



EUNOIA JUNIOR COLLEGE
JC2 Preliminary Examination 2020
General Certificate of Education Advanced Level
Higher 2

CANDIDATE
NAME

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CIVICS
GROUP

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INDEX
NUMBER

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CHEMISTRY

Paper 3 Free Response

9729/03

17 September 2020

2 hours

Candidates answer on the Question Paper

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, civics group, index number on all the work you hand in.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper. If addition space is required, you should use the pages at the end of this booklet. The question number must be clearly shown.

Section A

Answer **all** the questions

Section B

Answer **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.

For Examiner's Use	
Paper 3	
1	/ 22
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4	/ 20
5	/ 20
Total	/ 80

This document consists of **32** printed pages.

Section A

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

- 1 (a) Describe and explain the trend observed in the thermal stabilities of the carbonates of Group 2 elements. [3]
- (b) (i) Elements in period 3 can react with chlorine gas to form different chlorides. State the types of bonding in the chlorides of sodium, aluminium and silicon. [1]
- (ii) Write appropriate equations to illustrate the reactions, if any, when separate samples of sodium chloride, aluminium chloride and silicon chloride were added to excess water. [3]

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(c) Acids, bases and buffers play important roles in balancing biological systems.

(i) Explain what is meant by the term *buffer solution*.

Write equations to explain how an aqueous solution of ammonia and an ammonium salt maintains the pH when a little acid or base is added into it. [3]

(ii) Calculate the pH of the solution formed when 48 cm³ of gaseous ammonia (K_b of ammonia = 1.8×10^{-5} mol dm⁻³) is channeled into 20 cm³ of 0.05 mol dm⁻³ of sulfuric acid at room temperature and pressure.

Hence, predict the colour observed when a few drops of thymolphthalein is added to the resulting solution. [3]

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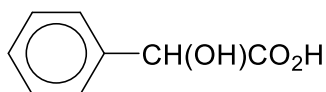
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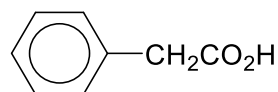
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(d) The following questions concern oxygen-containing organic compounds and their derivatives.

(i) The structures of mandelic acid and phenylacetic acid are shown below.



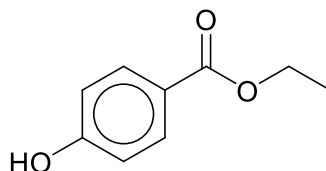
mandelic acid



phenylacetic acid

Suggest a simple chemical test that would distinguish mandelic acid from phenylacetic acid. State clearly the reagents and conditions used and write down the observations. [2]

(ii) Certain esters, like ethyl 4-hydroxybenzoate, are used as permitted anti-fungal preservatives.



ethyl 4-hydroxybenzoate

Draw the structures of the compounds formed when ethyl 4-hydroxybenzoate reacts with

- dilute NaOH, heat
- dilute HNO₃ at room temperature

[3]

(iii) **A**, C₄H₆O₄, is a neutral compound. When **A** is heated with reflux with aqueous sulfuric acid, it gives an organic acid **B**, C₂H₂O₄. On warming with concentrated sulfuric acid, **B** releases a mixture of a neutral toxic gas and an acidic gas which forms white precipitate with aqueous calcium hydroxide.

Suggest a possible identity of both **A** and **B**. Write balanced equations for the above reactions involving **A** and **B**. [4]

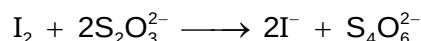
[Turn Over

- 2 (a) The following method was used to determine the concentration of dissolved oxygen in water at 288 K.

Approximately 700 cm³ of distilled water were shaken with air at 288 K for some time. 500 cm³ of this water was then placed in a 500 cm³ graduated flask.

1.00 cm³ of concentrated aqueous sodium hydroxide was delivered into the flask below the surface of the liquid, followed by 1.00 cm³ of concentrated aqueous manganese(II) chloride in the same way. The contents were gently agitated for a few minutes before allowing the precipitate to settle.

The stopper was then removed for the addition of potassium iodide crystals, followed by approximately 5 cm³ of concentrated hydrochloric acid. The contents of the flask were then titrated against 0.0200 mol dm⁻³ of sodium thiosulfate solution using starch as an indicator.



- (i) When sodium hydroxide and manganese(II) chloride were mixed, it caused the initial precipitation of manganese(II) hydroxide. This initial precipitate of manganese(II) hydroxide was oxidised by dissolved oxygen to form manganese(III) hydroxide as the only product.

Using oxidation states or otherwise, determine the number of moles of oxygen required to produce one mole of manganese(III) hydroxide. [2]

- (ii) In the presence of hydrochloric acid, manganese(III) hydroxide oxidises iodide ions to form iodine while itself is reduced to manganese(II) ions. Write an equation for this reaction. [1]

- (iii) The volume of aqueous thiosulfate required in the above titration was 30.00 cm³. Calculate the concentration of dissolved oxygen in water in mol dm⁻³. [3]

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- (b)** Explain why Co^{3+} is unstable in aqueous solution, but $[\text{Co}(\text{NH}_3)_6]^{2+}$ is stable. Support your answers with data from the *Data Booklet* where appropriate. [2]

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- (c) Copper minerals often contain copper sulfide mixed with sulfides of silver and zinc. After roasting in air to produce the oxides and reduction to the crude metals with carbon, the solid impure copper is purified with electrolysis.

With the aid of relevant data from the *Data Booklet*, describe the electrode reactions that take place during this electrolysis, and explain in detail how each of the two impurity metals is removed from the copper. [4]

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- (d) Carbonyl compounds undergo many reactions involving different nucleophiles with the general equation shown in Fig 2.1, of which the formation of a cyanohydrin (where $X = \text{CN}$) is one.

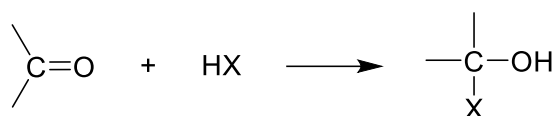


Fig 2.1

Chloral reacts in a similar way with water to give chloral hydrate as shown by the equilibrium in Fig 2.2. Chloral hydrate is a geminal diol, which is an organic compound that has two hydroxyl functional groups bonded to the same carbon atom.

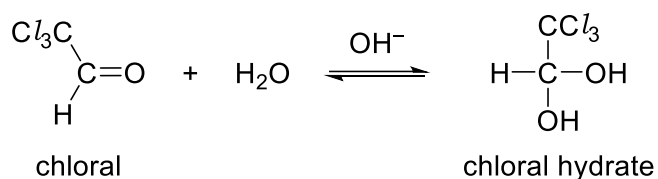


Fig 2.2

- (i) Both water and OH^- can act as nucleophiles. Explain why OH^- is a stronger nucleophile. [1]
- (ii) Given that OH^- acts as both a nucleophile and catalyst, suggest a mechanism for the reaction with chloral, showing clearly the flow of electrons. [3]
- (iii) Using your answer in (d)(ii), explain why the reaction shown in Fig 2.2 is faster when chloral is used as compared to $\text{CCl}_3\text{COCH}_3$. [1]
- (iv) State the type of reaction undergone by chloral with 2,4-dinitrophenylhydrazine and give the structural formula of the product formed. [2]

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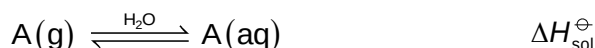
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PLEASE TURN OVER.

- 3** Henry's law is a gas law that states that, at a constant temperature, the amount of a given gas that dissolves in a given type and volume of liquid, is directly proportional to the partial pressure of that gas, in equilibrium with that liquid. The proportionality factor is called Henry's law constant.

Suppose gaseous A is in equilibrium with a solution of A in water:



The Henry's law solubility constant, K_H , of A in water, is given by

$$K_H = \frac{[A(aq)]}{p_{A(g)}}$$

where $p_{A(g)}$ is the partial pressure of A in the gaseous phase

$[A(aq)]$ is the concentration of A, in mol dm^{-3} , in the aqueous phase

- (a)** Soda manufacturers often inject cold liquid with pressurised carbon dioxide, then can the drink under high pressure.

On the average, a typical 355 cm^3 soda can possesses an internal pressure of 120 kPa when canned at 4°C , and 250 kPa when stored at room temperature.

The Henry's law constant, K_H , of CO_2 in water is $3.4 \times 10^{-7} \text{ mol dm}^{-3} \text{ Pa}^{-1}$ at room temperature.

- (i)** Explain why the internal pressure is so much higher than what is predicted by the ideal gas equation when the temperature is raised during storage. [1]
- (ii)** Calculate the concentration of CO_2 dissolved in a typical soda can at room temperature, in mol dm^{-3} . [1]

After opening a can of soda, the drink eventually goes flat when the dissolved CO_2 escapes into the atmosphere.

- (iii)** Assume that ambient air contains 0.04% by volume of CO_2 , and that the volume of a gas is proportional to the amount of the gas at the same pressure and temperature.

Calculate the partial pressure of CO_2 in air at room temperature and pressure, and hence the concentration of CO_2 in the can of flat soda. [2]

- (iv)** Using your answers to **(a)(ii)** and **(a)(iii)**, calculate the mass of CO_2 gas that has escaped into the atmosphere from the opened can of soda at room temperature, giving your answer to 4 decimal places. [1]

Glyoxal, OCHCHO , is the smallest dialdehyde. It is a crystalline solid, white at low temperatures and yellow near the melting point ($15\text{ }^{\circ}\text{C}$). The liquid is yellow, and the vapor is green.

The plot of $\ln(K_{\text{H}}/\text{mol dm}^{-3} \text{ Pa}^{-1})$ against $\frac{1}{T}/10^{-3} \text{ K}^{-1}$ for glyoxal over the temperature range between 278 K and 318 K is given in Fig. 3.1 below.

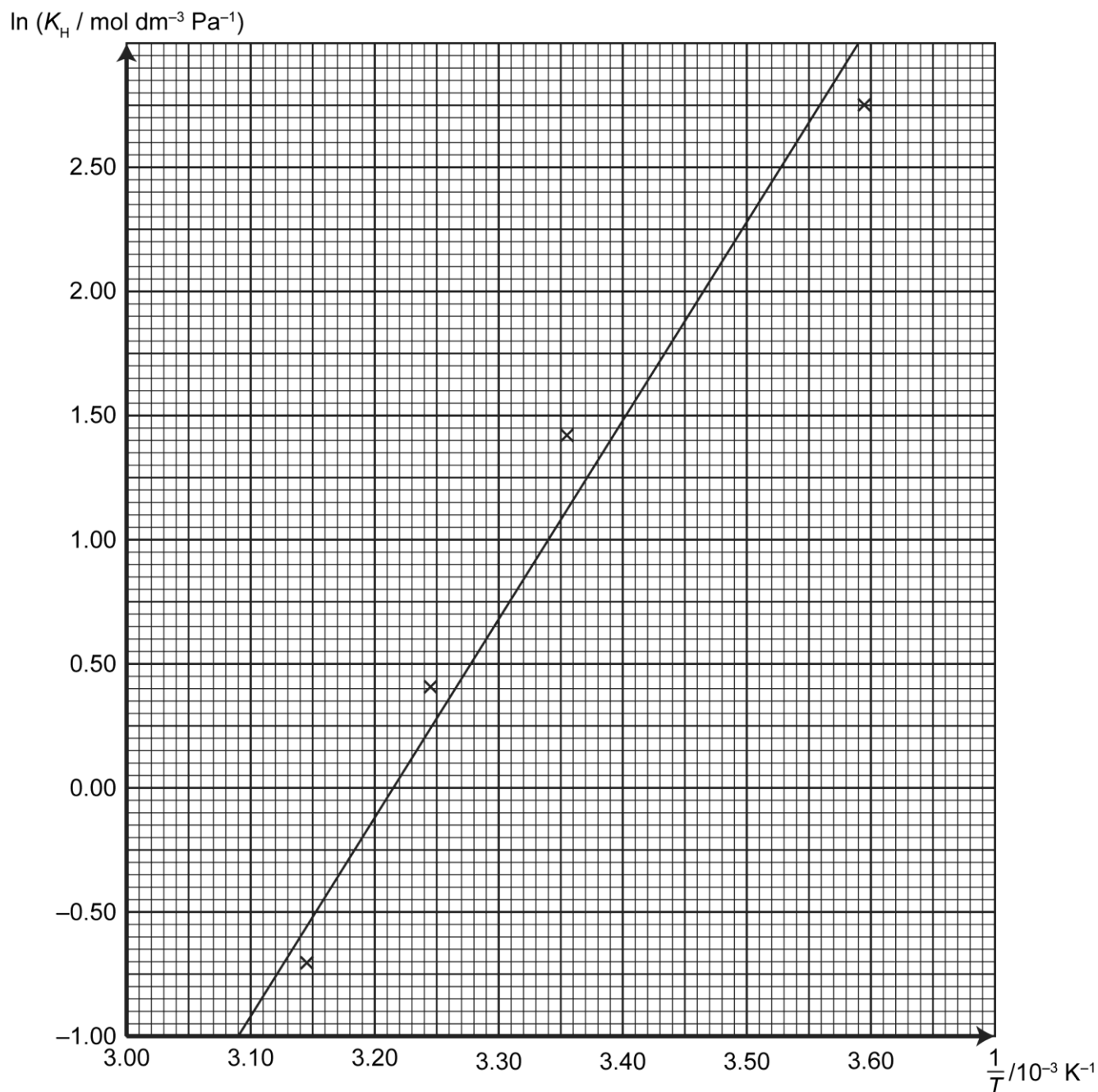


Fig. 3.1

- (b) Given that the standard Gibbs free energy change of solution, $\Delta G_{\text{sol}}^{\ominus}$, is related to the K_{H} , by the relationship

$$\Delta G_{\text{sol}}^{\ominus} = -RT \ln K_{\text{H}}$$

- (i) Determine using Fig. 3.1, a value for the standard enthalpy change of solution, $\Delta H_{\text{sol}}^{\ominus}$, of glyoxal. [2]
- (ii) Explain the significance of the sign of $\Delta H_{\text{sol}}^{\ominus}$ you have obtained in (b)(i) in terms of structure and bonding. [1]

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(c) Glyoxal can be converted into CO_2 .

(i) State the reagents and conditions for the conversion of glyoxal into CO_2 . [1]

(ii) Using Fig. 3.1, determine the Henry's law constant, K_H , for glyoxal at room temperature, in $\text{mol dm}^{-3} \text{ Pa}^{-1}$. [1]

(iii) Glyoxal is sold in bottles containing 40% of glyoxal by weight, which is approximately 11.5 mol dm^{-3} . Using your answer to (c)(ii), explain whether an opened bottle of glyoxal will rapidly lose glyoxal, like in the case of CO_2 in soda drinks. [1]

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Glyoxal is used in the synthesis of CL-20, a nitroamine explosive with the formula $C_6H_6O_{12}N_{12}$. One synthesis of CL-20 is shown in Fig. 3.2.

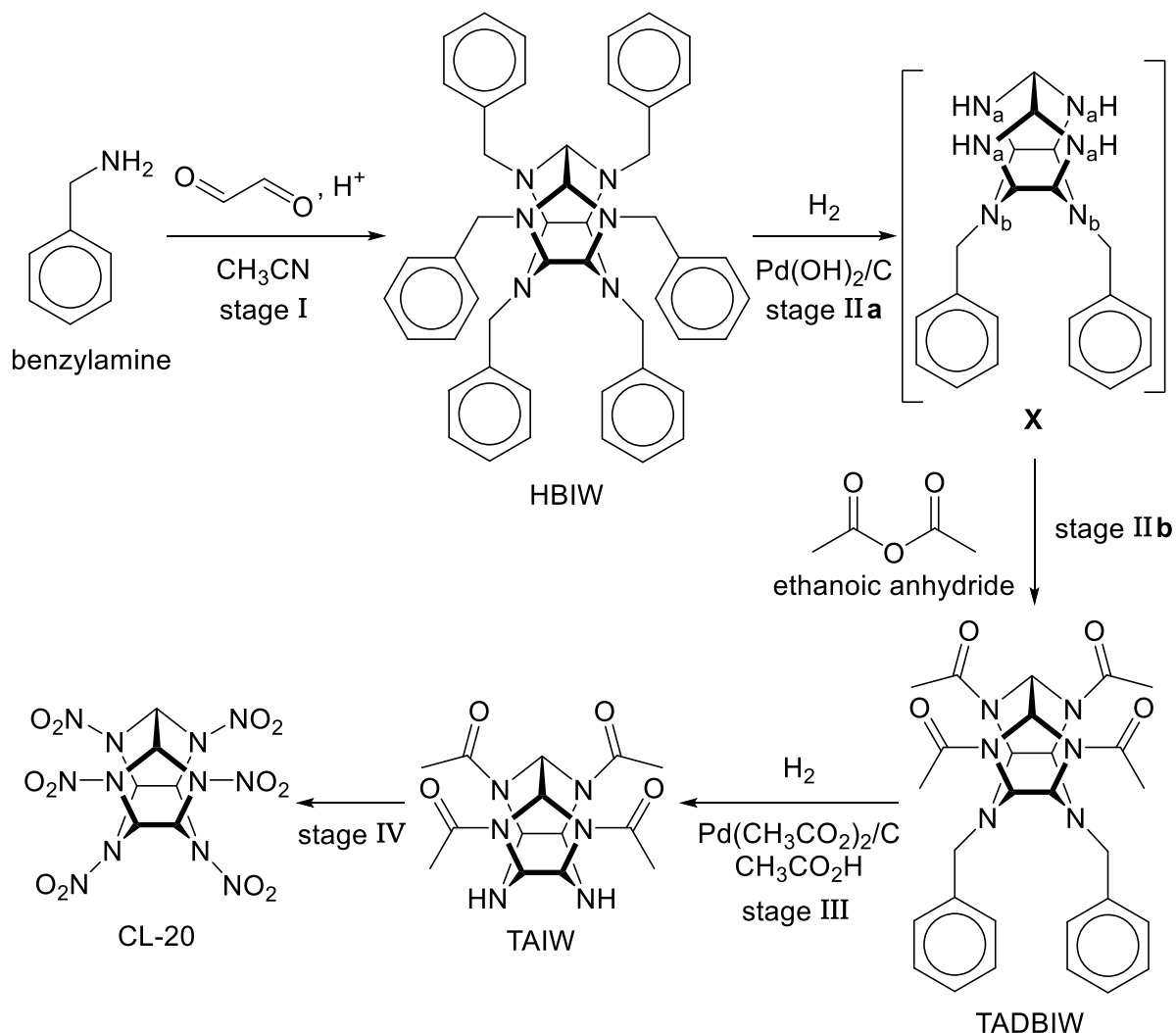
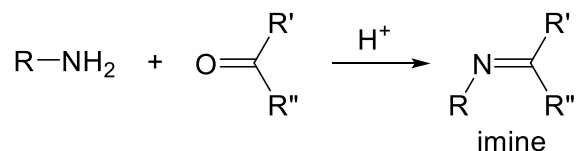


Fig. 3.2

(d) Stage I involves the reaction of glyoxal with benzylamine to give HBIW.

There are two types of reactions taking place in this stage, one involving the condensation between a primary amine and a carbonyl group to give an imine:



Name the **second** type of reaction involved, which results in the formation of the N-C-N linkage. [1]

(e) Stage **II** of the synthesis involves hydrogenation of HBIW in the presence of a palladium(II) catalyst, using ethanoic anhydride as the solvent, to give TADBIW. The reaction can be thought to proceed *via* the intermediate **X** which reacts with ethanoic anhydride *in situ*, to give TADBIW.

- (i) Explain why N_b is the more basic nitrogen atom among the two types of nitrogen atom, N_a and N_b , present in **X**. [1]
- (ii) Ethanoic anhydride is an ethanoylating agent like ethanoyl chloride. Explain why despite N_b being more basic than N_a , only N_a reacts with ethanoic anhydride in stage **IIb**. [1]

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(f) Methylbenzene is a by-product in stages **IIa** and **III**. State the type of reaction involved in these two stages. [1]

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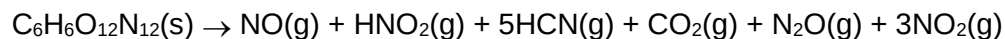
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(g) Stage **IV** involves the reaction of TAIW with the nitronium ion, NO_2^+ , to give CL-20. Suggest the reagents used. [1]

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- (h) (i) The detonation of solid CL-20, $\text{C}_6\text{H}_6\text{O}_{12}\text{N}_{12}(\text{s})$, leads to the formation of oxides of nitrogen, CO_2 and HCN , among other products:



Determine the standard enthalpy change of detonation of CL-20 using the data in Table 3.1.

Table 3.1

compound	$\Delta H_f^\ominus / \text{kJ mol}^{-1}$
CL-20(s)	+377.4
NO(g)	+91.3
HNO ₂ (g)	−79.5
HCN(g)	+135.1
CO ₂ (g)	−393.5
N ₂ O(g)	+81.6
NO ₂ (g)	+33.1

[2]

- (ii) By considering your answer in (h)(i) and the information given above, explain why the detonation of solid CL-20 is spontaneous. [1]

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[Total: 19]

Section B

Answer **one** question from this section.

- 4 (a) Nucleophilic substitution reactions can proceed via bimolecular or unimolecular mechanisms, which is often dependent on whether the halogenoalkane is primary, secondary, or tertiary.

Fig 4.1 shows the experimental data for a kinetics study for the reaction between aqueous sodium hydroxide and a solution of benzyl bromide, $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$, which is carried out at constant temperature.

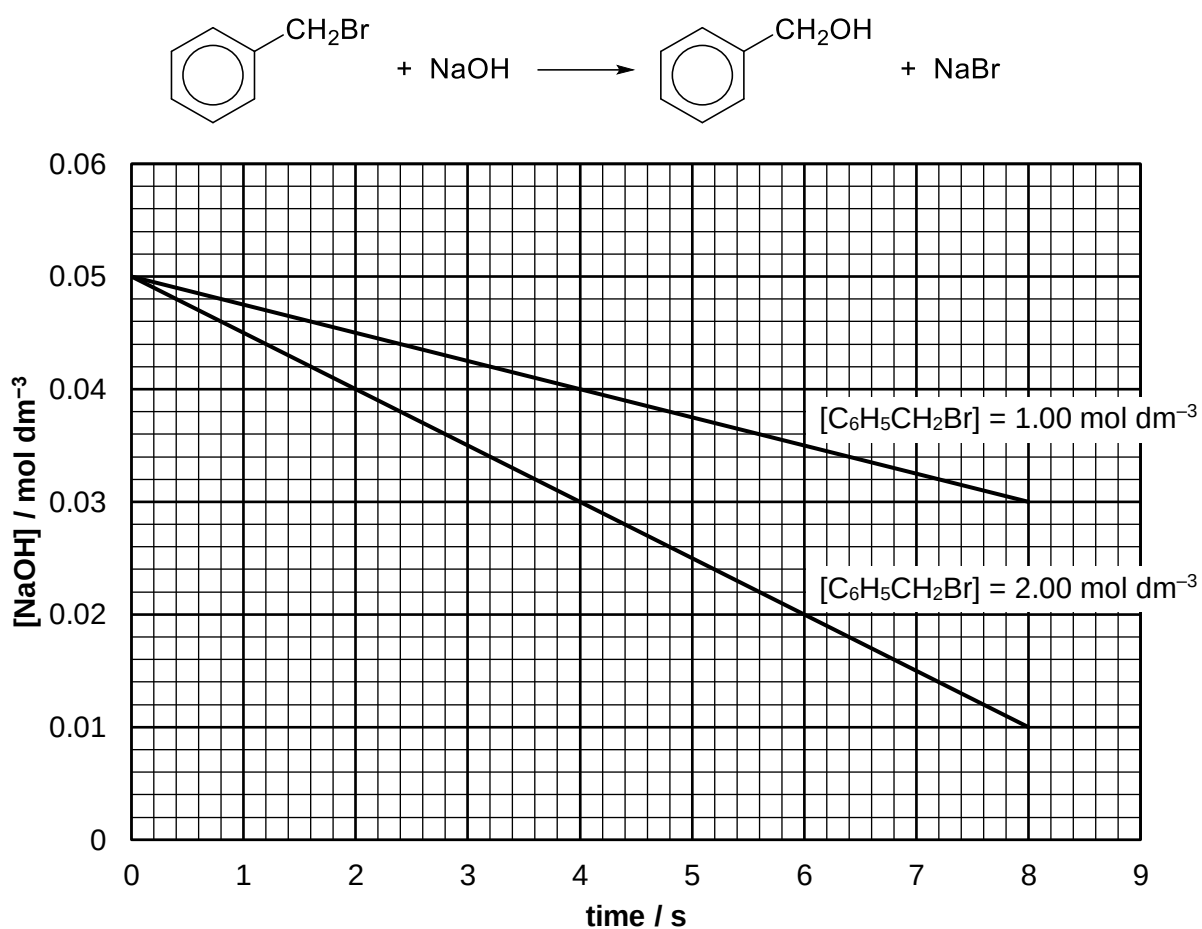


Fig 4.1

- (i) With reference to the graph shown in Fig 4.1, determine the orders of reaction with respect to NaOH and C₆H₅CH₂Br. [2]
- (ii) Hence, construct a rate equation for the reaction between NaOH and C₆H₅CH₂Br. [1]
- (iii) State and explain the type of mechanism for the reaction. Suggest how the structure of C₆H₅CH₂Br favours the type of mechanism you have stated. [2]
- (iv) Suggest and explain how the rate of reaction would change if aqueous potassium hydroxide of the same concentration was used in place of aqueous sodium hydroxide. [1]

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- (b) The concentration of Br^- ions in an aqueous sample of drinking water may be determined via a technique known as the Mohr method.

The Mohr method uses AgNO_3 as a titrant and K_2CrO_4 as an end point indicator. When AgNO_3 is first added, the Br^- ions precipitate as AgBr . The end point is indicated by the precipitation of the brick-red Ag_2CrO_4 .

At 298 K, the numerical values of the solubility product of AgBr and Ag_2CrO_4 are 5.40×10^{-13} and 3.01×10^{-12} respectively.

A 25.0 cm^3 of an analyte solution containing Br^- ions was titrated against $0.100 \text{ mol dm}^{-3}$ AgNO_3 solution. Before the titration, 0.100 cm^3 of $0.200 \text{ mol dm}^{-3}$ of K_2CrO_4 solution was added to the analyte. 24.55 cm^3 of AgNO_3 was required to reach the end point of reaction.

- (i) By determining the concentration of CrO_4^{2-} ions present at the end-point of the titration, calculate the concentration of Br^- remaining in the solution at the end point. [3]
- (ii) Hence, calculate the concentration of the Br^- ions present initially in the analyte solution. Assume that the precipitation of Ag_2CrO_4 causes a negligible change in the concentration of Ag^+ ions. [2]
- (iii) State and explain the effect of increasing pH on the accuracy of the titre value for the determination of Br^- ions obtained via the Mohr method. [1]

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(c) Compound **Q**, $\text{C}_8\text{H}_8\text{O}_2$ is formed when phenyl ethanoate, $\text{CH}_3\text{COOC}_6\text{H}_5$ is warmed with aluminum chloride. It is known that:

- Compound **Q** forms an orange precipitate with 2,4-DNPH, but does not produce a red precipitate with Fehling's solution.
- Compound **Q** reacts with alkaline aqueous iodine, followed by acidification, to produce compound **R**, $\text{C}_7\text{H}_6\text{O}_3$, which reacts with aqueous sodium hydroxide in a 1:2 mole ratio.
- Compound **Q** produces compound **S**, $\text{C}_8\text{H}_6\text{O}_2\text{Br}_2$, in bromine water.

(There is no need to explain the chemistry of the formation of compound **Q** from phenyl ethanoate.) [8]

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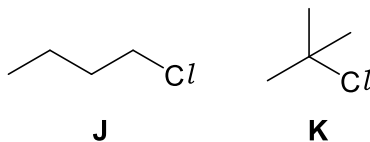
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5 Halocarbon compounds are compounds in which one or more carbon atoms are covalently bonded to one or more halogen atoms. They are important precursors in organic chemistry laboratories as they can be converted to many other different compounds.

- (a)** By means of a simple chemical test, distinguish between compounds **J** and **K**. You should include the reagents and conditions used, and the observations for each test compound.



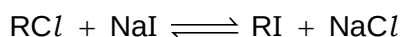
[2]

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- (b)** The Finkelstein reaction is another method that can be used to distinguish between primary and tertiary chloroalkanes. In this reaction, the test compounds are treated with NaI dissolved in acetone, (CH₃)₂CO.



The reaction conditions lead to an S_N2 reaction. The NaCl produced is insoluble in acetone, so a white precipitate will be observed if the chloroalkane tested undergoes a reaction.

- (i)** Explain how the Finkelstein reaction can be used to distinguish between primary and tertiary chloroalkanes. [1]
- (ii)** Describe the mechanism of the Finkelstein reaction with compound **J**.

Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows. [2]

- (iii)** Explain, with the aid of suitable diagrams, how NaI is able to dissolve in acetone. [2]
- (iv)** Explain why the equilibrium position lies largely to the right in the Finkelstein reaction. [1]

(c) To differentiate between a chloroalkane and an iodoalkane, separate portions of the two compounds can be heated with ethanolic silver nitrate. The respective insoluble silver halides will be produced.

- (i) The silver chloride formed from the chloroalkane dissolves upon addition of dilute ammonia, while the silver bromide formed from the bromoalkane does not.

Using relevant equations, account for the difference in the solubilities of the two halides in aqueous ammonia. [3]

- (ii) Given that the numerical value of the K_{sp} of silver chloride is 1.8×10^{-10} , show with the necessary calculations that the solubility of silver chloride is lower in a $0.200 \text{ mol dm}^{-3}$ solution of aqueous sodium chloride, as compared to water. [2]

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- (d) **L** is an optically inactive molecule with the molecular formula $C_8H_{16}O$. It decolourises aqueous bromine, produces white fumes with phosphorus pentachloride, but does not form a yellow precipitate with alkaline aqueous iodine. When heated with acidified $KMnO_4$, **L** is oxidised to produce **M** and carbon dioxide gas. When **M** is heated with a small amount of concentrated sulfuric acid, only a sweet-smelling cyclic compound **N** with the molecular formula $C_7H_{12}O_2$ is formed.

Deduce the structures of compounds **L**, **M** and **N**, giving reasons for your answer. [7]

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