Name:

Class: 13S\_\_\_\_\_

Reg Number: \_\_\_\_\_



MERIDIAN JUNIOR COLLEGE Preliminary Examination Higher 2

# Chemistry

## 9647/02

2 hours

**Paper 2 Structured Questions** 

19 September 2014

Additional Materials: Data Booklet

### INSTRUCTIONS TO CANDIDATES

Write your name, class and register number in the spaces provided at the top of this page.

Write your calculator brand and model/number in the box provided above.

Answer **all** questions in the spaces provided on the question paper.

All working must be shown clearly.

### **INFORMATION FOR CANDIDATES**

The number of marks is given in brackets [ ] at the end of each question or part question.

You are reminded of the need for good English and clear presentation in your answers.

Examiner's Use		
Paper 1	MCQ	/ 40
Paper 2	Q1	/ 12
	Q2	/ 12
	Q3	/ 11
	Q4	/ 13
	Q5	/ 14
	Q6	/ 10
Paper 3		/ 80
Total		/ 192
Percentage		
Grade		

This document consists of 20 printed pages.

#### 1 Planning (P)

The enthalpy change of neutralisation is the enthalpy change when one mole of water is formed in the reaction between an acid and a base.

 $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$ 

You are required to determine the enthalpy change of neutralisation between a strong base and a carboxylic acid through a series of experiments.

You may assume you are provided with the following:

- FA 1, aqueous sodium hydroxide, NaOH
- FA 2, 1.50 mol dm<sup>-3</sup> propanoic acid, CH<sub>3</sub>CH<sub>2</sub>COOH
- polystyrene (styrofoam) cups
- apparatus normally found in a school laboratory.

In separate experiments, different volumes of **FA 1** and **FA 2** are mixed while keeping the total volume of the reaction mixture constant. In each experiment, the temperature rise,  $\Delta T$ , is to be determined. When a graph of  $\Delta T$  against volume of **FA 1** used is plotted, it is observed that the temperature rise will increase, and then decrease when different volumes of **FA 1** are used.

Data from the graph can then be used to determine:

- the concentration of sodium hydroxide, NaOH, in FA1.
- the enthalpy change of neutralisation between NaOH and CH<sub>3</sub>CH<sub>2</sub>COOH.

It is given that 4.18 J is required to raise the temperature of 1  $\mbox{cm}^3$  of any solution by 1  $^{\rm o}\mbox{C}.$ 

(a) The total volume of the reaction mixture between **FA 1** and **FA 2** is constant. Explain why the temperature rise increases as more **FA 1** is added to the mixture.

[1]

(b) It is predicted that the maximum temperature change for the neutralisation would occur when the volume of **FA 1** mixed is between 35 cm<sup>3</sup> and 40 cm<sup>3</sup>.

Write a detailed plan on how you could determine the temperature changes for the series of reactions between **FA 1** and **FA 2**. The volume of **FA 1** used should be between 30 cm<sup>3</sup> and 45 cm<sup>3</sup> while the total volume of any mixture should be kept constant at 70 cm<sup>3</sup>.

**Comment [M1]:** Shifted the sentence down to make the flow of the question better.

3 Your plan should contain the following: all essential experimental details appropriate volumes of solutions to be used a tabulation of the experimental data to be collected (on the next page) ..... [Turn over Tabulation:

(c) (i) The following plots were plotted on a grid after an experiment. Draw suitable graphs through the plotted points.



[Turn over

[6]



- (ii) By using the graph in (i), calculate:
  - the concentration of sodium hydroxide in FA 1.
  - the enthalpy change of neutralisation between NaOH and CH<sub>3</sub>CH<sub>2</sub>COOH.

[4]

(d) Describe one major source of error for the experiment and suggest an improvement which could significantly increase the accuracy of the experiment.

[1]

[Total: 12]

**2** Chlorine is a yellow-green gas that was first synthesised around 1630. Nearly all the chlorine in the Earth's crust occurs as chloride in various ionic compounds. It forms a variety of oxides such as chlorate(V),  $C/O_3^-$ , chlorate(III),  $C/O_2^-$ , and chlorine dioxide,  $C/O_2$ .

Electrode Reaction	E° / V
$C/O_3(aq) + H_2O(l) + 2e^- = C/O_2(aq) + 2OH(aq)$	+0.33
$C/O_3(aq) + 2H^+(aq) + e^- = C/O_2(g) + H_2O(l)$	+1.15

The table below shows the reduction potentials for some oxides of chlorine.

 $ClO_2(g) + 4H^+(aq) + 5e^-$ 

(a) Draw a labelled diagram to show how the redox potential  $E^{\bullet}(ClO_3^{-}/ClO_2)$  could be measured in the laboratory.

 $\implies$  C $\Gamma$ (aq) + 2H<sub>2</sub>O(l)



+1.50

(b) Use the *Data Booklet* and the above information to predict what might happen when solutions of the two reagents are mixed together. In each case, calculate the  $E_{cell}^{e}$  and write an overall equation for any reaction that occurs.

Comment [M2]: Follow A-level phrasing N2004 P3 Q2

(i) mixing  $ClO_3$  (aq) with excess  $H_2O_2(aq)$ 

(ii) mixing  $ClO_2$  (g) with  $Fe^{2+}$  (aq).

[4]

[Turn over

7

- (c) It was found that chlorine gas has a density of 3.04 kg m<sup>-3</sup> at a temperature of 15 °C and a pressure of 1 atm.
  - (i) Assuming ideal behavior, calculate the relative molecular mass of chlorine.

(ii) Comment on the theoretical relative molecular mass of chlorine and that obtained in (i). Suggest reason for any discrepancy observed.

- (iii) Under what conditions of temperature and pressure would the behavior of real gases be more ideal?
- (iv) On the axes below, sketch the expected graph of density/pressure,  $\frac{\rho}{P}$ , against temperature, T, for an ideal gas.



(d) Chlorine dioxide, ClO<sub>2</sub>, is a useful agent in water treatment. Very pure chlorine dioxide is produced by electrolysis of aqueous sodium chlorate(V), NaClO<sub>3</sub>.

Calculate the current needed to produce 1 tonne of  $C/O_2$  gas per day. (1 tonne = 1000 kg)

[2]

[Total: 12]

- **3** Copper and cobalt are common transition elements.
  - (a) By quoting appropriate data from the Data Booklet,
    - (i) explain the difference between the atomic radii of copper and cobalt.

(ii) suggest an element in Period 2 that requires approximately similar energy to produce its ion in the +2 oxidation state as that of copper.

[3]

[Turn over

9

(b) Various potassium salts are known, some of which include anions containing cobalt complexed with cyanide ions, CN<sup>-</sup>.

Salt **A** has an empirical formula of  $K_4CoC_4N_4$ . Salt **B** has a composition by mass of K, 35.3%; Co, 17.7%; C, 21.7%; N, 25.3%.

(i) Determine the empirical formula of Salt B.

(ii) Suggest, by means of a diagram, the shape for the cobalt-containing anion of each salt.

Anion of Salt <b>A</b>	Anion of Salt <b>B</b>
shape:	shape:

(iii) State the oxidation number of cobalt in each salt.

Salt A: S	Salt <b>B</b> :
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(iv) Write the electronic configuration for cobalt in Salt B.

[6]

(c) Some salts of copper(I) such as CuC*l* or CuCN are insoluble in water. Solutions of other copper(I) salts generally convert readily into copper metal and copper(II) ions when left to stand.

When a solution of copper(II) sulfate,  $CuSO_4$ , is added to an excess of potassium cyanide, KCN, the corresponding copper(I) compound is formed, together with cyanogen,  $C_2N_2$ .

- (i) State the type of reaction when a solution of copper(I) ions are left standing for a while.
- (ii) Suggest an equation for the reaction between copper(II) sulfate and excess potassium cyanide.

[2]

[Total: 11]

- 4 The general formula of nitrosyl halide is NOX, where X is F, Cl or Br.
  - (a) (i) Draw a dot-and-cross diagram for nitrosyl fluoride, NOF, and hence use the Valence Shell Electron Pair Repulsion, VSEPR, theory to predict the shape of nitrosyl fluoride.

(ii) Arrange, in ascending order, the bond angle of NOF, NOC*l* and NOBr. Explain your answer.

[5]

- 13
- (b) Nitrosyl chloride undergoes dissociation according to the following equation.

$$2NOCl(g) \implies 2NO(g) + Cl_2(g)$$

Different amount of the three gases, nitrosyl chloride, NOC*l*, nitrogen monoxide, NO, and chlorine,  $Cl_2$ , were introduced into a closed vessel at 230 °C. At 10 minutes, the concentration of the three gases were determined and provided in the table below.

Temperature / °C	[NOC <i>l</i> ] /	[NO] /	[Cl <sub>2</sub> ] /
	mol dm <sup>-3</sup>	mol dm <sup>-3</sup>	mol dm <sup>-3</sup>
230	$2.00 \times 10^{-3}$	1.10 × 10 <sup>−3</sup>	$9.00 \times 10^{-3}$

(i) Write the expression for the equilibrium constant,  $K_c$ , for this reaction.

(ii) Given that the value of  $K_c$  at 230 °C is  $4.50 \times 10^{-2}$ , explain quantitatively if the system has attained equilibrium at 10 minutes.

(iii) Hence, deduce which direction the reaction will proceed in order for the system to attain equilibrium.

(iv) Suggest a reason why nitrosyl fluoride has the least tendency to dissociate.

(c) The experiment was repeated at 465 °C and the initial concentrations of the three gases are given in the table below.

Temperature / °C	[NOC <i>l</i> ] /	[NO] /	[Cl <sub>2</sub> ] /
	mol dm <sup>-3</sup>	mol dm <sup>-3</sup>	mol dm <sup>-3</sup>
465	$4.00 \times 10^{-4}$	$7.60  imes 10^{-3}$	$1.98 \times 10^{-4}$

(i) At equilibrium, the [NOC*l*] was found to be  $3.68 \times 10^{-4}$  mol dm<sup>-3</sup>. Calculate the value of  $K_c$  at 465 °C.

(ii) Hence, explain whether the forward reaction is exothermic or endothermic.

[4]

[Total: 13]

- 5 This question is about  $C_7H_{16}$  and the organic products that could be obtained from it.
  - (a) Of all the isomers of C<sub>7</sub>H<sub>16</sub>, only C and D can react with chlorine in the presence of ultraviolet light, each giving a tertiary monosubstituted halogenoalkane which is optically active.

The reaction between **C** and chlorine produced 3-chloro-3-methylhexane,  $CH_3CH_2C(Cl)(CH_3)CH_2CH_2CH_3$ .

- (i) Write an equation for the termination step of the reaction involving C to produce 3-chloro-3-methylhexane, showing clearly the structural formulae of all reactants and products involved.
- (ii) When only one form of enantiomers of C is reacted with chlorine, it was found that the termination step to produce 3-chloro-3-methylhexane resulted in a mixture that could **not** rotate plane-polarised light.

Draw the structures of the isomers formed in this mixture.

(iii) Suggest the type of hybridisation of the carbon atom containing a lone electron produced during the reaction in (ii).

Draw the hybridised orbitals for this carbon atom.

(iv) Suggest the structural formula of the monosubstituted halogenoalkane formed by **D**.

[4]

- (b) 3-chloro-3-methylhexane, can undergo elimination to produce 3-methylhex-3-ene. Such an elimination reaction usually involves a strong base such as an ethoxide ion, CH<sub>3</sub>CH<sub>2</sub>O<sup>-</sup>.
  - (i) The following shows the incomplete mechanism for the elimination reaction.

Complete the mechanism by drawing any missing lone pair, curly arrows and charges.





(ii) If 1-chloro-3-methylhexane is used instead of 3-chloro-3-methylhexane in (i), the mechanism shown would take place in one step instead of two steps.

Suggest a reason for this observation.

(iii) In (i), besides the elimination product for 3-chloro-3-methylhexane, it is possible that other unintended organic side products may be formed through other types of reaction.

Suggest the identity of a possible organic side product.

[4]

- (c) Another isomer of C<sub>7</sub>H<sub>16</sub> is heptane. Heptane can reform to produce methylbenzene and hydrogen gas.
  - (i) Write a balanced equation for the reformation reaction to produce methylbenzene, showing clearly the structures of all reactants and products.
  - (ii) The methylbenzene formed in (i) is reacted with bromine as well as other appropriate reagents and conditions to produce 4-bromomethylbenzene.

Describe the mechanism for this reaction.

[4]

- (d) Some bromine used in part (c)(ii) was accidentally contaminated with an excess of hot potassium hydroxide. A student attempted two different methods to deduce the amount of bromine contaminated.
  - (i) In Experiment 1, the student poured an excess of aqueous silver nitrate into the contaminated solution in an attempt to precipitate silver bromide.

Briefly explain how silver(I) nitrate would not allow the student to deduce the amount bromine contaminated.

(ii) In Experiment 2, the student evaporated the contaminated solution to dryness. Then he reacted the resulting residual solid with concentrated sulfuric acid.

Briefly explain why this method would not be able to obtain the accurate amount of bromine contaminated.

[2]

[Total: 14] [Turn over 6 Acetals are compounds formed when aldehydes or ketones are reacted with an alcohol and an acid catalyst.

The reaction between ethanal and methanol was studied in the inert solvent dioxan.  $H^+$ 

$$CH_3CHO + 2CH_3OH \implies CH_3CH(OCH_3)_2 + H_2O$$
  
an acetal

(a) When the initial rate of this reaction was measured at various starting concentrations of the two reactants with H<sup>+</sup> concentration of 0.05 mol dm<sup>-3</sup>, the following results were obtained.

Experiment	[CH <sub>3</sub> CHO] / mol dm <sup>-3</sup>	$[CH_3OH]$ / mol dm <sup>-3</sup>	Relative rate
1	0.20	0.10	1.00
2	0.25	0.10	1.25
3	0.25	0.16	2.00

- (i) Determine the order of reaction with respect to the following reactants, explaining how you arrive at your answer.
  - CH<sub>3</sub>CHO
  - CH<sub>3</sub>OH
- (ii) Hence, write the rate equation for the reaction, including the units of the rate constant.
- (iii) When the  $H^+$  concentration used in Experiment 2 was increased to 0.10 mol dm<sup>-3</sup>, the relative rate had a value of 2.50.

State the value of the relative rate when the concentrations of CH<sub>3</sub>CHO, CH<sub>3</sub>OH and H<sup>+</sup> used are 0.20 mol dm<sup>-3</sup> each.

[4] [Turn over (b) The reactants  $CH_3CHO$  and  $CH_3OH$  can be synthesised from the same bromoalkane.

Draw the full structural formula of this bromoalkane, and provide a suitable synthesis route, of **not** more than four steps, to form  $CH_3CHO$ .

[4]

(c) The acetal group does not react with bases or reducing agents, which the carbonyl group is susceptible to. For instance, both NaBH<sub>4</sub> and LiA/H<sub>4</sub> do not react with the acetyl group.

Hence it is possible to use the formation of acetals from carbonyl compounds as a way to protect the carbonyl groups from these reagents. Subsequently one can restore the carbonyl functional group by acidic hydrolysis since the formation of acetals is a reversible reaction.

By using OH OH as the alcohol to form an acetal group in the inert solvent dioxan as a first step, suggest a suitable synthesis route for the following conversion.



End of Paper 2

[2]

[Total: 10]