HWA CHONG INSTITUTION
C2 Preliminary Examinations
Higher 2

CANDIDATE NAME		**CT GROUP**	**12S**
CENTRE NUMBER		**INDEX NUMBER**	

CHEMISTRY

9647/03

Paper 3 Free Response

20 September 2013

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Data Booklet

INSTRUCTIONS TO CANDIDATES

Write your name and class on all the work you hand in.

Write in dark blue or black pen.

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 **new** 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 together.

Write down the **question numbers** for the questions that you have attempted on the **cover page** provided.

Answer any **four** questions.

1 **(a)** Sodium chloride and sodium iodide react differently when warmed with concentrated sulfuric acid.

Describe what you would observe when these reactions are carried out, write equations for the reactions that occur and suggest an explanation for these different reactions.

Include state symbols in your equations.

[5]

Solvent extraction is an analytical technique which involves extracting a solute dissolved in one solvent with another solvent. The two solvents must be immiscible with each other. The ratio of the concentrations of the solute in the two solvents at equilibrium is a constant value called the *partition coefficient.*

For this partition law to hold true, the solute must exist in the same molecular form in both solvents.

(b) At room temperature, an aqueous solution of iodine containing 1.20×10^{-3} mol dm^{-3} of iodine was found to be in equilibrium with a solution in tetrachloromethane containing 0.102 mol dm^{-3} of iodine.

Calculate the partition coefficient of iodine between tetrachloromethane and water, and comment on the significance of the value obtained.

[2]

(c) When iodine is dissolved in aqueous potassium iodide, it forms the triiodide complex ion according to the following equilibrium.

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq) \qquad \textbf{reaction 1}$$

To determine the equilibrium constant of the above reaction, a solution of iodine dissolved in 0.100 mol dm^{-3} aqueous potassium iodide was shaken with tetrachloromethane until equilibrium was reached at room temperature.

The tetrachloromethane layer contained 0.0850 mol dm^{-3} of I_2. The aqueous layer was found to contain I_2 and I_3^- at a total combined concentration of 0.0170 mol dm^{-3}.

(i) Use the value of the partition coefficient calculated in **(b)** to determine the concentration of I_2 in the aqueous layer.

(ii) Calculate the concentrations of I_3^- and I^- in the aqueous layer.

(iii) Write an expression for K_c for **reaction 1** and calculate its value. Indicate units in your answer.

[6]

(d) Chlorine and iodine can form many interhalogen compounds. One such interhalogen compound is iodine monochloride, ICl.

Iodine monochloride can be used to halogenate benzene. When this reaction is carried out in a suitable polar solvent, a Lewis acid catalyst is not required.

(i) Suggest why a Lewis acid is not required in the reaction.

(ii) Describe the reaction mechanism for the reaction between benzene and iodine monochloride.

[4]

(e) Iodine monochloride disproportionates when warmed with sodium hydroxide.

(i) State, with a reason, which of the two halogen atoms in iodine monochloride undergoes disproportionation.

(ii) Give an equation for the disproportionation of iodine monochloride in aqueous sodium hydroxide.

[3]

[Total: 20]

2 Carbonyl compounds react with HCN to form cyanohydrins via a nucleophilic addition reaction.

(a) In an experiment to study this reaction, propanone, HCN and KCN were mixed in the following concentrations.

Propanone	:	0.100 mol dm^{-3}
HCN	:	0.010 mol dm^{-3}
KCN	:	0.010 mol dm^{-3}

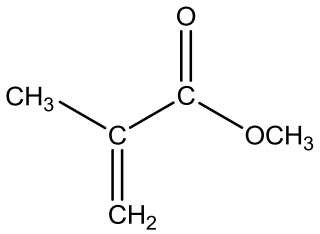
The concentration of HCN was monitored as the reaction proceeds.

(i) Based on your knowledge of the mechanism for the reaction, sketch the graph of [HCN] vs time that you would expect to obtain.

(ii) In the experiment, the half-life of propanone was 20.0 s. Predict and explain the half-life of propanone if the concentration of KCN used was 0.020 mol dm^{-3} instead.

[2]

(b) The reaction between propanone and HCN is an important step used to synthesise the monomer methyl methacrylate, in the production of acrylic glass.



methyl methacrylate

(i) Draw the displayed formula of the product obtained when propanone reacts with HCN under suitable conditions.

(ii) Starting with the product in **b(i)**, outline a three-step reaction scheme to obtain methyl methacrylate.

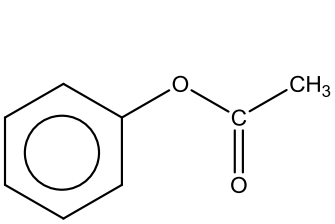
Your answer should include clearly the reagents and conditions in each step, and the structures of all intermediates formed.

[4]

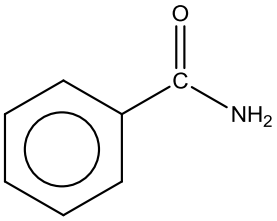
(c) For each of the three compounds given below, suggest a simple chemical test that will identify it from the other two via a positive result.

For each test, give reagents and conditions and state the observations for **each** of **A**, **B** and **C**.

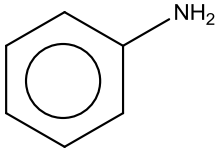
Your test(s) may rely on a preliminary breaking-up of the compound, and subsequent testing of the reaction products.



A



B



C

[6]

(d) One mole of hydrocarbon **R** (M_r = 136), reacts with three moles of hydrogen gas in the presence of nickel catalyst. Prolonged oxidation of **R** yields carbon dioxide, **S** ($C_4H_6O_3$) and **T** (C_3H_6O) in mole ratio 3:1:1. Both **S** and **T** react with alkaline aqueous iodine to give a pale yellow precipitate. Compound **U** can be synthesized by reacting **S** with thionyl chloride ($SOCl_2$), followed by ethylamine.

(i) Determine the molecular formula of **R**.

(ii) Deduce the structures of compounds **R**, **S**, **T** and **U**, and explain the reactions described. Equations are not required.

[8]

[Total: 20]

3 In 2009, archaeologists discovered a well-preserved vial of perfume in the tomb of Queen Hatshepsut, a female pharaoh who ruled the Ancient Egypt. The 2.0 g of fluid in the vial contained plant extracts like methyl butanoate, which made up 18.4 % by mass. Some ethanol and water were also present.

(a) The human nose can detect the strawberry smell of methyl butanoate at a minimum concentration of 10 ppm (parts per million) by mass. Assuming that all the fluid found in the vial was extracted and vapourised, calculate the volume of a room above which the smell of methyl butanoate can no longer be detected by the human nose.

Assume density of the air in the room is 1.20 kg m^{-3}.
[1 ppm by mass is 1 g in 1 x 10^6 g]

[2]

Ancient Egyptian perfumes uncovered by archaeologists had seldom retained their aromas. Instead the aromas were often replaced with the rancid smell of carboxylic acids. These acids could react with the clay mineral of the vial, $Al_2O_3.2SiO_2.2H_2O$, causing the perfume to evaporate through the thinned walls.

(b) Suggest **two** possible carboxylic acids that could be present in the perfume of Queen Hatshepsut and explain how they could have been formed.

[2]

(c) Explain how increasing the temperature would affect the rate of formation of these carboxylic acids.

[2]

(d) Explain how the acids can cause the thinning of the vial walls.

[1]

(e) The aluminum oxide present in the clay mineral can exist as gibbsite, $Al(OH)_3$, and boehmite, AlO_2H. Both decompose at high temperature to form aluminium oxide and steam only.

(i) Write an equation **each** for the decomposition of gibbsite, $Al(OH)_3$, and boehmite, AlO_2H.

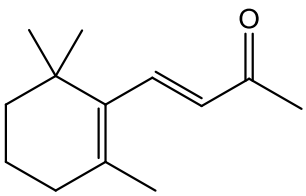
(ii) The following table lists some $\Delta H_{f}^{\ominus}$ values.

compound	$\Delta H_{f}^{\ominus}$ / kJ mol^{-1}
gibbsite, $Al(OH)_3(s)$	–1293
boehmite, $AlO_2H(s)$	–996
H_2O g)	–242

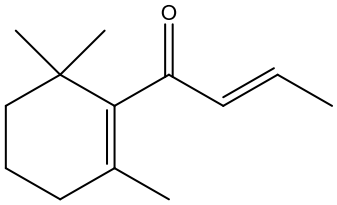
The enthalpy change for the decomposition of gibbsite is +102 kJ mol^{-1}. Use the data above to calculate the $\Delta H_{f}^{\ominus}$ of $Al_2O_3(s)$. Hence, determine the enthalpy change for the decomposition of boehmite, $AlO_2H(s)$.

[6]

Two carbonyl compounds, β-ionone and β-damascone, were used to reconstruct Queen Hatshepsut's perfume.



β-ionone (in violet oil extract)



β-damascone (in rose oil extract)

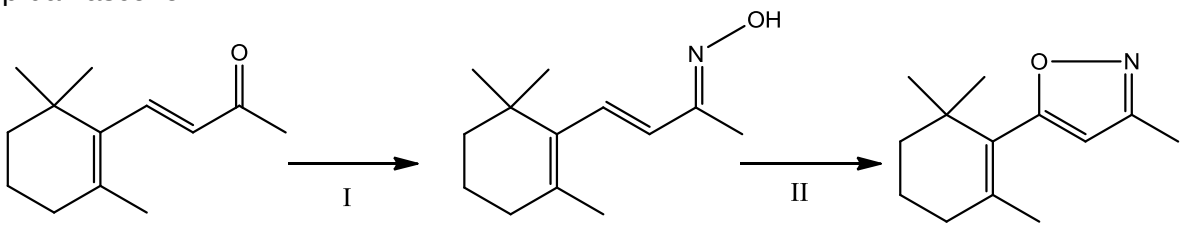
(f) Molecules which give characteristic smells in perfumes can be classified into head, heart or base notes.

Head Note	Light molecules that give the initial impact and generally last a few minutes on the skin
Heart Note	Molecules that form the bulk of the perfume and last for a few hours e.g. β-ionone
Base Note	Less volatile molecules of the fragrance

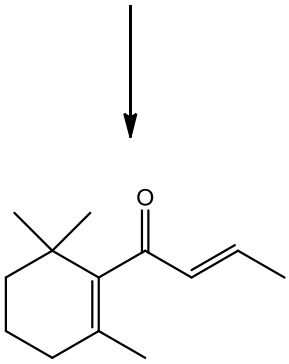
Methyl butanoate and β-damascone are classified under different notes. Suggest their classifications and explain your choice in terms of bonding.

[3]

(g) The synthesis of β-damascone from β-ionone via an electrochemical route was patented in 1984. It involved the formation of ketoxime via condensation in step **I**, followed by an anodic oxidation in step **II**. In the last step, the oxygen-nitrogen bond was cleaved to give β-damascone.



β-ionone ketoxime



β-damascone

(i) Suggest the reagent in step **I**.

(ii) Construct a balanced half-equation for the oxidation of ketoxime in step **II** under acidic conditions.

(iii) Draw the structures of all the **four** stereoisomers of ketoxime.

[4]

[Total: 20]

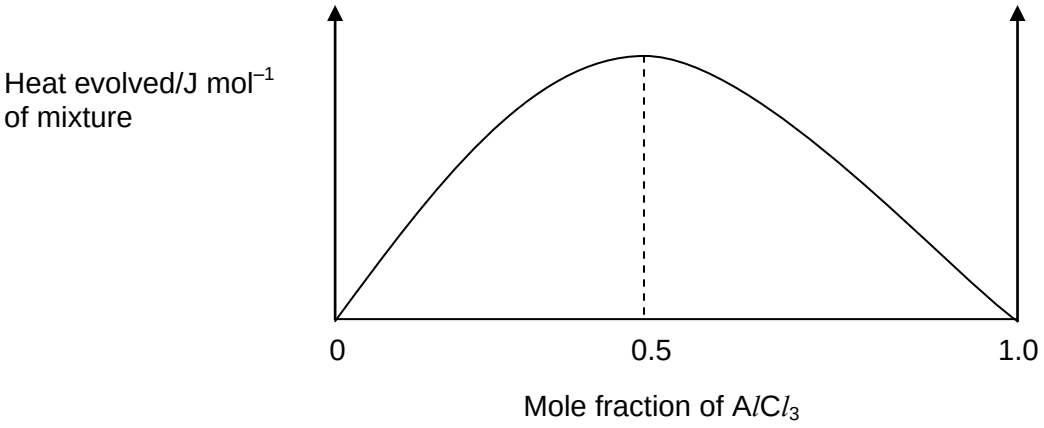
4 **(a)** There is said to be a 'diagonal relationship' between elements of the second and third periods of the Periodic Table, exemplified by lithium and magnesium, and by beryllium and aluminium.

(i) By considering the trends in electronegativity across the period and down the group, suggest why the 'diagonal relationship' exists.

(ii) Beryllium chloride dissolves in water to give $[Be(H_2O)_4]^{2+}$. Predict and explain the pH of the solution.

[3]

(b) When aluminium chloride, $AlCl_3$, is mixed with ammonia, heat is evolved. The amount of heat evolved per mole of the mixture is shown in the diagram below.



(i) What can you deduce from the diagram about the molar ratio of the aluminium chloride and ammonia reaction? Draw a diagram to illustrate the nature of the bonding in the product formed, and indicate the values of the bond angles clearly.

(ii) Sketch the curve you would expect to obtain for the heat evolved for mixtures of beryllium chloride, $BeCl_2$, and ammonia. Label your axes clearly.

[3]

(c) Beryllium oxide was heated with a mixture of potassium fluoride and hydrogen fluoride. An ionic compound was formed, which dissolved in water. When the resultant solution was added to aqueous lead(II) nitrate, an immediate white precipitate, **A**, containing only beryllium, fluorine and lead was obtained. The white precipitate contained 3.08 % by mass of beryllium.

(i) Given that the relative formula mass of **A** is approximately 290, deduce the empirical formula of **A**.

(ii) The anion in compound **A** is also formed when beryllium difluoride reacts with excess potassium fluoride.

Draw a dot-and-cross electron diagram of this anion and hence deduce its shape.

[4]

(d) The 'rare earth' elements play a crucial role in the manufacture of modern electronic gear such as mobile phones. They are formed as a result of filling in of the penultimate f-subshell, which consists of seven degenerate orbitals. Europium, Eu, is one of the rare earth elements.

The ground state electron configuration of Eu can be written as [Xe] $4f^7$ $6s^2$.

(i) What is meant by the term 'ground state'?

(ii) Draw the 'electron-in-box' diagram for the valence electrons of the Eu^{2+} ion.

(iii) Europium(II) nitrate decomposes on heating in the same way as Group II nitrates. Would you expect the decomposition temperature of $Eu(NO_3)_2$ to be higher or lower than that of $Be(NO_3)_2$? Explain your answer.

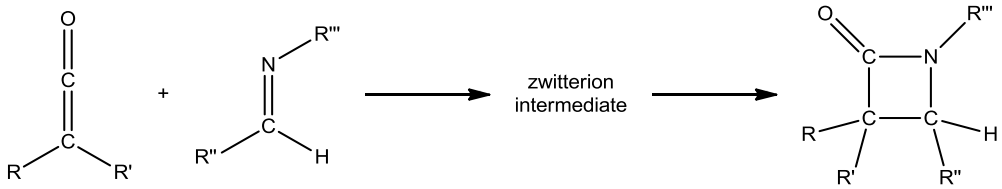
[4]

(e) Ketene, C_2H_2O, is a member of a class of unsaturated organic compounds that is widely used in organic synthesis.

$CH_2=C=O$
ketene

(i) Suggest chemical tests (reagent, conditions and observations) that you may use to confirm **each** of the functional groups in ketene. Write a balanced equation for **each** test you use.

(ii) The Staudinger synthesis is an important step in the synthesis of penicillin. It involves the reaction of a ketene with an imine to form a cyclic amide. It is suggested that in the rate-determining step of the mechanism, the imine acts as a nucleophile to attack the ketene, forming a zwitterion intermediate.



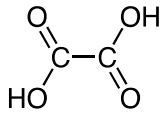
ketene imine

By means of curly arrows and labeling the relevant charges, show clearly the movement of electrons in this rate-determining step and suggest the structure of the zwitterion formed.

[6]

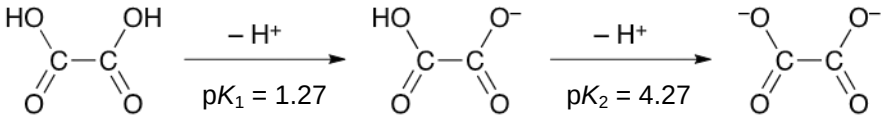
[Total: 20]

5 In 1824, Wöhler prepared oxalic acid (also known as ethanedioic acid), possibly the first synthesis of an organic molecule.



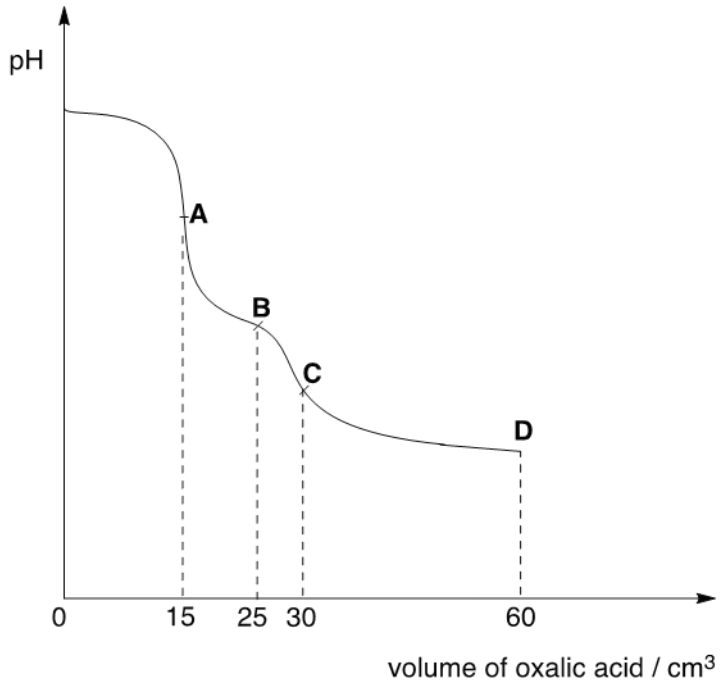
oxalic acid

(a) Despite being an organic acid, oxalic acid is a rather strong acid, with two pK_a values:



(i) Suggest **two** reasons why the pK_1 value of oxalic acid is lower than the pK_a value of formic acid, HCO_2H (pK_a = 3.7).

When a solution of 0.100 mol dm^{-3} oxalic acid is added slowly to a 30.0 cm^3 solution of 0.100 mol dm^{-3} NaOH, the following titration curve was obtained.



(ii) The major organic species present at points **A** and **C** are $^-O_2C–CO_2^-$ and $HO_2C–CO_2^-$ respectively. Explain this observation fully.

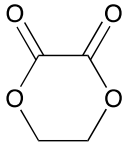
In your answer, include an equation for the reaction that occurred to produce **each** of these two species.

(iii) Calculate the pH value at point **B**, showing clearly your working.

(iv) Explain, with the aid of an equation, how the mixture at point **D** can resist pH change upon the addition of a small amount of aqueous NaOH.

[9]

(b) Starting with oxalic acid as the only organic reagent, propose a synthetic scheme to obtain the following compound.



Your answer should include reagents and conditions used, as well as any intermediate compound.

[2]

(c) **(i)** Oxalate ions, $C_2O_4^{2-}$, are toxic to the human body. If sufficient amounts are ingested and released into the bloodstream, the high concentration of oxalate ions would cause the precipitation of calcium oxalate in the urine, which can accumulate into painful kidney stones.

Assuming that the body excretes an average of 250 mg of calcium ions per litre of urine, what is the minimum concentration of oxalate ions needed to precipitate calcium oxalate in the urine?

Numerical value of solubility product of calcium oxalate, CaC_2O_4: 2.7×10^{-9}

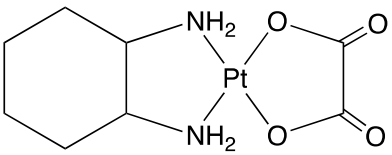
(ii) A student added an excess amount of calcium oxalate in water to obtain a saturated solution at equilibrium.

I Write an equation to show why the saturated solution has a pH above 7 at 25 ^oC.

II Predict and explain what happens when excess dilute HC*l* is added to the saturated solution.

[5]

(d) The oxalate ion, $C_2O_4^{2-}$, forms a *complex* with platinum in oxaliplatin, a drug used in cancer treatment.



oxaliplatin

(i) Explain why oxaliplatin is considered a *complex*.

(ii) State the oxidation number and coordination number of platinum in oxaliplatin.

(iii) Explain why a complex can be formed between platinum and oxalate ion, unlike calcium in **(c)** which forms a precipitate.

[4]

[Total: 20]