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The Enthalpy of Decomposition of Hydrogen Peroxide

A General Chemistry Calorimetry Experiment

Charles J. Marzzacco

Department of Physical Sciences, Rhode Island College, Providence, RI 02908-1991; cmarzzacco@ric.edu

Thermochemistry is an important topic in high school and college introductory chemistry courses. Laboratory experiments on this topic usually involve measurements of heat of acid—base neutralizations, heat of solution, or heat of displacement reactions using Styrofoam cup calorimeters (1–3). The experiment described here involves the determination of the enthalpy change for a simple decomposition reaction. In its simplest form, the experiment can be performed in less than one hour and is therefore suitable for the short laboratory periods that exist in many high schools. The chemicals are inexpensive and present no disposal problems.

The experiment involves the decomposition of aqueous H_2O_2 using $Fe(NO_3)_3$ as a catalyst. Household hydrogen peroxide (3.0 mass %, density = 1.00 g/mL) is used as the source of H_2O_2 . The decomposition reaction is shown below:

$$2H_2O_2(aq) \rightarrow 2H_2O(\ell) + O_2(g)$$

It should be noted that the oxygen is initially formed as $O_2(aq)$, which is then released to the atmosphere as $O_2(g)$. During the course of the reaction, most of the oxygen produced is given off as a gas.

The molarity of the H_2O_2 in the solution can be calculated from the mass percentage of H_2O_2 in the solution. Assuming a 3.0% concentration and a density of 1.00 g/mL, the concentration of the H_2O_2 is 0.88 M. For more accurate work, the concentration of H_2O_2 in the solution can be determined by titration with standard KMnO₄.

Procedure

A thermometer covering the range of 15 to 50 °C and precise to 0.01 °C is suspended in a 6-ounce Styrofoam cup on a magnetic stirrer in the usual way. Fifty milliliters of the household hydrogen peroxide solution and a stir bar are added to the cup. The solution is stirred slowly and the temperature is recorded every minute for four minutes. At the 5-minute mark, 10.0 mL of 0.50 M Fe(NO₃)₃ is added to the solution. The temperature is again measured at the 6-minute mark and every succeeding minute up to a total of about 20 minutes. The resulting time–temperature graph is shown in Figure 1. The initial temperature is obtained by extrapolating the five points prior to adding the catalyst to the point of mixing. The final temperature is obtained by extrapolating the linear portion of the graph (10 to 20 minutes) to the point of mixing.

Calculations

The specific heat of the reaction mixture was taken as $4.18~J~^{\circ}C^{-1}~g^{-1}$. The value for the calorimeter constant used in this experiment was obtained from the measured temperature change that occurs when a measured quantity of warm water is added to a measured quantity of room-temperature water in the calorimeter. The calorimeter constant depends on the

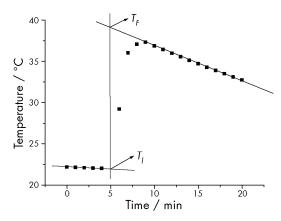


Figure 1. The temperature-vs-time graph for the decomposition of $H_2O_2(aq)$. The calorimeter initially contained 50.0 mL of 0.921 M H_2O_2 . Ten milliliters of 0.50 M Fe(NO₃)₃ was added at the 5-minute mark. The extrapolated initial and final temperatures were 21.94 and 39.10 °C, respectively.

volume of solution used. For the experimental conditions of this experiment, a calorimeter constant of 5 J °C⁻¹ was obtained. A detailed procedure for the measurement of the calorimeter constant is given in the *JCE Online* Lab Documentation that accompanies this paper.^W

The calculations presented here are based on the results shown in Figure 1. The experiment involved mixing 50.0 mL of 0.921 M $\rm H_2O_2(aq)$ with 10.0 mL of 0.50 M Fe(NO₃)₃(aq). According to the graph, the initial temperature was 21.94 °C and the final temperature was 39.10 °C.

The heat change for the solution is given by the formula q_{soln} = -specific heat of solution × mass of solution × ($T_{\text{F}} - T_{\text{I}}$) = -(4.18 J g⁻¹ °C⁻¹)(60.0 g)(39.10 °C - 21.94 °C) = -4.30 × 10³ J.

The heat change for the calorimeter is

$$q_{\text{calorimeter}} = -\text{C}(T_{\text{F}} - T_{\text{I}})$$

= -(5.0 J °C⁻¹) (39.10 °C - 21.94 °C)
= -86 J

Thus,

$$q_{\mathrm{total}} = q_{\mathrm{soln}} + q_{\mathrm{calorimeter}} = -4.39 \times 10^{3} \,\mathrm{J}$$

The number of moles of H_2O_2 reacted equals the molarity times the volume of H_2O_2 solution:

$$n = MV$$

 $n = (0.921 \text{ M})(0.0500 \text{ L}) = 0.0461 \text{ mol}$
 $\Delta H = q/n = -9.52 \times 10^4 \text{ J mol}^{-1} = -95.2 \text{ kJ mol}^{-1}$

This value agrees well with the literature value of -94.6 kJ mol⁻¹

calculated from the enthalpies of formation of the reactant and products for the reaction

$$H_2O_2(aq) \to H_2O(\ell) + \frac{1}{2}O_2(g)$$

Discussion

The experiment presented here is simple, yet gives good results. The chemical reaction that is investigated is colorful and interesting. The Fe(NO₃)₃(aq) solution has a pale yellow color due to the presence of Fe(OH)(H₂O)₅²⁺. When it is added to the H₂O₂ solution, a dark amber color is produced. This color is presumably due to the presence of a complex between H_2O_2 and Fe^{3+} (4). There is a rapid evolution of bubbles of oxygen. As the reaction proceeds to completion, the color of the solution slowly changes to the original pale yellow. This clearly shows that the catalyst takes part in the mechanism of the reaction but is not used up.

This experiment can be extended to include measurement of the enthalpy of formation of $H_2O_2(aq)$. This is done by combining the literature value for the enthalpy of formation of $H_2O(\ell)$ with this experimental value for the enthalpy

of decomposition of H₂O₂(aq). The following two thermochemical equations are used:

$$\begin{split} &H_2(g)+{}^{1}\!\!/_{\!\!2}\,O_2(g) \to H_2O(\ell) \quad \Delta \textit{H} = -285.8 \text{ kJ (lit.)} \\ &H_2O(\ell)+{}^{1}\!\!/_{\!\!2}\,O_2(g) \to H_2O_2(aq) \ \Delta \textit{H} = +95.2 \text{ kJ (exptl)} \end{split}$$

$$H_2(g) + O_2(g) \rightarrow H_2O_2(aq)$$
 $\Delta H = -190.6 \text{ kJ}$

The literature value for the enthalpy of formation of $H_2O_2(aq)$ is -191.2 kJ/mol.

Note

WSupplementary materials for this article, including instructions for the students and notes for the instructor, are available on JCE Online at http://jchemed.chem.wisc.edu/Journal/issues/1999/Nov/abs1517.html.

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