Gas Pressure Monitored Iodide-Catalyzed Decomposition Kinetics of H_2O_2: Initial-Rate and Integrated-Rate Methods in the General Chemistry Lab

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Hansen *(1)* suggested a closed-system gas pressure determination of the kinetics of the iodide-catalyzed H_2O_2 decomposition as a general chemistry lab experiment in 1996:

$$2H_2O_2(aq) \xrightarrow{I^-} 2H_2O(l) + O_2(g) \qquad (1)$$

Although based on an initial-rate approach, reactions were run to completion because the initial rate was calculated based on a final reaction pressure change ($\Delta P_{O_2,\infty}$)

$$\frac{d[H_2O_2]_t}{2dt} = \frac{d\Delta P_{O_2,t}}{dt} \times \frac{[H_2O_2]_0}{\Delta P_{O_2,\infty}} \qquad (2)$$

where $[H_2O_2]_0$ is the initial hydrogen peroxide concentration in the solution and $\Delta P_{O_2,t}$ is the additional pressure due to the oxygen generated from the catalyzed reaction (eq 1) at time t. The Hansen procedure can be greatly simplified: (i) Air does not need to be evacuated. (ii) A test tube can be used in place of a filtering flask and the solution volume reduced to 5.00 mL. (iii) Reagents can be added to an open test tube and then the test tube closed; the reaction has a significant period in which the pressure–time plot is linear. (iv) With the data-logger displaying a plot of pressure versus time, students can determine when enough data points have been collected; typically 10–20 data points are collected over 20–40 s. (v) The initial rate is

$$\frac{d[H_2O_2]_t}{2dt} = \frac{1}{2} \times \frac{d\Delta P_{O_2,t}}{dt} \times \frac{V(g)}{RT(g)} \times \frac{2\ \text{mol}\ H_2O_2(aq)}{1\ \text{mol}\ O_2(g)} \times \frac{1}{V(H_2O_2(aq))} \qquad (3)$$

where R is the gas constant, V(g) is the volume of the gas phase, T(g) is the temperature of the gas phase, and $V(H_2O_2(aq))$ is the volume of the solution. This lab has been published previously *(2)*.

In the integrated-rate method, the reaction is processed for an extended period of time. To prevent significant pressure buildup, a 250 mL Erlenmeyer flask is recommended. Given there is 5–10 s during which the solution becomes saturated with $O_2(aq)$ from the reaction, the last reagent can be added to an open flask. Reaction mixtures are shown in Table 1. Only one reaction, run 1, needs to be run to completion to obtain $\Delta P_{O_2,\infty}$.

Table 1. Reagent Volumes

Run	V(30% H_2O_2)/mL	V(2.00 M KI)/mL	V(H_2O)/mL
1	0.50	5.00	5.00
2	0.50	3.00	7.00
3	0.50	2.00	8.00
4	0.50	1.00	9.00
5	0.50	0.50	9.50

Table 2. The Effect of the Iodide Concentration on the Rate Constants

Run	[KI]/M	k'/s^{-1}	k/(L mol^{-1} s^{-1})
1	0.95238	0.01265	0.01329
2	0.57143	0.00690	0.01208
3	0.38095	0.00496	0.01302
4	0.19048	0.00255	0.01336
5	0.09524	0.00119	0.01247

If the reaction is first order with respect to H_2O_2, the applicable equations are

$$-\ln\left(\frac{[H_2O_2]_t}{[H_2O_2]_0}\right) = -\ln\left(\frac{\Delta P_{O_2,\infty} - \Delta P_{O_2,t}}{\Delta P_{O_2,\infty}}\right) = 2k't \qquad (4)$$

$$k' = k[I^-]^i \qquad (5)$$

where $\Delta P_{O_2,\infty}$ is the difference between the final pressure (complete reaction) and the initial pressure at the start time and $P_{O_2,t}$ is the difference between the pressure at time t and the initial pressure at the start time. A value of 46.0 kPa was found for $\Delta P_{O_2,\infty}$. A plot of $-\ln([H_2O_2]_t/[H_2O_2]_0)$ versus time for run 1 is linear with an equation $y = 0.02531x - 0.07469$ and $R^2 = 0.9989$, indicating that the order of the reaction with respect to H_2O_2 is 1 and $k' = 0.01265\ s^{-1}$. The k' values for runs 1–5 are shown in Table 2. From data in Table 2, the order with respect to I^- is 1 and the average rate constant is 0.01273 ± 0.00055 L mol^{-1} s^{-1}. The calculations for both the initial-rate and integrated-rate approaches are best accomplished in the Excel spreadsheet.

When students explore both the initial-rate and the integrated-rate approaches on the same reaction and using the same measured parameter, they are much better able to compare and

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contrast the two approaches. A colleague has suggested that the integrated-rate method may be better suited for the physical chemistry laboratory.

Hazards

Hydrogen peroxide is a strong oxidizer and contact with other material may cause fire. It is corrosive and can cause burns to the eyes, skin, and respiratory tract.

Literature Cited

1. Hansen, J. C. *J. Chem. Educ.* **1996**, *73*, 728–732.
2. Nyasulu, F.; Barlag, R. *Chem. Educ.* **2008**, *13*, 227–230.

Supporting Information Available

Instructor notes; lab writeup; postlab Excel sheet with sample data. This material is available via the Internet at http://pubs.acs.org.