

NATIONAL JUNIOR COLLEGE
SH2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE
NAME

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SUBJECT
CLASS

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REGISTRATION
NUMBER

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CHEMISTRY

Paper 2 Structured Questions

9729/02

Monday 16 September 2019
2 hours

Candidates answer on the 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.

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

For Examiner's Use

1	/17
2	/9
3	/17
4	/18
5	/14
P2 Total	/75

	Marks	Weightings
Paper 1	/30	15 %
Paper 2	/75	30 %
Paper 3	/80	35 %
Paper 4	/55	20 %

Overall Percentage	
Grade	

This document consists of **20** printed pages.

[Turn over

- 1 (a) Brass is a mixture of copper and zinc. When a piece of brass is placed in dilute hydrochloric acid, only one of the metals present dissolves.

Explain the observation and write an equation for the reaction that occurs.

.....

[3]

- (b) Copper and zinc are the two electrodes in a *Daniell* cell. The cell is set up as shown in Fig 1.1.

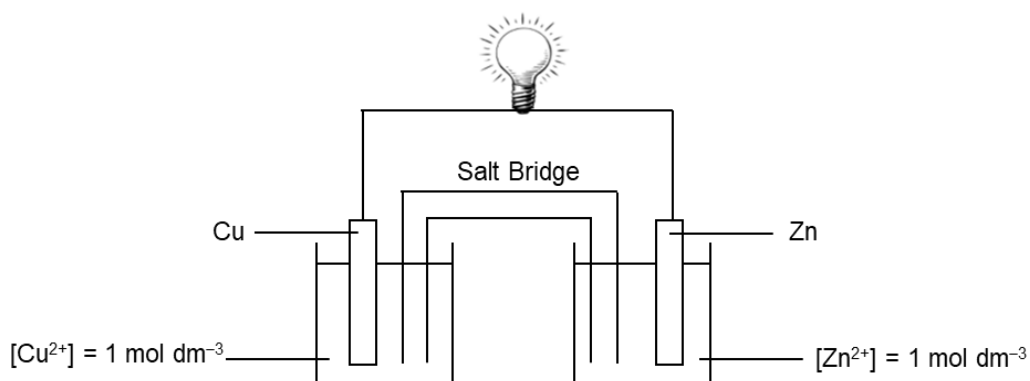


Fig 1.1

- (i) Indicate the direction of electron flow on Fig 1.1. [1]
- (ii) Write the equation for the reaction taking place and calculate ΔG° for the reaction.

.....

[3]

(iii) Discuss the effect of the following changes on the cell potential of the above cell.

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(I) adding excess amount of aqueous ammonia into the Zn^{2+}/Zn half-cell

.....
.....
.....
.....
..... [2]

(II) using a smaller copper electrode

.....
.....
.....
.....
..... [2]

(iv) How many hours will it take for this galvanic cell to plate 15.0 g of metallic copper from 1 mol dm⁻³ solutions of $\text{Cu}^{2+}(\text{aq})$ and $\text{Zn}^{2+}(\text{aq})$ using a current of 5.0 A?

[2]

- (v) The Nernst equation is an equation that relates the cell potential, E_{cell} , of an electrochemical reaction to the standard cell potential, $E^{\ominus}_{\text{cell}}$. It can be simplified and written as

Nernst equation :
$$E_{\text{cell}} = E^{\ominus}_{\text{cell}} - \frac{RT}{zF} \ln Q$$

where R is the ideal gas constant

z is the number of electron transferred

Q is $\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$ for the *Daniell* cell

T is temperature in Kelvin

F is Faraday's constant

Using the above equation, calculate Q for the overall redox reaction of the *Daniell* cell when it reaches equilibrium at 25 °C.

[2]

- (vi) In another set-up conducted at 25 °C, the concentration of Cu^{2+} ions and Zn^{2+} ions have been adjusted to 0.125 mol dm⁻³ and 0.002 mol dm⁻³ respectively.

Using the Nernst equation, calculate the e.m.f. of this cell.

[2]

[Total: 17]

Question 2 starts on the next page

- 2 Saccharin is an artificial sweetening agent used in some soft drinks and produced in various ways. Fig 2.1 shows the original route by *Remsen and Fahlberg*, starting with methylbenzene undergoing electrophilic substitution reaction using chlorosulfonic acid, $\text{Cl/SO}_3\text{H}$. This is also known as aromatic sulfonation process.

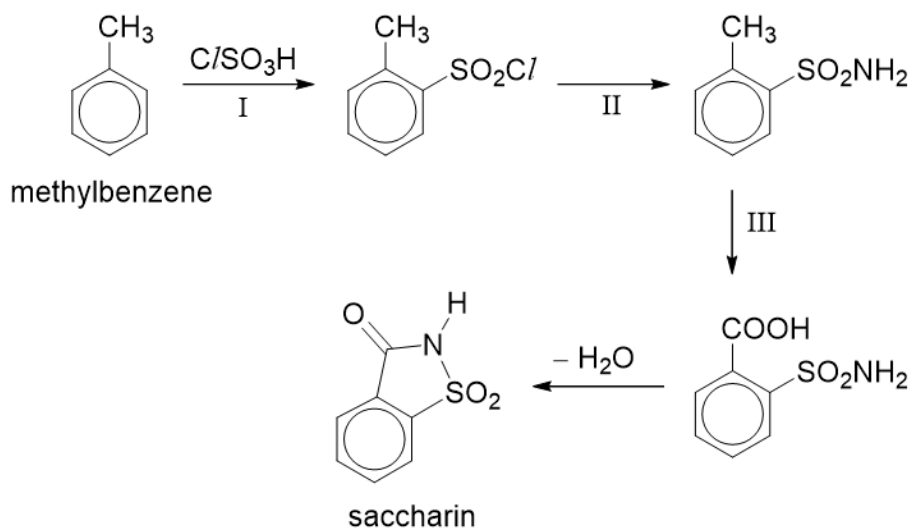


Fig 2.1

- (a) Draw a dot-and-cross diagram of chlorosulfonic acid, $\text{Cl/SO}_3\text{H}$ and hence state the bond angle for Cl-S-O .

Cl-S-O bond angle : [2]

- (b) (i)** Reaction I of the aromatic sulfonation process involves the formation of an electrophile. Identify the electrophile.

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Electrophile :

[1]

- (ii)** Hence, describe the mechanism for reaction I of the reaction. Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows.

[2]

- (iii)** State the types of reaction that occur during reactions II and III.

reaction II :

reaction III :

[2]

- (iv)** Suggest reagents and conditions for reactions II and III.

reaction II :

reaction III :

[2]

[Total : 9]

- 3** Perchlorate (ClO_4^-) compounds are used as oxidisers in some fireworks to aid the combustion reaction. These perchlorates can contaminate bodies of water near fireworks displays. Elevated concentrations of perchlorate in water can affect wildlife and it may also affect human health if it contaminates drinking water.

- (a)** One common perchlorate present in fireworks is ammonium perchlorate, NH_4ClO_4 . Given that the solubility of ammonium perchlorate is 30.6 g per 100 cm^3 , express its solubility in mol dm^{-3} and hence, calculate the solubility product, K_{sp} , for NH_4ClO_4 .

[2]

- (b)** A group of NJC students conducted a study to determine the perchlorate content of the water in the Singapore River before and after the fireworks display in the National Day Parade Rehearsal.

They followed the methodology described below one week before the rehearsal:

- Collect a 100.0 cm^3 sample of the river water and acidify it with 10 cm^3 of 1 mol dm^{-3} sulfuric acid.
- The resulting solution is added to an excess of 50 cm^3 of 5×10^{-5} mol dm^{-3} iron(II) sulfate solution. The mixture is then made up to 250 cm^3 . This is solution **X**.
- A 25.0 cm^3 sample of solution **X** is pipetted into a conical flask.

The 25.0 cm^3 solution is titrated against 1×10^{-6} mol dm^{-3} potassium manganate(VII) to determine the amount of remaining iron(II) ions in the sample.

- (i)** Write the half equation for the conversion of perchlorate ions to chlorine in the acidic medium and hence the overall equation for the reaction between perchlorate and iron(II) ions.

Half equation :

Overall equation :

[2]

- (ii)** Describe how you would recognise the endpoint of the titration.

..... [1]

- (iii) The 25.0 cm³ sample of solution X required 30.00 cm³ of potassium manganate(VII) for complete reaction.

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Calculate the concentration of perchlorate ions in the river water.

[3]

- (iv) Given that the perchlorate concentration in the Singapore River increased by 20% in the 24 hours after the fireworks display for the National Day Parade rehearsal, calculate the concentration of perchlorate ions in the river 24 hours after the fireworks display.

If you did not manage to work out an answer for (b)(iii), you may assume the concentration of perchlorate ions in the river water is $2.5 \times 10^{-6} \text{ mol dm}^{-3}$.

[1]

- (v) Table 3.1 shows the health effects on fishes due to varying concentration of perchlorate ion in the river.

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types of fish	abnormalities in skeletal growth	increased angiogenesis	myocardial infarction
stickleback	$5 \times 10^{-6} \text{ mol dm}^{-3}$	$1 \times 10^{-4} \text{ mol dm}^{-3}$	$1.5 \times 10^{-4} \text{ mol dm}^{-3}$
pike	$5 \times 10^{-7} \text{ mol dm}^{-3}$	$2 \times 10^{-6} \text{ mol dm}^{-3}$	$1 \times 10^{-5} \text{ mol dm}^{-3}$
catfish	$1 \times 10^{-7} \text{ mol dm}^{-3}$	$1 \times 10^{-6} \text{ mol dm}^{-3}$	$5 \times 10^{-5} \text{ mol dm}^{-3}$

Table 3.1

Using your answer in **b(iv)**, predict the type of health effect(s) experienced by each type of fish 24 hours after the fireworks display. Write "nil" if there is no effect.

types of fish	health effect(s)
stickleback	
pike	
catfish	

[2]

- (c) Perchlorate ions can be metabolized in the tissue of stickleback fish. The fish tissue concentration of perchlorate ions was investigated for one of the stickleback fish found in the Singapore River.

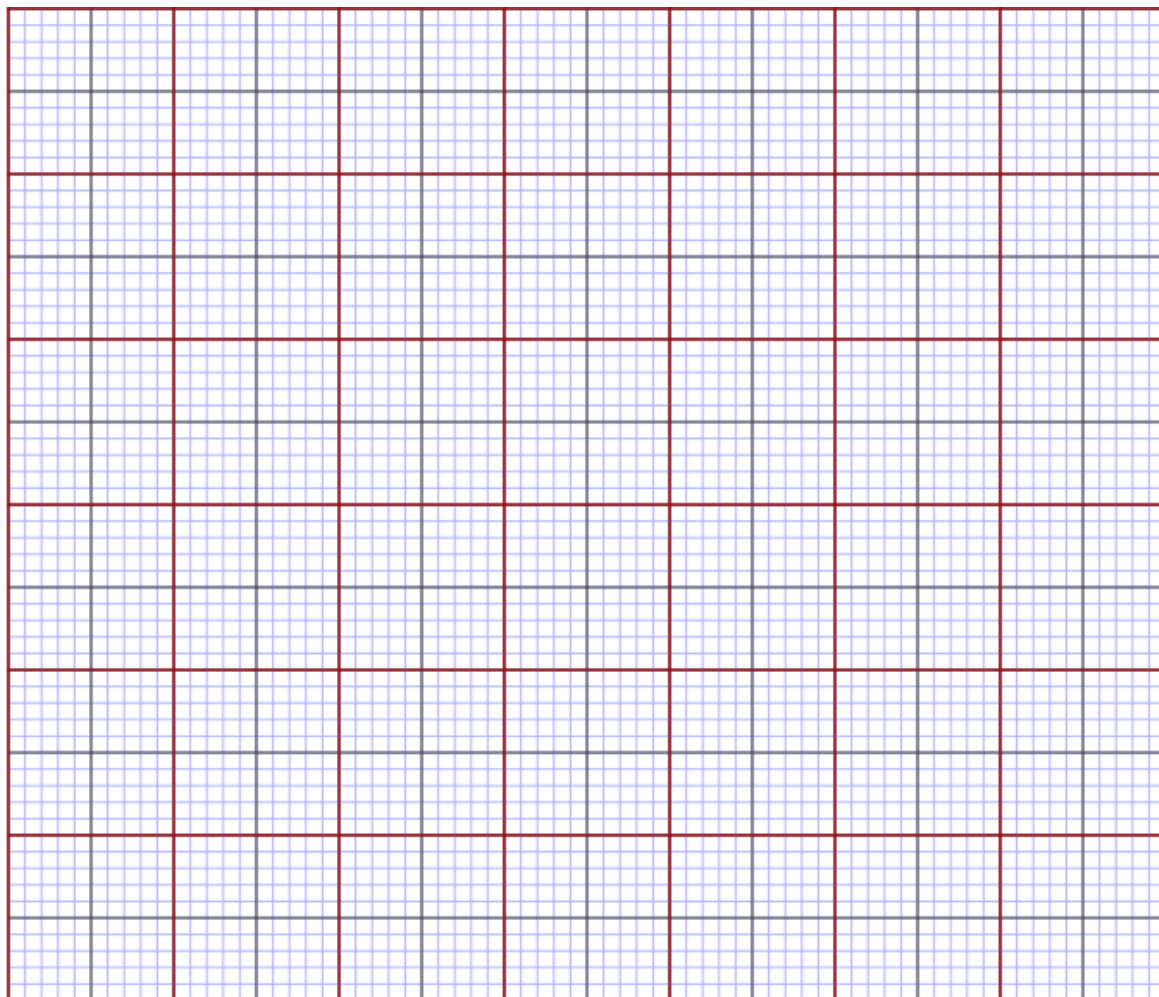
The following results was obtained.

Time/ hour	$[\text{ClO}_4^-] / \times 10^{-9} \text{ mol dm}^{-3}$
0	100
4	70
8	49
12	34
16	24
20	17
24	12

Table 3.2

- (i) Plot the data from Table 3.2 on the grid provided and use your graph to prove that the order of reaction with respect to perchlorate is one.

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[3]

- (ii) Using your graph in **c(i)**, determine the rate constant, k . Include units in your answer.

[2]

- (iii) Hence, estimate the time taken for the perchlorate ions to reach 1% of its initial concentration.

[1]

[Total : 17]

- 4 Alkalinity refers to the capability of water to neutralize acid. Alkalinity is important for fish and aquatic life because it protects or buffers against rapid pH changes. Living organisms, especially aquatic life, function best in a pH range of 6.0 to 9.0.

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In the ocean, dissolved carbon dioxide from the atmosphere is in equilibrium with seawater concentrations of carbonic acid, H_2CO_3 and hydrogen carbonate, HCO_3^- . The ocean has a very large buffering capacity made possible with the presence calcium carbonate rocks in lakes and streams.

Relevant chemical equations and equilibrium constants at 293K that affects the ocean's pH and buffering capacity are shown below.

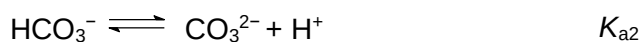
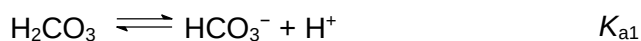


Fig 4.1 shows the molar fraction of H_2CO_3 , HCO_3^- and CO_3^{2-} in a sample of river water at 293K.

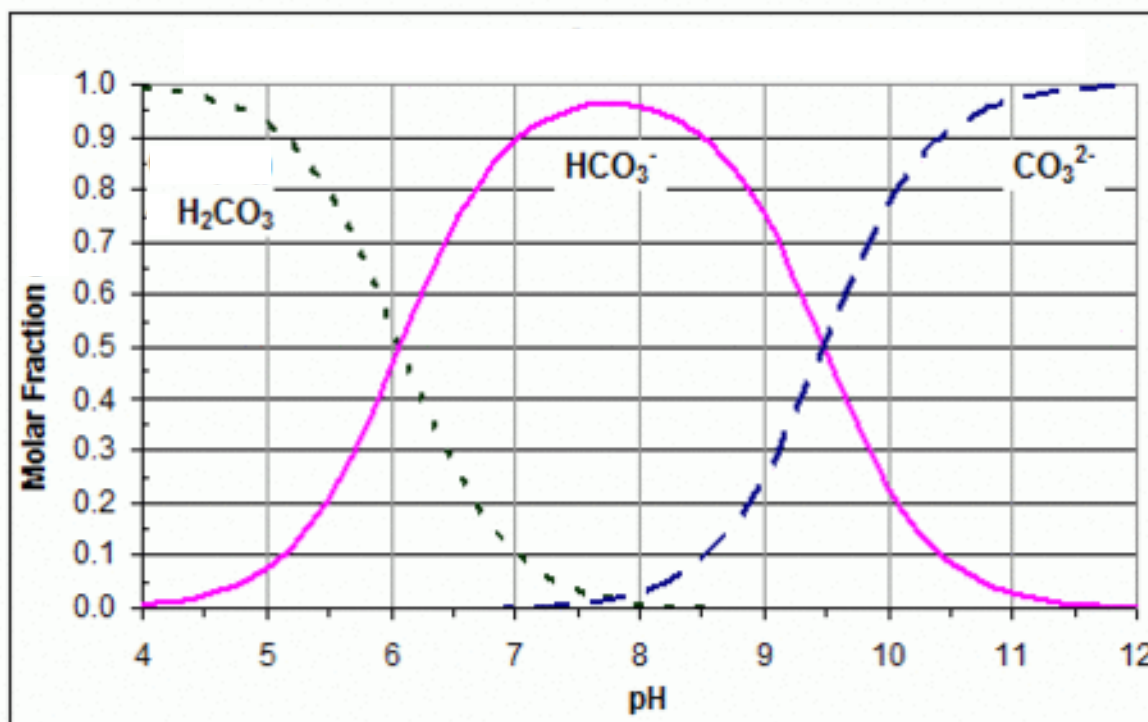


Fig 4.1

- (a) (i) With reference to Fig 4.1, state the two pH values where the mixture are at its maximum buffering capacity.

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pH of maximum buffering capacity : and

[1]

- (ii) Hence deduce the values for K_{a1} and K_{a2} .

[2]

- (iii) Explain why the calculated value of K_{a1} is larger than K_{a2} ?

.....

[1]

- (iv) Aquatic organisms survive within specific pH range.
 Suggest with equations, how the hydrogen carbonate and carbonate system in natural water ensures the survival of aquatic organisms.

.....

[3]

- (v) Table 4.1 gives the corresponding component of the gas in atmosphere. Determine the concentration of carbon dioxide in mol dm^{-3} in the atmosphere and hence determine the concentration of carbon dioxide dissolved in pure water at room temperature and pressure.

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component in dry air	volume ratio of gas in dry air / ppm
oxygen	209 500
nitrogen	780 840
carbon dioxide	399
argon	9300

Table 4.1

[ppm refers to parts per million]

[3]

- (vi) The concentration of dissolved O_2 is found to be $2.5 \times 10^{-4} \text{ mol dm}^{-3}$.
With the aid of a diagram, show how oxygen can dissolve in water.

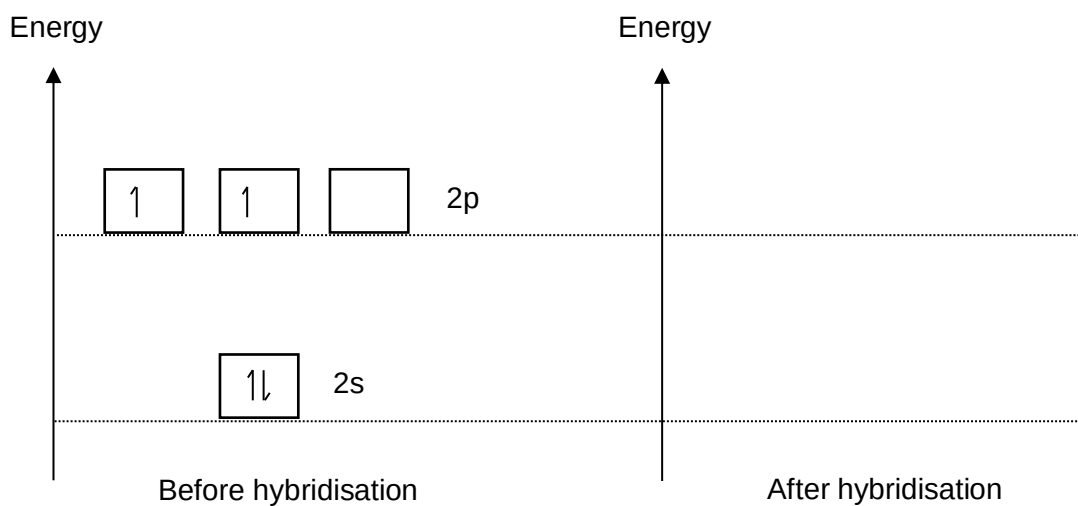
[1]

- (b) (i) Draw the labelled diagram to show the orbitals that form the C=O bond in CO₂, and state the type of hybridisation involved.

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Use

[2]

- (ii) Indicate the energy level of the orbitals involved in the σ (sigma) and π (pi) bonding of CO₂ on the energy level diagram provided. You should use boxes to represent the orbitals and half arrows to represent electrons.

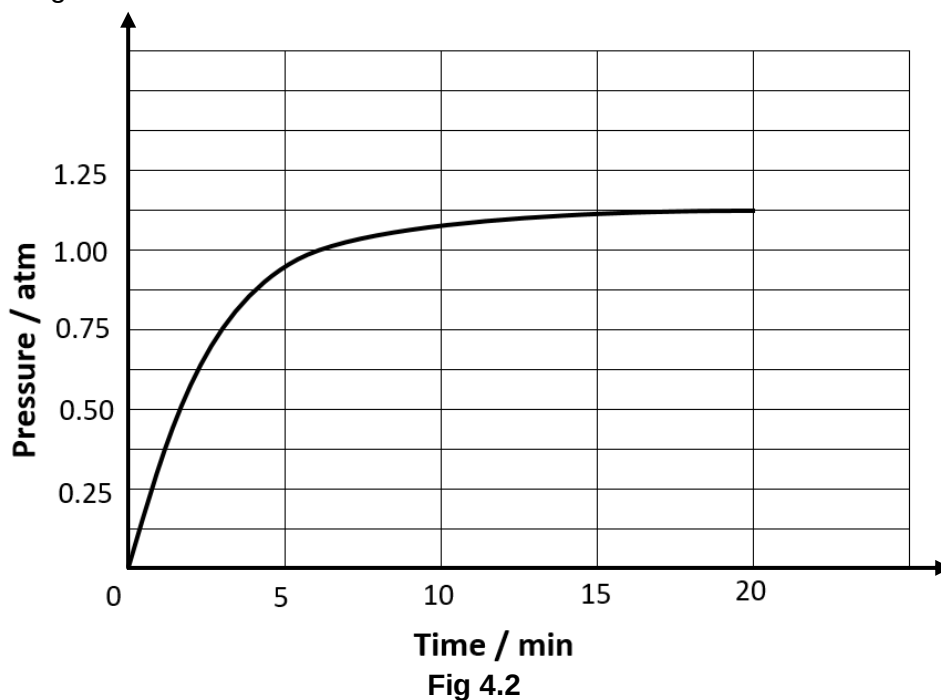


[2]

- (c) Calcium carbonate is an important compound that ensures the alkalinity of river water. When calcium carbonate is heated, it decomposes according to the equation below.



In a study of the decomposition of calcium carbonate, a student added a 50.0 g sample of solid CaCO_3 to a rigid 1 dm^3 container. The student sealed the container, pumped out all the gases, then heated the container in an oven at 1100K . As the container was heated, the total pressure of the $\text{CO}_2(\text{g})$ in the container was measured over time. The data are plotted in Fig 4.2.



- (i) The student repeated the experiment, but this time the student crushed another 50.0 g sample of $\text{CaCO}_3(\text{s})$ into powdered form. Sketch the resultant graph **on the same axis provided in Fig 4.2**. [1]
- (ii) After 20 minutes, some $\text{CO}_2(\text{g})$ was injected into the container, initially raising the pressure to 2.5 atm while keeping the temperature constant. Would the final pressure inside the container be less than, greater than, or equal to its initial pressure at 20 minutes? Explain your reasoning.

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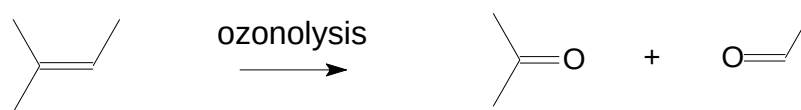
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.....

.....[2]

[Total : 18]

- 5 (a) Alkene can undergo oxidation with ozone, O_3 , to give carbonyl compounds. This reaction is known as *ozonolysis*.



Alkene **J**, $C_{11}H_{14}$, undergoes *ozonolysis* to give compound **K**, C_8H_8O , and compound **L**, C_3H_6O .

Compound **K** gives a brick red precipitate when warmed with alkaline Cu^{2+} tartrate complex.

Compound **L** gives a yellow precipitate when warmed with alkaline I_2 .

Alkene **J** gives compound **L** and benzoic acid, $C_6H_5CO_2H$, as the only organic products when heated with acidified $KMnO_4$.

- (i) Suggest the structures of compounds **J**, **K** and **L**. [3]

Compound J	Compound K	Compound L

- (ii) Write an equation for the reaction of alkene **J** with $KMnO_4$, using $[O]$ to represent the oxidising agent.

[1]

- (iii) Draw the structure of O_3 to illustrate its shape and show any dative covalent bond it may contain.

[1]

- (b) Cycloalkenes can undergo *syn* and *anti* addition as shown in Fig 5.1.

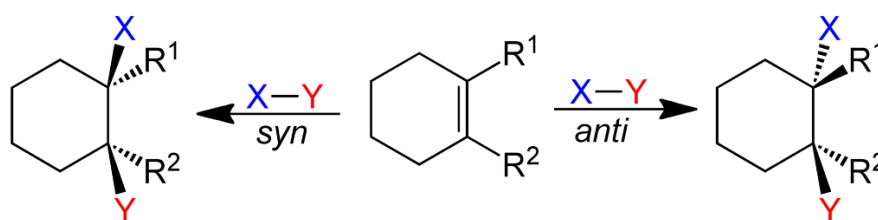


Fig 5.1

An example of *syn* addition is the oxidation of alkene to diol.

An example of *anti* addition is the bromination of alkene.

Using information from Fig 5.1, suggest the structure of the product for the reaction of 1,2-dimethylcyclohexene with the following reagents.

cold alkaline KMnO_4	
Br_2 in CCl_4	

[2]

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- (c) Fig 5.2 shows the reaction of cyclohexa-1,4-diene with HBr(g) .

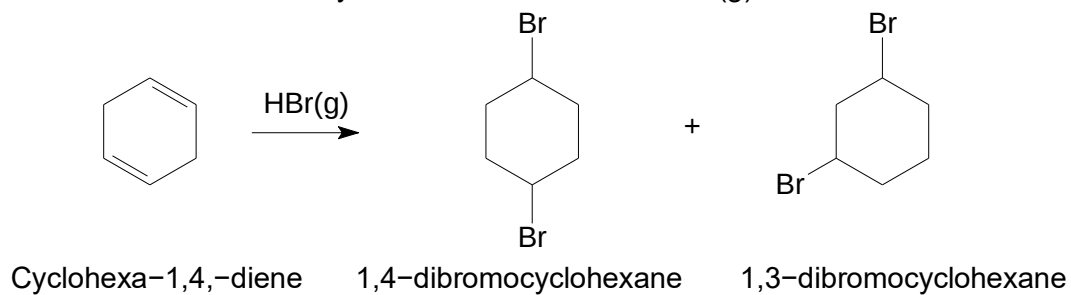


Fig 5.2

- (i) 1,4-dibromocyclohexane exhibits cis-trans isomerism.

Draw the structures of the stereoisomers.

cis isomer	trans isomer

[2]

- (ii) 1,3-dibromocyclohexane contains two chiral carbons. This gives rise to only three stereoisomers, of which two are optically active.

Suggest the structure of the *optically inactive* stereoisomer and explain why it has no optical activity.

.....

.....

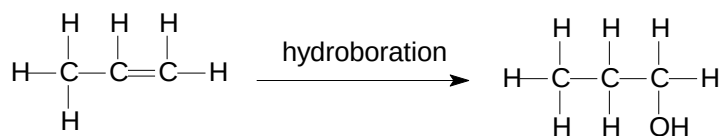
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.....

.....[2]

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- (d) Hydroboration can be used to convert an alkene to an alcohol.



Hydroboration involves a two-step reaction as shown in Fig 5.3:

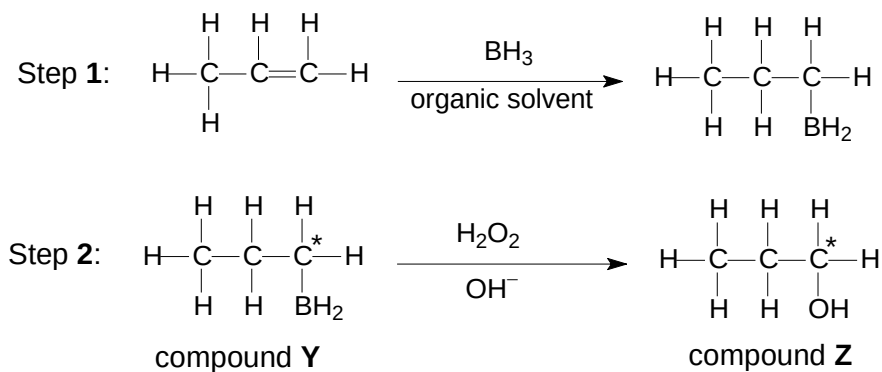


Fig 5.3

The electronegativity data for some elements are given in Table 5.1.

element	B	C	H	O
electronegativity	2.0	2.5	2.1	3.6

Table 5.1

- (i) Step 1 is an electrophilic addition reaction. Draw the structure of the carbocation intermediate involved in step 1.

[1]

- (ii) State the oxidation number of the carbon atoms labelled * in compound Y and Z, and hence deduce the role of H₂O₂ in step 2.

Oxidation number of C* in Y is

Oxidation number of C* in Z is

Role of H₂O₂:

[2]

[Total : 14]