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.

(ii) By considering the partial charges in IC*l*, explain how water reacts with IC*l*.

(iii) Hence construct an equation for the reaction of IC*l* with water.

[3]

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

(i) Draw the structure of **A**.

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

[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.

(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}

[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.

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

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

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

[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]

(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.

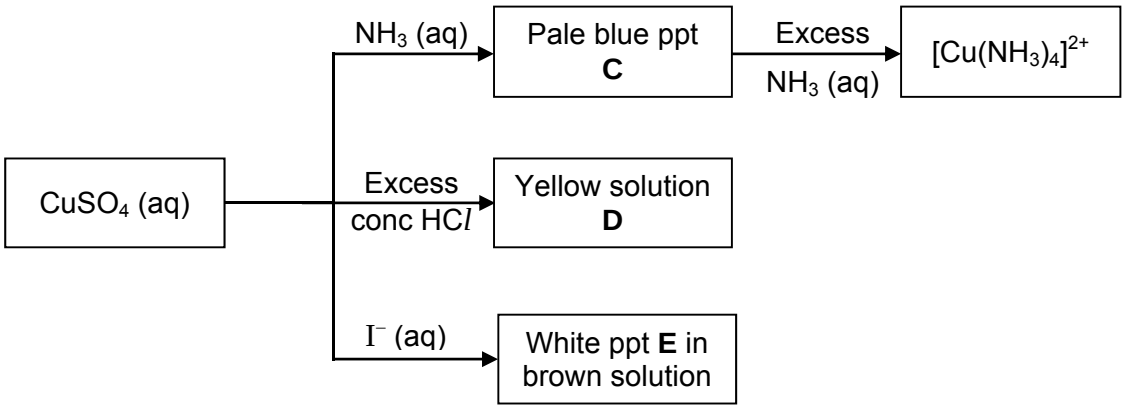
The brick red solid, Cu_2O, is isolated through filtration. It is soluble in excess ammonia to give a colourless solution **B.** When left exposed to air, the colourless solution **B** turns into a deep blue solution, containing the complex ion $[Cu(NH_3)_4]^{2+}$.

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

(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.

[6]

(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).

(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**.

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.

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

[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.

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

[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.

(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.

[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.

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

[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.

(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.

(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?

[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.

(ii) Describe, with the aid of an equation, how H_3PO_3 can be prepared from PCl_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.

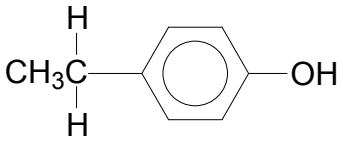
(I) Suggest a formula for **F**, and describe its shape.

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

[8]

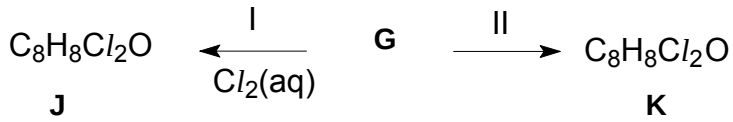
[Total:20]

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 **G** **K**

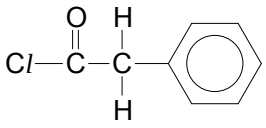
(a) **(i)** Suggest a structural formula for **J**.

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

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

[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:

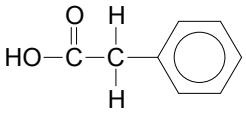
L > K > J

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

[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.

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

[2]

(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*.

(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**.

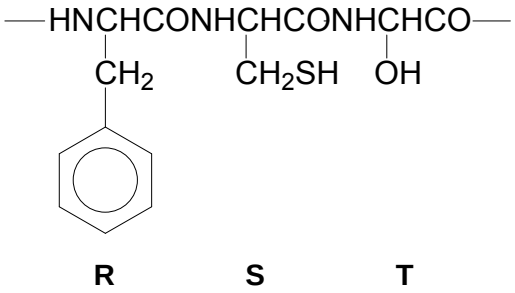
[9]

[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 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.

(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.

(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.

[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

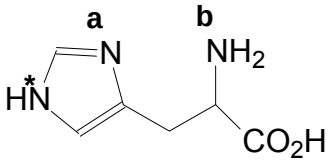
When chymotrypsin was added to polypeptide **U**, the following fragments were obtained.

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.

[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.

(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

[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.

[3]

[Total:20]