

# Belousov - Zhabotinsky Reaction: Velocity of Wave fronts with Temperature Gradient

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## Introduction

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Oscillatory systems are found throughout physics but seldom in chemistry. The oscillating chemical systems that are known and studied today have very important implications. Naturally occurring chemical oscillatory systems include the heart's pacemaker, and the sinoatrial node. Both reactions have trigger mechanisms that are closely analogous to the oscillating waves of the Belousov-Zhabotinsky reaction.

Soviet physicist Boris Belousov discovered what is now known as the Belousov-Zhabotinsky reaction (BZ reaction) in 1951. Initially, his results were heavily denied because of a misinterpretation of the 2<sup>nd</sup> law of thermodynamics (Hill 2-3). Critics wrongly believed that reactions could not progress backwards at any point in time because "all reactions must approach equilibrium." It was believed to have violated the 2<sup>nd</sup> law of thermodynamics. In actuality, on average the reaction must approach equilibrium. The BZ Reaction oscillates forward towards its equilibrium values. Put simply, the average value of reactants was strictly approaching equilibrium. This did not necessitate a strictly linear approach.

It was not until another soviet physicist Anatol Zhabotinsky, Belousov's graduate student, recreated the reaction some three years later, that the results gained traction amongst the leading chemists of the time (Hill 2-3). The initially proposed mechanism was immensely complicated and would do little to yield quantitative results or really any insight what so ever. For this reason, Field and Noyes took to simplifying the proposed model. They simplified it down to the most comprehensible model available today, the Oregonator (discussed more in depth in the theory section) (Noyes 1-2).

The original experiments studied only temporal oscillations, ones that occur under constant stirring. The more illuminating and interesting oscillations are the spatial oscillations (see figure 1). The presence of intermediate reactants and the diffusion of those reactants leads to the initiation of the reaction at various radii from the originating cite, seen as the propagation of a wave front (see below).



Figure 1: The spatial waves of the BZ Reaction - pictured at 2 minutes apart from each other.

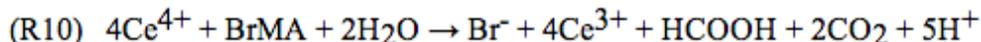
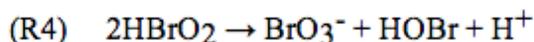
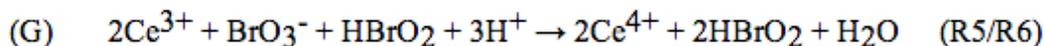
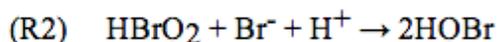
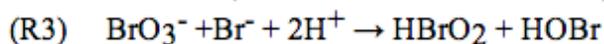
## Theory

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In general, the BZ reaction is perpetuated by Ce(III)/Ce(IV) oxidizing  $\text{CH}_2(\text{COOH})_2$  by  $\text{BrO}_3^-$  in  $\text{H}_2\text{SO}_4$ . To isolate only the oscillatory nature of the system, it is best to carry out the reaction in a closed, constantly stirred system. This was the method that Belousov used in his initial, accidental discovery of the reaction. In our case, we wanted to visualize the pattern formation and spontaneity of the oscillations (shown in figure 1). To better see this we carried the reaction out in a petri dish and forewent stirring the reactants.

There are many different proposed mechanisms for this reaction. Currently, no chemist, in good conscience, could give a definitive mechanism for this reaction. The two most robust mechanisms are close to seventy unique steps with over twenty unique intermediate species. There are many different, simpler reaction mechanisms. In this experiment, as opposed to previously done experiments in Dr. Kleinfeld's/Dr. Tsai's Physics 173 class, the Oregonator model of the reaction is presented and analyzed. It is given below:

### OREGONATOR (Condensed FKN Mechanism)

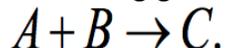


The reactions above are numbered from top to bottom as; (I), (II), (III), (IV), and (V).

So how do we get oscillations? Reaction (I) lowers the concentration of bromide and increases bromine. This allows for the bromination of malonic acid in (II). When the concentration of  $\text{Br}^-$  has been lowered enough, (III) dominates. This causes an exponential increase in bromous acid and oxidizes the metal ion catalyst and indicator cesium (Ferroun). Bromous acid is subsequently converted into bromate and HOBr in (IV). Meanwhile,  $\text{Ce}^{4+}$  (Ferroun) is reduced to  $\text{Ce}^{3+}$  (reduced Ferroun) in (V) and the bromide concentration is again increased. This change in cesium (Ferroun) is what results in the color change, or movement of the wave front. Once the concentration of bromide is high enough it reacts with bromate and HOBr in (I) and (II). Consequently, the process begins again (Hill 3-4).

The reason this reaction schematic is used as opposed to others is that this schematic is proven more robust and segues easily into mathematical analysis. In order to evaluate the rate equations it is necessary to know the k-values (rate constants). Since we are interested in these values at non-equilibrium positions of the reaction we cannot use the coefficients on the reactants. Instead, the k-values must be determined experimentally. The reaction schematic above has well defined experimental k-values discovered by Fields, Noyes and Koro (Noyes 1-2). The other commonly used model does not. That is the basis and strategic advantage of using the Oregonator model.

Rate equations are an important aspect of chemistry. They allow the concentration of reactants to be known at any period of time. Take the following general equation:



The elements A and B decrease with respect to time. Their derivatives can be expressed as  $-r$ , where  $r$  is the reaction rate. The corresponding rate equation is:

$$r = kAB$$

Again, the  $k$ -value is the experimentally determined rate constant.

The above schematic of the Oregonator model, and their accompanying rate equations can be written as:

$A + Y \rightarrow X + P$	$r = k_3AY$
$X + Y \rightarrow 2P$	$r = k_2XY$
$A + X \rightarrow 2X + 2Z$	$r = k_5AX$
$2X \rightarrow A + P$	$r = k_4X^2$
$B + Z \rightarrow \frac{1}{2}fY$	$r = k_0BZ$

The corresponding rate constants are;  $k_0 = 1$ ,  $k_2 = 2.4E6$ ,  $k_3 = 1.28$ ,  $k_4 = 3E3$ , and  $k_5 = 33.6$  (all with units  $M^{-1}s^{-1}$ ) (Dodd 6-10).

We could then solve the five coupled differential equations with varying initial conditions to determine the concentration with respect to time of the reactants. The one we focused on most was  $Ce^{4+}$  in its oxidized state because this is what resulted in the blue coloration. The graph of the concentration of  $Ce^{4+}$  with respect to time is shown below along with the graph for  $HBrO_2$  (Dodd 16-18, 23).

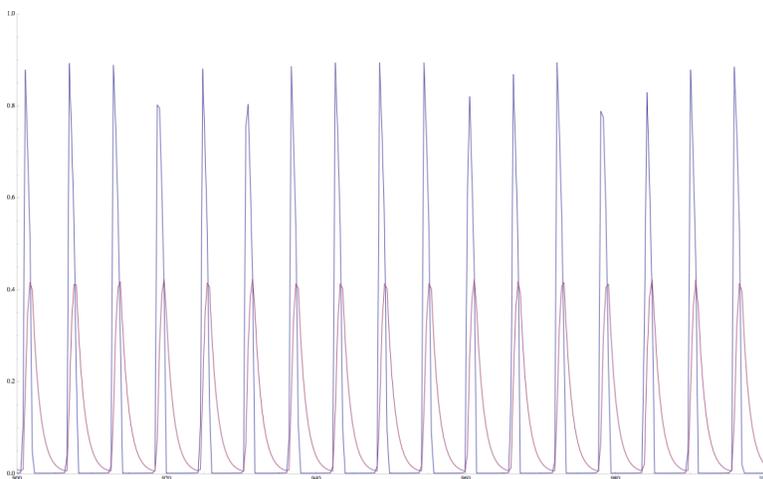


Figure 2:  $Ce^{4+}$  concentration with respect to time as indicated by the smaller peaks.  $HBrO_2$ 's concentration at different times is indicated by the larger peaks.

## Experiment and Methods

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In this experiment, Ferroin, a commonly used indicator, was elicited to help visualize the oscillations of the reaction. It is important to note that Ferroin is also used to replace cesium. This is largely due to the cost of cesium relative to Ferroin. Ferroin is much cheaper and a less toxic alternative. Ferroin also boasts a more dramatic color change making it more than a suitable alternative. The reactants were stock compounds; sodium bromate, potassium bromide, and malonic acid. Sulfuric acid was used to place all of the compounds into solution and yield the desired concentration of protons in the mixed solution. Furthermore Triton X-100 was used as a detergent to relieve surface tension and make imaging the reaction easier.

The steps for preparing the solutions are:

**Solution A:** Combine 0.0522 grams of potassium bromide in 1.25 ml of 0.6 molar sulfuric acid.

**Solution B:** Combine 0.280 grams of sodium bromate in 2.00 ml of 0.6 molar sulfuric acid.

**Solution C:** Combine 0.195 grams of Malonic Acid in 2.00 ml of 0.6 molar sulfuric acid.

Then combine solutions A, B, and C in a petri dish and allow it to rest for a few minutes until any yellowing fades. Then add 0.6 ml of Ferroin and four drops of Triton-X 100 (10% solution) to the reaction. Lastly, mix the reactants thoroughly and allow the reaction to settle. The reaction typically begins within two minutes.

There were two main experiments done on the BZ reaction. One was just the standard reaction done in open air on a light table. The second experiment was done under a temperature gradient. The apparatuses are pictured below:



Figure 3: This is the simple set-up, a Petri dish in open air on a light table. The camera set-up is composed of the silver crossing bars at the top of the picture.

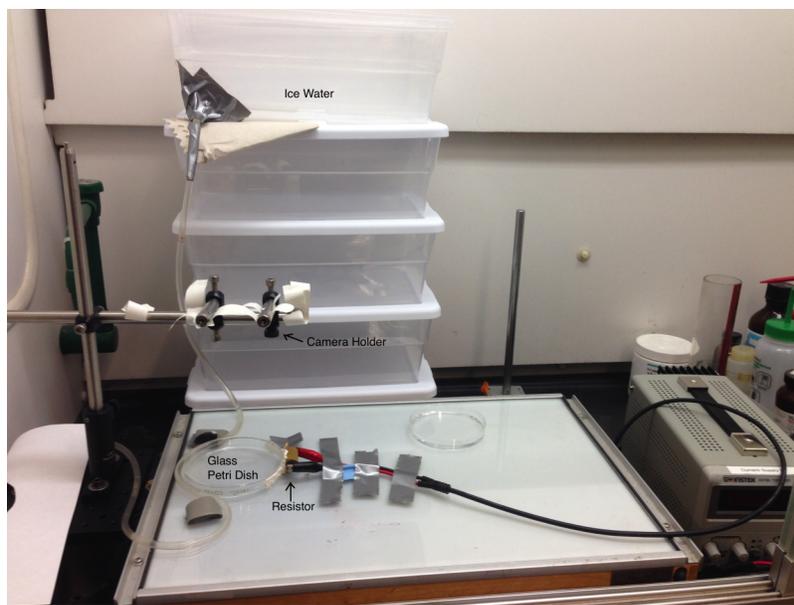


Figure 4: The complex set-up with the important aspects labeled.

The heat gradient was established using a tube with a constant flow of cold water. This cold side typically reached 10–14 Celsius. On the hot side, we used thermal putty and a resistor with current running through it to generate heat. The hot side remained between 38 and 42 Celsius. So a fairly large gradient was established in the reaction.

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## Goals

We wanted to first recreate the results of the previous two experiments. Being able to successfully complete the most basic form of the reaction is an important foundation to have when strong adaptations are going to be made. Moving on, we then tried to evaluate the frequency of oscillations of the reaction under different conditions; first under standard normal conditions, and then under the temperature gradients.

Furthermore we wanted to solve the five, coupled differential equations in Mathematica. This would allow us to track the theoretical concentrations of reactants as a function of time as well as gain a feel for the general shape of the concentration curves.

Lastly, we tried to determine the speed of the wave fronts for the two reaction environments and compare them to what we would expect given the model as well as values from literature.

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## Results and Analysis

We needed to develop a robust method of imaging the reaction. Filming proved difficult given the equipment. Eventually, we settled on using an iPad and a basic, free time-lapse application called Osnap to image each reaction. We took stills every second of the reaction (roughly 3600 - 4000 photos per reaction). We then developed a code in MatLab that allows us to pick a single

pixel and chart the oscillations of the pixel as the reaction progresses. We also wrote a MatLab code that allows us to track individual wave fronts through the images (See appendix for the MatLab code).

We ran two simple reactions but ended up only taking data from twenty pixels across the two reactions. The simple data had peak values ranging between 7.62 and 9.18 with a mean of 8.4. We would expect the data for the hot and cold reactions to fall on either side of these values. A graph of how one pixel's blue value oscillated through every photo of the reaction (the concentration of oxidized Ferroin with respect to time) is shown below.

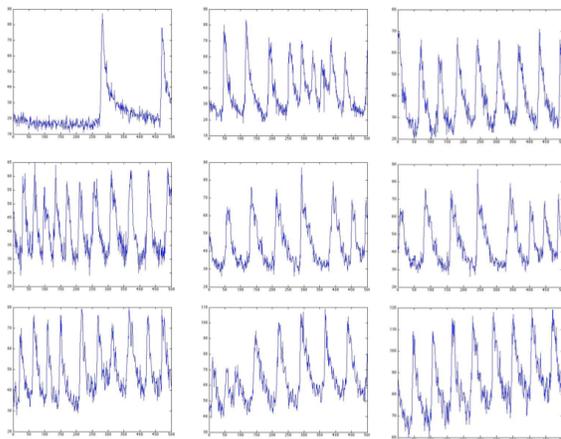


Figure 4: The oscillation of Ferroin with respect to time for the simple reaction.

We ran two of the complex reactions as well and then sampled from different time points. We obtained sixty different samples and graphs similar to figure 4, from various points in the petri dish. We then recorded the number of peaks this pixel corresponded too as well as whether it was on the hot or cold side. That data is provided in the appendix as well.

After examining the data, you can see there is a significant difference between the frequency of oscillations in the hot and cold side. The data suggests that on the hot side the number of oscillations is between 10.86 and 12.64. It also suggests that the frequency of cold oscillations is between 4.84 and 6.53. It is important to note that the probability of the hot and cold side peak values overlapping is 1/10000 at best. We can with absolute certainty state that the results from each half of the reaction are statistically different.

Moving on to our analysis of speed, we had two methods of determining speeds that both yielded similar results. The MatLab code yields a graph of pixel number and time. The slope of this graph is the speed of the wave-front. A few examples can be seen below in figure 5. We can also measure the width of the oscillations from figure 4 and divide this by the width of the wave in pixels to determine the pixels traveled per period of seconds. Then we can apply the “pixels in a centimeter” constant to determine the speed in cm/s. The latter method was used more because it was easier to do quickly in excel, and more dependable. The data for speeds is also given in the appendix right next to the data for peak number.

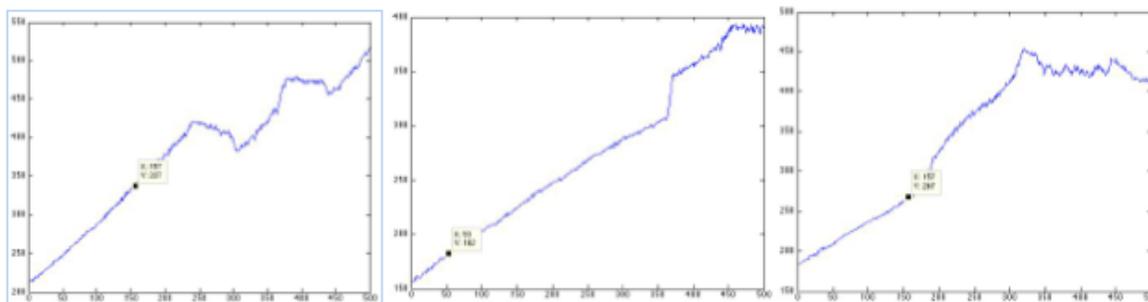


Figure 5: Graphs of the wave-front location (by pixel number) with respect to time for three different wave-fronts in the simple reaction.

Much like the peak number, we saw that the speeds were also statistically significant and followed the trend we expected. Further analysis of the data, showed that the results were between  $1.36\text{E-}02$  cm/s and  $1.58\text{E-}02$  cm/s for the hot side and between  $6.04\text{E-}03$  cm/s and  $8.16\text{E-}03$  cm/s for the cold side. For the simple reaction we determined the speeds were between  $9.53\text{E-}03$  cm/s and  $1.15\text{E-}02$  cm/s.

## Conclusions

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After analyzing the data we were able to conclude that running the reaction in the presence of a heat gradient significantly distorts the frequency of oscillations on both sides of the petri dish. This is in line with what we expect to see.

Furthermore, the heat gradient did significantly affect the speed of the wave fronts moving through the petri dish. The trend for both oscillation frequency and speed was cold < room temperature < hot. This is precisely what we would expect given the linear dependence of rate equations on temperature as well as LeChatelier's principle.

## General Discussion and Future Endeavors

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Initially, the aim of the experiment was to be able to successfully use the visual clues of Ferroin to determine the concentrations of elements as a function of time and then compare it to the results derived in MatLab. Determining what shades of blue correspond to what concentrations of Ferroin proved immensely difficult. Perhaps in the future, this question can be revisited. We were unable to determine a true number for the concentration of oxidized Ferroin throughout the reaction. Furthermore, because of our lack of data on concentration solving the rate equations proved to be only useful for determining the expected shape of the concentration curve.

The first true issue arose with imaging. We first imaged the reactions by taking one photo every two minutes. However, we then discovered the waves moved too quickly for our MatLab code to effectively track. We tried taking pictures every thirty seconds but still the waves could not be tracked. Eventually we settled on a single frame per second. This was not ideal because the photo number was now close to 4,000 per reaction. We took about three weeks to finally solve the imaging issues. With this increase in photo number, we took close to four weeks actually analyzing the data.

It is important to note also that there was one limiting aspect of our MatLab code. The MatLab code only worked in one dimension. The y-motion or the x-motion of the wave fronts was all that could be tracked. This is not ideal because the waves are curved and move out in all directions as well as collide with other waves. Moving forward, adapting the code to allow for tracking diagonally would greatly improve the analysis of the data.

The results were consistent with what we expected. Numerous scientific articles stated that the speed of the wave fronts at room temperature is right around  $10E-3$  to  $10E-2$  cm/s. So the data is remarkably close to the true value, which suggests that the data is accurate and consistent with other experimental techniques. It is this fact that substantiates the robustness of our MatLab codes and our general mechanism of determining wave speed. However, in the future it would make sense to add a control for reactions run in just the cold setting and just the hot setting. This would help us further analyze the results of applying the temperature gradient. Given more time this would have been done.

All in all, the data is quite pleasing. All of the goals we set out to achieve were done so in some capacity or another.

## Works Cited

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Dodd, Melody . "The Belousov-Zhabotinsky Oscillator: An Overview." Melody Dodd Lecture. Colorado State University. , . 10 Dec. 2010. Lecture.

Hill, Dan, and Timothy Morgan. "Pattern Formation and Wave Propagation in the Belousov-Zhabotinsky Reaction ." *University of California, San Diego – Physics Department 1: 12. Physics 173/BGGN 266*. Web. 23 Mar. 2014.

Noyes, Richard M. and Richard Field and Endre Koro. "Oscillations in Chemical Systems: Detailed Mechanism in a System Showing Temporal Oscillation" *Journal of the American Chemical Society* 1972 94 (4), 1394-1395

## Appendix

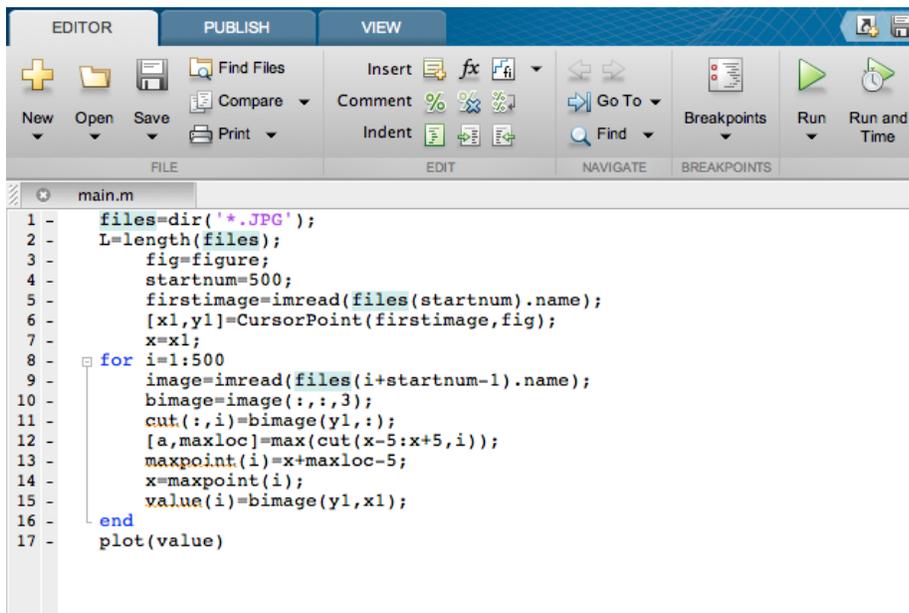
### MatLab Code Used:

```
function [x1,y1]= CursorPoint(A,fig)

imagesc(A);
dcm_obj = datacursormode(fig);
set(dcm_obj, 'DisplayStyle','datatip',...
    'SnapToDataVertex','on','Enable','on')

pause                                % Wait while the user does this.

c_info = getCursorInfo(dcm_obj);
x1 = c_info.Position(1);
y1 = c_info.Position(2);
```



```
main.m
1 - files=dir('*.JPG');
2 - L=length(files);
3 - fig=figure;
4 - startnum=500;
5 - firstimage=imread(files(startnum).name);
6 - [x1,y1]=CursorPoint(firstimage,fig);
7 - x=x1;
8 - for i=1:500
9 -     image=imread(files(i+startnum-1).name);
10 -    bimage=image(:, :, 3);
11 -    cut(:,i)=bimage(y1,:);
12 -    [a,maxloc]=max(cut(x-5:x+5,i));
13 -    maxpoint(i)=x+maxloc-5;
14 -    x=maxpoint(i);
15 -    value(i)=bimage(y1,x1);
16 - end
17 - plot(value)
```

## Data for the Complex Reactions

<b>N</b>	<b>HOT PEAK NUM.</b>	<b>COLD PEAK NUM.</b>	<b>HOT SPEED</b>	<b>COLD SPEED</b>
1	8	3	2.50E-04	9.38E-05
2	9	9	2.81E-04	2.81E-04
3	13	6	4.06E-04	1.88E-04
4	12	2	3.75E-04	6.25E-05
5	7	3	2.19E-04	9.38E-05
6	12	3	3.75E-04	9.38E-05
7	14	9	4.38E-04	2.81E-04
8	8	6	2.50E-04	1.88E-04
9	9	3	2.81E-04	9.38E-05
10	12	2	3.75E-04	6.25E-05
11	15	8	4.69E-04	2.50E-04
12	12	7	3.75E-04	2.19E-04
13	10	9	3.13E-04	2.81E-04
14	17	14	5.31E-04	4.38E-04
15	13	11	4.06E-04	3.44E-04
16	15	2	4.69E-04	6.25E-05
17	14	3	4.38E-04	9.38E-05
18	14	9	4.38E-04	2.81E-04
19	13	5	4.06E-04	1.56E-04
20	12	10	3.75E-04	3.13E-04
21	14	12	4.38E-04	3.75E-04
22	17	11	5.31E-04	3.44E-04
23	11	4	3.44E-04	1.25E-04
24	11	5	3.44E-04	1.56E-04
25	16	10	5.00E-04	3.13E-04
26	14	5	4.38E-04	1.56E-04
27	13	7	4.06E-04	2.19E-04
28	15	8	4.69E-04	2.50E-04
29	16	6	5.00E-04	1.88E-04
30	13	11	4.06E-04	3.44E-04
31	10	1	3.13E-04	3.13E-05
32	6	2	1.88E-04	6.25E-05
33	10	1	3.13E-04	3.13E-05
34	8	1	2.50E-04	3.13E-05
35	11	2	3.44E-04	6.25E-05
36	3	0	9.38E-05	0.00E+00
37	11	0	3.44E-04	0.00E+00
38	3	0	9.38E-05	0.00E+00
39	6	1	1.88E-04	3.13E-05
40	7	1	2.19E-04	3.13E-05
41	11	8	3.44E-04	2.50E-04
42	12	7	3.75E-04	2.19E-04
43	10	7	3.13E-04	2.19E-04
44	14	2	4.38E-04	6.25E-05
45	10	6	3.13E-04	1.88E-04
46	14	7	4.38E-04	2.19E-04
47	11	6	3.44E-04	1.88E-04

48	13	6	4.06E-04	1.88E-04
49	10	6	3.13E-04	1.88E-04
50	10	5	3.13E-04	1.56E-04
51	7	7	2.19E-04	2.19E-04
52	12	9	3.75E-04	2.81E-04
53	14	5	4.38E-04	1.56E-04
54	19	7	5.94E-04	2.19E-04
55	14	6	4.38E-04	1.88E-04
56	12	6	3.75E-04	1.88E-04
57	13	9	4.06E-04	2.81E-04
58	10	7	3.13E-04	2.19E-04
59	12	5	3.75E-04	1.56E-04
60	23	8	7.19E-04	2.50E-04
<b>AVERAGE</b>	11.75	5.68	3.67E-04	1.78E-04
<b>VARIANCE</b>	12.39	11.24	1.21E-08	1.10E-08
<b>STAN. DEV</b>	3.52	3.35	1.10E-04	1.05E-04
<b>STAN. ERROR</b>	0.45	0.43	1.42E-05	1.35E-05
<b>CONFIDENCE</b>				
LOWER	10.86	4.84	3.39E-04	1.51E-04
UPPER	12.64	6.53	3.95E-04	2.04E-04
<b>TIME</b>		<b>UNITS</b>		
RED (min)	0-8.3	SPEED (RED)	cm/s	
BLUE (min)	25-33.3	SPEED (BLUE)	cm/s	
GREEN (min)	33.3-41.7	SPEED (GREEN)	cm/s	

## Data for the Simple Reactions

SIMPLE

N	PEAK NUM.	PEAK SPEED
1	9	1.13E-02
2	11	1.38E-02
3	8	1.00E-02
4	5	6.25E-03
5	7	8.75E-03
6	9	1.13E-02
7	10	1.25E-02
8	8	1.00E-02
9	9	1.13E-02
10	10	1.25E-02
11	9	1.13E-02
12	7	8.75E-03
13	12	1.50E-02
14	8	1.00E-02
15	9	1.13E-02
16	7	8.75E-03
17	6	7.50E-03
18	8	1.00E-02
19	9	1.13E-02
20	7	8.75E-03

	PEAK NUM.	PEAK SPEED
<b>AVERAGE</b>	8.4	1.05E-02
<b>VARIANCE</b>	2.78	4.34211E-06
<b>STAN. DEV</b>	1.67	0.002083772
<b>STAN. ERROR</b>	0.37	0.000465946

<b>CONFIDENCE</b>		
LOWER	7.62	9.53E-03
UPPER	9.18	1.15E-02

TIME	UNITS		
BLUE (MIN)	25-33.3	SPEED (BLUE)	cm/s
GREEN (MIN)	33.3-41.7	SPEED (GREEN)	cm/s