NATIONAL JUNIOR COLLEGE
SH2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME			
SUBJECT CLASS		REGISTRATION NUMBER	

CHEMISTRY **9729/03**
Paper 3 Free Response **Wednesday 18 September 2019**
2 hours

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

READ THE 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 staples, paper clips, glue or correction fluid.

Section A
Answer **all** questions.

Section B
Answer **one** question.

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

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 from this section.

1 Potassium is an element found in Period 4 of the Periodic Table.

(a) **(i)** Write an equation for the second ionisation energy of potassium. [1]

(ii) Fig 1.1 shows the second ionisation energy for the consecutive elements from Period 3 and Period 4.

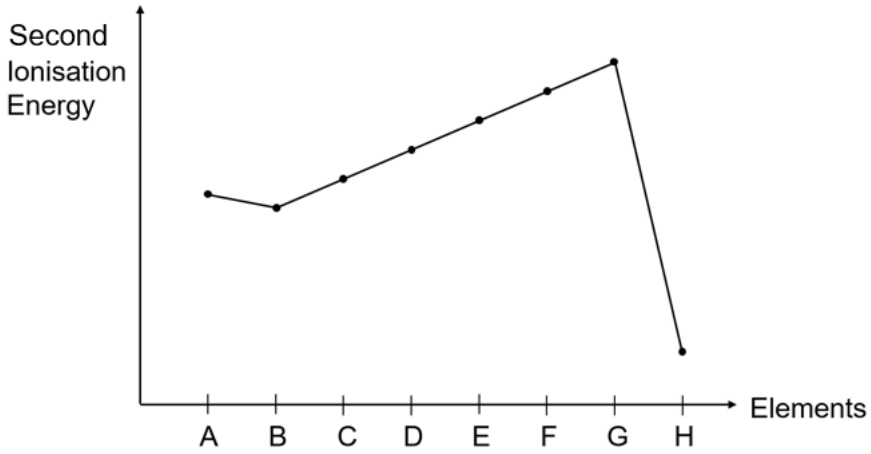


Fig 1.1

Suggest which of the above elements, **A** to **H**, is potassium. [2]

(b) When 0.400 g of potassium dichromate(VI), $K_2Cr_2O_7$, was heated using a strong flame, a yellowish green solid mixture was obtained and a gas was evolved. The gas collected ignited a glowing splint. Upon adding water to the yellowish green solid, part of the solid dissolved to give a yellow solution of K_2CrO_4, leaving a green solid.

(i) State the identity of the gas. [1]

(ii) The green solid that remained was collected and dried. It weighed 0.052 g and was found to be 68.4% chromium by mass and contains only chromium and oxygen.

Determine the chemical formula of the green solid. [2]

(iii) Using your answers to **b(i)** and **b(ii)**, write the equation for the decomposition of potassium dichromate(VI). [1]

(c) State **two** physical properties of chromium that differs from calcium.
Explain the reasons for those differences. [2]

(d) Vanadate(V) ion, VO_3^-, changes into pale yellow oxovanadium(V) ions, VO_2^+, when acid is added. Upon addition of excess zinc, the pale yellow solution changes to blue, to green and finally to violet.

(i) With the aid of an equation, explain the type of reaction that occurs when vanadate(V) ion changes into oxovanadium(V) ions. [2]

(ii) Explain why vanadium is able to exhibit variable oxidation states. [1]

(iii) With the aid of the *Data Booklet*, deduce the final oxidation state of vanadium in the violet solution. [3]

Solid vanadium(V) oxide, V_2O_5, is used as a catalyst for reaction 1.

reaction 1: $SO_2(g) + \frac{1}{2}O_2(g) \rightarrow SO_3(g)$

(iv) State the type of catalysis and outline the mode of action when V_2O_5 is used for reaction 1. [3]

(v) NO_2 can also act as a catalyst for reaction 1.

Write two equations to show how NO_2 acts as a catalyst in reaction 1. [2]

[Total : 20]

2 Lithium oxide, Li_2O, is used in traditional ceramic glazing to create a blue hue with copper on ceramics.

(a) Using the data below and any appropriate data from the *Data Booklet*, construct a labelled energy level diagram to calculate the standard enthalpy change of formation of $Li_2O(s)$.

	/ kJ mol^{-1}
first electron affinity of oxygen	–141
second electron affinity of oxygen	+798
lattice energy of lithium oxide	–2863
standard enthalpy change of atomisation of lithium	+159

[5]

(b) Lithium oxide is produced during the thermal decomposition of lithium peroxide, Li_2O_2, at 450 ^oC.

$$Li_2O_2(l) \longrightarrow Li_2O(s) + \frac{1}{2}O_2(g)$$

(i) Given that the standard enthalpy change of formation of $Li_2O_2(l)$ is –606 kJ mol^{-1} and using your answer in **(a)**, calculate the enthalpy change for the thermal decomposition of Li_2O_2. [1]

(ii) Explain why the thermal decomposition of Li_2O_2 is feasible. [2]

(c) Table 2.1 gives the melting points of two lithium ionic compounds.

compound	melting point / ^oC
Li_2O	1400
Li_2O_2	195

Table 2.1

Explain the difference in the melting points. [2]

(d) Similar to lithium peroxide, Li_2O_2, lithium nitrate, $LiNO_3(s)$, undergoes thermal decomposition to produce oxygen and a brown gas.

(i) Write a balance equation, with state symbols, for the thermal decomposition of lithium nitrate. [2]

(ii) Among the Group 1 metal nitrates, only lithium nitrate undergoes thermal decomposition.

Explain why lithium nitrate can undergo thermal decomposition. [2]

(e) Ethylenediamine tetraacetate, $[EDTA]^{4-}$, is a chelating agent that is widely used to remove transition metal ions such as copper(II) ions from aqueous solutions.

(i) Suggest a synthesis of ethylenediamine tetraacetate, $[EDTA]^{4-}$, starting from methanal and 1,2−diaminoethane ($NH_2CH_2CH_2NH_2$), according to the scheme in Fig. 2.1. Deduce the structure of compound **A**. Include reagents and conditions for all reactions, and the structures of all other intermediate compounds, in your answer.

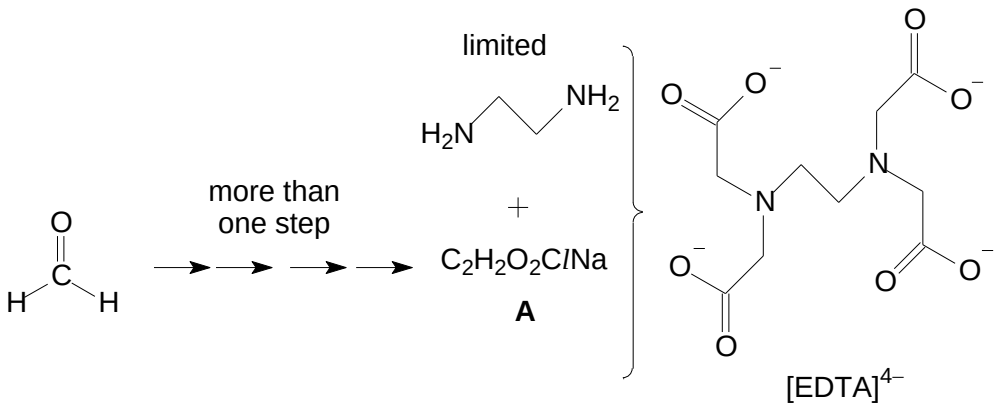


Fig 2.1

[5]

(ii) When aqueous ammonia is added to a solution of $CuSO_4$, a blue precipitate is formed which dissolves in excess aqueous ammonia to give a deep blue solution. On addition of $Na_4(EDTA)$ solid to the mixture, the colour of the solution turns light blue.

Suggest explanations for the above observations, writing equations as appropriate.
[3]

[Total : 22]

3 (a) Phenol is a white crystalline solid that is volatile. It is mildly acidic and requires careful handling as it can cause chemical burns.

Table 3.1 shows the physical properties for phenol and its derivatives.

compound	melting point / °C	K_a / mol dm^{-3}
phenol	41	1.12×10^{-10}
2−nitrophenol	46	5.89×10^{-8}
4−nitrophenol	114	7.08×10^{-8}

Table 3.1

(i) Explain the difference in melting points between 2−nitrophenol and 4−nitrophenol. [2]

(ii) Explain the difference in the acidities of phenol and 2−nitrophenol. [2]

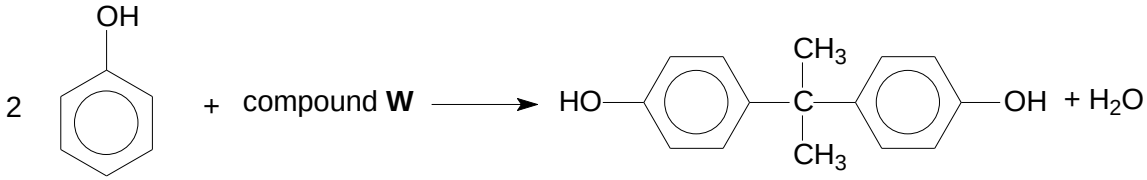
(iii) Suggest how 2,6−dibromo−4−nitrophenol can be synthesised from phenol in a 2−step synthesis. In your synthesis, you should state the reagents and conditions needed for each step, and show clearly the structure of any intermediate compounds. [3]

(b) When aqueous neutral $FeCl_3$ is added to a solution containing phenol, a violet solution containing the complex ion $[Fe(C_6H_5O)_6]^{3-}$ is formed.

(i) Draw the structure of the complex ion. [1]

(ii) The violet complex ion $[Fe(C_6H_5O)_6]^{3-}$ is not observed in **both** acidic and alkaline solutions. Suggest explanations for the above observation. [2]

(c) Phenol can react with compound **W** under suitable conditions to give bisphenol-A (BPA).



BPA

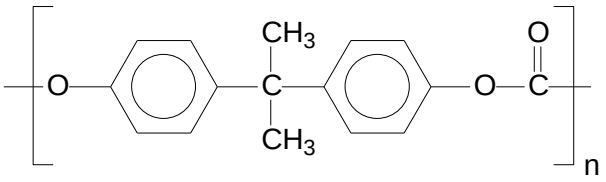
The use of the table of characteristic infra-red absorption frequencies for some selected bonds in the *Data Booklet* is relevant to this question.

Infra-red absorptions can be used to identity functional groups in organic compounds. For example, phenol shows absorption at 3200−3600 cm^{-1} due to the O−H bond.

The analysis of compound **W** shows absorptions at 1670−1740 cm^{-1}.

Identify the bond present in compound **W** and suggest its structure. [2]

(d) BPA can react with another monomer **X** to produce polycarbonates. Polycarbonates are commonly used in the manufacturing of water bottles.



Polycarbonates

(i) Identify the new functional group formed in the polycarbonates. [1]

(ii) Suggest the structure of monomer **X**. [1]

(iii) Research has shown that BPA can leach into beverages from the polycarbonate water bottles under certain conditions. Exposure to BPA is a concern because of possible health effects of BPA on the brain.

Discuss whether it is safe to consume cold lemon juice stored in a polycarbonate water bottle. [1]

(e) BPA can react with epoxides to form epoxy resins. Fig 3.1 shows the simplified equations for the reaction.

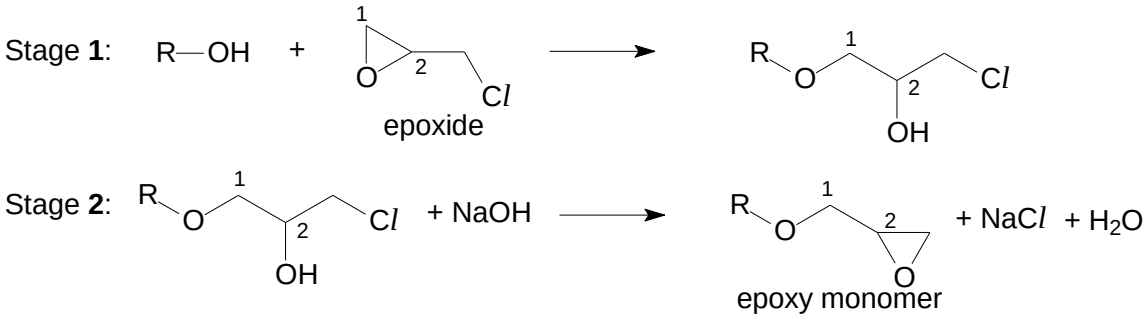


Fig 3.1

(i) For stage **1**, the phenol group of BPA acts as the nucleophile. Suggest why the nucleophile attacks C^1 instead of C^2. [1]

(ii) For stage **2**, state the type of reaction and the role of NaOH in the reaction. [2]

[Total : 18]

Section B
Answer **one** question from this section.

4 (a) Diphenylmethanone can be synthesized from methylbenzene in three steps as shown in Fig 4.1.

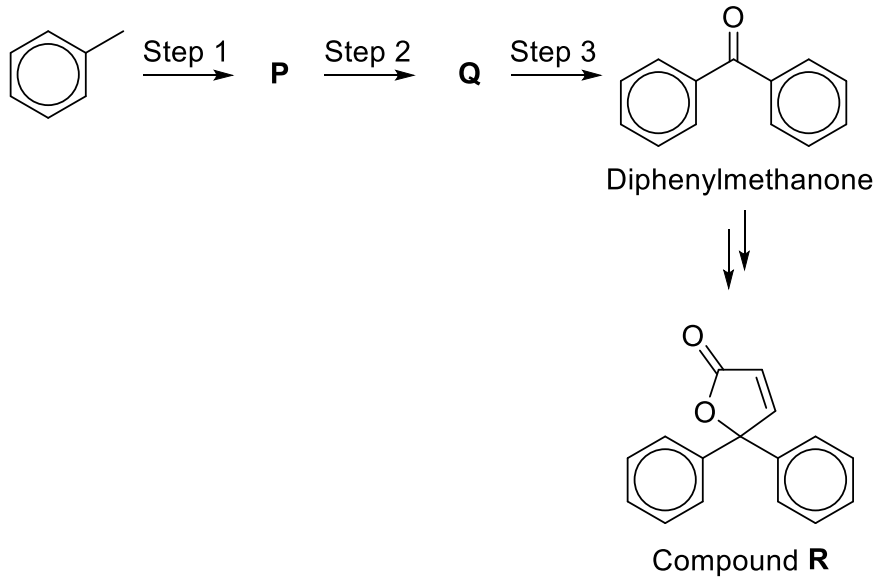
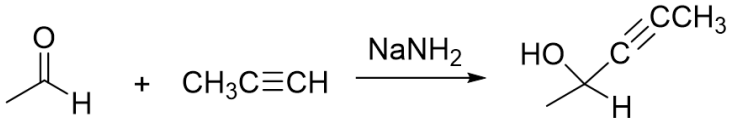


Fig 4.1

(i) Suggest the reagents and conditions for steps **1**, **2** and **3**, and draw the structures for compounds **P** and **Q**. [5]

(ii) When compound **R** is heated with acidified $KMnO_4$, compound **S** is formed as the only organic product. Suggest the structure of compound **S**. [1]

(b) Propyne, $CH_3C{\equiv}CH$, is a weak acid. It can react with an aldehyde in the presence of trace amount of strong base such as $NaNH_2$.



When propyne reacts with NH_2^-, propynyl ion, $CH_3C{\equiv}C^-$ is formed.

(i) State the type of reaction that occurred between propyne and ethanal. [1]

(ii) Describe the mechanism for this reaction. Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows. [2]

(iii) Suggest if the organic product formed from this reaction would rotate plane−polarised light. [2]

(c) The mechanism for the reaction between compounds **T** and **U** is as shown.

Step 1: **T** + **U** $\rightleftharpoons$ **V**

Step 2: **T** + **V** $\longrightarrow$ **W** (slow)

(i) Write a balanced overall equation for the reaction between compounds **T** and **U**. [1]

(ii) Write an expression for K_c for step 1, stating its units. [2]

(iii) Using the information given in the question and your answer to **c(ii)**, derive the rate equation for the reaction between compounds **T** and **U**. [2]

(iv) A concentration−time graph was plotted for step 1 as shown in Fig 4.2. Equilibrium was established at t_0. At t_1, a change was introduced.

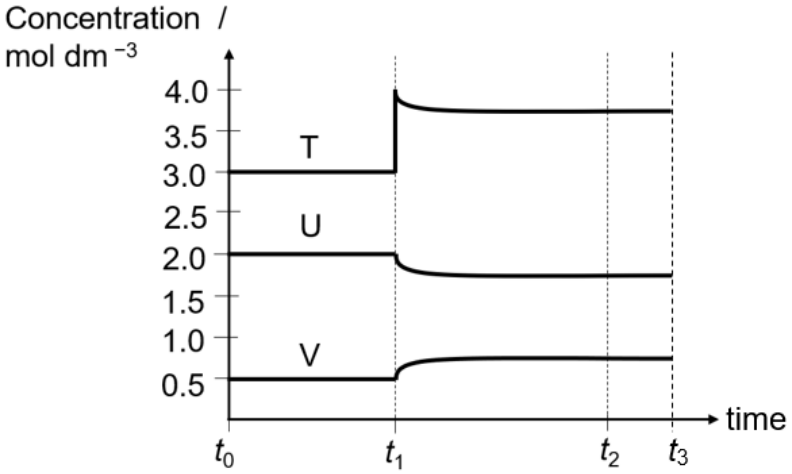


Fig 4.2

State the change that occurred at t_1. Explain the trend observed in the graph from t_1 to t_2. [2]

(v) Suggest whether there would be any change in the individual concentrations of compounds **T**, **U** and **V** when a catalyst is added to the reaction mixture at t_3. [2]

[Total : 20]

5 **(a)** Describe and explain the variation in volatility of the elements in Group 17. [2]

(b) *Use of the Data Booklet is relevant to this question.*

Explain the following observations in terms of the relative thermal stabilities of the hydrides of the Group 17 elements.

compound	HC*l*	HBr	HI
decomposition behaviour	does not decompose even on strong heating	strong heating yields reddish brown fumes of Br_2	purple fumes of I_2 obtained when red-hot rod is plunged into jar of HI

[2]

(c) State and explain the observations when separate solutions of chloride and iodide ions are mixed with aqueous silver nitrate, followed by excess aqueous ammonia. [3]

(d) Carbon monoxide in a sample of polluted air can readily be determined by passing through solid iodine(V) oxide, I_2O_5, to give carbon dioxide and iodine.

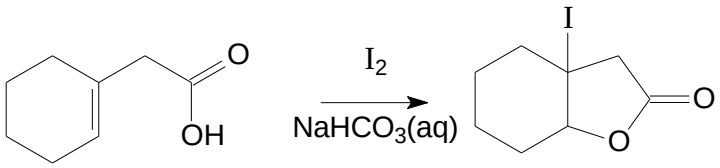
(i) Write a balanced equation for the reaction between carbon monoxide and iodine(V) oxide. [1]

(ii) The iodine produced is dissolved in a suitable solvent and titrated with aqueous sodium thiosulfate, $Na_2S_2O_3$.

1 dm^3 sample of air produced iodine that required 20.0 cm^3 of 0.10 mol dm^{-3} sodium thiosulfate to discharge the iodine colour.

Calculate the mass of carbon monoxide in this sample of polluted air. [2]

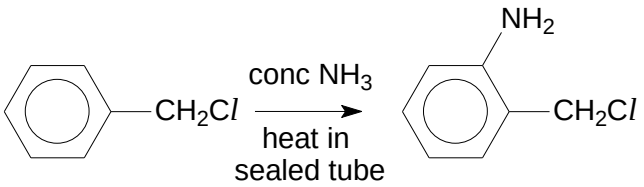
(e) In the presence of aqueous sodium hydrogencarbonate, iodine does not add across the C=C bond of compound **D** as might be expected. Instead, the following reaction occurs.



compound **D**

The first step of the mechanism involves a fast acid-carbonate reaction. Describe the mechanism for this electrophilic addition reaction. Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows. [2]

(f) A student attempted to make compound **E** from (chloromethyl)benzene as shown.



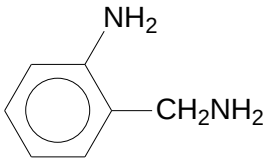
(chloromethyl)benzene compound **E**

However, a different product with molecular formula C_7H_9N was obtained.

(i) Draw the displayed formula of the product obtained from the reaction. [1]

(ii) Explain why compound **E** was not obtained. [1]

(g) The pK_b values of the two amine groups in compound **F** are 3.4 and 9.1.



compound **F**

(i) Copy the structure of compound **F** to your answer booklet and assign the pK_b values to the two amine groups. Explain your answer. [2]

(ii) Calculate the initial pH of 0.100 mol dm^{-3} of compound **F**. [2]

(h) Explain the observations when Br_2(aq) is added to the two samples.

sample	phenylamine	phenylamine dissolved in excess sulfuric acid
observations	orange Br_2 (aq) decolourises and white precipitate forms	orange Br_2 (aq) remains

[2]

[Total : 20]

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