

BZ Reaction in Electric Field
Ben Huh
Corinne Teeter
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The behavior of wavefronts in the BZ reaction were investigated under the influence of electric field. It has been previously shown that depending on the polarity of the electric field, wave fronts within the field are accelerated or slowed. The results of this experiment did not exhibit this effect. This could be due to experimental difficulties such as differences between experiments or difficulty in analysis due to a lack of steady state wave propagation being reached before too many bubbles took over.

Introduction

The following introduction and basic methodology has been taken from Hill and Morgan's 2003 lab writeup. I include it here (with permission of the author) instead of simply referencing it so that future students who may reference this paper will have all the necessary information in one place.

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, Koros, 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."

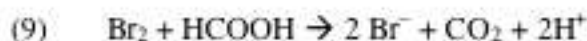
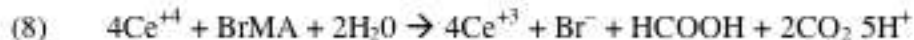
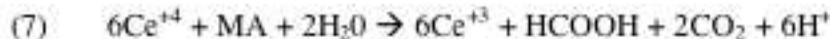
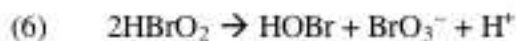
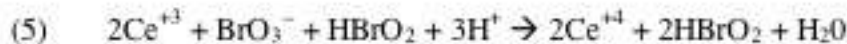
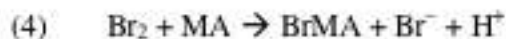
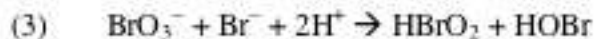
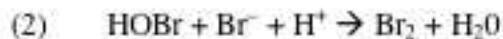
Belousov's original experiment studied only temporal oscillations in a well-stirred solution; however, much more interesting is the formation of spatial patterns in an unstirred solution. In these cases, if the reaction begins at a given point, the concentrations of intermediates will propagate outward 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 [HBrO₂]. This is eventually checked by a reaction that converts HBrO₂ 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.).



Important Points:

- When [Br⁻] is high, (1) dominates the reduction of bromate
- When [Br⁻] is low, (5) dominates the reduction of bromate
- (5) includes the autocatalytic production of HBrO₂; when (5) is dominant, HBrO₂

- 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 ratelimiting 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:

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

(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:

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

EXPERIMENT & METHODS

Reagents

Rather than use cerium as a catalyst and indicator, as Field, Koros, 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:

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

The specific recipe used was 2 mL of 0.9375 M NaBrO₃, 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.

In this experiment, the effects of electric field on the BZ reaction was investigated. Previous papers have claimed that the electric fields on the order of 10-50 V/cm can influence wave propagation. (Sagues & Epstein 2003, Sevcikova Et. Al. 1992). Observed phenomena include acceleration of wave propagation, wave splitting, and directional propagation reversal. Figure 1 (taken from Sevcikova Et. Al. 1992) shows that when the electric field is reversed the wave propagation changes directions. In order to observe some of these phenomena in a one dimensional system the following experiment was constructed.

Experimental Procedures:

The BZ solution was inserted into capillary tubes. Two wires were placed at a distance of approximately 4 cm apart perpendicular

to the capillary tubes with a voltage difference of 400 V across them. This corresponds to an electric field of approximately 15-40 V/cm (since the electric field falls off as $1/r$ for a wire).

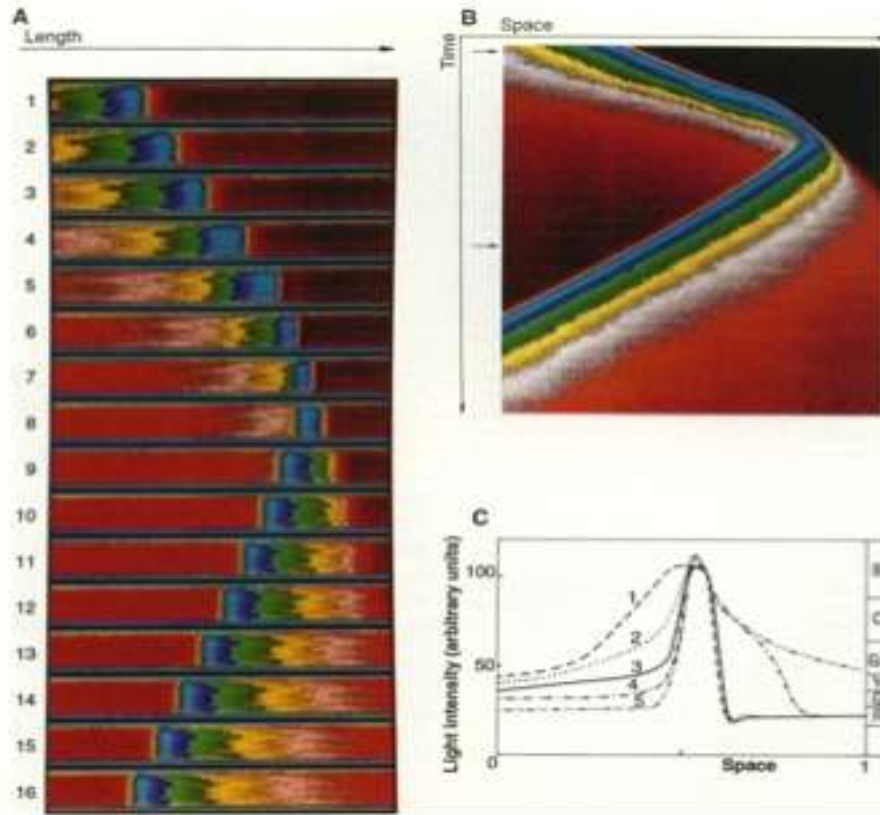


Fig. 2. Reversal of the direction of the wave propagation in the gelled system observed from the side ($E = 10$ V/cm). (A) Time series of video images of the cuvette taken at 16-s intervals. In plates 1 to 3, the wave moves from the left to the right toward the anode. Between plates 3 and 4, the polarity of the field is reversed. This is immediately reflected in the enlargement of the blue zone representing the oxidized state of the medium (C). This zone then shrinks again (plates 5 to 7), and the concentration gradient of the wave back becomes steeper (the dark blue, green, yellow, and gold zones in plates 5 to 8 become narrower). In plate 7, wave back and wave front have approximately the same steepness. In plate 8, the former wave front is converted into the wave back, and the former wave back, now the wave front, starts moving backwards toward the anode. The next eight plates show the development of the wave back. Pictured length of the capillary = 6.64 mm. (B) Space-time plot established along the central axis of the cuvette in (A), with the same false colors. Pictured time interval = 450 s; pictured length of the capillary = 7.54 mm. Arrows mark the time interval shown in (A) in detail. (C) Evolution of the spatial wave profile during wave reversal. Time instants after plate 5 of (A) are: 1 = 0 s; 2 = 16 s; 3 = 40 s; 4 = 64 s; and 5 = 128 s. Space unit = 3.6 mm. The scale on the right indicates the false colors used in (A) and (B) (B, blue; C, dark blue; Gr, green; Y, yellow; G, gold; and R, red).

Figure 1. Taken From Sevcikova, Et Al. 1992

Results

No effect of electric field was seen. The characteristic behavior of the system usually involved the solution oscillating together initially and then then propagating waves would emerge. Figure 2 shows the data from one capillary tube in electric field. At first the solution oscillates together (first 3 to 4 vertical lines on left) and then

waves start to propagate. In this case two waves start to propagate from opposite directions. An electric field effect on the speed of wave propagation should be seen here by speeding up propagation in one direction and slowing it in the other. In addition since the electric field is not constant across the preparation the speed of the waves should change along the y axis. Instead the slope is equal and constant in opposite directions. Figure 3 shows a capillary tube with no electric field. The speed of the wave fronts in this preparation is 0.08 mm/s as opposed to 0.1 mm/s in figure 1. Although there is a slight difference it could be due to a difference between preparations.

Overall the data was hard to analyze. Figure 4 shows data from another trial with out electric field. The yellow streaks running across the image along the time dimension correspond to the bubbles that develop while the reactants are being used up. Bubbles basically create a barrier between different parts of the capillary tube making it difficult for waves to propagate. Other interesting phenomena were also seen in preparations without electric field such as that seen in Figure 5 and 6. These examples show that it was hard to get good, consistent data across preparations.

Conclusions

Although no results were found, the BZ reaction is super cool. It can be viewed as a model for all sorts of biological phenomena such as retinal waves, forest fires, amoeba slime molds, and has even been proposed as a model for computation. It is endlessly fun to watch due to the variety of different patterns and phenomena that develop. The lack of results in this experiment could be accounted for by the fact that this is a very dynamic system that exhibits very different behavior from preparation to preparation. However it is very strange that there was no effect at all. The electric field across our preparation was in the range in which changes in the speed of wave front propagation has been observed before. It is possible that we didn't see any affect because the solution didn't reach a steady wave propagation state before bubbles started to interfere with the data. However, this experiment was also done in a two dimensional petri dish where bubbles didn't create huge barriers and the electric field was even stronger and still no effect was seen.

For future experiments it would be beneficial to find out how other experimentalists dealt with bubbles. In addition, applying an electric field with plates instead of wires would be better to assure a constant electric field across the solution.

In all of the following figures color corresponds to intensity. The y axis is an arbitrary distance and the x axis is an arbitrary time.

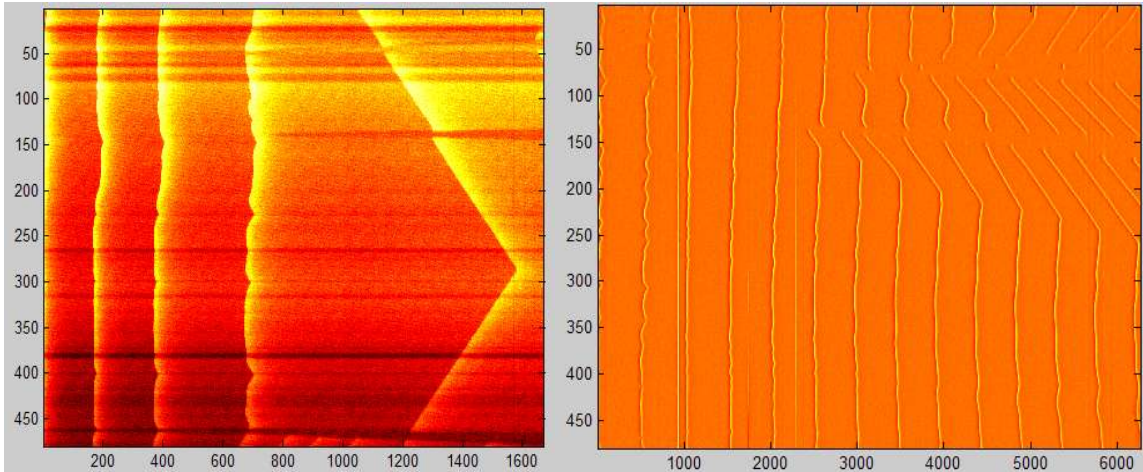


Figure 2 Left capillary tube in $\sim 15-40$ V/cm
Figure 3 Right. Capillary tube in no electric field.

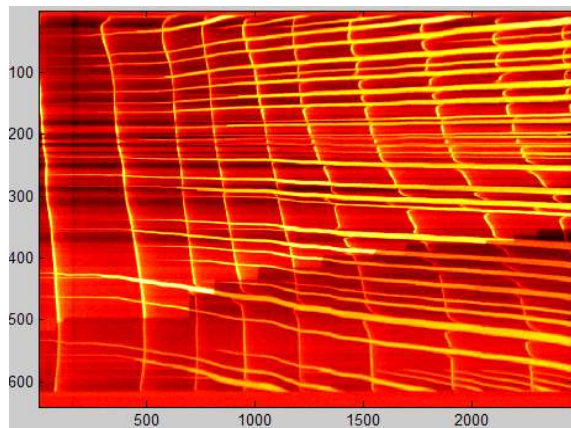


Figure 4. Capillary tube with no electric field. Horizontal yellow lines correspond to bubbles developing in the solution

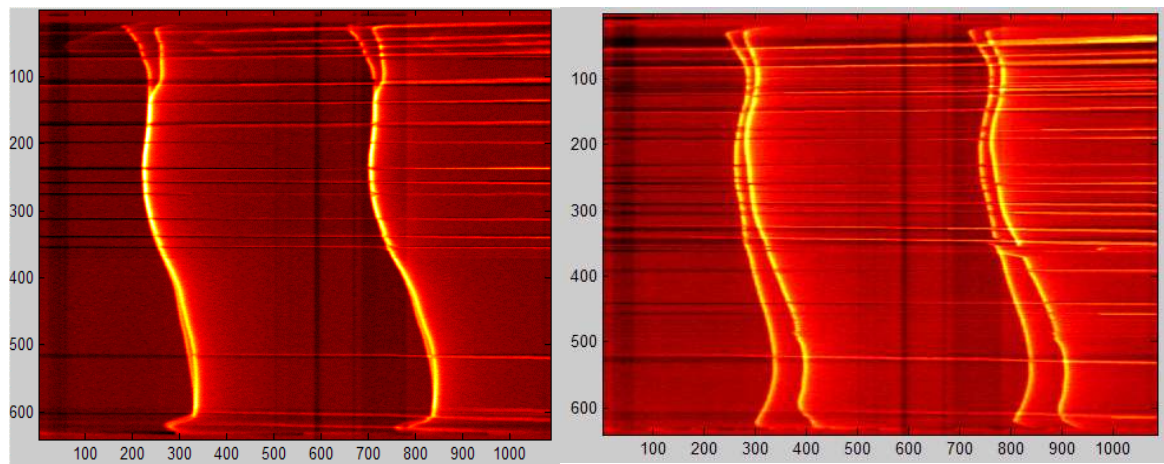


Figure 5 & 6 other interesting phenomena that develop

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