

**Investigating the relationship between the concentration of  $\text{MnO}_2$  catalyst powder and the first-order rate constant in the decomposition of  $\text{H}_2\text{O}_2$  using measurements of pressure.**

**Research Question:** How does changing the concentration of solid  $\text{MnO}_2$  catalyst powder suspended in aqueous 1.1 % (v/v)  $\text{H}_2\text{O}_2$  (aq) affect the first-order rate constant for its decomposition at  $24^\circ\text{C}$ ?

September 8, 2025

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.<sup>[1]</sup> Manganese, in the form of  $\text{MnO}_2$ , 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  $\text{H}_2\text{O}_2$ , by measuring the concentration of  $\text{H}_2\text{O}_2$  indirectly through the amount of oxygen gas released.

## 2 Background Information

Most existing studies use  $\text{MnO}_2$  catalysts immobilized on solid supports<sup>[2]</sup> or embedded in porous materials<sup>[4]</sup>. In contrast, this investigation uses fine  $\text{MnO}_2$  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<sup>[1]</sup> or colorimetric methods<sup>[2]</sup>, 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 [5, 7, 6]. Additionally, the results reveal that the decomposition of  $\text{H}_2\text{O}_2$  follows pseudo-first order kinetics:

$$-\frac{d[\text{H}_2\text{O}_2]}{dt} = k_{\text{app}}[\text{H}_2\text{O}_2] \quad (2.1)$$

and thus:

$$\ln \left( \frac{[\text{H}_2\text{O}_2]}{[\text{H}_2\text{O}_2]_0} \right) = -k_{\text{app}}t \quad (2.2)$$

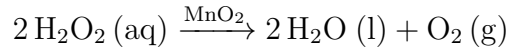
where  $k_{\text{app}}$  is the apparent first-order rate constant, and  $[\text{H}_2\text{O}_2]$  and  $[\text{H}_2\text{O}_2]_0$  are the concentrations of  $\text{H}_2\text{O}_2$  in the solution at any time  $t$  and time zero, respectively.[3]”

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  $k_{\text{app}}$  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			
$n(\text{H}_2\text{O}_2)$	$\text{H}_2\text{O}_2$ in solution at time $t$	$P$	Pressure at time $t$
$n(\text{O}_2)$	$\text{O}_2$ released up to $t$	$P_0$	Initial pressure
$n_0$	Initial $\text{H}_2\text{O}_2$ in solution	$P_\infty$	Final pressure
$n_{\text{air}}$	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



We use this to compute  $n(\text{H}_2\text{O}_2)$  in terms of  $n(\text{O}_2)$ :

$$n(\text{O}_2) = 2(n_0 - n(\text{H}_2\text{O}_2)) \implies n(\text{H}_2\text{O}_2) = n_0 - \frac{n(\text{O}_2)}{2} \quad (2.3)$$

By the definition of concentration,

$$[\text{H}_2\text{O}_2] = n(\text{H}_2\text{O}_2) \cdot V_l^{-1}$$

Substituting (2.3) into the above yields

$$[\text{H}_2\text{O}_2] = \left( n_0 - \frac{n(\text{O}_2)}{2} \right) V_l^{-1} \quad (2.4)$$

$$[\text{H}_2\text{O}_2]_0 = n_0 \cdot V_l^{-1} \quad (2.5)$$

The ideal gas law states

$$PV_g = (n_{\text{air}} + n(\text{O}_2))RT$$

Solve for  $n(\text{O}_2)$  in this expression:

$$n(\text{O}_2) = PV_g R^{-1} T^{-1} - n_{\text{air}} \quad (2.6)$$

Substituting this into (2.4) yields

$$\begin{aligned}
[\text{H}_2\text{O}_2] &= \left( n_0 - \frac{n(\text{O}_2)}{2} \right) V_l^{-1} \\
&= \left( n_0 - \frac{PV_g R^{-1} T^{-1} - n_{\text{air}}}{2} \right) V_l^{-1} \\
&= \frac{1}{2} (2n_0 + n_{\text{air}} - PV_g R^{-1} T^{-1}) V_l^{-1}
\end{aligned} \tag{2.7}$$

Notice that when all  $\text{H}_2\text{O}_2$  is decomposed,  $n(\text{H}_2\text{O}_2) = 0$  and (2.3) yields  $n(\text{O}_2) = 2n_0$ . Hence  $2n_0$  is the final amount of  $\text{O}_2$  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

$$\begin{aligned}
[\text{H}_2\text{O}_2] &= \frac{1}{2} (P_\infty V_g R^{-1} T^{-1} - PV_g R^{-1} T^{-1}) V_l^{-1} \\
&= \frac{1}{2} (P_\infty - P) V_g R^{-1} T^{-1} V_l^{-1}
\end{aligned} \tag{2.9}$$

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

$$\begin{aligned}
-k_{\text{app}} t &= \ln \left( \frac{[\text{H}_2\text{O}_2]}{[\text{H}_2\text{O}_2]_0} \right) \\
&= \ln \left( \frac{\frac{1}{2} (P_\infty - P) V_g R^{-1} T^{-1} V_l^{-1}}{n_0 \cdot V_l^{-1}} \right) \\
&= \ln \left( (P_\infty - P) \cdot \frac{V_g}{2n_0 RT} \right)
\end{aligned}$$

Solve for  $P$  to finish:

$$\begin{aligned}
e^{-k_{\text{app}} t} &= (P_\infty - P) \\
\frac{2n_0 RT}{V_g} \cdot e^{-k_{\text{app}} t} &= P_\infty - P \\
P &= P_\infty - \frac{2n_0 RT}{V_g} \cdot e^{-k_{\text{app}} t}
\end{aligned}$$

For clarity, set

$$c = 2n_0RTV_g^{-1} \quad (2.10)$$

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  $P_\infty$ ,  $c$ , and  $k_{\text{app}}$ .

$$P = P_\infty - c \cdot e^{-k_{\text{app}}t} \quad (2.11)$$

## 2.2 Existing Results

For porous MnO<sub>2</sub> on carbon nanotube (CNT) supports, the highest reported *specific* rate constant is

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

measured at 25°C in 100 mL of solution containing 1000 ppm H<sub>2</sub>O<sub>2</sub>.<sup>[4]</sup> The existence of such a specific rate constant suggests that the observed rate constant is roughly proportional with the mass of MnO<sub>2</sub> used.

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

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

measured at room temperature in 200 mL of solution containing 29.4 mM H<sub>2</sub>O<sub>2</sub>.<sup>[2]</sup> This suggests that the rate constant is proportional to the concentration of MnO<sub>2</sub> 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<sub>2</sub> and  $k_{\text{app}}$  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 <sub>2</sub> O <sub>2</sub> (aq), diluted to 3.3%	10 ± 0.5 mL per trial
Pure distilled water	20 ± 0.5 mL per trial
Fine MnO <sub>2</sub> powder	≈ 1 g total
Equipment	
200 mL Erlenmeyer flask	Thermometer
20 mL Medical syringe (±0.5mL)	Electronic scale (±0.001g)
Vernier Pressure sensor <sup>1</sup>	Rubber stopper
Magnetic stir bar and stir plate	Parafilm

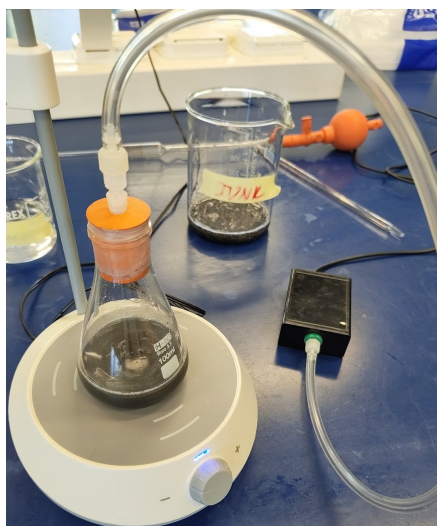


Figure 1: Apparatus

#### Pressure sensor specifications.

Range: 0–140 kPa    Accuracy: ±2 kPa    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 ( $\leq 140$  kPa) pressure.

## 3.2 Process

**Before trials:** Prepare the necessary amount of  $\text{H}_2\text{O}_2$  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  $\text{MnO}_2$  powder and add in the flask. Confirm that the solution is at  $24^\circ\text{C}$ . 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%  $\text{H}_2\text{O}_2$  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.

## 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).



## 4 Results and Discussion

Data, calcs, results, error all here.

$$V_f = 0.345l$$

$$V_l = 0.050l$$

## 5 Conclusion

## References

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