NATIONAL JUNIOR COLLEGE
SH2 PRELIMINARY EXAMINATION
Higher 2

H

CANDIDATE NAME			
SUBJECT CLASS		REGISTRATION NUMBER	

CHEMISTRY
Paper 3 Free response

9647/03
Mon 14 Sept 2015
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.

Answer any **four** questions.

1 A student analysed a can of beer to verify its alcohol content. The alcohol content is the percentage by volume of pure ethanol in the beer at room temperature. The alcohol content printed on the can is 4.2 %.

The analysis is carried out by titrating 10.0 cm^3 of the beer with 0.20 mol dm^{-3} acidified potassium manganate(VII). It is found that 17.80 cm^3 of potassium manganate(VII) is required to reach the end-point.

(a) **(i)** Write an overall equation for the reaction between potassium manganate(VII) and ethanol.

(ii) Using the titration result, calculate the number of moles of potassium manganate(VII) reacted and hence calculate the mass of ethanol in 10.0 cm^3 of the beer sample.

(iii) Given that the density of ethanol is 0.789 g cm^{-3}, determine the alcohol content of this beer sample.

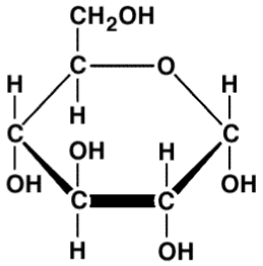
(iv) Give a reason why the alcohol content of the beer calculated is different from that printed on the can.

(v) Explain how you would determine the end-point of this titration.

(vi) Ethanol is highly soluble in water. Explain why the solubility of alcohols in water decreases with increasing carbon chain lengths.

[9]

(b) In the brewing of beer, yeast is added to break down the starch from malt or barley into glucose, $C_6H_{12}O_6$, which is further converted to ethanol and carbon dioxide.
The structure of glucose is as shown:



(i) Write a balanced equation for the conversion of glucose to ethanol.

(ii) Describe a simple chemical test to distinguish between glucose and ethanol. Give an equation for the reaction.

[4]

(c) Ethanol can be used to synthesise ether. Due to the low reactivity of ether, it is a suitable solvent for many chemicals reactions.

One method to synthesise ether, RCH_2OCH_2R', is through the Williamson ether synthesis as shown in the equation below.

$$RCH_2O^- + R'CH_2Cl \rightarrow RCH_2OCH_2R' + Cl^-$$

(i) Describe the mechanism for the above reaction, including curly arrows showing the movement of electrons and all charges.

(ii) Suggest a synthetic route for the formation of diethyl ether, $CH_3CH_2OCH_2CH_3$, using ethene as the only organic reactant.

[7]

[Total: 20]

2 The earthquake that hit Nepal in April 2015 was the worst natural disaster to strike Nepal since 1934. Hundreds of thousands of people were made homeless.

During an earthquake, the heat generated by the friction of the fault in the Earth's crust may be large enough to decompose the mineral rocks present in the fault, releasing chemicals like sulfur dioxide, SO_2, and aluminium oxide, Al_2O_3.

One method for the removal of SO_2 is to absorb it in a slurry of magnesium oxide, to produce magnesium sulfite, $MgSO_3$.

(a) **(i)** Name the type of reaction between magnesium oxide and sulfur dioxide and write a balanced equation for the reaction.

(ii) Based on your knowledge of chemical periodicity, suggest whether Al_2O_3 can also be used to remove sulfur dioxide.

[2]

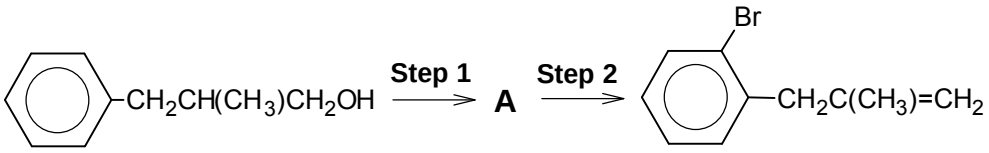
(b) **(i)** State and explain the pH of the solutions formed when MgO, Al_2O_3 and SO_2 are separately added to water.

(ii) When an excess of aqueous sodium hydroxide was added to a solid mixture of $MgSO_3$ and Al_2O_3 and filtered, a white residue and colourless filtrate were obtained. Write an equation to show the formation of the species in the filtrate.

[4]

(c) Aluminium is the third most abundant element found as minerals in the Earth's crust. Its compounds are of importance in the synthesis of many organic compounds.

(i) Compounds **A** and **B** below can be synthesised using two **different** aluminium-containing compounds in **Steps 1** and **2**.

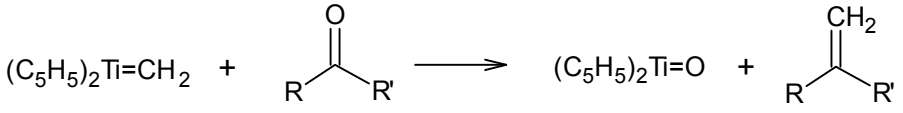


B

Give the reagents and conditions for **Steps 1** and **2**.

(ii) Describe the mechanism in **Step 1**, including curly arrows showing the movement of electrons and all charges.

(iii) Trimethylaluminium, $Al(CH_3)_3$, is an important precursor for the Shrock carbene, $(C_5H_5)_2Ti{=}CH_2$. The Shrock carbene can then be used to convert carbonyl compounds to alkenes in one step:



Draw the structure of the carbonyl compound that would give compound **B** when reacted with Shrock carbene.

[6]

(d) Aluminium chloride and magnesium chloride are separately added to two beakers, each containing 20 cm^3 of water. The pH of the solution containing aluminium chloride is 2.65.

(i) Given that the pK_a of $Al^{3+}(aq)$ is 5.01, write the K_a expression of $Al^{3+}(aq)$ and calculate the mass of $AlCl_3$ used.

(ii) Explain how the pK_a of $Mg^{2+}(aq)$ would compare to that of $Al^{3+}(aq)$.

(iii) A student suggested that an aqueous solution containing Mg^{2+} and Al^{3+} ions can be separated by adding an appropriate concentration of aqueous sodium phosphate, Na_3PO_4.

Use the data given in the table below to calculate the concentration of sodium phosphate necessary for an effective separation of a solution containing 0.10 mol dm^{-3} Mg^{2+} and 0.50 mol dm^{-3} Al^{3+} ions, and briefly describe how the separation is to be carried out.

salt	K_{sp} (at 25°C)
$Mg_3(PO_4)_2$	1.3×10^{-16}
$AlPO_4$	6.3×10^{-19}

[8]

[Total: 20]

3 Use the following data on Group II elements to answer **(a)** – **(c)** of this question.

	$E^{\ominus}$ [M^{2+}(aq)/M(s)] / V	metallic radius / nm	ionic radius / nm	ionic speed / mm s^{-1}
Mg	–2.38	0.160	0.065	0.549
Ca	–2.87	0.197	0.099	0.616
Sr	–2.89	0.215	0.113	0.616
Ba	–2.90	0.217	0.135	0.658

(a) Describe and explain the relative reactivities of Mg and Ba with water.

[2]

(b) **(i)** Write a balanced equation for the thermal decomposition of strontium nitrate.

(ii) Using data provided in the table, describe and explain how the thermal stabilities of the nitrates of the Group II metals vary from magnesium to barium.

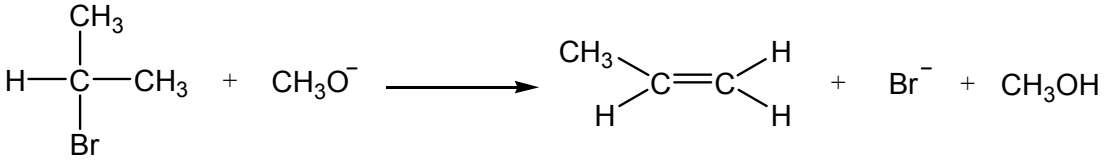
[3]

(c) Ionic speeds show how fast aqueous ions move under standard conditions. Explain why the ionic speeds of calcium and strontium ions are identical even though their ionic radii are different.

[2]

(d) The presence of lone pair of electrons on the O of alkoxides (RO^-) enables them to act as either bases or nucleophiles in organic reactions.

2-Bromopropane reacts with $NaOCH_3$ in methanol according to the following equation:



(i) Name the type of reaction occurring in the above equation.

(ii) State whether CH_3O^- acts as a base or nucleophile.

(iii) The kinetics of the reaction were studied and the experimental results given in the table below.

Experiment	[$NaOCH_3$] / mol dm^{-3}	[2-bromopropane] / mol dm^{-3}	Rate / mol dm^{-3} min^{-1}
1	0.100	0.150	0.06
2	0.150	0.150	0.09
3	0.200	0.200	0.16

Use the data to determine the orders of reaction with respect to $NaOCH_3$ and 2-bromopropane.
Hence, write a rate equation for the reaction and calculate the value of the rate constant, stating its units.

(iv) The above reaction takes place in a one-step mechanism as described in the following sequence.

- CH_3O^- abstracts a proton from C–H group and a new C–C π bond is formed;
- Simultaneously, the C–Br bond is broken to give Br^-.

Describe the mechanism using the above information, including curly arrows to show the movement of electrons and all charges. The name of the mechanism is **not** required.

(v) Explain whether the mechanism in **d(iv)** is consistent with the rate equation you obtained in **d(iii)**.

(vi) Assuming that the reaction proceeds via the same mechanism as in **d(iv)**, explain how the rate of reaction may change

I when 2-chloropropane is used instead of 2-bromopropane;

II when $NaOCH_2CH_3$ is used instead of $NaOCH_3$.

[13]

[Total: 20]

4 Sulfate and thiosulfate ions are examples of polyatomic anions that are involved in a variety of redox processes.

(a) When aqueous bromine is added to aqueous sodium thiosulfate, $Na_2S_2O_3$, followed by the addition of aqueous barium chloride, a white precipitate is formed.

(i) Identify the white precipitate and hence write an ionic equation for the reaction between aqueous bromine and thiosulfate ions.

(ii) The above experiment is repeated with aqueous iodine instead of aqueous bromine. Describe how this reaction would differ.
You should include in your answers:
- data from the *Data Booklet*,
- balanced equation,
- any observation,
- changes in oxidation states.

[6]

(b) Anodising is a process used to increase the thickness of the natural oxide on the surface of metal parts. Aluminium is a common metal which can be anodised as it is a reactive metal that is readily oxidised by the oxygen in air to form a layer of aluminium oxide, Al_2O_3, making it resistant to corrosion.

(i) Using $H_2SO_4(aq)$ as the electrolyte, draw a set-up to show how a small piece of aluminium can be anodised.

(ii) Write equations to show the reactions at the anode during the anodisation of aluminium.

(iii) The small piece of aluminium has a surface area of 25.20 cm^2. How long would it take to form a protective layer of Al_2O_3 of thickness 0.25 mm when a current of 1.8 A is passed through the set-up?
(density of Al_2O_3 is 3.95 g cm^{-3})

[6]

(c) Compound **B**, $C_9H_{12}O_2$, is optically active and does not react with aqueous sodium carbonate. However, it can dissolve in aqueous sodium hydroxide.

When **B** reacts with hot acidified potassium dichromate(VI), the solution turns from orange to green. **B** also decolourises aqueous bromine to form a white precipitate **C**, $C_9H_{10}O_2Br_2$.

Upon heating with excess concentrated sulfuric acid, **B** gives only compound **D**, $C_9H_{10}O$, which exhibits geometric isomerism. **D** gives compound **E** and ethanoic acid on addition of hot acidified potassium manganate(VII) solution.
Deduce the structures of **B** – **E**.

[8]

[Total: 20]

5 Syngas, or synthetic gas, is a fuel gas mixture consisting primarily of carbon monoxide and hydrogen. It is produced by reacting methane with steam in the presence of a nickel catalyst. Syngas is then used to produce diesel or synthesise ammonia or methanol.

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) \qquad \Delta H = \text{positive}$$

(a) In a typical plant, a 1:1 ratio of methane and steam is passed over a nickel catalyst at 1000 K.
Calculate the equilibrium pressure, in atm, that will produce a 90% conversion at 1000 K, given that K_p for this reaction is 0.033 atm^2.

[3]

(b) **(i)** State *Le Chatelier's* Principle.

(ii) Describe and explain how the position of equilibrium and the K_p value might alter when:

I the size of the reaction vessel is decreased,

II the temperature is decreased.

[5]

(c) When syngas is passed over a mixture of copper, zinc oxide and alumina catalyst, methanol, CH_3OH, is formed. One of the largest uses of methanol is to produce methanal, HCHO.

(i) Give the reagents and condition used in the laboratory to convert methanol to methanal.

(ii) State the type of hybridisation around each carbon in the methanol and methanal molecules and sketch the shapes of the hybrid orbitals.

[3]

(d) Other than to produce syngas, reactions of methane include combustion and free radical substitution.

(i) Give the reagents and conditions required to convert methane into chloromethane, CH_3Cl.

(ii) Write two equations to represent the propagation stage of this reaction.

[2]

(e) Some information about halogenoalkanes and acyl halide are shown below.

	chloropropane	iodopropane	propanoyl chloride
boiling point / °C	46	101	79
reaction with hot NaOH(aq) followed by acidified $AgNO_3$(aq)	white precipitate forms after 10 minutes	yellow precipitate forms almost immediately	white precipitate forms immediately
conditions required for reaction with concentrated NH_3	heat in a sealed tube	heat in a sealed tube	room condition

(i) Explain why the boiling point of chloropropane is lower than that of iodopropane.

(ii) With the aid of relevant data from the *Data Booklet*, explain the relative rate of formation of precipitate upon reacting chloropropane and iodopropane separately with hot NaOH(aq), followed by acidified $AgNO_3$(aq).

(iii) State and explain the observations when bromobenzene is reacted with the same reagents and conditions as stated in **e(ii).**

(iv) Suggest a reason for the different conditions required when chloropropane and propanoyl chloride are reacted separately with concentrated NH_3.

[7]

[Total: 20]

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Answer Cover page for Paper 3

Tie this cover page in front of your writing paper.
Please **circle the question numbers** which you have attempted.

Question	For Examiner's Use
1	
2	
3	
4	
5	
Total	