Name:		Class:	

ST ANDREW'S JUNIOR COLLEGE

JC2 Preliminary Examinations

Chemistry **9647/03**
Higher 2 **14 September 2015**
Paper 3 **2 hours**

Candidates answer on separate paper.

Additional Materials: Writing paper, Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and civics group 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.

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.

This document consists of **15** printed pages including this page.

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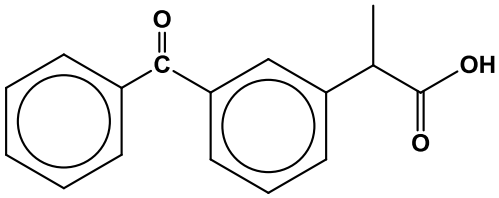
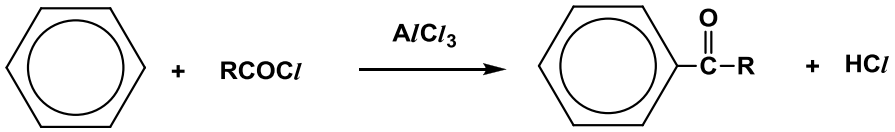
1 (a) Organic compounds have various applications. For instance, Ketoprofen is a kind of nonsteroidal anti-inflammatory drug, which can be used as a substitute for aspirin.

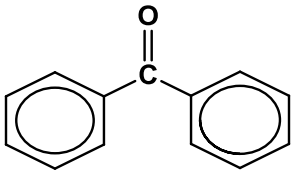


Ketoprofen

(i) Friedel Craft Acylation was first discovered by Charles Friedel and James Crafts in 1877. This reaction allowed for the acylation of an aromatic ring with acyl chloride. One such example is given below.



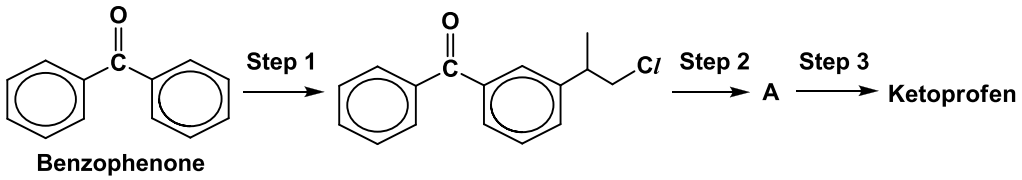
Benzophenone, which can be used to synthesise Ketoprofen, has the structure below.



Benzophenone

Suggest the reagent needed to convert 2 moles of benzene into 1 mole of benzophenone. **[1]**

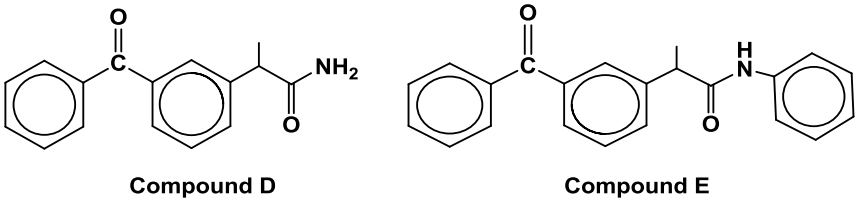
1 (a) (ii) Ketoprofen may be synthesised from benzophenone in the following route.



State the reagents and conditions for **Steps 1** to **3**.
Draw the structural formula of **A**. **[4]**

(iii) Ketoprofen is commonly sold as its sodium salt form for better absorption by the body, which is made up of 70% water. Explain, with the aid of a diagram, how this better absorption comes about. **[2]**

(iv) Nitrogen-containing derivatives of Ketoprofen may be synthesised and some examples are as shown.



Describe a simple chemical test to distinguish between compound **D** and compound **E**. **[2]**

(v) Ketoprofen can react with cold alkaline HCN to form a product which exists as a mixture of 4 stereoisomers.
Give the structure of the product formed. Hence, state the type of isomerism exhibited by this product and draw the stereoisomers. **[4]**

1 (b) Another use of organic compounds is in the area of food preservation. To prevent food spoilage, the pH of food should not fluctuate too much. Hence, a mixture of lactic acid, $CH_3CH(OH)COOH$, and sodium lactate is commonly added in yoghurt to act as a pH regulator.

(i) Explain how the mixture of lactic acid and sodium lactate can function as a pH regulator when an acid is added. Include any relevant equation.

[2]

(ii) The pH of yoghurt is usually maintained at about 4.2.
Calculate the ratio of the concentrations of lactate ion to lactic acid in yoghurt, given that the pK_a of lactic acid is 3.86. **[1]**

(iii) Given that the concentration of lactic acid in a sample of yoghurt is 0.05 mol dm^{-3} and using your ratio in **(b)(ii)**, calculate the concentration of lactate ion. **[1]**

(iv) Perfluorooctanoic acid is a common food contaminant. In yoghurt, this monobasic acid will dissociate completely. Calculate the new pH of the yoghurt when 0.05 mol of perfluorooctanoic acid is added to 5 dm^3 of the yoghurt in **b(iii)**.
Hence, calculate the change in pH. **[3]**

[Total: 20 marks]

2 (a) Transition metals are known to have many uses, ranging from materials, medicine to catalysts. Explain what is meant by the term *transition metal*. **[1]**

(b) Aqueous copper(II) sulfate is blue and this is due to the presence of hexaaquacopper(II) ion, $[Cu(H_2O)_6]^{2+}$. When 1,2-diaminoethane, $H_2NCH_2CH_2NH_2$, and ammonia are added separately to a sample of copper(II) sulfate solution, the following reactions occur. (Note: "en" represents $H_2NCH_2CH_2NH_2$)

Reaction 1:

$[Cu(H_2O)_6]^{2+}$ (aq) + en (aq) $\longrightarrow$ $[Cu(en)(H_2O)_4]^{2+}$ (aq) + $2H_2O$ (*l*)

$\Delta H^{\ominus} = -52$ kJ mol^{-1}

Reaction 2:

$[Cu(H_2O)_6]^{2+}$ (aq) + $2NH_3$ (aq) $\longrightarrow$ $[Cu(NH_3)_2(H_2O)_4]^{2+}$ (aq) + $2H_2O$ (*l*)

$\Delta H^{\ominus} = -48$ kJ mol^{-1}

(i) State the full electronic configuration of Cu^{2+}. **[1]**

(ii) With reference to relevant bonds, suggest why the two enthalpy changes are similar in value. **[1]**

(iii) By considering the entropy and enthalpy changes of **Reaction 1** and **Reaction 2**, suggest and explain the difference in magnitude of the standard Gibbs free energy change of the two reactions. **[2]**

(iv) Copper(II) sulfate can combine with $H_2NCH_2CH_2NH_2$ and sodium cyanide to form a compound, where the co-ordination number of copper is 6. The formula unit of this compound contains two sodium ions and an anion.

Draw the structure of the anion to illustrate its shape.

You may use  to represent $H_2NCH_2CH_2NH_2$. **[1]**

2 (c) Partition coefficient, K_D, is an example of an equilibrium constant. It is the ratio of equilibrium concentrations of a species in a mixture of two immiscible solvents. From the value of K_D, the difference in solubility of a species in two immiscible solvents can be determined.

When an aqueous solution of ammonia was shaken with dichloromethane at room temperature, an equilibrium was established as shown.

$$NH_3\,(aq) \rightleftharpoons NH_3\,(\text{in } CH_2Cl_2) \qquad K_D = 0.04$$

(i) State the solvent in which ammonia has a higher solubility. With reference to interactions involved, explain your answer. **[2]**

(ii) Write the K_D expression. **[1]**

(iii) 100 cm^3 of 1.00 mol dm^{-3} aqueous ammonia solution was mixed with dichloromethane. 100 cm^3 of 0.0133 mol dm^{-3} chromium(III) sulfate was then added to the water-dichloromethane mixture. This resulted in complex formation as shown below. All the Cr^{3+} reacted with some ammonia in the aqueous layer.

$$Cr^{3+} + n\,NH_3 \rightleftharpoons [Cr(NH_3)_n]^{3+}$$

The setup was then left to stand and the dichloromethane layer was found to contain 0.0184 mol dm^{-3} of ammonia.

Using your answer to **c(ii)**, calculate the concentration of ammonia left in the aqueous layer after complex formation. **[1]**

(iv) Using your answer to **c(iii)**, calculate the value of n in the formula $[Cr(NH_3)_n]^{3+}$. **[1]**

2 (d) The production of "elephant toothpaste" involves the decomposition of hydrogen peroxide. The equation for this reaction is as given.

$$2\ H_2O_2 \longrightarrow 2\ H_2O + O_2$$

(i) It is postulated that this reaction involves a highly reactive species with an unpaired electron. With the use of curly arrows to represent the movement of electrons, show how the reactive species may be formed from H_2O_2. **[1]**

(ii) Using data from the *Data Booklet*, calculate $E^{\ominus}_{cell}$ for the decomposition of hydrogen peroxide. **[1]**

(iii) ΔG and $E^{\ominus}_{cell}$ values are related by the following equation.

$$\Delta G = - zFE^{\ominus}_{cell}$$

Where ΔG is in Joules per mole, z is the number of moles of electrons transferred and F is the Faraday constant.

Based on the given information, calculate ΔG for the decomposition of hydrogen peroxide. State the significance of your answer. **[2]**

(iv) When a sample of hydrogen peroxide was left to decompose, the rate of production of gas was slow. Suggest a reason for this observation. **[1]**

(v) Fe^{2+} is known to aid the decomposition of hydrogen peroxide. By referring to the following $E^{\ominus}$ value and relevant data from the *Data Booklet*, show how Fe^{2+} carries out its role. You should give relevant equations in your answer.

$$FeO^{2+} + 2\ H^+ + 2\ e^- \rightleftharpoons Fe^{2+} + H_2O \qquad E^{\ominus} = +1.55\ V$$ **[3]**

(vi) Besides its role in hydrogen peroxide decomposition, Fe^{2+} (aq) is commonly used in redox titration. Although both acidified potassium manganate(VII) and acidified potassium dichromate(VI) can be used to titrate Fe^{2+} (aq) in volumetric analysis, acidified potassium manganate(VII) is the preferred titrant to improve the reliability of experiment. Suggest a reason why this is so. **[1]**

[Total: 20 marks]

3 (a) Chlorine is a useful reagent for chemical synthesis. It has desirable applications, such as in the production of drugs, fire-fighting and purification of water.

(i) Chlorine may be produced from the electrolysis of concentrated sodium chloride. Write equations for the reactions at the anode and cathode. **[1]**

(ii) By considering their reactions with thiosulfate ion and with reference to changes in oxidation number, compare the oxidising ability of Cl_2 and I_2. Write relevant equations where appropriate. **[3]**

(iii) A student attempted to synthesise trichloromethane from methane using an aqueous solution of chlorine. However, this was unsuccessful. Suggest and explain what went wrong in the synthesis. **[1]**

(b) Chlorine dioxide gas, ClO_2, is widely used as a bleaching agent. It is commonly manufactured from the reaction between chlorine and sodium chlorite.

$$Cl_2\,(g) + 2\,NaClO_2\,(s) \rightarrow 2\,ClO_2\,(g) + 2\,NaCl\,(s)$$

(i) Calculate the mass of ClO_2 produced when 15.0 g of $NaClO_2$ is reacted with 2000 cm^3 of Cl_2 at 290 K and under 1.50 atm. **[3]**

(ii) Draw dot-and-cross diagrams of ClO_2 and ClO_2^-. **[2]**

(iii) ClO_2 is known to oxidise Fe^{2+} easily. With reference to your answer in **(b)(ii)**, suggest a reason for this. **[1]**

(iv) Despite being highly unstable, iodite ion, IO_2^-, has been detected as an intermediate in some reactions. State and explain if the bond angle in IO_2^- is greater or smaller than that in ClO_2^-. **[2]**

3 (c) Figure 1 shows the change in pV with increasing pressure at 298 K for an ideal gas and four real gases. The amount for each gas is 1 mole.

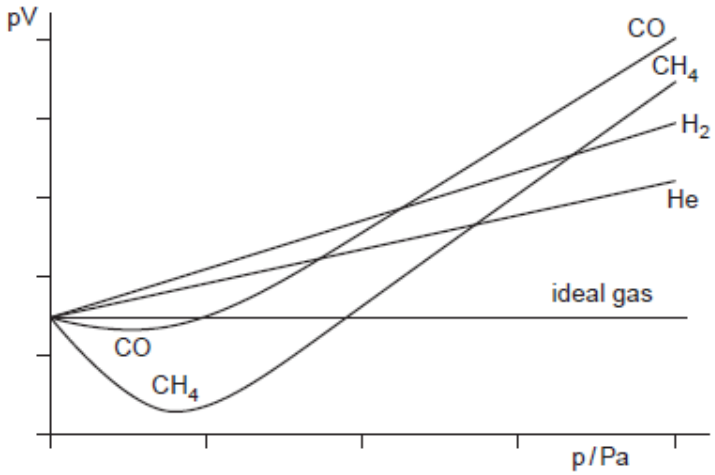
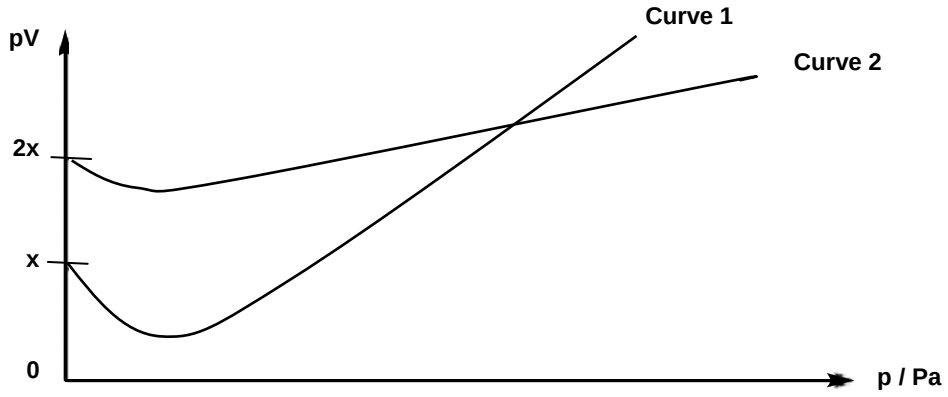


Figure 1

(i) Explain the deviation from ideality as shown by the real gases. **[1]**

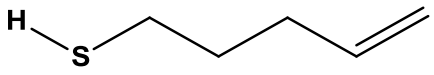
(ii) The following curves show the behaviour of methane under different conditions.
Curve 1 shows the behavior of 1 mole of CH_4 at 298 K.
What does **curve 2** represent?



[1]

[Turn over

3 (d) Organic compounds which contain sulfur typically have an odour. One such example is as shown.

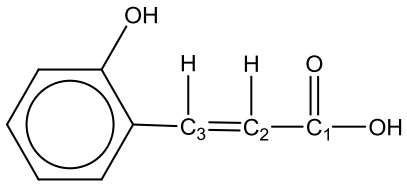


(i) Describe the mechanism for the reaction between this compound and chlorine molecule in CCl_4. **[3]**

(ii) The product formed in **d(i)** can undergo further reaction to form **Z** with a molecular formula of C_5H_9SCl.
Suggest the structure of **Z** and the type of reaction involved. **[2]**

[Total: 20 marks]

4 (a) Compound **A** is a commonly used starting material to synthesise a class of anti-bacterial drugs known as quinolones.



Compound **A**

(i) There are two acidic groups in compound **A**.

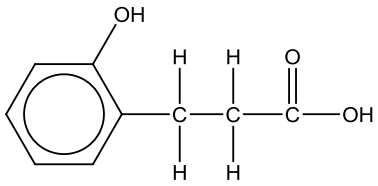
Explain the difference in the acidities of these two groups. Show the difference in their acidities by writing an equation to represent the reaction between compound **A** with sodium carbonate. **[4]**

(ii) C_1, C_2 and C_3 are carbon atoms which undergo the same type of hybridisation when forming compound **A**.

I – State the type of hybridisation and draw a labelled diagram to show all the orbitals of any of these carbons.

II – Explain how sigma and pi bonds arise between these orbitals. **[4]**

(iii) Compound **B** is formed when compound **A** is hydrogenated.



Compound **B**

With reference to your answer in **a(ii)**, suggest why the carboxylic acid group in compound **A** is more acidic than that in compound **B**. **[1]**

(iv) Upon oxidation, both compounds **A** and **B** yield compound **C** with molecular formula $C_7H_6O_3$. Compound **C** is less soluble in water than compounds **A** and **B**. Suggest the structure of compound **C** and explain its lower solubility in water.

[2]

[Turn over

4 (b) When agricultural lime containing $CaCO_3$ is heated to a high temperature in a lime kiln, quicklime is produced. Quicklime is allowed to cool and a calculated amount of water is added. A highly exothermic reaction takes place and a white powder called slaked lime is produced.

(i) Write balanced equations for the **two** reactions described above. **[2]**

(ii) Agricultural lime is used to increase the pH of the soil.
Using an equation, show how agricultural lime carries out this role. **[1]**

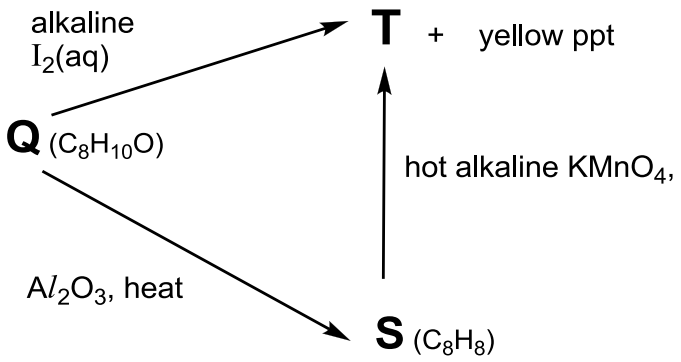
(iii) $CaCO_3$, the main active component in agricultural lime, has a lower melting point than quicklime.
Suggest an explanation for the difference in their melting points. **[3]**

(iv) Predict how the decomposition temperature of $Al_2(CO_3)_3$ would compare with that of $CaCO_3$ in agricultural lime.
Explain your answer using relevant data from the *Data Booklet*. **[3]**

[Total: 20 marks]

5 (a) Compound **P**, $C_{10}H_{12}O_3$, is insoluble in water. It does not dissolve in aqueous NaOH at room temperature but upon heating with aqueous NaOH, compound **P** gives two compounds, **Q**, $C_8H_{10}O$, and **R**, sodium 2-hydroxyethanoate.

Q was found to undergo the following reactions:



(i) Based on the above information, state the functional groups for which the three oxygen atoms in **P** belong to. Explain your answer. **[2]**

(ii) Draw the displayed formulae of **P**, **Q**, **S** and **T**. **[4]**

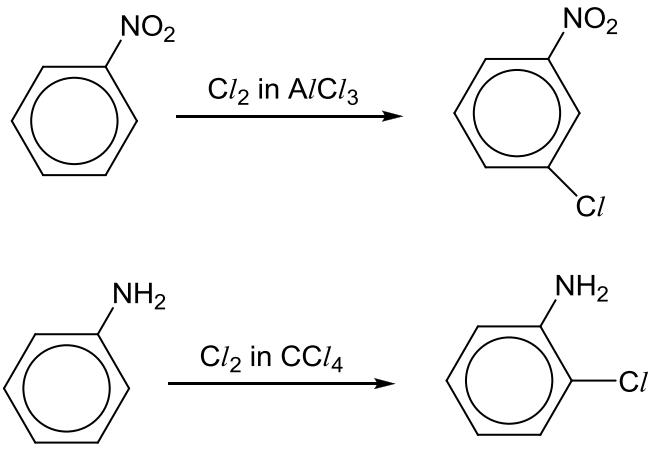
(iii) A student proposed to synthesise **P** from acidified **R** by the following route.

$$HOCH_2CO_2H \xrightarrow{PCl_5} \text{Intermediate} \xrightarrow{\mathbf{Q}} \mathbf{P}$$

Explain what is wrong with his proposed synthetic route. Suggest how he could synthesise **P** from acidified **R** instead. **[2]**

(iv) Upon reacting acidified **R** with hot $KMnO_4$, carbon dioxide is obtained as the only carbon-containing product. Write an equation for this oxidation reaction.
Use [O] to represent the formula of the oxidising agent. **[1]**

5 (b) Nitrobenzene and phenylamine react with Cl_2 under different conditions as shown.



(i) State the role of $AlCl_3$ in the reaction. **[1]**

(ii) Explain clearly the difference in the conditions needed for the two reactions. **[2]**

(c) Aluminium can be combined with oxygen and chlorine to make different compounds. Alumina, Al_2O_3, is the refractory oxide of aluminium with a very high melting point of about 2070 °C. Aluminium chloride, $AlCl_3$, which can be manufactured from Al and HCl at temperatures between 650 to 750 °C, has a much lower melting point of about 192 °C.

(i) Write an equation to show how $AlCl_3$ can be manufactured from Al and HCl.
State the type of reaction involved. **[2]**

(ii) State the type of structures of Al_2O_3 and $AlCl_3$.
Explain the difference in structures. **[3]**

(iii) A student is given an unknown white solid which can either be Al_2O_3 or $AlCl_3$. Describe how you would carry out a simple test to determine its identity. Explain the difference in observations and include relevant equations where applicable.
[3]

[Total: 20 marks]

~ END OF PAPER ~