NATIONAL JUNIOR COLLEGE
SH2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME			
SUBJECT CLASS		REGISTRATION NUMBER	

CHEMISTRY
Paper 3 Free response

9647/03
Monday 29 Aug 2016
2 hour

READ THESE INSTRUCTIONS FIRST

Answer any **four** questions.

A Data Booklet is provided.

The use of an approved scientific calculated is expected, where appropriate.

You are reminded of the need for good English and clear presentation in your answers.

At the end of the examination, fasten all your work securely behind the cover page.

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

This paper consists of **11** printed pages.

Answer any **four** questions.

1 **(a)** Alums are salts formed when a monovalent cation with a large radius (e.g. K^+ or NH_4^+) and a trivalent cation with a small radius (e.g. Al^{3+}, Fe^{3+} or Cr^{3+}) combine with sulfate ions.

An ammonium iron alum has the formula $(NH_4)_aFe(SO_4)_b.12H_2O$.

To determine the chemical formula of the alum, two separate samples of 0.500 g of the alum were each dissolved in 100 cm^3 of water.

An excess of NaOH(aq) was added to the first alum solution and the mixture was boiled. The ammonia gas evolved exactly neutralised 5.2 cm^3 of 0.200 mol dm^{-3} HCl(aq).

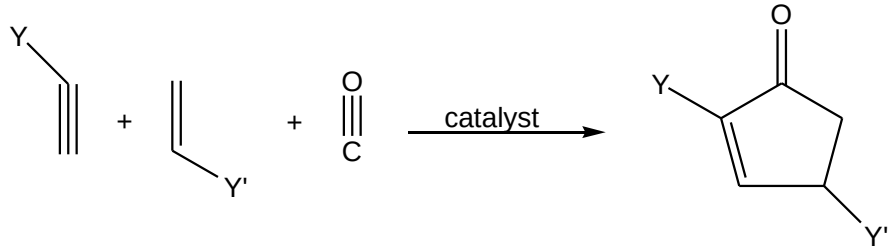
An excess of zinc was added to the second alum solution, which reduced Fe^{3+} to Fe^{2+}, and the resulting solution was filtered. The filtrate collected required 10.4 cm^3 of 0.0200 mol dm^{-3} acidified $KMnO_4$(aq) for complete reaction.

(i) Calculate the amount of NH_4^+ ions present in 0.500 g of the alum. [1]

(ii) Write an equation for the reaction between the filtrate and acidified $KMnO_4$. Hence, calculate the amount of Fe^{3+} ions present in 0.500 g of the alum. [2]

(iii) Using your answers in **(i)** and **(ii)**, determine the values of **a** and **b**. [2]

(b) The Pauson-Khan reaction is a gas phase reaction between an alkyne, an alkene and carbon monoxide to form a cyclic carbonyl compound, as shown below.



where Y and Y' can be Cl or H.

An organic compound **A** was produced from the Pauson-Khan reaction. The compound has the following composition by mass; 51.5 % C, 13.7% O, 30.5% Cl and 4.3% H. M_r of **A** is 116.5.

Upon heating with ethanolic $AgNO_3$, **A** gave a white precipitate.

(i) Determine the molecular formula of **A** and draw its structural formula. [3]

(ii) By quoting relevant data from the *Data Booklet* and given that the bond energy of C≡O is 1079 kJ mol^{-1}, prove that the enthalpy change of reaction in the Pauson-Khan reaction to form **A** is −221 kJ mol^{-1}. [2]

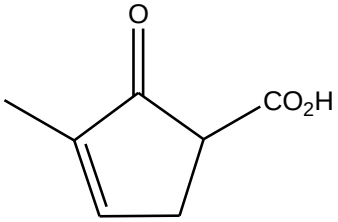
(iii) Predict the sign of the entropy change for the formation of **A** in the above reaction. Hence, deduce if the reaction is feasible at a high or low temperature.

[2]

(iv) With the aid of a Boltzmann diagram, predict and explain the effect on the rate of the Pauson-Khan reaction without a catalyst.

[3]

(c) Another possible product of the Pauson-Khan reaction is shown below:



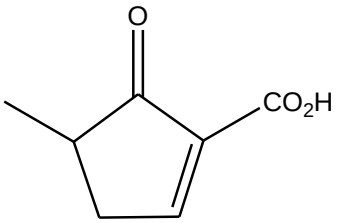
B

(i) Draw the product formed when **B** reacts with each of the following.

I. cold $KMnO_4$(aq) in KOH(aq)
II. H_2, Pt
III. $LiAlH_4$

[3]

(ii) Compound **C** is an isomer of **B**, and has the structure shown below:



C

Deduce which compound, **B** or **C**, is more acidic.

[2]

[Total: 20]

2 Bovine serum albumin (BSA) is a serum albumin protein which is a main constituent of cow milk. It is often used as a protein concentration standard in laboratory experiments. The BSA molecule is a single chain of 607 amino acids, 66% of which are incorporated into β-pleated sheets. It is a globular protein and takes up a roughly spherical shape in water.

Six of the most common amino acids in the BSA molecule are listed below.

Amino acid	**Formula of side chain (R in $RCH(NH_2)CO_2H$)**
Isoleucine	$-CH(CH_3)CH_2CH_3$
Methionine	$-CH_2CH_2SCH_3$
Tyrosine	$-CH_2C_6H_4OH$
Asparagine	$-CH_2CONH_2$
Lysine	$-CH_2(CH_2)_3NH_2$
Asparate	$-CH_2CO_2H$

Table 1

(a) **(i)** There are three pK_a values associated with lysine: 2.17, 9.04, 12.48.

Make use of these pK_a values to suggest the major species present in aqueous solutions of lysine with the following pH values:

- pH 1
- pH 3
- pH 10
- pH 14

[4]

(ii) Suggest **two** positive tests (stating reagents, conditions and observations) that could be used to confirm the identity of two amino acids: asparagine and tyrosine.

[2]

(b) **(i)** Describe the conditions needed to hydrolyse a protein non-enzymatically.

[1]

(ii) Briefly describe what is meant by the *primary structure of proteins*.

[1]

(iii) Describe how a polypeptide chain is held in the shape of a β-pleated sheet.

[1]

(iv) With the aid of a diagram and using suitable amino acids from *Table 1*, describe how hydrogen bonding maintains the tertiary structure of proteins.

[2]

(v) The following recipe illustrates how a lemon sponge cake can be made.

Steps:

1. Cream butter and sugar until light and fluffy.
2. Beat in eggs.
3. Sift over the flour, add lemon juice and rind.
4. Bake for 10 minutes at 180 ºC.

Suggest how any of the **two** steps described above can cause denaturation, making specific reference to suitable pairs of amino acids present in BSA.

[4]

(c) When a beam of $^{3}_{1}T^{+}$ particles is passed through an electric field, the angle of deflection is found to be +5.00º. You may assume that all the $^{3}_{1}T^{+}$ particles travel at the same speed through an electric field of constant strength.

(i) Calculate the angles of deflection if $^{3}_{1}T^{+}$ is replaced with the following, leaving your answers to 2 decimal places:

- $^{32}S^{2-}$
- $^{56}Fe^{3+}$

[2]

The mass of particle **D** is 25 times that of $^{3}_{1}T^{+}$. When a beam of **D** is passed through the same electric field as that used for $^{3}_{1}T^{+}$, the angle of deflection is found to be +0.60º.

(ii) Determine the overall charge on a particle of **D**.

[1]

(iii) A particle of **D** contains 27 protons. Deduce the number of electrons in this particle and hence write its electronic configuration.

[1]

(iv) A nuclear reaction is a reaction in which there is a change in the atomic nucleus.
An experimental nuclear reactor uses ^{13}C and tritium, $^{3}_{1}T$, as fuel. A nuclear reaction between these two atoms are described below (n is a neutron).

$$^{13}C + {}^{3}T \rightarrow X + n + {}^{4}He$$

Suggest the identity of **X** with the aid of the *Data Booklet*.

[1]
[Total: 20]

3 **(a)** The kinetics of the hydrolysis of methyl ethanoate may be investigated by determining the concentration of ethanoic acid produced.

$$CH_3CO_2CH_3 + H_2O \rightarrow CH_3CO_2H + CH_3OH$$

In a 1 dm^3 vessel, 0.350 mol of $CH_3CO_2CH_3$ was heated with dilute hydrochloric acid which acted as a catalyst. The following results were obtained.

Time / s	$[CH_3CO_2H]$ / mol dm^{-3}
0	0
340	0.105
680	0.185
1080	0.243
1440	0.278

(i) What is meant by the term *order of reaction*? [1]

(ii) By drawing a suitable graph using the data given above, determine the order of reaction with respect to methyl ethanoate.

[3]

(iii) Given that the hydrolysis reaction is first order with respect to hydrochloric acid, write the rate equation for this reaction. [1]

(b) Esters can also undergo reduction in the presence of a strong reducing agent such as lithium aluminium hydride, $LiAlH_4$. The reaction produces two alcohols.

$$RCO_2R' \rightarrow RCH_2OH + R'OH$$

Using this information, and that provided below, draw out the full mechanism for the formation of ethanol from methyl ethanoate.

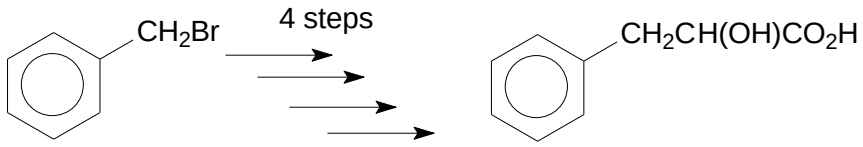
- There is an initial nucleophilic attack by hydride ion, H^-, on the ester to generate a negatively charged ion.
- The C=O π bond reforms and the –OR' group is eliminated from the ester, forming an aldehyde.
- A second hydride ion attacks the aldehyde to generate an alkoxide ion.
- The alkoxide ion is then protonated to form the alcohol.

[3]

(c) Besides esters, nitriles can also undergo reduction to give aldehydes in the presence of another strong reducing agent, diisobutyl aluminium hydride (DIBAL).

$$RCN \rightarrow RCHO$$

(i) By considering the change in oxidation states of the reacting carbon, suggest why the conversion of a nitrile to an aldehyde is a reduction reaction. [1]



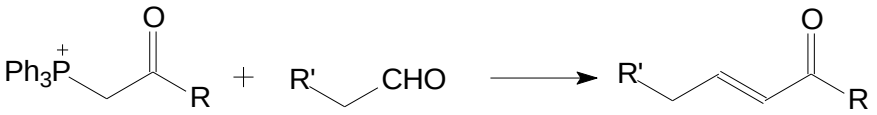
Compound **E**

(ii) Compound **E** can be synthesised using DIBAL as a reducing agent in one of the steps above.

Suggest the reagents and conditions required for each step of synthesis and identify all the intermediate compounds.

[5]

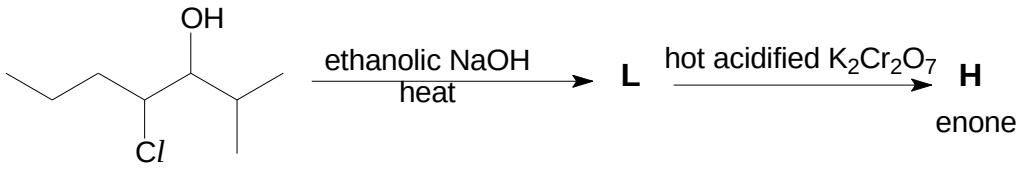
(d) A Wittig reagent can convert an aldehyde to an enone, a ketone with an adjacent double bond.



Wittig reagent enone

(where 'Ph' represents $-C_6H_5$)

Wittig reagent **F** was reacted with an aldehyde **G** to give an enone **H**. **H** was then reacted with hot acidified potassium manganate(VII) to give two different compounds, **J** and **K**.
H can also be synthesised by the following route.



(i) Suggest the identities of compounds **H**, **J**, **K** and **L**. [4]

(ii) Suggest the identities of compounds **F** and **G**. [2]

[Total: 20]

4 **(a)** The question below is related to some compounds of Group II elements.

(i) Write an equation, with state symbols, for the thermal decomposition of strontium nitrate. [1]

(ii) Use the *Data Booklet* to explain how the thermal stability of zinc nitrate might compare to strontium nitrate. [3]

(iii) The chemical properties of beryllium and its compounds show similarity to those of aluminium. Beryllium form complexes of coordination number 4.

I. Aluminium chloride, $AlCl_3$, dimerises to form Al_2Cl_6.
Draw the displayed formula of Al_2Cl_6, showing clearly the bond angle about Al. [1]

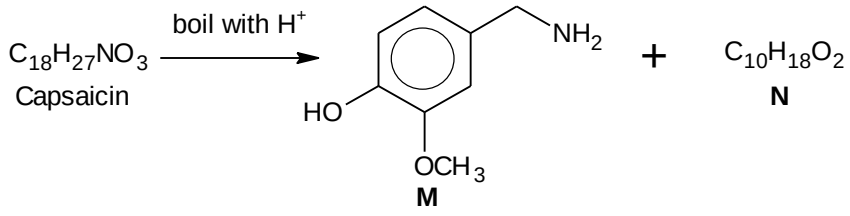
II. Explain why $AlCl_3$ dimerises. [1]

III. Explain, using a relevant equation, why a solution of beryllium chloride is acidic. [2]

IV. Beryllium oxide, similar to aluminium oxide, is amphoteric. Suggest the nature of bonding in beryllium oxide. [1]

V. Write equations for the reaction of beryllium oxide with HCl(aq) and NaOH(aq). [2]

(b) Capsaicin is a slightly acidic compound responsible for the burning sensation of chilli peppers. Its molecular structure can be deduced by the following reaction scheme.
[Assume that $-OCH_3$ group is inert.]



(i) When **N** is heated with concentrated acidified potassium manganate(VII), **P**, $C_6H_{10}O_4$, and **Q**, C_4H_8O, are formed.

P is formed from the reaction of $Br(CH_2)_4Br$ with hot ethanolic KCN followed by hydrolysis. **Q** can be reduced to an alcohol, **R**, which is optically active.

Deduce the structures of **N**, **P**, **Q, R** and capsaicin. [5]

(ii) Draw the organic compound formed when **M** reacts with CH_3CH_2COCl. [1]

(c) Peroxodisulfate(VI) ion, $S_2O_8^{2-}$, is capable of oxidising tartaric acid, $(CH(OH)CO_2H)_2$, to carbon dioxide and methanoic acid.
The $E^{\ominus}_{cell}$ of the reaction is +0.99 V.

$$(CH(OH)CO_2H)_2 + 3S_2O_8^{2-} + 2H_2O \rightarrow 2CO_2 + 2HCO_2H + 6H^+ + 6SO_4^{2-}$$

The reaction is very slow, even when temperature is increased.
However, the reaction rate can be increased by adding a suitable catalyst.

The half equation for the reduction of carbon dioxide to tartaric acid is

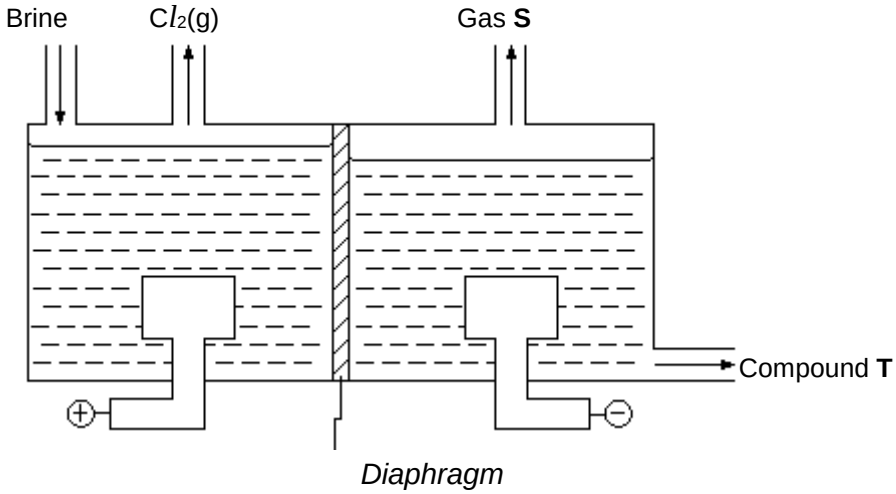
$$2CO_2 + 2HCO_2H + 6H^+ + 6e^- \rightarrow (CH(OH)CO_2H)_2 + 2H_2O$$

Using the *Data Booklet*, show how cobalt(III) ion can act as a homogenous catalyst.

[3]

[Total: 20]

5 **(a)** Chlorine is manufactured from brine (concentrated NaC*l*) by electrolysis using inert electrodes at room temperature. The anode and cathode compartments are separated by a diaphragm which is a permeable membrane.



(i) Suggest the identities of gas **S** and compound **T**. [1]

(ii) Using relevant $E^{\ominus}$ data from the *Data Booklet,* suggest a reason why the electrolysis of dilute NaC*l*(aq) produces mainly oxygen at the anode, whereas the electrolysis of brine produces mainly chlorine gas.

[2]

(iii) Suggest the products that might be formed if the diaphragm is removed and the solution is stirred. Write an equation for any reaction that occurs.

[1]

(b) Orchids can be made into jewellery that gleams with either a reddish tint of copper or shiny gold. In copper-plating, orchids are coated with a thin layer of graphite paste before placing them in a bath of aqueous copper(II) sulfate and electroplating.

(i) Suggest a reason why orchids are first coated with graphite. [1]

(ii) To ensure high standards of electroplated orchids, the copper coating must be at least 0.5 mm thick. Given that the total surface area of a typical orchid is 10 cm^2 and the operating current is 20 A, calculate the time required to electroplate an orchid.
[Density of copper = 8.96 g cm^{-3}]

[3]

(c) The use of *Data Booklet* is relevant to this question.

When iron is heated with bromine, $FeBr_3$ is produced. However, when heated with iodine, FeI_2 is produced instead.

(i) Write the **two** equations for the formation of $FeBr_3$. [2]

(ii) Hence explain why when iron is heated with iodine, FeI_2 is produced but not FeI_3. [2]

(iii) An unknown element **U** is diatomic and is below iodine in Group VII of the Periodic Table. The hydride of **U**, H**U**, and hydride of iodine, HI, differ in their physical properties and reactivities.

(I) Suggest and explain how the polarities of H-**U** and H-I bonds differ.

(II) Suggest and explain how the boiling points of H**U** and HI differ.

(III) Suggest and explain how the acidities of H**U** and HI differ when dissolved in water.

[4]

(d) Methane and steam react to give hydrogen and carbon monoxide as follows.

$$CH_4(g) + H_2O(g) \rightleftharpoons 3\,H_2(g) + CO(g)$$

A mixture of 3.0 mol of CO and 8.0 mol of H_2 is heated in a closed container of 2 dm^3 and allowed to reach dynamic equilibrium at 300 K. The amount of hydrogen at equilibrium was found to be 6.5 mol.

(i) Determine the amounts of methane and steam at equilibrium. [2]

(ii) Write the expression for the equilibrium constant, K_c, for the above equilibrium and calculate the K_c at 300 K.

[2]

[Total: 20]