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AP Chemistry, Period 0
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Temperature Effects on an Oscillating Reaction

Research Question:

How do changes in temperature affect the oscillation of the Briggs-Rauscher reaction?

Introduction:

Most reactions that are known either proceed to completion or to equilibrium. Even in equilibrium reactions, and change in color is one-way, always toward equilibrium. However, since the beginning of the 20th century, a few select reactions have been discovered that do not proceed linearly, but rather they oscillate. Concentrations and colors shift cyclically, and it seems to conflict with the Second Law of Thermodynamics, which states that within a given system, entropy is always non-decreasing. If the reaction switches back and forth between two states, and those states are at different entropies, then there would appear to be a violation. Fortunately, the iron law does not crumble in the face of this reaction, but Briggs-Rauscher and others like it garnered increased attention and study to its effects on equilibrium behavior.

My experiment will directly investigate the effects of changing the temperature at which the reaction occurs. I will keep the concentrations of all of the reactants constant in addition to stir rates, order of preparation, and air pressure. Much of the procedure and set-up comes from an MIT lab that effectively replicates the already known Briggs-Rauscher reaction, but the measuring and testing of the effects from changing temperature are my own.

Materials List:

The following is copied from the MIT OpenCourseWare:

1. 3 Liters of distilled water
2. 410 mL 30% Hydrogen peroxide, H_2O_2
3. 43 g, potassium iodate KIO_3 4.3 mL 18M sulfuric acid H_2SO_4
4. 16 g malonic acid, $CH_2(CO_2H)_2$
5. 3.4 g manganese(II) sulfate monohydrate
6. 0.3 g soluble starch
7. 20 g sodium thiosulfate, $Na_2S_2O_3$
8. 4- 2 L beakers
9. Disposable gloves
10. Hot plate glass stirring rods Beakers,
11. 100 mL & 50 mL magnetic stirrer,
12. 2" stirring bar

My additional materials list:
1. Thermometer
2. Paper towels
3. Two metal pots
4. Parafilm
5. Tape and sharpie (for labelling)
6. Three graduated cylinders
7. 3 200mL beakers
8. 1 250mL beaker

Procedure:

The main lab procedure I used to prepare the three reactant solutions is not my own procedure. It comes from MIT OpenCourseWare, see works cited.[1]

I will summarize the procedure. The first reactant solution was 1 Liter of 12% Hydrogen Peroxide from dilution. The second was dissolved potassium iodate (dissolved with heating and concentrated sulfuric acid). The third is malonic acid (reactant), manganese sulfate (catalyst), and starch (indicator), again through a somewhat complex heating/stirring procedure.

What follows is my own:

With one liter of each solution, it is now easy to test the effects of changing temperatures on the oscillations. The following represents the procedure that I only realized to use by the end of my trials. For all temperature variations, the procedure is much the same.

1. Pour 100 mL of each solution into separate 200 mL beakers. This is enough for two trials.
2. While the solutions are in these beakers, the temperature can now be adjusted by placing beakers in a pot of water with ice for cooling, or in a pot of water on a hot plate for heating.
3. With thermometer, measure temperature of each solution, not the water, until the solutions themselves have reached the desired temperature.
4. Measure 50 mL of each solution into separate graduated cylinders.
5. In a new 250 mL flask, place the stir bar inside and begin stirring before pouring any solution. Then briskly pour in solution A, followed by solution B, followed by solution C, and then observe the reaction.
6. As reaction nears its end indicated by less distinct oscillation phases, measure temperature of reaction once more.
7. Once the reaction is completed, as indicated by a very dark brown color and the expulsion of elemental iodine, follow disposal instructions, which is from the MIT source.

Observations, Data, Analysis:

Most observations were conducted by watching the video of the reaction after the fact for more accurate measurements.

      Failed Attempt: While waiting for malonic acid delivery, I made solution C with acetone as a substitute in equimolar quantities. When I performed the full reaction with the substitution, there was no color switch to blue, but rather the amber became increasingly darker amber like in the end of the working reaction.

Control Reaction at Room Temperature (22° C):

Justin surprised at the initial "fast" color change. This diluted blue is very unmistakable in the first few oscillations.

The clear phase in every oscillation.

Once 2.5 minutes have elapsed, the unmistakable blue from the "fast" change is now a dull, blue-amber color. Additionally, the change from the deep amber to this color takes more time.


The darker amber color shortly before the "fast" change to blue. This picture happens to be later in the reaction.

Eventually, the oscillation stops and the solution settles on this very dark amber color (far darker than at any point during oscillation).

Overall, the color cycle for the reaction is from clear to increasingly amber until a sharp change to the blue color, which then fades back to clear in short time. As the reaction progresses, color changes become more gradual, the colors themselves become less distinguished, and the time between oscillations increases. Additionally, as indicated below, oscillations quicken, then remain relatively constant before slowing as the final reactants are reacted.

Time Between Oscillations as Reaction Progresses
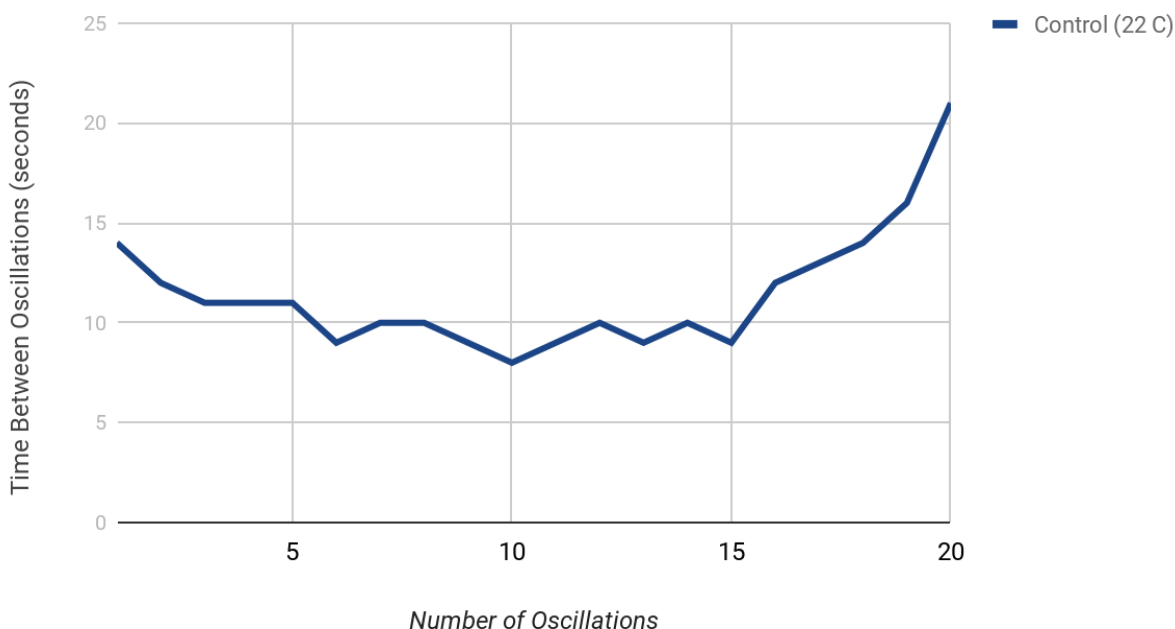

Hot Reaction (70.1 ºC):

This reaction was marked by the distinct absence of any blue color at any point during any oscillation. Rather, the color changes to and from amber happened sharply, distinctly, and rapidly, with the change itself lasting under 1/5 of a second. I believe that the blue color is absent not because the tri-iodide ions (I_3^-) weren't forming (a crucial step of one of the reaction pathways), but because the starch indicator was denatured in some way or it never bound to the (I_3^-) to actually produce the blue color.

Below is a purely conceptual model for the intensity of color where zero represents some middle, 'equilibrium' value, which will be discussed more later:
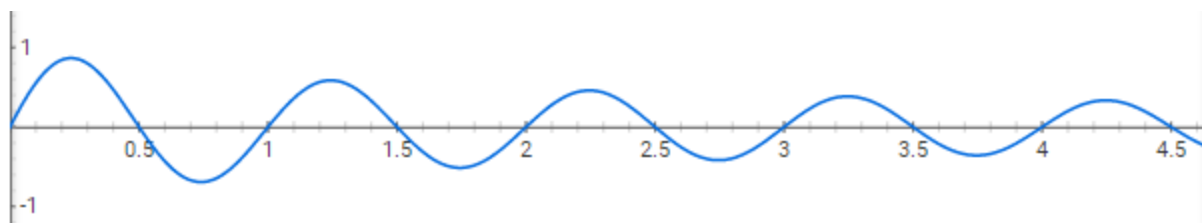
Oscillation proceeds at a relatively constant rate (1 second period), but the maximum color intensity (or lack thereof) decreases as the reaction progresses to eventually settle on a diluted amber color. However, once settled for approximately 20 seconds at the end of the reaction, the light amber suddenly changed to dark brown and elemental iodine (gas) was expelled very rapidly, far more so than in the control or 'cold' reactions.

Oscillation of Hot Reaction

Number of Oscillations
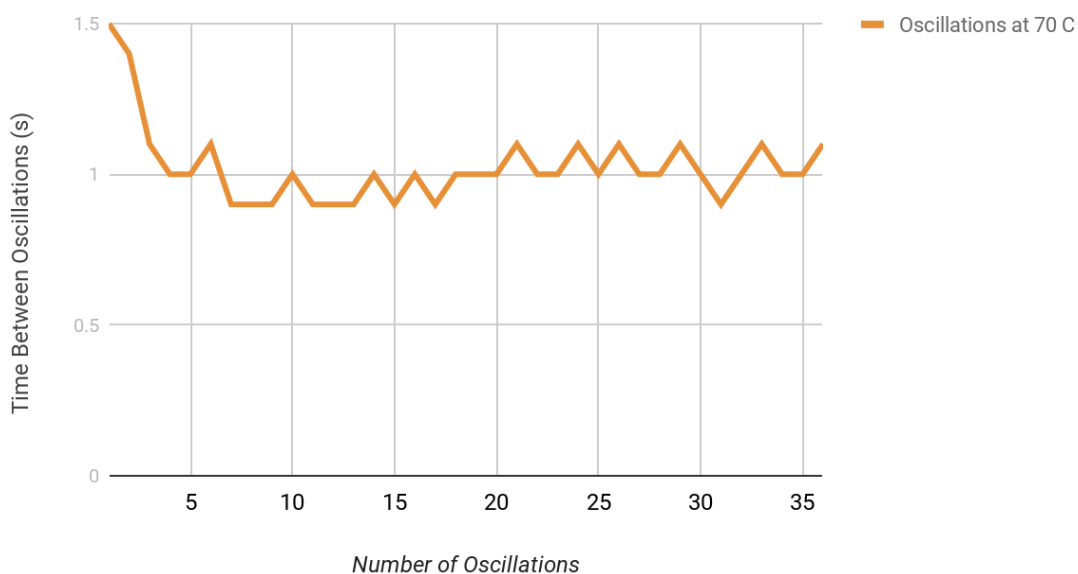
Cold Reaction (10° C):

As indicated in the below chart and table, each oscillation lasted significantly longer than in the control despite the reaction occurring roughly ten degrees lower in temperature. In addition, the total number of oscillations were roughly the same, but each oscillation took almost twice as long as in the control, as did the total reaction time. Additionally, the increase of time is not spread evenly between the amber and blue phases of the reaction. At two separate, representative points in the control reaction, the ratio of time from clear-amber and from dark blue-clear was about **1:2 (approx. 3 seconds to approx. 6-7 seconds)**. For the cold reaction, this ratio was closer to **1:1.5** or **1:1.4 (approx. 7 seconds to approx 10 seconds)**. While confounding from other variables is possible, this would seem to indicate that decreasing the

temperature more dramatically decreases the time of the clear-amber phase than the blue-clear phase.
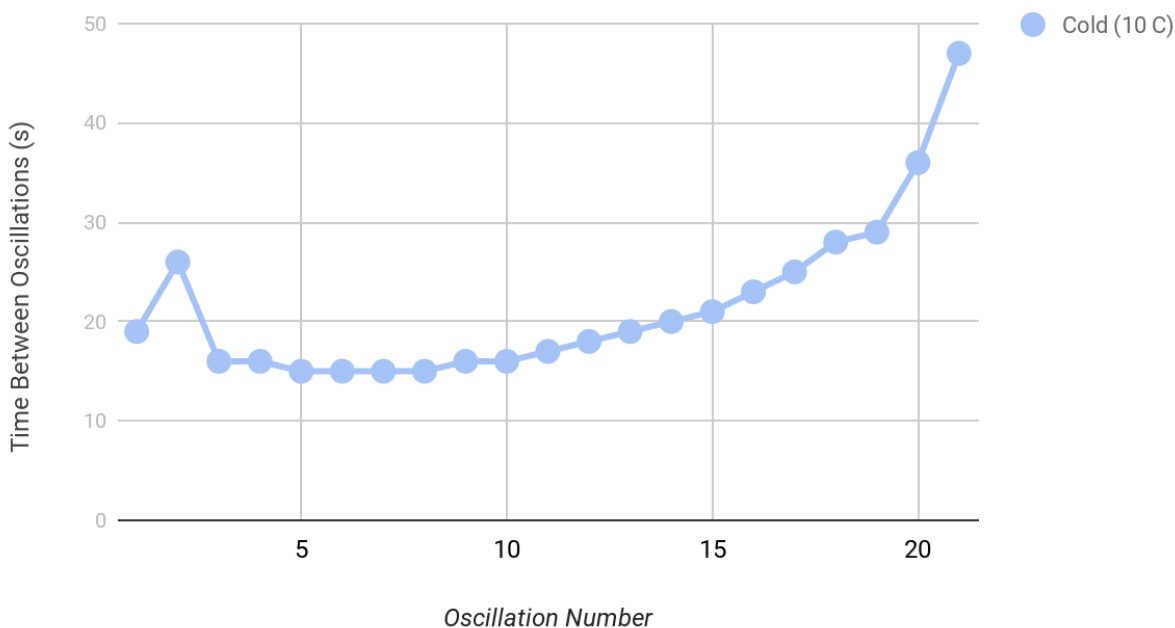
Oscillation of Cold Reaction

Table combining summary measurements of the three trials:

Temp. (°C)*	Average Oscillation Time (s)	Total Oscillations	Total Reaction Time (s)
10.0	21.5	21	432
22.0	11.4	20	228
70.1	1.02	36	59

*Temperature measurement was a flaw in my procedure as practiced. For control (22°C) and the hot temperature, I only measured the room temperature and water bath temperature as opposed to the actual temperature of the solutions, which I did do for the cold temperature reaction. Also, the cold temperature reaction mixture had risen to 18°C by the time the reaction had finished oscillating, so **RECORDED TEMPERATURES REPRESENT INITIAL VALUES.**

Discussion: The goal of this experiment was not to investigate the nature of the Briggs-Rauscher reaction itself, so i will briefly summarize **why** the colors appear to oscillate and why the 2nd law of thermodynamics is not truly violated.

Here is the overall reaction: $IO_3^- + 2\ H_2O_2 + CH_2(COOH)_2 + H^+ \rightarrow ICH(COOH)_2 + 2\ O_2 + 3\ H_2O$
The reaction pathway is currently being researched and debated by chemists, because it contains *many* steps. The process comes from the two sources cited, summarized in my words[2, 3]

1. Essentially, a radical process converts Hydrogen Peroxide and Iodate into Iodine and Oxygen, and a non-radical process which converts Iodine into Iodide in the presence of Iodate and Malonic Acid.
2. The radical process (using Manganese as catalyst) consumes some iodide and can only operate at LOW iodide concentrations. The non-radical process produces iodide as an intermediate.
3. The amber color is Iodine (I_2) and the blue color comes from the accumulation of iodide AND Iodine with the starch indicator to form penta-iodide (I_5^-).
4. Both processes happen simultaneously, but in varying proportions, and both contribute to the overall one way conversion of Hydrogen Peroxide, Malonic Acid, and Iodate into Oxygen, Water, and $ICH(COOH)_2$.
5. The radical process begins, turning the clear solution into Iodine while being able to consume the Iodide produced by the non-radical process.
6. However, the non-radical process produces Iodine faster with increasing Iodine concentrations, so much so that once the reaction is a dark amber (high iodine concentration), the non-radical process produces Iodide extraordinarily quickly and the radical process is unable to operate, so the iodine and iodide are in high concentrations and combine to form the penta-iodide which produces the deep blue color.
7. Once radical process ceases, iodine is no longer produced, but the non-radical process still proceeds which essentially removes Iodine from penta-iodide converting it back into clear iodide ions. The process slows once the solution is clear (from lack of Iodine), allowing process B to start up again, thus completing the cycle.

Even though there is oscillation, the overall reaction is not in any kind of equilibrium, but rather two competing process produce intermediates that are colored, but both process in a way accomplish the overall reaction (not to say that either process could be isolated to produce the overall reaction). Therefore, the overall entropy of the system is not inherently non-increasing.

Both the radical and non-radical processes are affected by change in temperatures. Since cooling the reaction increased the length of the clear-amber phase, it likely slowed the radical process significantly, thus delaying the increase in Iodine concentration which causes the non-radical process to take longer to overpower the radical to produce the blue color.

Works Cited:

1. *MIT OpenCourseWare. Splendor of One Chemical Reaction.* Massachusetts Institute of Technology, Fall 2012.

2. Anne Marie Helmenstine. *Briggs-Rauscher Oscillating Color Change Reaction.* ThoughtCo.com, 27 June 2018.

3. Furrow, S. D. in Field, R. J. and M. Burger (1985), *Oscillations and Traveling Waves in Chemical Systems*, J. Wiley & Sons, New York.