RIVER VALLEY HIGH SCHOOL
YEAR 6 PRELIMINARY EXAMINATION

CANDIDATE NAME								
CLASS	6							
CENTRE NUMBER	S					INDEX NUMBER		

H2 CHEMISTRY 9647/03

Paper 3 Free Response **18 September 2012**

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 **11** printed pages and **1** blank page.

Answer any **four** questions.

1 **(a)** One common characteristic of transition elements is the ability to form complexes. Transition elements react with carbon monoxide to form a class of complexes known as metal carbonyls. One aspect of metal carbonyls that is unusual for metallic compounds is that they are often volatile.

Nickel carbonyl was first synthesised in 1890 by Ludwig Mond by passing carbon monoxide over nickel metal. Nickel carbonyl has a boiling point of 43 °C and is extremely poisonous.

(i) Draw the 'dot-and-cross' diagram of carbon monoxide.

(ii) Explain in terms of structure and bonding why nickel carbonyl has a low boiling point.

(iii) A 2.00 g sample of nickel carbonyl was vaporised and found to occupy a volume of 314 cm^3 at 50 °C and 1 atmosphere pressure.

Determine the M_r of nickel carbonyl.

(iv) Nickel carbonyl has the general formula $Ni(CO)_x$. Using the answer in **(iii)**, determine the coordination number of nickel in nickel carbonyl and suggest the shape of the complex. [7]

(b) Transition metal compounds are often coloured.

(i) Explain why transition metal compounds are often coloured.

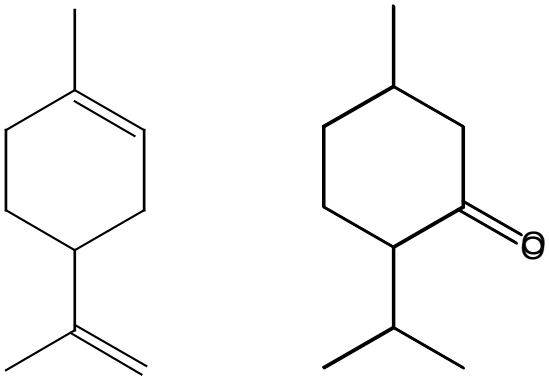
(ii) When a solution of dilute sulfuric acid was electrolysed using copper electrodes, a blue solution was obtained. On heating this solution to dryness, an anhydrous white solid was eventually obtained.

When concentrated hydrochloric acid was electrolysed using copper electrodes in a separate experiment, a yellow solution was obtained. On adding water, the colour of the solution turned from yellow to green and eventually blue.

Explain these observations. State clearly the formula of any coloured species. [9]

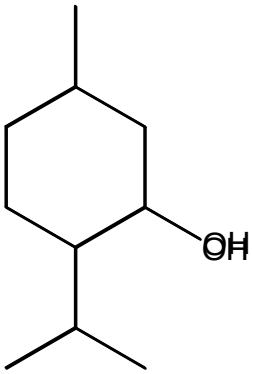
(c) Menthol, menthone and limonene are members of a class of compounds called isoprenoids which are derived from isoprene, $CH_2=C(CH_3)CH=CH_2$.

Limonene and menthone are intermediates in the biosynthesis of menthol. The many reactions in the biosynthesis of menthol are catalysed by different enzymes. In the laboratory, transition metal catalysts can be used to catalyse many of these reactions instead of enzymes.



limonene

menthone



menthol

Describe how you would distinguish these three compounds by means of simple chemical tests. [4]

[Total: 20]

2 **(a)** Hydrocarbons like alkanes are commonly used for fuels. Increasingly, biofuels are gaining increased public and scientific attention, driven by concerns over oil prices and greenhouse gas emission. Biofuels, like methanol and butan-1-ol, which can be produced by the fermentation of biomass, are increasingly being used for fuels over hydrocarbons.

(i) Using common oxidation numbers for H and O, calculate the oxidation number of carbon in methanol, CH_3OH.

(ii) Using **only** the elements C, H and O, suggest the structural formulae of two compounds, each containing a single carbon atom with an oxidation number of zero and +2 respectively.

In an experiment to determine the standard enthalpy change of combustion of butan-1-ol, ΔH_c, a quantity of the fuel was burned underneath a 200 g copper can containing 515 g of water. It was found that the temperature of water rose from 23 °C to 58 °C after 2.30 g of butan-1-ol has been burned completely.

(iii) Write an equation for the complete combustion of butan-1-ol.

(iv) Using the experimental results and relevant data from the *Data Booklet*, calculate the apparent ΔH_c of butan-1-ol. You can ignore the heat capacity of the copper can.

(v) The true value of ΔH_c of butan-1-ol is - 2670 kJ mol^{-1}. Compare this value to the one you have calculated in **(iv)** and suggest a reason for the discrepancy. [7]

(b) The following table compares the pK_a values of two dicarboxylic acids.

$$HO_2C\text{-}(CH_2)_n\text{-}CO_2H \overset{pK_1}{\rightleftharpoons} HO_2C\text{-}(CH_2)_n\text{-}CO_2^- \overset{pK_2}{\rightleftharpoons} {}^-O_2C\text{-}(CH_2)_n\text{-}CO_2^-$$

acid	formula	pK_1	pK_2
propanedioic acid	$HO_2CCH_2CO_2H$	2.85	5.70
butanedioic acid	$HO_2CCH_2CH_2CO_2H$	4.20	5.60

(i) Suggest a reason why the pK_1 value of propanedioic acid is so much less than the pK_1 of butanedioic acid.

(ii) Suggest a reason why the pK_2 value of propanedioic acid is higher than its pK_1 value.

(iii) Calculate the pH of 0.25 mol dm^{-3} of butanedioic acid (ignoring the effect of pK_2 on the pH).

(iv) Sketch the pH-volume added curve you would expect to obtain when 60 cm^3 of 0.25 mol dm^{-3} NaOH is added to 20 cm^3 of 0.25 mol dm^{-3} butanedioic acid. On your curve, include all relevant information and highlight any buffer regions. [7]

(c) When chlorine gas is passed over heated aluminium in a hard glass tube, a vapour is produced which condenses to a yellow-white solid. At low temperatures, the vapour has the empirical formula $AlCl_3$ and an M_r of 267.

(i) Suggest the molecular formula of the vapour, and draw a 'dot-and-cross' diagram to describe the bonding.

The yellow-white solid reacts with water in two different ways. When a few drops of water are added to the solid, steamy white fumes are evolved and a white solid remains, which is insoluble in water. When a large volume of water is added to the solid, a clear, weakly acidic solution is produced.

(ii) Write equations, including state symbols, for these two reactions and explain the observations. [6]

[Total: 20]

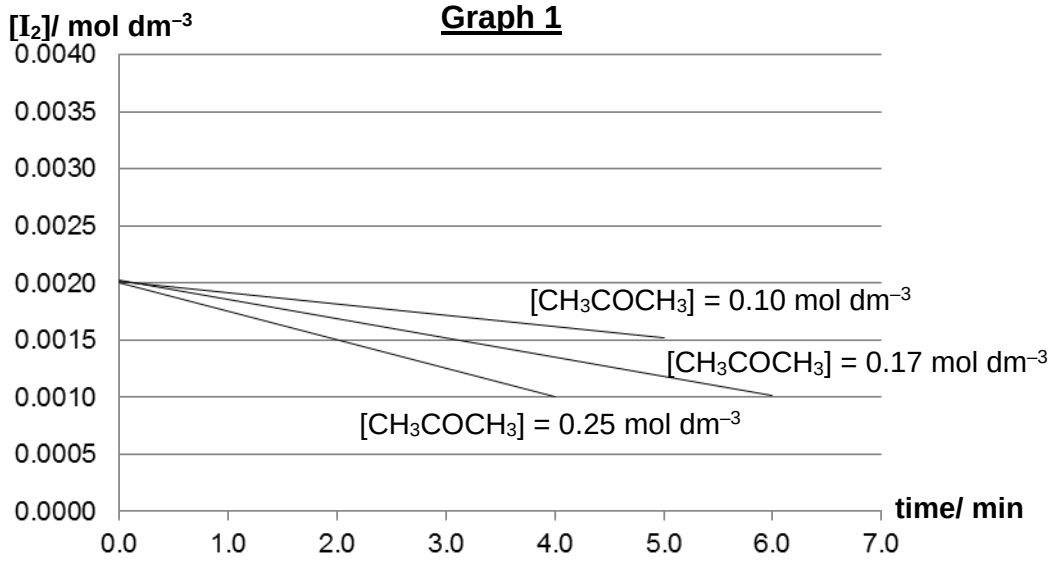
3 Alcohols and ketones are two classes of organic compounds with great importance in both industrial processes and in biological systems.

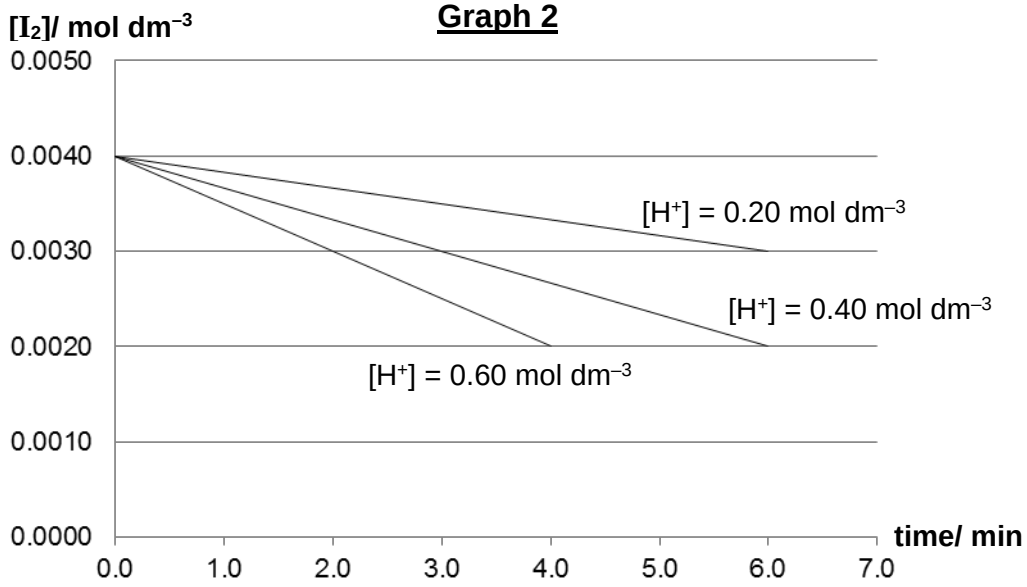
(a) The iodination of propanone under acidic conditions is shown by the following equation:

$$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + H^+(aq) + I^-(aq)$$

The rate of the reaction was studied via a colorimetric method, in which the colour intensity of iodine was measured at regular intervals.

Three sets of separate experiments were performed in which the initial concentration of iodine, propanone and acid was varied in turn, with the other two being kept constant. The results are shown in Graphs 1 and 2 below:





(i) Suggest another method, other than a colorimetric method, that can be used to investigate the rate of the reaction. Include the variables to be measured.

(ii) Using the graphs above, deduce the orders of reaction with respect to propanone, iodine and H^+.

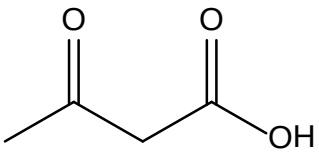
(iii) Hence, write the rate equation for this reaction.

A mechanism for the reaction is suggested as below:

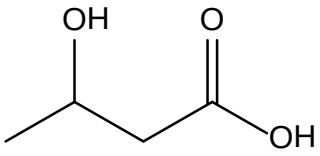
$$CH_3COCH_3 \xrightarrow[\text{stage 1}]{H^+ \text{ as catalyst}} CH_2{=}C(OH)CH_3 \xrightarrow[\text{stage 2}]{I_2} CH_3COCH_2I$$

(iv) From your answers from **(iii)**, what can be deduced about the relative rate of the two stages given in the mechanism above? Explain your answer. [8]

(b) Ketone bodies are three water-soluble organic compounds that are produced as by-products when fatty acids are broken down for energy in the liver. The three ketone bodies found in humans are propanone, 3-oxobutanoic acid and 3-hydroxybutanoic acid.



3-oxobutanoic acid



3-hydroxybutanoic acid

(i) 3-oxobutanoic acid can be converted to 3-hydroxybutanoic acid in a chemistry laboratory. State the reagents required for this conversion and the type of reaction undergone.

(ii) Under suitable conditions, 3-hydroxybutanoic acid can be converted to 3-bromobutanoic acid.

Compare the acid strength of 3-bromobutanoic acid and butanoic acid. Explain your answer.

(iii) The accumulation of ketone bodies in blood can cause an alarming decrease in the pH of blood. Suggest how this is prevented in the human body. [5]

(c) Compound **P** is a drug used to treat narcolepsy, a condition where a person falls asleep uncontrollably. **P** has a molecular formula of $C_4H_8O_3$ and is structurally related to one of the ketone bodies. **P** can be oxidised to give compound **Q**, which then reacts with alkaline copper(II) ions to give a brick-red precipitate and the salt of an acid, **R**. 1 mole of **P** and **R** will each react with sodium metal to produce 1 mole of hydrogen gas.

When **P** is warmed with a few drops of concentrated sulfuric acid, a neutral compound **S**, with the molecular formula $C_4H_6O_2$, can be isolated.

Deduce the structures of **P**, **Q**, **R** and **S**. Explain your reasoning. [7]

[Total: 20]

4 Organic compounds containing halogens are widely used in industry and society as flame retardants, refrigerants, propellants, solvents and pharmaceuticals.

(a) Methylbenzene can be converted to 1-chloro-2-methylbenzene.

(i) State the reagents and conditions required for the conversion.

(ii) State the type of reaction and describe the mechanism for the conversion of methylbenzene to 1-chloro-2-methylbenzene.

(iii) Calculate the percentage yield of the conversion given that 92.4 g of 1-chloro-2-methylbenzene was obtained from 118 g of methylbenzene.

(iv) Another mono-chlorinated compound was also formed in significant amounts. Suggest the structure of this other compound. [7]

(b) Suggest a two-step synthesis to convert 1-chloropropane to butanoic acid, giving the structure of the intermediate. [3]

(c) Compound **A** is an optically active compound with molecular formula $C_{10}H_{13}Br$. When heated with aqueous sodium hydroxide, compound **A** gives compound **B** which forms a yellow precipitate when warmed with alkaline iodine.

When compound **A** is heated under reflux with sodium hydroxide dissolved in ethanol, it forms compound **C** which has molecular formula $C_{10}H_{12}$. When cold, alkaline potassium manganate(VII) is added to compound **C**, compound **D** with molecular formula, $C_{10}H_{14}O_2$, is formed. On the other hand, when compound **C** is heated with acidified potassium manganate(VII), the products are compound **E** with molecular formula, $C_8H_6O_4$, and ethanoic acid.

Deduce the structures of compounds **A**, **B**, **C**, **D** and **E**. Explain the chemistry of the reactions involved. [10]

[Total: 20]

5 Sulfur is a chemical element with the symbol S and an atomic number of 16. It is an abundant, multivalent non-metal. It can be found in amino acids and as a precursor to other chemicals such as H_2SO_4. H_2SO_4 is a common mineral acid with many uses. It can be used as an electrolyte and an oxidising agent.

(a) Anodising is a process used to increase the thickness of the natural oxide, on the surface of metal parts. Aluminium is a common metal which can be anodised as aluminium is a reactive metal and is readily oxidised by oxygen in air. This forms a layer of aluminium oxide (Al_2O_3), making it resistant to corrosion.

(i) Using H_2SO_4(aq) as the electrolyte and an inert electrode, draw an electrolysis set-up to show how an iPod Nano®, which is made of Al, can be anodised.

(ii) Write chemical equations to show the reactions at the anode and cathode during anodisation.

(iii) The iPod Nano® has a surface area of 29.21 cm^2 which can be anodised. How long will it take to form a 0.2 mm protective layer of Al_2O_3 on the iPod Nano® if a current of 2.0 A is passed through the set-up?

(density of Al_2O_3 is 3.95 g cm^{-3}) [10]

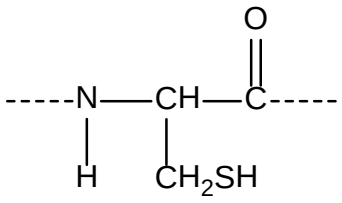
(b) Heating solid halides with concentrated H_2SO_4 is one of the ways to obtain hydrogen halides. However, the halides have different reactivity with concentrated H_2SO_4.

(i) Write an equation to show the reaction of NaCl with concentrated H_2SO_4.

(ii) With reference to the *Data Booklet*, explain why chlorine cannot be isolated by the action of concentrated sulfuric acid with sodium chloride. [3]

(c) Sulfur is an essential element for all life, and is widely used in biochemical processes. Sulfur is a component of some amino acids such as cysteine.

(i) Using the cysteine residue, as shown in the diagram below, construct an equation to show the formation of the disulfide bridge between two cysteine residues.



(ii) Denaturation of proteins involves the disruption and possible destruction of the tertiary structure of the protein. Addition of heavy metal ions can cause denaturation through the disruption of R group interactions.

State and explain, in chemical terms, how R group interactions are disrupted by the addition of heavy metal ions. [4]

(d) Group II elements are shiny, silvery-white reactive metals. Down the group, reactivity of the elements changes.

(i) With reference to the *Data Booklet*, state and explain the trend in reactivity, in terms of reducing power, from Mg to Ba.

(ii) State the differences in reactivity of Mg and Ba with water. [3]

[Total: 20]