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Elephant's toothpaste used as a qualitative demonstration of rate vs. temperature

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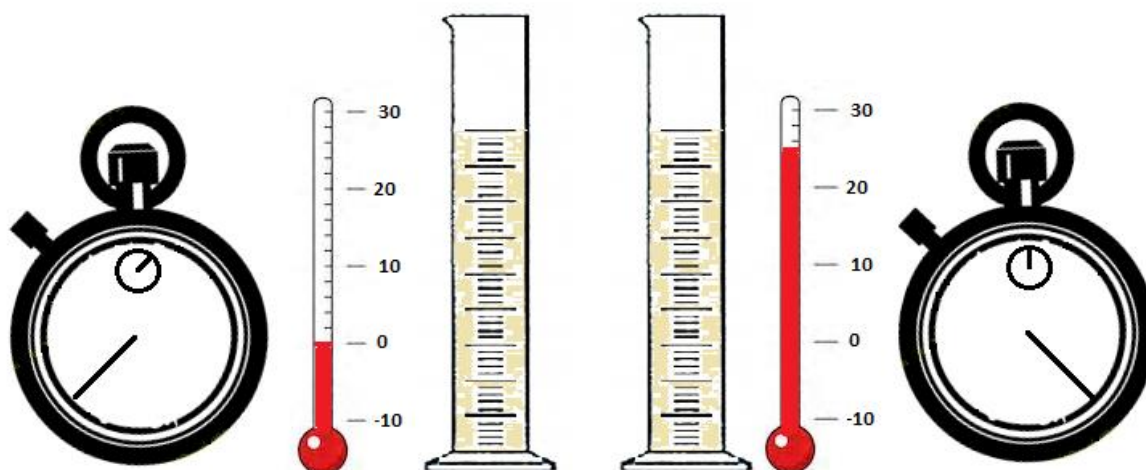
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ABSTRACT

The popular elephant's toothpaste demonstration can be used to demonstrate the effect of temperature on reaction rate qualitatively. Our version is designed for simplicity of execution and to require little class time. Two runs of the reaction are performed at easily achieved temperatures (ice and ambient), the latter being approximately three times as fast. The reaction behind the demonstration, the iodide-catalyzed decomposition of hydrogen peroxide (along with some complicating side-reactions), are discussed in some detail.

Graphical Abstract



KEYWORDS

Audience: High School/Introductory, First Year Undergraduate/General Chemistry

Domain: Demonstrations

Topic: Kinetics, Mechanism of reactions

INTRODUCTION

This demonstration is intended as an easily performed qualitative demonstration of the effect of temperature on reaction rate. The effect of temperature is one aspect of reaction kinetics (an important topic in chemistry^{1, 2}) comprising the interrelated topics of collision theory,³ transition state theory,⁴ activation energy,⁵ potential-energy diagrams,⁶ the Arrhenius equation,^{7 - 9} and the Maxwell-Boltzmann distribution.^{10 - 12} The elephant's toothpaste demonstration and the iodide-catalyzed decomposition of hydrogen peroxide, which drives it, are widely used to illustrate or study a variety of topics¹³ including catalysis,^{14, 15} rate laws,^{14, 16, 17} heat of reaction,^{6, 16} and activation energy,^{14, 18, 19} among others.^{19, 20} The elephant's toothpaste demonstration can be easily adapted to illustrate the effect of temperature on reaction rate qualitatively, but vividly. The effect of temperature change on reaction rate is the subject of many experiments^{1, 2, 6, 14, 18, 21 - 36} and relatively few lecture demonstrations.^{32, 37 - 45}

The demonstration described here, is designed to meet several goals:

- Easily performed
- Suitable for a large class
- Easily seen and interpreted
- Use simple apparatus and easily achieved temperature control
- Reasonably safe

- Qualitative
- Engaging
- Performed in five minutes or less

For instructors with similar restrictions, this demonstration may be more suitable than other demonstrations which may be difficult to interpret,³⁸ use or produce hazardous materials,^{39, 41, 45} require a long time,^{39, 41} be unsuitable for a large class,^{37, 41, 43} involve complicated apparatus,³² or require precise temperature control.^{37, 40, 41}

Instructors need not go into detail about the reaction mechanism which, as discussed below, is generally oversimplified. Rather, it can be presented as the iodide-catalyzed decomposition of hydrogen peroxide into water and oxygen. The oxygen is captured in bubbles by added detergent or other surfactant, much in the way carbon dioxide is captured by detergent in the familiar vinegar-baking soda volcano.⁴⁶ The rate of the reaction is reflected in the time required for the oxygen foam to rise from the 100 mL mark to the 500 mL mark in a 500 mL graduated cylinder. One or more students can be asked to time it.

DEMONSTRATION

A 500 mL graduated cylinder, with a magnetic stir bar, is charged with 20 mL of 14 % w/w hydrogen peroxide (40 ml of 36 % hydrogen peroxide diluted to 100 mL) and 10 mL of detergent solution. The mixture is stirred for a few minutes, as it will be throughout the reaction. (The solution should be made basic and stirred rapidly, as discussed below.) Then, 20 mL of a freshly-prepared solution of potassium iodide (10 g per 100 mL) is added. It is helpful to have a tub immediately underneath the graduated cylinder to catch the foam that

overflows the graduated cylinder. The use of laundry and dishwashing detergents have disadvantages. They are found to be acidic (See discussion below.), or contain dyes which may react with hydrogen peroxide, or leave stubborn residue on the glassware. A solution of 1 g of Alconox in 100 mL of solution works quite well. See Supporting Information for details.

A low temperature run is performed identically, except that the graduated cylinders with the hydrogen peroxide and detergent mixture and with the potassium iodide solution have both been cooled in ice-baths for approximately 20 minutes before mixing. (The ice bath for the 500 mL graduated cylinder, if sufficiently large, will serve to receive overflow.) The contrast between the two runs is better emphasized if the low temperature run is done first, in that the ambient temperature run goes about three times as fast. Both runs can be performed in five minutes or less total. Each run should use different 500 mL graduated cylinders.⁴⁷ The demonstration has been well-received by the classes of chemistry students for whom it was performed. The demonstration is similar to, but more easily performed than, a previously published method.¹⁵ Figure 1 is a photograph taken after the demonstration. The graduated

Figure 1. A photograph taken after the demonstration to lecture class



cylinder on the right is the low temperature run, which is completed before beginning the high temperature run (the large graduated cylinder on the left). The high temperature run produced 500 mL of foam and its overflow in the same time that low temperature run produced only its overflow. This shows that the high temperature run goes faster.

HAZARDS

If the concentrations and amounts of hydrogen peroxide, potassium iodide and Alconox called for in this article are used, the reaction should proceed at a safe rate. Nonetheless, proper precautions are in order. Splash goggles, a lab coat, closed shoes, and nitrile gloves should be worn. Demonstrators should review safety guidelines⁴⁸⁻⁵⁰ and Safety Data Sheets of the materials they use. Hydrogen peroxide and iodine (which may be produced^{55,56}) are oxidizing agents, corrosive, and cause severe burns skin and eyes. Oxygen will, and hydrogen peroxide and iodine may, be present in the foam, which should be treated accordingly. Hydrogen peroxide may cause fire in contact with other materials and may cause cancer. On decomposition, hydrogen peroxide produces oxygen which will accelerate combustion and this effect is important when oxygen lingers in clothing. Iodine is toxic. The American Conference of Governmental Industrial Hygienists (ACGIH) set the short term exposure limit (STEL) for iodine vapor at 0.1 ppm. At 25 °C, the vapor pressure of iodine is 0.305 mm Hg (4,010 ppm). Recalling the exothermicity of the decomposition of hydrogen peroxide, the vapor pressure of iodine (in mm. Hg) as a function of temperature, between 273 K and 328 K, can be summarized as $\ln[\text{vapor pressure (mm Hg)}] \approx 0.000002503 T^3 - 0.002555 T^2 + 0.9398 T - 120.6$.⁵¹ The demonstration should be conducted in a well-ventilated environment, such as a fume hood. Contact of eyes and skin with potassium iodide should be avoided. Potassium iodide

irritates mucus membranes. Universal Indicator is flammable, and, while the SDS may not indicate carcinogenicity, it contains phenolphthalein which was considered sufficiently carcinogenic to be removed from Ex-Lax and Feen-A-Mint, OTC laxatives, in 1997. Alconox causes skin irritation and severe eye irritation and damage. The decomposition of hydrogen peroxide is highly exothermic and the graduated cylinder and solution become quite hot.⁵⁵ Take care not to touch the cylinder during, or soon after, the reaction and then handle with caution.

DISCUSSION

Immediately before the potassium iodide solution is added and afterwards, the material should be stirred as rapidly as practical. Rapid stirring ameliorates the apparent rate-retarding effect attributed to oxygen supersaturation.⁵²

It is useful to understand what is taking place in the examples instructors use. To this end, the basic reaction, as well as complicating side reactions are discussed. Although this demonstration comprises some imperfectly understood reactions, a reasonable examination follows.

The commonly-presented mechanism for the iodide-catalyzed decomposition of hydrogen peroxide is a two-step reaction (Reactions 1 and 2)^{53, 54} for an acidic solution. All materials, except oxygen, are in aqueous solution.



In a basic medium, these reactions become



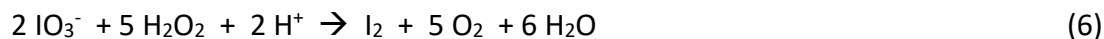
This mechanism is an oversimplification because, among other things, iodine, I_2 , is produced during the reaction,^{55, 56} something which neither of the above mechanisms explains.

Nonetheless, reactions 1' and 2' suffice for instructors who follow our recommendation of performing the demonstration at pH 9.

Iodine production can be thought to arise from materials present during the reaction (Reaction 3), as well as from disproportionation of HOI (Reaction 4),⁵⁷ although the expected low concentration of HOI makes disproportionation seem unlikely.



The presence of iodine complicates matters in two ways. First, it means the decrease of the concentration of the iodide catalyst. Since iodine and iodide can combine to form the triiodide ion ($K_{eq} \approx 700$),⁵⁹ which “does not react directly with hydrogen peroxide,”⁵⁹ the amount of iodide catalyst is further lowered. The iodine can also volatilize from the solution. Second, it may open (or widen) a bridge to the Bray-Liebafsky oscillatory reaction. The skeleton mechanism of this reaction has been simply summarized⁶⁰ as Reactions 5 and 6.



While Reactions 5 and 6 can be seen to produce the same amount of oxygen per hydrogen peroxide as Reactions 1 and 2, they, nonetheless, introduce an alternative overall reaction and rate. Further, the mechanism of the Bray-Liebafsky reaction is not clearly understood.⁶¹ A long list of possible reaction steps and intermediates have been suggested to be involved in the reaction,⁶¹ some involving radical species^{62 - 67} and some not.^{57, 60, 68, 69} A radical mechanism^{63, 67} provides a pathway for iodine's participation in the Bray-Liebafsky reaction. (Radical participation has been proposed for the iodide-peroxide reaction as well.⁷⁰) Some proposed mechanisms of the Bray-Liebafsky reaction invoke the production of singlet oxygen.^{60, 61, 64}

The above illustrates the complexity the Bray-Liebafsky reaction could introduce. The decomposition of hydrogen peroxide by iodine, itself, involves a complex set of reactions.⁷¹ If, indeed, molecular iodine is key to such pathways, a way to suppress iodine production before the boundaries are breached would seem worthy of investigation.

A side reaction (Reaction 7) of the iodide-catalyzed decomposition of hydrogen peroxide bears closer scrutiny. The side reaction is yet another example of a reaction that although "studied



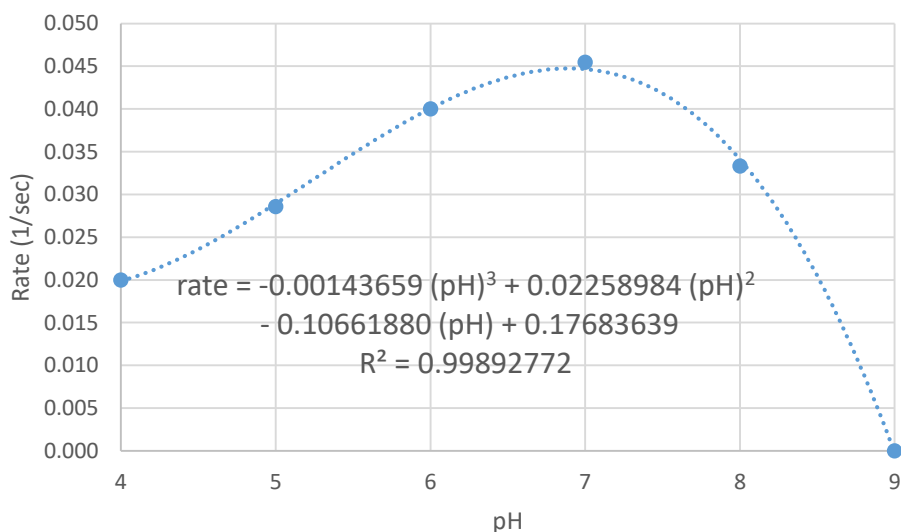
for at least a century the detailed reactions involved in the mechanism are still not clearly understood."⁷² Nonetheless, for a mixture of hydrogen peroxide and iodide, as in the hydrogen peroxide iodine-clock reaction,^{5, 14} it is found that at low pH, no oxygen is produced as the oxidation product (only I_3^-). "The complete *transformation* [*sic*] of iodide into iodine, [by Reaction 7]... is possible at sufficiently high concentration of hydrogen ion...."⁷³ It is clearly seen that in acid (pH 4.7) medium there is stoichiometric oxidation of I^- into I_3^- by H_2O_2 ... without

oxygen formation.”⁷² At sufficiently high pH, oxygen is produced and the production of I_3^- greatly reduced in that the reaction, Reaction 7, of iodide, hydrogen ion and hypoiodous acid has a rate constant of $1.3 \times 10^{10} \text{ M}^{-2}\text{s}^{-1}$.⁷² This suggests that there is a pH-dependent competition between I^- and H_2O_2 for the HOI (or OI^-) formed.^{72, 74} The effect of pH on this competition is amplified by the fact that the reaction of OI^- with H_2O_2 (or HOO^- with HOI) to produce oxygen is 10^5 to 10^7 times faster than the reaction of HOI with H_2O_2 .⁷² (Perrin⁷⁵ lists the pK_a of hydrogen peroxide as 12.11 – 12.23 at 0 °C, 11.92 at 10 °C, 11.81 at 20 °C, 11.34 at 35 °C and 11.21 at 50 °C and the pK_a of hypoiodous acid as 12.4 at 20 °C, 9.7 at 22 °C, and 10.64 at 25 °C.) This pH dependence is consistent with Wright and Reedy’s data.⁷⁶ They gave ranges of time for a clock reaction to reach the starch-iodine endpoint when performed at a series of pHs. While Wright and Reedy specified that the concentrations of the reducing agent (vitamin C, 0.0005 moles), hydrogen peroxide, starch and iodine were held constant, they did not specify the temperature at which the reactions were run and the buffers, of which the same volumes were used in all of these experiments, were only identified as “commercially available.” For the six pHs in the range from 4 to 9, curve-fitting of the inverse of the maxima of each time range (the lowest rates) versus pH gave the best correlation. (Since no endpoint was reached at pH 9—“At pH 9 there is no more I_3^- formation....”⁷²—, the time for pH 9 was taken as infinity, that is, a rate of zero.) This is shown in Figure 2. The increase of rate with increase of pH (for the first four points) may be attributable to the finding that $\frac{-d[H_2O_2]}{dt} \propto 1/a_{H^+}^2$,⁵⁹ since the consumption of hydrogen peroxide, Reaction 1, is the rate-determining precursor to iodine production,⁷⁷ Reaction 3. The decrease in the rate of iodine production (in the last three points) may be attributed to the increased concentration of IO^- or HOO^- which react with H_2O_2 or HOI,

respectively, producing oxygen rather than iodine. The maximum of the plot reflects the transition of dominance between iodine and oxygen production from the hypiodous species.

Figure 2. Rate (1/time to consume 0.0005 moles of ascorbic acid) vs pH for Wright and Reedy's

iodine-clock reaction

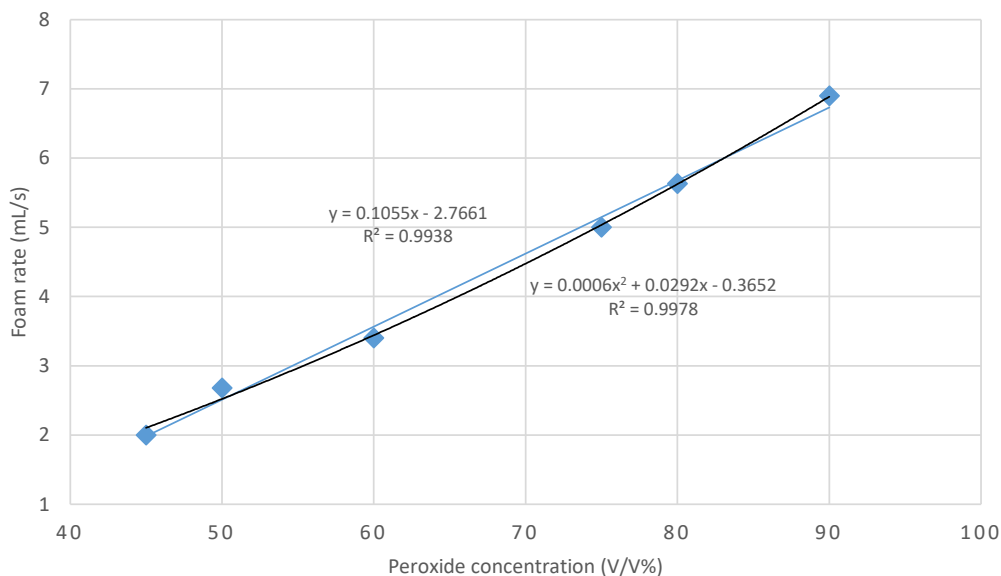


Applying the quadratic formula to the first derivative of equation of the curve yielded a maximum at pH 6.9 for a hydrogen peroxide to iodide ratio of 3.6:1. (Corresponding plots of 1/midrange and 1/minimum versus pH had $R^2 = 0.9965$, with the maximum at pH 6.9 and $R^2 = 0.9917$, with a maximum at pH 6.8, respectively.)

Examination of Hansen's data for reaction rate, as measured by oxygen production, versus potassium iodide concentration (in his Figure 4 or Table 2)⁷⁸ show a downward curvature with increasing iodide concentration, rate (atm/s) = $-0.009275 [KI]^2 + 0.01583 [KI] - 0.0002203$ for $[KI] = 0.100$ to 0.400 . The decrease in rate increase with increased iodide concentration is consistent with increasing success in competition for hypiodous acid (or hypiodite) by iodide as its concentration increases. Similarly, Hernando, Laueruta, Kuijl, Laurin, Sacks, and Ciolino's plot of rate versus hydrogen peroxide concentration (Figure 3)²⁰ appears to have an upward

curvature with increasing hydrogen peroxide concentration (approximately, rate (mL/second) = $0.0006 (V/V\% \text{ H}_2\text{O}_2)^2 + 0.0306 (V/V\% \text{ H}_2\text{O}_2) - 0.4178$), reflecting the increasing success of hydrogen peroxide in that competition.

Figure 3. Comparison of linear vs. quadratic fit to rate vs. concentration data



High pH is not enough to completely obviate iodine production. Evans and Upton found that 0.4 % of the oxygen produced by iodide-catalyzed decomposition of hydrogen peroxide is singlet oxygen.⁷⁹ Kepka and Grossweiner found that singlet oxygen readily oxidizes iodide, with $\Delta F^0 \approx -30$ kJ/mole and with a measurable rate constant.⁸⁰ The mechanism of this oxidation is discussed by Braathen, Chou, and Frei⁸¹ who found the rate constant for the formation of I_3^- to be equal to the rate constant of $\text{O}_2(^1\Delta)$ decay which they found to be $(8.7 \pm 0.2) \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$.

Variations in the procedure might increase student interest. The addition of universal (pH) indicator to the two solutions, which can be adjusted to pH 9 with sodium hydroxide or potassium hydroxide, **not** ammonium hydroxide (Iodine, if produced, can react with ammonia

to form “nitrogen triiodide,” which is explosive.⁸²), which will obviate significant iodine production. Although running the reaction at pH 9 does not show dramatic pH change during the production of 500 mL of foam, as with thiosulfate present (as Sorum *et al.* found; see their Figure 5.)⁸³ a gradual drop in pH of about two units can be observed. The indicator will give a colored solution which may increase the visibility of the foam. (Note that the effect of thiosulfate would be to increase the induction period and cause pH fluctuation, but not ultimately interfere with iodine production.) Instructors may wish to experiment with other initial pHs. Another alternative would be to lower the hydrogen peroxide to iodide ratio and to add starch. When, toward the end of the reaction, enough hydrogen peroxide would be consumed (the iodide concentration being maintained by Reaction 2') iodide could successfully compete for hypoiodous acid to form iodine. This would result in a clock reaction-like color change. Clearly, instructors may change the foam volume difference to be timed, as well as quantities of materials to accommodate time restrictions or other exigencies.

Reactions 1 and 1' are rate determining and have different activation energies:⁷⁷ $E_{a_{k_1}}$ = 56.07 kJ/mole and $E_{a_{k_1}}$ = 43.72 kJ/mole. This means that the apparent E_a will be pH-dependent and, as a result, so will the change in rate with change in temperature. This pH-dependence may, in part, account for the differing values found for E_a in student laboratory experiments.^{14, 18, 19}

CONCLUSION

The Elephant's Toothpaste demonstration can be used to demonstrate the effect of temperature on reaction rate. While the mechanism of the reaction behind this demonstration

is commonly given as a two-step reaction, it cannot account for the acknowledged by-product, iodine or triiodide. The possible complexity giving rise to and, consequently, arising from the production of iodine or triiodide has been outlined, amply illustrating the desirability of giving students a simplified discussion of the mechanism, if any. Nonetheless, we feel that it is desirable that, should students ask questions, instructors be aware of this complexity and controversy and have access to relevant reference materials (sampled here). Among the complications comprised by the demonstration are the opposing effects on the (first order in hydrogen peroxide) reaction rate of diminishing reactant concentration resulting from the reaction's progress and the increase in temperature, absent temperature control, caused by the reaction's high exothermicity,^{6, 19, 55, 84, 85} $\Delta H \approx -94.6 \text{ kJ mol}^{-1}$,⁸⁵ to $-98.2 \text{ kJ mol}^{-1}$.⁸⁴

ASSOCIATED INFORMATION

Supporting information

Supporting information giving a description of how the demonstration can be done is available at

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The authors declare no competing financial interest.

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