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.

Question A1

Marks

a) Prince Yussupov, the nephew of Tsar Nicholas II, attempted to poison the 'mad monk' Gregory Rasputin. He added the highly toxic cyanide ions, $CN^-(aq)$, as potassium cyanide, KCN(s), to some cakes.

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.

Atmospheric carbon dioxide, $CO_2(g)$, can react with water from the damp air according to the following equation:

Equation 1: $\mathbf{CO_2\,(g) + H_2O(l) \rightleftharpoons H_2CO_3\,(aq)}$

This carbonic acid, $H_2CO_3(aq)$, can then react further with the potassium cyanide to form hydrogen cyanide, HCN(g), and potassium hydrogencarbonate, $KHCO_3(aq)$:

Equation 2: $\mathbf{H_2CO_3(aq) + KCN(aq) \rightarrow KHCO_3(aq) + HCN(g)}$

The hydrogen cyanide gas evolves from the reaction mixture leaving the harmless potassium hydrogencarbonate behind.

When hydrogen cyanide dissolves in water it acts as a weak acid.

i. Write the equation for the reaction of hydrogen cyanide with water. — 1 mark

ii. Identify the two conjugate acid-base pairs involved in question **a)i**. — 2 marks

iii. Write the expression for the acid ionisation constant, K_a, for hydrogen cyanide. — 1 mark

iv. Calculate the pH of a 5.00×10^{-1} dm^3 aqueous solution containing 1.35 g of hydrogen cyanide. — 3 marks

v. With reference to **equation 2** above, deduce whether the pK_a of carbonic acid is higher or lower than that of hydrogen cyanide. Justify your answer. — 2 marks

Given: atomic molar masses in g mol^{-1}: H: 1.01 ; C: 12.0 ; N: 14.0 ;
pK_a (HCN(aq)) = 9.31 at the experimental conditions.

Question A1		
	Page 2/2	**Marks**
b)	A 2.00 x 10^{-2} dm³ sample of a hydrogen cyanide solution, HCN(aq), of concentration 1.00 mol dm^{-3}, was titrated using a 1.00 mol dm^{-3} solution of potassium hydroxide, KOH(aq).	
	i. Write the equation for the reaction of this titration.	2 marks
	ii. Calculate the pH of the potassium hydroxide solution used in the titration.	2 marks
	iii. Show by calculation, that the pH of the solution after the addition of 1.00 x 10^{-2} dm^3 of the potassium hydroxide solution, corresponds to the pK_a of hydrogen cyanide, pK_a (HCN(aq)) = 9.31.	4 marks
	Given: pK_w = 14.00 at the experimental conditions.	
c)	Buffer solutions resist changes in pH upon the addition of small quantities of acid or alkali.	
	i. Describe two methods to prepare a buffer solution using a weak acid HY(aq) (calculations are not required).	2 marks
	ii. Give two equations to show how a buffer solution (HY(aq)/Y^-(aq)) resists changes in pH upon the addition of acid or base.	2 marks
d)	The hydrogencarbonate ion, HCO_3^-(aq), is amphoteric.	
	i. Show its amphoteric behavior in water using two equations.	2 marks
	ii. Give the two conjugate acid/base pairs involving the hydrogencarbonate ion.	2 marks

Question A2

Page 1/3 | **Marks**

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.

a) Bleach can be produced by passing chlorine gas, $Cl_2(g)$, through a dilute sodium hydroxide solution, NaOH(aq). The process is described by the following unbalanced **equation 1**:

Equation 1: $Cl_2(g) + OH^-(aq) \rightarrow Cl^-(aq) + ClO^-(aq) + H_2O(l)$

When chlorine reacts with hot concentrated sodium hydroxide solution, a different reaction takes place, which is described in the unbalanced **equation 2**. One of the products formed, sodium chlorate, $NaClO_3$, was used in the past as weed killer.

Equation 2: $Cl_2(g) + OH^-(aq) \rightarrow Cl^-(aq) + ClO_3^-(aq) + H_2O(l)$

i. Determine the oxidation number of chlorine in Cl_2, Cl^-, ClO^-, and ClO_3^-. — 2 marks

ii. Identify, using the oxidation numbers, the redox couples involved in **equation 1**. — 2 marks

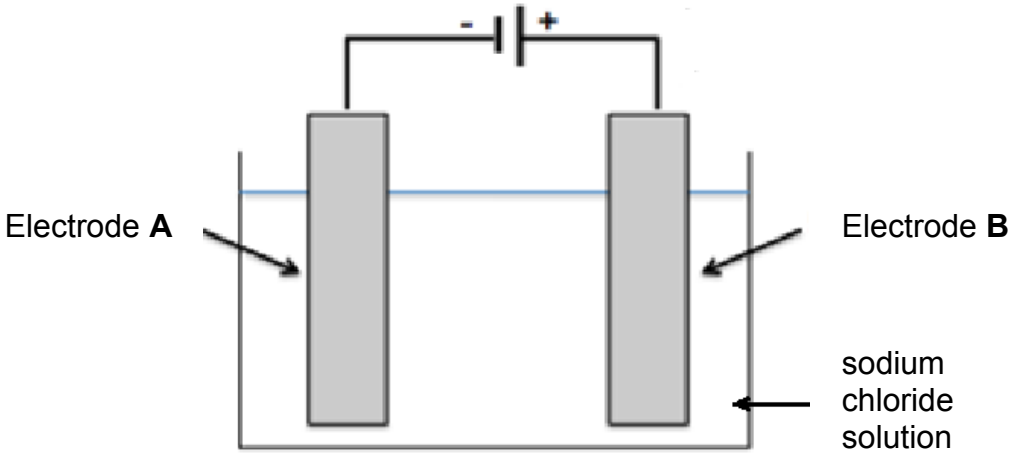
iii. Balance **equation 1**. — 1 mark

iv. Balance **equation 2**. — 2 marks

Question A2

	Page 2/3	Marks

b) Chlorine is produced by the electrolysis of a sodium chloride solution, NaCl(aq).



The equation for the overall reaction is:

$$\mathbf{2\ H_2O(l) + 2\ Cl^-(aq) \rightarrow H_2\,(g) + Cl_2(g)\ + 2\ OH^-(aq)}$$

i. Give the half-equation for oxidation and specify at which electrode (**A** or **B**) it takes place. — 2 marks

ii. Is the formation of hydrogen, $H_2(g)$, and chlorine, $Cl_2(g)$, expected according to the standard redox potentials? Explain your answer. — 3 marks

iii. Calculate the time required for the production of 1.00×10^4 dm^3 of chlorine, $Cl_2(g)$, if the current is 1.50×10^4 A. — 3 marks

Given: Standard redox potentials:

Redox couple	E^θ **/ V**
$Cl_2\,(g) / Cl^-(aq)$	+1.36
$O_2\,(g) / H_2O(l)$	+1.23
$H_2O(l) / H_2(g)$	-0.83
$Na^+(aq) / Na(s)$	-2.71

Molar volume of chlorine gas:

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

1 Faraday = 9.65×10^4 C mol^{-1}

Question A2

Marks

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^3) of chlorine, $Cl_2(g)$, that is released under **standard conditions** by 1.00 dm^3 of bleach in a reaction with an acid, according to the equation:

$$\mathbf{ClO^-(aq) + Cl^-(aq) + 2H^+(aq) \rightarrow Cl_2(g) + H_2O(l)}$$

He used the following method to determine the concentration of the hypochlorite ions, $ClO^-(aq)$, in the bleach:

- He made a tenfold dilution (1:10) of the concentrated commercial bleach solution.
- He took a sample of 10.0 cm^3 of the diluted bleach solution and added an excess of acidified potassium iodide solution, KI(aq).
- After stirring, he titrated the iodine produced, $I_2(aq)$, with a 1.00×10^{-1} mol dm^{-3} sodium thiosulfate solution, $Na_2S_2O_3(aq)$. Shortly before the end of titration he added some starch solution.

The end-point of the titration occurred when 10.6 cm^3 of the sodium thiosulfate solution had been added to the sample.

i. Using the relevant couples given below**,** write the equation for the reaction between the hypochlorite ion, $ClO^-(aq)$, and the iodide ion, $I^-(aq)$, under acidic conditions. — 2 marks

ii. Using the relevant couples given below, write the equation for the reaction between the thiosulfate ion, $S_2O_3^{2-}(aq)$, and iodine, $I_2(aq)$. — 2 marks

iii. Describe how the end-point is observed experimentally in the titration with thiosulfate ion, $S_2O_3^{2-}(aq)$. — 1 mark

iv. Determine the concentration of the hypochlorite ions, $ClO^-(aq)$, in the diluted bleach solution. — 3 marks

v. Deduce the chlorometric degree of the concentrated commercial bleach solution. — 2 marks

Given: Redox couples:

$ClO^-(aq) / Cl^-(aq)$
$I_2(aq) / I^-(aq)$
$S_4O_6^{2-}(aq) / S_2O_3^{2-}(aq)$

Molar volume of chlorine gas: V_m = 22.4 dm^3 mol^{-1} under **standard conditions**.

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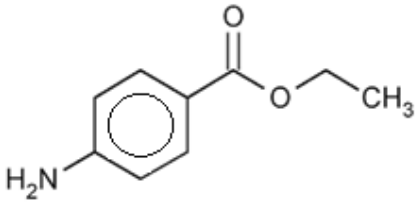
Question B1

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

Question B1	
Page 2/2	**Marks**
c) Consider the following compounds: **A.** propanoic acid **B.** 2,2-dimethylpropanoic acid **C.** 2-fluoropropanoic acid	
i. Give the structural formulas for the two compounds **B** and **C**.	2 marks
ii. Arrange **A**, **B** and **C** in order of increasing acid strength. Justify your response by comparing their structures.	3 marks
d) Benzocaine (ethyl-4-aminobenzoate) is the principle active ingredient in several anaesthetic medicinal products.  **Benzocaine** In the laboratory benzocaine is synthesised in the reaction between 4-aminobenzoic acid and ethanol. Some concentrated sulfuric acid, $H_2SO_4(l)$, is added to the reaction mixture.	
i. Give the overall equation for this reaction using structural formulas.	2 marks
ii. State the type of reaction taking place.	1 mark
When 2.60 g of 4-aminobenzoic acid reacts with 1.15 g of ethanol, 1.81 g of benzocaine is obtained.	
iii. Show, by calculation, that the limiting reactant is 4-aminobenzoic acid i.e. that the ethanol is in excess.	2 marks
iv. Calculate the percentage yield in this synthesis.	2 marks
v. Explain the role of the concentrated sulfuric acid.	1 mark
Given: Molar molecular mass (in g mol^{-1}): 4-aminobenzoic acid: 137 ; Ethanol: 46.0 ; Benzocaine: 165	

Question B2

Page 1/3 | **Marks**

a) Amines have a wide range of applications including the manufacture of polymers and dyes. They show basic properties.

i. Draw the structural formula of ethylamine, C_2H_7N. — 1 mark

ii. Explain why ethylamine can act as a base. — 1 mark

iii. Write the equation for the reaction of ethylamine with water using structural formulas. — 2 marks

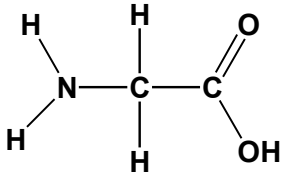
iv. Explain, why ethylamine has a high solubility in water. — 2 marks

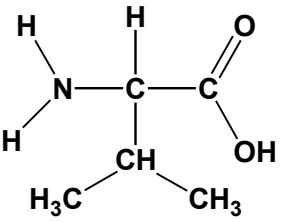
Aminobenzene (phenylamine), $C_6H_5NH_2$, is an aromatic amine ($pK_b = 9.37$), which is significantly less basic than ethylamine ($pK_b = 3.30$).

v. Explain why aminobenzene has a relatively high pK_b and why ethylamine has a relatively low pK_b. — 2 marks

b) Amino acids are the building blocks of proteins. There are approximately 20 naturally-occurring amino acids, two of which are shown below:

glycine





valine

i. By reference to its structure, explain why valine can show optical isomerism. — 2 marks

The isoelectric point of glycine is 5.97 in aqueous solution.

ii. Draw the structural formula of the predominant species of glycine present at the following pH values. — 3 marks

A. pH = 2.00 ; B. pH = 5.97 ; C. pH = 12.00

iii. 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. — 1 mark

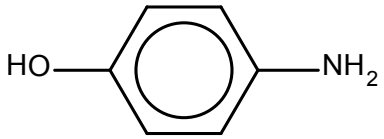
Glycine and valine can form dimers with different structures.

iv. State how many different dipeptides can be formed in a mixture of glycine and valine. — 1 mark

v. Give the structural formulas of two of these dipeptides. — 2 marks

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.

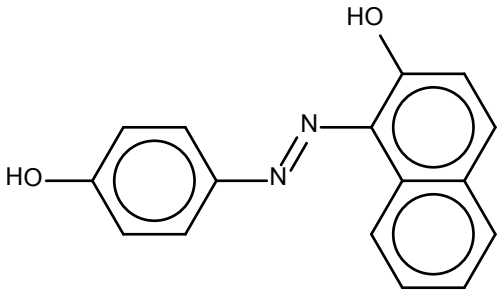


compound P

First step in the synthesis: $NaNO_2$ + HCl

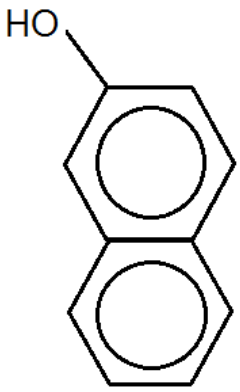
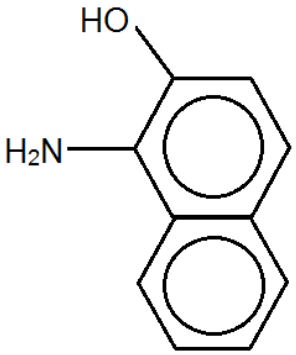
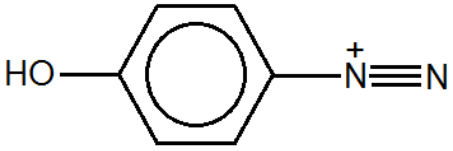
intermediate compound Q

Second step in the synthesis: NaOH + **compound R**



compound S

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

Question B2	
Page 3/3	**Marks**
ii. Identify compounds **Q** and **R** from the following three molecules **1**, **2** and **3**: **1.**  **2.**  **3.**  The final compound formed, **S**, is coloured.	2 marks
iii. Explain this property by referring to the chemical structure of **S**.	3 marks
iv. Give the general name for the class of compounds to which **S** belongs.	1 mark