

# Differential Rates of $\text{H}_2\text{O}_2$ Decomposition by Halogen Anion Catalysis ( $\text{Cl}^-$ , $\text{Br}^-$ and $\text{I}^-$ )

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## 1.0 | Introduction

### 1.1 | An Overview of $\text{H}_2\text{O}_2$ and Iodide Catalysis

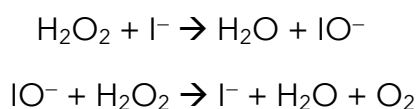
**Hydrogen peroxide ( $\text{H}_2\text{O}_2$ )** is a dangerous and highly reactive by-product of many physiological processes. In eukaryotic cells, electron leakage in the electron transport chain partially reduces molecular oxygen ( $\text{O}_2$ ) to  $\text{H}_2\text{O}_2$  and its metastable counterpart, superoxide ( $\text{O}_2^{\bullet-}$ ). Additional  $\text{H}_2\text{O}_2$  is produced through the destruction of toxic  $\text{O}_2^{\bullet-}$  by the superoxide dismutase enzymes (SODs). To counter this fatal flow of  $\text{H}_2\text{O}_2$  from diverse sources, eukaryotic cells employ a variety of brilliantly created strategies. Before exploring this arsenal, a question must be answered: “Why is  $\text{H}_2\text{O}_2$  dangerous?”

The primary reason is that the central O–O of  $\text{H}_2\text{O}_2$  bond is quite weak – much weaker than the O=O bond in  $\text{O}_2$ . When hit with high-energy radiation (like UV rays), the weak O–O bond breaks, producing two hyper-reactive **hydroxyl radicals ( $\text{OH}^\bullet$ )**. Likewise, the reduction of  $\text{H}_2\text{O}_2$  by free cytoplasmic  $\text{Fe}^{2+}$  ions produces hydroxyl radicals via the Fenton Reaction. These molecules are the core reason behind the danger of  $\text{H}_2\text{O}_2$  to eukaryotic cells, for hydroxyl radicals will react indiscriminately with all biomolecules. Their oxidative power is able to deactivate enzymes, mutate DNA, and set off a chain reaction of lipid peroxidation which can destroy the entire cell membrane.

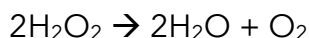
With this understanding, we can now observe the methods by which eukaryotic cells combat hydrogen peroxide. In human cells, the ultra-specific enzyme catalase converts  $\text{H}_2\text{O}_2$  to harmless  $\text{H}_2\text{O}$  and  $\text{O}_2$ . Plus, there are the glutathione peroxidases (GPxs), a class of enzymes which break down not only  $\text{H}_2\text{O}_2$  but also organic peroxides.\*

Yet of particular relevance to this study is another method known to be employed by marine algae – the use of *inorganic* iodine as a catalyst for  $\text{H}_2\text{O}_2$  decomposition [1]. Shocking enough is a biological catalysis occurring non-enzymatically; but even more shocking is the fact that the catalyst is in elemental form, as the **iodide** ( $\text{I}^-$ ) ion.

The iodide catalyst operates via a simple two step reaction mechanism:



$\text{I}^-$  ion is regenerated over the steps of the reaction, fitting the definition of a catalyst. Overall, the net reaction is identical to the reaction for catalase catalysis (GPxs do not produce  $\text{H}_2\text{O}$  and  $\text{O}_2$  as by-products – only  $\text{H}_2\text{O}$ ), which proceeds as follows:



The instantaneous rate law for the iodide-catalyzed decomposition of  $\text{H}_2\text{O}_2$  is second order overall, and first order in each of the reactants: **rate =  $k[\text{H}_2\text{O}_2][\text{I}^-]$** .

## 1.2 | Beyond Iodide Catalysis – The Experimental Idea

With the iodide catalysis in mind, a question naturally arises: “How do the lower period halogens compare to  $\text{I}^-$  in catalytic efficiency for the  $\text{H}_2\text{O}_2$  decomposition reaction?”

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\* The GPxs are distinguished by an intriguing property – some contain the trace element selenium (Se).

This is the question that arose in my mind after learning about iodide catalysis. After rolling the idea round for a while, I decided that fluorine would not be feasible to test since it notoriously reactive. Moreover, the fluoride ion ( $F^-$ ) is notably basic, behaving primarily in the protonated form (HF).<sup>\*</sup> Conversely, the strong hydrohalic acids – HCl, HBr and HI – shed their protons 100% in solution, their halogen anions being such weak bases that re-protonation is essentially nonexistent. Thus, as far as general safety and acid-base activity are concerned, the best halogens to test as comparisons to iodine are bromine (Br) and chlorine (Cl). The anions of all three can be easily obtained by dissolving a salt of each element in solution (see Section 2.1).

Now the only difficulty comes in actually *measuring* the reaction rates. The solution to this difficulty is the idea of measuring the  $O_2$  gas which bubbles out solution during the reaction (see Section 1.1). Eventually, we determined to make the measurements with a digital pressure sensing instrument. (See Section 7 for information on the individuals who contributed to the critical experimental design steps detailed in this paragraph.)

## 2.0 | Materials

### 2.1 | Chemicals

- Potassium Iodide (KI),  
0.1 M aqueous solution
- Potassium Bromide (KBr),  
dry powder / crystals
- Sodium Chloride (NaCl),  
sea salt crystals
- Hydrogen Peroxide ( $H_2O_2$ ),  
3% aqueous solution (~0.88 M)
- Distilled Water ( $H_2O$ ),  
Arrowhead brand
- San Pellegrino Beverage, for  
testing Gas Pressure Sensor

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<sup>\*</sup> I say “behaving” because recent evidence suggests that HF really is a strong acid, and only “behaves” as a weak acid because the ion pair ( $H_3O^+ \cdots F^-$ ) is so tightly bound that the acidic proton is neutralized.

## 2.2 | Apparatus

- Erlenmeyer Flasks (150 and 250 mL), for housing stock solutions
- Erlenmeyer Flask (50 mL), to act as the reaction chamber
- Go Direct® Gas Pressure Sensor, from Vernier Science Equipment
- Accompanying Vernier Graphical Analysis software,
- 3.0 mL pipettes, for applying small amounts of solutions
- Transfer beaker (50 mL), for pouring catalyst solutions
- Long plastic stirrers, for mixing stock solutions
- Professional Digital Mini Scale, accuracy  $\pm 0.001$  g

## 3.0 | Purpose and Hypothesis

The purpose of this experiment is to compare the reaction rates of iodide-, bromide- and chloride-catalyzed  $\text{H}_2\text{O}_2$  decomposition. Accordingly, I will present my hypothesis about the relative catalytic rates of each halogen anion.

I think that  $\text{I}^-$  will have the highest catalytic rate for two main reasons:

1. Iodide catalysis is the method employed by marine algae – and it is definitely plausible that the most efficient method would be found in nature.
2. Chemical evidence also points toward  $\text{I}^-$  producing the fastest rate.

This evidence is comprised of some general trends regarding element families on the Periodic Table and comparison between the halogen and chalcogen families. Firstly, “Heavier elements are more polarizable (‘softer’) than lighter ones...this usually leads to more rapid electrophilic and nucleophilic substitutions at the element” [2]. In redox chalcogen chemistry, this idea has been enthusiastically embraced in research papers that compare the reactivities of sulfur and its heavier congener, selenium. Just as one might predict from the family trend, selenium comes out on top in terms of reactivity.

Fundamentally, the reason for selenium's higher reactivity is that its "...outer valence electrons...are...more loosely held than those of sulfur" [2]. Colloquially, selenium's outer electrons have been "...described as 'easy in, easy out' relative to sulfur..." [3].

By way of extrapolation, this logic can be applied to the halogens. Iodide anion is the largest and most polarizable of the three halogen anions to be tested, and therefore it should be the most nucleophilic and reactive of the three. Reactivity should decrease up the halogen family; bromide should show less reactivity than iodide, but more than chloride. Therefore, my hypothesis for the relative catalytic reaction rates of the three halogen anions is as follows, from fastest to slowest:  $I^- > Br^- > Cl^-$ .

## 4.0 | Procedures

### 4.1 | Preparing Stock Solutions

We obtained  $H_2O_2$  in a standard over-the-counter brown bottle, at a concentration of 3%, which  $\approx 0.88$  M. We also obtained iodide anion as a 0.1 M aqueous solution of KI. However, we were only able to bromide anion as dry crystals of KBr. Thus, we needed to make the KBr solution ourselves. In order to maintain concentration consistency, we performed the necessary calculations for the creation 0.1 M KBr solution.

The desired volume of KBr solution was 0.2 L (200 mL). Using the formula  $n = CV$ :

$$\frac{0.1 \text{ mol}}{L} \times 0.2 \text{ L} = \mathbf{0.02 \text{ mol}}$$

Then, converting to grams via the molar mass of KBr:

$$\frac{119.0 \text{ g}}{1 \text{ mol}} \times 0.02 \text{ mol} = \mathbf{2.38 \text{ g}}$$

Using the Digital Mini Scale, we weighed out 2.381 g of dry, crystalline KBr powder and added enough water to obtain 200 mL of the solution. The resulting stock solution was housed in a 250 mL Erlenmeyer flask, which was put aside until further use.

To obtain the final halogen anion – chloride – we crushed pure sea salt (NaCl) into a fine crystalline powder. The difference in alkali metal cation between this salt and the other two halogen salts (Na vs. K) is of no concern to the purposes of this experiment. The desired volume of NaCl solution was 0.15 L (150 mL). Using the formula  $n = CV$ :

$$\frac{0.1 \text{ mol}}{L} \times 0.15 L = \mathbf{0.015 \text{ mol}}$$

Then, converting to grams via the molar mass of NaCl:

$$\frac{58.5 \text{ g}}{1 \text{ mol}} \times 0.015 \text{ mol} = \mathbf{0.8775 \text{ g}}$$

Using the Digital Mini Scale, we weighed out 0.878 g of dry, crystalline NaCl powder and added enough water to obtain 150 mL of the solution. The resulting stock solution was housed in a 150 mL Erlenmeyer flask, which was put aside until further use.

Thus, we ensured that all three catalytic halogen solutions had a 0.1 M concentration.

## 4.2 | Experimental Design

As explained in Section 1.2, the key to measuring the reaction rates of halogen-anion-catalyzed  $\text{H}_2\text{O}_2$  decomposition is tracking the rate of  $\text{O}_2$  gas production over time. To do this, we employed the Go Direct® Gas Pressure Sensor, manufactured by Vernier Science Equipment. This Pressure Sensor corks into the mouth of a 50 mL Erlenmeyer flask, which acts as the reaction chamber. The pressure data collected by the Sensor is displayed in real-time on a computer, using the Vernier Graphical Analysis software.

In all the trials except for the Control, we employed a 30 mL / 30 mL volumetric ratio of substrate reactant (H<sub>2</sub>O<sub>2</sub>) to halogen catalyst solution. However, due to concentration differences between the substrate and catalyst solutions, the actual mole *amounts* of chemicals differed significantly. The formula  $n = CV$  gives the mole amounts for H<sub>2</sub>O<sub>2</sub>:

$$\frac{0.88 \text{ mol}}{L} \times 0.03 L = \mathbf{0.0264 \text{ mol}}$$

And likewise, for each of the three catalytic halogen anions (I<sup>-</sup>, Br<sup>-</sup>, Cl<sup>-</sup>):

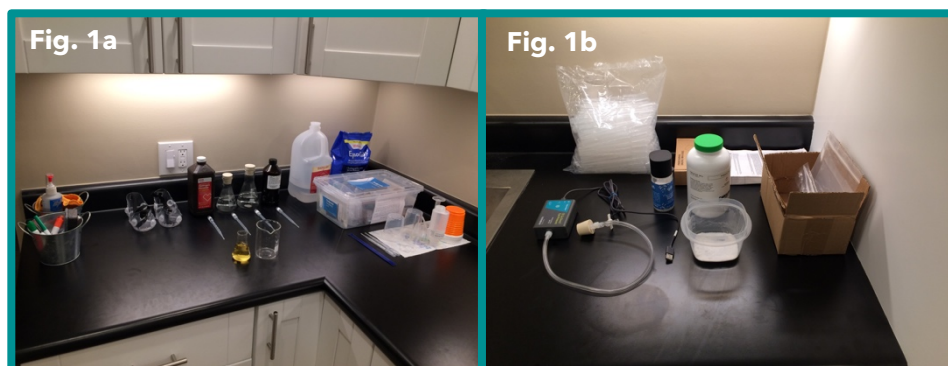
$$\frac{0.1 \text{ mol}}{L} \times 0.03 L = \mathbf{0.003 \text{ mol}}$$

The difference of these values is 0.0234 mol excess H<sub>2</sub>O<sub>2</sub>, which may seem too high. However, the stoichiometry of the reaction (see Section 1.1) demonstrates that two H<sub>2</sub>O<sub>2</sub> molecules are destroyed for each halogen anion X<sup>-</sup> that is used in catalysis. Plus, X<sup>-</sup> is regenerated at the end of each catalytic cycle, so it is actually quite logical to use a smaller amount of halogen catalyst than H<sub>2</sub>O<sub>2</sub> substrate. Equimolar amounts of H<sub>2</sub>O<sub>2</sub> and catalyst would cause the reaction to proceed so quickly that pressure data would assume an unreasonably steep curve. Furthermore, the volume of O<sub>2</sub> gas generated almost instantaneously might create dangerous pressure. All things considered, the 30/30 ratio of reactant substrate to halogen catalyst was suitable for this experiment.

Finally, it must be noted that the 30/30 reactant/catalyst ratio has an important effect on the solution concentrations. When the two solutions are mixed in the reaction flask, the total volume is doubled; as a result, the **concentration of each solution is halved**. Thus, the halogen catalyst solutions have a **constant** "experimental concentration" of **0.05 M**. Similarly, the **initial** experimental concentration of the H<sub>2</sub>O<sub>2</sub> reactant solution is **~0.44 M**. Because the H<sub>2</sub>O<sub>2</sub> concentration is *not* constant, this idea of concentration halving will be critical to the calculations presented in Section 5.2.

### 4.3 | Control, Trials 1-3, and Bonus Trial

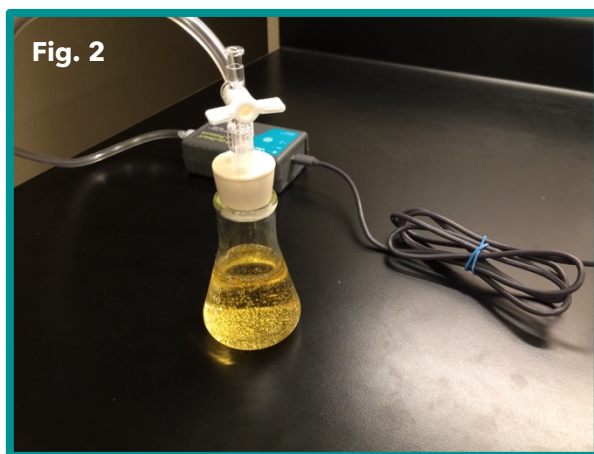
As this experiment is heavily dependent on gas pressure, it is good to give a couple data points about the ambient conditions of the laboratory where this experiment was performed. The lab's ambient pressure was found to be  $\sim 100.8$  kPa, while its ambient temperature was measured to be  $22.9$  °C ( $\sim 296$  K). **Fig. 1** shows the lab in which the experiment was performed. The larger surface **(a)** was used for running the reactions; the smaller surface **(b)** was used for preparing the KBr and NaCl stock solutions. As the general safety protocols would demand, there was a sink present in the laboratory; its edge can be seen on the left-hand side of **Fig. 1b**.



**Control:** We placed 30 mL of 3%  $\text{H}_2\text{O}_2$  into a 50 mL Erlenmeyer flask, which acted as the reaction chamber for the trials of this experiment. (Between each trial, the flask was rinsed and swabbed with Q-Tips in order to prevent contamination between different solutions.) After swiftly securing the cork in the flask neck, we monitored  $\text{O}_2$  pressure for 10 minutes using the Gas Pressure Sensor, and the data was graphed in real-time using the Graphical Analysis software. The resulting graph is shown in Section 5.1.



**Trial 1 – Iodide Catalysis:** We measured out 30 mL of 0.1 M KI stock solution into the 50 mL transfer beaker. Next, we placed 30 mL of 3% H<sub>2</sub>O<sub>2</sub> into the reaction chamber flask. After pouring in the KI solution into the reaction chamber, we swiftly secured the cork in the neck of the flask. We had originally intended to use the Pressure Sensor to measure O<sub>2</sub> production for a duration of 10 minutes, but by a little over 8 minutes, the pressure in the flask had become so extreme\* that we were forced to terminate data collection. The resulting graph is shown in Section 5.1. **Fig. 2** shows the experimental set-up described in Section 4.2, using Trial 1 as an example. (The yellow color in the flask is due to a side reaction unrelated to the main catalytic reaction; see Section 5.1).



**Trial 2 – Bromide Catalysis:** All procedures were the same as those in Trial 1, but we used 30 mL of 0.1 M KBr stock solution rather than the KI solution. In contrast to the dramatic color change of Trial 1, the solution in the reaction chamber stayed entirely colorless, and we terminated data collection after about 8 minutes because of the unnoticeable levels of reaction (see Section 5.1 for pressure graph).

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\* During the reaction, the cork was blown off multiple times by the high O<sub>2</sub> pressure which the reaction generated. However, we managed to keep the cork on long enough to get a relatively accurate graph.

**Trial 3 – Chloride Catalysis:** All procedures were the same as those in the previous two trials, but this time we used 30 mL of 0.1 M NaCl stock solution. As with Trial 2, no noticeable reaction occurred within the reaction chamber, and we again terminated data collection after about 8 minutes (see Section 5.1 for pressure graph).

**Bonus Trial – Iodide Catalysis:** Due to the spectacular nature of the reaction carried out in Trial 1, we decided to run a bonus trial with 0.1 M KI as the catalytic solution. All procedures were the same as in Trial 1, except this time, we were more prepared for the high levels of O<sub>2</sub> gas pressure generated by the reaction and were therefore able to prevent the cork from blowing off as often (see Section 5.1 for pressure graph).

#### 4.4 | Possible Sources of Error

Before moving on to the presentation and analysis of the data that we collected, it is necessary to list a few possible sources of error for this experiment:

- Failure to secure the cork quickly enough into the neck of the flask; this would result in the Pressure Sensor missing the opening seconds of the reaction.
- Failure to secure the cork tightly enough into the neck of the flask; the escaping gases would cause the Pressure Sensor to record values that are too low.
- Contamination from residual solution from previous trials (this is a low-risk error source, as the flask was meticulously rinsed and swabbed between each trial).
- Contamination from cotton Q-Tip fibers deposited in the flask by swabbing; this could result in some of the halogen anions forming ion-dipole attractions with the polar hydroxyl groups of the cotton fibers, effectively leaching the ions out of solution and hindering their catalytic ability to react with H<sub>2</sub>O<sub>2</sub> molecules.

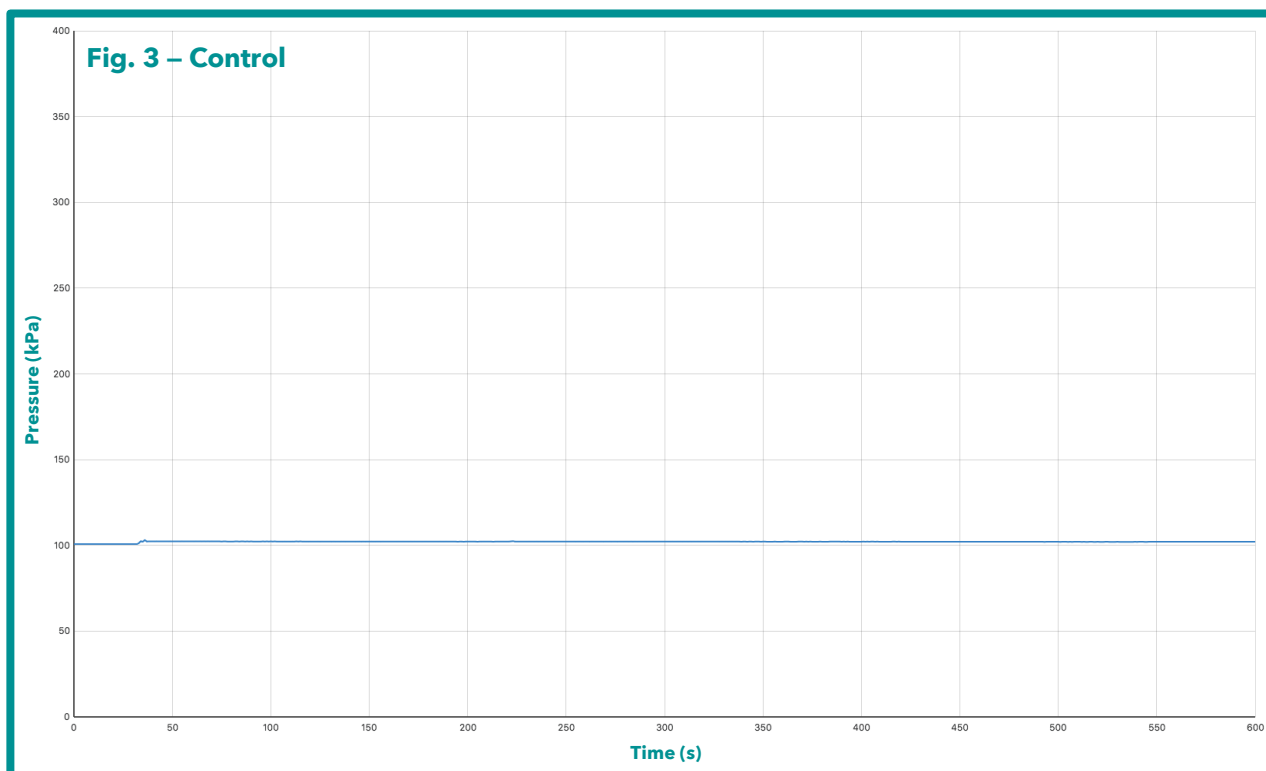
#### 5.0 | Results and Discussion

## 5.1 | Data for the Experiment

Presented here are the data – both qualitative and quantitative – for this experiment. Included are all five of the O<sub>2</sub> pressure graphs, as well as qualitative observations for the Control, Trials 1-3, and the Bonus Trial.

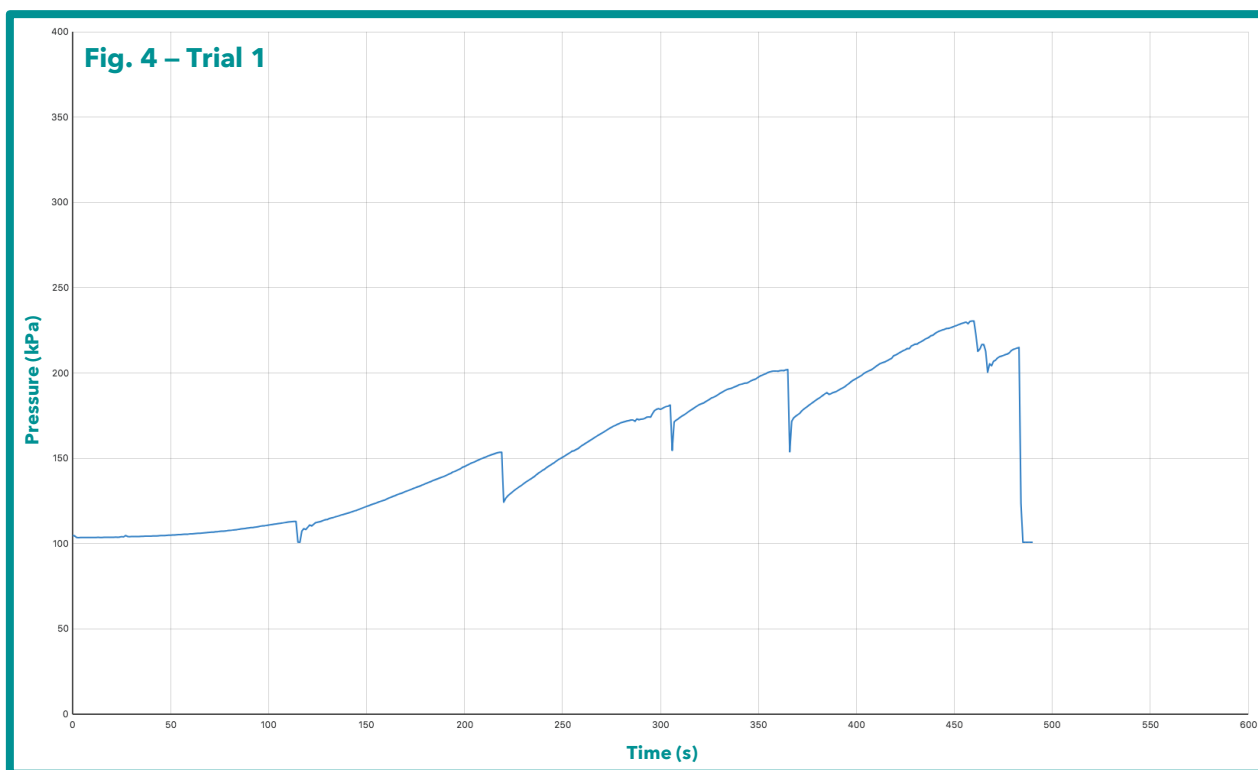
**Control:** The graph below (**Fig. 3**) gives a “pressure baseline” for the experiment – a reference point for all the other trials. As shown in the graph, the measured pressure flatlines a small amount above\* the ambient pressure (~100.8 kPa). This slight rise in pressure is presumably due to the slow, natural decomposition of H<sub>2</sub>O<sub>2</sub>; alternatively, it could be due simply to the presence of a liquid volume in the reaction chamber flask.

Therefore, for any of the following trials to display catalytic activity, they must exhibit pressures that are at least a little above the baseline shown in the graph. To give hard values, we will set the “control pressure” for this experiment at 102.2 kPa, a value that starts to appear consistently after about 120 seconds from  $T = 0$ .

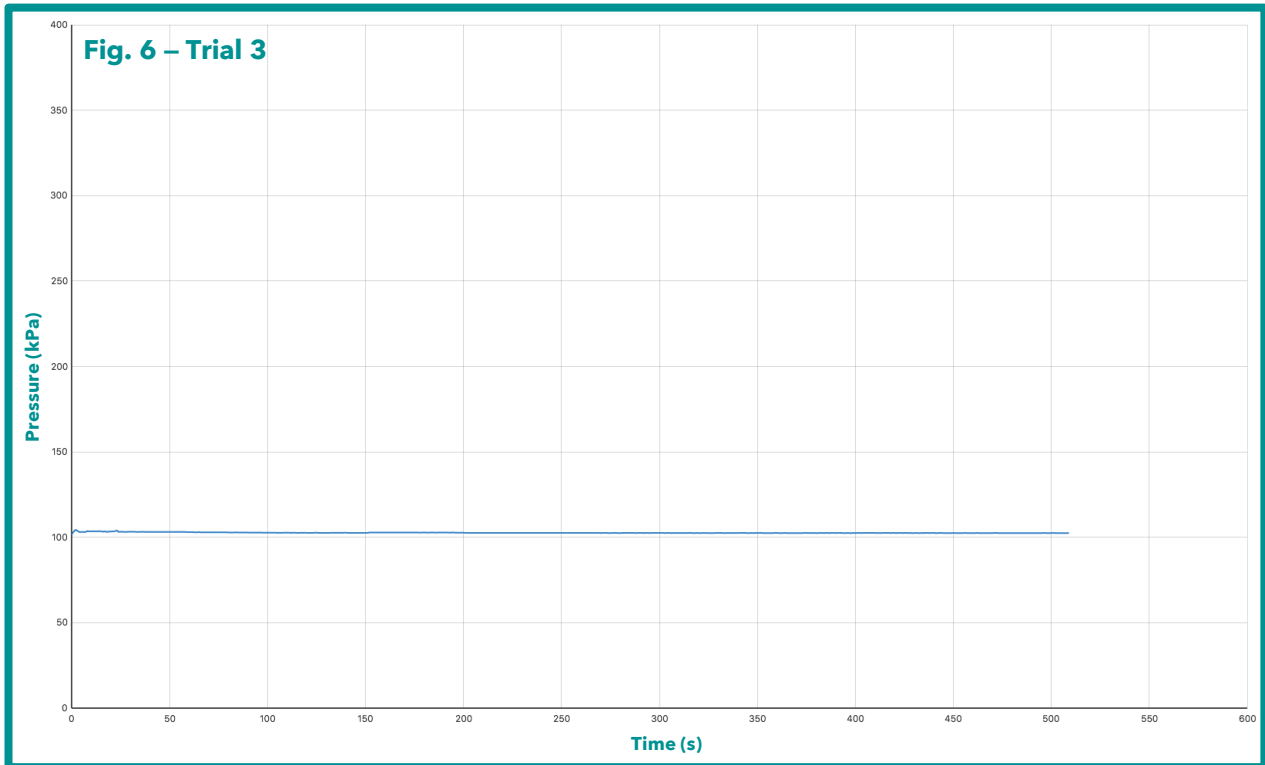
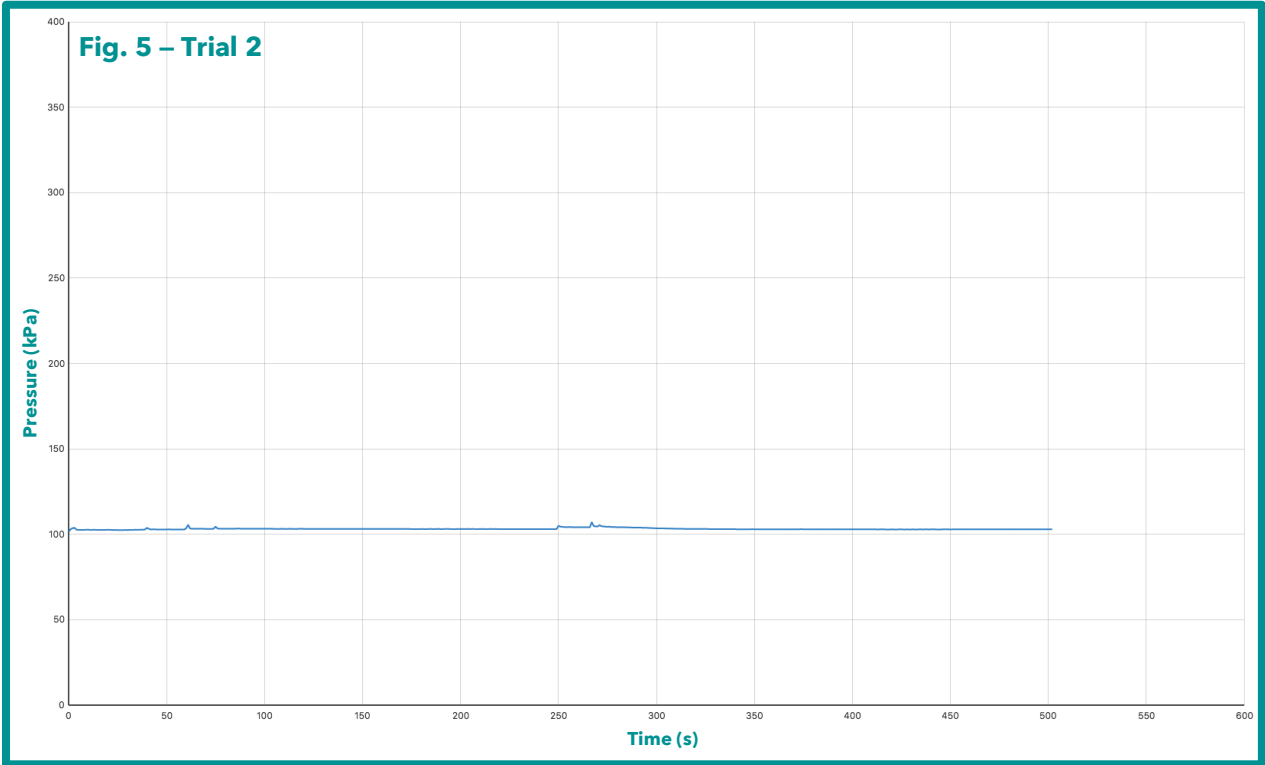


**Trial 1 – Iodide Catalysis:** Out of the three halogens tested, the iodide anion was the clear winner in terms of catalytic efficiency. There was simply no comparison between the iodide catalysis reaction and the other two halogen ions – neither qualitatively nor quantitatively. Qualitatively, the reaction between  $I^-$  and  $H_2O_2$  proceeded vigorously, producing an abundance of  $O_2$  gas bubbles which streamed up through the solution. The solution also turned a bright yellow color, which we initially inferred as being due to the presence of the intermediate,  $IO^-$ , since all other reacting species are colorless. This hypothesis gave rise to the idea of using color as a “reaction clock” – i.e., the return of the solution to its colorless state would signal the ending of the reaction. However, upon further research, we determined that the color was really caused by an unrelated side reaction, involving the oxidation of  $I^-$  to triiodide ( $I_3^-$ ) [4]. These ions are brown in high concentrations and yellow in low concentrations (as in this experiment). Thus, the “reaction clock” idea had to be discarded in continuation of this experiment.

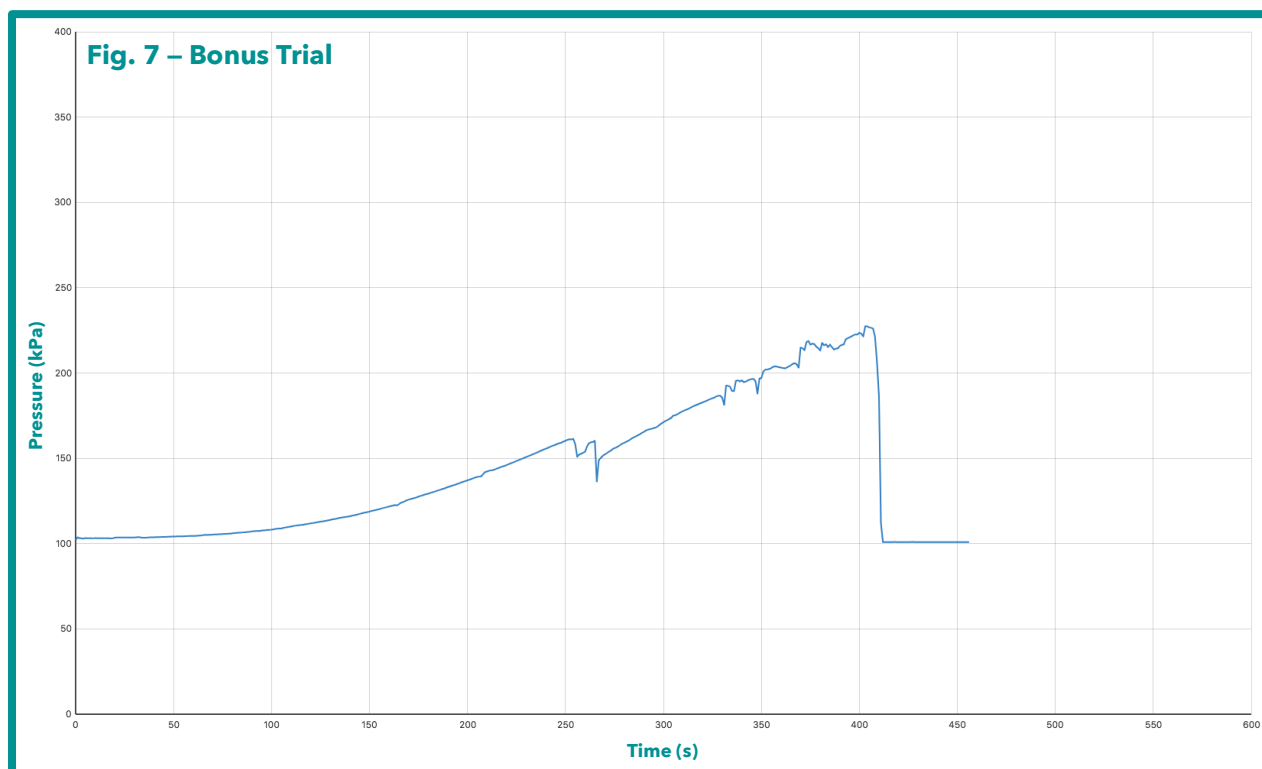
The pressure per time graph for Trial 1 (**Fig. 4**) takes the form of a steady curve, which starts off a bit slow and gradually ramps up. The sudden drops in the pressure curve are reflections of when the strong  $O_2$  gas pressure blew the cork off the reaction flask. Peak pressure was recorded at 230.5 kPa at 460 seconds.



**Trials 2 & 3 – Bromide & Chloride Catalysis:** The results of Trial 2 were the greatest deviation from the hypothesis given in Section 3.0. While we expected the catalytic efficiency of  $\text{Br}^-$  to fall somewhere between the efficiencies of  $\text{I}^-$  and  $\text{Cl}^-$ , the rate of bromide catalysis showed no discernable positive difference from the rate of chloride catalysis, neither qualitatively nor quantitatively. Both solutions remained crystal clear, and no vigorous bubbling (like that seen in Trial 1) was observed in either case. Note that the little spikes in bromide graph (**Fig. 5**) were caused by our auxiliary securing of the cork and do not represent reaction bursts. An examination of our Supplementary Data will show that **Fig. 5** and **Fig. 6** have no statistically significant differences.



**Bonus Trial – Iodide Catalysis:** The qualitative results of the Bonus Trial were identical to those observed in Trial 1. The solution quickly turned yellow, and vigorous bubbling was seen. Quantitatively, the trial yielded similar results to those observed in Trial 1, as can be seen in the graph below (**Fig. 7**). The main difference between the two graphs is that there are less hard pressure drops in the Bonus Trial graph, because this time, we were more prepared for the intense  $O_2$  pressure generated by the reaction.



## 5.2 | Mathematical Analysis for Iodide Catalysis

The qualitative data and graphs presented in the preceding section show that iodide is the most efficient of the three catalytic halogens tested – hands down. But what can we learn from this in terms of mathematical reaction rates of iodide catalysis?

**From Pressure to Moles:** The first step in any mathematical reaction rate is to convert the pressure data in the graphs into mole data. Knowing the moles of O<sub>2</sub> gas produced at a given time  $t$  would allow us to find the moles of H<sub>2</sub>O<sub>2</sub> reacted at  $t$  via a simple multiplication by 2, thanks to the stoichiometry of the reaction (see Section 1.1). How can we do this? The key comes in the form of the Ideal Gas Law:

$$PV = nRT$$

Where  $P$  = pressure,  $V$  = volume,  $n$  = moles,  $R$  = the Ideal Gas Constant (with the right units!) and  $T$  = temperature in Kelvins. We know all these variables except for  $n$ , so the equation is rearranged to solve for  $n$  as follows:

$$n = \frac{RT}{PV}$$

Now we can proceed to insert the values that we know and find  $n$ . Firstly,  $R$  will be the Ideal Gas Constant with pressure units in kPa, since these are the pressure units on all of the pressure graphs. This gives the following number:

$$\frac{8.314 \text{ L} \cdot \text{kPa}}{\text{K} \cdot \text{mol}}$$

Secondly,  $T$  is simply the ambient temperature, measured as 296.05 (see Section 4.3). Thirdly,  $P$  is a pressure value which we will take from the graph of the Bonus Trial. (As explained earlier, this graph had less hard pressure drops than the graph of Trial 1, making the Bonus Trial Graph more accurate in terms of data recording.) According to the Graphical Analysis software, a value of **223.6 kPa** appears when  $t = \mathbf{400 \text{ seconds}}$ . This is the value that we will insert for  $P$ , as it arises from a time when the reaction had progressed significantly. Finally,  $V$  is the only variable which proves somewhat elusive. The question that presents us is, "What is the volume that we should consider the O<sub>2</sub> gas to occupy?" We have found two main answers to this question.



According to the Vernier Go Direct® Gas Pressure manual [5], the Pressure Sensor has an internal volume of **0.8 mL**, which is a miniscule  **$8 \times 10^{-4}$  L**. Such a value seems too small, and when placed in the Ideal Gas Law, produces value for  $n$  that seems absurdly small. Thus, it is worth also considering the volume of the tubing running from the flask to the Sensor *and* the volume of the flask neck. To that end, we measured the distance between the solution surface and the bottom of the cork, obtaining a length of 3.0 cm. The diameter of the flask was 2.4 cm, making its radius 1.2 cm. Putting these values into the equation for the volume of a cylinder ( $V = \pi r^2 h$ ) gives us a value of 13.6 cm<sup>3</sup> or 13.6 mL (**0.0136 L**). We can also think of the tubing as a cylinder; its length was measured as 45 cm and its diameter as 0.7 cm, making its radius 0.35 cm. Putting these values into the  $V$  equation, we obtain a value of 17.3 cm<sup>3</sup> or 17.3 mL (**0.0173 L**). Now we can add both of these values to the original Pressure Sensor internal volume, giving a total volume of **0.0317 L**. This is the more reasonable of the two values but nevertheless, we will run calculations of  $n$  with both values, beginning with the smaller value.

Putting the values into the equation rearranged for  $n$ , we obtain the following result:

$$n = \frac{223.6 \text{ kPa} \times 8 \times 10^{-4} \text{ L}}{\frac{8.314 \text{ L} \cdot \text{kPa}}{\text{K} \cdot \text{mol}} \times 296.05 \text{ K}} = 7.27 \times 10^{-5} \text{ mol}$$

Multiplying by 2 gives the mole amount of H<sub>2</sub>O<sub>2</sub> reacted at  $T = 400$ :  **$1.45 \times 10^{-4}$  mol**. Recalling the initial mole amount of H<sub>2</sub>O<sub>2</sub> – **0.0264 mol** – this value, after 400 seconds of reaction time seems to be far too small. However, the amount of I<sup>-</sup> catalyst initially present was only 0.003 mol, so this value is not impossible – just surprising.

Running the numbers again with the expanded volume gives a more rational result:

$$n = \frac{223.6 \text{ kPa} \times 0.0317 \text{ L}}{\frac{8.314 \text{ L} \cdot \text{kPa}}{\text{K} \cdot \text{mol}} \times 296.05 \text{ K}} = 0.00288 \text{ mol} = 2.88 \times 10^{-3} \text{ mol}$$

Multiplying by 2 gives a much larger (and more reasonable) result for the mole amount of H<sub>2</sub>O<sub>2</sub> reacted after 400 seconds: **5.76 x 10<sup>-3</sup> mol**, or simply **0.00576 mol**. For the remaining calculations in this paper, this second value is the one that we shall utilize. Placed alongside the original starting value of 0.0264 mol H<sub>2</sub>O<sub>2</sub>, **0.00576 mol** H<sub>2</sub>O<sub>2</sub> reacted after 400 seconds seems more reasonable than the alternative value of only 1.45 x 10<sup>-4</sup> mol, which is considerably smaller.

**From Moles to Rates:** Having decided on 0.00576 mol H<sub>2</sub>O<sub>2</sub> as the value with which to continue, the next natural step might seem to divide the value by the time it took to reach it – 400 seconds. This would produce a rate of catalytic H<sub>2</sub>O<sub>2</sub> decomposition of 1.44 x 10<sup>-5</sup> mol/s. Yet we cannot simply stop with this linear rate, because the real rate is a curve (see **Fig. 7**). Therefore, we must find a *rate law equation* – i.e., an *integrated rate law equation*, which allows for changes in concentration. How can this be done?

Earlier in this paper, we stated that the instantaneous rate law for the iodide-catalyzed decomposition of H<sub>2</sub>O<sub>2</sub> is **rate = k[H<sub>2</sub>O<sub>2</sub>][I<sup>-</sup>]**. But this is only an *instantaneous* rate law, and while the [I<sup>-</sup>] stays constant throughout the reaction (because I<sup>-</sup> is a catalyst), [H<sub>2</sub>O<sub>2</sub>] decreases. However, this equation is still helpful, for it tells us that H<sub>2</sub>O<sub>2</sub> – the reactant whose concentration changes over the course of the reaction – is *first order*. Thus, we now know which integrated rate law to use – the **first order integrated rate law**:

$$\ln[A]_t - \ln[A]_0 = -k \times t$$

Where  $t$  is a given time in seconds (400 seconds in this case) and  $k$  is the rate constant (which we will ultimately calculate).  $[A]_t$  is the concentration of the reactant in question at the time  $t$ , while  $[A]_0$  is the initial concentration.  $A$  in this case is H<sub>2</sub>O<sub>2</sub>, and we know its initial concentration: **~0.44 M** (see Section 4.2). However, we have only calculated a *mole* amount of H<sub>2</sub>O<sub>2</sub> reacted at time  $t$ . To obtain a  $[A]_t$ , we proceed as follows.

Firstly, we subtract the 0.00576 mol (= moles of H<sub>2</sub>O<sub>2</sub> reacted after 400 seconds) from the initial mole amount of H<sub>2</sub>O<sub>2</sub>: 0.0264 – 0.00576 = **0.02064 mol**. This means that 0.02064 mol H<sub>2</sub>O<sub>2</sub> remains in solution at t = 400 seconds. Secondly, recalling the 30/30 ratio of reactant solution to catalyst solution (see Section 4.2), we can treat the volume of the reaction flask solution as a constant throughout the reaction at **60 mL (0.06 L)**. Then, employing the formula  $C = n/V$ , we find the concentration at t = 400 seconds:

$$\frac{0.02064 \text{ mol}}{0.06 \text{ L}} = \mathbf{0.344 \text{ M}}$$

Now we know all the values that we need to solve for  $k$ , the rate constant, via the first order integrated rate law. First, we will rearrange the equation to solve for  $k$  as follows:

$$k = -\left(\frac{\ln[A]_t - \ln[A]_0}{t}\right)$$

Now, plugging in all of the known values into the rearranged equation:

$$k = -\left(\frac{\ln(0.344) - \ln(0.44)}{400 \text{ s}}\right) = \frac{\mathbf{6.15 \times 10^{-4}}}{\mathbf{s}}$$

Note that the  $k$  value is only constant for a given temperature, which we have reported earlier as 296.05 K. Therefore, the integrated rate law equation for **iodide-catalyzed H<sub>2</sub>O<sub>2</sub> breakdown** at an ambient laboratory temperature of 296.05 K is

$$\ln[H_2O_2]_t - \ln[H_2O_2]_0 = -\frac{\mathbf{6.15 \times 10^{-4}}}{\mathbf{s}} \times t$$

Finally, we can use this  $k$  value to find the half-life ( $t_{1/2}$ ) as given by the formula:

$$t_{1/2} = \frac{0.693}{k}$$

Plugging in the calculated value for  $k$ , we obtain the following half-life value:

$$t_{1/2} = \frac{0.693}{\frac{6.15 \times 10^{-4}}{s}} = 1127 \text{ s} = \mathbf{18.8 \text{ min}}$$

Beginning with only pressure-time data, we have derived not only mole amounts of the reactant  $\text{H}_2\text{O}_2$ , but also the half-life and integrated rate law equation for the reaction!!

## 6.0 | Conclusions and Next Steps

In this experiment, we compared the catalytic efficiencies of the iodide, bromide, and chloride ions for the decomposition of hydrogen peroxide reaction. As way to measure reaction progress, we monitored the pressure from the  $\text{O}_2$  gas generated by each trial and used a software program to graph the pressure data over time. Both qualitatively and quantitatively, our results show that **the  $\text{I}^-$  anion is the clear winner** in the catalysis competition, with rates far exceeding those of the bromide and chloride trials, and the Control. The supremacy of iodide as a catalyst for  $\text{H}_2\text{O}_2$  decomposition is in line with our hypothesis. Moreover, the only notable deviation from our hypothesis was the total lack of disparity between the reaction rates for bromide and chloride catalysis, which were qualitatively and quantitatively indistinguishable.

This leads to a reasonable next step for the reaction – investigating why bromide did not catalytically out-perform chloride like we expected. Such investigation may involve running trials similar to those run in this experiment but utilizing more concentrated solutions of bromide and chloride salts. For it may be that the concentrations utilized in this experiment were too dilute, resulting in zero catalytic activity being observed. Regardless, this experiment shows that of the three halogen anions tested, **iodide ( $\text{I}^-$ )** is the most efficient at catalyzing the  $\text{H}_2\text{O}_2$  breakdown reaction.

## 7.0 | References and Acknowledgements

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5. Go to <https://www.vernier.com/manuals/gdx-gp/> and click the button labeled *Download Manual PDF* – The piece of data referenced in Section 5.2 is on **p. 2**.

The author declares no conflict of interest.

The experiment was done out of purely self-directed initiative.

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