

## CHEMISTRY

**DATE :** 7 June 2016

**DURATION OF EXAMINATION :**

3 hours (180 minutes)

**PERMITTED EQUIPMENT :**

Calculator : TI-Nspire in 'Press-to-Test' mode

**INSTRUCTIONS :**

- Answer both A questions and both B questions.
- Use a separate answer sheet for each of the four main questions.

**EUROPEAN BACCALAUREATE 2016: CHEMISTRY**

<b>Question A1</b>		
	<b>Page 1/2</b>	<b>Marks</b>
<p><b>a)</b> Prince Yussupov, the nephew of Tsar Nicholas II, attempted to poison the 'mad monk' Gregory Rasputin. He added the highly toxic cyanide ions, <math>\text{CN}^-(\text{aq})</math>, as potassium cyanide, <math>\text{KCN}(\text{s})</math>, to some cakes.</p> <p>Rasputin is reputed to have eaten several of these cakes, laced with the poison. It is thought he survived because Yussupov stored the potassium cyanide in damp conditions.</p> <p>Atmospheric carbon dioxide, <math>\text{CO}_2(\text{g})</math>, can react with water from the damp air according to the following equation:</p> <p><b>Equation 1:</b> <math>\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{CO}_3(\text{aq})</math></p> <p>This carbonic acid, <math>\text{H}_2\text{CO}_3(\text{aq})</math>, can then react further with the potassium cyanide to form hydrogen cyanide, <math>\text{HCN}(\text{g})</math>, and potassium hydrogencarbonate, <math>\text{KHCO}_3(\text{aq})</math>:</p> <p><b>Equation 2:</b> <math>\text{H}_2\text{CO}_3(\text{aq}) + \text{KCN}(\text{aq}) \rightarrow \text{KHCO}_3(\text{aq}) + \text{HCN}(\text{g})</math></p> <p>The hydrogen cyanide gas evolves from the reaction mixture leaving the harmless potassium hydrogencarbonate behind.</p> <p>When hydrogen cyanide dissolves in water it acts as a weak acid.</p> <p><b>i.</b> Write the equation for the reaction of hydrogen cyanide with water. <span style="float:right">1 mark</span></p> <p><b>ii.</b> Identify the two conjugate acid-base pairs involved in question <b>a)i.</b> <span style="float:right">2 marks</span></p> <p><b>iii.</b> Write the expression for the acid ionisation constant, <math>K_a</math>, for hydrogen cyanide. <span style="float:right">1 mark</span></p> <p><b>iv.</b> Calculate the pH of a <math>5.00 \times 10^{-1} \text{ dm}^3</math> aqueous solution containing 1.35 g of hydrogen cyanide. <span style="float:right">3 marks</span></p> <p><b>v.</b> With reference to <b>equation 2</b> above, deduce whether the <math>\text{p}K_a</math> of carbonic acid is higher or lower than that of hydrogen cyanide. Justify your answer. <span style="float:right">2 marks</span></p> <p><b>Given:</b> atomic molar masses in <math>\text{g mol}^{-1}</math>: H: 1.01 ; C: 12.0 ; N: 14.0 ;  <math>\text{p}K_a(\text{HCN}(\text{aq})) = 9.31</math> at the experimental conditions.</p>		

**EUROPEAN BACCALAUREATE 2016: CHEMISTRY**

Question A1		
	Page 2/2	Marks
<p><b>b)</b> A <math>2.00 \times 10^{-2} \text{ dm}^3</math> sample of a hydrogen cyanide solution, <math>\text{HCN(aq)}</math>, of concentration <math>1.00 \text{ mol dm}^{-3}</math>, was titrated using a <math>1.00 \text{ mol dm}^{-3}</math> solution of potassium hydroxide, <math>\text{KOH(aq)}</math>.</p>		
<p>i. Write the equation for the reaction of this titration.</p>		2 marks
<p>ii. Calculate the pH of the potassium hydroxide solution used in the titration.</p>		2 marks
<p>iii. Show by calculation, that the pH of the solution after the addition of <math>1.00 \times 10^{-2} \text{ dm}^3</math> of the potassium hydroxide solution, corresponds to the <math>\text{p}K_{\text{a}}</math> of hydrogen cyanide, <math>\text{p}K_{\text{a}}(\text{HCN(aq)}) = 9.31</math>.</p>		4 marks
<p><b>Given:</b> <math>\text{p}K_{\text{w}} = 14.00</math> at the experimental conditions.</p>		
<p><b>c)</b> Buffer solutions resist changes in pH upon the addition of small quantities of acid or alkali.</p>		
<p>i. Describe two methods to prepare a buffer solution using a weak acid <math>\text{HY(aq)}</math> (calculations are not required).</p>		2 marks
<p>ii. Give two equations to show how a buffer solution (<math>\text{HY(aq)}/\text{Y}^{-}(\text{aq})</math>) resists changes in pH upon the addition of acid or base.</p>		2 marks
<p><b>d)</b> The hydrogencarbonate ion, <math>\text{HCO}_3^{-}(\text{aq})</math>, is amphoteric.</p>		
<p>i. Show its amphoteric behavior in water using two equations.</p>		2 marks
<p>ii. Give the two conjugate acid/base pairs involving the hydrogencarbonate ion.</p>		2 marks

**EUROPEAN BACCALAUREATE 2016: CHEMISTRY**

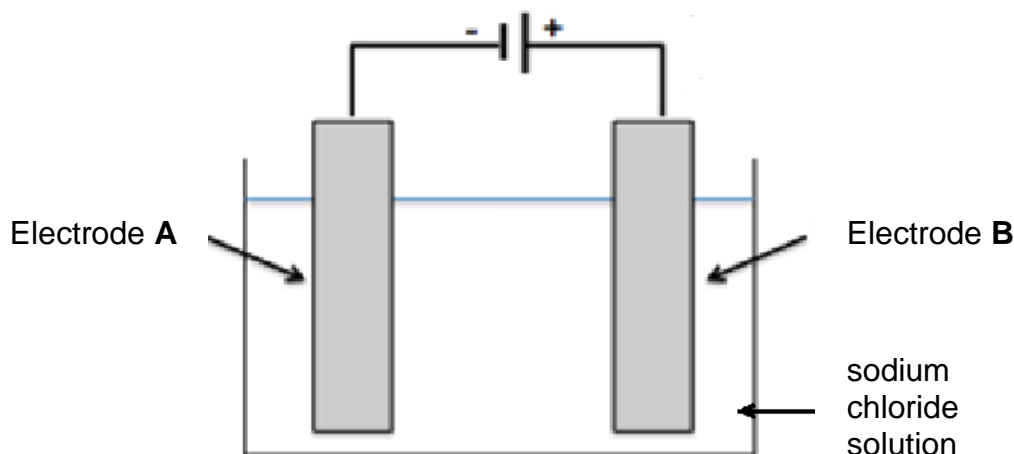
<b>Question A2</b>		
	<b>Page 1/3</b>	<b>Marks</b>
<p>A typical bleach is a basic solution of sodium hypochlorite, NaClO(aq), and sodium chloride, NaCl(aq). It is mainly used for its disinfectant or bleaching properties.</p> <p><b>a)</b> Bleach can be produced by passing chlorine gas, Cl<sub>2</sub>(g), through a dilute sodium hydroxide solution, NaOH(aq). The process is described by the following unbalanced <b>equation 1</b>:</p> <p align="center"><b>Equation 1: Cl<sub>2</sub>(g) + OH<sup>-</sup>(aq) → Cl<sup>-</sup>(aq) + ClO<sup>-</sup>(aq) + H<sub>2</sub>O(l)</b></p> <p>When chlorine reacts with hot concentrated sodium hydroxide solution, a different reaction takes place, which is described in the unbalanced <b>equation 2</b>. One of the products formed, sodium chlorate, NaClO<sub>3</sub>, was used in the past as weed killer.</p> <p align="center"><b>Equation 2: Cl<sub>2</sub>(g) + OH<sup>-</sup>(aq) → Cl<sup>-</sup>(aq) + ClO<sub>3</sub><sup>-</sup>(aq) + H<sub>2</sub>O(l)</b></p>		
<b>i.</b>	Determine the oxidation number of chlorine in Cl <sub>2</sub> , Cl <sup>-</sup> , ClO <sup>-</sup> , and ClO <sub>3</sub> <sup>-</sup> .	2 marks
<b>ii.</b>	Identify, using the oxidation numbers, the redox couples involved in <b>equation 1</b> .	2 marks
<b>iii.</b>	Balance <b>equation 1</b> .	1 mark
<b>iv.</b>	Balance <b>equation 2</b> .	2 marks

## Question A2

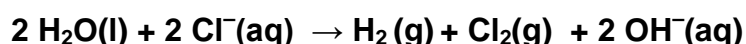
Page 2/3

Marks

- b) Chlorine is produced by the electrolysis of a sodium chloride solution,  $\text{NaCl(aq)}$ .



The equation for the overall reaction is:



- Give the half-equation for oxidation and specify at which electrode (**A** or **B**) it takes place. 2 marks
- Is the formation of hydrogen,  $\text{H}_2\text{(g)}$ , and chlorine,  $\text{Cl}_2\text{(g)}$ , expected according to the standard redox potentials? Explain your answer. 3 marks
- Calculate the time required for the production of  $1.00 \times 10^4 \text{ dm}^3$  of chlorine,  $\text{Cl}_2\text{(g)}$ , if the current is  $1.50 \times 10^4 \text{ A}$ . 3 marks

**Given:** Standard redox potentials:

Redox couple	$E^\ominus / \text{V}$
$\text{Cl}_2\text{(g)} / \text{Cl}^{\text{-(aq)}}$	+1.36
$\text{O}_2\text{(g)} / \text{H}_2\text{O(l)}$	+1.23
$\text{H}_2\text{O(l)} / \text{H}_2\text{(g)}$	-0.83
$\text{Na}^{\text{+(aq)}} / \text{Na(s)}$	-2.71

Molar volume of chlorine gas:

$V_m = 24.5 \text{ dm}^3 \text{ mol}^{-1}$  under the experimental conditions.

1 Faraday =  $9.65 \times 10^4 \text{ C mol}^{-1}$

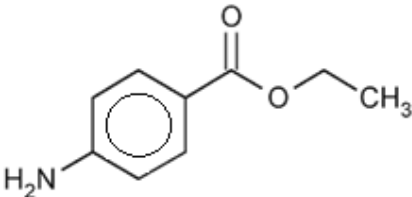
# EUROPEAN BACCALAUREATE 2016: CHEMISTRY

Question A2		
	Page 3/3	Marks
<p>c) A lab-technician checked the label on a commercial bottle of bleach: 14° Chl (14 chlorometric degrees). The chlorometric degree represents the volume (in dm<sup>3</sup>) of chlorine, Cl<sub>2</sub>(g), that is released under <b>standard conditions</b> by 1.00 dm<sup>3</sup> of bleach in a reaction with an acid, according to the equation:</p> $\text{ClO}^-(\text{aq}) + \text{Cl}^-(\text{aq}) + 2\text{H}^+(\text{aq}) \rightarrow \text{Cl}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$ <p>He used the following method to determine the concentration of the hypochlorite ions, ClO<sup>-</sup>(aq), in the bleach:</p> <ul style="list-style-type: none"> <li>• He made a tenfold dilution (1:10) of the concentrated commercial bleach solution.</li> <li>• He took a sample of 10.0 cm<sup>3</sup> of the diluted bleach solution and added an excess of acidified potassium iodide solution, KI(aq).</li> <li>• After stirring, he titrated the iodine produced, I<sub>2</sub>(aq), with a 1.00 × 10<sup>-1</sup> mol dm<sup>-3</sup> sodium thiosulfate solution, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>(aq). Shortly before the end of titration he added some starch solution.</li> </ul> <p>The end-point of the titration occurred when 10.6 cm<sup>3</sup> of the sodium thiosulfate solution had been added to the sample.</p>		
i.	Using the relevant couples given below, write the equation for the reaction between the hypochlorite ion, ClO <sup>-</sup> (aq), and the iodide ion, I <sup>-</sup> (aq), under acidic conditions.	2 marks
ii.	Using the relevant couples given below, write the equation for the reaction between the thiosulfate ion, S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> (aq), and iodine, I <sub>2</sub> (aq).	2 marks
iii.	Describe how the end-point is observed experimentally in the titration with thiosulfate ion, S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> (aq).	1 mark
iv.	Determine the concentration of the hypochlorite ions, ClO <sup>-</sup> (aq), in the diluted bleach solution.	3 marks
v.	Deduce the chlorometric degree of the concentrated commercial bleach solution.	2 marks
<p><b>Given:</b> Redox couples:</p> <div style="border: 1px solid black; padding: 10px; width: fit-content; margin: 10px auto;"> <p>ClO<sup>-</sup>(aq) / Cl<sup>-</sup>(aq)</p> <p>I<sub>2</sub>(aq) / I<sup>-</sup>(aq)</p> <p>S<sub>4</sub>O<sub>6</sub><sup>2-</sup>(aq) / S<sub>2</sub>O<sub>3</sub><sup>2-</sup>(aq)</p> </div>		
<p>Molar volume of chlorine gas: V<sub>m</sub> = 22.4 dm<sup>3</sup> mol<sup>-1</sup> under <b>standard conditions</b>.</p>		

# EUROPEAN BACCALAUREATE 2016: CHEMISTRY

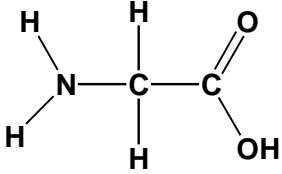
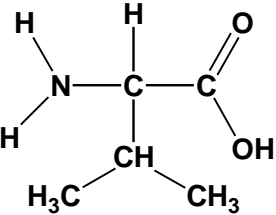
Question B1		
	Page 1/2	Marks
<p><b>a)</b> A primary alcohol <b>X</b> has the following composition, by mass:  C : 59.9% ; H : 13.5% ; O : 26.6%</p> <p><b>i.</b> Confirm, by calculation from the mass percentages, that the empirical formula of compound <b>X</b> is <math>C_3H_8O</math>.</p> <p>The molar molecular mass of alcohol <b>X</b> is <math>60.1 \text{ g mol}^{-1}</math>.</p> <p><b>ii.</b> Determine the molecular formula of <b>X</b>.</p> <p><b>iii.</b> Give the structural formula and the systematic (IUPAC) name for alcohol <b>X</b>.</p> <p><b>Given:</b> Molar atomic mass (in <math>\text{g mol}^{-1}</math>): C: 12.0 ; H: 1.01 ; O: 16.0</p>		
<p><b>b)</b> Oxidation of alcohol <b>X</b> using limited amounts of acidified potassium dichromate (VI) solution, <math>K_2Cr_2O_7(aq)</math>, produces organic compound <b>Y</b> and chromium(III) ions, <math>Cr^{3+}(aq)</math>.</p> <p><b>i.</b> Give the separate half-equations and the overall equation for the reaction between alcohol <b>X</b> and acidified potassium dichromate(VI) solution.</p> <p><b>ii.</b> Give the systematic (IUPAC) name for compound <b>Y</b>.</p> <p>Further oxidation of compound <b>Y</b> using Fehling's solution produces the organic compound <b>Z</b>.</p> <p><b>iii.</b> Give one observation that can be made, when compound <b>Y</b> reacts with Fehling's solution.</p> <p><b>iv.</b> Give the structural formula and the systematic (IUPAC) name for <b>Z</b>.</p>		

**EUROPEAN BACCALAUREATE 2016: CHEMISTRY**

<b>Question B1</b>		
	<b>Page 2/2</b>	<b>Marks</b>
<p><b>c)</b> Consider the following compounds:</p> <p><b>A.</b> propanoic acid</p> <p><b>B.</b> 2,2-dimethylpropanoic acid</p> <p><b>C.</b> 2-fluoropropanoic acid</p> <p><b>i.</b> Give the structural formulas for the two compounds <b>B</b> and <b>C</b>.</p> <p><b>ii.</b> Arrange <b>A</b>, <b>B</b> and <b>C</b> in order of increasing acid strength. Justify your response by comparing their structures.</p>		
		2 marks
		3 marks
<p><b>d)</b> Benzocaine (ethyl-4-aminobenzoate) is the principle active ingredient in several anaesthetic medicinal products.</p> <div align="center">  </div> <p align="center"><b>Benzocaine</b></p> <p>In the laboratory benzocaine is synthesised in the reaction between 4-aminobenzoic acid and ethanol. Some concentrated sulfuric acid, <math>\text{H}_2\text{SO}_4(\text{l})</math>, is added to the reaction mixture.</p> <p><b>i.</b> Give the overall equation for this reaction using structural formulas.</p> <p><b>ii.</b> State the type of reaction taking place.</p> <p>When 2.60 g of 4-aminobenzoic acid reacts with 1.15 g of ethanol, 1.81 g of benzocaine is obtained.</p> <p><b>iii.</b> Show, by calculation, that the limiting reactant is 4-aminobenzoic acid i.e. that the ethanol is in excess.</p> <p><b>iv.</b> Calculate the percentage yield in this synthesis.</p> <p><b>v.</b> Explain the role of the concentrated sulfuric acid.</p> <p><b>Given:</b> Molar molecular mass (in <math>\text{g mol}^{-1}</math>):  4-aminobenzoic acid: 137 ; Ethanol: 46.0 ; Benzocaine: 165</p>		
		2 marks
		1 mark
		2 marks
		2 marks
		1 mark



**EUROPEAN BACCALAUREATE 2016: CHEMISTRY**

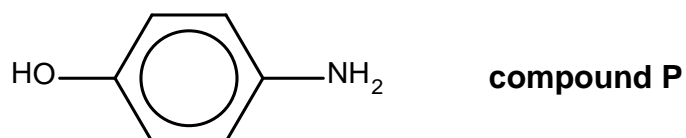
<b>Question B2</b>		
	<b>Page 1/3</b>	<b>Marks</b>
<p><b>a)</b> Amines have a wide range of applications including the manufacture of polymers and dyes. They show basic properties.</p> <p><b>i.</b> Draw the structural formula of ethylamine, <math>C_2H_7N</math>. <span style="float:right">1 mark</span></p> <p><b>ii.</b> Explain why ethylamine can act as a base. <span style="float:right">1 mark</span></p> <p><b>iii.</b> Write the equation for the reaction of ethylamine with water using structural formulas. <span style="float:right">2 marks</span></p> <p><b>iv.</b> Explain, why ethylamine has a high solubility in water. <span style="float:right">2 marks</span></p> <p>Aminobenzene (phenylamine), <math>C_6H_5NH_2</math>, is an aromatic amine (<math>pK_b = 9.37</math>), which is significantly less basic than ethylamine (<math>pK_b = 3.30</math>).</p> <p><b>v.</b> Explain why aminobenzene has a relatively high <math>pK_b</math> and why ethylamine has a relatively low <math>pK_b</math>. <span style="float:right">2 marks</span></p> <p><b>b)</b> Amino acids are the building blocks of proteins. There are approximately 20 naturally-occurring amino acids, two of which are shown below:</p> <div style="display: flex; justify-content: space-around; align-items: center; margin: 10px 0;"> <div style="text-align: center;"> <p><b>glycine</b></p>  </div> <div style="text-align: center;">  <p><b>valine</b></p> </div> </div> <p><b>i.</b> By reference to its structure, explain why valine can show optical isomerism. <span style="float:right">2 marks</span></p> <p>The isoelectric point of glycine is 5.97 in aqueous solution.</p> <p><b>ii.</b> Draw the structural formula of the predominant species of glycine present at the following pH values. <span style="float:right">3 marks</span></p> <p style="margin-left: 40px;">A. <math>pH = 2.00</math> ; B. <math>pH = 5.97</math> ; C. <math>pH = 12.00</math></p> <p><b>iii.</b> Explain why glycine at a pH of 5.97, will not move towards the anode nor the cathode when placed in a uniform electric field. <span style="float:right">1 mark</span></p> <p>Glycine and valine can form dimers with different structures.</p> <p><b>iv.</b> State how many different dipeptides can be formed in a mixture of glycine and valine. <span style="float:right">1 mark</span></p> <p><b>v.</b> Give the structural formulas of two of these dipeptides. <span style="float:right">2 marks</span></p>		

## Question B2

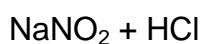
Page 2/3

Marks

- c) Compound **P**, the structure of which is shown below, is used as a starting material for the synthesis of another organic compound **S**, also shown below.

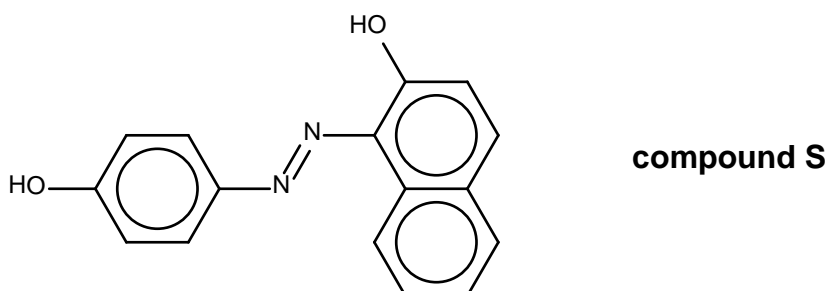


First step in the synthesis:



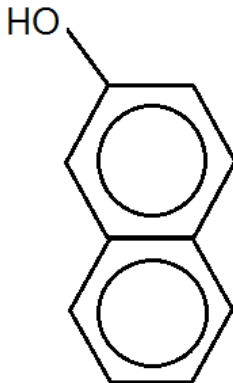
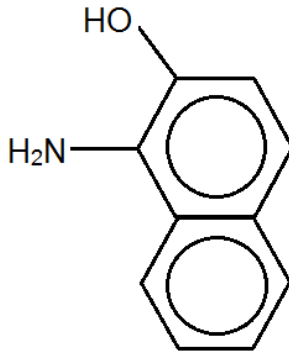
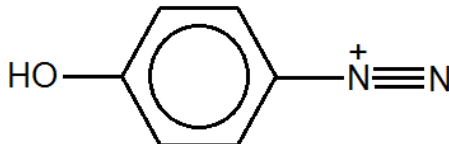
**intermediate compound Q**

Second step in the synthesis:



- i. Copy the structural formula of compound **P**. Circle and name two functional groups. 2 marks

**EUROPEAN BACCALAUREATE 2016: CHEMISTRY**

Question B2		
Page 3/3		Marks
<p>ii. Identify compounds <b>Q</b> and <b>R</b> from the following three molecules <b>1</b>, <b>2</b> and <b>3</b>:</p> <div style="display: flex; justify-content: space-around; align-items: flex-start;"><div style="text-align: center;"><p><b>1.</b></p></div><div style="text-align: center;"><p><b>2.</b></p></div></div> <div style="text-align: center; margin-top: 20px;"><p><b>3.</b></p></div>		2 marks
<p>The final compound formed, <b>S</b>, is coloured.</p> <p>iii. Explain this property by referring to the chemical structure of <b>S</b>.</p> <p>iv. Give the general name for the class of compounds to which <b>S</b> belongs.</p>		3 marks 1 mark