ST ANDREW'S JUNIOR COLLEGE

JC2 Preliminary Examinations

Chemistry
Higher 2 **9647/02**
Paper 2 **10 September 2012**
2 hours

Candidates answer in the spaces provided on the question paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

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 **all** 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.

For Examiner's Use:

Question	Marks
1	
2	
3	
4	
5	
Total	

This document consists of **17** printed pages **including** this page.

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1 **Planning (P)**

Four aqueous solutions are provided. Each solution contains one of the following:
Aluminium bromide, Zinc sulfate, Silver nitrate, Barium hydroxide

You are to plan a series of test-tube experiments using **only** the four solutions and solid potassium carbonate, in order to deduce which compound is present.
No other reagents should be used.

You should commence your plan by adding potassium carbonate to each of the solutions. Your completed plan should include observations, deductions and balanced equations for positive tests.

[12]

No.	Experiment	Observations	Deductions with relevant balanced equations
1.	Add ½ spatula of solid potassium carbonate to each separate samples (1 cm^3) of the 4 solutions in clean, dry test tubes.		
2.			

3			

[Turn Over

2 (a) Transition metals are often used to produce ornamental stained-glass windows. Iron–based colours and pigments have been used since ancient times for stained-glass windows in European churches.

(i) Explain why iron compounds are usually coloured.

(ii) Explain why the melting point of iron is significantly higher than that of calcium.

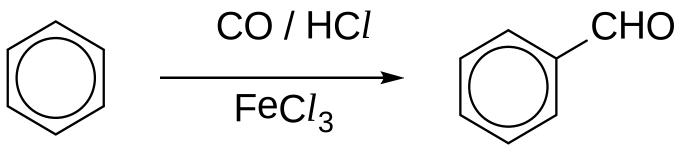
Stained-glass windows are darkened from corrosion and age. Microprobe analysis showed that the tiny cracks and defects on the glass surface were enriched with insoluble MnO_2.

(iii) Using the *Data Booklet*, suggest a suitable reducing agent to dissolve MnO_2 without reducing iron (III) to iron (II).

[7]

[Turn Over

2 (b) Iron (III) chloride is often used as a catalyst in the conversion of benzene to produce carbonyl compounds.



(i) Write an equation to show the generation of the electrophile to form benzaldehyde.

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(ii) Explain why iron (III) chloride must be anhydrous in order to generate the electrophile.

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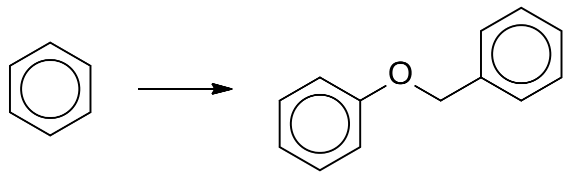
[3]

2 (c) By making use of the reaction in **2(b)** and suitable starting materials, suggest a synthetic pathway (in no more than 4 steps) to convert benzene into the following compound. State clearly the reagents and conditions for each stage, and draw the structural formulae of every intermediate formed.



[4]

2 (d) Iron (III) chloride can also be used in the alkylation of benzene to yield alkyl benzene, for example methylbenzene (toluene). Toluene is less toxic than benzene, and thus can replace benzene as an aromatic solvent in chemical preparation.

Using the following data,

	ΔH^{θ}/ kJ mol^{-1}
Enthalpy change of formation of CO_2 (g)	- 393.5
Enthalpy change of formation of H_2O (*l*)	- 285.8
Enthalpy change of combustion of $C_6H_5CH_3$ (*l*)	- 3910
Enthalpy change of vaporisation of $C_6H_5CH_3$ (*l*)	+ 38

(i) Calculate the standard enthalpy change of formation of toluene, $\Delta H_f^{\theta} C_6H_5CH_3$ (*l*).

(ii) Using your answer to **2 (d)(i)**, relevant data from the table above and the *Data Booklet,* draw an appropriate energy cycle to determine the enthalpy change of formation of benzyl radical $C_6H_5CH_2\bullet$ (g).

2 (d) **(iii)** Hence, deduce the thermodynamic stability of the product, benzyl radical $C_6H_5CH_2\bullet$ as compared to its reactants. Explain.

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[7]

[Total: 21 marks]

3 (a) Chelation is the formation of coordinate bonds between a ligand and a single central atom or metal ion. The ethanedioate ion ($C_2O_4^{2-}$) is an example of a chelating ligand. Two complexes which are successfully synthesised are $[Al(C_2O_4)_3]^{3-}$ and $[Al(C_2O_4)_2]^{-}$.

(i) Draw a dot-and-cross diagram for $C_2O_4^{2-}$. Hence, suggest the bond angle about either carbon atom.

(ii) State the coordination number of aluminium in the complex $[Al(C_2O_4)_3]^{3-}$.

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[3]

3 (b) Aluminium is able to form ethanedioate complex such as $K_{2n-3}[Al(C_2O_4)_n]$. To determine the identity of the complex, the complex is first decomposed in an acidic solution to give ethanedioic acid and then titrated against potassium manganate (VII).

$$Al(C_2O_4)_n^{(3-2n)} + n\ H_2SO_4 \rightarrow n\ H_2C_2O_4 + Al^{3+} + n\ SO_4^{2-} \quad (n = 2 \text{ or } 3)$$

$$2\ H^+ + 2\ CO_2 + 2\ e \rightleftharpoons H_2C_2O_4 \qquad E = -\ 0.49\ V$$

Volumetric Analysis for ethanedioate content	
Step 1	Weigh 1.77 g of the complex, $K_{2n-3}[Al(C_2O_4)_n]$, in a 50 cm^3 beaker.
Step 2	Dissolve it in deionised water and transfer to a 250 cm^3 volumetric flask and top up to the mark with deionised water.
Step 3	Pipette 25.0 cm^3 of the solution into a conical flask and add about 40 cm^3 of aqueous H_2SO_4.
Step 4	Warm the solution to about 50 ^{0}C.
Step 5	Titrate the contents of the flask with potassium manganate (VII) from a burette until the first pink colour appears.

(i) Use the *Data Booklet* to explain how the results of titration would differ when HC*l* is used instead of H_2SO_4 in **Step 3.**

(ii) By using collision theory of reaction kinetics, explain why the solution needs to be warmed in **Step 4.**

[4]

[Turn Over

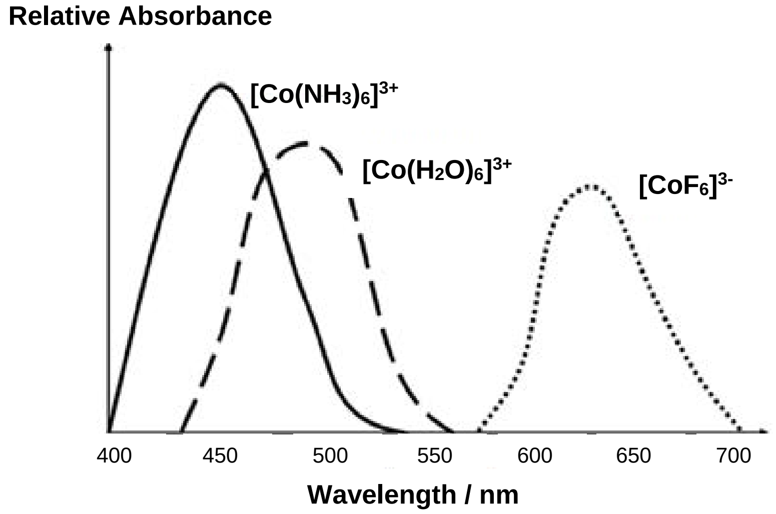
3 (b) (iii) Given that 27.50 cm^3 of 0.0213 mol dm^{-3} potassium manganate (VII) is needed to reach equivalence point, calculate the % by mass of ethanedioate ion in the aluminium complex.

(iv) Hence, determine the value of ***n***.

[4]

3 (c) Other chelating ligands such as F^-, H_2O and NH_3 can also be used to form cobalt complexes.

The UV-visible absorption spectra of the three aqueous solutions are shown below:



(i) With the aid of the spectrum above, account for the difference in the wavelength for each complex.

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(ii) With the addition of another chelating ligand such as $EDTA^{4-}$ to $[Co(H_2O)_6]^{2+}$, $[CoEDTA]^{2-}$ complex is formed according to the following equation:

$$[Co(H_2O)_6]^{2+}(aq) + EDTA^{4-}(aq) \rightleftharpoons [CoEDTA]^{2-}(aq) + 6H_2O\,(l)$$

Explain why this reaction is spontaneous at all temperatures.

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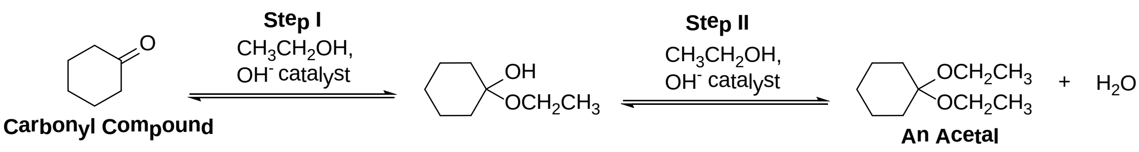
[5]

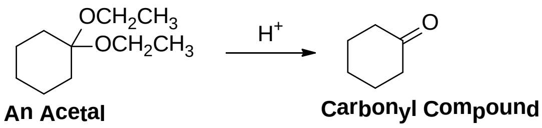
[Total: 16 marks]

4 (a) Acetal is relatively inert and can be made from a carbonyl compound. The carbonyl functional group may be restored by adding aqueous acid.

Formation of Acetal



Carbonyl functional group is restored by adding aqueous H^+



(i) Suggest the type of reaction which occurs in **Step I**.

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(ii) Suggest why OH^- catalyst is needed in **Step I**.

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(iii) Outline a mechanism for **Step I.** In your answer, show any relevant charges, lone pairs of electrons and movement of electrons.

4 (a) **(iv)** Explain why anhydrous calcium chloride is added after **Step II.**

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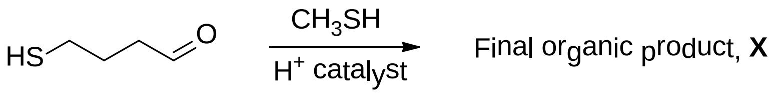
[7]

(b) Thiols (RSH) are sulfur analogs of alcohols.



(i) Compound **X** has the following composition by mass.

C: 51.2%; H: 7.7%; S: 27.4%; O:13.7%

Using the given data, calculate the empirical formula of the final organic product **X.**

(ii) When a sample of 0.219 g of compound **X** was vaporised using a suitable apparatus, the vapour occupied 38.2 cm^3 at 95 ^0C and 150 kPa.

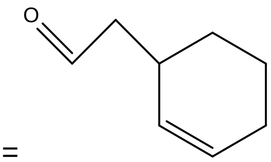
Calculate the Mr of compound **X.**

[3]

[Total: 10 marks]

5 (a) The rate of the reaction between **A** and Cl_2 (*l*) has the following rate law:

Rate = k[**A**]^m [Cl_2]

Where **A** =  and

k is the rate constant with units of $mol^{-2}dm^6s^{-1}$.

Two experiments to study the kinetics of this reaction were carried out and the data obtained are tabulated below.

Experiment	Initial [**A**] / $mol\ dm^{-3}$	[Cl_2] / $mol\ dm^{-3}$	Initial rate / $mol\ dm^{-3}\ s^{-1}$
1	0.40	0.08	R
2	0.20	***y***	½ R

(i) What is the value of ***y*** in Experiment **2**?

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(ii) Given that the half-life of Cl_2 in Experiment **1** was 4.5 seconds, predict a value for the half-life of Cl_2 in Experiment **2**, giving your reasoning.

[3]

(b) **(i)** Predict the products formed when $BaCl_2$ reacts with concentrated H_2SO_4.

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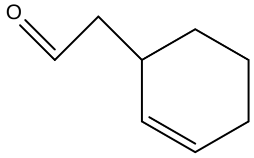
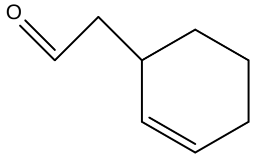
5 (b) (ii) Hence, identify the structural formula for the organic product formed when



reacts with $BaCl_2$ and concentrated H_2SO_4.

[2]

(c) The reaction scheme below shows how an ester is generated from



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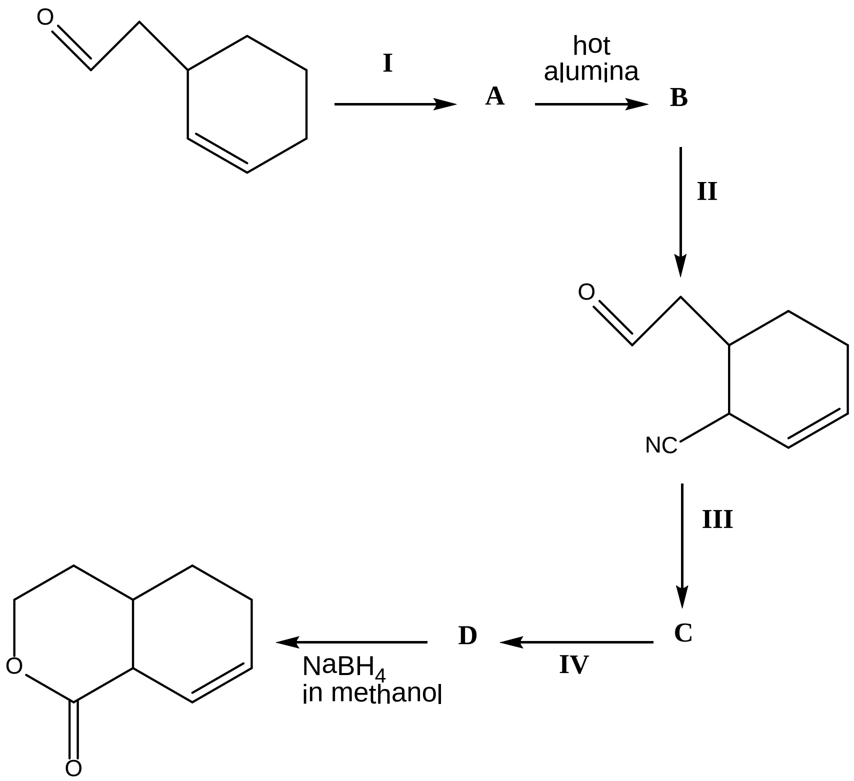
Complete the reaction scheme below by writing the structural formulae of the organic products and the reagents and conditions in the spaces provided.



5 (c)

A	B
C	**D**

Step	Reagents and conditions
I	
II	
III	
IV	

[8]

[Total: 13]

~~~ END ~~~