PIONEER JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION
HIGHER 2

CANDIDATE NAME	

CT GROUP	1	1				INDEX NUMBER						

CHEMISTRY **9647/02**

Paper 2 Structured **10 September 2012**

2 hours

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, index number and name on all work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough workings.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

FOR EXAMINER'S USE			
Paper 2			
1	/ 12	6	/ 12
2	/ 9	7	/ 9
3	/ 15		
4	/ 7	Penalty	sf units
5	/ 8	Total	/ 72

This document consists of **19** printed pages.

Answer **all** the questions in the spaces provided.

1 Planning (P)

You are provided with solutions **FA 1**, **FA 2** and **FA 3**.

FA 1 and **FA 2** are either
1.0 mol dm^{-3} nitric acid **or**
1.0 mol dm^{-3} ethanoic acid

whereas **FA 3** is 2.0 mol dm^{-3} sodium hydroxide.

You are to plan an experiment that will enable you to identify **FA 1** and **FA 2**, and hence, calculate the enthalpy change of neutralisation for the reaction between ethanoic acid and sodium hydroxide.

You are provided with the following apparatus:

a thermometer,
a polystyrene cup,
other common apparatus in the laboratory

(a) State the independent and dependent variables when determining the identity of each solution, **FA 1** and **FA 2**. [1]

Independent variable ……………………………………………………………………

Dependent variable ……………………………………………………………………..

(b) Plan an experiment to identify which of the two solutions, **FA 1** and **FA 2**, is 1.0 mol dm^{-3} nitric acid and which is 1.0 mol dm^{-3} ethanoic acid.

Your plan must identify the acids solely based on the change in temperature. Mathematical processing of the temperature change is thus **not** required.

Your plan should give a step by step description of the method including:

- the apparatus used for measurement
- appropriate volumes of reagents
- how you would measure the various variables

[3]

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(c) Either a burette with 0.1 cm^3 interval or a measuring cylinder with 1 cm^3 interval can be used to measure the volume of **FA 3** required.

It is known that the error (or uncertainty) that is associated with each reading when using a measuring cylinder with 1 cm^3 interval is ±0.5 cm^3, while that using a burette with 0.1 cm^3 interval is ±0.05 cm^3.

Assuming that the volume of **FA 3** measured is V cm^3, calculate the maximum total percentage error (or uncertainty) in the measurement of the volume of **FA 3**, in terms of V, when using:

(i) a measuring cylinder with 1 cm^3 interval,

(ii) a burette with 0.1 cm^3 interval.

[2]

(d) Explain clearly how you could determine the identity of the acids using the difference in temperature rise in the experiment proposed in **(b)**. [2]

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(e) **(i)** Define the term *standard enthalpy change of neutralisation.*

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(ii) Show the mathematical expression for the enthalpy change of neutralisation between ethanoic acid and sodium hydroxide, using the volumes proposed in **(b)**.

The temperature change measured in **(b)** should be represented by ΔT.

[You may assume that 4.2 J of heat energy raised the temperature of 1 cm^3 of any solution by 1^oC.]

[3]

(f) A student suggests titrating **FA 3** against **FA 1** and **FA 2** separately, using phenolphthalein as indicator, to identify two acids. Explain why this proposed method cannot work. [1]

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[Total: 12]

2 Nitrogen dioxide, NO_2 undergoes dimerisation to form dinitrogen tetraoxide, N_2O_4.

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

(a) **(i)** Draw the dot-and-cross diagram of NO_2.

(ii) State the shape and bond angle of the O–N–O bond in NO_2.

Shape ……………………………………………

Bond angle ……………………………………………

(iii) Draw the dot-and-cross diagram of NO_2^- ion. With reference to your answer in **(a)(i)** and **(ii)**, suggest a bond angle of the O–N–O in NO_2^- ion, as compared to NO_2. Explain your answer.

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[5]

The general rate equation for the dimerisation of nitrogen dioxide can be represented as:

$$\text{Rate} = k(p_{NO_2})^{\boldsymbol{n}},$$

where ***n*** represents the order of reaction with respect to nitrogen dioxide.

To determine the value of ***n***, an experiment was carried out to collect experiment data on the partial pressure of nitrogen dioxide (p_{NO_2}) measured at a constant temperature of 500 K. The results were given below.

Time/ s	p_{NO_2} / atm	Rate / atm s^{-1}	
0	0.917	9.48×10^{-5}	
1000	0.827	7.75×10^{-5}	
2000	0.753	6.45×10^{-5}	
3000	0.691	5.45×10^{-5}	
4000	0.638	4.67×10^{-5}	

Table 1

(b) **(i)** Given that ***n*** is 2, process the results in the Table 1 to produce data that would enable you to plot a **straight line graph**.

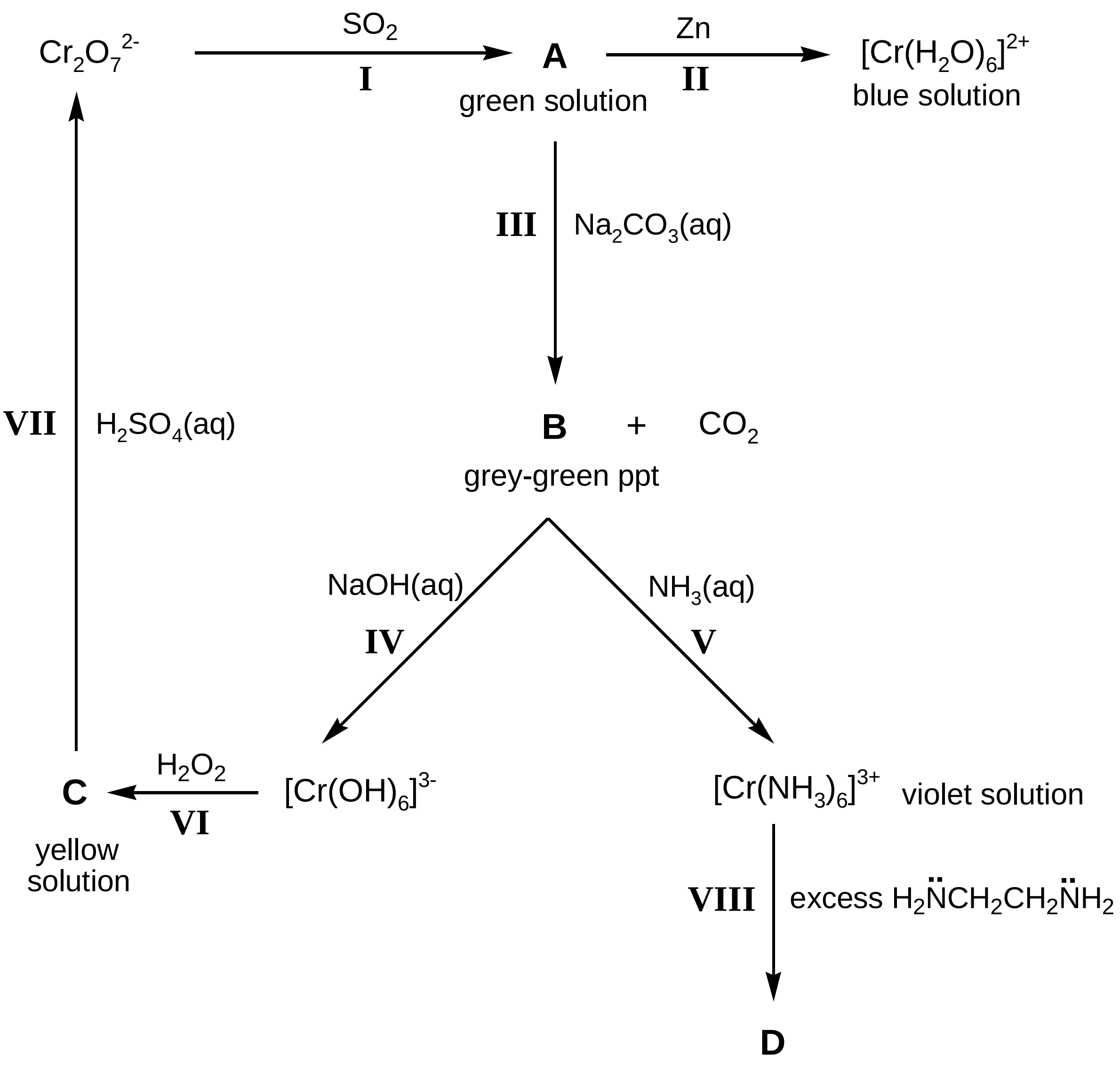
(ii) Hence, use the processed data above to plot the graph on the grid below.

(iii) A student repeated the experiment at the temperature of 250 K. Sketch, on the same axes in **(ii)**, the graph obtained by this student. Label this graph as **250 K**.

[4]

[Total: 9]

3 The following reaction scheme shows the chemistry of some chromium-containing species in aqueous solution.



(a) **(i)** Write the formulae of the following chromium-containing species.

A: ....

B: ....

C: ....

(ii) State the type of reaction that has occurred in **VIII**. Construct a balanced equation to represent the reaction.

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(iii) Hence, using your knowledge of Gibbs free energy, explain why the reaction in **(a)(ii)** occurs spontaneously.

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[7]

(b) Explain why carbon dioxide is evolved when Na_2CO_3(aq) is added to **A** in **III**. Include any relevant equations in your answer. [2]

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(c) Explain why aqueous solutions of chromium ions are coloured. [3]

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(d) In a separate experiment, a chemist prepared two compounds with the general formula $CrCl_3.6H_2O$. Upon adding $AgNO_3$(aq) to aqueous solutions of compounds **E** and **F** separately, he noted the following:

Solution containing	Amount of Ag*Cl* precipitated per mole of compound
compound **E**	1
compound **F**	2

Based on these observations, deduce the formula of compounds **E** and **F** in the solutions. Explain your answer. [3]

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[Total: 15]

4 In the vapour phase, ethanoic acid associates to form dimers and an equilibrium is established as shown.

$$2CH_3COOH(g) \rightleftharpoons (CH_3COOH)_2(g)$$

At 177 °C and 1 atm, 0.084 g of the equilibrium mixture occupies 37.8 cm^3.

(a) **(i)** Calculate the average relative molecular mass of the gaseous mixture, giving your answer to 1 decimal place.

(ii) Calculate the proportion of ethanoic acid and its dimer in the equilibrium mixture.

(iii) Hence, calculate the value of K_p for the dimerisation of ethanoic acid at 177 °C, giving its units.

[4]

(c) State and explain the effect of an increase in temperature on the average M_r of the equilibrium mixture. [3]

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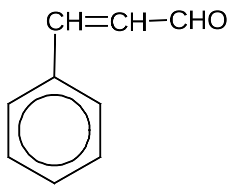
[Total: 7]

5 Cinnamaldehyde is an essential oil with the distinctive odour of cinnamon.



cinnamaldehyde

(a) Sketch the shapes of the hybrid orbitals around one carbon atom in the cinnamaldehyde molecule, indicate clearly the hybridisation of the carbon atom. [1]

(b) A yellow oil is suspected to be cinnamaldehyde.

(i) Assuming the oil is cinnamaldehyde, complete the table below, giving the reagent and conditions to confirm the presence of the two functional groups. Give the expected observation for each test.

Functional group	Reagent and conditions	Expected observation
Alkene		
Aldehyde		

(ii) Write an equation for the reaction between cinnamaldehyde with the reagent you have chosen to test for presence of the aldehyde.

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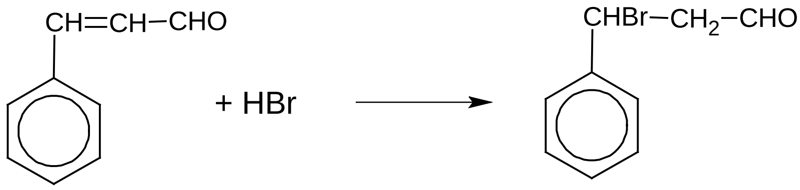
[3]

(c) Cinnamaldehyde undergoes electrophilic addition with hydrogen bromide according to the equation as shown.



Draw the mechanism of the reaction and explain why the product obtained does **not** rotate the plane of polarised light. [4]

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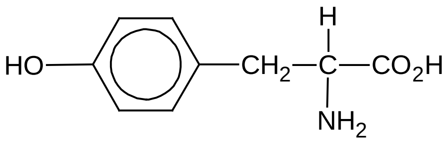
[Total: 8]

6 (a) Tyrosine, one of the 20 α-amino acids commonly found in proteins, was discovered 1846 by German chemist Justus von Liebig in the protein casein from cheese. It has the following structure.



tyrosine

The Hell-Volhard-Zelinskii reaction is the one of oldest methods of α-amino acids synthesis. It involves α bromination of a carboxylic acid by treatment with Br_2 and PBr_3, followed by the conversion of the α-bromo acid to the α-amino acid.

$$R\text{-}CH_2CO_2H \xrightarrow[\text{2. } H_2O]{\text{I: 1. } Br_2,\ PBr_3} R\text{-}CHBrCO_2H \xrightarrow{\text{II}} R\text{-}CH(NH_2)CO_2H$$

(i) Give the structure of the carboxylic acid that could be converted to tyrosine by the above reaction scheme.

(ii) Suggest reagent and condition for step **II**.

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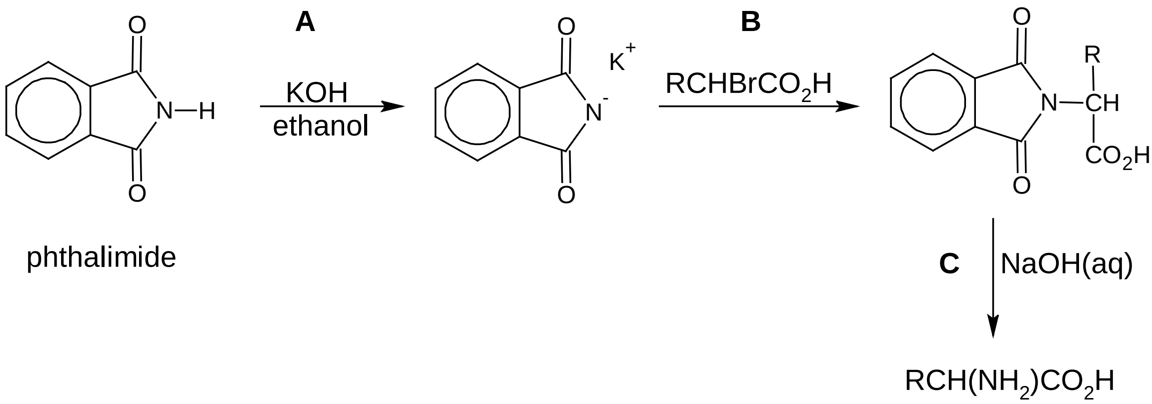
The yield of the amino acid obtained in step **II** of the above reaction scheme tends to be low. A better method is to carry out the Gabriel amine synthesis, which involves the use of phthalimide as shown.



(iii) State the role of KOH in step **A**.

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(iv) What is the type of reaction in step **B**?

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(v) Suggest a reason for the low yield of the amino acid obtained in step **II** of Hell-Volhard-Zelinskii the reaction. Hence, explain how the use of phthalimide in Gabriel amine synthesis would give a higher yield.

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(vi) The protons of amide (-$CONH_2$) are not known to be acidic (pK_a > 500). Explain why the proton of phthalimide is acidic (pK_a = 8.3).

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(vii) Give the structure of the other organic product obtained when alkaline hydrolysis is carried out in step **C** of the Gabriel amine synthesis.

[9]

(b) The three pK_a values associated with tyrosine are 2.20, 9.11 and 10.13.

Make use of these pK_a values to suggest the major species present in solutions of tyrosine with the following pH values.

pH 1

pH 6

pH 11

[3]

[Total: 12]

7 Benzoic acid can be prepared by the oxidation of benzaldehyde using alkaline potassium manganate(VII) as described below.

Data about the benzaldehyde and benzoic acid are given below.

compound	density / g cm^{-3}	melting point / °C	boiling point / °C
benzaldehyde	1.05	-26	179
benzoic acid	1.27	122	229

Preparation of impure benzoic acid

1 Place 2.00 g of solid potassium manganate(VII), 30 cm^3 of 1 mol dm^{-3} sodium hydroxide and 1.5 cm^3 of benzaldehyde in a round-bottomed flask. Swirl the flask carefully to mix the contents thoroughly.

2 Fit a reflux condenser onto the round-bottomed flask and boil the mixture gently for 10 minutes.

3 Filter off the brown precipitate of manganese(IV) oxide formed, collect the filtrate in a 100 cm^3 beaker and allow the filtrate to cool.

4 Carefully add concentrated hydrochloric acid, with constant swirling, to the filtrate till the mixture is acidic enough to precipitate the benzoic acid.

(a) By means of two ion-electron half-equations, write an equation for the oxidation of benzaldehyde by alkaline potassium manganate(VII). [2]

(b) Show by calculation, which reagent, benzaldehyde or potassium manganate(VII), is in excess. [2]

(c) Draw a diagram of the assembled apparatus for heating under reflux. Indicate clearly how water enters and leaves the condenser. [2]

Purification of impure benzoic acid

5 Filter the benzoic acid that has been precipitated and wash it once with cold water.

6 The crude benzoic acid product is purified by recrystallisation from water.

7 Filter the recrystallised solid, wash with water and dry the solid by pressing it under several layers of filter paper.

8 Weigh the solid obtained.

(d) Give a description of the procedure you would use to purify the crude benzoic acid. [1]

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(e) Explain how you would check for purity of the benzoic acid. [1]

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(f) Given that 1.40 g of benzoic acid is obtained from the preparation, calculate the percentage yield of the reaction. [1]

[Total: 9]

END OF PAPER