

Pattern Formation and Wave Propagation in the Belousov-Zhabotinskii Reaction

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INTRODUCTION

The Belousov-Zhabotinskii (BZ) reaction is the earliest well-understood example of a chemical system that results in oscillations and pattern formation. It was discovered in 1951 by the Soviet biophysicist Boris Belousov. At the time, chemists were skeptical of the possibility of chemical oscillators because of a misconception about the second law of thermodynamics. As a result, Belousov was unable to get his work published. A decade later, another Soviet scientist named Anatol Zhabotinskii reproduced Belousov's experiment and successfully persuaded more chemists to accept the idea of chemical oscillators. In 1972, three researchers at the University of Oregon, Field, Körös, and Noyes, published a complete mechanism describing the BZ reaction, known as the FKN mechanism. However, their equations were too complex for numerical analysis by the computers of the time. Consequently, Field and Noyes distilled their model to a set of ordinary differential equations with only three variables, dubbed "the Oregonator."

Belousov's original experiment studied only temporal oscillations in a well-stirred solution; however, much more interesting is the formation of spatial patterns in an unstirred solution. In these cases, if the reaction begins at a given point, the concentrations of intermediates will propagate outward via diffusion, initiating the reaction in the adjacent regions. This is known as a trigger wave. Periodically the reaction will reinitiate at the nucleation point resulting in successive bands (in a one-dimensional test tube reaction) or concentric rings (in a two-dimensional Petri dish reaction).

Systems of chemical oscillators are of great interest in biological systems. For example, the sinoatrial node, the heart's pacemaker, causes trigger waves which, though electrical in nature, propagate in much the same way as BZ trigger waves. The generation of cyclic adenosine monophosphate in aggregating *Dictyostelium discoideum* slime mold colonies creates spiral patterns nearly identical to those of the BZ reaction. RNA has been found to self-replicate, with fronts of increased RNA concentration moving outward via diffusion. (All examples Epstein and Pojman.)

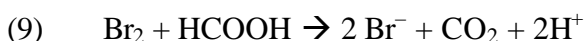
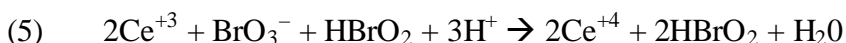
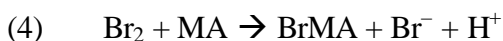
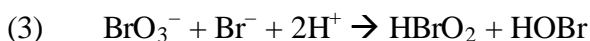
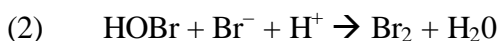
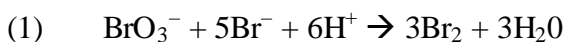
THEORY

As stated before, early skeptics of the BZ reaction held that chemical oscillators would violate the 2nd law of thermodynamics. They believed the second law meant that all chemical concentrations in a reaction must move directly towards equilibrium. Many compared the BZ reaction to a damped pendulum, which passes through its equilibrium position during each oscillation and eventually comes to rest. A chemical system that did this would indeed violate the second law of thermodynamics. Passing through the equilibrium point and then moving away from it would require an increase in Gibbs free energy, which must always decrease. However, the BZ reaction (like all other chemical oscillators) does not reach its equilibrium point until after the oscillations are finished—oscillatory behavior is a process involving only intermediates. The BZ reaction is actually a system of several chemical reactions with dozens of elementary steps, but the overall process is the oxidation of malonic acid by bromate producing carbon dioxide. As the system slowly progresses towards equilibrium, the concentrations of several

intermediate species oscillate while the concentrations of products move monotonically towards equilibrium.

The following is a quick summary of the development of oscillatory behavior: Normally bromide reduces the bromate. This reaction is fast, quickly using up the available bromide. Once bromide drops below a critical level, bromous acid takes over the reduction of bromate in a reaction that autocatalytically produces more bromous acid. This leads to exponential growth in $[\text{HBrO}_2]$. This is eventually checked by a reaction that converts HBrO_2 to HOBr and bromate. Meanwhile, the decomposition of malonic acid results in the reduction of bromine to bromide, nearly restoring the initial concentration and allowing the whole process to begin again.

Much of our understanding of the BZ reaction stems from the FKN mechanism. Below is an overview of the FKN mechanism. (For a more thorough treatment, see Tyson.) The key steps are:



Important Points:

- When $[\text{Br}^-]$ is high, (1) dominates the reduction of bromate
- When $[\text{Br}^-]$ is low, (5) dominates the reduction of bromate
- (5) includes the autocatalytic production of HBrO_2 ; when (5) is dominant, HBrO_2 increases exponentially until limited by (6)
- (7), (8), and (9) are the final processes, oxidizing malonic and bromomalonic acid
- The rates of (7), (8), and (9) are much slower than those of the other reactions
- Double- and triple-brominated malonic acid also occur, but in much smaller concentrations than BrMA , so the FKN mechanism neglects these. They would be oxidized in a manner similar to BrMA .

Oscillations occur in the following manner: Process (1) lowers the bromide concentration and increases bromine, allowing for the bromination of malonic acid by

(3). When $[\text{Br}^-]$ has been significantly lowered, (5) causes an exponential increase in bromous acid and the oxidized form of the metal ion catalyst and indicator, cerium. Bromous acid is subsequently converted to bromate and HOBr. Meanwhile, the rate-limiting steps (7), (8), and (9) reduce the cerium to Ce^{+3} and simultaneously increase bromide concentration. Once the bromide concentration is high enough, it reacts with bromate and HOBr in (1) and (2) to form bromine, and the process begins again. The different absorption spectra of the two ionization states of cerium causes the solution to change from yellow to clear and back as their relative concentrations change, allowing the oscillations to be observed visually.

Two-dimensional spatial patterns can either form spontaneously or by stimulation depending on the set-up of the experiment. When the reaction nucleates at a point, diffusion brings bromide from the surrounding region into the nucleation point. This facilitates the resetting mechanism at the nucleation point while simultaneously allowing process (5) to dominate in the surrounding region, oxidizing the metal ion catalyst and perpetuating the front of lowered bromide concentration. In this manner, a circular wave will progress outward from the nucleation point. If the conditions are such that oscillations will continue, a second circular wave will begin at the nucleation point, and the end result will be many concentric rings in a “target pattern.” If the nucleation point does not continue to oscillate, a single wavefront will expand until it is annihilated at the edge of the container. Field and Noyes discovered experimentally that the wavefront velocity is given by:

$$v = 0.04 \text{ cm}^2\text{sec}^{-1}\text{M}^{-1}([\text{H}^+][\text{BrO}_3^-])^{1/2}$$

(Tyson, p85). Furthermore, there is a curvature dependence on the velocity. For very small target patterns, the curvature is relatively high and this slows the reaction's progress because diffusion from a point is less than diffusion from a line. This dependence is given by the eikonal equation:

$$v^* = v + DK$$

(Epstein, p123), where D is the diffusion constant (on the order of $10^{-5} \text{ cm}^2\text{sec}^{-1}$), $K = \pm r^{-1}$ is the curvature (positive for a contracting circle and negative for an expanding circle), and v is the propagation velocity for the reaction at zero curvature.

Using the above equations and typical numbers for hydrogen and bromate concentrations and D , we can estimate v and v^* . Using the following values:

$$\begin{aligned} [\text{BrO}_3^-] &= 0.3 \text{ M} \\ [\text{H}^+] &= 0.25 \text{ M} \\ D &= 10^{-5} \text{ cm}^2 / \text{sec} \end{aligned}$$

results in:

$$\begin{aligned} v &= 6.5727 \text{ mm / min} \\ v^* &= 5.9727 \text{ mm / min (200 } \mu\text{m expanding circle)} \\ v^* &= 6.5697 \text{ mm / min (4 cm expanding circle)} \\ v^* &= 6.5757 \text{ mm / min (4 cm contracting circle)} \\ v^* &= 7.1727 \text{ mm / min (200 } \mu\text{m contracting circle)} \end{aligned}$$

EXPERIMENT & METHODS

Reagents

Rather than use cerium as a catalyst and indicator, as Field, Körös, and Noyes did, we used ferroin, which has a more conspicuous color change between its two ionization states, from dark red to bright blue. The reactants were stock solutions of sodium bromate, potassium bromide, and malonic acid dissolved in sulfuric acid. The ferroin used was a 0.025 M stock solution in water. The initial concentrations in the experiment were:

$[\text{BrO}_3^-]$	=	0.3 M
$[\text{Br}^-]$	=	0.05 M
$[\text{MA}]$	=	0.3 M
$[\text{Ferroin}]$	=	0.004 M
$[\text{H}^+]$	=	0.25 M

The specific recipe used was 2 mL of 0.9375 M NaBrO_3 , 1.25 mL of 0.25 M KBr , 2 mL of 0.9375 M malonic acid, and 1 mL of 0.025 M ferroin. All stock solutions except for ferroin were made in 0.3 M sulfuric acid, in order to achieve the final acid concentration of 0.25 M.

A 0.1% solution of Triton X-100 was also used in our experiment.

Apparatus

To capture video images of our reaction, our set-up involved a camera overlooking a light-box. The light-box contained a blue sheet of plastic that served as a filter which closely matched the transmission wavelength (blue) of ferroin, the reduced form of ferroin. The use of the light filter provided the greatest possible contrast between the two states in the video output. In order to initiate target patterns we used a 9-volt battery with silver leads which we taped to the light-box.

A CCD video camera mounted above the dish outputted a black-and-white video signal to a CRT and to a computer IMAQ card. A framegrabber written in LabVIEW captured images from the camera with a user-controlled framerate (usually 1 fps). A timestamp was also saved for each frame.

Experiment

The amount of solution used in our experiments was 6.25 mL in a 10 cm diameter polystyrene Petri dish, resulting in a depth of 0.8 mm. This was shallow enough that the system was essentially two-dimensional. In other words, the reaction progressed at the same rate on the top surface and bottom surface; there was no variation in the z -direction. A similar experimental setup has been described for carrying out lecture demonstrations of chemical pattern formation (Shakashiri).

The reactants were combined in a beaker, first by adding bromide to bromate (producing bromine, turning the solution yellow), then adding malonic acid, which slowly eliminated the bromine. When the solution was clear again, a drop of 0.1% Triton

X-100 detergent was added to facilitate spreading of the solution in the dish by reducing surface tension. Finally, ferroin was added. The beaker was then swirled several times. With the initial concentrations listed above, the solution will typically oscillate once while being swirled, turning blue, then back to red. After this, the solution was poured into the Petri dish and swirled carefully so that it spread evenly throughout the dish.

The positive lead (silver wire) of a 9V battery was touched to the center of the dish for 1-2 seconds and the negative lead to the outer edge. Although several past experimenters used this method, none of the literature explains why this works. However, it seems likely that the silver is ionized and thus reduces bromate in the vicinity, starting off the reaction. Simply using a piece of silver wire to seed the reaction (with no battery) is almost as effective, reducing the bromate in the same manner, but without the added push of a voltage source. After the wires are removed, a small blue dot will appear in the center and propagate outward. With the initial concentrations listed above, oscillations will continue at the nucleation point, creating target patterns.

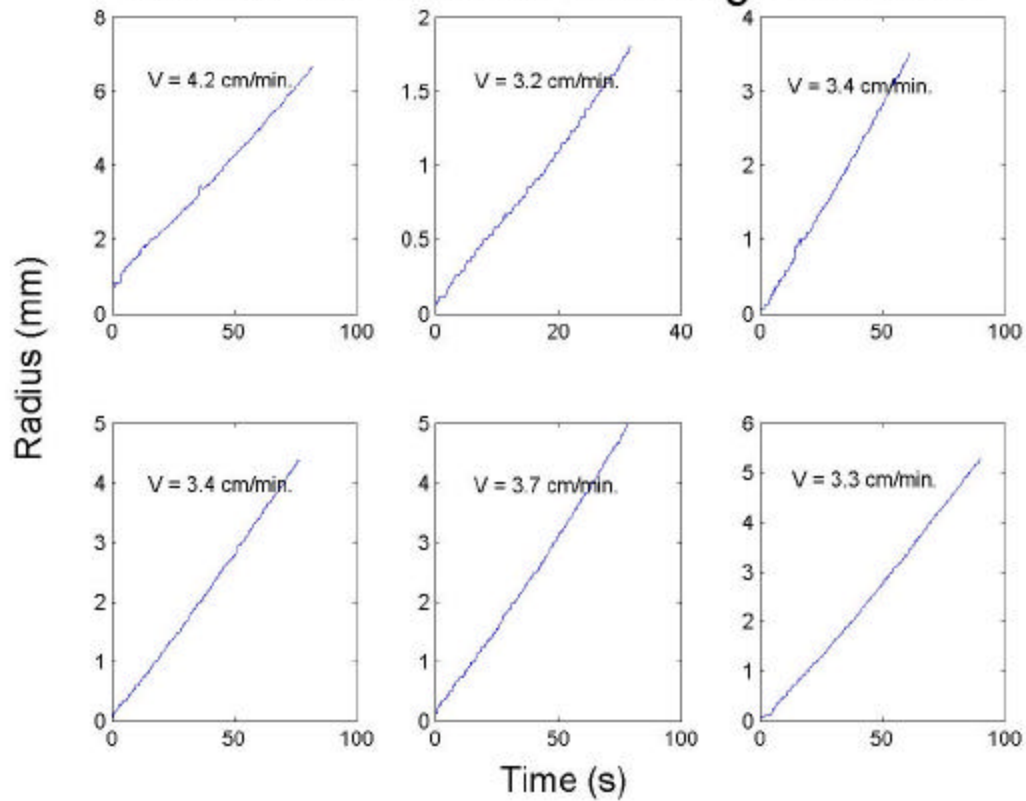
One problem with the above recipe is that, because the solution is so close to the oscillatory regime, the reaction can spontaneously nucleate, especially in regions of inhomogeneity, for example along the edge of the dish. For this reason, circular trigger waves often develop along the edge and progress inward, annihilating the planned target patterns when the two wavefronts meet.

One way to reduce the excitability of the solution is to reduce the malonic acid concentration. Diluting the malonic acid threefold (in 0.3 M sulfuric acid) resulted in a solution in which the outer edge was unlikely to spontaneously nucleate trigger waves. In this solution, target patterns were unlikely to develop as well, as the reaction will not continue without stimulus by the battery or wire. In this case, one sees only single trigger waves resulting from each stimulus. However, this mixture is ideal for studying spirals, which are self-propagating, and can continue even if the solution is in the excitable (but not oscillatory) regime. Spiral patterns can be made by breaking a wavefront, either physically (with a pipette tip or a blast of air from a micropipette) or chemically (with a *small* drop (10 μ L or less) of dilute (0.1 M or less) KCl (chloride ion limits the reaction)). When a wave front is broken, the two ends will begin to spiral in on themselves.

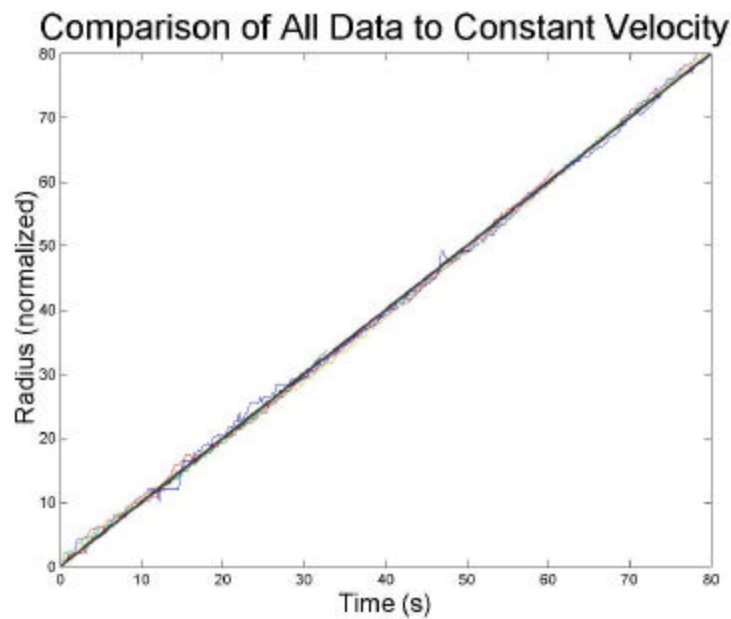
RESULTS AND ANALYSIS

Our main experimental goal was to determine whether the rate of expansion of a circle pattern was dependent on curvature. That is, is velocity a function of radius? In order to calculate velocity, we stimulated individual circle patterns and recorded them for analysis with a computer. For each of six circle patterns, we captured approximately 300 frames taken every 500 ms where each image was 640 by 480 pixels or about 2.4 by 1.6 cm. Each video was filtered for noise and had an average background image subtracted from it. The videos were then analyzed with an algorithm that found a best-fit circle for each image as determined by a maximum correlation between the circle and the image. The magnitude of the radius over time was then plotted to compare it to a straight line (the constant velocity hypothesis). Here are these plots.

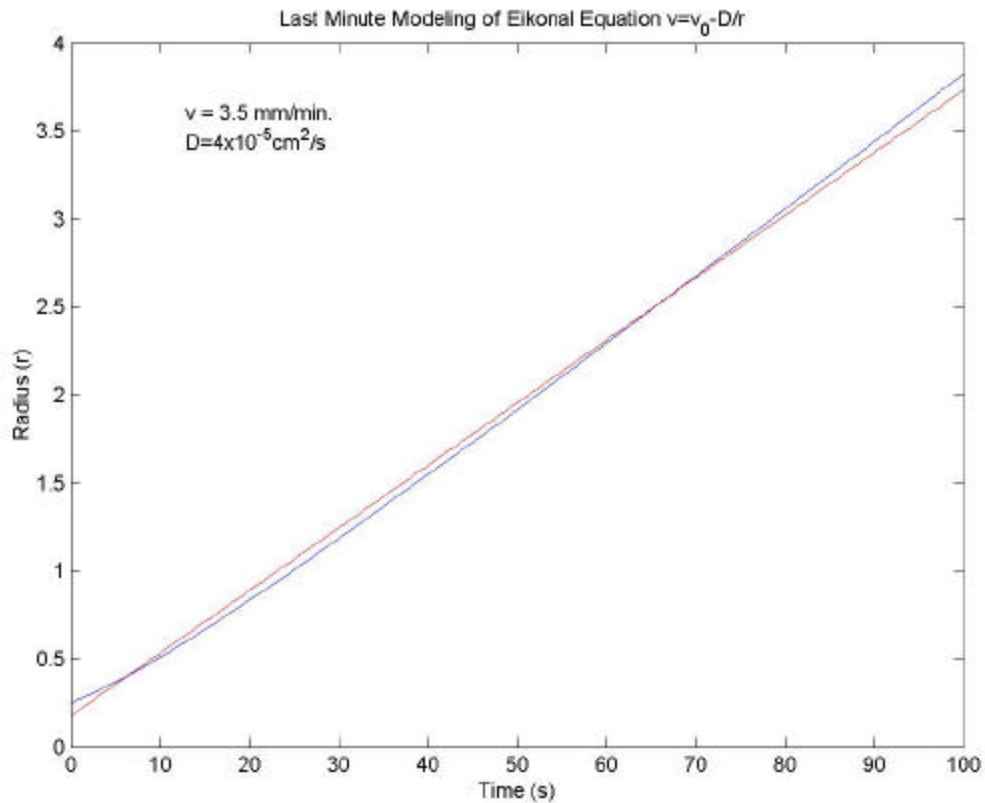
Radius Vs. Time for Six Target Patterns



By normalizing and shifting each set of data so that its best fit line was $x=y$, we can compare all plots to a constant velocity on the same graph.



There appears a definite trend of velocity increasing with radius and/or time. This agrees with the eikonal equation described earlier. We did not attempt to fit the eikonal equation to our data, but here is an example of the eikonal equation predicted velocity for parameters consistent with our experiments.



We attempted two other experiments during the quarter. One was to model a BZ reaction wavefront using the Oregonator model. The equations we used were:

$$\left(\frac{\partial X}{\partial t}\right) = D_x \left(\frac{\partial^2 X}{\partial r^2}\right) + k_3 A B Y - k_2 A X Y + k_5 A B X - 2k_4 X^2$$

$$\left(\frac{\partial Y}{\partial t}\right) = D_y \left(\frac{\partial^2 Y}{\partial r^2}\right) - k_3 A B Y - k_2 A X Y$$

where

A = [H⁺]

B = [BrO₃⁻]

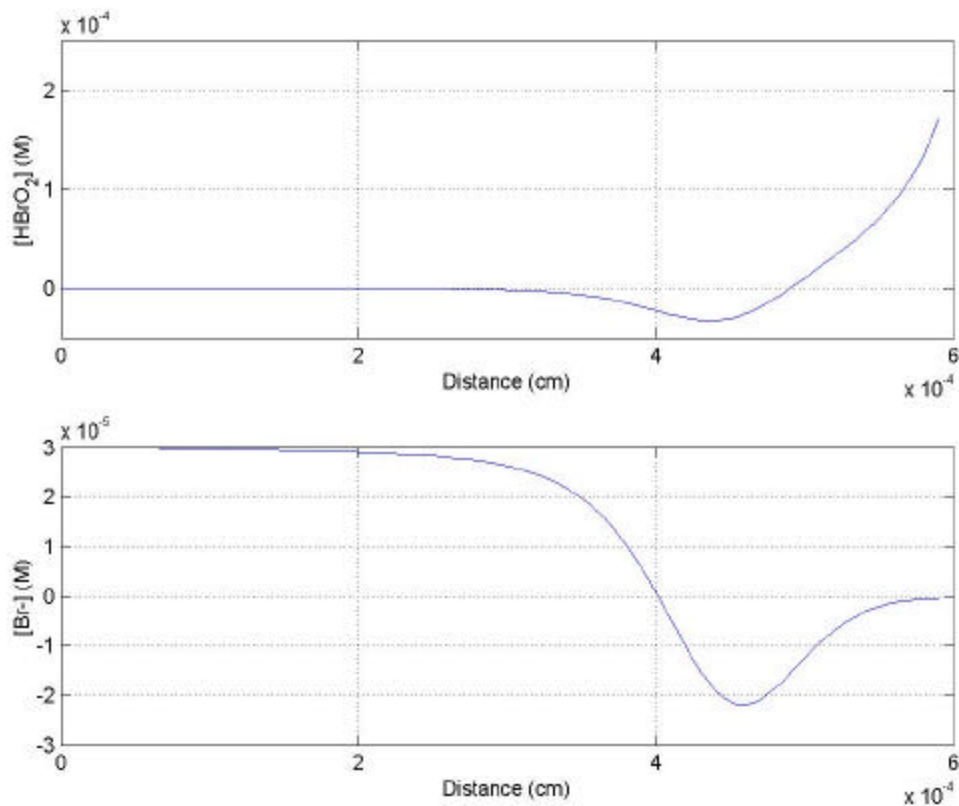
X = [HBrO₂]

Y = [Br⁻]

D is a diffusion constant

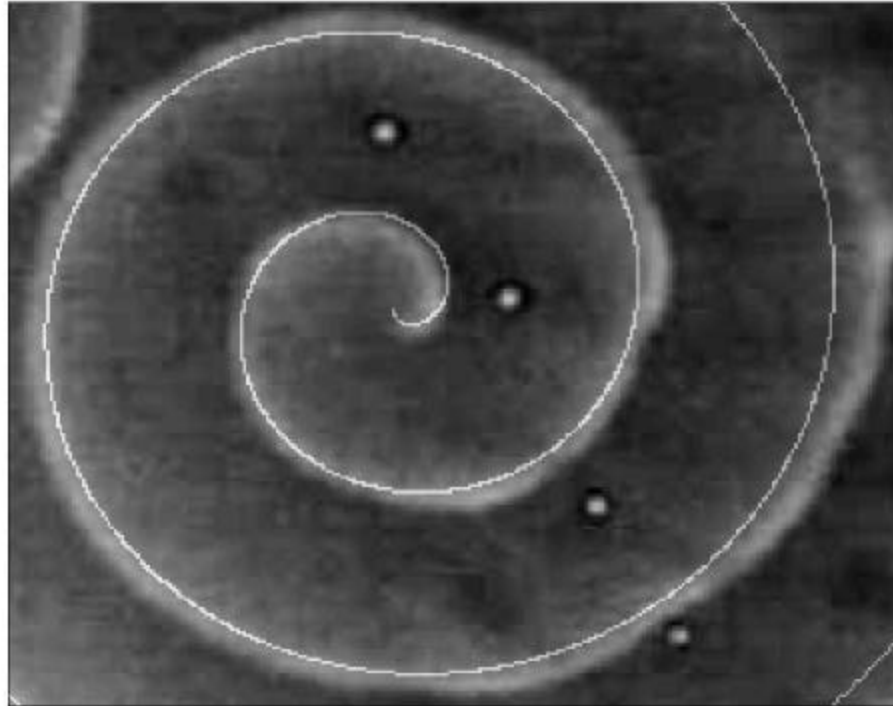
k is a reaction rate

A and B were assumed to be constants. In order to solve these as ordinary differential equations we assumed constant velocity and were thus able to remove the partial derivative with respect to time. We used initial conditions given by (Field and Noyes) and numerically solved these equations in MATLAB. We found the following plots of X and Y .



Although the direction of change and timescale are approximately correct for these reactants, the wavefront is not physically realistic since it involves negative concentrations.

Finally, we attempted to fit a spiral to an image of one of our spiral patterns. The particular spiral equation we used was an Archimedes spiral which assumes that the increase in radius of curvature per turn is constant. Since the increase in the radius of curvature for circle patterns is approximately constant, we hypothesized this would be true for spirals as well. We fit one spiral pattern satisfactorily with the Archimedes spiral $r = (.97\text{mm})\theta$.



As far as future experiments, we would have liked to continue the modeling effort to obtain reasonable simulated behavior with an ODE or PDE model. This should be a realizable goal since there are multiple MATLAB implementations of BZ models available through a Google search. One property of the BZ reaction we never verified experimentally is that although the wavelength of individual target patterns may vary in a single solution, the velocity of all patterns should be a constant of the solution. This could be verified by stimulating multiple target patterns in a dish simultaneously. Similarly, spiral patterns have constant periods and velocities. Finally, it should be possible to observe 3-dimensional patterns such as scroll waves in thicker solutions. It was left unexplored what changes to the experimental set-up are necessary to form these patterns.

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