releasing alkyl group) which helps to further disperse the charge of the conjugate base from **J**, making it more stable than phenoxide. Therefore **J** is a stronger acid.

(iii) Give the reagent and conditions for the formation of **K**.

Cl_2(g), UV light or high temp

[4]

(b) Under suitable conditions, 4-ethylphenol can be converted to compound **L.**



L

(i) **J**, **K** and **L** are halogen–containing compounds which can react with a nucleophile under suitable conditions.

Explain why the reactivity of **J**, **K** and **L** towards nucleophilic substitution is as follows:

L > **K** > **J**

When compounds **J, K** and **L** react with nucleophiles, C-Cl bond is substituted. **L** is most susceptible to nucleophilic attack because the carboxyl carbon is the most partial positive due to additional highly electronegative O attached. On the other hand, carbon in
carboxyl carbon of **J** is the least partial positive as the continuous overlap of p orbital of Cl with pi orbital of benzene partially offset the partial positive charge of this carbon. This makes it most resistant towards nucleophilic reaction.

OR

C-Cl bond of **J** is the strongest as the continuous overlap of p orbital of Cl with pi orbital of benzene results in double bond character in C-Cl bond.This makes it most resistant towards nucleophilic reaction as it is more difficult to overcome the stronger C-Cl bond.

(ii) Hence, describe suitable chemical tests to distinguish **J**, **K** and **L**.

Upon addition of $AgNO_3(aq)$ to three separate samples of **J**, **K** and **L**, **L** gives white ppt while the **J** and **K** do not.

When **J** and **K** are separately
(i) heated with aq NaOH (ii) cool, excess HNO_3 (iii) add $AgNO_3(aq)$

White ppt observed with **C** only.

OR

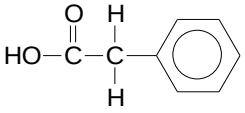
	J	**K**	**L**
$AgNO_3$ (aq)	No precipitate	No precipitate	White precipitate
(i) heated with aq NaOH (ii) cool, excess HNO_3 (iii) add $AgNO_3(aq)$	No precipitate	White precipitate	

[5]

(c) Compound **L** can easily form other acid derivatives when reacted with suitable reagents such as phenol and methylamine.

(i) Phenol reacts with **L** to form an ester. Suggest and explain the condition required to carry out such a conversion.

NaOH reacts with phenol to form phenoxide. This is to increase the electron density at oxygen making it a stronger nucleophile.

(ii) Suggest the structural formula of the product formed when methylamine is reacted with  instead of **L**.

$CH_3NH_3^+$ $C_6H_5CH_2COO^-$

(d) **(i)** Compound **M**, $C_xH_yO_2$, has a relative molecular mass of 152. Given that 3.04 g of **M** gives 4.32 dm^3 of CO_2 and 2.16 g of H_2O at room temperature and pressure, determine the values of *x* and *y*.

$$\eta_{CO_2} = \frac{4.32}{24} = 0.18mol \qquad \eta_{H_2O} = \frac{2.16}{18.0} = 0.12mol \qquad \therefore \eta_H = 0.24mol$$

Simplest ratio of C:H = 3: 4

M_r of $(C_3H_4)_nO_2$ = 152
n = 3 ∴ x and y are 9 and 12 respectively.

(ii) The following are a series of reactions carried out to elucidate the structure of **M.**

1. **M** reacts with acidified potassium dichromate(VI) to form **N**, $C_9H_8O_3$.
2. **M** does not decolorise aqueous bromine.
3. When **M** reacts with acidified potassium manganate(VII), it forms benzene–1,2– dicarboxylic acid.
4. Both **M** and **N** react with alkaline iodine to give a yellow precipitate.
5. The other organic product obtained from **M** in **reaction 4** is acidified to form compound **P**, $C_8H_8O_3$.
6. Compound **Q**, $C_8H_6O_2$, is formed when **P** is reacted with concentrated H_2SO_4.

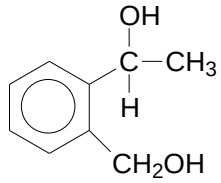
Deduce, with reasoning, the structures of **M**, **N**, **P** and **Q**.

E: $C_9H_{12}O_2$ vs C_9H_{20}

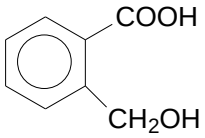
Degree of unsaturation is 4: benzene likely to be present.

Reaction	Explanation	Deduction
1	oxidation **E**:$C_9H_{12}O_2$ ---→ **F**: $C_9H_8O_3$ -4H + 1O	**F** likely to have a ketone and COOH **E** has 1° and 2° alcohol at side chain **Or E** has alcohol groups that can be oxidised
2		Absence of activated benzene ring, absence of C=C
3	Side chain oxidation	Benzene has two substituent at 1,2 position to each other.
4		**F** has methyl ketone while **E** has methyl 2°alcohol (-CH(OH)CH_3) Therefore there must be a -CH(OH)CH_3 and -CH_2OH substituent at 1,2 position of benzene.
5		**G**
6	**G** to **H** involves elimination of H_2O	Intramolecular reaction between COOH and alcohol.

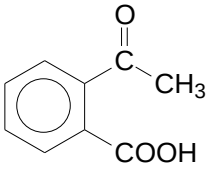
E:



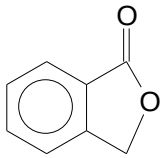
G:



F:



H:



[9]

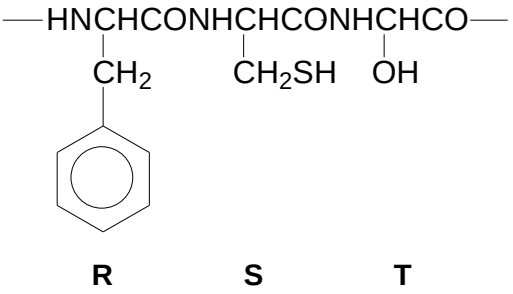
[Total:20]

5 Enzymes are large protein molecules that adopt highly specific three-dimensional structures.

(a) **(i)** Briefly describe how an enzyme maintains its three-dimensional shape.

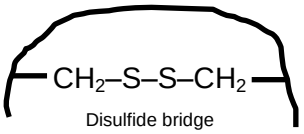
The three-dimensional shape of enzyme is maintained by the **R group interactions** between the amino acids along the polypeptide chain, namely **ionic bond, hydrogen bond, disulfide bridge and van der Waals interaction**.

The diagram below shows the structure, at pH 7, of a fragment from polyphenoloxidase enzyme which contains three amino acid residues, **R**, **S**, and **T**.



R **S** **T**

(ii) Draw a diagram to show how the side chain on amino acid **S** could be involved in maintaining the tertiary structure of polyphenoloxidase. State the type of reaction that occurs.



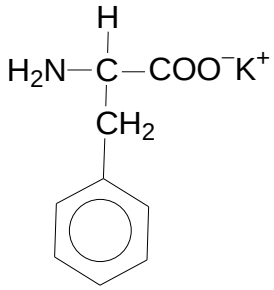
Type of reaction: Oxidation

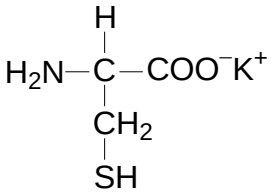
(iii) Cut fruits such as apples turn brown on exposure to air due to a chemical reaction caused by polyphenoloxidase.

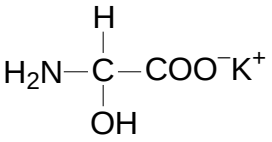
To prevent the browning of cut apple, lemon juice is commonly added to the fruits. Explain how lemon juice helps to prevent the browning of cut apple.

The low pH of lemon juice **denatures** polyphenoloxidase enzyme as **H^+ protonates COO^- which disrupts the ionic bonds** or **H^+ protonates NH_2 which disrupts H bonds** that stabilise the tertiary structure by of the enzyme causing it to **lose its catalytic ability** and thus **preventing the browning of the cut apple**.

(iv) Draw the structures of the amino acids formed when polyphenoloxidase is heated under reflux with 3 mol dm^{-3} potassium hydroxide, and state the type of reaction occurring.







Type of reaction: Alkaline hydrolysis

[10]

(b) Enzymes, trysin and chymotrypsin, are secreted by the pancreas to aid the digestion of proteins in the small intestine.

When trypsin was added to polypeptide **U**, the following fragments were obtained.

phe
gly-lys-phe
ser-lys-ala-phe

When chymotrypsin was added to polypeptide **U**, the following fragments were obtained.

ala-phe-gly-lys
phe-ser-lys
phe

Using the above results, deduce the **shortest** possible amino acid sequence of polypeptide **U**. Show your reasoning.

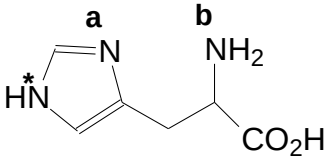
Reasoning

phe
phe-ser-lys
ser-lys-ala-phe
ala-phe-gly-lys
gly-lys-phe
phe

phe-ser-lys-ala-phe-gly-lys-phe

[2]

(c) Histidine is an essential amino acid in human. It can be catalysed by an enzyme to produce histamine that is responsible for allergic body reactions. The following shows the structure of histidine.



histidine

(i) By considering the number of electron domains about the nitrogen atoms, state the type of hybridisation of the nitrogen atoms, ^{a}N and ^{b}N, in histidine.

^{a}N: sp^2 hydridisation

^{b}N: sp^3 hydridisation

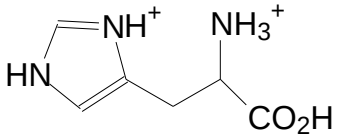
(ii) In histidine, ^{a}N is ***less basic*** than ^{b}N and *****N is found to be ***inert to chemical reaction.***

There are three pK_a values associated with histidine: 1.8, 6.1, 9.2.

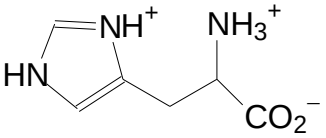
Make use of these pK_a values to suggest the major species present in solutions of histidine with the following pH values.

- pH 1
- pH 3
- pH 7

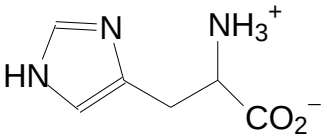
pH = 1



pH = 3



pH = 7



[5]

(d) The hydrolysis of sucrose can be catalysed by the enzyme sucrase, or by dilute acids. The initial reaction of the hydrolysis can be represented by:

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

The following results were obtained using hydrochloric acid as the catalyst.

experiment	[sucrose] / mol dm^{-3}	[HC*l*] / mol dm^{-3}	initial rate / mol dm^{-3}s^{-1}
1	0.05	0.05	0.100
2	0.06	0.06	0.144
3	0.08	0.06	0.192

Use these data to deduce the order of reaction with respect to HC*l* and sucrose. Hence, write the rate equation for the reaction.

Using Expt 2 & 3,

$[\text{sucrose}]_{\text{Expt 3}} = 4/3\ [\text{sucrose}]_{\text{Expt 2}}$, $\text{rate}_{\text{Expt 3}} = 4/3\ \text{rate}_{\text{Expt 2}}$

1st order of reaction w.r.t sucrose

Using Expt 1 & 2,

$$\frac{\text{rate}_2}{\text{rate}_1} = \frac{[\text{sucrose}]_2[\text{HC}l]_2^{\text{n}}}{[\text{sucrose}]_1[\text{HC}l]_1^{\text{n}}}$$

$$\frac{0.144}{0.100} = \left(\frac{0.06}{0.05}\right)\left(\frac{0.06}{0.05}\right)^{\text{n}}$$

n = 1

1st order of reaction w.r.t HC*l*

rate = k[sucrose][HC*l*]

[3]

[Total:20]