EUNOIA JUNIOR COLLEGE
JC2 Preliminary Examination 2021
General Certificate of Education Advanced Level
Higher 3

CANDIDATE NAME	

CIVICS GROUP	2	0	–			INDEX NUMBER		

CHEMISTRY

9813/01

Paper 1

23 September 2021

2 hours 30 minutes

Candidates answer on Question Paper.

Additional Materials: Data Booklet
Insert

READ THESE INSTRUCTIONS FIRST

Write your name, civics group and registration 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 staplers, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper. If additional 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** questions.

Section B
Answer **two** questions.

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	
Section A	
1	**/ 20**
2	**/ 11**
3	**/ 10**
4	**/ 19**
Section B	
5	**/ 20**
6	**/ 20**
7	**/ 20**
Total	**/ 100**

This document consists of **35** printed pages and **1** blank page.

Section A

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

1 The information provided in the insert is taken from several published scientific articles. Other published articles may not agree with all of this information.

You should read the whole insert before you start to answer any questions and use the information it contains to answer the questions.

(a) **(i)** Write an equation for the main reaction in the carbonator, including state symbols. [1]

(ii) Suggest a likely source for the calcium carbonate input. [1]

(iii) Besides CO_2, suggest the identity of two other gases which are likely to be the main constituent of flue gases. [1]

(iv) With reference to your answer to **(a)(iii)**, suggest the principle component of Gas Y exiting from the carbonator. [1]

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(b) One of the impurities in flue gases is sulfur dioxide from the combustion of sulfur-containing fuels. This can react in the carbonator to form calcium sulfate, which can accumulate over successive cycles and reduce the efficiency of the process.

(i) Write an equation for the reaction of sulfur dioxide with calcium carbonate and oxygen to give two products, of which one is calcium sulfate. [1]

(ii) By comparing the thermal stability of calcium sulfate and calcium carbonate, explain why calcium sulfate accumulates over successive cycles. [3]

(iii) Name another impurity in flue gases and explain how this impurity comes about. [2]

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(c) Direct air capture (DAC) is a process which takes carbon dioxide directly from the air therefore avoiding any sulfur dioxide contamination. However, this process can be expensive to run due to the energy required to overcome thermodynamic barriers.

(i) Besides avoiding sulfur dioxide contamination, state the main difference between using flue gas and air as the source of CO_2. [1]

(ii) Write an equation, including state symbols, for the reaction in the

- air contactor
- pellet reactor. [2]

(iii) Water is consumed in the slaker, but the demand for water is balanced in the overall process. Use your answer to **(c)(ii)** to explain why this is so. [1]

(iv) Use your answer to **(c)(ii)** and the standard enthalpy change of formation data at 298 K given below, calculate the standard enthalpy change for the reaction which occurs in the air contactor.

compound	$\Delta H_f^{\ominus}$ / kJ mol^{-1}
$CaO(s)$	–634.9
$CaCO_3(s)$	–1207.6
$Ca(OH)_2(s)$	–985.2
$KOH(aq)$	–482.4
$K_2CO_3(aq)$	–1181.9
$CO_2(g)$	–393.5
$H_2O(l)$	–285.8

[2]

(v) What is the standard enthalpy change at 298 K for the sum of the reactions in the four reactors. Explain your answer. [2]

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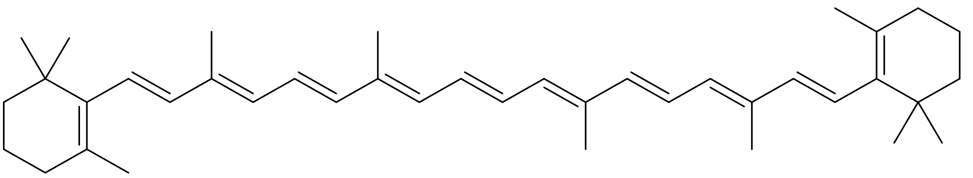
(d) The calcium loop in Fig. 1.1 uses a solid sorbent, CaO, while the DAC in Fig. 1.2 uses an aqueous basic solution, KOH(aq), as the capture media.

Give one disadvantage each, for the use of solid CaO sorbent and the use of aqueous KOH solution as the capture media. [2]

[Total: 20]

2 **(a)** β-carotene is an organic, strongly coloured pigment abundant in fungi, plants and fruits. It absorbs most strongly in the wavelength of 448 nm, and is often displayed as a red-orange pigment.



β-carotene

The absorption spectrum of β-carotene is shown in Fig. 2.1

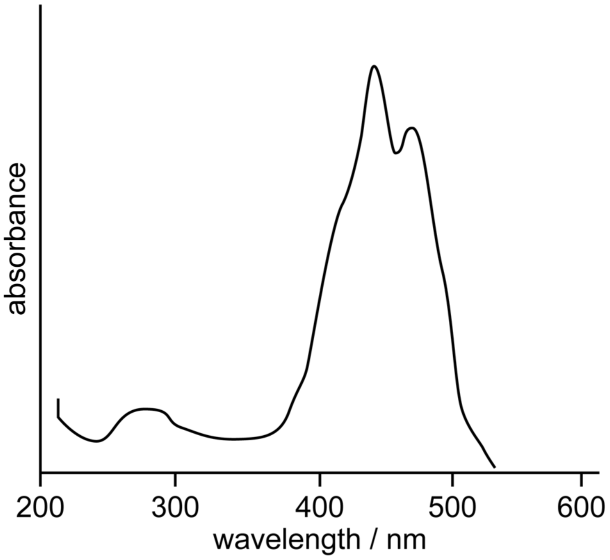


Fig. 2.1

(i) State the electronic transition occurring and suggest why there is more than one absorption peak of varying intensity in the range of 400 nm – 500 nm. [2]

The difference between energy levels, ΔE, is related to the length (in metres) of a polyene (alternating double and single bonds), L, via

$$\Delta E = \frac{(2n+1)h^2}{8m_eL^2}$$

where m_e is the rest mass of the electron, and
n is the number of double bonds in the molecule

(ii) Calculate the energy difference, ΔE, for the UV absorption peak at 448 nm in β-carotene. [1]

(iii) Using your answer to **(ii)**, suggest the minimum length of β-carotene, in nm. [2]

(b) Water can act as an extreme Lewis base to reduce F_2 to F^-, which is given by the reaction:

$$2H_2O + 2F_2 \rightarrow 4F^- + 4H^+ + O_2$$

(i) Sketch a molecular orbital diagram for fluorine molecule, clearly indicating the symmetry of the molecular orbitals, as well as the HOMO and LUMO. [3]

(ii) With reference to MO diagram you have sketched in **(i)**, suggest how water can reduce F_2. [1]

(iii) By considering the molecular orbitals of chlorine and bromine, and your answer to **(b)(ii)**, suggest why their reduction by water, is increasingly unfavourable. [2]

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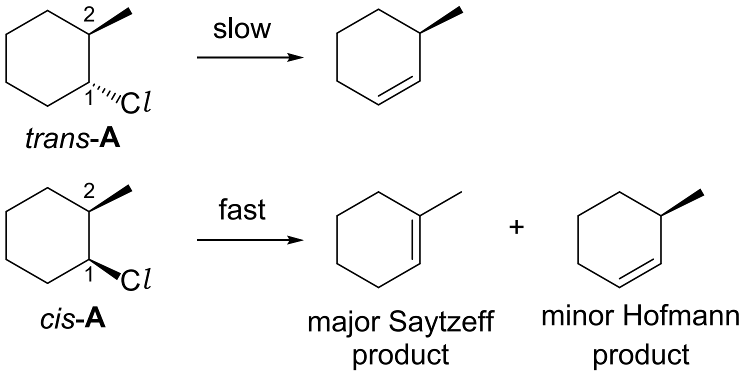
[Total: 11]

3 **(a)** The reaction of 1-chloro-2-methylcyclohexane, **A**, with potassium ethoxide, C_2H_5OK, in ethanol results in the elimination of HBr and the formation of cyclohexene derivatives:

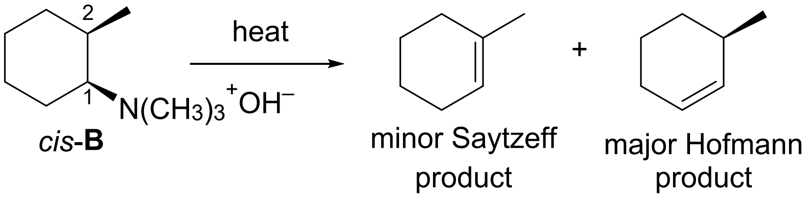


(i) State and explain whether the E1 or E2 mechanism is operating under the conditions of this elimination. [1]

(ii) Suggest explanations for the differences in the elimination reactions of *cis*- and *trans*-**A**. [4]

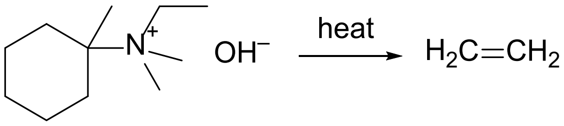
(b) Although the elimination of *cis*-**A** gives predominantly the Saytzeff product. However, changing the leaving group changes the regiochemistry altogether, in what is known as the Hofmann elimination.

(i) Heating the tetraalkylammonium hydroxide, *cis*-**B**, results in an elimination reaction affording the Hofmann product as the major product instead:



Assuming that both *cis*-**A** and *cis*-**B** undergoes a similar type of elimination mechanism, explain why the Hofmann product is the major product. [2]

(ii) Suggest why heating compound **D** gives ethene as the only alkene product.



D

[3]

[Total: 10]

4 **(a)** Compound **F** is used as a local anesthetic. **F** contains C, H, N and O. Its mass spectrum and ^{1}H nuclear magnetic resonance (NMR) spectrum are shown in Fig. 4.1 and Fig. 4.2 respectively.

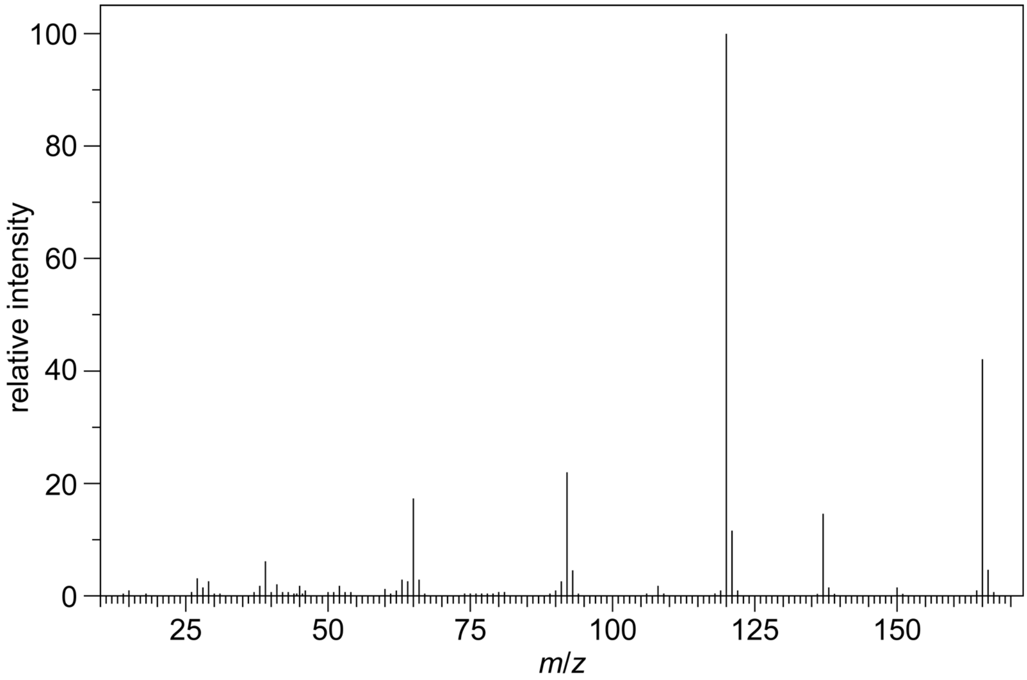


Fig. 4.1

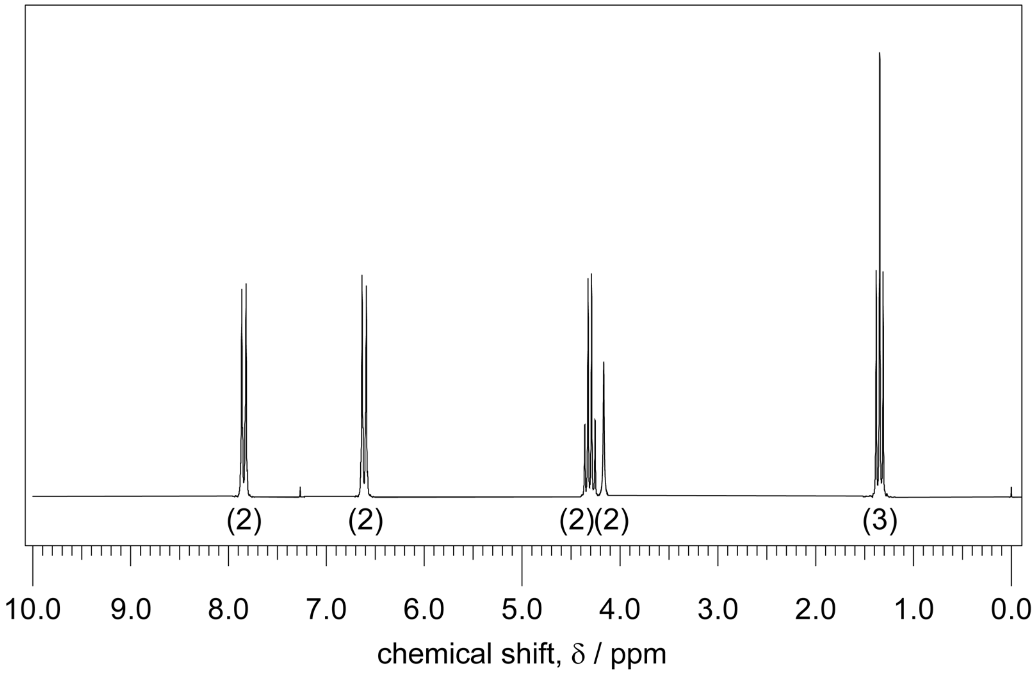


Fig. 4.2

The integration of each peak in the NMR spectrum is shown in brackets beneath each peak. On shaking the sample with D_2O, the peak at δ 4.16 disappears.

(i) Outline the basic principles of ^{1}H NMR spectroscopy. [3]

(ii) Deduce the molecular formula and the structural formula of compound **F**. Show your reasoning. [7]

(iii) Using the structural formula of **F** deduced in **(a)(ii)**, suggest the structure of the fragment at *m/z* 92 in the mass spectrum, Fig. 4.1. [1]

(iv) Explain why the peak at δ 4.16 in Fig. 4.2 disappears in the presence of D_2O.[1]

(b) **G** ($C_8H_9NO_2$) is another drug and is used for pain relief.

Hydrolysis of **G** yields **H** and ethanoic acid.

Both **G** and **H** give a violet colour when treated with neutral $FeCl_3$. However, 1 mole of **G** reacts with only 2 moles of aqueous bromine, while 1 mole of **H** reacts with 4 moles of aqueous bromine.

In the ^1H NMR spectrum of **G**, the splitting pattern in the δ 6.0 – 8.0 region is similar to that in Fig. 4.2.

(i) Identify compounds **G** and **H**, and explain the above observations. [5]

(ii) Suggest how the infra-red spectra of **F** (from **(a)**) and **G** would differ. [2]

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Section B

Answer **two** questions from this section.

5 **(a)** Enzymes exhibit substrate-specificity which is achieved by having active sites that have complementary shape, charge and hydrophobic or hydrophilic characteristics to substrates. The kinetics of an enzymatic reaction mechanism typically involves the binding on an enzyme, **E**, to a substrate, **S**, to form the enzyme-substrate complex, **ES**. The **ES** in turn reacts to form the enzyme-product complex *via* an alternative pathway with lower activation energy, and releases a product, **P**.

The enzyme-catalysed reaction may be represented schematically by:

$$\mathbf{E}+\mathbf{S} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \mathbf{ES} \xrightarrow{k_{cat}} \mathbf{E}+\mathbf{P}$$

(i) By considering the rates of the appropriate reactions, construct two separate expression for the rate of change of $[\mathbf{ES}]$, $\frac{d[\mathbf{ES}]}{dt}$, and the rate of formation of **P**, $\frac{d[\mathbf{P}]}{dt}$, in terms of $[\mathbf{E}]$, $[\mathbf{S}]$ and $[\mathbf{ES}]$. [2]

The initial concentration of the enzyme, $[\mathbf{E}]_0$, is the sum of the concentration of the enzyme, $[\mathbf{E}]$, and the concentration of the enzyme-substrate complex, $[\mathbf{ES}]$, at any time, *t*. That is, $[\mathbf{E}]_0 = [\mathbf{E}] + [\mathbf{ES}]$.

(ii) By assuming that $[\mathbf{ES}]$ can be considered as constant, that is, $\frac{d[\mathbf{ES}]}{dt} = 0$.

Use your answer to **(a)(i)** to derive an expression for $[\mathbf{ES}]$ in terms of $[\mathbf{E}]_0$, $[\mathbf{S}]$, k_b, k_f and k_{cat}, and hence show that the rate of product formation for the enzyme-catalysed reaction may be given by the Michaelis-Menten equation:

$$\frac{d[\mathbf{P}]}{dt} = k_{cat}[\mathbf{E}]_0 \frac{[\mathbf{S}]}{K_M + [\mathbf{S}]}, \text{ where } K_M = \frac{k_b + k_{cat}}{k_f}$$ [4]

(iii) Sketch a graph of rate of reaction, $\frac{d[\mathbf{P}]}{dt}$, against substrate concentration, $[\mathbf{S}]$.

With reference to the Michaelis-Menten equation or otherwise, state and explain the order of the reaction with respect to the substrate when:

- the substrate concentration is very low
- the substrate concentration is very high [3]

(iv) With reference to Table 5.1 or otherwise, suggest the effect on the maximum rate of reaction between an enzyme and substrate, when substrate **I** is replaced with substrate **J**.

Table 5.1

type of substrate	K_M with same enzyme
substrate **I**	4000
substrate **J**	8000

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Concern has been expressed about the presence of a type of bacteria, called *listeria*, which is present in soft cheese and can be harmful. The danger is most acute due to the growth of *listeria* when the cheese is brought from a refrigerator to room temperature.

At the temperature of the refrigerator (3 °C), the number of *listeria* cells doubles in 18 hours but, at room temperature (20 °C), the doubling time is reduced to 7 hours. This increase in rate can be attributed to the increase in the rate of enzyme-catalysed reaction.

(b) The relationship between the doubling time τ and the rate constant *k* of a reaction is given by:

$$k\tau = \ln 2\,.$$

(i) Suggest and explain the order of reaction for the enzyme-catalysed reaction. [1]

(ii) Calculate the rate constants for the enzyme-catalysed reactions in *listeria* at

- 3 °C,
- 20 °C. [2]

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The Arrhenius equation shows how the rate constant varies with activation energy and absolute temperature:

$$k = Ae^{\frac{-E_a}{RT}}$$

(iii) Show that the when the temperature increases from T_1 to T_2, the increase in rate constant from k_1 to k_2 is given by

$$\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$ [2]

(iv) Hence, calculate the activation energy for the enzyme-catalysed reaction in *listeria*. [1]

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(c) The activation energy of the reaction would be doubled if it were not enzyme-catalysed. Explain the **quantitative** effect this would have on the following:

(i) rate of population growth of *listeria* at 3 ºC, [2]

(ii) the ratio $\frac{k_2}{k_1}$. [2]

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[Total: 20]

6 **(a)** Nucleophilic substitution is key mechanism in synthesis chemistry. Fundamental findings of the mechanism are derived from reactions with halogenoalkanes.

Leaving groups in a nucleophilic substitution reaction, whether S_N1 or S_N2, can affect the relative rate of the reaction. Examples of leaving groups are the halides. The pK_a values of the hydrohalic acid, HX, can be found in Table 6.1.

Table 6.1

HX	pK_a
HF	+3
HCl	–7
HBr	–9
HI	–10

(i) Using the *Data Booklet* and Table 6.1, predict and explain the trend for the relative rate of nucleophilic substitution of CH_3F, CH_3Cl, CH_3Br and CH_3I. [3]

Substituents can improve the rate of reaction for S_N2 mechanisms by stabilising the transition state. Table 6.2 describes the relative rates of S_N2 reactions of alkyl chlorides with iodide ions.

Table 6.2

$R–Cl + I^- \rightarrow R–I + Cl^-$	
alkyl chloride	relative rate
CH_3Cl	200
$(CH_3)_2CHCl$	0.02
$CH_2CHCH(CH_3)Cl$	79

(ii) By considering the p orbitals of the carbon atoms, draw a structure showing the shape of the transition state for the S_N2 reaction of $CH_2CHCH(CH_3)Cl$ with I^-. [1]

(iii) Hence or otherwise, explain the differences in the relative rates for the alkyl chlorides. [2]

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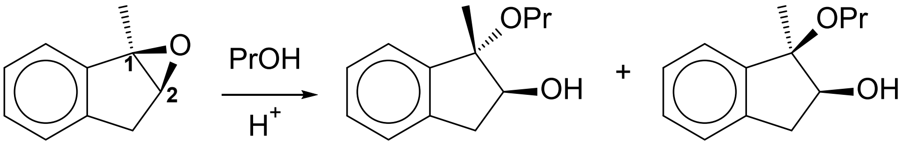
(b) Compound **K** can react with PrOH (where Pr refers to the propyl group, $CH_3CH_2CH_2–$), under different conditions to give different products. Fig 6.1 shows one specific condition that gives compound **L** and **M**.



K **L** **M**

Fig. 6.1

(i) Assign the stereochemistry at C1 and C2 of compound **K** and explain your reasoning. [2]

(ii) Describe the role of the acid in the reaction. Justify your answer. [1]

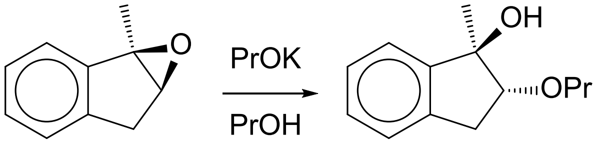
(iii) Describe the predominant mechanism for the reaction in Fig. 6.1. [3]

(iv) Draw the energy profile diagram for the reaction and provide the rate equation. [2]

(v) Compound **L** and **M** are not produced in equal amounts.

Suggest which is the major product and explain your reasoning. [1]

When a different set of conditions as shown in Fig. 6.2 were used, **K** gives a different product **N**.



K **N**

Fig. 6.2

(vi) By comparing the stability of intermediates formed, if any, and the stereochemistry of the products formed in both reactions, state and explain whether the reaction in Fig. 6.2 proceed by the same mechanism in **(b)(iii)**. [2]

(vii) Explain why PrOK is used for the reaction in Fig. 6.2 instead of pure PrOH. [1]

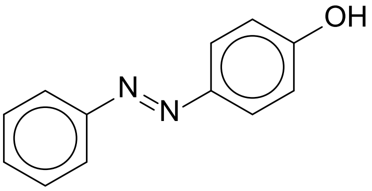
(viii) **N** and **O** are a pair of *diastereomers*.

Define the term *diastereomers* and draw the diasteromer **O**. [2]

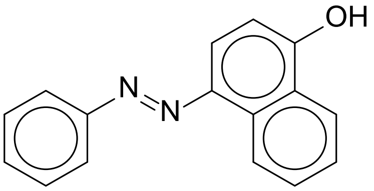
[Total: 20]

7 Azo compounds are chemical compounds with the general formula R–N=N–R′, where R and R′ can be either aryl (aromatic) or alkyl (aliphatic) substituents.

(a) Aryl diazo compounds such as **X** and **Y** are commonly used as dyes for textiles due to their bright colours.



X



Y

(i) Identify the feature in **X** and **Y** which gives them bright colours. Explain your reasoning in terms of electronic transition. [1]

(ii) Given that **X** is yellow in colour, suggest the colour of **Y**. Give a reason for your answer. [2]

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(b) Aryl diazo compounds are synthesised *via* coupling reactions (reaction II) involving aryl diazonium halides, $ArN_2^+X^-$, which are in turn prepared *in-situ* from phenylamine, hydrochloric acid and nitrous acid (reaction I).

reaction I $\quad Ar{-}NH_2 + HNO_2 \overset{+\ HX}{} \longrightarrow Ar{-}\overset{+}{N}{\equiv}N\ X^- + 2H_2O$

reaction II $\quad Ar{-}\overset{+}{N}{\equiv}N + Ar'{-}H \longrightarrow Ar{-}N{=}N{-}Ar' + H^+$

The unstable diazonium salts, $ArN_2^+X^-$, are prepared at 0–5 °C, and are usually not isolated due to the hazards associated with isolating them.

(i) Suggest the type of reaction in reaction I. Give a reason for your answer. [2]

(ii) Describe the mechanism for reaction II to produce compound **X** in **(a)**. [3]

A common precursor used in the synthesis of aryl diazo compounds is 4-bromophenylamine, which is synthesised from phenylamine *via* the use of a "protecting group".

(iii) Explain why phenylamine cannot be directly converted into 4-bromophenylamine with aqueous bromine. [2]

(iv) The synthesis of 4-bromophenylamine from phenylamine involves "protecting" the amine by converting it into a weaker electron-donating group. After bromination, the protecting group is removed to furnish 4-bromophenylamine. Suggest the reagents and conditions for each step in the synthesis. [2]

(v) Benzene does not react with the diazonium ion in reaction II. Suggest the product, if any, when 4-bromophenylamine is reacted with nitrous acid, hydrogen chloride and methylbenzene. Explain your answer. [1]

Unlike aryl azo compounds, alky diazo compounds are not brightly coloured.

Dialkyl diazo compounds decompose when heated in the gas phase, according to the following steps (R = alky group, such as CH_3).

step 1 $R–N=N–R(g) \rightarrow 2R\bullet(g) + N_2(g)$ ΔH_1

step 2 $2R\bullet(g) \rightarrow R–R(g)$ ΔH_2

(c) **(i)** Copy step 1, and insert in curly arrows for the reaction. [1]

(ii) Use relevant data from the *Data Booklet* to calculate a value for ΔH_1. [1]

(iii) Suggest the sign for the entropy change of the overall reaction (step 1 + step 2). Explain your reasoning. [1]

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The exact values for ΔH_1 and the activation energy, E_a, depend on the nature of the alkyl group R.

Table 7.1 shows the results when a series of dialkyl diazo compounds with different R groups was decomposed.

Table 7.1

R in R–N=N–R	ΔH_1 / kJ mol^{-1}	E_a / kJ mol^{-1}
CH_3	+33	+52
CH_3CH_2	+29	to be calculated
$(CH_3)_3C$	+24	+45

The Bell-Evans-Polanyi Principle relates the activation energies of a series of related reactions to their enthalpy changes.

(d) **(i)** Calculate a value for the activation energy for following reaction, using the data in Table 7.1. [3]

$$CH_3CH_2–N=N–CH_2CH_3(g) \rightarrow 2CH_3CH_2\bullet(g) + N_2(g)$$

(ii) Suggest why the values of ΔH_1 decreases down Table 7.1. [1]

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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.

EUNOIA JUNIOR COLLEGE
JC2 Preliminary Examination 2021
General Certificate of Education Advanced Level
Higher 3

CHEMISTRY

9813/01

Paper 1
INSERT

23 September 2021

2 hours 30 minutes

INSTRUCTIONS

This insert contains information for Question 1. **Do not write your answers on the insert**.

This document consists of **3** printed pages and **1** blank page.

Information for Question 1
Flue gas is the gas exiting to the atmosphere *via* a flue, which is a pipe or channel for conveying exhaust gases from a fireplace, oven, furnace, boiler or steam generator. Quite often, the flue gas refers to the combustion exhaust gas produced at power plants.

Abstract 1 (*Applied Energy*, 2016, 162, pp 787–807)

Calcium Looping

Carbon dioxide (CO_2) capture and storage, or CSS, is a process in which CO_2 is separated from industrial and energy-related sources, compressed and transported to be stored underground or used in other applications such as Enhanced Oil Recovery (EOR). CCS is recognized as a necessary technology for meeting greenhouse gas emissions reduction targets.

Among the different techniques under study, the Calcium Looping (CaL) technology is a potentially low cost second generation technology emerged in the last years. The process is based on the use of CaO as a regenerable sorbent through carbonation/calcination cycles as schematised in Fig. 1.1.

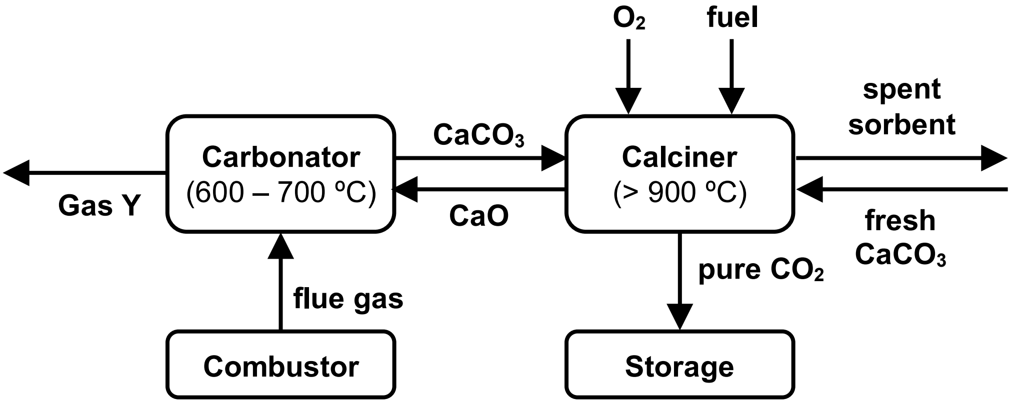

Fig. 1.1

Thus, CO_2 present in the flue gas stream (in a volume concentration of ~15%) is captured by partial carbonation of the CaO particles in a fluidised bed reactor (carbonator) operating at 650 °C under atmospheric pressure. This temperature ensures a low value of the equilibrium CO_2 concentration (around 1% vol) and, at the same time, a fast enough reaction kinetics for carbonation to take place in short residence times, which allows efficiently reducing the concentration of CO_2 in the gas leaving the carbonator reactor.

The partially carbonated particles are subsequently circulated into a second reactor (calciner) where calcination of $CaCO_3$ to regenerate the sorbent is carried out at temperatures typically above 930 °C under a highly concentrated CO_2 environment (between 70% and 90% vol). The CO_2 gas exiting the calciner is thus ready for condensation, compression and transport. The high temperatures needed for efficient calcination at practical rates is achieved by burning fuel in the calciner under a flow of pure O_2 (oxycombustion) in order to avoid CO_2 dilution.

Abstract 2 (*Joule*, 2018, 2(8), pp 1–22)

Direct Air Capture (DAC)

The capture of CO_2 from ambient air was commercialised in the 1950s as a pre-treatment for cryogenic air separation. In the 1960s, capture of CO_2 from air was considered as a feedstock for production of hydrocarbon fuels using mobile nuclear power plants. In the 1990s, Klaus Lackner explored the large-scale capture of CO_2 as a tool for managing climate risk, now commonly referred to as direct air capture (DAC).

One such process comprises two connected chemical loops (Fig. 1.2). The first loop (left) captures CO_2 from the atmosphere using an aqueous solution with ionic concentrations of roughly 1.0 M OH^-, 0.5 M CO_3^{2-}, and 2.0 M K^+. A second calcium loop (right) drives the removal of carbonate ion and thus the regeneration of the alkali capture fluid.

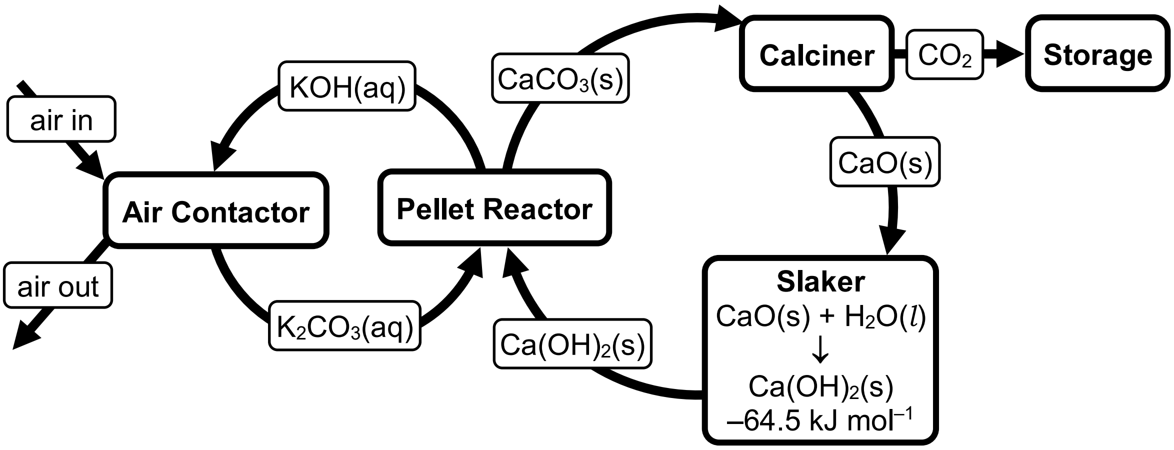

Fig. 1.2

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