NATIONAL JUNIOR COLLEGE
SH2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME			
SUBJECT CLASS		REGISTRATION NUMBER	

CHEMISTRY

9729/03
Paper 3 Free Response
27 August 2021
2 hours

Candidates answer on Question Paper.
Additional Materials: 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.

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

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

For Examiner's Use	
Section A	
1	**/20**
2	**/16**
3	**/24**
Section B	
4	**/20**
5	**/20**
Paper 3 Total	**/80**

This document consists of **28** printed pages.

Section A

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

1 **(a)** Nicotine ($C_{10}H_{14}N_2$) is a drug present in tobacco. In aqueous solution, nicotine ionises as shown.

$$C_{10}H_{14}N_2 + H_2O \rightleftharpoons C_{10}H_{15}N_2^+ + OH^- \qquad pK_b\ (C_{10}H_{14}N_2) = 6.0$$

(i) Calculate the pH of a 0.100 mol dm^{-3} $C_{10}H_{14}N_2$ solution. [2]

(ii) Suggest a suitable indicator for the titration of aqueous nicotine with HNO_3(aq). Explain your answer. [2]

(iii) Calculate the pH of a 5.00 dm^3 solution consisting of 0.100 mol dm^{-3} $C_{10}H_{14}N_2$ and 0.200 mol dm^{-3} $C_{10}H_{15}N_2^+$. [1]

(iv) Calculate the number of moles of HNO_3 that needs to be added to the solution in **(a)(iii)** to obtain a buffer solution of pH 7.40. [2]

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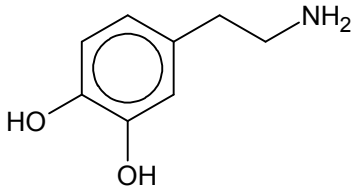
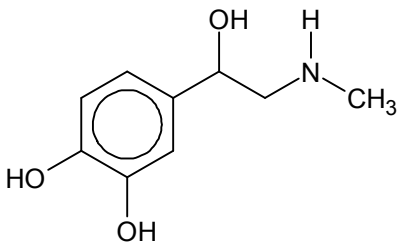
When a cigarette is smoked, nicotine-rich blood stimulates the release of many chemical messengers including dopamine and epinephrine.



dopamine



epinephrine

(b) **(i)** Name the type of isomerism exhibited by epinephrine and draw the isomers. [2]

(ii) Give the structure of the product when dopamine is reacted with excess concentrated HNO_3. [2]

(iii) A reaction between dopamine and chloromethane, CH_3Cl, forms a compound with formula $C_{11}H_{18}NO_2Cl$. Suggest a structure for this compound and how the yield of this compound can be maximised. [2]

(iv) Suggest a chemical test to distinguish the two chemical messengers, dopamine and epinephrine. [2]

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Cigarette smoke contains many harmful chemicals such as Period 4 elements, chromium, nickel and arsenic.

(c) Give the full electronic configuration of chromium and arsenic. [2]

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(d) Chromium and nickel are transition elements.

(i) State what is meant by the term *transition elements*. [1]

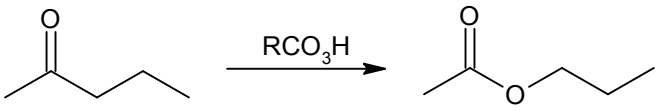
(ii) Suggest why the first ionisation energies of chromium and nickel are similar. [2]

[Total : 20]

2 Baeyer-Villiger reaction is an organic reaction that forms an ester from a ketone.

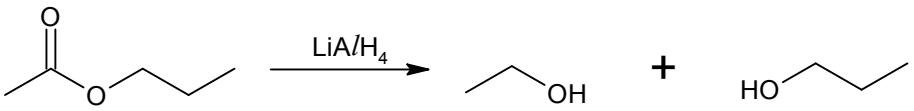
Pentan-2-one can be converted into propyl ethanoate using a peroxyacid, RCO_3H.

equation 2.1



Ester can be reduced by $LiAlH_4$ to give alcohols. An example of the reduction of propyl ethanoate is shown below.

equation 2.2



(a) **(i)** Suggest the type of reaction shown in equation 2.1. [1]

(ii) Suggest the products formed when ethyl benzoate is reacted with $LiAlH_4$. [2]

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(b) Fig 2.1 shows a reaction scheme involving a cyclic ester, compound **C**.

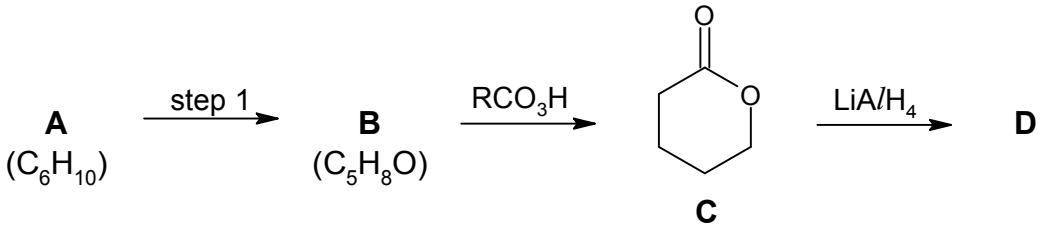

Fig 2.1

(i) State the reagents and conditions required for step 1 and suggest structures for the organic compounds **A**, **B** and **D**. [4]

(ii) Compound **C** can also be synthesised from $HOOC(CH_2)_3CH_2OH$.

Suggest the reagents and conditions required for this synthesis. [1]

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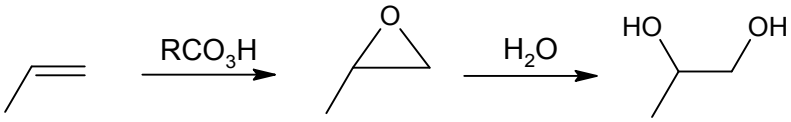
(c) Peroxyacid, RCO_3H, also converts alkene into epoxide, a cyclic ether with three-atom ring that approximates an equilateral triangle.

Epoxide reacts with water readily to give a diol.



Use your knowledge of VSEPR theory to explain the high reactivity of epoxide. [2]

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(d) Describe the mechanism for the reaction of propene with $Cl-I$.
In your answer, show any relevant charges, dipoles or lone pairs of electrons you consider important in this mechanism. [3]

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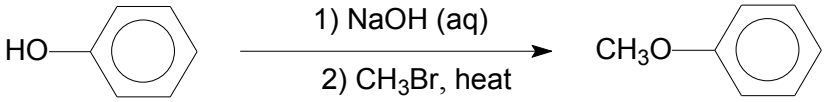
(e) Organic halogen compounds are widely used in synthetic reactions.

Bromoalkanes are often used in the synthesis of ethers from phenols in the Williamson ether synthesis, an example of which is shown below.



(i) Suggest why aqueous NaOH is required in this reaction. [1]

(ii) The rate of the synthesis decreases when $CH_3C\mathit{l}$ is used in place of CH_3Br.

With the use of the *Data Booklet*, suggest an explanation for this difference in the rate of reaction. [2]

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[Total : 16]

3 **(a)** Some data on three nitrogen-containing compounds are given in the table below:

compound	boiling point/ °C
NO_2	21
N_2O_4	21
N_2O_5	47

(i) With reference to the structure and bonding, explain why the boiling points of NO_2 and N_2O_4 are the same. [3]

(ii) N_2O_5 is a symmetrical molecule $O_2N{-}O{-}NO_2$.

Draw the full structural formula of N_2O_5 and suggest the N−O−N bond angle. [2]

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(b) reaction 3.1 $2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$ $\Delta H = +110$ kJ mol^{-1}

The overall order of reaction for reaction 3.1 is one and the reaction proceeds via a two-step mechanism.

(i) Sketch a graph of concentration of N_2O_5 against time for reaction 3.1. The reaction has a half-life of 5 minutes and N_2O_5 at an initial concentration of 2.00 mol dm^{-3}. [1]

(ii) Determine the value of the rate constant, k, for reaction 3.1, stating its units. [1]

(iii) The slow step of the two-step reaction mechanism produces a NO_3 intermediate.

Write equations to show a possible reaction mechanism for reaction 3.1. [2]

(iv) Sketch an energy profile diagram for the proposed mechanism for reaction 3.1. Label your diagram clearly, including the reactants and the products formed. [2]

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(c) reaction 3.2 $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $\Delta H = +58\ kJ\ mol^{-1}$

Some amount of dinitrogen tetroxide, N_2O_4, is placed in a gas syringe and allowed to achieve the equilibrium. At room temperature and pressure, 0.100 g of an equilibrium mixture of reaction 3.2 takes up a volume of 31.7 cm^3.

(i) Write the K_p expression for reaction 3.2. [1]

(ii) Calculate the average relative molecular mass of the mixture. [1]

(iii) Use your answers to **(c)(ii)** to calculate the percentage of N_2O_4 in the equilibrium mixture and hence the value of K_p (in atm) for reaction 3.2 at r.t.p. [3]

(iv) The gas mixture is compressed to a volume of 20 cm^3. Explain how would the percentage of N_2O_4 be affected as compared to your answer in **(c)(iii)**. [2]

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(d) NO_2, an air pollutant, is sometime found in car exhaust emissions.

(i) Give one environmental impact of NO_2. [1]

(ii) Explain how NO_2 is produced in car engine. [1]

(iii) To reduce pollution from motor vehicles, catalytic converters containing rhodium and platinum are fixed onto the exhaust pipes. These catalysts convert the pollutants to less harmful compounds.

Write an equation to show how catalytic converter removes CO and NO_2. [1]

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(e) NH_3, CH_3CONH_2 and $C_6H_5NH_2$ are nitrogen containing compounds.

Arrange these compounds in order of increasing basicity. Explain your answer. [3]

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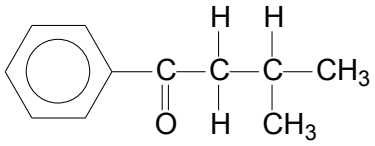
[Total: 24]

PLEASE TURN OVER

Section B

Answer **one** question from this section.

4 **(a)** When phenyl-3-methylbutanone reacts with bromine in the presence of UV light, three mono-brominated compounds are formed.



phenyl-3-methylbutanone

(i) Draw the structures of the three mono-brominated compounds and hence predict the ratio of the three compounds formed [2]

(ii) After bromination is carried out, the products are analysed. It is found that the three mono-brominated compounds are formed in approximately equal amount.

Suggest an explanation for the difference between this ratio and the one you gave in **(a)(i)** [2]

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(b) With reference to the data given below and any relevant data from the *Data Booklet*, answer the following questions concerning the chemistry of sodium bromide.

Standard enthalpy change of formation of solid sodium bromide	– 361 kJ mol^{-1}
First electron affinity of bromine	– 325 kJ mol^{-1}
Standard enthalpy change of atomisation of sodium	+ 107 kJ mol^{-1}
Lattice energy of sodium bromide	– 753 kJ mol^{-1}

(i) Define standard enthalpy change of formation of solid sodium bromide. [1]

(ii) Construct an energy level diagram and use it to calculate the standard enthalpy change of vapourisation of bromine. [5]

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(c) Long-term exposure to bromate(V) ions may increase consumers' risk of cancer, according to the US government's Environmental Protection Agency.

Aqueous bromate(V) ions acts as a strong oxidising agent in acidic solution as shown in the equation below:

$$2BrO_3^-(aq) + 12H^+(aq) + 10e^- \rightleftharpoons Br_2(aq) + 6H_2O(l) \quad E^\ominus = +1.48\ V$$

(i) Draw a labelled diagram to show how the standard electrode potential of the $BrO_3^-(aq)/Br_2(aq)$ electrode can be measured. [3]

(ii) When $AgNO_3(aq)$ is added to the $BrO_3^-(aq)/Br_2(aq)$ half-cell in the **(c)(i)** set-up, white precipitate is formed.

Explain the effect on the electrode potential of the half-cell. [2]

(iii) Effervescence is observed when excess zinc is added to acidified bromate(V) ions. The final solution is colourless.

Write balanced equations for the reactions. [3]

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(d) Describe and explain how the volatilities of the halogens vary from chlorine to iodine. [2]

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[Total : 20]

5 **(a)** Ethanedioate ion, $C_2O_4^{2-}$, is a found in some food such as spinach and beets.

(i) Draw the dot-and-cross diagram for $C_2O_4^{2-}$, which contains a C−C bond. [1]

(ii) All the carbon-oxygen bond lengths in ethanedioate ion, $C_2O_4^{2-}$ are determined to be a value between the C−O and C=O bond lengths. Account for this observation. [2]

(iii) When heated to high temperature, MgC_2O_4 undergoes thermal decomposition to give magnesium oxide, carbon monoxide and carbon dioxide. It is observed that thermal stability of Group 2 ethanedioate increases down the group.

Explain the thermal stability trend of Group 2 ethanedioate. [2]

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(b) Ethanedioic acid, $H_2C_2O_4$, is a toxic substance found in rhubarb leaves.

20.0 g of rhubarb leaves was crushed, and the ethanedioic acid present was extracted using water. The volume of the extracted sample was made up to 50.0 cm^3 using water.

10.0 cm^3 of the solution containing ethanedioic acid was pipetted into a conical flask and titrated with 0.020 mol dm^{-3} acidified potassium manganate(VII), $KMnO_4$. The following reaction occurs.

$$2MnO_4^-(aq) + 16H^+(aq) + 5C_2O_4^{2-} \longrightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g)$$

The average titre was 9.25 cm^3.

(i) State the endpoint colour change of this titration. [1]

(ii) Calculate the percentage mass of ethanedioic acid, $H_2C_2O_4$, present in the rhubarb leaves sample. [3]

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(c) One of the uses of carbon dioxide is in the manufacture of carbonated drinks.

Cylinders of pressurised carbon dioxide are used to produce cola, a carbonated drink. A commercial cola drink was manufactured using such cylinders, each with internal volume of 5 dm^3 and contains 2.58 kg of carbon dioxide.

(i) Calculate the pressure the carbon dioxide would exert inside the cylinder at 25 °C. [1]

(ii) The actual pressure inside each of the cylinder was found to smaller than the pressure you calculated in **(c)(i)**. Explain this observation. [1]

The amount of carbon dioxide dissolved in a carbonated drink is affected by three reversible reactions.

reaction 5.1 $CO_2(g) \rightleftharpoons CO_2(aq)$

reaction 5.2 $CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$

reaction 5.3 $H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$

(iii) Henry's law state that the amount of dissolved gas in a liquid is proportional to its partial pressure above the liquid.

$$K_H = \frac{[CO_2(aq)]}{P_{CO2}}$$

The Henry's law constant, K_H, for CO_2 is 3.4×10^{-2} mol dm^{-3} atm^{-1} at 25 °C.

The pressure of $CO_2(g)$ in an unopened sealed bottle is 250 kPa at 25 °C.

Calculate the concentration of dissolved CO_2 in the unopened bottle at 25 °C. [1]

(iv) Deduce the effect on the pH of the drink when the bottle is opened. Explain your reasonings in terms of the effect on the equilibrium reactions above. No calculation is required for this question. [3]

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(d) Sucrose is the most common natural food sweetener, often known as table sugar. In acidic solution, sucrose is readily hydrolysed to a 1:1 mixture of glucose and fructose. The reaction is catalysed by aqueous H^+ ions.

$$\underset{\text{(sucrose)}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+(aq)} \underset{\text{(glucose)}}{C_6H_{12}O_6} + \underset{\text{(fructose)}}{C_6H_{12}O_6}$$

A series of experiments were carried out at 25 °C to investigate the kinetics of this reaction, using 0.79 mol dm^{-3} sucrose solution and 1.25 mol dm^{-3} hydrochloric acid. The data obtained was presented in Table 5.1.

Table 5.1

Expt	Volume of sucrose /cm^3	Volume of HC*l* /cm^3	Volume of water /cm^3	Initial rate of reaction /mol dm^{-3} min^{-1}
1	20	20	10	0.00125
2	20	30	0	0.00188
3	10	30	10	0.000938

(i) Explain why varying volume of water was used in the 3 experiments. [1]

(ii) Using the data in Table 5.1, deduce the rate equation and hence, calculate the rate constant for the reaction, stating its units. [4]

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[Total : 20]

Additional answer space

If you use the following pages to complete the answer to any question, the question number must be clearly shown.