

Data-based application questions: Physical and Inorganic Chemistry

- 1 Hydrogen peroxide (H_2O_2) is a high value green-oxidant used in Chemistry. Although it is toxic, using H_2O_2 appropriately in contexts such as water treatment helps to save the environment in a cost-efficient way.

Currently, H_2O_2 is industrially produced through energy intensive methods. A new field of research is emerging to electrochemically synthesise H_2O_2 through hydrogen, oxygen and/or water.

2 known methods of electrochemical synthesis are discussed in this question.

Method 1: An electrochemical cell to produce H_2O_2 from H_2 and O_2 . This method is known as the 2e-ORR (2 electron oxygen reduction reaction).

Method 2: An electrolytic cell to produce H_2O_2 from H_2O . This method is known as the 2e-WOR (2 electron water oxidation reaction).

- (a) **Fig 1.1** illustrates a simplified setup of an electrochemical cell to produce H_2O_2 using the 2e-ORR.

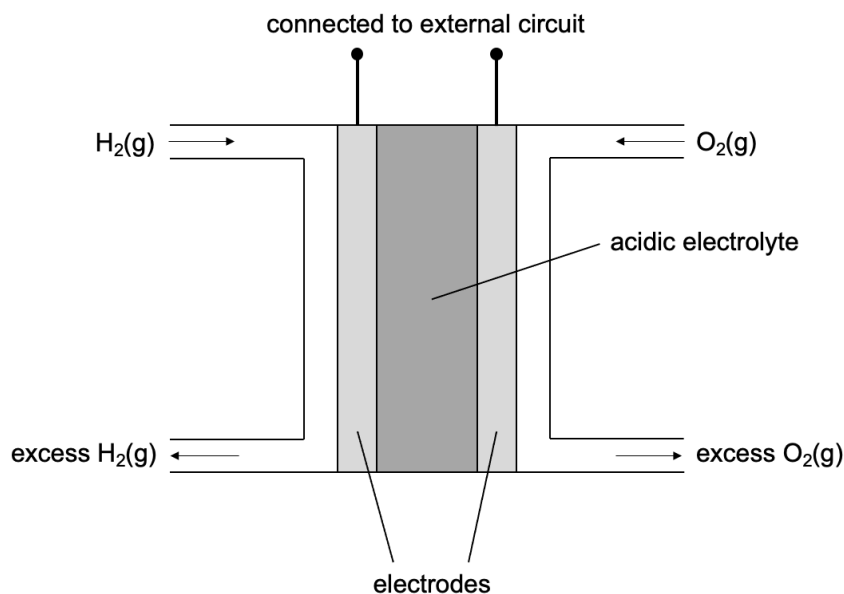


Fig 1.1

- (i) On **Fig 1.1**, indicate the cathode and anode, and their polarities; and direction of electron flow on the wires connected to both electrodes. [3]
- (ii) Write half-equations occurring at both the anode and the cathode. [1]

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(iii) Researchers using the 2e-ORR to produce hydrogen peroxide often realise that another product was formed.

Identify this product. Using your answer from (ii), explain whether this product or H₂O₂ is more likely to be formed. [3]

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In the 2e-WOR method, 3 competing reactions may occur. Apart from the 2e-WOR, the 2 other reactions are the 1e-WOR (producing the •OH(aq) radical) and the 4e-WOR (producing O₂(g)).

Fig 1.2 illustrates how the 4e-WOR proceeds under the presence of an electrocatalyst.

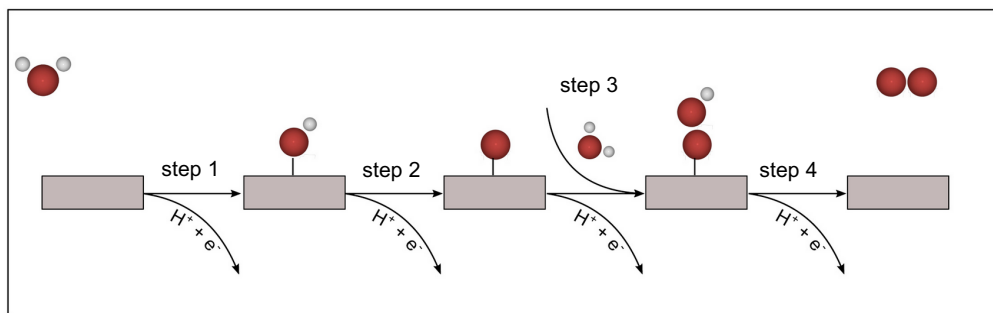


Fig 1.2

In the first step, one H₂O molecule will occupy a vacant active site on the electrocatalyst, forming the •OH radical which is adsorbed onto the catalyst.

This is represented by equation 1.



The * indicates an unoccupied active site, while OH* represents an adsorbed •OH radical on the electrocatalyst.

- (b) (i) With reference to **Fig 1.2**, write balanced half-equations for steps 2, 3 and 4. [3]

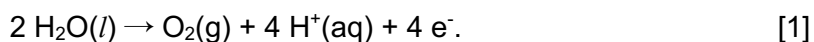
You do not need to indicate any unpaired electrons on the species when it is adsorbed onto the catalyst.

step 2

step 3

step 4

- (ii) Show that the half-equations in steps 1 to 4 add up to give the half-equation:



- (iii) The 2e-WOR proceeds via 2 steps. The first step is as per step 1 in **Fig 1.2**.

Suggest a half-equation for the second step. [1]

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- (c) The 3 competing reactions in the 2e-WOR would imply that the choice of an electrocatalyst is critical for a high yield of H_2O_2 .

The free energy of formation (ΔG) of the following species from $\text{H}_2\text{O}(l)$ is shown in **Fig 1.3** below. All ΔG values are positive.

Species	$\Delta G / \text{eV}$	Reactions the species are involved in
$\text{H}_2\text{O}(l)$	0	1e, 2e and 4e-WOR
OH^*	x	1e, 2e and 4e-WOR
$\bullet\text{OH}(\text{aq})$	2.38	1e-WOR
O^*	y	4e-WOR
$\text{H}_2\text{O}_2(\text{aq})$	3.52	2e-WOR
$\text{O}_2(g)$	4.92	4e-WOR

Fig 1.3

The values x and y depend on the electrocatalyst used. x and y are positive numbers.

- (i) The electrocatalyst used must have its values of x and y in a certain range. By considering the information in (b), state the range of values x and y must take in order for H_2O_2 to be formed. Explain your answer. [3]

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- (ii) Hence, tick the catalyst(s) that should be used to produce H_2O_2 . [1]

Tick here	Catalyst	Value of x	Value of y
	IrO_2	0.25	1.7
	PtO_2	1.2	3.25
	TiO_2	2.25	4.9

- (d) The Faradaic efficiency (FE) for H_2O_2 production in the 2e-WOR may be determined by:

$$\text{FE} = \frac{\eta_{\text{H}_2\text{O}_2 \text{ detected}}}{\text{theoretical maximum } \eta_{\text{H}_2\text{O}_2}} \times 100\%$$

In an experiment, a current of 0.10 mA was passed through the setup consisting of 20.0 cm^3 of aqueous electrolyte for 20 min. 5.0 cm^3 of the electrolyte required 4.70 cm^3 of $1.00 \times 10^{-5} \text{ mol dm}^{-3}$ of acidified KMnO_4 for complete reaction.

Calculate the FE for H_2O_2 production for this experiment. [4]

(e) Suggest 2 advantages of using the 2e-WOR over the 2e-ORR to produce H_2O_2 . [2]

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(f) H_2O_2 cannot be stored for prolonged periods of time. This is because H_2O_2 can spontaneously break down into water and oxygen gas.

With reference to a bond energy from the Data Booklet, explain why H_2O_2 can break down easily. [1]

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[Total: 23]

2 In 1952, Miller and Urey sought to find the origin of life. They wanted to test the hypothesis that under the presence of lightning, amino acids can be formed through reactions in a reducing atmosphere, which gave rise to the first hints of life after Earth was formed.

The well-known Miller-Urey experiment was hence born.

Fig 2.1 illustrates a schematic diagram for the Miller-Urey experiment.

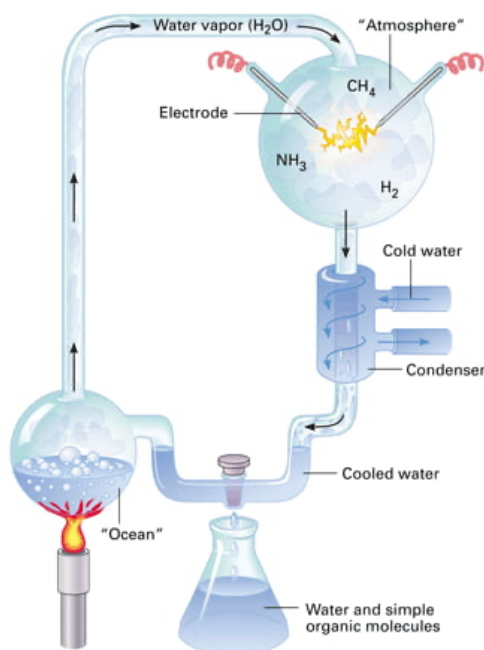


Fig 2.1

A flask of water was boiled to simulate the then hot environment after the Earth was formed. In the simulated atmosphere, a potential difference was created to simulate lightning. There, the simulated reducing atmosphere contains NH_3 , CH_4 , H_2 . The products formed, and any excess water vapour was then cooled. Organic compounds formed were isolated for analysis.

- (a) Suggest why the atmosphere is termed as a “reducing” one. [1]

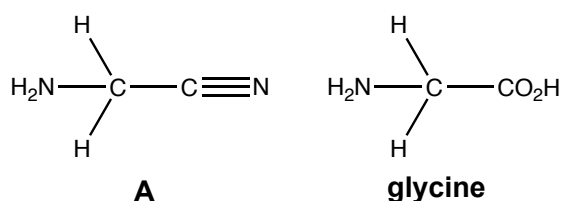
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- (b) (i) It is found that ammonia and methane can react together to form hydrogen cyanide (HCN) and hydrogen gas.

Write a balanced equation for this reaction. [1]

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- (ii) Following the formation of HCN, many chemists propose that the intermediate **A** was formed.



Suggest whether glycine, an amino-acid, can be produced from **A** in the Miller-Urey experiment. Explain your answer. [1]

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- (iii) Explain the difference in the solubilities of **A** and glycine in cold water with reference to structure and bonding. [2]

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Other chemists and physicists sought to find how the 4 of the most common elements in nature, carbon, hydrogen, oxygen and nitrogen, were formed after the universe was born from the Big Bang Theory.

The proton-proton (pp) chain was proposed to explain the formation of hydrogen and helium.

The pp chain contains a few branches. In the next part of the question, we will study branch 1 of the pp chain.

It may be helpful to understand the following terms, and their symbols in brackets ()::

- Positron (e^+): It has the same elementary charge and mass as an electron, but is positively charged instead.
- Neutrino (ν): A particle that has zero charge and has an extremely small mass.
- Gamma ray (γ): A particle that carries high amounts of energy when a nuclear reaction occurs. A nuclear reaction refers to a reaction between 1 or more nuclei.

Branch 1 of the pp chain

Step 1: 2 protons combine together to form a deuterium (^2H) nucleus, a positron and neutrino

Step 2: A proton combines with a deuterium nucleus to form a ^3He nucleus, releasing a gamma ray.

Step 3: 2 ^3He nuclei combine together to form a ^4He nucleus (alpha particle), releasing 2 other particles. The particles are of the same type.

(c) (i) Write balanced equations for steps 1 and 3. [2]

You are to indicate the mass number and relative charges where possible.

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(ii) Explain why the pp chain only occurs at high temperatures of more than 10 MK (mega Kelvins). [1]

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Following the formation of alpha particles, carbon and oxygen may be created via the triple-alpha process.

This proceeds in 3 steps. The first 2 steps are shown below. The species indicated in the 2 equations below only represent their respective nuclei.



(d) (i) In order for ^{12}C to be formed, step 2 must proceed at a certain rate.

Calculate the minimum ratio

$$\frac{\text{rate of step 1}}{\text{rate of step 2}}$$

in order for there to be an overall release of energy.

[1]

(ii) An alpha particle can combine with a proton to form a lithium-5 nucleus. However, this nucleus is very unstable and decays with a constant half-life of 3.7×10^{-22} s.

Calculate the rate of depletion of lithium-5 nuclei when 2.5 moles of lithium-5 nuclei are present.

Calculate how long it takes for 10^{-6} moles of lithium-5 nuclei are left to be decayed.

[3]

- (iii) Show clearly that the **nuclei**: ${}^2\text{H}$, ${}^4\text{He}$, ${}^8\text{Be}$, ${}^{12}\text{C}$ and ${}^{16}\text{O}$, separately, will deflect at the same angle when passed through the same electric field. [2]

[Total: 14]

- 3 Osmium is one of the rarest and densest metals on Earth. It happens to be amphoteric too.

In this question, we will examine the chemical properties of osmium.

- (a) (i) Fully describe the structure and bonding in osmium.

Include a relevant diagram in your answer. [3]

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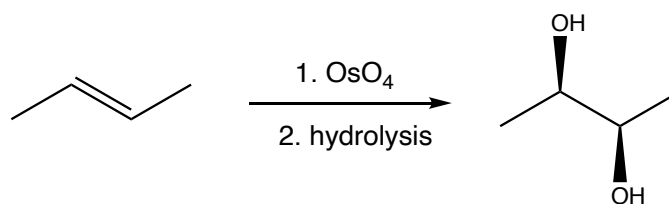
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- (ii) Draw 2 isomers of the complex ion $\text{OsO}_4(\text{OH})_2^{2-}$. State the type of isomerism that exists between them. [2]

Osmium tetroxide is a selective oxidant used in organic chemistry.



When an alkene is oxidised by OsO_4 , a diol is formed. OsO_4 is reduced to an unknown osmium compound. An example is shown above.

Because osmium tetroxide is so toxic, this oxidation is done with a small amount of OsO_4 . A non-toxic oxidant is added to reoxidise the reduced osmium compound to OsO_4 again. However, this oxidant does not react with the $\text{C}=\text{C}$ bond to form a diol.

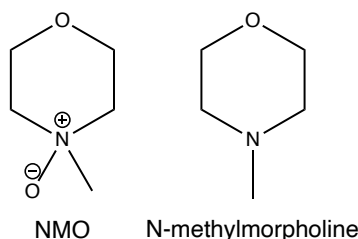
- (iii) Explain the role of OsO_4 in the reaction. [2]

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- (iv) Equal amounts of the reduced osmium compound and NMO reacts together to reform OsO_4 and N-methylmorpholine as a side product.

Find the oxidation state of Os in the reduced osmium compound.

[1]



- (v) Suggest why in some cases, KMnO_4 is **not** used to form a diol from an alkene. [1]

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- (b) Osmium metal is produced through nickel and copper refining. Osmium is usually present in small amounts in ores extracted.

- (i) In the first stage, the ore undergoes electrolysis. The ore is placed at the anode. Some raw metals fall through and remains unreacted. Osmium is one of them.

What can you conclude about $E(\text{Os}^{x+}/\text{Os})$ with respect to $E(\text{Ni}^{2+}/\text{Ni})$? [1]

x represents the oxidation state of osmium in the hypothetical aqueous Os^{x+} ion.

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- (ii) Under extremely strong oxidising conditions, osmium, alongside other metals, are oxidised to their highest oxidation state.

The ore contains gold, whose oxide is not amphoteric.

Suggest how you would separate gold from osmium. [1]

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- (iii) In the final stage, the OsO_4 separated from other metals is purified by distillation. The boiling point of OsO_4 is around 130 degrees Celsius.

With reference to structure and bonding, explain why OsO_4 has a rather low boiling point. [1]

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- (c) The Haber Process to produce ammonia first used osmium as a catalyst.

Now, the Haber Process uses finely divided iron (and its oxides sometimes).

Explain why using iron, instead of osmium as a catalyst, does **not** affect the yield of ammonia. State another reason of using iron instead of osmium in the Haber Process. [2]

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[Total: 14]

- 4 Iodine deficiency is of special concern in Georgia because it occupies a region where iodine is scarce in soil and water. Iodine deficiency can be effectively and inexpensively prevented if salt for human consumption is fortified with small amounts of iodine. Current regulations in Georgia stipulate that iodised salt must contain between 25 ppm and 55 ppm of iodine.

- (a) Most salt is iodised by fortification with potassium iodate (KIO_3). Iodate content can be determined in salt samples using iodometric titration.

In an experiment, 10.000 g of an iodized salt sample is dissolved in 100 cm^3 of 1.0 mol dm^{-3} aqueous HCl to which 1.0 g KI has been added. The solution is then titrated with $0.00235 \text{ mol dm}^{-3}$ aqueous $\text{Na}_2\text{S}_2\text{O}_3$. 7.50 cm^3 of $\text{Na}_2\text{S}_2\text{O}_3$ is required for the endpoint to be reached.

- (i) Write a balanced equation for the reaction between the iodate and iodide ion. The iodine-containing species in the product is only I_2 . [1]

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- (ii) The iodine liberated from the reaction between the iodate and iodide ions reacts with $\text{Na}_2\text{S}_2\text{O}_3$.

Write a balanced equation for this reaction.

[1]

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- (iii) Using suitable calculations, explain if this sample of salt meets Georgia's regulations for iodised salt.

[3]

1 ppm of iodine is equivalent to 1 mg of iodine per kg of salt.

- (b) A less common chemical used to iodise salt is potassium iodide, KI.

An iodometric titration cannot easily be used to measure the content of iodine.

Instead, the Sandell-Kolthoff reaction is used.

Under the presence of a small amount of catalytic KI, H_3AsO_3 reacts with $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$ to form Ce^{3+} and H_3AsO_4 in acidic conditions.

- (i) H_3AsO_3 acts like a monoprotic acid.

Suggest why H_3AsO_3 and $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$ react with each other slowly without the presence of a catalyst.

[1]

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The concentration of KI can be determined through the kinetics of the Sandell-Kolthoff reaction.

In order to understand the kinetics of this reaction, 3 trial runs were performed with the initial concentrations of H_3AsO_3 , $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$ and KI shown in **Fig 4.1**. The pH of the solution was 0 for all 3 runs.

Run	concentration of H_3AsO_3 / mol dm^{-3}	concentration of $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$ / mol dm^{-3}	concentration of KI / mol dm^{-3}
1	0.01250	0.00120	1.43×10^{-6}
2	0.00625	6.00×10^{-4}	1.43×10^{-6}
3	0.01250	0.00120	7.15×10^{-7}

Fig 4.1

The absorbance of the reaction mixture was monitored. For each run, the absorbance recorded is directly proportional to the concentration of $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$. The results are recorded in **Fig 4.2**.

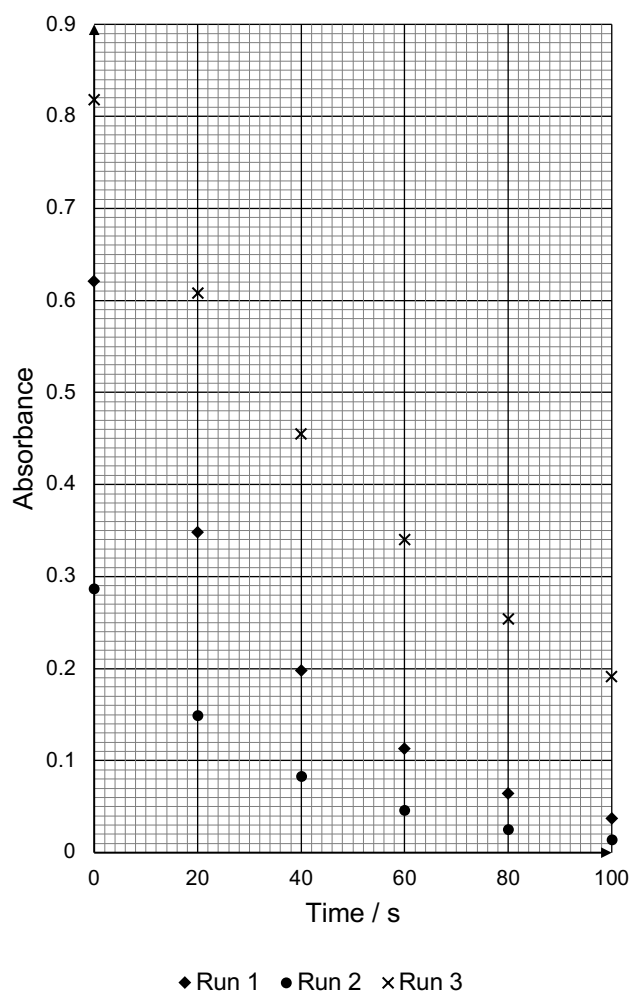


Fig 4.2

Fig 4.3 shows the raw data recorded.

Time / s	Absorbance recorded for		
	Run 1	Run 2	Run 3
0	0.621	0.287	0.818
20	0.348	0.149	0.608
40	0.198	0.083	0.455
60	0.113	0.046	0.340
80	0.064	0.025	0.254
100	0.037	0.014	0.191

Fig 4.3

The first reading of the absorbance of the reaction mixture is recorded at time = 0 s. This is **not** the time when the reaction first starts.

The rate of reaction of this reaction is defined as the rate of change of absorbance with respect to time. The absorbance measurement has no units (i.e., it's dimensionless).

- (ii) Determine the order of reaction with respect to H_3AsO_3 , $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$ and KI.

[7]

You need to show all working. You may use the space on the next page to carry on with your working.

[Continue your working in the space below.]

- (iii) Hence or otherwise, determine the rate constant in the rate law of the Sandell-Kolthoff reaction using data from Run 1. State its units.

[2]

- (iv) A 1.000 g sample of iodised salt was dissolved in 10.0 cm³ of deionised water. A 0.0500 cm³ aliquot of this solution was added to a mixture of 1.000 cm³ of 0.0250 mol dm⁻³ H₃AsO₃. 0.800 cm³ of H₂SO₄ was added to adjust the pH. 0.200 cm³ of 0.0120 mol dm⁻³ (NH₄)₂ [Ce(NO₃)₆] was added to start the reaction. The starting pH of the reaction mixture was 0.

The absorbance of the solution was measured. The results are shown in **Fig 4.4**. The absorbance is proportional to the concentration of (NH₄)₂ [Ce(NO₃)₆].

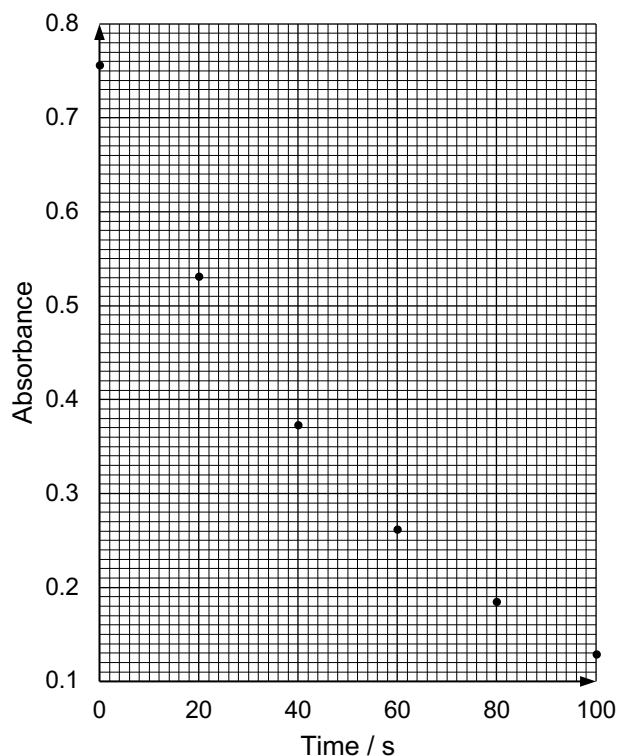


Fig 4.4

The initial absorbance recorded at time = 0 s is 0.756.

Without finding the initial rate of the reaction, determine the iodine level in ppm of this sample of salt using your answer from (ii) and (iii). [3]

