JURONG JUNIOR COLLEGE
2016 JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME	
CLASS	**16S**

CHEMISTRY

9647/03

Paper 3 Free Response

14 September 2016
2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class and exam index number on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any **four** questions.
A *Data Booklet* is provided.
The use of an approved scientific calculator is expected, where appropriate.
You are reminded of the need for good English and clear presentation in your answers.

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.

1 Methane, the main component of natural gas, is converted into a combustible mixture of gases by reaction with steam in the presence of a heated nickel catalyst.

reaction 1: $CH_4(g) + H_2O(g) = CO(g) + 3H_2(g)$

(a) **(i)** The total bond energy in the carbon monoxide molecule is 1046 kJ mol^{-1}.

Suggest why this value is higher than either of the bond energies between carbon and oxygen found in the *Data Booklet*. [1]

(ii) Using the given bond energy value for the carbon monoxide molecule and other relevant data from the *Data Booklet*, calculate the enthalpy change of reaction for *reaction 1*. [2]

(b) The standard Gibbs free energy change of a reaction can be calculated based on its standard enthalpy as well as its standard entropy change.

(i) The $\Delta G^{\ominus}$ for the forward reaction in *reaction 1* is +142 kJ mol^{-1}.

Using the given value for $\Delta G^{\ominus}$ and your answer in **(a)(ii)**, calculate $\Delta S^{\ominus}$ for the forward reaction in *reaction 1* at 25 °C. [2]

(ii) Calculate the temperature at which the reaction just becomes feasible. [1]

(c) When a 2:1 mole ratio of methane and steam at an initial total pressure of 5 atm is passed over the catalyst at 450 °C, the partial pressure of hydrogen at equilibrium is found to be 1.8 atm.

(i) Calculate the partial pressures of methane, steam and carbon monoxide at equilibrium. [1]

(ii) Write an expression for the equilibrium constant, K_p, and calculate its value, giving its units. [2]

(iii) Calculate the percentage yield of hydrogen gas at equilibrium under the above given conditions. [1]

(iv) Suggest what conditions of temperature and pressure would increase the yield of hydrogen gas. Explain your answer in each case. [3]

(d) The hydrogen gas from *reaction 1* can be harnessed and used as a fuel in fuel cells. Oxygen from air is pumped into the fuel cell at the cathode. An alkali such as warm aqueous potassium hydroxide can be used as an electrolyte.

(i) Write the half–equations of the reactions which would take place at the anode and the cathode of such a fuel cell. [2]

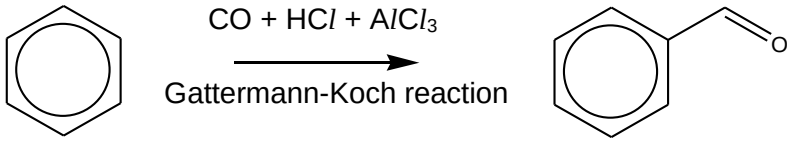
(ii) Using relevant $E^{\ominus}$ values from the *Data Booklet,* calculate the standard cell potential of the above fuel cell. [1]

(iii) One refinement of the fuel cell design is to replace the alkaline electrolyte solution with a film of solid OH^- ion-conducting polymer.

Briefly explain why this would be an improvement. [1]

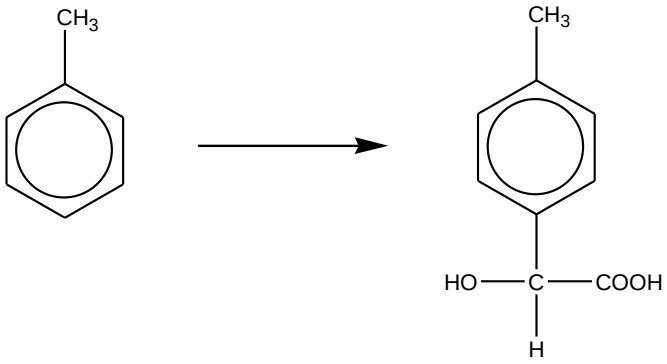
1 (e) The carbon monoxide attained from *reaction 1* is also useful for the production of aromatic aldehydes from various aromatic compounds, including derivatives of benzene.

One such example is the *Gattermann–Koch* reaction, in which carbon monoxide, hydrochloric acid, and aluminium chloride are used to react with benzene to produce benzaldehyde.



Using the *Gattermann-Koch* reaction as the **first step** of the synthesis, show how compound **G** can be formed from methylbenzene in a three-step synthesis.

You should suggest the reagents and conditions to be used for the second and third steps and identify the intermediates involved.



Compound **G**

[3]

[Total: 20]

2 **(a)** By passing dry chlorine over aluminium metal, aluminium chloride, $AlCl_3$, a yellow-white solid that sublimes at low temperatures, can be prepared.

(i) Other than the formation of the yellow-white solid, describe another observation that you can make between the reaction of aluminium and chlorine. [1]

(ii) Describe and explain what you would see when a sample of solid $AlCl_3$ is added to a solution of litmus in water.

Include relevant equation(s) in your answer. [3]

(iii) When NaOH(aq) is added dropwise to the resulting solution formed in **(a)(ii)**, a white precipitate forms, which is soluble on adding excess NaOH(aq).

With the aid of suitable equations with state symbols, explain these observations. [3]

(b) $AlCl_3$ is used to catalyse electrophilic substitution reactions such as the chlorination of benzene.

Chlorination of benzene takes place in several steps.

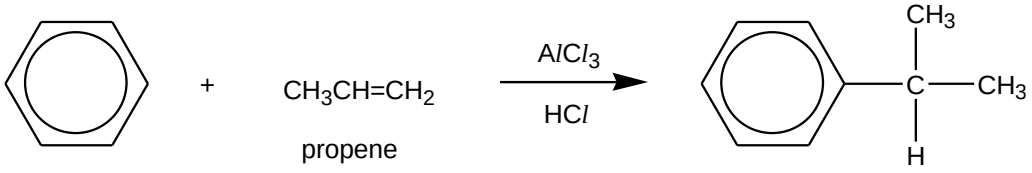
- The first step is the reaction between Cl_2 and $AlCl_3$.

$$Cl_2 + AlCl_3 \longrightarrow Cl^+ + AlCl_4^-$$

- The benzene ring is then attacked by the Cl^+ cation in the second step.

Alkylation of benzene can also be catalysed by $AlCl_3$ in a similar way.

When benzene and propene react together in the presence of $AlCl_3$ and HCl, cumene is formed in a high yield.

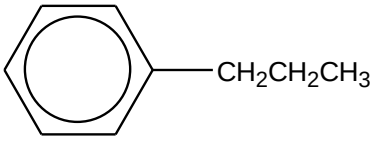


cumene

(i) By considering the structure of cumene, write a balanced equation showing the formation of the carbocation obtained from the reaction of $CH_3CH=CH_2$, $AlCl_3$ and HCl. [1]

(ii) Hence, using the above information provided, describe the mechanism for the reaction between the carbocation and benzene to give cumene. In your answer, show relevant charges and use curly arrows to show the movements of electron pairs. [2]

(iii) In the above reaction between benzene and propene, propylbenzene is obtained in small quantities. Suggest a reason for this.



propylbenzene [1]

2 **(b)** **(iv)** When cumene is treated with a small quantity of bromine in the presence of ultraviolet light, only two monobrominated compounds can be formed.

Suggest the structure of an isomer of cumene that will also give only two monobrominated products under the same reaction conditions.

Assume no bromination takes place on the benzene ring. [1]

(v) Describe a simple chemical test to distinguish the isomer drawn in **(b)(iv)** from cumene. [2]

(c) Phosphorus and sulfur are in the same Period as aluminium. In addition to forming halides like aluminium, both phosphorus and sulfur form oxyhalides that are commonly used as chlorinating agents in organic syntheses. These include $POCl_3$ and $SOCl_2$.

(i) Draw the shape for the $SOCl_2$ molecule. [1]

(ii) $POCl_3$ boils at 106 °C while $SOCl_2$ boils at 75 °C.

Account for the difference in boiling points between the two oxyhalides. [2]

(d) Phosphoric(V) acid, H_3PO_4, is one of the most well-known triprotic acids. Apart from phosphoric(V) acid, there exists other phosphorus-containing acids that dissociate to give more than three protons per molecule. One such acid is **W**, which can be formed when H_3PO_4 reacts with $POCl_3$. HCl gas is also produced during the reaction.

W has the following composition by mass: P, 34.8%; O: 62.9%; H, 2.3%.

(i) Calculate the empirical formula of **W**. [1]

(ii) Given that the empirical formula of **W** is the same as its molecular formula and that the constituent atoms in **W** show their usual valencies, suggest the structure of molecule **W**. [1]

(iii) Write an equation for the reaction between H_3PO_4 and $POCl_3$. [1]

[Total: 20]

3 Thermogravimetry is an analytical method used to determine the composition of solids which decompose on heating. The change in mass which is measured during the heating process provides information about the composition of the mixture analysed.

A mixture of calcium oxalate, CaC_2O_4, and magnesium oxalate, MgC_2O_4, was heated up to 900 °C. During this process, the mass of the mixture was measured continuously. It is known that the following two decomposition reactions take place at around 400 °C.

$$MgC_2O_4(s) \rightarrow MgO(s) + CO(g) + CO_2(g)$$

$$CaC_2O_4(s) \rightarrow CaCO_3(s) + CO(g)$$

At 700 °C, a third decomposition with the evolution of an acidic gas is observed.

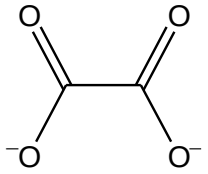
(a) **(i)** Write an equation to illustrate the third decomposition reaction. [1]

(ii) At 500 °C, the mass of the mixture obtained was 3.06 g.
At 900 °C, the mass of the mixture obtained was 2.03 g.

Calculate the ratio $\frac{\text{moles of } MgC_2O_4}{\text{moles of } CaC_2O_4}$ prior to heating. [3]

(b) Other than bonding with Group II metal ions, the oxalate ion, $C_2O_4^{2-}$, is known to act as a bidentate ligand to transition metal ions to form complex ions. An example is the light green $Fe(C_2O_4)_3^{3-}$ complex ion.

The structure of the oxalate ion is as follows.



(i) What do you understand by the term, *ligand*? [1]

(ii) State the oxidation number of iron in $Fe(C_2O_4)_3^{3-}$. [1]

(iii) Draw the structure of the $Fe(C_2O_4)_3^{3-}$ complex ion, showing the geometry around Fe. [2]

(iv) Briefly explain how the light green colour of $Fe(C_2O_4)_3^{3-}$ arises. [3]

(v) Explain why iron forms complex ions while calcium does not. [1]

(c) Compound **K** has the molecular formula, $C_4H_7NO_2$. When compound **K** was warmed with aqueous sodium hydroxide, a colourless pungent gas was evolved. Acidification of the resulting solution gives compound **L**, $C_4H_6O_3$.

L gives an orange precipitate with 2,4-dinitrophenylhydrazine but has no reaction with Fehling's solution. Effervescence was observed when **L** was treated with aqueous sodium hydrogencarbonate. When lithium aluminium hydride was added to **L**, compound **M**, $C_4H_{10}O_2$, was produced.

M can also be obtained from the reaction of cold acidified potassium manganate(VII) with compound **N**, C_4H_8.

Deduce the structures of compounds **K**, **L**, **M** and **N** and explain the reactions described.

[8]

[Total: 20]

4 This question concerns chemical reactions of halogens, halides and the organic derivatives of halogens.

(a) Chlorine-containing bleaches are usually made by reacting chlorine gas with cold aqueous sodium hydroxide.

State the type of reaction and the products formed in this reaction.

Write an equation to illustrate what happens when chlorine gas reacts with hot aqueous sodium hydroxide instead. [3]

(b) Three unmarked jars contain HC*l*, HBr and HI respectively.

Describe how plunging a red hot glass rod into each of the jars in turn can help to identify the gaseous hydrogen halide present.

Explain your answer in terms of relevant bond energies. Where relevant, include equation(s) to support your answer. [3]

(c) Both halogenoalkanes and hydrogen halides undergo hydrolysis under specific reagents and conditions.

(i) Suggest reasons why reaction **I** must be heated for some time for it to occur, whereas reaction **II** takes place almost instantaneously at room temperature.

I $CH_3CHBrCH_2CH_3(l) + NaOH(aq) \rightarrow CH_3CH(OH)CH_2CH_3(aq) + NaBr(aq)$

II $HBr(aq) + NaOH(aq) \rightarrow H_2O(l) + NaBr(aq)$ [2]

(ii) How would the rate of the reaction between $CH_3CHClCH_2CH_3$ and NaOH compare to that of reaction **I**? Explain your answer with the aid of the *Data Booklet*. [2]

(iii) In reaction **I**, an inversion of the stereochemical configuration of the organic product was observed.

Describe the mechanism for reaction **I**. Show relevant lone pairs and dipoles, and use curly arrows to indicate the movement of electron pairs. [2]

(iv) Write the rate equation for reaction **I**.

With the help of your rate equation, estimate the effect on the rate of reaction **I** of diluting the solution with an equal volume of solvent. Explain your answer. [3]

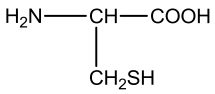
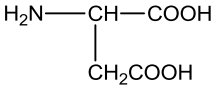
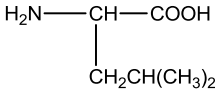
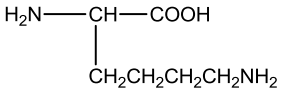
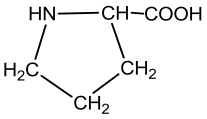
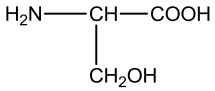
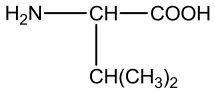
(v) Rates of reactions can also be dependent on the temperature used. Describe, and explain in molecular terms, how the rate of a reaction is affected by a change in temperature. You should include a reference to the Boltzmann distribution in your answer. [3]

(d) With the use of NaOH(aq) and another reagent, describe how you could distinguish 1-bromopropane from 2-bromopropane. [2]

[Total: 20]

5 Ovalbumin, OVA, is the predominant protein in egg white, making up approximately 54% of the total protein content. It is also a key reference protein used in protein research, vaccination experiments and immunology.

Some of the predominant and significant amino acids found in OVA are listed in the table below.

name	abbreviation	structural formula
cysteine	cys	
aspartic acid	asp	
leucine	leu	
lysine	lys	
proline	pro	
serine	ser	
valine	val	

(a) Research has shown that the C-terminal sequence of OVA is “cys-val-ser-pro”, with proline being the last amino acid residue of the polypeptide chain.

Draw the structure of this C-terminal portion at pH 1. [2]

(b) When heat is applied, OVA undergoes denaturation. The structure of OVA, when denatured by heat, exists mostly in the form of *β*-pleated sheets.

(i) Define what a *β-pleated sheet* is. Sketch a diagram to show how a polypeptide chain is held in the shape of a *β*-pleated sheet. [3]

(ii) Explain what is meant by the term *denaturation*.

Using suitable pairs of amino acids from the table above, draw labelled diagrams to illustrate **two** different types of side-chain interactions that will be affected by the heat-induced denaturation. [4]

(iii) Aggregation of the *β*-pleated sheets formed during the heat-induced denaturation of OVA results in the formation of a white insoluble solid.

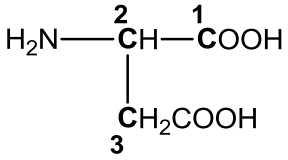
From the given table, suggest **three** amino acids whose side chains are on the outside of the *β*-pleated sheets such that the denatured OVA is insoluble in water. [1]

5 **(c)** OVA can be administered to treat suspected poisoning by heavy metal ions via ingestion.

In this treatment, consumption of a small amount of OVA causes the heavy metal ions in the gastrointestinal tract to be "trapped" by the protein, thus preventing the ions from being absorbed by the body.

Suggest possible chemical interactions between OVA and heavy metal ions in this treatment. [2]

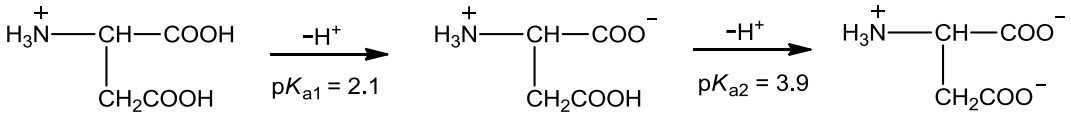
(d) Aspartic acid, which can be found in OVA, is a non-essential amino acid that can be synthesised by the human body. It plays a vital role in the construction of biochemicals in the citric acid cycle and assists the liver in removing excess ammonia and other toxins from the bloodstream.



It is found that the length of the **C_1-C_2** bond is shorter than the **C_2-C_3** bond. Suggest a reason for this difference. [1]

(e) There are three pK_a values associated with aspartic acid: 2.1, 3.9 and 9.8.

Starting with the cationic form, aspartic acid undergoes the first two stages of acid dissociation as shown below:



(i) Explain why the α-COOH dissociates in preference to the side-chain –COOH in the first stage of dissociation. [2]

(ii) Ignoring the effect of pK_{a2} and pK_{a3} on the pH, calculate the pH of a 0.050 mol dm^{-3} solution of aspartic acid. [1]

A solution of aspartic acid can resist pH changes when a small amount of acid or base is added.

(iii) Draw the structures of the species responsible for this characteristic of the solution at pH 9.8. [2]

(iv) With the aid of equations, show how this solution of aspartic acid can maintain its pH at 9.8. [2]

[Total: 20]

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