		Calculator Model / N	
Name MERIDIAN J JC2 Prelimin Higher 2	Class: UNIOR COLLEGE ary Examination	Reg Number:	
CHEMISTRY		9647/02	
Paper 2 Structured Question	S	19 September 2011 2 hours	
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.

FOR EXAMINER'S USE			
Q1	/ 12		
Q2	/ 17		
Q3	/ 21		
Q4	/ 10		
Q5	/ 12		
Total	/ 72		

This document consists of **<u>20</u>** printed pages.

# 1 Planning (P)

You are provided with solutions FB 3, FB 4 and FB 5.

**FB 3** and **FB 4** are either 1.0 mol dm<sup>-3</sup> nitric acid **or** 2.0 mol dm<sup>-3</sup> ethanoic acid

whereas **FB 5** is  $1.0 \text{ mol dm}^{-3}$  sodium hydroxide.

You are to plan experiments that will enable you to identify the solution that matches each of **FB 3** and **FB 4**, hence, calculate  $\Delta H_{neutralisation}$  for the reaction between ethanoic acid and sodium hydroxide.

You are provided with the following apparatus:

 $-10 \,^{\circ}$ C to  $110 \,^{\circ}$ C thermometer, 100 cm<sup>3</sup> beaker, 50 cm<sup>3</sup> measuring cylinder

The measuring cylinder should be rinsed thoroughly before each use.

(a) (i) When determining the identity of the two acids listed above,

the independent variable is the nature or strength of acids

the dependent variable is temperature change

(ii) Plan an experiment to find which of the solutions is  $1.0 \text{ mol } \text{dm}^{-3}$  nitric acid and which is 2.0 mol  $\text{dm}^{-3}$  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 experiment(s) must use only the solutions and apparatus above.

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

Method

- 1. Measure 25 cm<sup>3</sup> of FB 5 using the 50 cm<sup>3</sup> measuring cylinder, and transfer it into the 100 cm<sup>3</sup> beaker.
- 2. Measure and record the initial temperature in the 100cm<sup>3</sup> beaker using a thermometer.
- 3. Measure 25 cm<sup>3</sup> of FB 3 using the 50 cm<sup>3</sup> measuring cylinder.
- 4. Carefully transfer the FB 3 into the 100 cm<sup>3</sup> beaker, stir, and record the highest temperature reached.
- 5. Repeat steps 1-4 by mixing FB 4 with FB 5.
- (b) Explain clearly how you could determine the identity of the acids using the difference in temperature rise in the experiment proposed in (a).

[2]

[4]

Ethanoic acid is a weak acid and nitric acid is a strong acid. The temperature rise will be lower when 2.0 mol dm<sup>-3</sup> ethanoic acid is used compared to 1.0 mol dm<sup>-3</sup> nitric acid for the same number of moles of water formed.

This is because some of the energy evolved from the neutralisation process is used to further dissociate the ethanoic acid completely.

(c) Show the mathematical expression for the enthalpy change of neutralization of sodium hydroxide, using the volume proposed in (a) with 25 cm<sup>3</sup> of ethanoic acid.

The temperature change measured in (a) should be represented by  $\Delta T$ .

[4.2 J of heat energy raised the temperature of 1 cm<sup>3</sup> of any solution by 1°C.] [2]

Energy evolved by neutralization reaction =  $mc\Delta T$ = 210 $\Delta T$  J

 $\Delta H_{neutralisation} = -210\Delta T / 0.025$  $= -8400\Delta T J mol^{-1}$ 

- (d) A student accidentally diluted both the ethanoic acid and nitric acid prior to conducting the experiment above.
  - (i) With an aid of a pH meter, a titrimetric method could still be used to differentiate the diluted ethanoic acid from the diluted nitric acid, even though their exact concentrations are not known.

Briefly describe the measurements to be taken, and how the measurements may lead to the identification of the two acids.

Precise details of how a titration is performed, along with the apparatus used are <u>not</u> required, though the identity of any indicator (if used) should be clearly stated.

Titrate the diluted acids separately with NaOH(aq) using phenolphthalein. Record the pH of the end-point (or pH when solution changes colour) using a pH meter. The pH of the end point of ethanoic acid and NaOH should be greater than 7 or  $\sim$  9, and the pH of the end-point of HNO<sub>3</sub> and NaOH is  $\sim$  7

(ii) Other than the fact that a titrimetric method is more effective in the determination of the identity of a weak or strong acid when the concentration is unknown, compare the general reliability of using a titrimetric and thermochemical method in the determination of the identity of a weak or strong acid.

[4]

Heat could be lost from the beaker easily resulting in inaccurate results in the thermochemical method. However, pH resulting from the presence of  $CH_3COO^-$  in the solution is always higher than 7 at end point. Hence titration method is a better method.

[Total: 12]

**2(a)** Alkenes are very useful compounds, which are used as fuel and in the manufacture of a wide variety of polymers.



(i) Name and outline the mechanism in Step I to form A.

#### Free radical substitution



(ii) Draw the structure of **B**.



(iii) When C<sub>10</sub>H<sub>18</sub>Br<sub>2</sub> reacts with hot NaOH in ethanol in Step II, the rate of reaction is found to be faster. Explain why.

C-Br bond is weaker as compared to C-C*l* hence it is more susceptible to nucleophilic substitution. Therefore the rate of reaction is faster.

(iv) When **B** reacts with hot NaOH in ethanol in Step II, another sideproduct, **C** (M<sub>r</sub> = 228.0), is formed.

Suggest the structure of **C**.

OCH<sub>2</sub>CH<sub>3</sub> OCH<sub>2</sub>CH<sub>3</sub>

[7]

(b) The flow scheme below involves the reaction of **D**.



(i) Draw the structures for **E**, **F** and **G** in the boxes provided below.



(ii) State the reagents and conditions for **Step 1** and **2** in the spaces provided.

	Reagents	Conditions
Step 1	concentrated H <sub>2</sub> SO <sub>4</sub>	170°C
Step 2	KMnO <sub>4</sub> , dilute H <sub>2</sub> SO <sub>4</sub>	Heat

(iii) **G** contains a chiral carbon but the eventual reaction mixture was found to be optically inactive. Suggest a reason for this observation.

8

F undergoes  $S_N1$  mechanism to form G. Hence, there is an equal probability of the nucleophile,  $CH_3NH_2$ , attacking from either plane of the carbocation intermediate, which is trigonal planar in shape. This will lead to the formation of a racemic mixture. Hence, G is optically inactive.

(iv) State the type of hybridisation with respect to the carbon atom indicated below by the asterix \* in compound **D**.

 $CH_2 = *CHCH_2CH_2CH_2OH$ 

Sketch the shape of the hybrid orbitals of this carbon and indicate its bond angle.



(v) It was found that when **D** is reacted with bromine, **H**, ( $C_5H_9BrO$ ) was formed.

Suggest the structural formula of **H**.

[10]



[Total: 17]

**3** Old mine workings are often the cause of the pollution of mountain streams. One of the main chemical culprits of such pollution is iron pyrites, FeS<sub>2</sub>, in which iron has an oxidation state of +2.

The early miners unwittingly accelerated the chemical processes by grinding up unwanted rock containing some ore and dumping it in waste heaps.

(a) Oxygen in the air and rain water combined to oxidise the sulfide ions in solid iron pyrites to form an acidic solution of iron(II) sulfates.

Write a balanced ionic equation for this reaction.

[1]

 $2\text{FeS}_2(s) + 7\text{O}_2(g) + 2\text{H}_2\text{O}(I) \rightarrow 2\text{Fe}^{2+}(aq) + 4\text{SO}_4^{2-}(aq) + 4\text{H}^+(aq)$ 

- (b) The resulting ions then run off into the local streams where the iron(II) ions are oxidised.
  - (i) By considering the appropriate E<sup>e</sup> values in the *Data Booklet*, explain why the water in the streams must be acidic for oxygen to oxidise the iron(II) ions.

E<sup>e</sup>/v

From the Data Booklet

O <sub>2</sub> + 2H <sub>2</sub> O + 4e 🛁	4OH <sup>-</sup>	+0.40
Fe <sup>3+</sup> + e 🔫	Fe <sup>2+</sup>	+0.77
O <sub>2</sub> + 4H <sup>+</sup> + 4e 🛁	$2H_2O$	+1.23

If solution is acidic,

$$\begin{split} E^{\Theta}_{cell} &= E^{\Theta}_{red} - E^{\Theta}_{oxd} \\ &= 1.23 - 0.77 \\ &= +0.46V \\ \text{Since } E^{\Theta}_{cell} > 0, \text{ reaction is feasible.} \end{split}$$

If solution is not acidic,

$$\begin{split} E^{e}_{cell} &= E^{e}_{red} - E^{e}_{oxd} \\ &= 0.40 - 0.77 \\ &= -0.37 \ V \\ Since \ E^{e}_{cell} < 0, \ reaction \ is \ not \ feasible. \end{split}$$

(ii) Hence, write an equation for the oxidation of iron(II) ions in the stream water under acidic conditions.

 $4Fe^{2+}(aq) + O_2(g) + 4H^+(aq) \rightarrow 4Fe^{3+}(aq) + 2H_2O(I)$ 

- (c) Aqueous iron(III) ions are present in the stream as *complex ions*.
  - (i) What is meant by the term 'complex ion'?

A complex ion is one which contains a central metal atom or ion closely surrounded by ions or molecules called ligands through dative bonds.

(ii) Draw a diagram to show the shape of the aqueous iron(III) complex ions.



- (d) The iron(III) ions are hydrolysed in the stream to form a precipitate which is basic in nature. The precipitate is referred to as '*yellow boy*' by the miners.
  - (i) Suggest the formula of the precipitate which gives rise to the yellow colour of 'yellow boy'.

Fe(OH)<sub>3</sub>

(ii) Write an equation to show the hydrolysis of aqueous iron(III) ions in water to form the '*yellow boy*', given that the final solution is acidic in nature.

[2]

[4]

[2]

 $[Fe(H_2O)_6]^{3+}(aq) = Fe(OH)_3(s) + 3H_2O(I) + 3H^+(aq)$ 

- (e) As a result of the increased acidity of the stream water, other d-block metal ions are leached into the water. Zinc(II) ions are often found in the water but are not noticed because they are colourless.
  - (i) Suggest a reason why zinc(II) ions are colourless.

Zn(II) ions has fully filled 3d subshell/orbitals. Hence, d-d transition could not occur.

(ii) Explain why iron compounds are usually coloured.

[4]

- In a compound, the iron ions have partially filled 3d orbitals.
- In the presence of ligands, the d orbitals in Fe ions are split into two groups with different energy levels. This effect is known as d orbital splitting.
- The d electron undergoes d-d transition and is promoted to the higher d orbital.
- During the transition, the d electron absorbs a certain wavelength of light from the visible region of the electromagnetic spectrum and emits the remaining wavelength which appears as the colour of the complex observed.
- (f) Very dilute solutions of iron(III) ions are almost colourless. Addition of potassium thiocyanate, KSCN, leads to a deep red coloured complex.
  - (i) What type of reaction has occurred?

### Ligand exchange

(ii) Suggest a technique (other than titration) you could use to determine the concentration of the complex formed.

Colorimetry

(g) When potassium cyanide is added to stream water, iron(III) ions form a orange red complex, [Fe(CN)<sub>6</sub>]<sup>3-</sup>.

In an experiment, the standard electrode potential of the  $[Fe(CN)_6]^{3-}$  |  $[Fe(CN)_6]^{4-}$  system is measured.

(i) By means of a fully labelled diagram, show how the standard electrode potential of the  $[Fe(CN)_6]^{3-}$  |  $[Fe(CN)_6]^{4-}$  system can be measured.



(ii) The presence of  $CN^{-}$  significantly decrease the oxidising ability of an acidic solution of Fe(III) ions. Illustrate this effect by selecting appropriate  $E^{\circ}$  values from the *Data Booklet*.

In water, the more positive  $E^{e}$  (Fe<sup>3+</sup>/Fe<sup>2+</sup>) = +0.77 V indicates that Fe<sup>3+</sup> is unstable with respect to Fe<sup>2+</sup> and should be spontaneously reduced to Fe<sup>2+</sup> (*e.g.* by water itself).

On the other hand, in the presence of  $CN^{-}$  ligands, the reduction potential decreases to  $E^{e}$  ([Fe(CN)<sub>6</sub>]<sup>3-</sup>|[Fe(CN)<sub>6</sub>]<sup>4-</sup> = +0.36V, means that  $CN^{-}$  ligand stabilises the Fe<sup>3+</sup> with respect to Fe<sup>2+</sup>.

Smaller  $E^-$  means that  $[Fe(CN)_6]^{3-}$  is less readily reduced compared to  $Fe^{3+}$ , rendering it less oxidising.

(iii) From the list of standard electrode potentials in the booklet, Identify a gas that would reduce  $[Fe(CN)_6]^{3-}$  to  $[Fe(CN)_6]^{4-}$ .

Explain your answer.

$$SO_{4}^{2^{-}} + 4H^{+} 2e \implies SO_{2} + 2H_{2}O \qquad E^{e} = +0.17V$$

$$[Fe(CN)_{6}]^{3^{-}} + e \implies [Fe(CN)_{6}]^{4^{-}} \qquad E^{e} = +0.36V$$

$$E^{e}_{cell} = E^{e}_{red} - E^{e}_{oxd}$$

$$= 0.36 - 0.17$$

$$= +0.19V$$

Since  $E^{\Theta}_{cell} > 0$ , reaction is feasible.

The gas is SO<sub>2</sub>.

[Total : 21]

4 Silver ions are used to make silver ethanoate (AgC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>). It is an important ingredient in the manufacture of chewing gum and lozenges to aid cessation of smoking as it produces a repulsive taste when combined with cigarette smoke.

The solubility product for silver ethanoate can be found by the following method.

Preparation of saturated silver ethanoate solution by precipitation from solutions of salts

- 1. Using a burette, transfer 40.00 cm<sup>3</sup> of 0.20 mol dm<sup>-3</sup> silver nitrate into a 100 cm<sup>3</sup> beaker.
- 2. Using another burette, transfer 40.00 cm<sup>3</sup> of 0.20 moldm<sup>-3</sup> sodium ethanoate into the beaker containing the silver nitrate.
- 3. Keep the contents well shaken.
- 4. Leave the mixture to stand for some hours at a temperature of 25°C.
- 5. Filter the mixture into a clean, dry 250 cm<sup>3</sup> beaker.

## Determination of [Ag<sup>+</sup>] by titration with standard KSCN solution

- 6. Pipette 20.0 cm<sup>3</sup> of the saturated solution into a 250 cm<sup>3</sup> conical flask.
- 7. Add 6 drops of nitric acid into the conical flask.
- 8. Add 6 drops of iron (III) solution to act as an indicator.
- 9. Keep the contents well shaken.
- 10. The mixture was then titrated against 0.10 moldm<sup>-3</sup> potassium thiocyanate.
- 11. The end-point being when the titration mixture turned red.

The volume of aqueous potassium thiocyanate required was 14.90 cm<sup>3</sup>.

(a) Explain why the mixture was initially kept at 25°C (Step 4).

[1]

[1]

[1]

The solubility product has a fixed value at a fixed temperature. Hence the temperature has to be kept constant at 25°C.

(b) Explain why there is a need to filter the mixture (Step 5).

This was done to remove  $AgC_2H_3O_2$  formed.

(c) State the purpose of adding dilute nitric acid to the solution (Step 7).

To prevent the formation of Fe(OH)<sub>3</sub>.

(d) The end point of the titration was obscured by the formation of a white precipitate (Step 11).

State the identity of the white precipitate and write an equation with state symbols for its formation.

[2]

AgSCN

 $Ag^{+}(aq) + SCN^{-}(aq) \longrightarrow AgSCN(s)$ 

(e) (i) Calculate the number of moles of KSCN required to react with  $Ag^+$ .

No of moles of KSCN required =  $\frac{14.90}{1000} \times 0.10 = 1.49 \times 10^{-3}$ 

(ii) Calculate the concentration of Ag<sup>+</sup> in the filtrate.

No of moles of Ag<sup>+</sup> required =  $\frac{14.90}{1000}$  x0.10 = 1.49x10<sup>-3</sup>

 $[Ag^+] \text{ in the filtrate} = \frac{1.49x10^{-3}}{\frac{20.0}{1000}} = 0.0745 \text{ mol dm}^{-3}$ 

(iii) Hence, calculate the solubility product of  $AgC_2H_3O_2$ .

 $[Ag^+]$  in the saturated solution of  $AgC_2H_3O_2$ 

 $= 0.0745 \text{ mol dm}^{-3}$ 

 $K_{sp} = [Ag^+][C_2H_3O_2] = (0.0745)^2 = 5.50 \times 10^{-3} \text{ mol}^2 \text{ dm}^{-6}$ 

(iv) When a precipitate is formed,  $\Delta G_{ppt}^{e}$  in J mol<sup>-1</sup> is given by the following expression:

$$\Delta G^{\Theta}_{ppt} = 2.303 RT lg K_{sp}$$

Given that the standard enthalpy change of formation of the precipitate of AgC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> is -17.5 kJ mol<sup>-1</sup>, and using your answer in (iii), calculate  $\Delta S^{e}_{ppt}$  for the formation of the AgC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>.

$$\Delta G_{ppt}^{\Theta} = 2.303 RT lg K_{sp}$$
$$= -1.29 \times 10^{4} J mol^{-1}$$
$$\Delta S_{ppt}^{\Theta} = \frac{\Delta H - \Delta G}{T}$$
$$= -15.4 J mol^{-1} K^{-1}$$

(v) Explain the significance of the sign of your answer in (iv).

[5] [Total: 10]

Since  $\Delta S_{ppt}^{\theta} < 0$ , it implies that entropy decrease when a precipitate is formed as there is a decrease in disorder.

5 An electride is a special type of ionic compound that can be formed from Group I metals (such as Na and Cs) and has 'trapped' electrons taking on the role of anions. It has the general formula [ML<sub>n</sub>]e, where M, L and e refer to the metal, ligand and electron respectively. For example,

Na + 6NH<sub>3</sub> 
$$\rightarrow$$
 [Na(NH<sub>3</sub>)<sub>6</sub>]e

A generalised energy cycle for the formation of electrides is shown below.



(a) (i) Define, with an aid of an equation, what is meant by the first ionisation energy of a metal **M**.

 $M(g) \rightarrow M^+(g) + e$ 

First ionisation of a metal M is the energy required to remove 1 mole of electrons from 1 mole of M gaseous atoms to form 1 mole of singly positively charged M<sup>+</sup> gaseous ions.

(ii) Step 1 is proposed to be the determining factor in whether the formation of the electride is possible.

Based on this, which of the group I metals of sodium or caesium is predicted to form electrides most readily? Explain your answer.

Caesium is predicted to form electrides the most readily. Cs has the lowest first IE in Group I. Its valence electron is furthest away from the nucleus hence the electrostatic forces of attraction between valence electron the nucleus is the weakest.

(ii) **J** is a hexadentate ligand, (CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N that can be used in the formation of an electride.

When the ligand  ${\bf J}$  binds to a  $Cs^{\scriptscriptstyle +}$  ion, the enthalpy change for the reaction is as follows:

$$Cs^{+}(g) + J(g) \rightarrow CsJ^{+}(g) \qquad \Delta H^{\theta}{}_{r} = -277 \text{ kJ mol}^{-1}$$

Using the additional data given in the table below, calculate a value for the enthalpy change of formation of the electride, [CsJ]e (s), defined as follows:

 $Cs(s) + J(g) \longrightarrow [CsJ]e(s)$ 

enthalpy change of atomisation of Cs	+77 kJ mol <sup>-1</sup>
first ionisation energy of Cs	+378 kJ mol <sup>-1</sup>
lattice energy of [CsJ]e	-292 kJ mol <sup>-1</sup>

[7]



#### By Hess' Law,

 $\Delta$  H<sub>f</sub> of [CsJ]e (s) = -114 kJ mol<sup>-1</sup>

The structures of some electrides are studied and they are said to be remarkably similar to that of sodium and caesium chlorides. The diagram below shows the crystal lattice structures for both sodium chloride and caesium chloride.



crystal lattice of CsCl and NaCl

In the crystal lattice of sodium and potassium chloride, the co-ordination number of each ion is 6. However, in the crystal lattice of caesium chloride, CsC*l*, the co-ordination number has a different value.

(b) (i) From the diagrams, deduce the co-ordination number in CsC*l* lattice. Suggest an explanation for the co-ordination number in the CsC*l* lattice being different from those in NaC*l* and KC*l*.

The coordination number is 8.

 $Cs^+$  is a larger cation than Na<sup>+</sup> or K<sup>+</sup>. More  $Cl^-$  anions can surround the larger  $Cs^+$  cation, thus the coordination number in CsCl (ie. 8) is different than in NaCl and KCl.

(ii) It is proposed that  $[Na(NH_3)_6]e$  has the same crystal lattice structure as NaCl. In the diagram below, label the particles present in the structure.



(iii) Unlike Na which forms [Na(NH<sub>3</sub>)<sub>6</sub>]*e*, lithium forms the electride [Li(NH<sub>3</sub>)<sub>4</sub>]*e* instead.

Suggest a reason why this is so.

Unlike Na, lithium is a period 2 element and has no energetically accessible vacant 3d orbitals to accommodate more than eight electrons, hence can only accommodate a maximum of 8 electrons.

(iv) Suggest whether an electride can conduct electricity in the solid state. Explain your reasoning fully.

[5]

# [Total: 12]

There are no free mobile ions and the 'trapped' electrons are localised/ not delocalised' in the structure of electrides. Hence they are unable to conduct electricity.

## END OF PAPER