NATIONAL JUNIOR COLLEGE
PRELIMINARY EXAMINATIONS
Higher 2

CANDIDATE NAME			
SUBJECT CLASS		REGISTRATION NUMBER	

CHEMISTRY

9647/02

Paper 2 Structured

Fri 14 Sept 2012

Answer on the Question Paper.

2 hours

Additional Materials: Data Booklet

READ THE INSTRUCTIONS FIRST

Write your subject class, registration number and name on all the work you hand in.
Write in dark blue or black ink in the spaces provided.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use paper clips, highlighters, glue or correction fluid.

Answers **all** questions.

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

For Examiner's Use	
1	/12
2	/10
3	/18
4	/11
5	/6
6	/15
Total	/72

This document consists of **17** printed pages and **1** blank page.

For Examiner's Use

1 Planning (P)

The hydroxides of Group I metals (LiOH, NaOH, KOH, RbOH, CsOH) are highly corrosive white solids which rapidly absorb water vapour on exposure to the atmosphere.

All of these solids dissolve exothermically in water.
The enthalpy change of solution, ΔH_{soln}, is the energy change associated with the following reaction.

$$MOH(s) + (aq) \rightarrow M^{+}(aq) + OH^{-}(aq)$$

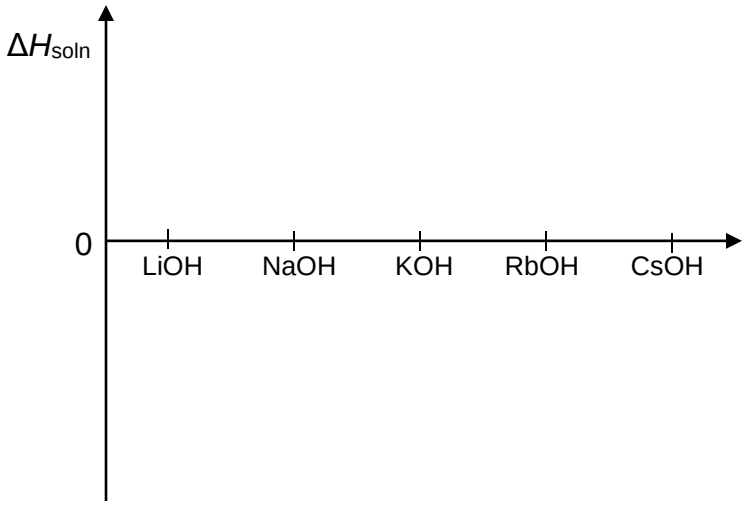
where *M* represents the Group I metal.

Both lattice energy and hydration enthalpy play an important part in determining the magnitude of ΔH_{soln}.

Lattice energy and hydration enthalpy are both more exothermic when ions carry higher charges and/or ions have smaller radii.

When comparing Group I hydroxides, changes in $\Delta H_{hydration}$ are more significant than changes in lattice energy.

(a) Sketch the likely trend in ΔH_{soln} from LiOH to CsOH and explain your answer.



Explanation:

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. ……..

[2]

[Turn over

For Examiner's Use

(b) Without considering heat loss, based on the information given, identify **one** *possible* source of error in the experiment to determine ΔH_{soln} of the hydroxides of Group I metals. State how you would minimise the effect of this source of error.

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[1]

(c) Identify a safety risk in the experiment and suggest how you would minimise it when carrying out the experiment.

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[1]

(d) Given the enthalpy change of solution of lithium hydroxide is approximately - 21 kJ mol^{-1}, describe the procedure you would carry out to find its enthalpy change of solution.

Your plan should give a step-by-step description of the method, including appropriate masses and volumes of reagents. You may use the apparatus normally found in a school or college laboratory.

The following data may be of use in planning the details of your experiment.

*A*r: Li, 6.9; O, 16.0; H, 1.0 4.3 J are required to raise the temperature of 1.0 cm^3 of any solution by 1°C.

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[4]

(e) A student was interested to investigate how the enthalpy change of neutralisation, $\Delta H_{neutralisation}$, varies when acids such as hydrochloric acid, HC*l* and ethanedioic acid, $(CO_2H)_2$ are neutralised with aqueous solutions of a Group I hydroxide such as RbOH.

The student proposed measuring the temperature change when each of the given acids reacts with 30.0 cm^3 of 2.0 mol dm^{-3} rubidium hydroxide.
Identify one aspect of the experimental procedure that must be kept the same to ensure comparable results.

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[1]

[Turn over

For Examiner's Use

(f) **(i)** In each experiment, 30.0 cm^3 of 2.0 mol dm^{-3} RbOH is to be used.
There is to be an excess of rubidium hydroxide, RbOH.

Suggest appropriate volumes and concentrations for each of the acids to be used in the individual experiments such that the experiments are equivalent.
Justify your answer with respect to ethanedioic acid with relevant working.
Complete the table below.

Acid	Volume / cm^3	Concentration / mol dm^{-3}
Hydrochloric acid HCl		
Ethanedioic acid $(CO_2H)_2$		

[2]

(ii) Show the mathematical expression for the enthalpy change of neutralisation of rubidium hydroxide with ethanedioic acid, using the volume and concentration from **(f) (i)** and ΔT to represent the temperature change.

[1]

[Total:12]

2 The Dissolved Oxygen Concentration (DOC) in rivers and lakes is important for aquatic life. If DOC falls below 5 mg dm^{-3}, most species of fish cannot survive.

For Examiner's Use

Environmental chemists can determine the DOC in water using the procedure below.

> A sample of water is shaken with aqueous Mn^{2+} and aqueous alkali. The dissolved oxygen oxidises the Mn^{2+} to Mn^{3+}, forming a pale brown precipitate of $Mn(OH)_3$.
>
> $O_2(aq) + Mn^{2+}(aq) + 8\ OH^-(aq) + 2\ H_2O(l) \rightarrow 4\ Mn(OH)_3(s)$
>
> The $Mn(OH)_3$ precipitate is then reacted with an excess of aqueous potassium iodide, which is oxidised to iodine, I_2.
>
> $2\ Mn(OH)_3(s) + 2I^- \rightarrow I_2(aq) + 2\ Mn(OH)_2(s) + 2\ OH^-(aq)$
>
> The iodine formed is then determined by titration using aqueous sodium thiosulfate, $Na_2S_2O_3$ (aq).

(a) A student decided to analyse the National Junior College's pond water using the above procedure. The student found that a 20.0 cm^3 sample of the pond water required 18.60 cm^3 of 0.00100 mol dm^{-3} of $Na_2S_2O_3$ (aq) for titration.

(i) Calculate the DOC of the sample of pond water, in mg dm^{-3}.

DOC = …… mg dm^{-3}

(ii) Comment on whether there is enough dissolved oxygen in the pond water for the carps to survive.

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[4]

For Examiner's Use

(b) Another d-block element, rhenium is similar in many ways to manganese. The standard electrode potential E^{θ} for the change between 2 oxidation states of rhenium is + 0.3V.

$$ReO_4^-(aq) + 4H^+(aq) + 3e \rightleftharpoons ReO_2(s) + 2H_2O(l)$$

$ReO_4^-(aq)$ is colourless while ReO_2 is a dark solid.

(i) Draw a fully labelled diagram for the apparatus that can be used to determine this standard electrode potential.

[3]

(ii) Using the *Data Booklet,* show that a reaction occurs when an aqueous solution containing sodium sulfite, Na_2SO_3 is added to aqueous ammonium perrhenate, NH_4ReO_4.
Describe the observation(s) and write a balanced equation for the reaction.

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[3]

[Total: 10]

For Examiner's Use

3 Copper, silver and gold share certain attributes: they have one s-orbital electron in addition to a filled d-shell. The filled d-shells in these elements do not contribute much to the interatomic interactions, which are dominated by the s-electrons through metallic bonds. Contrary to metals with incomplete d-shells, metallic bonds in copper are relatively weak. Thus pure copper is soft and malleable.

Alloys are made to alter the mechanical properties of copper, to induce hardness and ductility. Brass and bronze are typical substitutional alloys in which some of the copper atoms are substituted by zinc in the former, and by tin in the latter.

The table below gives the hardness of copper and these two alloys as measured on the Brinell Scale.

	copper	brass	bronze
Hardness	42	114	241

(a) Using relevant information from the *Data Booklet*, account for the difference in the hardness of copper, brass and bronze.

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[3]

(b) Although both copper and zinc are 3-d elements, zinc is not classified as a transition metal. Explain why zinc is not classified as a transition metal.

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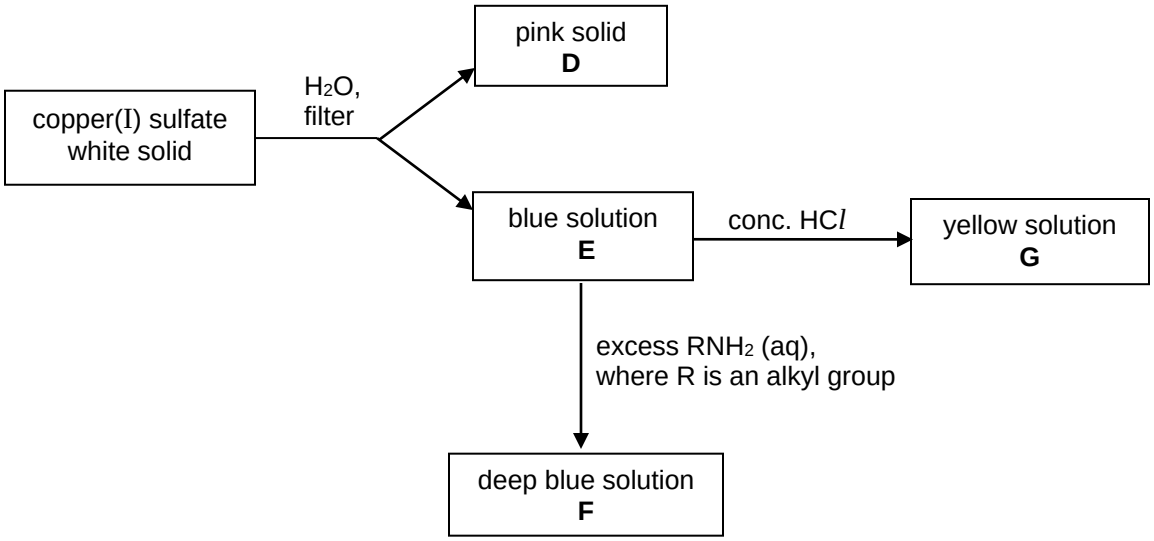
[1]

For Examiner's Use

(c) Copper forms compounds with variable oxidation states. Copper(I) compounds are unstable in water. The following flow scheme shows the reactions between different compounds of copper.



(i) State the type of reaction between copper(I) sulfate and water. Using relevant data from the *Data Booklet*, explain why this reaction occurs.

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(ii) Give the formulae of the complex ions in **F** and **G**.

F: ……

G: ……

(iii) When solution **G** was diluted with water, it changed from yellow to green and finally blue. Explain the colour changes.

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[7]

For Examiner's Use

(iv) Describe what you would observe when potassium iodide solution is added to solution **E**. Write an equation for the reaction that occurs.

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(v) Explain why solution **E** is blue.

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[5]

(d) Copper has remarkable resistance to corrosion. However, many well-known architectural structures built with copper, such as the Statue of Liberty in the United States and the Royal Observatory in Edinburgh, on centuries of exposure to the elements, appear green due to the formation of the basic carbonate, $Cu(OH)_2.CuCO_3$.

Explain the formation of the basic copper carbonate.

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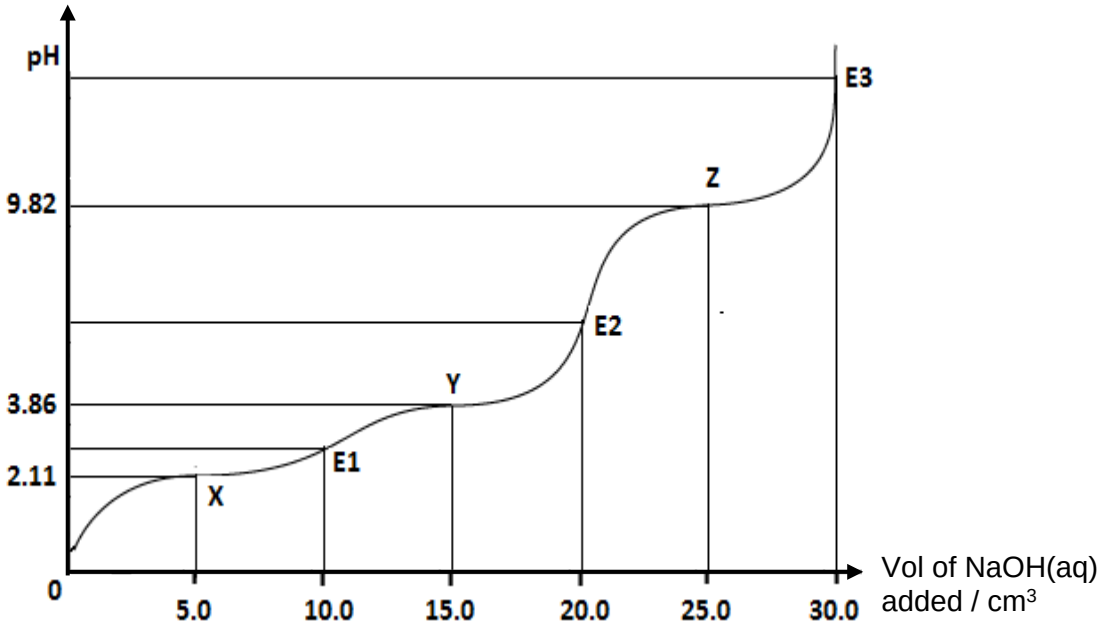
[2]

[Total:18]

For Examiner's Use

4 (a) Aspartic acid, $HO_2CCH_2CH(NH_2)CO_2H$, is one of the two acidic essential amino acids.

A 25.0 cm^3 solution of fully protonated aspartic acid, $HO_2CCH_2CH(NH_3^+)CO_2H$, is titrated with 0.500 mol dm^{-3} NaOH (aq). The titration curve is shown below. The label '**E1'**, **'E2'** and '**E3'** denotes equivalence point 1, 2 and 3 respectively.



(i) The species present at **E1** is $HO_2CCH_2CH(NH_3^+)CO_2^-$. Identify the species present at **E2** and **E3**.

(ii) The equation for the first acid dissociation constant, K_{a1}, of the fully protonated aspartic acid can be written as follows:

$$HO_2CCH_2CH(NH_3^+)CO_2H \rightleftharpoons HO_2CCH_2CH(NH_3^+)CO_2^- + H^+$$

Using the titration curve, determine K_{a1}.

K_{a1} = …… mol dm^{-3}

For Examiner's Use

(iii) Explain why the shape of the graph at **E3** differs from that at **E1**.

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(iv) At pH = 4.0, the mixture can act as a buffer. Identify the two species present in this buffer and calculate the ratio of the concentrations of these two species at this pH.

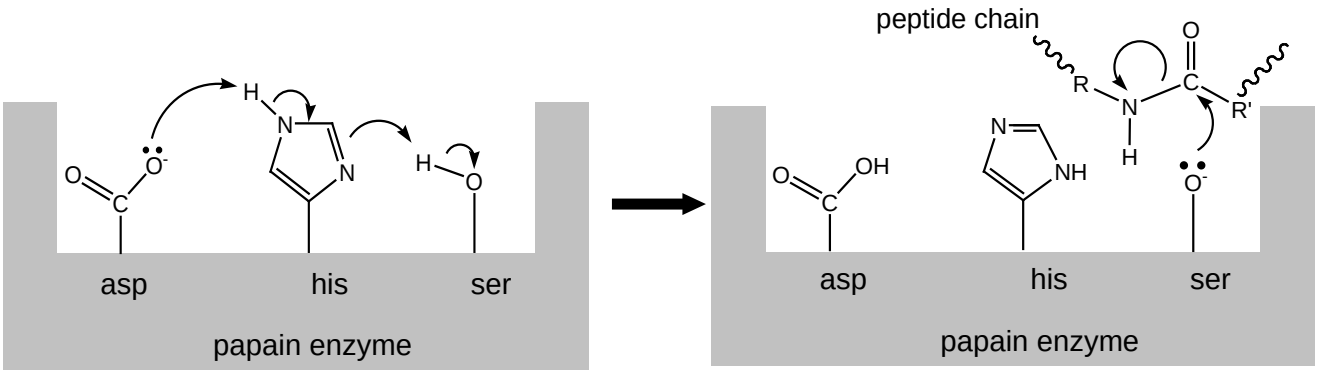
[8]

For Examiner's Use

(b) Papain, an enzyme in fresh papaya juice is used as a meat tenderiser. It is responsible for catalysing the hydrolysis of certain proteins in muscle tissues, causing the tough meats to soften during the cooking process.

Papain is a relatively heat resistant enzyme, with an optimal temperature range of 60-70 °C. The three main amino acids involved in the catalytic activity of papain are His48, Asp102 and Ser185.

The first stage in the mechanism of the action of papain is illustrated in the figure below.



(i) Name the region of the papain enzyme that is illustrated above.

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(ii) With reference to the figure above, explain why the action of this enzyme would be inhibited if the pH was too low.

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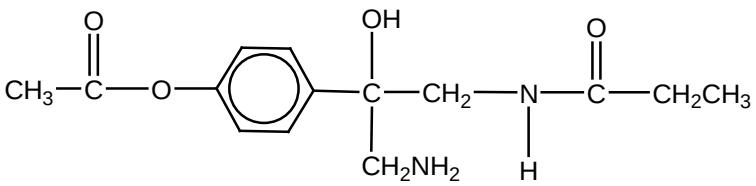
[3]

[Total:11]

5



Q

(i) Name the four functional groups in compound **Q**, other than the phenyl group.

1) ……

2) ……

3) ……

4) ……

(ii) Draw the structural formulae of the compound(s) when compound **Q** is treated with

- Cold HC*l*(aq)

- Hot NaOH (aq)

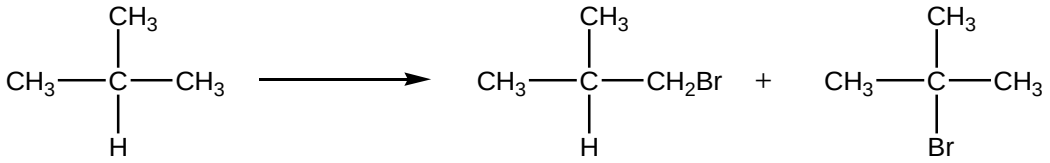
[6]

[Total:6]

For Examiner's Use

For Examiner's Use

6 (a) 2-methylpropane reacts with Br_2 to give a mixture in which the major products are two monobrominated alkanes.



63% 37%

(i) State the conditions required for this reaction.

……..

(ii) Outline the mechanism for the formation of 1-bromo-2-methylpropane from 2-methylpropane under the conditions stated in **(i)**.

(iii) Discuss two factors which are responsible for the observed percentages of the two monobrominated alkanes.

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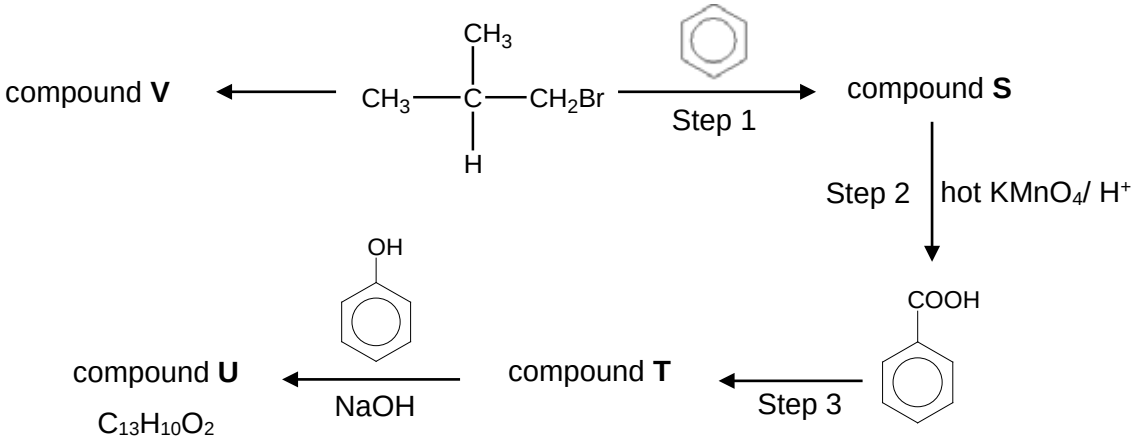
[6]

For Examiner's Use

(b) 1-bromo-2-methylpropane undergoes a series of reactions as shown by the given flow scheme.



(i) State the conditions needed for step 1.

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(ii) Explain as fully as you can why the conditions you stated in **(i)** are required.

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(iii) Draw the structures of compounds **S**, **T** and **U** in the boxes provided below.

S	**T**	**U**

(iii) When an alkaline solution of complexed $Cu^{2+}(aq)$ is added to compound **V**, a reddish-brown precipitate is observed.

Propose a 2-step synthesis for compound **V** from 1-bromo-2-methylpropane.

[9]

[Total:15]

–End of Paper –