NATIONAL JUNIOR COLLEGE

SH2 PRELIMINARY EXAMINATION

Higher 2

CANDIDATE NAME			
SUBJECT CLASS		REGISTRATION NUMBER	

CHEMISTRY

9647/02

Paper 2 Structured Questions

Friday 28 August 2015
2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your subject class, registration number and 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 paper clips, highlighters, glue or correction fluid/tape.

Answers **all** questions.
A Data Booklet is provided.

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

For Examiner's Use	
1	/12
2	/12
3	/ 7
4	/15
5	/ 8
6	/13
7	/ 5
Total	/72

This document consists of **20** printed pages

Answer **all** the questions

1 Planning (P)

The label on a bottle in your school chemistry laboratory is found to be missing and you are to help identify the organic compound in the bottle. The compound in the bottle is one of the following:

- ethanal
- propanamide
- 1-iodopentan-2-one
- benzaldehyde
- phenylamine

(a) Plan a series of simple chemical tests that would allow you to confirm the identity of the compound in the bottle through a positive test. You are reminded that most of the compounds listed are *flammable* liquids.
Your plan must include the following:

- the reagents and conditions to be used, but **not** the quantities of reagent used.
- observation(s) for each test.

[6]

(b) Assuming the unknown compound to be ethanal, it can react with 2,4-dinitrophenylhydrazine (2,4-DNPH) to form a crystalline solid derivative (melting point 165 °C).

(i) Draw the displayed formula of the derivative formed between ethanal and 2,4-DNPH.

[1]

(ii) Write a plan for the preparation of the 2,4-DNPH derivative of ethanal.

In your plan you should:

- give a full description of the procedure you would use to prepare and purify the derivative;
- explain how you would check the purity of your sample.

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....[4]

(c) Identify one potential safety hazard and state how you would minimise this risk.

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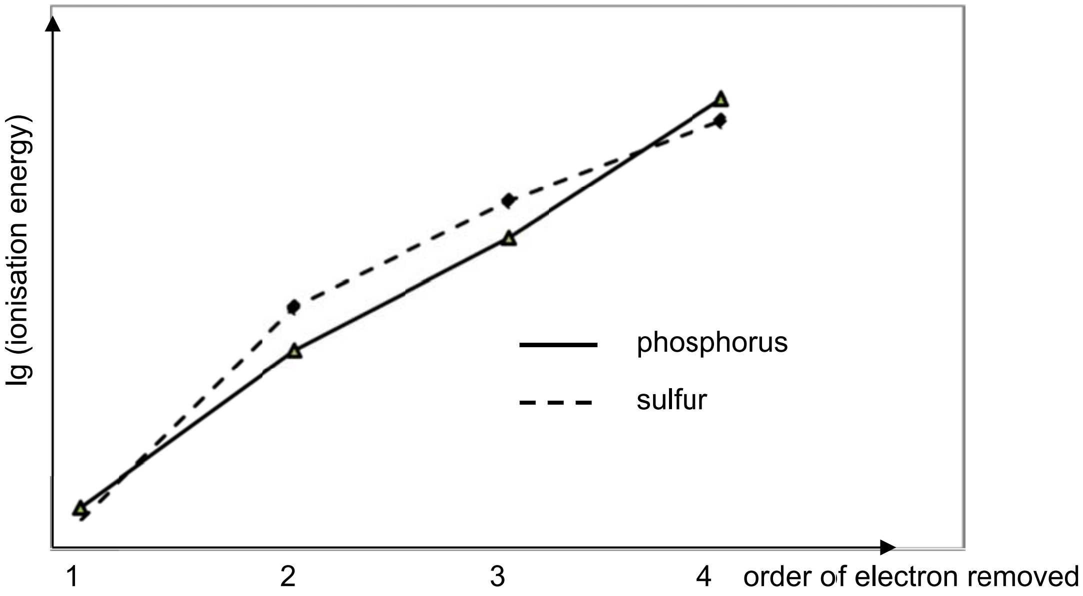
....[1]

[Total: 12]

2 **(a)** The diagram below shows the first four successive ionisation energies of sulfur and phosphorus.



(i) Write the full electronic configurations for sulfur and phosphorus.

P: ……………………………………………………………………

S: ……………………………………………………………………

[1]

(ii) Explain why the first and fourth ionisation energies of sulfur are *both lower* than the corresponding ionisation energies of phosphorus.

First ionisation energy

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

Fourth ionisation energy

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………[2]

(b) The van der Waals' equation as shown below is often used to account for the discrepancies between experimental and theoretical behaviour of real gases.

$$(p + \frac{n^2a}{V^2})(V - nb) = nRT$$

where p is the pressure, V is the volume, T is the temperature, n is the amount of substance (in mol), and R is the gas constant. The van der Waals' constants a and b are characteristic of the substance and are independent of temperature.

(i) Given that the van der Waals' constants a and b for SO_2 are 0.687 Pa m^6 mol^{-2} and 5.68×10^{-5} m^3 mol^{-1} respectively, calculate the pressure exerted by 1 mol of SO_2 in a 0.50 dm^3 container at 25 °C.

[1]

(ii) Calculate the pressure exerted by SO_2 as described in **(b)(i)** if it obeys the ideal gas law.

[1]

(iii) Suggest a reason for the discrepancy in the pressures obtained in **(b)(i)** and **(b)(ii)**.

....

....

....[1]

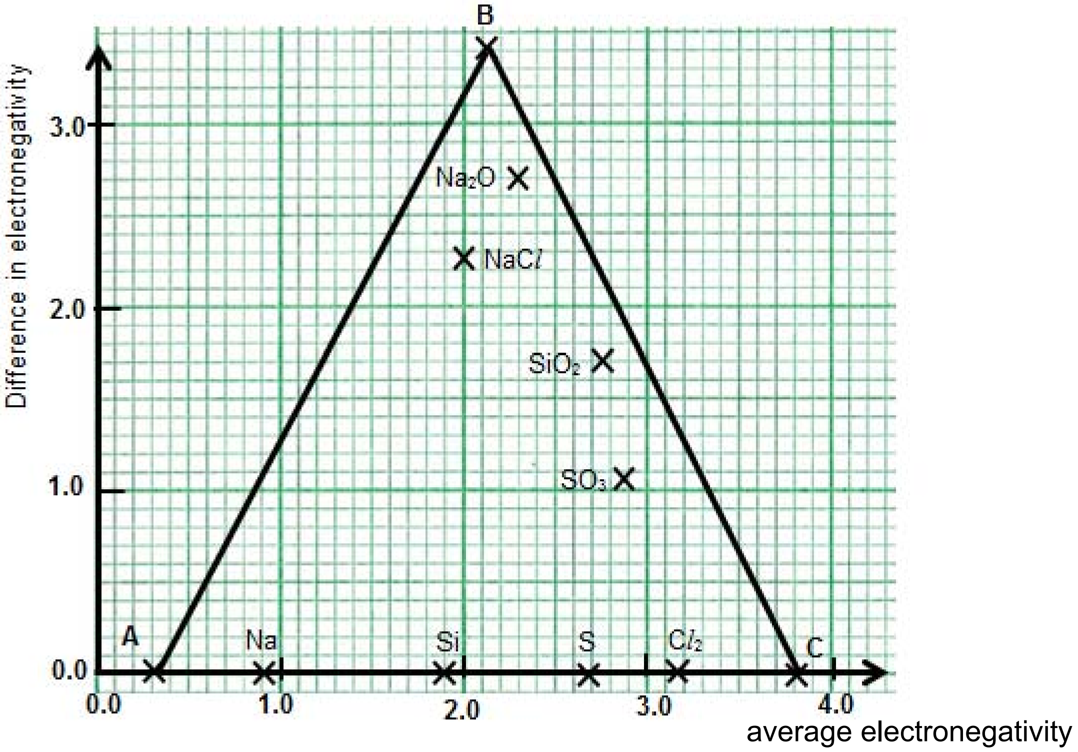
(c) The type of bonding (covalent, ionic or metallic) present in a substance can be determined and predicted using the van Arkel triangle based on the values of electronegativity of the element.

Difference in electronegativity between the element(s) is plotted along the *y–axis* and the average electronegativity of the element(s) is plotted along the *x–axis*.

The electronegativity data for oxygen and germanium, Ge, and some selected elements from Period 3 of the Periodic Table are given below.

element	electronegativity
Na	0.93
A*l*	1.61
Si	1.90
Ge	2.01
S	2.58
C*l*	3.16
O	3.61

In addition, some of the Period 3 elements and their compounds have been plotted on the van Arkel triangle given below.



(i) Using your knowledge of the Period 3 elements and their compounds plotted on page **6**, state *the type of bonding* present at each of these bonding extremes, labelled as **A**, **B** and **C**, on the triangle.

A: ……………………….

B: ……………………….

C: ……………………….

[2]

(ii) I On the van Arkel triangle of page **6**, **plot the point** corresponding to the oxide of germanium.

Use this point together with your knowledge of the properties of Period 3 elements and their compounds, decide whether the oxide of germanium is best described as an/a acidic, basic or amphoteric oxide.

Nature of germanium oxide: ……………………….

[2]

II Hence explain if the melting point of the oxide of germanium would be lower or higher than that of the oxide of silicon.

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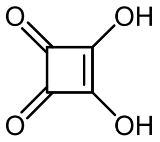
……………………………………………………………………………………….

……………………………………………………………………………………..[2]

[Total: 12]

3 Squaric acid is commonly used to make photosensitive dyes and inhibitors of protein tyrosine phosphatases. It has the following structure and is a *strong diprotic* acid.



squaric acid

The molecule is stable despite its high angle strain associated with a four-membered ring. At room conditions, it exists as a white crystalline powder and is very soluble in water.

(a) Explain why squaric acid is very soluble in water.

....

....

....

....[2]

(b) A 4.00 g of impure sample containing squaric acid was dissolved in 100 cm^3 of 0.250 mol dm^{-3} sodium hydroxide solution.

25.0 cm^3 of the resultant solution was titrated against 0.100 mol dm^{-3} hydrochloric acid and the excess alkali in the solution required 29.70 cm^3 of the acid for complete neutralisation.

(i) Write an equation for the reaction between squaric acid and sodium hydroxide.

[1]

(ii) Calculate the percentage purity by mass of squaric acid in the impure sample.

[3]

(c) After reacting with NaOH in part **(b)**, the structural analysis of the dianion of squaric acid revealed that it is completely symmetrical with identical C−C bond lengths.

With reference to your answers to **b(i)**, suggest why all the C−C bonds are identical in the dianion of squaric acid.

....

....

....[1]

[Total: 7]

4 Mercury(II) fulminate, $Hg(CNO)_2$, has been known as a super-sensitive explosive and its crystaline structure was determined in 2007. To avoid setting off an explosion, the solid compound has to be synthesised in the dark in a process that the researchers described as "quite tricky".

On detonation, mercury(II) fulminate decomposes to form mercury, nitrogen and carbon monoxide.

(a) **(i)** Write an equation, with state symbols, for the decomposition of $Hg(CNO)_2$.

....[1]

(ii) Calculate the standard enthalpy change of reaction for the decomposition of $Hg(CNO)_2$ using the following standard enthalpies of formation, $\Delta H_f^\ominus$.

compound	$Hg(CNO)_2$	CO
$\Delta H_f^\ominus$ / kJ mol^{-1}	+386	−111

[1]

(iii) By considering the entropy and enthalpy changes, determine whether the decomposition of $Hg(CNO)_2$ is energetically feasible.

....

....

....

....[2]

(b) HgO may also be produced from the decomposition of $Hg(CNO)_2$ under certain conditions.

(i) Using the following data and relevant data from the *Data Booklet*, construct a Born–Haber cycle to calculate a value for the lattice energy of HgO(s).

standard enthalpy change of atomisation of Hg	+64 kJ mol^{-1}
first ionisation energy of Hg	+1007 kJ mol^{-1}
second ionisation energy of Hg	+1810 kJ mol^{-1}
first electron affinity of O	−142 kJ mol^{-1}
second electron affinity of O	+844 kJ mol^{-1}
standard enthalpy change of formation of HgO(s)	−91 kJ mol^{-1}

[4]

(ii) Suggest, with a reason, how the magnitude of the lattice energy of HgO(s) might compare to that of HgF_2(s).

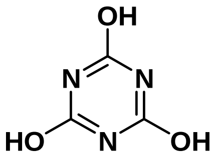
…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………[2]

(c) Mercury(II) cyanate is an isomer of mercury(II) fulminate. In fact cyanates and fulminates were the first known examples of isomers in chemistry. Cyanates can be converted to cyanuric acid, $(HNCO)_3$ under suitable conditions. There are two different structures for cyanuric acid which exist in equilibrium. One of the structures is given below.



cyanuric acid

(i) The hydroxyl group in the above structure of cyanuric acid is found to have phenolic character.
State the type of reaction involved and draw the structure of the organic product formed when it reacts with excess:

I NaOH(aq),

Type of reaction: ……………………………………………

Organic product:

II CH_3COCl.

Type of reaction: ....

Organic product:

[3]

(ii) **The use of the table of characteristic values for infra-red absorption in the *Data Booklet* is relevant to this question.**

Infra-red absorptions can be used to identity functional groups in organic compounds. For example, the given structure of cyanuric acid shows absorption at 3230−3550 cm^{-1} due to the O−H bond.

The analysis of the other structure of cyanuric acid shows absorptions at 1680−1750 cm^{-1} and 3350−3500 cm^{-1}.

Identify the bonds present in the other structure of cyanuric acid. Hence, draw the other structure.

infra-red absorption	bond
1680−1750 cm^{-1}	
3350−3500 cm^{-1}	

The other structure of cyanuric acid:

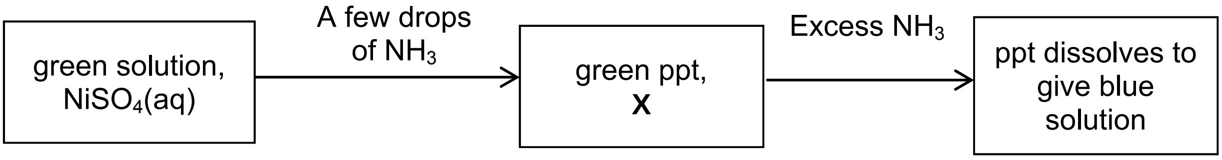
[2]

[Total: 15]

5 *Use of the Data Booklet is relevant to this question.*

Metal complexes involve ligands forming dative covalent bonds with central cations.

(a) When concentrated ammonia is added dropwise to a green solution of nickel(II) sulfate, the following observations are noted.



(i) Write an equation to account for the formation of **X** when a few drops of NH_3 are added to $NiSO_4(aq)$.

....[1]

(ii) Identify the nickel-containing species in the blue solution.

....[1]

(iii) When 2 cm^3 of the green solution of $NiSO_4$ is warmed with 1 g of solid NaC*l*, the solution turns yellow. Name the type of the reaction that has occurred.

....[1]

(b) The ligand in a complex affects the complex's redox properties and this is apparent from the relevant standard electrode potentials.

Suggest and explain the expected observations when $Na_2S_2O_3$ is separately added to:

(i) a solution of $CuSO_4(aq)$.

....

....

....

....

(ii) a solution mixture of $CuSO_4(aq)$ and concentrated NH_3.

....

....

....

....[3]

(c) Complex formation is used in estimating the concentrations of metal ions in solutions, for example the use of dimethylglyoxime (DMGH) in gravimetric analysis of nickel(II) salt.

A sample of a hydrated nickel(II) salt is analysed as described below.

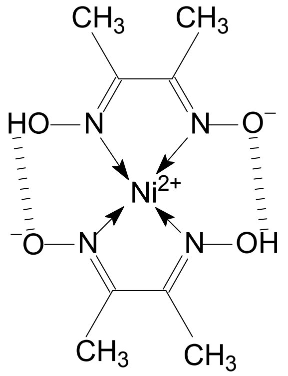
Step 1: The hydrated nickel(II) salt is dissolved in dilute acid.

Step 2: An excess of aqueous DMGH is added.

Step 3: An excess of aqueous ammonia is added and the mixture is heated, a red precipitate of $Ni(DMG)_2$ forms.

$$Ni^{2+}(aq) + 2\ DMGH(aq) + 2\ NH_3(aq) \rightarrow Ni(DMG)_2(s) + 2NH_4^+(aq)$$

The structure of $Ni(DMG)_2$ is shown below.



(i) State and explain the role of NH_3 in Step 3 mentioned above.

....[1]

(ii) State the coordination number of the nickel in $Ni(DMG)_2$.

Coordination number = ...[1]

[Total: 8]

6 Chemists and biochemists use pK_a values to compare the strengths of acids. The use of pK_a values is more convenient for comparing acid strengths than the K_a values.

pK_a values of several naturally occurring acids are shown in the table below.

name	structural formula	pK_a (at 25 °C)
benzoic acid	C_6H_5COOH	4.19
phenylethanoic acid	$C_6H_5CH_2COOH$	4.31
pyruvic acid	$CH_3COCOOH$	2.39
lactic acid	$CH_3CH(OH)COOH$	3.86

(a) Explain why benzoic acid has a lower pK_a value than phenylethanoic acid.

....

....

....

....[2]

(b) The 'magic tang' in many candies is obtained from acid buffers. A candy manufacturer carried out tasting tests with consumers and identified the acid taste that gave the 'magic tang' to a candy. The manufacturer was convinced that the 'magic tang' would give the company a competitive edge and the company's chemists were asked to identify the chemicals needed to generate the required taste. The chemists' findings would be a key factor in the success of the sales of the candies.

The team of chemists identified that a pH of 3.55 was required to give the 'magic tang'. They decided to use one of the acids from the table above and NaOH(s) to prepare this buffer.

(i) Identify the acid that is most suitable for preparing a buffer solution of pH 3.55 with the best buffering capacity.

....[1]

(ii) Calculate the relative concentrations of the acid and its salt needed to make this buffer.

[1]

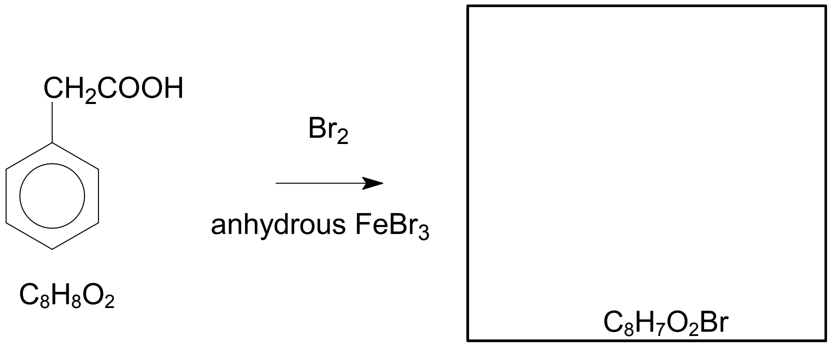
(iii) Hence, determine the mass of NaOH(s) to be added to a 500 cm^3 solution of 0.200 mol dm^{-3} of the chosen acid in **(b)(i)** to produce the buffer solution of pH 3.55.

[2]

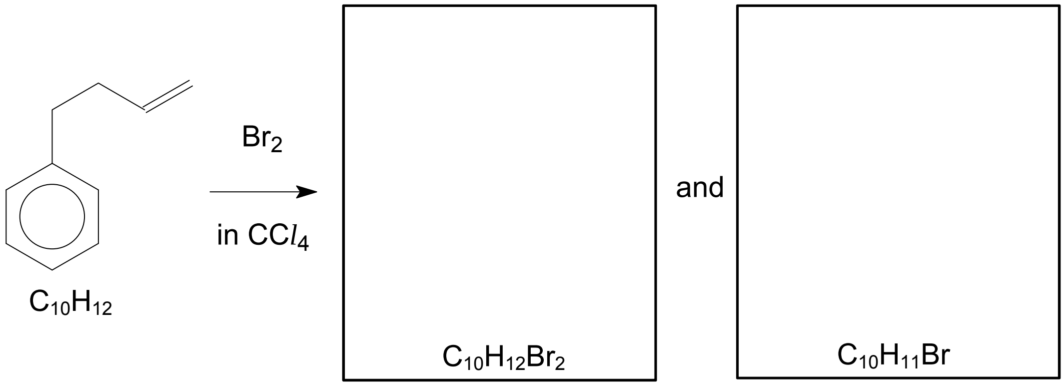
(c) Bromine can undergo electrophilic addition with alkenes and electrophilic substitution with arenes.

Give the structure of the bromine-containing organic products for the following reactions:

(i)

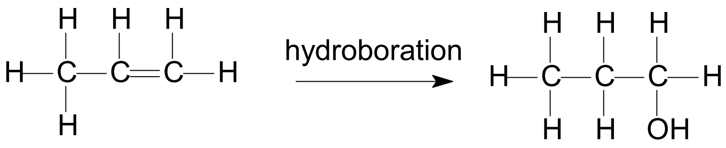


(ii)



[3]

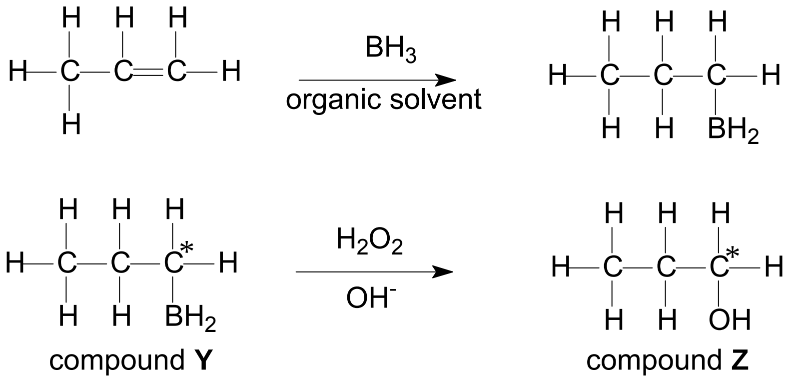
(d) Hydroboration can be used to convert an alkene to an alcohol as shown below



Hydroboration involves a two-step reaction as shown below:

Step 1:

Step 2:



The electronegativity data for some elements are given as follows.

element	B	C	H	O
electronegativity	2.0	2.5	2.1	3.61

With reference to the data above,

(i) identify the type of reaction and draw the structure of the intermediate for Step 1.

Type of reaction: ....

Intermediate:

[2]

(ii) state the oxidation number of the carbon atoms labelled *, and hence deduce the role of H_2O_2 in Step 2.

Oxidation number of C* in:

compound **Y**: .... compound **Z**: ....

Role of H_2O_2: ....[2]

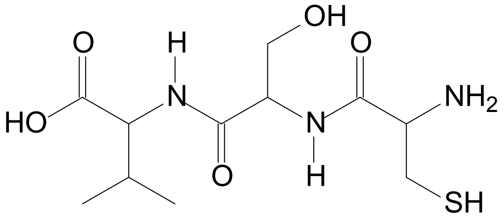
[Total: 13]

7 Amino acids are the basic building blocks of proteins. Proteins are important polymers found in living organisms.

Some common amino acids are listed in the table below.

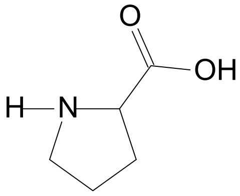
amino acid	formula of side chain (R in $RCH(NH_2)COOH$)
glutamic acid (glu)	$-CH_2CH_2COOH$
valine (val)	$-CH(CH_3)_2$
cysteine (cys)	$-CH_2SH$
phenylalanine (phe)	$-CH_2C_6H_5$
threonine (thr)	$-CH(OH)CH_3$
serine (ser)	$-CH_2OH$

(a) State the primary structure of the following tripeptide using the abbreviated names of the amino acids.



....[1]

(b) Proline acts as a “structural disruptor” in the alpha helix structure.



proline

(i) With the aid of an appropriate diagram, describe how a polypeptide chain is held in the shape of alpha-helix.

[3]

(ii) Explain why proline acts as a “structural disruptor” in the alpha helix structure.

……..…………………………………………………………………………………………...

…………………………………………………………………………………………………..[1]

[Total: 5]