Energy Diagram for the Catalytic Decomposition of Hydrogen Peroxide
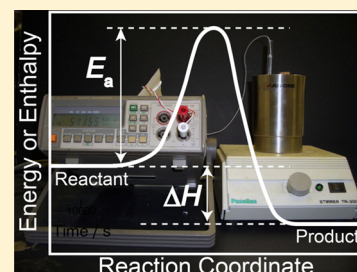
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Ⓢ Supporting Information

ABSTRACT: Drawing a schematic energy diagram for the decomposition of H_2O_2 catalyzed by MnO_2 through a simple thermometric measurement outlined in this study is intended to integrate students' understanding of thermochemistry and kinetics of chemical reactions. The reaction enthalpy, $\Delta_r H$, is determined by a conventional thermometric method, where a modified calorimetric vessel with negligible thermal leakage is used. Thermometric curves for the reactions at different initial temperatures can be converted to different series of kinetic rate data under nonlinearly changing temperatures. The apparent activation energy, E_a, is easily determined by the differential kinetic relationship at the fixed degree of reaction among the different series of kinetic rate data. By determination of both $\Delta_r H$ and E_a, students can draw a schematic diagram of the energy change accompanying the reaction. The laboratory activity and post lab data treatments are useful in general chemistry courses at the university or college level and also applicable in advanced chemistry courses in high schools.

KEYWORDS: First-Year Undergraduate/General, High School/Introductory Chemistry, Physical Chemistry, Laboratory Instruction, Hands-On Learning/Manipulatives, Kinetics, Laboratory Computing/Interfacing, Thermodynamics

Ⓢ implified energy diagrams are useful in visualizing chemical reactions from a different perspective, such as thermochemistry and reaction kinetics, topics that are covered in different learning units in conventional chemistry courses. It is expected that an experimental approach in drawing such an energy diagram might provide an opportunity to integrate students' understanding of these two topics into the process. The catalytic decomposition of hydrogen peroxide in aqueous solution,

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g) \qquad (1)$$
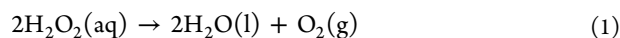
is one of the most widely used reactions for teaching different concepts of chemistry, such as oxygen generation, reaction stoichiometry, catalytic reactions, thermochemistry, and reaction kinetics. For evaluating the reaction enthalpy, $\Delta_r H$, in the catalytic decomposition of H_2O_2, student activities using conventional thermometric measurements have been reported.[1,2] Kinetic analysis of the catalytic decomposition of H_2O_2 is a widely utilized laboratory experiment with various experimental procedures. Decomposition rate behavior can be measured by the changes in the aqueous H_2O_2 concentration[3] and the amount of oxygen gas generated at a constant temperature.[4−9] Because the reaction is relatively exothermic with a standard reaction enthalpy of $\Delta_r H°_{298} = -98.3$ kJ mol^{-1},[8] thermometric measurements are also a viable procedure for measuring the kinetic rate data. Nyasulu and Barlag[2] reported an ingenious experimental procedure for determining $\Delta_r H$ and the order of reaction for the iodide-catalyzed decomposition of H_2O_2 by a thermometric measurement, where an initial rate approximation is applied to evaluate the reaction rate. Consequently, it is expected that a unified experimental approach to thermochemistry and kinetics of the catalytic decomposition of H_2O_2 in drawing the energy diagram

is possible by modifying the thermometric measurement and proposing a calculation procedure for evaluating the apparent activation energy, E_a, from thermometric curves. A laboratory activity for determining the $\Delta_r H$ and E_a values for the decomposition of H_2O_2 catalyzed by MnO_2 is presented. It is used in an advanced chemistry course in several high schools and in an introductory chemistry course at our university. It is usually carried out by student groups (3−4 members) in a 3-h session.

THERMOMETRIC MEASUREMENTS: SETUP AND CALIBRATION

Calorimeter

The apparatus for calorimetric measurements consists of a calorimetric vessel and a digital thermometer.[10] To obtain reliable kinetic rate data from the thermometric curve, any thermal leakage during the measurements should be minimized to realize the direct correspondence of the fraction of temperature change to the degree of reaction. Therefore, the calorimetric vessel requires modification to provide a higher thermal insulation. A simple modification is to nest several polystyrene cups and to cover the cups with a thick polystyrene lid. A homemade calorimetric vessel,[10] constructed from a stainless-steel vacuum-insulated vessel (250 cm^3, As-One Co., Japan) and a polystyrene cup (200 cm^3) with thick polystyrene lids, is used in this experiment. During the reaction, small temperature changes, for example, less than 4 K, are preferable to avoid thermal leakage during the measurements. To do this and to meet a requirement for the

kinetic analysis, a digital thermometer that can record three decimal places is required. Such thermometers with a thermistor sensor are commercially available and have been used in the student experiments.[2] If a digital multimeter with a data acquisition system is available, the thermometer can be constructed by purchasing a thermistor sensor that is reasonably priced. The homemade calorimetric vessel and the thermometric system employed in the student laboratory sessions are described in the Information for Instructors in the Supporting Information.

Calibration of Calorimeter

Calibration of the calorimeter is carried out by utilizing the temperature change while mixing water at two different temperatures, T_1 and T_2 ($T_1 > T_2$). Equal volumes (25 cm^3) of water at T_1 and T_2 are mixed in the calorimetric vessel by adding the water at T_1 into that at T_2 and the temperature change of the water is measured. By comparing the measured temperature of the mixed water, T_3, with the ideal temperature, $T_{ideal} = (T_1 + T_2)/2$, the energy calibration constant, K, is calculated by

$$K = \frac{T_{ideal} - T_2}{T_3 - T_2} \tag{2}$$

The K value functions as an empirical calibration constant for the difference of the apparent specific heat capacity of the overall calorimetric system from the specific heat capacity of water at 298 K. Details of this calibration procedure are described in the Information for Instructors and Instruction for Students in the Supporting Information.

■ EXPERIMENTAL OVERVIEW

Preparation of Reactant Solution

Reagent-grade $H_2O_2(aq)$ (ca. 30%) is diluted to approximately 0.5% with deionized−distilled water. The molar concentration of the H_2O_2 solution, c, is determined by redox titration with a standard aqueous solution of KMnO$_4$ (0.05 mol dm^{-3}).

Thermometric Measurement

About 100 cm^3 of $H_2O_2(aq)$ is placed in a beaker and its temperature is controlled in a range of 283−298 K by placing the beaker in a water bath. A 50 cm^3 aliquot of the temperature-controlled $H_2O_2(aq)$ is transferred to the calorimetric vessel using a transfer pipet with a safety pipetter. The calorimetric vessel is covered with polystyrene lids, and the reactant solution is left by standing for several minutes to stabilize the temperature. The thermometric measurement is started by setting a constant time interval of 1 s for data acquisition. The reaction is initiated by adding 25 ± 1 mg of MnO$_2$ as the catalyst. The measurements are repeated by changing the initial temperature of the reactant solution in the range from 283 to 298 K.

■ HAZARDS

Students are required to wear safety goggles and protective gloves during the experiment. Aqueous solutions of NaOH, H_2O_2, and KMnO$_4$ are hazardous in the case of skin contact, eye contact, or ingestion; H_2O_2 and KMnO$_4$ are strong oxidizers. The waste solutions generated from the redox titration of H_2O_2 should be disposed of in a designated container. The waste solutions generated from the calorimetric measurements should be appropriately disposed of after removal of MnO$_2$ by filtration.

■ EXPERIMENTAL RESULTS

Energy Calibration for the Calorimeter

Typical results for energy calibration for the calorimetric system are described in the Supporting Information. It is carried out by comparing the K values determined by the present method with those determined from enthalpy changes for the dissolutions of solid NaOH and KNO$_3$ in water. When using the homemade calorimetric vessel, the typical K value determined by mixing equal volumes of water at two different temperatures is 1.057 ± 0.005, which is virtually identical to those determined by dissolving NaOH and KNO$_3$ in water. The student results are within a 2% deviation of the above values. Sample data of the energy calibration is also provided as an MS-Excel spreadsheet in the Supporting Information.

Redox Titration

Determination of molar concentration of the aqueous H_2O_2 solution, c, is essential in evaluating $\Delta_r H$ of H_2O_2 decomposition. In the chemistry courses in high schools and in university, students determine the H_2O_2 concentration by conventional redox titration (3% deviation between students groups). If time is limited, the H_2O_2 concentration can be provided by the instructor.

Thermometric Measurement

Among the many catalysts for H_2O_2 decomposition such as Fe^{3+} and I$^-$, freshly prepared MnO$_2$ was selected for the experiments because of its high catalytic activity and the negligible temperature fluctuation induced when it is added to the reactant solution. MnO$_2$ can be prepared by the thermal decomposition of MnCO$_3$, and the preparation procedure is described in the Information for Instructors in the Supporting Information. Figure 1 shows typical thermograms for the decomposition of
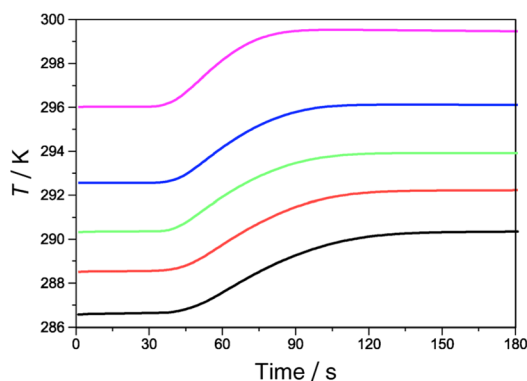

Figure 1. Typical thermograms for the decomposition of H_2O_2 catalyzed by MnO$_2$ at different starting temperatures. MnO$_2$ was added at 30 s at each temperature.

H_2O_2 catalyzed by MnO$_2$. After adding MnO$_2$, the temperature immediately increases and the reaction is complete within 120 s, even at the lowest temperature examined.

Reaction Enthalpy

The reaction enthalpy of the H_2O_2 decomposition, $\Delta_r H$, is calculated from the temperature change, ΔT, during the thermometric measurements according to:

$$\Delta_r H \ (\mathrm{J\,mol^{-1}}) = \frac{-1 \times \Delta T \times (m_0 - m) \times C_p \times K}{n(H_2O_2)} \tag{3}$$

where m_0, m, C_p, and $n(H_2O_2)$ are the mass of reactant solution, the calculated mass of oxygen produced by the reaction, specific

heat capacity of water (4.184 J g^{-1} K^{-1} at 298 K), and the initial molar amount of H_2O_2 in the reactant solution, respectively. In this calculation, the specific gravity of the reactant solution is assumed to be 1.0 g cm^{-3} and contribution of MnO_2 to the thermometric system is neglected. Table 1 lists the measured ΔT

Table 1. Typical Results of the Temperature Change ΔT (= $T_f - T_i$) during H_2O_2 Decomposition and the Calculated $\Delta_r H$ Value

No.	T_i^a/K	T_f^a/K	ΔT/K	$\Delta_r H$/(kJ mol^{-1})
1	286.640	290.318	3.678	−101.4
2	288.567	292.207	3.640	−100.4
3	290.357	293.919	3.562	−98.2
4	292.563	296.130	3.567	−98.3
5	296.030	299.534	3.504	−96.6
Average	-	-	3.590 ± 0.069	−99.0 ± 1.9

^{a}The molar concentration of H_2O_2 is 1.600×10^{-1} mol dm^{-3}.

values from the thermograms shown in Figure 1 and the $\Delta_r H$ values calculated from eq 3. The average $\Delta_r H$ value of −99.0 ± 1.9 kJ mol^{-1} is very close to the standard enthalpy change of $\Delta_r H°_{298} = -98.3$ kJ mol^{-1} and the experimental values previously reported in this *Journal* of $\Delta_r H = -95.2$ and -91.7 kJ mol^{-1}.[1,2] The $\Delta_r H$ values determined by our students are usually within a 5% deviation from the above value.

■ SIMPLIFIED KINETIC ANALYSIS

Kinetic Rate Data and Kinetic Equation

In thermometric measurements, the temperature change during the reaction is recorded, and any possible thermal leakage is negligible; thus, the thermograms can be converted to the kinetic rate data for H_2O_2 decomposition. The degree of reaction, α, is calculated according to:

$$\alpha = \frac{T - T_i}{T_f - T_i} \tag{4}$$

where T, T_i, and T_f are the measured temperature at time t, the initial temperature before the reaction starts, and the final temperature after the reaction is complete, respectively. The reduced reaction rate, $(d\alpha/dt)_i$, of the i-th order can be calculated as the difference quotient by

$$\left(\frac{d\alpha}{dt}\right)_i = \frac{(\alpha_i - \alpha_{i-1}) + (\alpha_{i+1} - \alpha_i)}{2\Delta t} \tag{5}$$

where Δt is the constant time interval of data acquisition. From this mathematical conversion, a series of kinetic rate data (t, T, α, $d\alpha/dt$)$_i$ are obtained from the respective thermograms shown in Figure 1. Figure 2 illustrates the typical kinetic rate data (t, T, α, $d\alpha/dt$). The data conversion can be easily carried out using a spreadsheet program. These numerical data are given as the sample data in an MS-Excel spreadsheet in the Supporting Information.

Owing to the temperature change during the reaction, kinetic rate data are characterized as those under nonlinearly changing temperature conditions. For analyzing such kinetic rate data under nonlinear nonisothermal conditions, the following differential kinetic equation can be applied.[11−14]

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \tag{6}$$
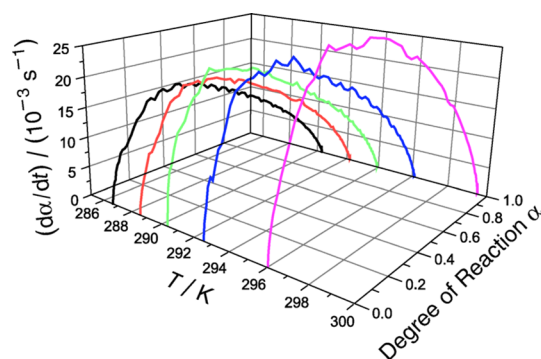

Figure 2. Typical kinetic rate data converted from the thermograms in Figure 1.

where A, E_a, and $f(\alpha)$ are the Arrhenius pre-exponential factor, apparent activation energy, and kinetic model function, respectively. When assuming the conventional nth order reaction, the kinetic model function is expressed by $f(\alpha) = (1 - \alpha)^n$.

Apparent Activation Energy

The E_a values can be calculated using the set of kinetic rate data converted from the different thermograms without assuming $f(\alpha)$. Taking the logarithm of eq 6, the following equation is obtained

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln[Af(\alpha)] - \frac{E_a}{RT} \tag{7}$$

Equation 7 indicates that, at a fixed α, a plot of $\ln(d\alpha/dt)$ against T^{-1} gives a straight line with a slope of $-E_a/R$ and an intercept of $\ln[Af(\alpha)]$. This method for evaluating E_a at fixed α is known as the Friedman method.[15] The nearest data points to the fixed α are selected from the different series of kinetic rate data (t, T, α, $d\alpha/dt$). Figure 3 shows the typical Friedman plot at $\alpha = 0.5$. It
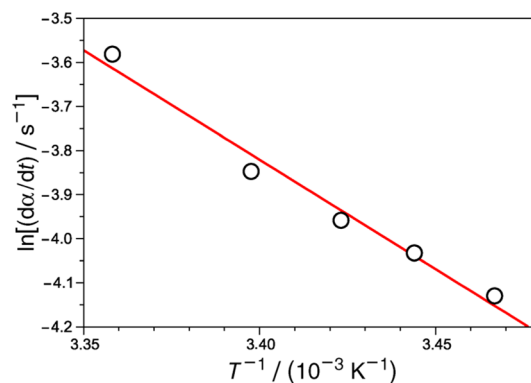

Figure 3. Typical plot of $\ln(d\alpha/dt)$ versus T^{-1} at $\alpha = 0.5$.

gives an acceptable straight line, from which $E_a = 41.3 \pm 3.5$ kJ mol^{-1} is determined. The E_a value is reasonable for the decomposition of H_2O_2 catalyzed by MnO_2.[16,17] The E_a values determined by students are within a 10% deviation from the above value.

■ SCHEMATIC ENERGY DIAGRAM

Using the experimentally determined $\Delta_r H$ and E_a values, students construct a schematic energy diagram for H_2O_2 decomposition as shown in Figure 4.
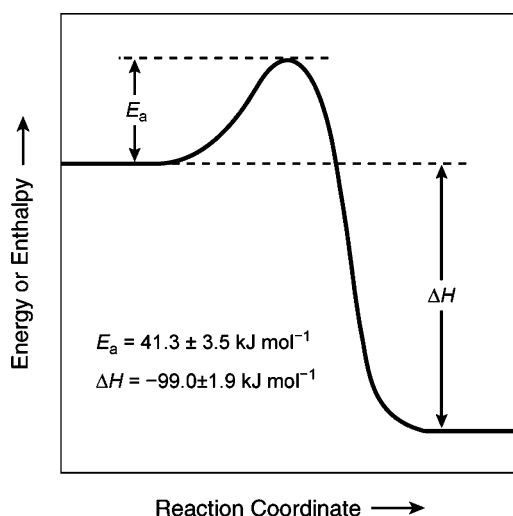
Figure 4. Schematic energy diagram for the decomposition of H_2O_2 catalyzed by MnO_2.

CONCLUSIONS

By minimizing any possible thermal leakage in conventional thermometric measurements performed in the student laboratory, the recorded thermograms for a chemical reaction can be utilized as both the calorimetric data and the kinetic rate data under nonlinear nonisothermal conditions. The $\Delta_r H$ and E_a values can be determined by the conventional calorimetric calculation and by the differential isoconversional method without assuming a kinetic model function, respectively. By solely determining $\Delta_r H$ and E_a from the thermometric data, students can draw an energy diagram for the reaction. The present experiment is useful in integrating students' understanding on thermochemistry and kinetics and is appropriate for advanced chemistry courses in high schools and for an introductory chemistry course at university.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Instructions for the students and information for instructors. MS-Excel spreadsheets with sample data. This material is available via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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636

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