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Many of the people I meet for the first time seem impressed to learn that I am a chemistry professor. This makes me feel good until they go on to tell me how much they disliked chemistry when they were in school. I love chemistry and most of the chemistry teachers I know love it too, yet it seems we have difficulty transferring our joy to so many of our students. This, I believe, is one of the major challenges facing our profession.

The effect of a change in the catalyst on the enthalpy of decomposition of hydrogen peroxide

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In an earlier article published in *Chem 13 News*, I presented an overhead projector demonstration of the catalytic decomposition of hydrogen peroxide.¹ One of the catalysts described in that article was ferric nitrate.

In a more recent article in the *Journal of Chemical Education*,² I described an introductory chemistry calorimetry experiment on the enthalpy of decomposition of H_2O_2 using $\text{Fe}(\text{NO}_3)_3(\text{aq})$ as a catalyst. The experiment is simple, inexpensive and colorful. In its simplest form, it can be performed in less than one hour. The experiment uses polystyrene coffee cups, requires inexpensive chemicals that present no disposal problems, and produces a large temperature change. The addition of the $\text{Fe}(\text{NO}_3)_3(\text{aq})$ catalyst produces a dramatic color change followed by the evolution of oxygen gas bubbles. At the completion of the reaction, the color returns to the original color of the catalyst.

In this article, I describe an extension of this experiment that involves an investigation of the effect of changing the catalyst on the enthalpy of decomposition of H_2O_2 . The two catalysts used in this experiment are a $\text{Fe}(\text{NO}_3)_3$ solution and a slightly basic NaI solution.

Background

Household hydrogen peroxide (3% by mass) is used in this experiment. The molarity of the solution can be determined by titration with standard KMnO_4 . Detailed procedures for the standardization of KMnO_4 and the determination of the H_2O_2 solution can be found in any analytical chemistry text and are also available from me on request. Alternatively, an approximate calculation of the molar concentration can be performed by assuming that the concentration is exactly 3% and that the density of the solution is 1.0 g/mL. Such a calculation leads to a value of 0.88 M. The actual molar concentration of such solutions is usually slightly larger than this. For example, I obtained a value of 0.919 M by analyzing my solution using the above procedures.

The two catalysts used in this experiment are a 0.10 M $\text{Fe}(\text{NO}_3)_3$ solution, and a 0.50 M NaI solution that is also 0.01 M in NaOH. The NaI solution is made slightly basic in order to prevent a side reaction involving the oxidation of I^- to I_2 by H_2O_2 . The $\text{Fe}(\text{NO}_3)_3$ solution should be prepared from the hydrated salt and should not be acidified. This solution will have an amber color due to a small concentration of $\text{Fe}(\text{H}_2\text{O})_5\text{OH}^{2+}$ resulting from the hydrolysis of the $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ ion.

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Procedure

To perform the calorimeter experiment, add 50.0 mL of the household H_2O_2 solution to a 6-oz polystyrene cup. Stirring can be performed by using a glass rod or by adding a stir bar and placing the cup on a magnetic stirrer. A thermometer covering the range of 20-40°C should be suspended in the solution. Ideally, this thermometer should be precise to 0.01°C, but a precision of 0.1°C is more than adequate. Alternatively, the temperature can be monitored as a function of time by using a temperature probe interfaced to a computer. The latter method was used in this study. Record the temperature every half-minute for four and a half minutes. At the 5-minute mark, add 50.0 mL of the first catalyst solution. Continue to make temperature readings until the 20-minute mark is reached. Repeat the entire procedure using the second catalyst.

To obtain good results, it is important that the hydrogen peroxide solution and the catalysts are initially at the same temperature. This can be assured by storing them in the same location for sufficient time for them to come into thermal equilibrium with their surroundings.

Results and calculations

Temperature vs time graphs are shown in Fig. 1 for the NaI catalyst and in Fig. 2 for the $\text{Fe}(\text{NO}_3)_3$ catalyst. The initial and final temperatures were found by extrapolating the two linear portions of the graph to the point of mixing. It can be seen that the two experimental temperature changes are quite similar.

In doing the calculations, it is assumed that the densities of the two solutions resulting from mixing the catalysts with the hydrogen peroxide are both 1.00 g mL⁻¹ and that the specific heats of these solutions are 4.18 J g⁻¹ °C⁻¹. The heat capacity of the calorimeter cup is taken as 5.0 J °C⁻¹. The molar concentration of the hydrogen peroxide solution used in this experiment was 0.919 M. The calculations for the reaction with the NaI catalyst are shown below.

$$\begin{aligned} \text{Amount of } \text{H}_2\text{O}_2 \text{ decomposed} \\ = n = CV = (0.919 \text{ mol L}^{-1})(0.0500 \text{ L}) = 0.0460 \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{Heat released to the solution} \\ = q_{\text{sol'n}} = -(\text{mass})(\text{specific heat})(\text{temperature change}) \\ = -(100.0 \text{ g})(4.18 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1})(10.24^\circ\text{C}) \\ = -4.28 \times 10^3 \text{ J} \end{aligned}$$

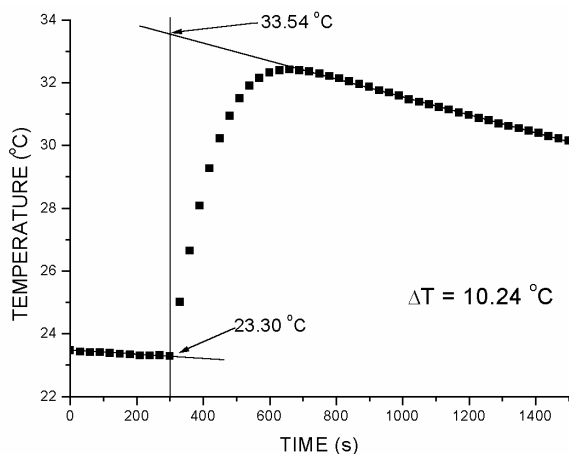


Figure 1. Temperature vs Time for the decomposition H_2O_2 using 0.50 M NaI with 0.01 M NaOH as a catalyst.

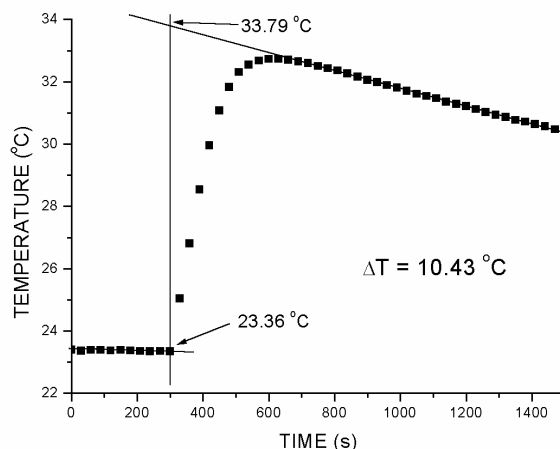


Figure 2. Temperature vs time plot for the decomposition of H_2O_2 using 0.10 M $\text{Fe}(\text{NO}_3)_3$ as a catalyst.

Heat released to the cup = q_{cup}
 $= -(\text{heat capacity of the calorimeter cup})(\text{temp change})$
 So, $q_{\text{cup}} = -(5.0 \text{ J } ^\circ\text{C}^{-1})(10.24^\circ\text{C}) = -51 \text{ J} = -0.051 \times 10^3 \text{ J}$

Total heat change = $q_{\text{total}} = q_{\text{sol'n}} + q_{\text{cup}}$
 $= -4.28 \times 10^3 \text{ J} - 0.051 \times 10^3 \text{ J} = -4.33 \times 10^3 \text{ J}$

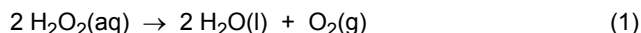
Enthalpy of decomposition
 $= \Delta H = q_{\text{total}}/n = -4.33 \times 10^3 \text{ J}/0.0460 \text{ mole}$
 $= -9.41 \times 10^4 \text{ J/mol.}$

So, $\Delta H = -94.1 \text{ kJ}/(\text{mol of } \text{H}_2\text{O}_2 \text{ decomposed})$

The data obtained for the $\text{Fe}(\text{NO}_3)_3$ catalyst yielded a value of -95.8 kJ/mol . These values compare reasonably well with the value of -94.66 kJ/mol obtained from the literature values of the standard enthalpies of formation of $\text{H}_2\text{O}_2(\text{aq})$, $\text{H}_2\text{O}(\text{l})$ and $\text{O}_2(\text{g})$.

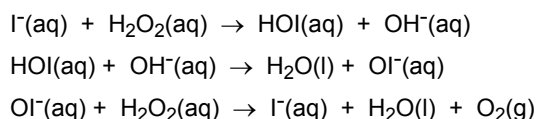
Discussion

The decomposition of hydrogen peroxide results in the following overall reaction:



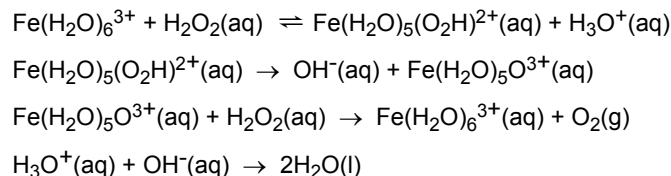
This reaction is very slow in the absence of a catalyst at room temperature. The $\text{Fe}(\text{NO}_3)_3$ and NaI solutions provide alternative mechanisms for the reaction to occur. The alternative paths that these catalysts provide require lower free energies of activation than is the case for the uncatalyzed reaction. However, the overall chemical reaction is the same when the reaction is performed in the presence of a catalyst as it is in the absence of a catalyst. Thus, the overall enthalpy of reaction is the same whether or not a catalyst is present. The enthalpy change should not depend on the nature of the catalyst. This experiment clearly demonstrates that this is so.

For the reaction catalyzed by I^- , the following mechanism has been proposed.³



More complicated mechanisms involving the free radicals I and OH have also been proposed.³

The iron-catalyzed reaction is an especially colorful one. The initial $\text{Fe}(\text{NO}_3)_3(\text{aq})$ solution has an amber color due to the small amount of $\text{Fe}(\text{H}_2\text{O})_5\text{OH}^{2+}$ present from the hydrolysis of the $\text{Fe}^{3+}(\text{aq})$ ion. The addition of this catalyst to the H_2O_2 solution results in the formation of a dark reddish-brown solution which is due to the formation of the $\text{Fe}(\text{H}_2\text{O})_5(\text{O}_2\text{H})^{2+}(\text{aq})$ intermediate, where HO_2^- results from the loss of a proton from H_2O_2 . This is followed by the evolution of oxygen bubbles. As the reaction goes to completion, the solution returns to the original amber color of the catalyst. A possible mechanism for this reaction is shown below.⁴



Other possible mechanisms for this reaction have been proposed.

As with any mechanism involving a catalyst, the sum of the steps of the mechanism must add up to the net overall reaction given in equation 1. Since the same net chemical reaction is occurring with either catalyst, the enthalpy change must be the same also.

References

1. C.J. Marzzacco, *Chem 13 News*, February 1995, page 1.
2. C.J. Marzzacco, *Journal of Chemical Education*, November 1999, pages 1517-1518.
3. P.G. Ashmore, in *Catalysis and Inhibition of Chemical Reactions*, Butterworths, 1963, page 62.
4. C. Walling, *Accounts of Chemical Research*, volume 8, pages 125-131 (1975). ■