NATIONAL JUNIOR COLLEGE

SH2 PRELIMINARY EXAMINATION

Higher 2

CANDIDATE NAME			
SUBJECT CLASS		REGISTRATION NUMBER	

CHEMISTRY

9729/03

Paper 3 Free Response

Monday 11 Sep 2017
2 hours

Candidates answer on separate paper.
Additional Materials: Data Booklet
Answer Paper

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 or graphs.
Do not use paper clips, highlighters, glue or correction fluid/tape.

Section A
Answers **all** questions.

Section B
Answers **one** question.

The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

This document consists of **11** printed pages and **1** blank page.

Section A

Answer **all** the questions in this section.

1 (a) (i) Write an equation for the thermal decomposition of barium carbonate. [1]

(ii) Describe and explain the trend observed in the ease of thermal decomposition of the carbonates of the Group 2 elements. [2]

(b) Monuments made of marble or limestone, such as the Taj Mahal in India and the Mayan temples in Mexico, are eroded by acid rain containing sulfuric acid. The carbonate stone is converted into sulfate by acid rain.

$$CaCO_3(s) + H_2SO_4(aq) \rightarrow CaSO_4(s) + H_2O(l) + CO_2(g)$$

The life of such monuments is now being extended by treating them with a mixture of urea, $(NH_2)_2CO$, and barium hydroxide solutions.

reaction 1: After soaking in the pores of the carbonate stone containing water, urea reacts gradually to give ammonia and carbon dioxide.

reaction 2: Carbon dioxide produced then reacts with barium hydroxide to form barium carbonate.

(i) State the shape and bond angle around the C atom of $(NH_2)_2CO$. [2]

(ii) Write balanced equations for **reactions 1** and **2**. [2]

(c) When carbon dioxide gas dissolves in water, carbonic acid, H_2CO_3, is formed.

$$CO_2(g) \rightleftharpoons CO_2(aq)$$
$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

In a school laboratory, a student was instructed to titrate 25.0 cm^3 of 0.100 mol dm^{-3} carbonic acid with 0.125 mol dm^{-3} NaOH using phenolphthalein indicator. (K_{a1} of H_2CO_3 = 4.3 × 10^{-7} mol dm^{-3})

(i) Calculate the pH of 0.100 mol dm^{-3} H_2CO_3. [1]

(ii) Calculate the volume of NaOH needed to completely react with 25.0 cm^3 of 0.100 mol dm^{-3} H_2CO_3. [1]

(iii) Calculate the pH of the solution when H_2CO_3 and HCO_3^- are in equal concentrations. [1]

(iv) Calculate the pH of the resulting solution when 20.0 cm^3 of NaOH is added to 25.0 cm^3 of H_2CO_3. [2]

(v) Using your answers in **(i)** to **(iv)**, sketch the shape of the pH curve during the titration. [2]

(d) Barium compounds also have other uses and soluble barium salts are highly poisonous. For example, barium sulfate is used as a 'barium meal' in X-ray diagnostic work for patients with digestive tract problems. On the other hand, barium carbonate is used in rat poison.

The solubility products of $BaCO_3$ and $BaSO_4$ at 25 ^oC are given in the table below.

	Numerical value of K_{sp}
$BaCO_3$	5.5×10^{-10}
$BaSO_4$	1.3×10^{-10}

(i) Calculate the solubility of barium carbonate in mol dm^{-3} at 25 ^oC.

[1]

(ii) When the concentration of Ba^{2+} ions exceeds 0.100 mol dm^{-3}, it is lethal. Suggest a reason why barium carbonate is poisonous when ingested by mouth whereas barium sulfate is safe. [2]

(e) The values of lattice energy of $CaSO_4$ and $BaSO_4$ are −2374 kJ mol^{-1} and −2480 kJ mol^{-1} respectively.

Some standard enthalpy changes of hydration are listed below.

	$\Delta H_{hyd}^{\ominus}$ / kJ mol^{-1}
Ca^{2+}	−1577
Ba^{2+}	−1305
SO_4^{2-}	−1099

Determine the enthalpy change of solution, $\Delta H_{sol}^{\ominus}$, for these two salts. Hence, comment on the difference in the solubilities of the two salts. [3]

[Total: 20 marks]

2 This question is about the chemistry of aluminium, iron and ruthenium, Ru.

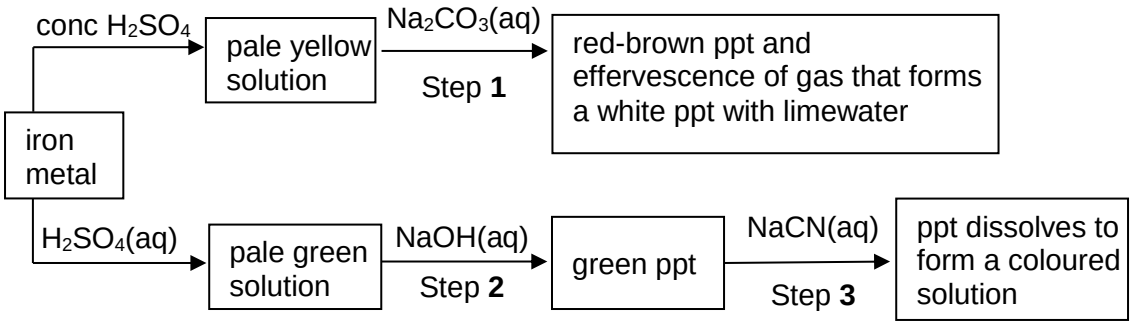
(a) Anodising is a process used to increase the thickness of the natural oxide on the surface of metal parts. Aluminium is a common metal which can be anodised as aluminium is a reactive metal that is readily oxidised by oxygen. This forms a layer of aluminium oxide, Al_2O_3, making it resistant to corrosion.

(i) Using $H_2SO_4(aq)$ as the electrolyte and an inert electrode, draw an electrolysis set-up to show how an iPhone 7®, which is made of Al, can be anodised. [2]

(ii) Write chemical equations to show the reactions at the anode during anodising. [2]

(iii) The iPhone 7® has a surface area of 93.0 cm^2 to be anodised. Calculate the time needed to form a 0.2 mm protective layer of Al_2O_3 on the iPhone 7® if a current of 2.0 A is passed through the set-up. [2]
(Density of Al_2O_3 is 3.95 g cm^{-3})

(b) Iron metal is dissolved in limited amounts of dilute and concentrated sulfuric acid solutions and the resultant solutions undergo a series of reactions as shown below.



(i) Account for the observations seen in step **1**. [2]

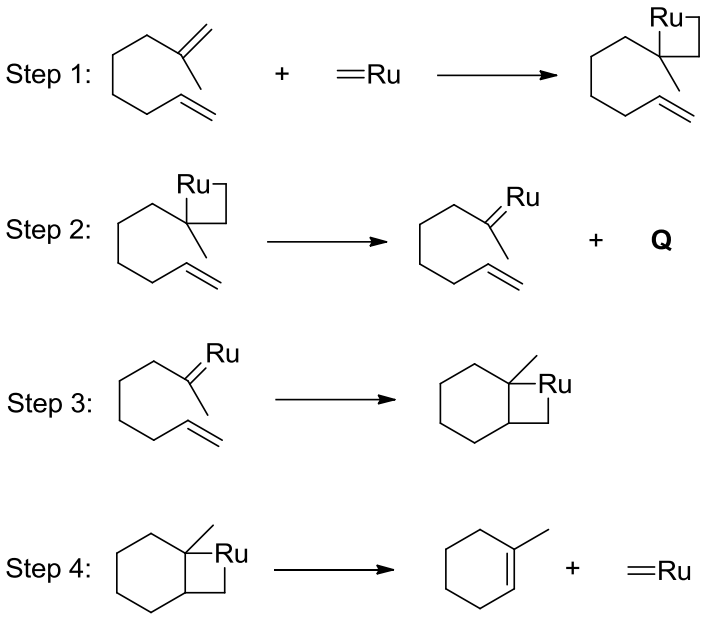
(ii) Write equations with state symbols to account for the observations in steps **2** and **3**. [2]

(c) When aqueous ruthenium(III) chloride is treated with zinc and aqueous ammonia, an orange compound is formed. The orange compound contains 36.9% ruthenium, 30.7% nitrogen, 25.8% chlorine and a certain percentage of hydrogen by mass. When aqueous silver nitrate is added, 1 mol of the orange compound forms 2 mol of AgCl precipitate.

Given that 1 mol of the orange compound contains only 1 mol of Ru, determine the molecular formula of the orange compound. Draw a diagram of the structure of the complex ion in the orange compound. [3]

(d) Robert H. Grubbs used catalysts containing ruthenium for ring-closing reactions involving dienes.

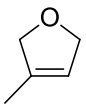
An example of such reactions is as shown.
(Note: ═Ru represents CH_2═Ru)



(i) Formation of **Q** thermodynamically drives this reaction forward.
State the identity of **Q**. [1]

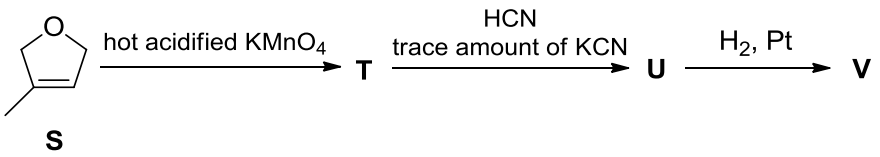
(ii) Copy step **4** onto your writing paper. Draw 2 full-headed curly arrows showing the movement of electrons to form the products. [1]

(iii) Suggest suitable reactants to synthesize **S** using the above method.



S [2]

(e)



S

The ether functional group, –CH_2–O–CH_2–, in compound **S** is inert.
V exists as a crystalline solid at 300 ^oC.
Draw the structures of **T**, **U** and **V**. [3]

[Total: 20]

3 **(a)** The colour of blackberries is due to a compound known as cyanidin. At certain pH, cyanidin (Cy) exist as CyH^+, which is red, and at higher pH as Cy, which is purple.

$$\underset{\text{red}}{CyH^+} \rightleftharpoons \underset{\text{purple}}{Cy + H^+}$$

(i) Write an expression for the acid dissociation constant, K_a of CyH^+. [1]

(ii) Given the K_a value of CyH^+ is 5×10^{-5}, calculate the ratio of $\frac{[CyH^+]}{[Cy]}$ in the blackberries fruit juice buffered at pH = 5.3 and hence predict the colour of the solution at pH = 5.3. [2]

(b) Fruit juices are often preserved by adding small quantities of sulfur dioxide, but SO_2 also reacts with both forms of cyanidin to give colourless compounds. For the red form, the reaction can be represented as follows:

$$CyH^+(aq) + SO_2(aq) + H_2O(l) \rightleftharpoons CySO_3H_2(aq) + H^+(aq) \quad \text{Equilibrium (1)}$$

When sufficient sulfur dioxide is added to a fruit juice buffered at pH = 3.0 to reach an equilibrium SO_2 concentration of 1.0×10^{-2} mol dm^{-3}, the intensity of the red colour decreases to **one tenth** of its original value.

(i) Write an expression for the equilibrium constant for equilibrium (1) and use the data to calculate its value. [2]

(ii) Would this decolourisation of the preserved fruit juice be more or less severe at pH = 4.0 compared to pH = 3.0? Explain your answer. [2]

(c) Primary fermentation of blackberries produces wine and carbon dioxide. It undergoes a secondary fermentation to convert compound **J** (M_r =134) to compound **K** (M_r =90) to decrease the acidity of the wine.

Compounds **J** and **K** undergo the following reactions.

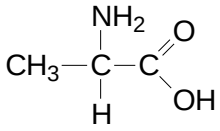
- Both **J** and **K** react with sodium carbonate and hot acidified $K_2Cr_2O_7$, but not with 2,4–dinitrophenylhydrazine.
- Both **J** and **K** react with excess hot concentrated H_2SO_4, but only **J** gives a mixture with a pair of cis-trans isomers.
- 0.234 g sample of **J** reacts completely with 35 cm^3 of 0.10 mol dm^{-3} NaOH(aq).
- **K** give a yellow precipitate with alkaline aqueous iodine.
- 7.5×10^{-4} mol of **K** produces 18 cm^3 H_2 gas at r.t.p. when excess Na is added.

Use the information above to deduce the structures of compounds **J** and **K**. Explain all the reactions involved. [5]

(d) Pyruvic acid, CH_3COCO_2H, can be produced from compound **K**. Explain why pyruvic acid is more acidic than benzoic acid. [2]

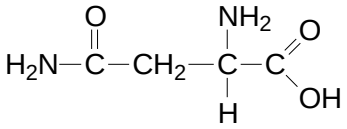
(e) Trace amount of amino acids could be found in fruits.

One of the amino acids, alanine, has the following structure.



(i) Suggest suitable reagents and conditions, and the structures of intermediate compounds formed, in the 3-steps synthesis of alanine from pyruvic acid. [4]

(ii) Describe a simple chemical test that you would carry out to distinguish alanine from asparagine.



asparagine

State the expected observations. [2]

[Total: 20]

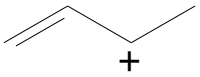
Section B

Answer **one** question from this section.

4 (a) Alkenes are commonly used as a precursor to make halogenalkanes.

(i) Describe the mechanism for the reaction of 1 mol of buta−1,3−diene with 1 mol of HBr. Show any relevant lone pairs, dipoles and charges, and indicate the movement of electron pairs with curly arrows.

The intermediate of the mechanism is shown below.

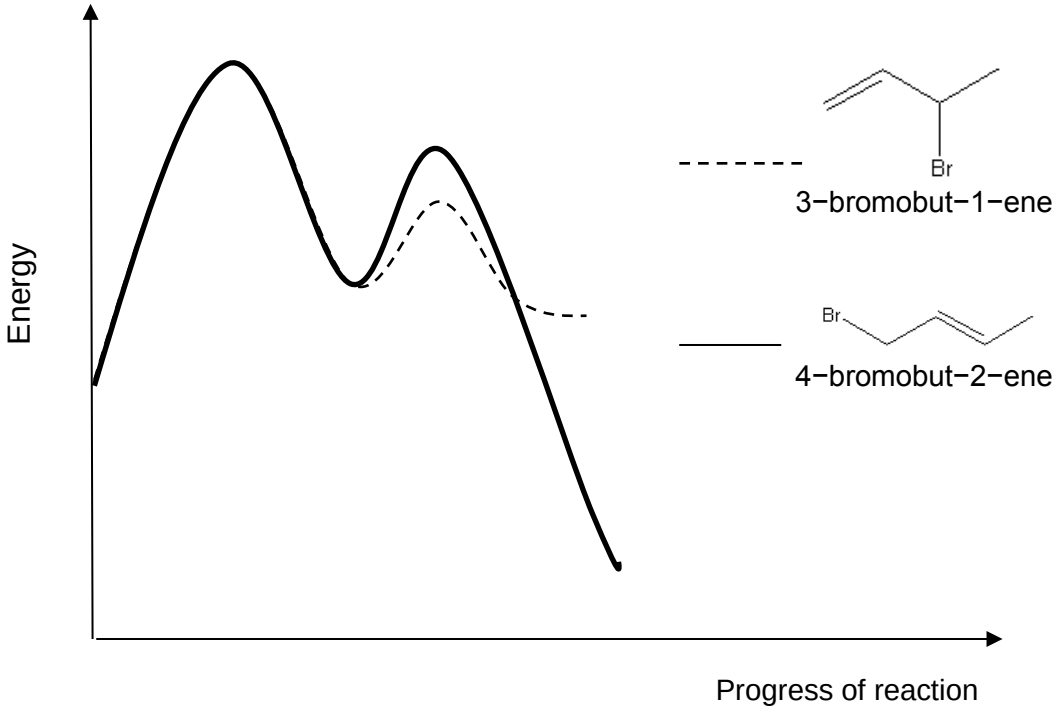


[3]

(ii) The intermediate in the above reaction in **(i)** can undergo a rearrangement to give a **primary** carbocation.

Draw the structure for the primary carbocation formed and show, with arrows, how the intermediate can be rearranged. [2]

(b) The diagram below shows the energy profile diagram for the formation of the products of the reaction of 1 mol of buta−1,3−diene with 1 mol of HBr.

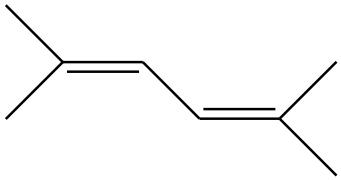


(i) Draw the Boltzmann distribution curve for the step 2 of the above reaction. Indicate their difference in activation energies that resulted in the two products formed. [2]

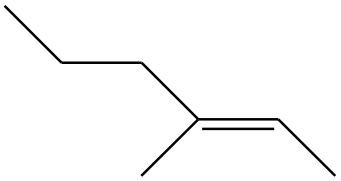
(ii) With reference to the Boltzmann distribution curve for the reaction, explain why 3−bromobut−1−ene is formed faster. [3]

(iii) With respect to the number of substituents on the C=C bond, suggest why 4−bromobut−2−ene is more stable than 3−bromobut−1−ene. [1]

(c) Separate bottles containing the following alkenes were mixed up.



compound **L**



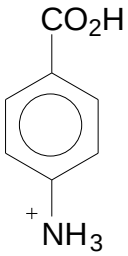
compound **M**

(i) Suggest a distinguishing test to determine the identity of the compounds and give the balanced equation for any reaction that occurs. [4]

(d) Arenes consist of 3 C=C bonds separated by C–C bonds, yet they exhibit different properties from alkenes.

(i) Explain why arenes cannot undergo electrophilic addition, unlike alkenes. [1]

(ii) Suggest suitable reagents and conditions, and the structures of intermediate compounds formed, for the synthesis of compound **N** from benzene.



compound **N** [4]

[Total: 20]

5 (a) Calcium chloride, $CaCl_2$, is commonly used as a desiccant to reduce humidity level of an enclosed space to allow the storage of articles that are prone to damage in high humidity. The lattice energy of $CaCl_2$ can be calculated from a Born–Haber cycle using the relevant data in the *Data Booklet* and the following data.

Enthalpy change of atomisation of calcium	= +177 kJ mol^{-1}
Enthalpy change of formation of calcium chloride, $CaCl_2$(s)	= −795 kJ mol^{-1}
First electron affinity of chlorine	= −364 kJ mol^{-1}

(i) Explain, with the aid of an equation, what is meant by *lattice energy* of $CaCl_2$. [1]

(ii) Construct a Born-Haber cycle for the formation of $CaCl_2$ and use it to calculate the lattice energy of $CaCl_2$. [4]

(iii) Explain how you would expect the magnitude of the lattice energy of aluminium oxide, Al_2O_3(s) might compare to that of $CaCl_2$(s). [2]

(iv) Calcium chloride can be prepared by the reaction of calcium oxide and chlorine gas.

$$2CaO(s) + 2Cl_2(g) \rightarrow 2CaCl_2(s) + O_2(g)$$

Using the data above and given that the enthalpy change of formation of calcium oxide is −635 kJ mol^{-1}, construct an energy cycle and use it to calculate the enthalpy change of reaction for the equation above. [2]

(b) Calcium chloride, $CaCl_2$ is a solid with a high melting point (775 °C) whereas aluminium chloride, $AlCl_3$, sublimes at 178 °C.

(i) Explain the difference in melting points between these two chlorides in terms of their structure and bonding. [3]

(ii) Aluminium chloride is a halogen carrier where it reacts with chloromethane gas to generate the electrophile in the electrophilic substitution of hydrogen atoms in benzene:

$$AlCl_3 + CH_3Cl \rightarrow AlCl_4^- + CH_3^+$$

Explain why aluminium chloride can react with chlorine gas. Draw a diagram to illustrate the bonding in $AlCl_4^-$ [2]

(iii) The reaction in **(ii)** is an important step in the synthesis of 3–methylbenzoic acid, a precursor used to make DEET, a well-known insect repellent.

Suggest suitable reagents and conditions for a 3-steps synthesis of 3–methylbenzoic acid from benzene. [3]

(c) A 0.505 g sample of gaseous aluminium chloride takes up a volume of 90 cm^3 at 300 °C and 10^5 Pa.

(i) Under what conditions of temperature and pressure would you expect the behaviour of gaseous aluminium chloride to be most like that of an ideal gas? [1]

(ii) Calculate the M_r of the vapour at this temperature. [1]

(iii) With reference to your answer in **(ii)**, draw a displayed formula to show the type of bonding in the molecules of the vapour. [1]

[Total: 20]

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