H

NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CHEMISTRY **9729/03**

Paper 3 Free Response **19 SEP 2017**

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Section A
Answer all questions.

Section B
Answer **one** question

The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

[Turn over

Section A

Answer **all** the questions in this section.

1 (a) (i) Suggest why the melting point of MgO, Al_2O_3 and SO_3 is decreasing in the following order

$$MgO > Al_2O_3 > SO_3$$ [2]

(ii) Explain how the electronegativity of the elements in the oxides determine the type of bonding and hence the acid-base nature in MgO and P_4O_{10}. [2]

(b) A student was given 3 unknown oxides A, B and C containing Na_2O, Al_2O_3, and P_4O_{10}, The labels A to C do not correspond to the identities of the oxides.

He was given 2 packets of sample mixture, each containing different mole ratios of oxides A to C given in the table.

The student dissolved each sample mixture in half a beaker of water and recorded the observations of the resulting solution.

Sample	A	B	C	Observation of resulting solution
1	1	1	7	Neutral solution
2	1	1	1	Highly acidic solution

(i) Write a balanced equation when NaOH reacts with

- Al_2O_3
- P_4O_{10} [2]

(ii) By considering the reactions of the oxides with water and the stoichiometric ratios obtained in **(i)**, account for the observations for samples 1 and 2. Hence deduce the identities of A, B and C. [4]

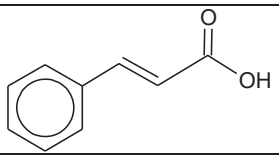
(c) The mineral dolomite is a double carbonate of magnesium and calcium, with the formula of $CaMg(CO_3)_2$. When a sample of impure dolomite was heated at 315 ^oC, ***x*** cm^3 of gas was collected which gave white ppt with lime water. When another sample of the same mass was heated at 530 ^oC, **2*x*** cm^3 of gas was collected. When 1.000g of dolomite was reacted with excess hydrochloric acid, 0.450 g of gas was collected.

(i) Write an equation to account for the reaction that took place at 315 ^oC. [1]

(ii) Account for the different volumes of gases collected at 315 °C and 530 °C. [3]

(iii) Determine the percentage purity of the impure dolomite sample. [2]

(d) The following are some of the commonly used acids in food and beverage industries for various purposes like flavouring, preservatives and improving the texture of food. Their pK_a values are given below.

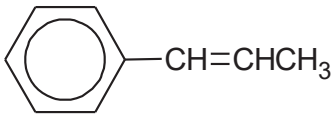
Name	Structure	pK_a
Carbonic acid	H_2CO_3	3.61
Ethanoic acid	CH_3CO_2H	4.72
Cinnamic acid		4.44

(i) By considering the structure of both acids, suggest and explain if ethanoic acid or cinnamic acid will react with NaOH(aq) first. [2]

(ii) Explain, using appropriate equations, what would happen when carbon dioxide is bubbled into a solution containing the salt formed in **(i)**. [2]

[Total: 20]

2 Phenylpropenes, for instance, 1−phenylpropene, has been used as precursors for a variety of effective insecticides.



1-phenylpropene

(a) Draw a labelled diagram to show the orbitals that form the C=C bond in 1−phenylpropene, and state the type of hybridisation involved. [2]

(b) 1−phenylpropene reacts with iodine monochloride, IC*l*, in the presence of an inert organic solvent.

(i) Describe the mechanism of this reaction, showing curly arrows, charges, dipoles and any relevant lone pairs. [2]

(ii) Suggest the structure of another carbocation that can be formed from the mechanism drawn in **(i)**. Hence, explain which is the preferred carbocation formed. [2]

(iii) 1−phenylpropene also reacts with aqueous iodine monochloride. When water is present, a different organic compound can be formed.

Suggest the structure of this organic compound, and explain how it is formed with reference to the mechanism you have described in **(i)**. [2]

(c) Hydroformylation is an industrial process for the production of aldehydes from alkenes. This chemical reaction entails the net addition of –CHO and a hydrogen atom to a carbon-carbon double bond.

When an equimolar mixture of $C_6H_5CH_2CH=CH_2$, CO and H_2 at an initial total pressure of 120 atm is allowed to reach equilibrium at 500 K, the partial pressure of $C_6H_5CH_2CH_2CH_2CHO$ is found to be 39.6 atm.

Write the K_p expression for this process and hence calculate a value for K_p at 500 K, stating its units. [3]

(d) Alcohol D, C_xH_yOH, is an alarm pheromones emitted by the Koschevnikov gland of honey bees.

When 0.10 cm^3 of liquid D was dissolved in an inert solvent and an excess of sodium metal added, 10.9 cm^3 of gas was produced.

When 0.10 cm^3 of liquid D was combusted in excess oxygen in an enclosed vessel, the volume of gas was reduced by 65 cm^3. The addition of excess KOH(aq) caused a further reduction in gas volume of 131 cm^3.

All gases were measured at 273 K.

(i) Use these data to calculate values for x and y in the molecular formula C_xH_yOH for D. [3]

Alcohol D reacts with acidified $K_2Cr_2O_7$, and can be dehydrated to alkene E. On treating E with an excess of hot acidified concentrated $KMnO_4$, an equimolar mixture of ethanoic acid and butanone is produced.

(ii) Use this information to deduce the skeletal formulae of D and E, explaining your reasoning. [2]

(iii) State and explain with two reasons whether E can show cis-trans isomerism. [1]

(e) Dinitrogen pentoxide, N_2O_5, has been used as a reagent to introduce the nitro group in arenes. It exists as a white solid of N_2O_5, with the structure $O_2N{-}O{-}NO_2$.

N_2O_5 can be produced by the following sequence.

I: $N_2(g) + O_2(g) \rightarrow 2NO(g)$ $\quad \Delta H = +180\ kJ\ mol^{-1}$
II: $NO(g) + ½\ O_2(g) \rightarrow NO_2(g)$ $\quad \Delta H = -57\ kJ\ mol^{-1}$
III: $2NO_2(g) + ½\ O_2(g) \rightarrow N_2O_5\ (g)$ $\quad \Delta H = -55\ kJ\ mol^{-1}$

(i) Draw the dot-and-cross diagram of N_2O_5. [1]

(ii) Given that the bond energy of N−O bond is 210 kJ mol^{-1} and using relevant data from the Data Booklet, estimate the average bond energy of the N=O bond. [2]

(iii) The standard enthalpy change of formation of solid N_2O_5 is +11.3 kJ mol^{-1}. Using the relevant enthalpies given, construct an energy cycle to calculate the enthalpy change of sublimation of N_2O_5. [2]

[Total: 22]

3 Proteins are macromolecules, consisting of one or more long chains of amino acid residues. Proteins perform a vast array of functions in the human body such as the transport of oxygen in the blood by haemoglobin, an iron-containing protein.

(a) Glycine, NH_2CH_2COOH is an amino acid. It is electrically neutral at pH 5.97. When placed in a solution of low pH, it exists as a dibasic acid, $^+NH_3CH_2COOH$. The two corresponding acid dissociation values are:

$K_{a\,(1)} = 4.57 \times 10^{-3}$ mol dm^{-3} for the −COOH
$K_{a\,(2)} = 2.51 \times 10^{-10}$ mol dm^{-3} for the $-NH_3^+$

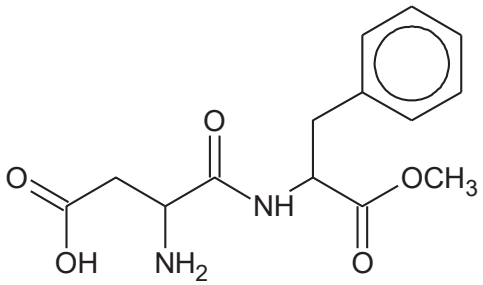
The acidic properties of glycine was studied when 25.0 cm^3 of 0.0500 mol dm^{-3} $^+NH_3CH_2COOH$ was titrated with 40.00 cm^3 of 0.100 mol dm^{-3} NaOH.

(i) Calculate the initial pH of a solution of $^+NH_3CH_2COOH$. [1]

(ii) Calculate the pH of the solution when $^+NH_3CH_2COOH$ is completely neutralised. [2]

(iii) Hence, sketch the pH-volume curve you would expect to obtain for the titration. Label the key points based on your calculations in **(i)** and **(ii)**, stating the maximum buffering capacity. You may assume that the final pH of the solution is 12.4. [3]

(b) Apart from having many biological functions, amino acids are used in a variety of applications in the food industry. Aspartame, an amino acid derivative is used as an artificial sweetener in many foods and beverages. However, it is not commonly used as a baking sweetener as it breaks down easily at high pH when heated.

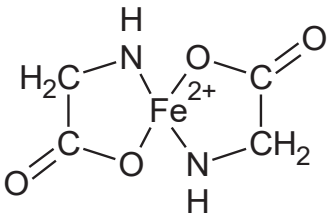


aspartame

Predict the products of aspartame when it is heated at high pH. [2]

(c) Amino acids are also widely applied in the health industry. They form chelates with metals ions by acting as ligands.

The following is an example of a chelated metal ion.



For the uptake of essential metal ions into the body, chelated metal ions are believed to be the preferred choice as health supplements because their complex structures better survive passage through the acidic environment of the stomach and subsequently absorbed into the body. On the other hand, free metal ions are typically flushed through the intestine without being absorbed into the bloodstream.

(i) The following equilibrium is established when iron(II) sulfate dissolves in acid.

$$FeSO_4(s) + 2H^+(aq) \rightleftharpoons H_2SO_4(aq) + Fe^{2+}(aq)$$

By considering the above equilibrium, suggest why non-chelated compounds such as iron (II) sulfate are not well absorbed by the body. [1]

The formation constant, K_f, is an indication of the stability of a complex ion. The K_f values of amino acid complexes of many health supplements are in the 10^4 to 10^5 range and are highly absorbed. For formation constants above 10^6, there will be minimal metal released and such compounds are essentially useless in biological systems.

The table below lists the K_f values of some iron and mercury complexes with amino acids and common ligands.

Ligand	Metal ions	
	Fe^{2+}	Hg^{2+}
cysteine	10^6	10^{14}
CN^-	10^{35}	10^{41}
$edta^{4-}$	10^{14}	10^{21}

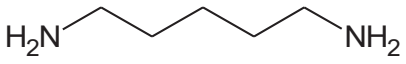
(ii) Given the equilibrium concentration of a solution of $[Fe(CN)_6]^{4-}$ is 0.65 mol dm^{-3}, calculate the concentration of cyanide ion present in equilibrium with the complex ion. [2]

(iii) In other cases, amino acids in the body such as cysteine are capable of forming a tightly bound complex with mercury, hence when taken in small amounts, mercury is not as toxic. However, exposure to high level of mercury will require chelation therapy, a medical procedure which involves injecting suitable ligands into the bloodstream to remove mercury ions from the body.

By using the K_f values, suggest an explanation whether the following ligands can be injected into the bloodstream for the chelation therapy.

- CN^-
- $edta^{4-}$ [2]

(d) Upon death, the proteins in body starts to decompose and produce ammonia in the lungs soon after death, and the ammonia diffuses outward through the nose and mouth. Within a few hours, the body starts to produce heavier amines such as 1,5-diaminopentane in its tissues, giving rise to the foul smell.



1,5-diaminopentane

(i) Suggest how the basicity of 1,5-diaminopentane and phenylamine might compare to that of ammonia. Explain your reasoning. [2]

(ii) Phenoxyethanol is used in embalming to disinfect and temporarily preserve human and animal remains. It can be made from phenol in two steps.

phenoxyethanol

State reagents and conditions for each of the two steps, and give the structure of the intermediate formed. [3]

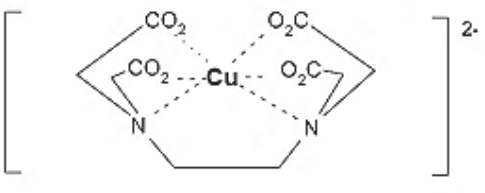
[Total: 18]

Section B

Answer **one** question from this section.

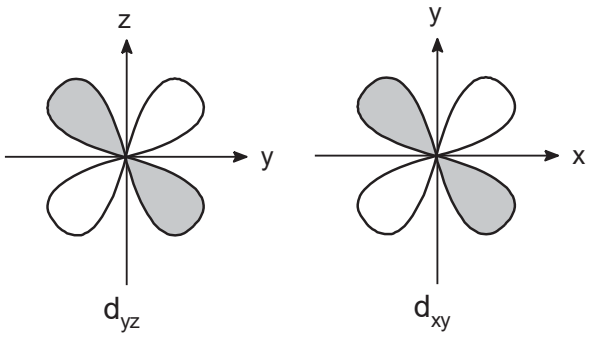
4 (a) Copper and the compounds it forms have a wide variety of uses.
Copper-EDTA complexes are commonly used in cosmetics and it gives the blue colour in many shampoos.

The structure of the copper-EDTA complex is given below.



(i) State the electronic configuration of this copper ion. [1]

(ii) Two of the d orbitals are given below. Sketch the shape of the other three d orbitals present in copper. [2]



(b) Copper produced from ore undergoes an electrolytic treatment at some stage via electrorefining. In the electrorefining of impure anodes, unwanted impurities are eliminated, yielding copper with high purity at the cathode.

When a particular ore was reduced, an alloy was obtained. It mainly consists of copper, but with silver and lead as minor impurities.

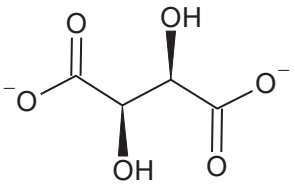
(i) Explain, with reference to relevant $E^{\ominus}$ values, and the information given above, what happens to the silver and lead impurities during the purification process. [3]

(ii) A current of I A was passed through the cell described in **(b)** for t min. It was found that the mass of the cathode increased from m_o g to m_x g. Using the information provided, deduce an expression for Avogadro's constant, L. [2]

(c) Tartrate and citrate salts are used with copper(II) ions in the preparation of Fehling's and Benedict's solutions that are used to test for presence of aldehydes and reducing sugars.

(i) Copper(II) ions can form a salt of formula $Cu_x(C_yH_zO_7)_2$ with citrate ions. The composition of this salt by mass is Cu: 33.55 %; C: 25.30 %; O: 39.40 %. Determine x, y and z. [2]

The structure of tartrate ion that is used in the preparation of Fehling's reagent is given below.



Tartrate ion

(ii) Explain why the tartrate ion is a
- Bronsted-Lowry base
- Lewis base [3]

(iii) Ethanedioic acid, HO_2CCO_2H, is another dibasic acid like tartaric acid, $HO_2CCH(OH)CH(OH)CO_2H$. Explain why pK_1 of ethanedioic acid is lower than pK_1 of tartaric acid. [1]

(d) Compound J, $C_9H_8O_4$, forms a non-chiral molecule K, $C_9H_{12}O_3$, when reacted with $LiAlH_4$ in dry ether. However, when J was reacted with $NaBH_4$ instead, a product of molecular formula $C_9H_{10}O_4$ was formed.
J gives an orange precipitate with 2,4-dinitrophenylhydrazine but does not give any precipitate when warmed with Fehling's reagent. K reacts with bromine water to form L, $C_9H_9O_3Br_3$.

(i) Suggest the structures of J, K and L. [3]

(ii) Write a balanced equation for the reaction of J with $LiAlH_4$. [1]

(iii) State two observations that you would expect to see when K reacts with bromine water to form L. [1]

(iv) $LiAlH_4$ reactions must be done in the absence of water as it will react spontaneously with water. Write a balanced equation for this reaction. [1]

[Total: 20]

5 The Kolbe electrolysis is an electrochemical method used to synthesise alkanes. Hermann Kolbe discovered the method in 1849 when he demonstrated the existence of carbon dioxide and ethane produced during the electrolysis of an aqueous solution of potassium ethanoate. The method has several advantages, for example the possibility to control the potential of the electrode and the simplicity of the reaction because no reducing or oxidizing agents are required.

The reaction mechanism is thought to involve a three-stage process.

In step I, the ethanoate ion CH_3COO^- is first converted into an ethoxy radical intermediate $CH_3COO\bullet$.

This intermediate then undergoes decarboxylation to form a methyl radical intermediate.

step II $\quad CH_3COO\bullet \rightarrow \bullet CH_3 + CO_2$

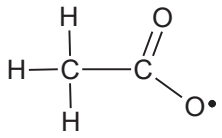
Finally two methyl radical intermediates dimerises to form the alkane product.

step III $\quad 2 \bullet CH_3 \rightarrow CH_3\text{-}CH_3$

(a) (i) Suggest and explain, in terms of change in oxidation number, the electrode where step I took place in the electrolysis process. Hence, write a half-equation for step I. [2]

(ii) A gas is obtained at the other electrode. Write the half-equation to explain how the gas is formed. Calculate the volume of gas produced at room temperature and pressure when a current of 500 mA is passed for 20 minutes through a solution of potassium ethanoate. [3]

(iii) Use information given above to draw out the full mechanism for steps II and III of the Kolbe Reaction. You are advised to use structural formulae for all species, such as



for $CH_3COO\bullet$ as well as appropriate curly arrows so that it is clear which bonds are broken and which are formed. Indicate any unpaired electrons by a dot (•). [2]

(b) Kolbe electrolysis of a single acid salt gives a symmetrical alkane. However, when a mixture of two mono-carboxylic acid salts is used, all probable alkanes are formed.

$$R'CO_2^- + RCO_2^- \Rightarrow R–R + R–R' + R'–R'$$

Electrolysing a mixture of ethanoate salt and the salt of another mono-carboxylic acid W produced three different alkanes: ethane, X and Y, which could be separated by fractional distillation.

(i) A gaseous sample of 0.30 g of X occupied 168 cm^3 at 300 K and 1 atm. Calculate the M_r of X and hence deduce its molecular formula. [2]

(ii) State 2 assumptions you have made in your calculation in **(i)**. [2]

(iii) Use information given above and your answer in **(i)** to suggest possible structures for the alkane Y and the acid W. [2]

(c) In another separate experiment, a new alkane Z, C_5H_{12}, was formed. When reacted with chlorine under ultraviolet light, Z produced only four monochloro compounds with the formula $C_5H_{11}Cl$. Some of the products is/are chiral. Suggest the structure of Z as well as that of the chiral product(s) formed. Explain your reasoning. [3]

(d) Red cabbage juice contains a pigment molecule called flavin that changes colours according to the pH of the solution as shown below.

pH	2	4	6	8	10	12
colour	red	pink	violet	blue	green	yellow

Suggest and explain, with the aid of equations, what would be observed if a few drops of red cabbage juice was added separately to the following solutions.

(i) Silicon chloride [2]

(ii) Ammonium chloride [2]

[Total: 20]