RIVER VALLEY HIGH SCHOOL
YEAR 6 PRELIMINARY EXAMINATION II

CANDIDATE NAME									
CLASS	6								
CENTRE NUMBER	S					INDEX NUMBER				

H2 CHEMISTRY 9647/03

Paper 3 Free Response

21 September 2016

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Cover Page
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class, centre number and index number on all the work you hand in.
Write in dark blue or black pen on both sides of 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.

Answer any **four** questions.
Begin each question on a fresh sheet of paper.
A Data Booklet is provided. Do not write anything on it.
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 together, with the cover page on top.

This document consists of **10** printed pages and **2** blank pages.

Answer any **four** questions.

1 Many compounds of chlorine are manufactured from brine, NaC*l*(aq). The electrolysis of brine produces Cl_2(g) and NaOH(aq). In some industrial electrolytic cells, these two substances are allowed to react further. The products formed in this second reaction dependp on the operating conditions used.

(a) Write balanced equations for the reaction between Cl_2(g) and

(i) cold aqueous NaOH; **[1]**

(ii) hot aqueous NaOH. **[1]**

(b) Chlorine dioxide, ClO_2, is used in the treatment of water. It is formed from ClO_3^- ions in an acidic solution.

$$ClO_3^- + 2H^+ + e^- \rightleftharpoons ClO_2 + H_2O$$

(i) Draw the dot-and-cross diagrams of ClO_2 and H_2O_2.

You may assume that there is no dative bond in either compound. **[2]**

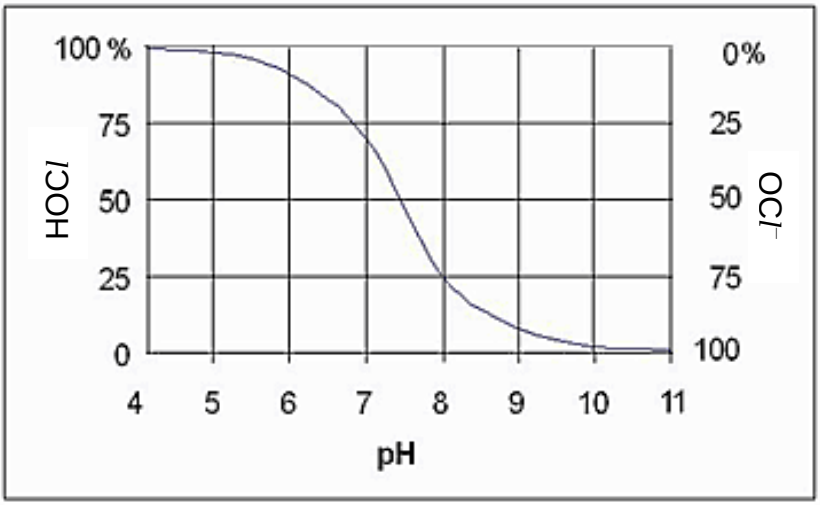
(ii) Construct the overall equation for the reaction of ClO_3^- ions with H_2O_2 in acidic solution. **[1]**

(iii) What is the role of H_2O_2 in the reaction? **[1]**

(c) Chlorine can also be used to disinfect water. When chlorine is added to water, it produces hypochlorous acid, HOC*l*. Hypochlorous acid is a weak acid that dissociates into hypochlorite ions, OCl^-, according to the following equation.

$$HOCl(aq) \rightleftharpoons H^+(aq) + OCl^-(aq)$$

Free chlorine refers to the total chlorine content in HOC*l* and OCl^-. The dissociation curve below illustrates the ratio of hypochlorous acid to hypochlorite at different pH values.



[Source: www.hach.com]

(i) Determine the pK_a of hypochlorous acid. **[1]**

(ii) Hence, calculate the pH of a 0.0025 mol dm^{-3} hypochlorous acid solution. **[2]**

To determine whether the free chlorine in a sample of tap water meets the regulatory limit (4 mg C*l* per litre), OC*l*$^-$ is quantitatively reduced to C*l*$^-$ by I^- ions, which is in turn oxidised to I_2. The I_2 is titrated with standard sodium thiosulfate. The following reaction takes place during the titration.

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

(iii) Construct a balanced equation between OC*l*$^-$(aq) and acidified KI(aq). **[1]**

(iv) When 2 dm^3 of tap water was tested, 6.0 cm^3 of 0.00455 mol dm^{-3} sodium thiosulfate was required to discharge the colour of iodine. Calculate the concentration of OC*l*$^-$ in the sample of water. **[2]**

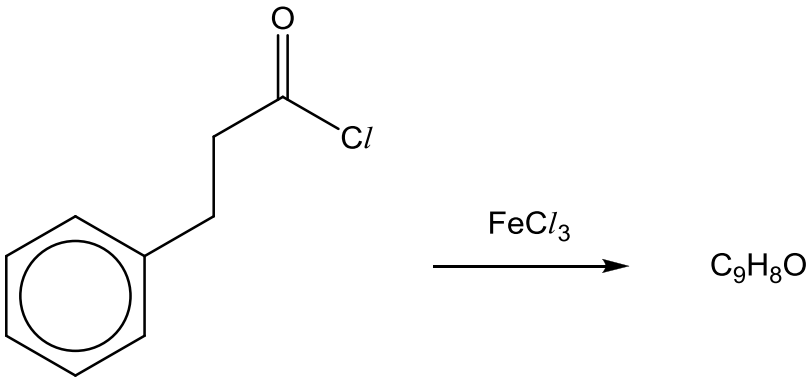
(v) Suggest why the calculated concentration of OC*l*$^-$ has the same value as the concentration of *free* chlorine. **[2]**

(vi) Determine if the sample of tap water is safe for consumption. **[2]**

(d) Chlorine is also used in organic chemistry to produce the Lewis acid catalyst, FeC*l*$_3$, for the reaction between methylbenzene and chlorine.

(i) Describe the mechanism of the above reaction. **[3]**

(ii) FeC*l*$_3$ reacts in a similar way with acyl chlorides. Predict the structure of the product of the following reaction.



[1]

[Total: 20]

2 **(a)** Nitrous oxide or dinitrogen oxide, N_2O, is commonly known as "laughing gas" due to the euphoric effects of inhaling it. It is used in surgery and dentistry for its anesthetic and analgesic effects. To produce N_2O, ammonium nitrate is decomposed at 170 °C. Water is a by-product of this reaction.

(i) Write an equation for the production of dinitrogen oxide from ammonium nitrate. **[1]**

(ii) In the manufacturing of N_2O gas, 1 kg of N_2O gas is produced for every 2.1 kg of ammonium nitrate used. Determine the percentage yield of dinitrogen oxide. **[2]**

(b) At 1200 K, in the presence of gold wire, dinitrogen oxide decomposes as shown:

$$2N_2O(g) \longrightarrow 2N_2(g) + O_2(g).$$

To follow the rate of reaction, the change in concentration of a sample of N_2O is measure against time. The results are shown below:

Time, t / s	**Concentration of N_2O / $\times 10^{-3}$ mol dm^{-3}**
0	2.50
1000	2.01
2000	1.62
3000	1.31
4000	1.05
5000	0.85
6000	0.68
7000	0.55

(i) What do you understand by the term *half-life* of N_2O? **[1]**

(ii) Plot the above data on a graph paper.

Use the following scale:

- 2 cm to represent 1000 s on the x-axis; and
- 2 cm to represent to represent 0.25 $\times 10^{-3}$ mol dm^{-3} on the y-axis. **[2]**

(iii) From your graph, deduce the order of the reaction with respect to N_2O. **[2]**

(iv) Calculate the rate constant for the reaction and state its units. **[2]**

(v) The gold wire acts as a *heterogeneous catalyst* in this reaction.

Explain the terms *in italics* and outline the mode of action of the catalyst. **[3]**

(c) Alkenes react with carbenes R_2C**:** to yield cyclopropanes.

One way to generate a substituted carbene is by reacting chloroform, $CHCl_3$, with a strong base.

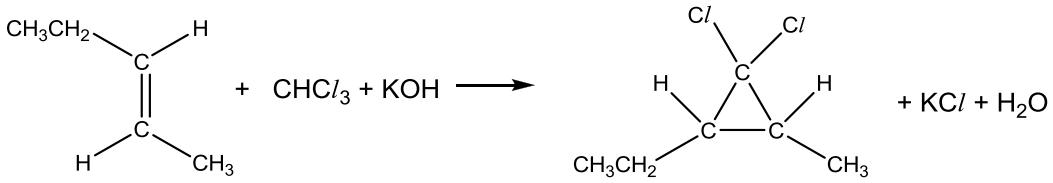
The mechanism to generate a carbene is described below.

1. Potassium hydroxide, KOH, removes the proton from $CHCl_3$, leaving behind the electron pair. An anionic intermediate is formed.
2. Cl^- is lost and a neutral dichlorocarbene is formed.

(i) Based on the description above, draw a mechanism to show the generation of dichlorocarbene.

Show relevant lone pairs and use curly arrows to indicate the movement of electron pairs. **[3]**

An example of a reaction between an alkene and a carbene is as shown:



(ii) Suggest the structure of the product formed when cyclohexene reacts with chloroform in the presence of KOH. **[1]**

(iii) Suggest the role of carbene in its reaction with an alkene. Explain your answer. **[2]**

(iv) Suggest the type of reaction when carbene reacts with an alkene. **[1]**

[Total: 20]

3 Copper is a rare element, constituting only 6.8×10^{-3} percent of the Earth's crust by mass. However, it has a wide range of uses such as in alloys, plumbing and in electrical cables. The common oxidation states of copper are +2 and +1.

(a) Copper can be obtained by roasting a copper ore, $CuFeS_2$, to give Cu_2S, which is further oxidised to form metallic copper. This impure copper can be purified by electrolysis.

(i) Draw a diagram to illustrate the electrolytic cell used in the purification of copper, using $CuSO_4(aq)$ as the electrolyte. **[2]**

(ii) If a current of 0.8 A was passed through the cell, calculate the time required for 0.25 g of pure copper to be collected. **[2]**

(b) Anhydrous copper(II) sulfate, $CuSO_4(s)$, is a white powder. It dissolves in water to form a pale blue solution.

(i) State the species responsible for the pale blue colour of the solution. **[1]**

(ii) Explain why the solution is pale blue in colour. **[3]**

(iii) Describe the colour changes observed when the following solutions are added to the pale blue solution, giving the formulae of all relevant species.

I. Dilute $NH_3(aq)$, until in excess;

II. $KI(aq)$. **[4]**

(c) When Na_2CO_3 is added to a solution of $CuSO_4$ and the resultant mixture is filtered, a green solid, cupric carbonate, is obtained. The formula of this solid is $Cu_2(OH)_{\boldsymbol{a}}(CO_3)_{\boldsymbol{b}}$.

0.10 mol of $Cu_2(OH)_{\boldsymbol{a}}(CO_3)_{\boldsymbol{b}}$ required 0.40 mol of hydrochloric acid for complete reaction. The products of this reaction include copper(II) chloride, carbon dioxide and water.

(i) Given that 2.4 dm^3 of CO_2 was formed at room temperature and pressure, determine the values of ***a*** and ***b***. **[2]**

(ii) Hence, write an equation for the reaction of cupric carbonate with hydrochloric acid. **[1]**

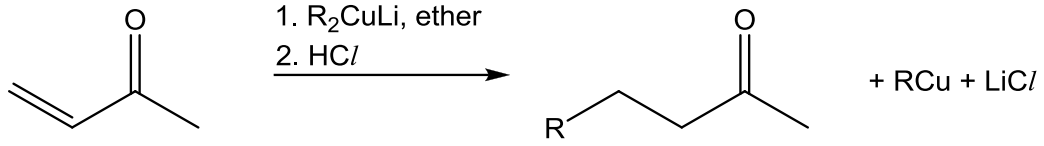
(d) Cu_2O, a brick red solid, is a compound where copper is in the oxidation state of +1. It can be formed by reacting an alkaline solution of complexed Cu^{2+} with a particular organic functional group.

(i) State the functional group that will produce Cu_2O with the alkaline solution of complexed Cu^{2+}. **[1]**

(ii) Name the type of reaction undergone by the functional group in **(i)**. **[1]**

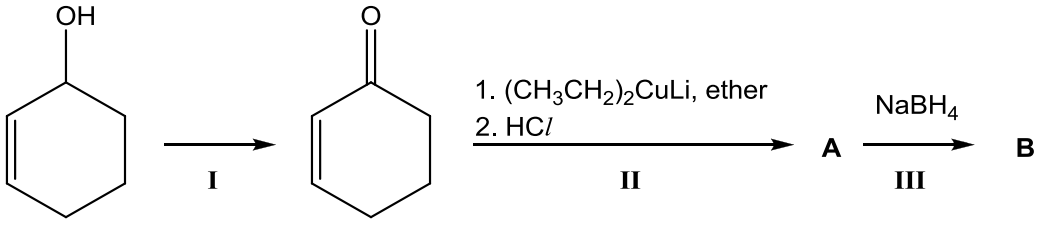
(e) Organocopper compounds are useful reagents in organic synthesis. One such class of compounds is the Gilman reagents, with the general formula R_2CuLi, where R represents an alkyl group.

Gilman reagents are effective nucleophiles used in conjugate addition reactions. Conjugate addition involves the addition of a nucleophile across a C=C bond instead of across a C=O bond. This is illustrated in the example below:



The Gilman reagent can be seen as providing the "R^-" nucleophile while a mineral acid (e.g. HC*l*) provides the proton that is added to one of the carbon atoms in the C=C bond.

The following synthesis involves a Gilman reagent for one of the steps:



Suggest the reagent and conditions for Step **I** and the structures of compounds **A** and **B**. **[3]**

[Total: 20]

4 **(a)** Copper(I) chloride is used as a precursor of a fungicide and a catalyst for a variety of organic reactions. It is sparingly soluble in water.

(i) Define the standard enthalpy change of hydration of an ion. **[1]**

(ii) Using the data given in the following table, draw an appropriate energy cycle and calculate the standard enthalpy change of solution for copper(I) chloride.

$\Delta H^{\ominus}_{hyd}(Cu^{+})$	–593 kJ mol^{-1}
$\Delta H^{\ominus}_{hyd}(Cl^{-})$	–378 kJ mol^{-1}
Lattice Energy of CuCl	–979 kJ mol^{-1}

[3]

(b) **(i)** Explain what is meant by the term *entropy* of a chemical system. **[1]**

Describe and explain how the entropy of the following systems will change during the stated process. Assume the pressure of each system remains at 1 atm throughout.

(ii) 1 mol of Cl_2(g) at 298 K is heated to 500 K. **[1]**

(iii) 1 mol of Cl_2(g) at 298 K is reacted with copper according to the following equation.

$$Cu(s) + Cl_2(g) \rightarrow CuCl_2(s)$$ **[1]**

(c) Copper(II) ions are pollutants found in water. One method of purification is via precipitation of $Cu(OH)_2$ and CuS.

	K_{sp} (298 K)
CuS	6.3×10^{-36}
$Cu(OH)_2$	2.0×10^{-19}

Using the above data, calculate:

(i) the minimum concentration of Cu^{2+} for a precipitate of CuS to form in 10 ppm S^{2-} solution;

(1 ppm = 1 mg dm^{-3}) **[2]**

(ii) the maximum pH of a solution containing 0.100 mol dm^{-3} Cu^{2+} ions. **[3]**

(d) Many organic compounds also contain chlorine. An example would be 1,2-dichlorocyclohexane, which exhibits both geometrical and optical isomerism.

(i) Explain why 1,2-dichlorocyclohexane can exhibit geometrical isomerism. **[1]**

(ii) The effect of plane polarised light on 1,2-dichlorocyclohexane was investigated. Three different types of 1,2-dichlorocyclohexane was identified:

- Molecule **X** rotated plane polarised light to the left
- Molecule **Y** rotated plane polarised light to the right
- Molecule **Z** had no effect on plane polarised light

Suggest an explanation for these observations. **[3]**

(e) Compounds **C** and **D** both have the molecular formula C_7H_7Cl. In an experiment, both compounds are separately heated under reflux for some time with aqueous sodium hydroxide. The resulting solutions are cooled and acidified with dilute nitric acid. When aqueous silver nitrate is added subsequently, a white precipitate is formed with **C** while no precipitate is formed with **D**.

Suggest the structures of **C** and **D**. Explain your reasoning for **each** compound. **[4]**

[Total: 20]

5 **(a)** The electrical conductivities of some Period 3 elements are shown below.

Element	Na	Mg	A*l*	P	S	C*l*
Electrical conductivity at 298 K / $\times 10^7$ S m^{-1}	2.1	2.3	3.5	Non-conductors		

(i) With reference to the data above, describe and explain the difference in electrical conductivities of the elements above. **[3]**

(ii) Silicon carbide (SiC), also known as carborundum and moissanite, is used in abrasive and cutting tools.

Suggest the structure and bonding of SiC. **[2]**

(b) Chlorides of Period 3 elements dissolve in water to give solutions of varying pH.

Explain the following pH values and write the chemical equations for any reactions that occur:

(i) A*l*C*l*$_3$ dissolves readily in water to form an acidic solution (pH = 3). **[3]**

(ii) SiC*l*$_4$(l) dissolves in water to form a strongly acidic solution (pH = 2). **[2]**

(c) Caffeic acid is an organic compound found in all plants as it is a key intermediate in the biosynthesis of lignin, one of the principal components of plant biomass.

Caffeic acid has the molecular formula $C_9H_8O_4$. Caffeic acid reacts with Br_2(l) to give $C_9H_8O_4Br_2$. When treated with hot $KMnO_4$ and H_2SO_4, caffeic acid reacts to give **F**, $C_7H_6O_4$, and a colourless gas that produces a white solid with Ca(OH)$_2$(aq). **F** reacts with PC*l*$_5$ to give **G**, $C_7H_5O_3C$*l*, with the production of steamy white fumes. **G** reacts with water to form an acidic solution. When added to neutral FeC*l*$_3$(aq), **G** also forms a violet colouration. **G** reacts with Br_2(aq) to give **H**, $C_7H_3O_4Br_3$.

Use the information above to deduce the structures of caffeic acid and compounds **F** to **H**, explaining all the reactions involved. **[10]**

[Total: 20]

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