TEMASEK JUNIOR COLLEGE

Preliminary Examinations
Higher 1

CANDIDATE NAME									
CIVICS GROUP			/						
CENTER NUMBER	S					INDEX NUMBER			

CHEMISTRY 8872/02

Paper 2 **29 August 2014**

Candidates answer Section A on the Question Paper. **2 hours**

Additional Materials: Answer Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Civics Group number and candidate name 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.

Section A
Answer **all** questions.

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

At the end of the examination, Section A and Section B will be handed in separately.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use		
Paper 1		/30
Paper 2	A1	/14
	A2	/8
	A3	/8
	A4	/10
	B	/20
	B	/20
Total		/110

For Examiner's use

Section A

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

1 This question is about Period 3 elements and compounds.

(a) The values below indicate the successive ionisation energies of a Period 3 element, **X**.

1000 2260 3390 4540 7000 8500 27110 31720

(i) Define first ionisation energy with the aid of an equation.

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(ii) Deduce the identity of **X**. Hence, write its electronic configuration.

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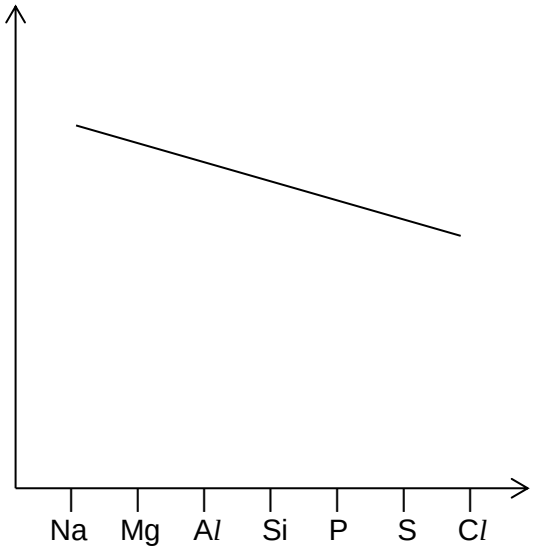
[5]

(b) Chlorine can react with oxygen to give Cl_2O_6 in the gaseous state. In the liquid or solid form, the compound ionises into ClO_2^+ and ClO_4^-. Draw the shape of the ions.

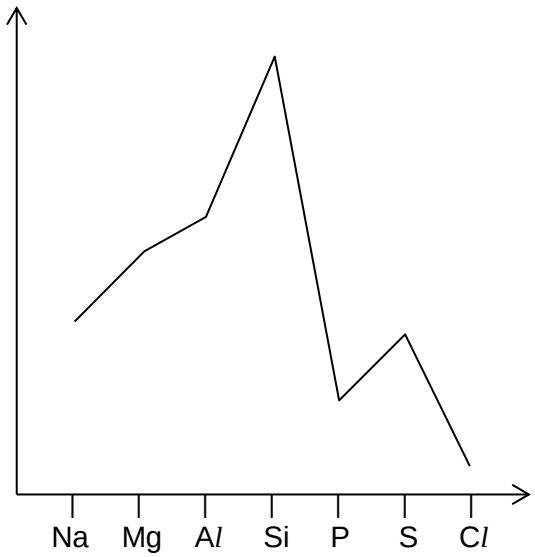
[2]

For Examiner's use

(c) Graphs **A** and **B** show the trends of two physical properties of Period 3 elements.



Graph A



Graph B

(i) Identify the physical properties represented by the two graphs.

Graph **A**: .....

Graph **B**: .....

(ii) In terms of structure and bonding, explain the trend shown by the last 4 elements in Graph **B**.

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[5]

[Turn over

For Examiner's use

(d) A solid mixture contains two oxides of Period 3 elements. To separate the oxides, water was added to the mixture, followed by filtration. Effervescence was observed when sodium carbonate was added to the filtrate. The residue does not react with dilute acid and dilute alkali.

(i) Identify the 2 oxides present in the mixture.

.....

(ii) Hence, write an equation for the reaction of one of the oxides with water.

.....

[2]

[Total: 14]

2 **(a)** Explain what is meant by the term *bond energy*.

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[1]

(b) Ethanoic acid burns as shown by the following equation:

$$C_2H_4O_2(l) + 2O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)$$

(i) Using bond energies given in the *Data Booklet*, calculate the enthalpy change for the combustion of ethanoic acid as shown in the equation above.

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(ii) Given that the experimentally determined value for enthalpy change of combustion of ethanoic acid is –209 kJ mol^{-1}, explain the discrepancy between this value and your answer in **(b)(i)**.

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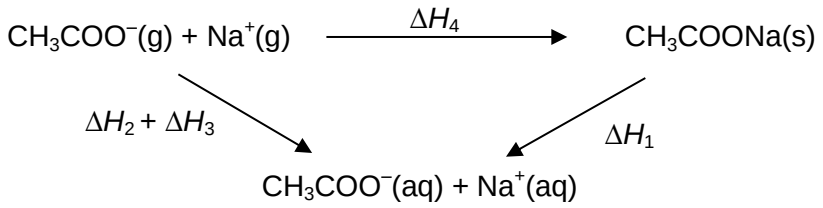
.....

[3]

(c) Sodium ethanoate is an inexpensive chemical that is widely used as a pickling agent. Pickling is a food preservation method that enhances flavor. Essentially, food to be pickled, such as a cucumber, is soaked in a solution of sodium ethanoate that imparts a salty and sour taste.

The enthalpy change for the solution of sodium ethanoate in water, ΔH_1 can be determined by using the energy cycle given below.



$\Delta H_2 = -375$ kJ mol^{-1}

$\Delta H_3 = -405$ kJ mol^{-1}

$\Delta H_4 = -763$ kJ mol^{-1}

(i) Name the enthalpy change that is represented by ΔH_4.

.....

(ii) With reference to the energy cycle and the data given above, calculate ΔH_1.

For Examiner's use

(iii) Would you expect the magnitude of the lattice energy of CH_3COOK to be larger or smaller compared to that of CH_3COONa? Explain your answer.

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.....

[4]

[Total: 8]

3 We usually think of iron occurring in compounds in the +2 or +3 oxidation states. However, other oxidation states of iron are possible; for example, potassium ferrate (VI), K_2FeO_4, contains iron in the +6 oxidation state. The FeO_4^{2-} ion is a stronger oxidizing agent than the MnO_4^- ion. In acidic conditions, FeO_4^{2-} ions are reduced to Fe^{3+} ions. Hence K_2FeO_4 can be used in analytical chemistry for redox titrations.

In one such titration, 25.0 cm^3 of 6.60 g dm^{-3} aqueous ethanedioic acid, $H_2C_2O_4$, is found to require 37.5 cm^3 of potassium ferrate (VI) solution for complete reaction.

Relevant half–equations for this reaction are given below.

$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$$

$$FeO_4^{2-} + 8H^+ + 3e^- \longrightarrow Fe^{3+} + 4H_2O$$

(a) Using oxidation numbers, explain why this reaction is described as a redox reaction.

.....

.....

[2]

(b) Use the two half–equations given above to construct a balanced ionic equation for the reaction between $C_2O_4^{2-}$ and FeO_4^{2-} ions, showing your working clearly.

For Examiner's use

[2]

(c) Hence calculate the concentration, in g dm^{-3}, of potassium ferrate (VI) used in the titration.

[A_r of Fe = 55.8]

[4]

[Total: 8]

For Examiner's use

4 Carboxylic acids may be decarboxylated to form alkanes by an electrochemical reaction known as the *Kolbe* electrolysis reaction.

When a mixture of the sodium salts of two different mono-carboxylic acids is electrolysed, a mixture of alkanes is produced.

$$R'CO_2^- + RCO_2^- \longrightarrow R\text{-}R + R\text{-}R' + R'\text{-}R' \quad (R = CH_3, C_2H_5 \text{ etc.})$$

Electrolysing a mixture of the sodium salts of the two mono-carboxylic acids **A** and **butanoic acid** produced three alkanes **hexane**, **B** and **C**, which could be separated by fractional distillation.

(a) 1.00 g sample of **B** was burned in an excess of oxygen. The gases that were produced were first passed through a U-tube containing phosphorus pentoxide (to absorb the water vapour) and then bubbled through concentrated NaOH (to absorb carbon dioxide). The phosphorus pentoxide U-tube increased in mass by 3.10 g, and the NaOH(aq) bottle increased in mass by 6.06 g.

(i) Write an equation for the reaction of carbon dioxide with concentrated NaOH.

.....

(ii) Use these data to calculate the H : C ratio in alkane **B**, and hence suggest its molecular formula.

(iii) Use your results in **(ii)** to deduce possible structures for the alkane **C** and the acid **A**.

[5]

For Examiner's use

(b) In another separate experiment, a new alkane **D**, C_6H_{14}, was produced. Alkane **D** undergoes free radical substitution to form compound **E,** 3-chloro-3-methylpentane.

(i) Compound **E** has 3 other positional isomers. Give the structural formulae of all 3 isomers.

(ii) Compound **E** undergoes elimination of HC*l* to form a mixture of isomeric alkenes.

Suggest the structural formulae of the isomeric alkenes formed. State the type of stereoisomerism (if any) shown.

Type of stereoisomerism: .....

[5]

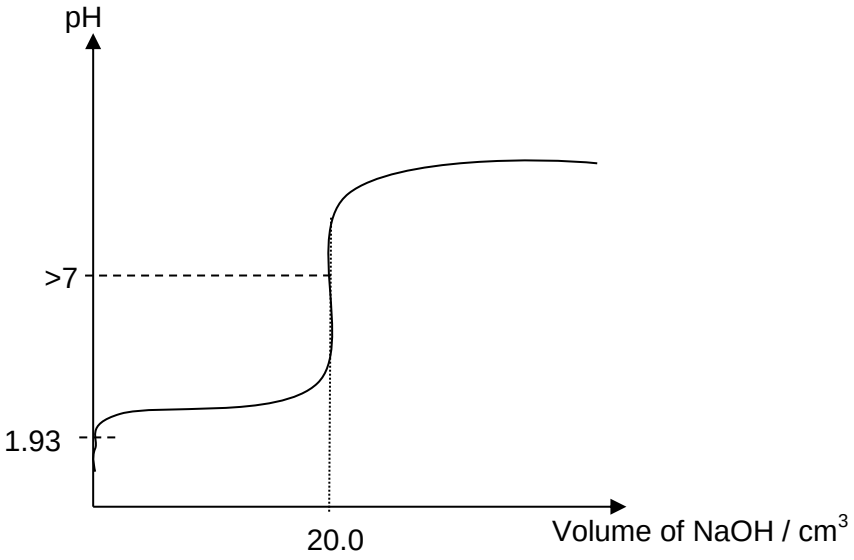
[Total: 10]

Section B

Answer **two** of the three questions in this section on separate paper.

5 Chloroethanoic acid, C*l*CH_2COOH is a chemical intermediate for production of various pharmaceuticals and insecticides.

(a) In an experiment, 20.0 cm^3 of 0.100 mol dm^{-3} of C*l*CH_2COOH is titrated with aqueous sodium hydroxide. The titration curve for the above titration was given below.



(i) Using the pH value of the chloroethanoic acid shown in the graph, calculate the concentration of the hydrogen ions in the solution of chloroethanoic acid.

(ii) Explain the difference between the concentration of $[H^+]$ calculated in **(i)** and the concentration of chloroethanoic acid.

(iii) The above titration experiment was done using screened methyl orange as an indicator. Deduce if screened methyl orange is a suitable indicator. If not, suggest an alternative suitable indicator for the above titration.

[4]

(b) A student titrated 20.0 cm^3 of 0.100 mol dm^{-3} of NaOH(aq) in the conical flask against 0.100 mol dm^{-3} of C*l*CH_2COOH in the burette. Deduce if an acidic buffer is formed when 10.0 cm^3 of C*l*CH_2COOH is added into the solution.

[1]

(c) A buffer solution was formed when 20.0 cm^3 of 0.100 $moldm^{-3}$ of C*l*CH_2COOH and 10 cm^3 of 0.100 $moldm^{-3}$ of C*l*CH_2COONa are mixed.

(i) Explain, using relevant equations, how the above buffer controls pH when a small amount of HC*l* (aq) or NaOH (aq) is added.

(ii) The pH of an acidic buffer solution can be calculated by the given equation,

$$pH = pK_a + lg \frac{[salt]}{[acid]}$$

where K_a is the acid dissociation constant of the organic acid.

Calculate the concentration of the salt and the acid in the acidic buffer solution formed and hence, calculate the pH of the buffer solution. [Given that K_a of C*l*CH_2COOH is 1.40 x 10^{-3} mol dm^{-3}.]

[5]

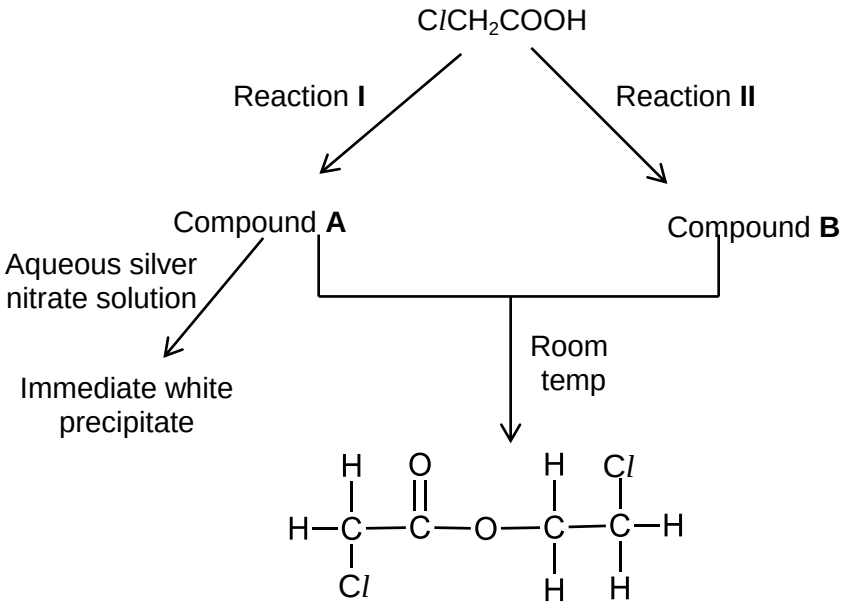
(d) The K_a values of three carboxylic acids are listed in the table below:

Acid	**K_a/ mol dm^{-3}**
CH_3COOH	1.8 x 10^{-5}
C*l*CH_2COOH	1.4 x 10^{-3}
Cl_2CHCOOH	5.5 x 10^{-2}

Describe and explain the acid strength illustrated by these values.

[3]

(e) 2-chloroethyl 2-chloroethanoate can be synthesised through the synthetic route shown below, starting with only chloroethanoic acid.



2-chloroethyl 2-chloroethanoate

(i) State the reagents and conditions for reaction **I** and **II**.

(ii) Draw the structural formula for Compound **A** and **B**.

(iii) Describe a simple chemical test that you could use to distinguish between chloroethanoic acid and compound **B**. You are to include reagents and conditions, observations and balanced equation(s) in your answer.

[7]

[Total: 20]

6 **(a)** The chlorides $MgCl_2$, $AlCl_3$ and $SiCl_4$ differ considerably in their structures and chemical properties. The chlorides become more acidic across the period.

Illustrate this statement by describing the reactions, if any, of the chlorides with water, suggesting the pH of the resulting solutions and writing equations where appropriate.

[6]

(b) Solid aluminium chloride sublimes at 180°C. In the vapour phase, an equilibrium is established between aluminium chloride and its dimer.

$$2\ AlCl_3\ (g) \rightleftharpoons Al_2Cl_6\ (g)$$

(i) Write an expression for the equilibrium constant, K_c, for this reaction and state its units.

Given that the value of K_c for the reaction is 4.0, calculate the equilibrium amount of Al_2Cl_6 when 0.4 moles of $AlCl_3$ is allowed to reach equilibrium in a 1 dm^3 vessel at high temperatures.

(ii) Describe and explain how will the composition of the equilibrium mixture be affected by

I increasing the pressure,

II increasing the temperature of the system.

[7]

(c) 2-hydroxybutanoic acid can be produced from propan-1-ol according to the reaction scheme given below:

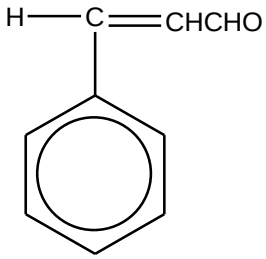
$$CH_3CH_2CH_2OH \xrightarrow{\textbf{I}} \textbf{X} \xrightarrow{\textbf{II}} \textbf{Y} \xrightarrow[\text{heat}]{HCl\ (aq)} CH_3CH_2CH(OH)COOH$$

(i) Identify compounds **X** and **Y**.

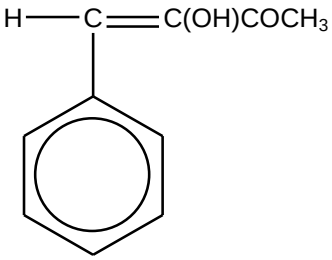
(ii) State the reagents and conditions for steps **I** and **II**.

[4]

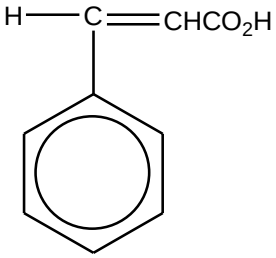
(d) For each of the compounds **A** to **C**, state the reagents and conditions for a positive test which would distinguish it from the other two and describe the observations that would be seen.



A



B



C

[3]

[Total: 20]

7 **(a)** Halogens react with hydrogen to form hydrogen halides. The reaction below has an activation energy of +173.2 kJ mol^{-1}.

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g); \Delta H = -9.6$ kJ mol^{-1}

The reaction is first *order* with respect to each of the reactant concentrations.

(i) What do you understand by the term *order of reaction*?

(ii) Calculate the activation energy of the reverse reaction.

(iii) State and explain how the rate constants k_f and k_b for the forward and reverse reactions and the equilibrium constant K_c for the reaction in **(a)** would change, if at all,

- with an increase in temperature,
- in the presence of a catalyst.

[6]

(b) Halogens also react with alkanes to form halogenoalkanes. However, synthesis of halogenoalkanes from alkanes is seldom employed as a synthetic route as there could be several isomeric products being formed in the reaction.

(i) 2-methylpropane reacts with bromine gas under ultraviolet light to form a mixture of two isomeric products, 1-bromo-2-methylpropane and 2-bromo-2-methylpropane.

The relative rates of abstraction of H atoms are given in the table below:

Type of H atoms	Relative rate of abstraction
Primary	1
Secondary	4
Tertiary	6

Predict and explain the ratio of the two isomeric products, taking into account the relative rates of abstraction.

(ii) Describe suitable chemical test(s) to distinguish the two isomeric molecules, 1-bromo-2-methylpropane and 2-bromo-2-methylpropane.

[4]

(c) An aromatic organic compound **A**, C_9H_{10}, decolourises bromine water and undergoes strong oxidation to give compound **B**, $C_8H_6O_4$. **B** forms intramolecular hydrogen bond.

A reacts with chlorine in the presence of sunlight to give compound **C**, C_9H_9Cl.

When **C** is heated under reflux with an ethanolic KCN followed by acid hydrolysis, compound **D** is formed. **D** liberates carbon dioxide with sodium carbonate.

Heating **D** under high pressure with a mixture of steam and phosphoric acid gives compound **E**. The resulting organic compound **E** gives a yellow solid with alkaline iodine solution.

Heating **E** under reflux with concentrated sulfuric acid gives a sweet smelling compound **F**, $C_{10}H_{10}O_2$.

Use all the above information to identify the organic compound **A**, **B**, **C**, **D**, **E** and **F** and draw a structural formula for each of them. Clearly show all of the deductions that you make from the information that you have been given: full marks cannot be gained by only giving the structures required.

[10]

[Total: 20]