Investigating the relationship between the concentration of MnO_2 catalyst powder and the first order rate constant in the decomposition of H_2O_2 using measurements of pressure.

Research Question: How does changing the concentration of solid MnO_2 catalyst powder suspended in aqueous $1.1\,\%\,(v/v)\,H_2O_2\,(aq)$ affect the first order rate constant for its decomposition at 24°C?

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Word count: 123

1   Introduction

Hydrogen peroxide is widely used in disinfection, bleaching, and environmental remediation. Its catalytic decomposition improves its oxidizing ability and is especially relevant in green chemistry due to the reduced waste generated. Transition metal ions such as manganese, iron, cobalt, and lead are commonly used to catalyze this reaction.[**Abuissa**] Manganese, in the form of MnO_2, is the catalyst of choice in this investigation because it is available in the school laboratory, being stable, inexpensive, and non-toxic in small quantities.

This investigation aims to establish a quantitative relation between the concentration of manganese oxide powder and the rate of decomposition of H_2O_2, by measuring the concentration of H_2O_2 indirectly through the amount of oxygen gas released. Theory states that for low amounts of MnO_2, the relationship between its mass and the observed first order rate constant.

2   Background Information

Most existing studies use MnO_2 catalysts immobilized on solid supports[**Do**] or embedded in porous materials[**Kim**]. In contrast, this investigation uses fine MnO_2 powder suspended in solution. This setup presents practical limitations, most notably that the catalyst in its powdered form cannot be directly recovered after the reaction, necessitating an additional separation process. Nonetheless, the powdered form offers simplicity for a school laboratory.

Most existing studies monitor the reaction utilizing methods such as titration on samples taken at specific intervals[**Abuissa**] or colorimetric methods[**Do**], both of which allow direct measurement of the concentration of hydrogen peroxide in the solution.

Instead, this experiment opts to evaluate the progress of the reaction by measuring the amount of oxygen gas released by the reaction over time. This can be calculated with information about the pressure of the sealed reaction vessel over time, assuming constant temperature. Gas pressure will be measured using a pressure sensor, allowing for precise, continuous data collection suitable for computer processing.

2.1 Relevant Theory

"The rate limiting reaction is believed to be the initial reaction between hydrogen peroxide and the iron oxides [**Miller1995**, **ValentineWang1998**, **Miller1999**]. Additionally, the results reveal that the decomposition of H_2O_2 follows pseudo-first order kinetics:

$$-\frac{d[H_2O_2]}{dt} = k_{app}[H_2O_2] \tag{2.1}$$

and thus:

$$\ln\left(\frac{[H_2O_2]}{[H_2O_2]_0}\right) = -k_{app}t \tag{2.2}$$

where k_{app} is the apparent first order rate constant, and $[H_2O_2]$ and $[H_2O_2]_0$ are the concentrations of H_2O_2 in the solution at any time t and time zero, respectively.[**Huang**]"

The data presented in **Section 4** agrees with theory, that the reaction is pseudo-first order. The aim of this investigation is to measure how k_{app} changes in relation to the amount of catalyst used.

Now a general expression for pressure as a function of time will be mathematically derived from (2.2).

Notation			
$n(H_2O_2)$	H_2O_2 in solution at time t	P	Pressure at time t
$n(O_2)$	O_2 released up to t	P_0	Initial pressure
n_0	Initial H_2O_2 in solution	P_∞	Final pressure
n_{air}	Initial air molecules	V_l	Solution volume
R	Ideal gas constant	V_f	Flask volume
T	Temperature	V_g	$= V_f - V_l$, Gas volume

The catalysed decomposition reaction taking place is described by

$$2\,H_2O_2\,(aq) \xrightarrow{\text{MnO}_2} 2\,H_2O\,(l) + O_2\,(g)$$
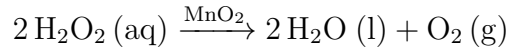
We use this to compute $n(H_2O_2)$ in terms of $n(O_2)$:

$$n(O_2) = 2(n_0 - n(H_2O_2)) \implies n(H_2O_2) = n_0 - \frac{n(O_2)}{2} \tag{2.3}$$

By the definition of concentration,

$$[H_2O_2] = n(H_2O_2) \cdot V_l^{-1}$$

Substituting (2.3) into the above yields

$$[H_2O_2] = \left(n_0 - \frac{n(O_2)}{2}\right) V_l^{-1} \tag{2.4}$$

$$[H_2O_2]_0 = n_0 \cdot V_l^{-1} \tag{2.5}$$

The ideal gas law states

$$PV_g = (n_{\text{air}} + n(O_2))RT$$

Solve for $n(O_2)$ in this expression:

$$n(O_2) = PV_g R^{-1} T^{-1} - n_{\text{air}} \tag{2.6}$$

3

Substituting this into (2.4) yields

$$
\begin{aligned}
[H_2O_2] &= \left(n_0 - \frac{n(O_2)}{2} \right) V_l^{-1} \\
&= \left(n_0 - \frac{PV_gR^{-1}T^{-1} - n_{\text{air}}}{2} \right) V_l^{-1} \\
&= \frac{1}{2} \left(2n_0 + n_{\text{air}} - PV_gR^{-1}T^{-1} \right) V_l^{-1}
\end{aligned}
\tag{2.7}
$$

Notice that when all H_2O_2 is decomposed, $n(H_2O_2) = 0$ and (2.3) yields $n(O_2) = 2n_0$. Hence $2n_0$ is the final amount of O_2 produced. Then $2n_0 + n_{\text{air}}$ can be interpreted as the final amount of gas present, so by the ideal gas law,

$$
(2n_0 + n_{\text{air}})RT = P_\infty V_g \implies 2n_0 + n_{\text{air}} = P_\infty V_g R^{-1} T^{-1}
\tag{2.8}
$$

Substituting this into (2.7) gives

$$
\begin{aligned}
[H_2O_2] &= \frac{1}{2} \left(P_\infty V_g R^{-1} T^{-1} - PV_g R^{-1} T^{-1} \right) V_l^{-1} \\
&= \frac{1}{2} \left(P_\infty - P \right) V_g R^{-1} T^{-1} V_l^{-1}
\end{aligned}
\tag{2.9}
$$

Finally, substitute (2.9) and (2.5) into (2.2).

$$
\begin{aligned}
-k_{\text{app}}t &= \ln \left(\frac{[H_2O_2]}{[H_2O_2]_0} \right) \\
&= \ln \left(\frac{\frac{1}{2} \left(P_\infty - P \right) V_g R^{-1} T^{-1} V_l^{-1}}{n_0 \cdot V_l^{-1}} \right) \\
&= \ln \left(\left(P_\infty - P \right) \cdot \frac{V_g}{2n_0 RT} \right)
\end{aligned}
$$

Solve for P to finish:

$$
e^{-k_{\text{app}}t} = \left(P_\infty - P \right)
$$

$$
\frac{2n_0 RT}{V_g} \cdot e^{-k_{\text{app}}t} = P_\infty - P
$$

$$
P = P_\infty - \frac{2n_0 RT}{V_g} \cdot e^{-k_{\text{app}}t}
$$

For clarity, set

$$c = 2n_0 RTV_g^{-1} \tag{2.10}$$

Notice that c is constant over time assuming that the temperature and volume do not change throughout the reaction. Then the pressure at time t always satisfies the following equation, for constants P_∞, c, and k_{app}.

$$P = P_\infty - c \cdot e^{-k_{\mathrm{app}}t} \tag{2.11}$$

2.2 Existing Results

For porous MnO_2 on carbon nanotube (CNT) supports, the highest reported *specific* rate constant is

$$k_{\mathrm{CNT}} = 35.48\,\mathrm{g}^{-1}\,\mathrm{min}^{-1},$$

measured at 25°C in 100 mL of solution containing 1000ppm H_2O_2.[**Kim**] The existence of such a specific rate constant suggests that the apparent rate constant is roughly proportional with the mass of MnO_2 used.

For pyrolusite (the primary manganese ore) powder, the highest reported specific rate constant is

$$k_{\mathrm{pyro}} = 0.061\,\mathrm{min}^{-1}\,\mathrm{mM}^{-1},$$

measured at room temperature in 200 mL of solution containing 29.4mM H_2O_2.[**Do**] This suggests that the rate constant is proportional to the concentration of MnO_2 in solution.

The results obtained in this investigation will be compared with these two results.

Hypothesis. Ideally a proportional relationship between the mass of MnO_2 and k_{app} is observed in this investigation, and the result does not deviate majorly from the above values.

3 Experimental

3.1 Materials & Apparatus

Materials	
33% (v/v) H_2O_2 (aq), diluted to 3.3%	10 ± 0.5mL per trial
Pure distilled water	20 ± 0.5mL per trial
Fine MnO_2 powder	≈ 1g total

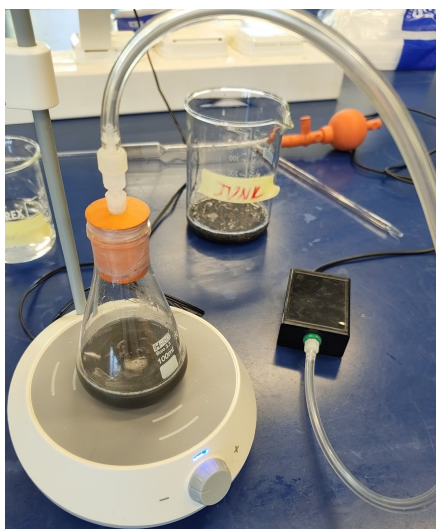| Equipment	
220 mL Erlenmeyer flask	Thermometer
20 mL Medical syringe (± 0.5mL)	Electronic scale (± 0.001g)
Vernier Pressure sensor[1]	Rubber stopper
Magnetic stir bar and stir plate	Parafilm

Figure 1: Apparatus

Pressure sensor specifications.

Range: 0–140 kPa   Accuracy: ± 2kPa   Sampling rate: 1 Hz

Data is recorded automatically using Logger Pro.

Illustration. The stir bar is in the flask, which is sealed airtight with a rubber stopper wrapped in parafilm. The tapered valve connector of the pressure sensor is wrapped in parafilm and inserted in the hole of the rubber stopper. A minimal setup, with the aid of parafilm and pressure-rated tubing aims to minimize leakage at moderate ($\leq$ 140kPa) pressure.

3.2   Process

Before trials: Prepare the necessary amount of H_2O_2 solution, diluted to 3.3% (v/v). Confirm the pressure sensor is ready for data collection and is connected to the valve connector with tubing.

For each trial: Add 20 mL water to the empty Erlenmeyer flask. Measure the desired amount of MnO_2 powder and add in the flask. Confirm that the solution is at 24°C. Add the stir bar and stir at 600 rpm. Wrap the sides of the rubber stopper in parafilm and push it in the flask, sufficiently deeply to minimize leakage. Draw 10 mL of 3.3% H_2O_2 in the syringe. Wrap the tapered area of the valve connector in parafilm. Then, inject the contents of the syringe into the flask through the hole in the stopper, and (quickly) insert the tapered valve connector into the hole.

When pressure reaches 140kPa, carefully withdraw the valve connector from the stopper. Confirm the temperature of the solution has remained roughly the same as before the reaction. Then the trial is finished; reset the apparatus and repeat.

3.3   Analytical Method

With data on the relation between pressure and time, simply use Logger Pro's 'fit curve' functionality to automatically fit a curve with the general form derived in (2.11).

The curve will be fit on the data between 120 kPa and 140 kPa. This interpolation always uses well above 80 data points. It avoids the beginning of the data collection which contains an unwanted artifact that results from connecting the valve. Using the Auto Fit functionality also automatically gives the error radius for k_{app}, which is the only error in dependent variables that needs to be considered. To establish proportionality with respect to catalyst concentration, the error radius of MnO_2 mass and solution volume are
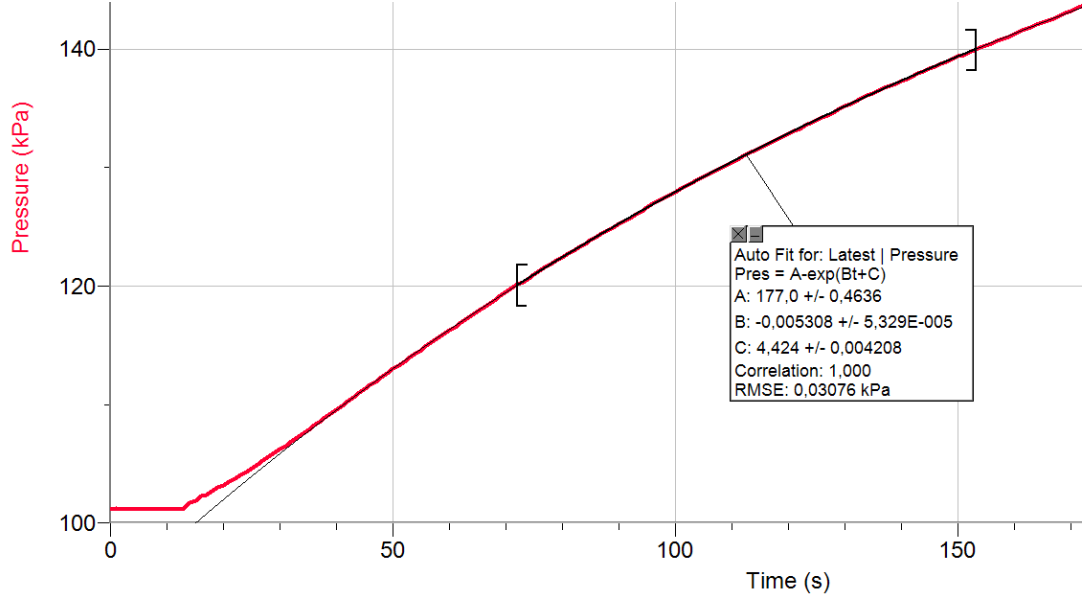
Figure 2: Logger Pro Auto Fit Curve for 0.25g trial

also necessary.

In **Figure 2**, $A = P_\infty$, $B = -k_{\mathrm{app}}$, and $C = \ln(c)$, in relation to the constants in (2.11). Only the value of k_{app} is ultimately needed, but P_∞ is a useful sanity check, to ensure no major systematic error is taking place.

4   Results and Discussion

4.1   Computing Theoretical Final Pressure

We compute the theoretical final pressure and compare it to the experimental values given by Logger Pro, to avoid major errors.

$$\rho(\mathrm{H_2O_2}) = 1.45 \text{ g mL}^{-1}, \qquad M(\mathrm{H_2O_2}) = 34.0 \text{ g mol}^{-1},$$

$$V_l = 30 \pm 1 \text{mL}$$

$$\implies V_{\text{H}_2\text{O}_2} = 0.33 \pm 0.011 \text{mL}$$

$$\implies m = \rho V = 0.33 \cdot 1.45 = 0.4785 \pm 0.0160 \text{g},$$

$$n(\text{H}_2\text{O}_2) = \frac{m}{M} = \frac{0.4785}{34.0} = 0.0141 \pm 0.00047 \text{mol} \tag{4.1}$$

This decomposes into $0.00705 \pm 0.00024 \text{mol } \text{O}_2$. Assuming constant gas volume and temperature, the ideal gas law states

$$\Delta P = (\Delta n) R T V^{-1} \qquad \text{for } R \approx 8.314 L \text{ kPa } K^{-1} \text{ mol}^{-1} \tag{4.2}$$

Initial conditions for the headspace gas:

$$P_i = 101 \pm 1 \text{kPa}, \qquad V_g = 200 \pm 10 \text{mL} = 0.20 \pm 0.01 \text{L}, \qquad T = 24 \pm 1°\text{C} = 297.15 \pm 1\text{K}$$

Then numerically $\Delta P = \dfrac{0.00705 \cdot 8.314 \cdot 297.15}{0.20} \approx 88 \pm 7 \text{kPa}$. The final pressure P_∞, in theory, is $P_0 + \Delta P \approx 88 + 102 = 190 \pm 8$ kPa. This is a rough range close to which the experimental final pressure should belong.

4.2   Data and Processing

m(MnO$_2$)	P_∞	$k_a pp$

Table 1: Table to test captions and labels.

5   Conclusion