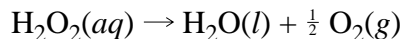


THERMOCHEMISTRY

OBJECTIVE: To determine the heat of decomposition of hydrogen peroxide in aqueous solution, and to use this datum to calculate the dissociation energy of the O-O bond in H_2O_2 .

INTRODUCTION: The decomposition of hydrogen peroxide in aqueous solution proceeds according to the equation:



In the absence of a catalyst the reaction is quite slow, but in the presence of powdered MnO_2 , the reaction takes place rapidly with a measurable evolution of heat.

In this experiment, the heat of decomposition will be measured in an isothermal calorimeter consisting of a Dewar flask, stirrer and thermometer. The calorimeter will be calibrated under conditions similar to those used in the actual experiment so that elaborate corrections for the heat exchanged between the calorimeter and its surroundings will be unnecessary.

The calorimeter is calibrated by observing the temperature rise resulting from the addition of concentrated sulfuric acid to water. It is possible to determine the heat which is evolved by comparing the concentration of the acid solution with tabulated data on the heat of solution of sulfuric acid. The effective heat capacity of the calorimeter is then defined as follows:

$$\text{Effective heat capacity} = \frac{\text{Total heat liberated (in Joules)}}{\text{Temperature rise (in } ^\circ\text{C)}}$$

This value may then be used to calculate the amount of heat evolved which corresponds to some observed temperature rise in this calorimeter.

Since the observed changes in temperature are the result of the combined effect of simultaneous heating and cooling processes on the solution it is necessary to correct for the cooling effect when calculating the effective temperature rise. This is usually done by taking temperature readings until the temperature is falling steadily and extrapolating this linear cooling curve back to the time when the acid or catalyst was added. Because of the negligible slope of the extrapolated line, however, the effective maximum temperature may be approximated by the maximum observed temperature in the case of the hydrogen peroxide decomposition, thus eliminating the need for further temperature readings once a steady maximum temperature has been attained.

PROCEDURE: (a) Determination of the Energy Equivalent of the Calorimeter.

Before starting, ensure that the Dewar flask, stirrer and thermometer are clean and dry. Transfer 505 mL of distilled water into the calorimeter, set the lid in place and carefully position the stirrer and thermometer. Be certain the stirrer paddle will not strike the thermometer or side of the Dewar flask when rotating. Switch on the stirrer, adjust to a moderate speed and take temperature readings at two minute intervals until a steady temperature reading is obtained. Because the temperature changes are so small in this experiment, all temperature readings should be made to the nearest 0.02°C using the magnifying glass provided.

Once a steady temperature has been reached add approximately 5 mL of concentrated sulfuric acid using a small graduated cylinder. Take care that the acid is added directly to the water. Continue taking temperature readings at intervals until the temperature remains steady or falls regularly for at least 10 minutes. Open the calorimeter and determine the concentration of the dilute sulfuric acid by titrating two 10 mL aliquots of the acid with the standardized 0.1 M NaOH provided. Titrate to the phenolphthalein color end point.

The temperature rise due to the addition of the sulfuric acid may be determined by plotting the temperature T against the time and extrapolating back to the time when the acid was added. Because of the time required to completely mix the solution some of the first temperature readings may be higher or lower than should be the case and should be disregarded when extrapolating the graph. Only the linear portion of the graph corresponding to a steadily decreasing temperature should be extrapolated. The difference between the temperature at the time the acid was added and the temperature of the water before the addition of the acid will be the observed temperature rise.

The quantity of heat evolved may be determined from the measured concentration of acid and the following data on the heat of solution of sulfuric acid.

| <u>Joules/100 mL H₂O</u> | <u>Final M of solution</u> |
|-------------------------------------|---|
| 803 | 0.109 |
| 1013 | 0.139 |
| 1979 | 0.276 |

Plot the data given using the Least Squares Fit Program (on your calculator or on the computer in the lab) and by interpolation find the heat corresponding to the molarity of the acid in your calorimeter. The effective heat capacity of your calorimeter and contents can then be calculated.

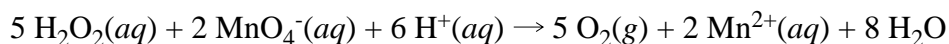
This procedure should be repeated and an average of the effective heat capacities should be calculated.

(b) Determination of the Heat of Decomposition of H₂O₂.

Again be certain that the Dewar flask, stirrer and thermometer are clean and dry before starting. Transfer 550 mL of distilled water into the calorimeter and add 10 mL of 30% hydrogen peroxide. **MIX THOROUGHLY.** Remove two 25 mL aliquots into a clean and dry 100 mL beaker for subsequent titration against the 0.02 M potassium permanganate solution provided. Position the cover, stirrer and thermometer carefully and set the stirrer for a moderate stirring speed. Take temperature readings every-two minutes until a steady reading is obtained. Add approximately 6 g of powdered MnO₂ to catalyze the decomposition of the peroxide.

Continue taking temperature readings until the temperature remains steady or is falling regularly. Obtain the temperature rise by taking the difference between the maximum temperature and the temperature before addition of the MnO₂. (The extrapolation procedure takes 30 min. or more and is not generally worthwhile in this part.)

To determine the the concentration of H₂O₂ in the initial solution, pipette out 10 mL aliquots from your 100 mL beaker and add 25 mL of distilled water and 25 mL of dilute (3 M) sulfuric acid and titrate with the 0.02 M permanganate solution. The reaction taking place in the titration is



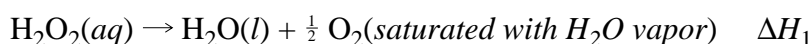
The above procedure should be repeated.

Calculation of the Heat of Solution and D(HO-OH)

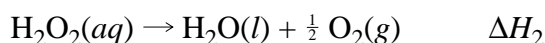
The total heat liberated in the calorimeter by the decomposition is:

$$\text{Heat liberated} = (\text{Effective heat capacity}) \times (\text{Temp. rise})$$

From the analysis of the hydrogen peroxide solution the number of moles of H_2O_2 present and hence the heat liberated per mole may be calculated. The value obtained represents the heat evolved in the reaction,



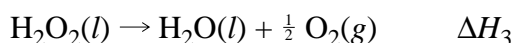
To calculate the heat liberated in the reaction,



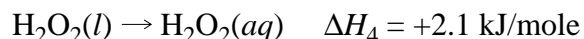
it is necessary to correct for the heat of vaporization of the water required to saturate the oxygen leaving the calorimeter. At the temperature of the experiment, the water vapor pressure may be taken as 18 mm Hg and heat of vaporization as 44.35 kJ/mole. Observe that for each mole of H_2O_2 decomposed, half a mole of O_2 is produced. For each mole O_2 produced at 760 mm Hg, 15/760 moles of water are vaporized. Hence:

$$\Delta H_2 = \Delta H_1 - (\frac{1}{2})(18/760)\Delta H_{\text{vap}}(\text{H}_2\text{O})$$

To obtain ΔH for the reaction

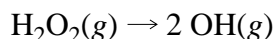


a further correction in the form of the heat of solution of H_2O_2 must be applied. The heat evolved for the reaction,



For dilute solutions, $\Delta H_3 = \Delta H_2 + \Delta H_4$.

The dissociation energy of the O-O bond in H_2O_2 is ΔH for the reaction,



Given that $\Delta H_f(\text{H}_2\text{O}, liq) = -285.85 \text{ kJ mole}^{-1}$, and $\Delta H_{\text{vap}}(\text{H}_2\text{O}_2, liq) = 51.63 \text{ kJ mole}^{-1}$, calculate $\Delta H_f(\text{H}_2\text{O}_2, gas)$.

Finally calculate D(HO-OH), given that $\Delta H_f(\text{H}_2\text{O}, gas) = -241.84 \text{ kJ mole}^{-1}$, $\Delta H_f(\text{H}, gas) = +217.95 \text{ kJ mole}^{-1}$ and that for the reaction,

