

Improved Data Analysis for an Adiabatic Kinetics Experiment

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Abstract

Dichromate-catalyzed decomposition of hydrogen peroxide was carried out in a Dewar flask and the temperature was recorded as a function of time. The data were corrected for heat loss and used to find the enthalpy and the activation energy of the reaction. All calculations were done using a standard spreadsheet.

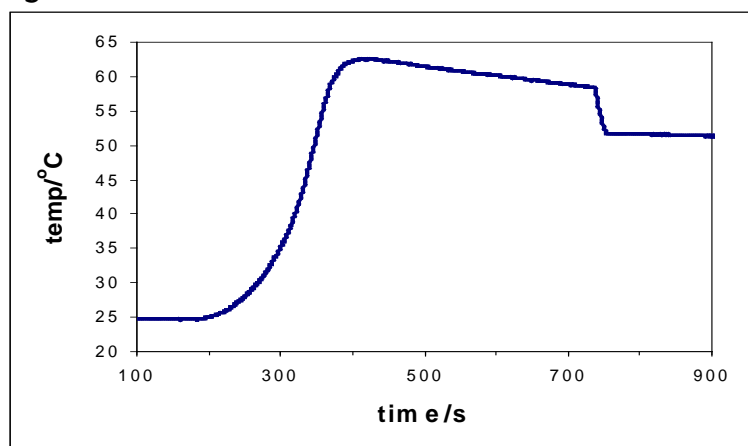
Experimental

The reaction was run by the method of Keusch.¹ The reaction vessel was a 100 mL glass Dewar equipped with a 2-hole rubber stopper, magnetic stir bar and temperature probe (Vernier TMP-BTA). The vessel was charged with 25.00 mL of 10% H₂O₂. Temperature recording was started and 10.00 mL of 0.10M dichromate, equilibrated to the same temperature as the peroxide, were added. The temperature was recorded every second for 1000 seconds, with signal averaging over each 1s interval.

To facilitate our data analysis, 10.00mL of room-temperature water was added approximately 400s after the maximum temperature was reached. To determine the exact concentration of hydrogen peroxide, 1.00 mL of the 10% solution was added to 0.5M H₂SO₄ and titrated with KMnO₄.² The KMnO₄ was standardized by titrating K₂C₂O₄ in 0.5M H₂SO₄.³

Raw Data

Figure 1. Raw Data



Results and Data Analysis

1. Heat capacity

On addition of 10.00 mL (9.972g) of water, the temperature of the water and the system changed by 27.42°C and -6.69°C respectively (Fig. 1, ~ 750s; temperatures linearly extrapolated to time of addition). Using an average value of $C_p = 75.3 \text{ J/mol}^\circ\text{C}$ for water, the heat capacity of the reaction system was found to be 171 J/°C.

2. Standardization of peroxide

The H_2O_2 was found to be 2.873 M, so 0.0718 mol of H_2O_2 were present initially.

3. Correction for heat loss

Heat loss from the Dewar is apparent in the raw data after 400s. The data from 500s to 700s were fit to the expression

$$(1) \quad \ln[T(t)-T_r] = a - b(t-500),$$

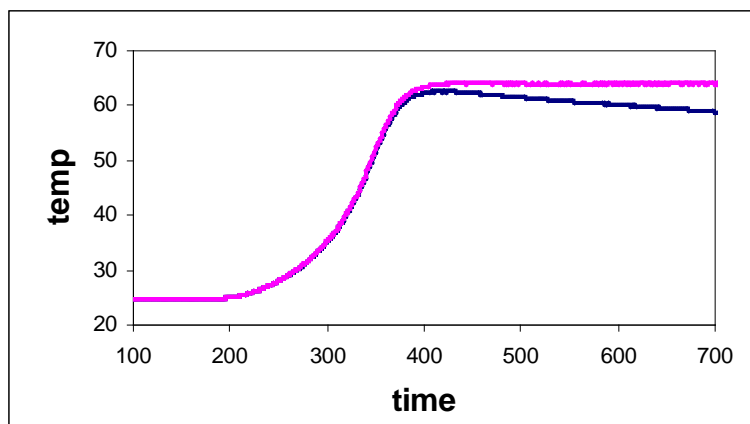
in which $T(t)$ is the temperature at time t , T_r is room temperature. b , the thermal constant of the apparatus, was found to be $(3.71 \pm 0.01) \times 10^{-4} \text{ s}^{-1}$.

For the purpose of determining the amount of heat liberated by the reaction, temperatures were “corrected” by numerical integration of the heat lost during each 1s time interval:

$$(2) \quad T_c(n) = T(n) + b \times 1\text{s} \times \sum_{i=0}^n (T(i) - T_r)$$

$T_c(n)$ is the corrected temperature (i.e. the temperature the system would have if adiabatic) at time = n seconds and T_r is room temperature.

Figure 2: Corrected and measured temperatures



4. Reaction enthalpy

ΔH was calculated from the corrected temperature change, the system heat capacity and the number of moles of H_2O_2 reacted. Loss of 0.036 mol of water-saturated O_2 at temperatures from 25 to 64°C results in a loss of 189J in heat of vaporization. The heat evolved by the reaction is:

$$(3) \quad q = 39.25^\circ\text{C} \times 171 \text{ J}/^\circ\text{C} + 189\text{J} \\ = 6.90\text{kJ}.$$

Division by the moles of H_2O_2 reacted gives

$$\Delta H = -95.9 \text{ kJ/mol } \text{H}_2\text{O}_2.$$

The heat capacity changes by ~0.4% as the composition and temperature of the calorimeter's contents change; an average value was used in the foregoing calculations. Likewise, an average value of ΔH_{vap} of water was used (43kJ/mol) but the vapor pressure was computed at each temperature.⁴

5. Rate and rate constant

The amount (moles) of H_2O_2 remaining at any time during the reaction was

$$(4) \quad n(t) = n(0) \times \frac{T_c(\infty) - T_c(t)}{T_c(\infty) - T_r},$$

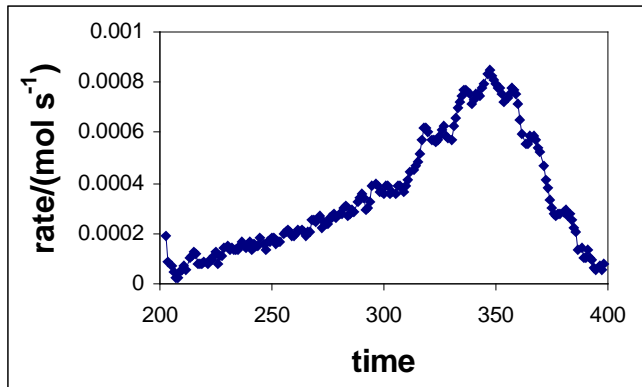
in which $T_c(\infty)$ is the final corrected temperature.

The reaction rate in mol s^{-1} was found using 5-point smoothing:⁵

$$(5) \quad \text{rate}(t) = -\frac{dn}{dt} \sim -\left[\frac{-2n(t-2) - n(t-1) + n(t+1) + 2n(t+2)}{10} \right].$$

The first-order rate constant (which depends on catalyst concentration) was obtained by dividing $\text{rate}(t)$ by $n(t)$.

Figure 3: Reaction rate



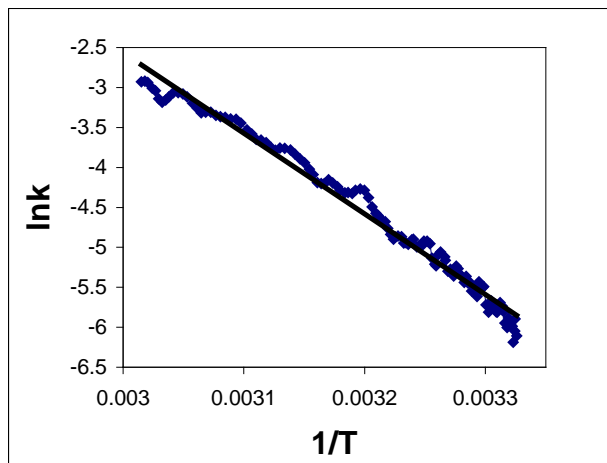
6. Activation energy

The data from 240 to 370s fit fairly well to the Arrhenius equation

$$(6) \quad \ln k = \ln A - \frac{E_a}{RT},$$

with $E_a = 84 \pm 1 \text{ kJ/mol}$ and $\ln(A/\text{s}^{-1}) = 27.7 \pm 0.4$.

Figure 4: Arrhenius plot



References

- ¹ Peter Keusch, "Kinetics: Decomposition of Hydrogen Peroxide catalyzed by Potassium Iodide", http://www.uni-regensburg.de/Fakultaeten/nat_Fak_IV/Organische_Chemie/Didaktik/Keusch/chembox_KJ-e.htm
- and "Kinetics: Decomposition of Hydrogen Peroxide catalyzed by Potassium dichromate", http://www.uni-regensburg.de/Fakultaeten/nat_Fak_IV/Organische_Chemie/Didaktik/Keusch/chembox_per_di_T-e.htm
- ² T.Greco, L.Rickard and G.Weiss, *Experiments in General Chemistry*, Prentice-Hall, Upper Saddle River, NJ (2002) pp. 203-208
- ³ G.H.Ayres, *Análisis Químico Cuantitativo*, Harper & Row, Madrid (1970), pp. 649-650
- ⁴ Thermal data were obtained from the NIST Chemistry Webbook: <http://webbook.nist.gov/cgi/cbook.cgi?Name=water&Units=SI>
- ⁵ A. Savitsky and M. Golay, "Smoothing and differentiation of data by simplified least squares procedures," *Analytical Chemistry*, 36, 1627-1638, (1964)