SERANGOON JUNIOR COLLEGE
General Certificate of Education Advanced Level
Higher 1

Candidate Name
Class

CHEMISTRY **8872/02**
JC2 Preliminary Examination **13th Sep 2017 (AM)**
Paper 2 **2 hours**

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark or blue pen.
You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

The use of an approved scientific calculator is expected, where appropriate.

Section A
Answer **all** the questions

Section B
Answer **two** questions on a separate answer paper.

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 of part question.

FOR EXAMINER'S USE		
P1 (MCQ)		/30
P2	Section A	
	1	/15
	2	/15
	3	/10
	Section B	
		/20
		/20
Total		/110

This document consists of **15** printed pages and **1** blank page.

For Examiner's Use

Section A

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

1 **(a)** An excess of water was added to 3.9 g of unknown phosphorus chloride, PCl_x, and the resulting solution was made up to 250 cm^3 in a standard flask. 25.0 cm^3 of this solution was titrated with 0.40 $moldm^{-3}$ NaOH and required 37.40 cm^3 for neutralisation.

(i) Write equations, for the reactions of PCl_5 and PCl_3 with water. [1]

……

……

(ii) Calculate the total amount, in moles, of H^+ ions present in the 250 cm^3 standard flask. [2]

(iii) Hence, calculate the numerical value of x. [2]

(iv) Draw out the Lewis structure of H_3PO_4. State the bond angles and shape about any central atoms. [3]

(v) Explain why PCl_5 exist but not NCl_5. [1]

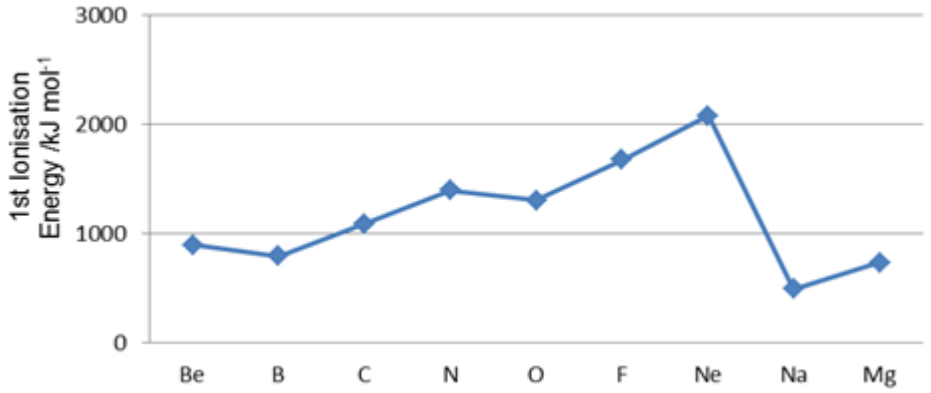
……

……

……

For Examiner's Use

(b) The graph below shows the first ionisation energy of the elements beryllium to magnesium.



(i) Define the term *first ionisation energy*. [1]

……

……

……

(ii) Account for the increasing ionisation energy from beryllium to neon. [2]

……

……

……

……

……

(iii) Explain why the first ionisation energy decreases from beryllium to boron and nitrogen to oxygen. [2]

……

……

……

……

……

……

……

……

For Examiner's Use

(iv) Explain why the first ionisation energy decreases sharply from neon to sodium. [1]

……

……

……

……

……

……

[Total: 15]

For Examiner's Use

2 Ethyl propanoate can be hydrolysed according to the following equation.

$$C_2H_5OCOCH_2CH_3 + H_2O \rightarrow C_2H_5OH + CH_3CH_2CO_2H$$

The kinetics of the above hydrolysis may be investigated by measuring the concentration of propanoic acid produced. In this investigation, 0.240 moles of the ester was mixed with a suitable catalyst in 1 dm^3 of water and the mixture was kept at a constant temperature of 35 °C.

10 cm^3 samples were withdrawn periodically at hourly intervals and rapidly cooled by the addition of cold water. The resulting solution was then titrated against a solution of standard sodium hydroxide every hour over a period of four hours. The following results were obtained.

Time / h	Concentration of propanoic acid / mol dm^{-3}
0	0.000
1	0.084
2	0.140
3	0.178
4	0.195

(a) (i) Identify the role of the cold water used prior to the titration and explain why it is necessary. [2]

……

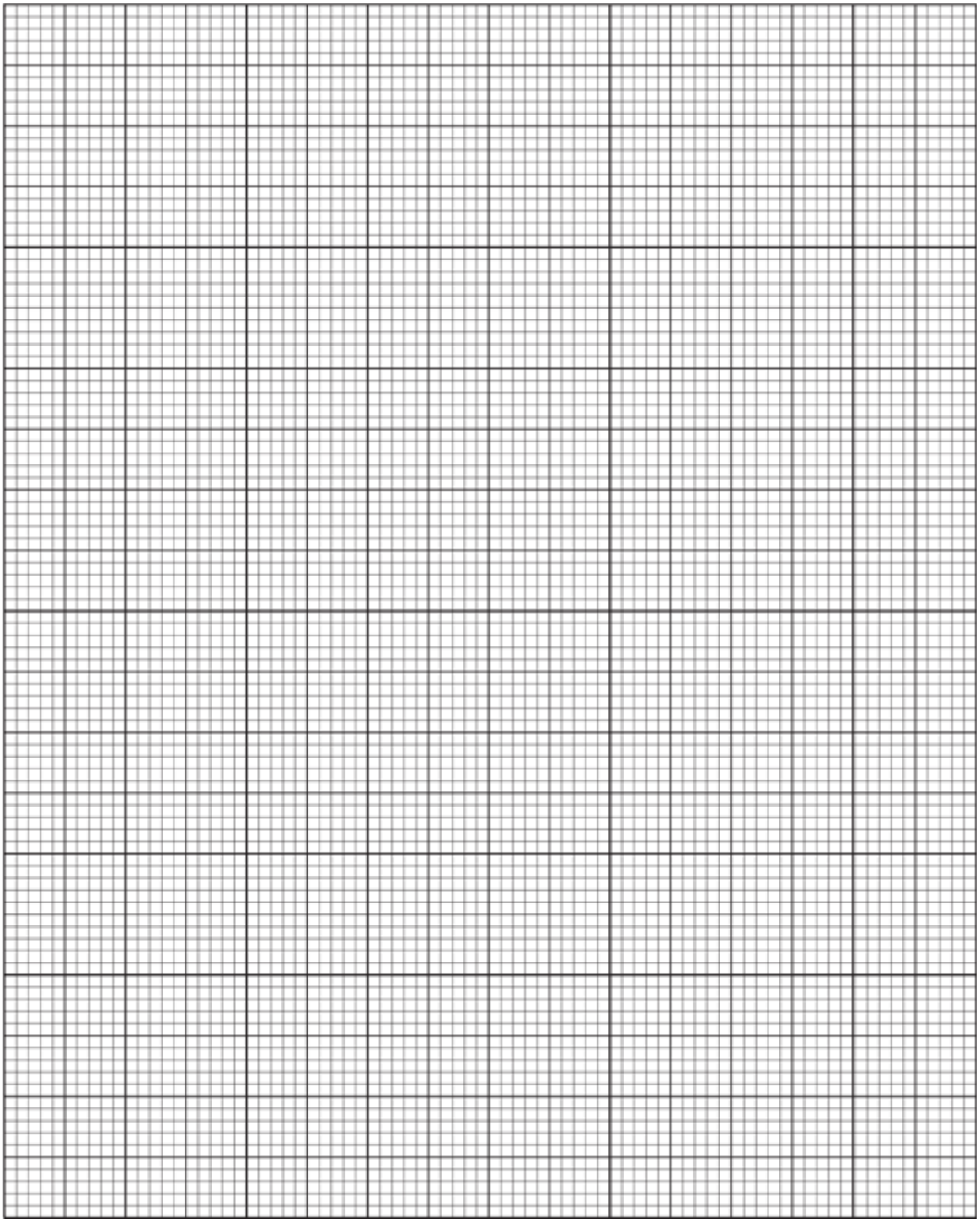
……

……

……

For Examiner's Use

(ii) By using a suitable graphical method, determine the half-life of the reaction and hence show that the hydrolysis reaction is first order with respect to the ester. [4]



For Examiner's Use

(b) The ester, ethyl propanoate, can also undergo base hydrolysis and the reaction is monitored using the initial rates method. The initial rate of the hydrolysis reaction between the ester and NaOH(aq) was measured in three separate experiments at a constant temperature.

The results are obtained below:

Experiment	Temperature / ^{o}C	Initial [NaOH] / mol dm^{-3}	Initial [ester] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	T_1	0.020	0.015	2.70×10^{-3}
2	T_1	0.030	0.015	4.05×10^{-3}
3	T_1	0.060	0.020	r_1
4	T_2	0.120	0.020	4.32×10^{-2}

(i) Deduce the order of reaction with respect to NaOH. [2]

……

……

……

(ii) Given that the reaction is first order with respect to the ester, calculate the initial rate of reaction, r_1, for Experiment 3. [1]

(iii) Calculate the value of the rate constant in experiment 1 and experiment 4, specifying the correct unit. Hence, deduce whether T_1 or T_2 is higher. [3]

……

……

……

……

……

……

For Examiner's Use

(iv) Draw the Maxwell-Boltzmann distribution curve, explain how the increase in temperature increases the rate of reaction. [3]

……

……

……

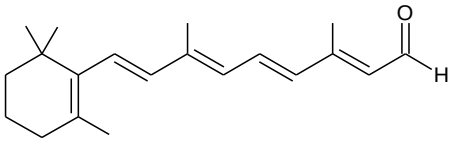
……

[Total: 15]

For Examiner's Use

3 This question revolves around carbonyl compounds involved in biological applications in living things.

(a) Retinal is one of the many forms of vitamin A, bound to proteins called opsins. It is the chemical basis of vision in animals and humans as well as allowing certain microorganisms to convert light into metabolic energy.



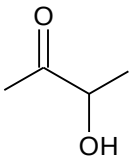
Retinal

(i) State the number of geometrical isomers for retinal. [1]

……

(ii) Draw all the organic products formed when retinal is reacted with cold acidified potassium manganate(VII). [1]

(b) Acetoin is a colorless or pale yellow liquid with a pleasant buttery odour. It is a neutral, four-carbon molecule used as an external energy store by a number of fermentive bacteria.



Acetoin

(i) Suggest a chemical test to **positively** distinguish acetoin from retinal, including relevant chemical equations. [3]

……

……

……

……

……

……

For Examiner's Use

(ii) Compound **F** is an isomer of acetoin and contains an aldehyde and a tertiary alcohol. **F** was reacted in a sequential procedure as shown below.

Step 1:
It is reacted with aqueous hydrogen cyanide at low temperatures.

Step 2:
Hot acidified potassium dichromate(VI) added to product formed earlier

Step 3:
2,4-dinitrophenylhydrazine added to product formed in step 2 to form compound **G**.

Draw the structures of compounds **F** and **G** and state the types of reactions taken place. [5]

Step 1: ……..……

Step 2: ……..……

Step 3: ……..……

F	**G**

[Total: 10]

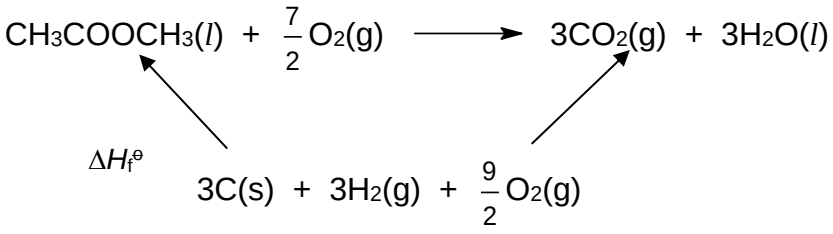
Section B

Answer **two** questions from this section on separate answer paper.

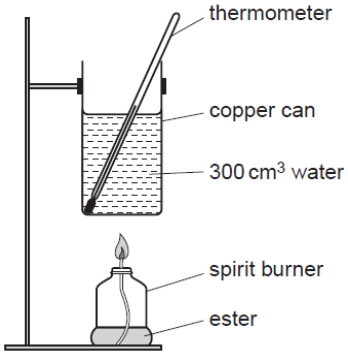
1 (a) (i) Define standard enthalpy change of formation. [1]

(ii) Use the energy cycle below and the standard enthalpy changes of combustion, $\Delta H_c^{\ominus}$, in the table to calculate the standard enthalpy change of formation, $\Delta H_f^{\ominus}$, of methyl ethanoate, CH_3COOCH_3. [2]

	$\Delta H_c^{\ominus}$ / kJ mol^{-1}
carbon	–393.5
hydrogen	–285.8
methyl ethanoate	–1592.1



(b) A student used the apparatus shown to carry out experiments to determine the standard enthalpy change of combustion of methyl ethanoate, CH_3COOCH_3.



Mass of copper can = 250 g

An initial experiment was carried out using methyl ethanoate. This ester was burnt in a spirit burner underneath a copper can so that the flame from the burner heated 300 cm^3 of water in the can. It was found that 0.980 g of ester was required to raise the temperature of the water in the can by 10.0 ^{o}C

(i) Calculate the heat gain by the water given that the specific heat capacity of water is 4.18 J g^{-1} K^{-1}. Take the density of water to be 1.00 g cm^{-3}. [1]

(ii) Given that the **total** heat energy gain is 13.5 kJ, calculate the specific heat capacity of the copper can used in this experiment. [2]

(iii) Using the $\Delta H_c^{\ominus}$ of methyl ethanoate given in the table of part **(a)**, calculate the total theoretical heat energy **in kJ** released by the mass of methyl ethanoate burnt in this experiment. [2]

(iv) Calculate the percentage efficiency of heat transfer in this experiment and suggest a reason for this value. [2]

(c) Methane is used to produce synthesis gas (syngas), a mixture that includes carbon monoxide and hydrogen, by reacting with steam on a nickel catalyst in a 2 dm^3 vessel. Syngas is then used to produce liquid hydrocarbons and methanol.

$$CH_4\,(g) + H_2O\,(g) \rightleftharpoons CO\,(g) + 3H_2\,(g) \qquad \Delta H > 0$$

The equilibrium mixture was found to contain 1 mole of methane, 1 mole of steam, 1.5 moles of carbon monoxide and 4.5 moles of hydrogen gas.

(i) State Le Chatelier's Principle. [1]

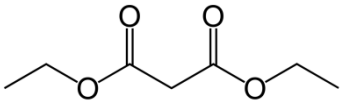
(ii) Write an expression for the equilibrium constant, K_c and determine its value, including units. [2]

(iii) Define the term *endothermic reaction*. [1]

(iv) With reference to the above equilibrium, predict and explain the effect of **separately** increasing pressure and decreasing temperature on the position of equilibrium, yield and K_c. [6]

[Total : 20]

2 Diethyl malonate, also known as DEM exist as a colourless liquid, commonly used in the manufacture of perfumes, artificial flavourings and vitamins. The structure of diethyl malonate is shown below.

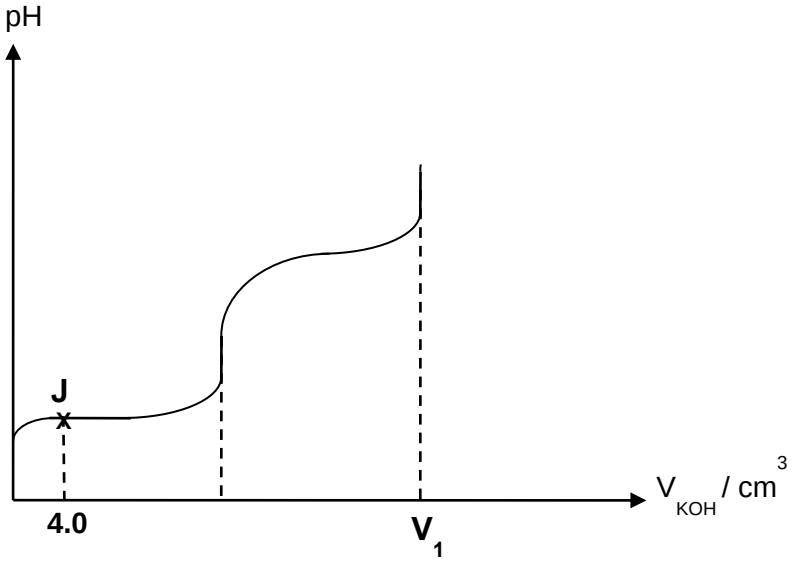


diethyl malonate

(a) **(i)** Diethyl malonate is synthesised from the esterification of malonic acid and an alcohol. Draw the structure of malonic acid and state the reagents and conditions required for this process. Write a balanced chemical equation for this synthesis. [3]

(ii) State the number of moles of H_2 gas produced per mole of malonic acid with Mg. [1]

(b) 7.0 grams of malonic acid was dissolved in 250 cm^3 of distilled water. The following titration curve was obtained when 25 cm^3 of this solution was titrated against 0.40 mol dm^{-3} potassium hydroxide.



The dissociation of malonic acid (H_2A) can be regarded as follows.

$H_2A \rightleftharpoons HA^- + H^+$ $\quad K_{a1} = 1.479 \times 10^{-3}$

$HA^- \rightleftharpoons A^{2-} + H^+$ $\quad K_{a2} = 2.042 \times 10^{-6}$

(i) Suggest why K_{a2} is much smaller than K_{a1}. [1]

(ii) Write an expression for K_{a1} stating its units. [2]

(iii) Ignoring the effects of K_{a2}, hence, or otherwise, calculate the initial pH of the solution. [2]

(iv) Calculate the volume of KOH, $\mathbf{V_1}$, required to completely neutralise malonic acid in 25 cm^3 of solution. [1]

(v) Explain what it means to be a buffer solution. [1]

(vi) The pH of a buffer solution can be determined by the following equation.

$$pH = -\lg K_a + \lg \frac{[\text{conjugate base}]}{[\text{acid}]}$$

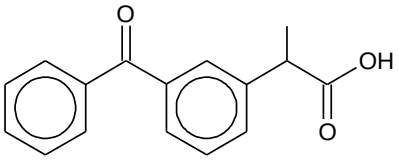
Identify the species present at point **J**. Calculate the amount of malonic acid remaining, and use the above equation to calculate the pH. [3]

(vii) The pH at the second end point is more than 7. Explain this observation with the aid of relevant equations. [2]

(c) Account for the relative acidities of ethanoic acid, ethanol and fluoroethanoic acid. [4]

[Total: 20]

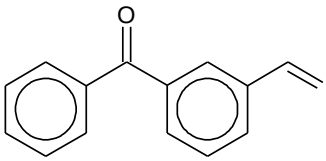
3 Ketoprofen, is one of the propionic acid class of nonsteroidal anti-inflammatory drugs (NSAID) with analgesic and antipyretic effects. It is generally prescribed for arthritis-related inflammatory pains or severe toothaches that result in the inflammation of the gums.



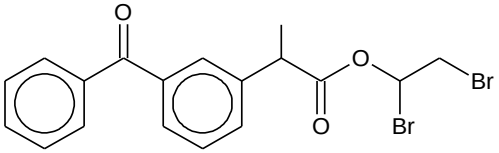
Ketoprofen

(a) Describe the bonding in benzene in terms of orbital overlap, illustrating your answer with a suitable diagram. [3]

(b) Propose a synthetic pathway for the formation of ketoprofen from the structure below. [3]



(c) Ketoprofen is reacted with an alcohol and forms an ester as shown.

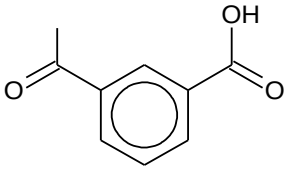


(i) Name the alcohol used in forming the ester. [1]

(ii) The alcohol was heated in the presence of aluminum oxide. Draw the structures of the two isomeric products formed and name them accordingly. [2]

(iii) Predict the relative boiling points of the products formed, giving reasons for your answer. [1]

(d) Compound **K**, a sweet smelling liquid, is an isomer of ketoprofen. Upon heating **K** with dilute sulfuric acid, compound **L** and benzoic acid are produced. Compound **L** is an alcohol which also produces a silver mirror with Tollens' reagent and a blue solution with Fehling's solution. It also reacts with hot acidified potassium dichromate(VI) to form compound **M** as shown below.



Compound **M**

Compound **L** reacts with hot acidified potassium manganate(VII) to form carbon dioxide and compound **N** which will subsequently react with liquid bromine and anhydrous aluminium bromide solid to form compound **O**.
Deduce, with reasoning, the structures for compounds **K**, **L**, **N** and **O.** [10]

[Total: 20]

END OF PAPER