Chemical Waves in the Belousov-Zhabotinsky Reaction: Determining a Rate Constant with a Ruler

John A. Pojman
Department of Chemistry and Biochemistry,
The University of Southern Mississippi,
Hattiesburg, MS 39406-5035
www.pojman.com

Goal: Determine the rate constant for the autocatalytic step in the BZ reaction using the velocity dependence of the chemical waves in the unstirred BZ system.

Prelaboratory Exercise

(1) Name the type and units of the data you expect to gather.

(2) What is an excitable media and how does this relate to waves and spirals in an unstirred reaction mix?

(3) Does the velocity of a wave depend upon the concentration of the catalyst? Does the velocity of the wave depend upon the viscosity of the media? Does the velocity of the wave depend upon the thickness of the media?

Background

If an autocatalytic reaction is left unstirred, extremely interesting behavior can be observed. Diffusion, instead of causing concentration gradients to disappear, can couple the autocatalytic reactions to produce reactions that propagate through the medium.

Exothermic reactions can be autocatalytic if sufficient heat is produced to accelerate the rate of reaction. In well-stirred reactors, such systems exhibit bistability and sometimes oscillatory behavior. When allowed to proceed in unstirred reactors, chemical reaction fronts may develop.

The simplest example to consider is that of burning paper: The system consists of a high free energy material (paper) and oxygen. The system is not at equilibrium, which would be a combination of carbon dioxide, water and heat. However, the configuration is metastable in that a "push" is necessary to get the reaction started, after which it will proceed toward equilibrium. This can be accomplished with a match, which provides sufficient energy to begin the reaction. The burning is itself exothermic so that it produces heat that diffuses by heat conduction to adjacent, unreacted paper, stimulating that material to react. This process proceeds in a chain reaction and a reaction front is observed moving along the material. The rate at which this front propagates is a function of the rate of chemical reaction (burning) and the ease by which the heat is conducted through the paper. In this way heat is coupled to conduction to cause a front.

Directly analogous behavior can be observed in autocatalytic solution reactions. If a reaction mixture is in a metastable state and can react toward equilibrium by producing products that catalyze the reaction (autocatalysis), then a chemical wave front may occur. Simple systems have been found in which a reaction produces hydrogen ions (H^+) and the reaction is acid catalyzed. Here, the H^+ plays the same role as the heat in our burning paper example. The reaction spreads because the H^+ diffuses, stimulating neighboring regions to react. Diffusion replaces heat conduction. Like the paper and oxygen system, the solution requires initiation with the autocatalytic species. Such reactions are described in one dimension by the so-called reaction diffusion equation, which applies to any unstirred reaction.

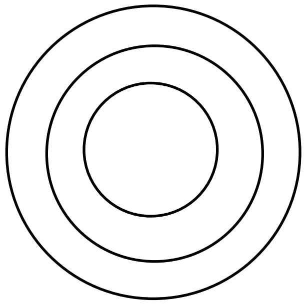
$$\frac{\partial C_i(x,t)}{\partial t} = D_i \frac{\partial^2 C(x,t)}{\partial x^2} + R\,\{\,C_i\,\}$$

The equation says that the rate of change of the concentration of the i^{th} chemical species at position x is affected by two factors. The first term describes the change from diffusion in which D_i (cm^2/s) is the diffusion coefficient, which is multiplied times the rate of change of the gradient of the concentration at the position. (This second derivative with respect to position is called the one-dimensional Laplacian and is a measure of how sharply the concentration changes with position.) The second term indicates that there are chemical reactions, which also are occurring and affect the concentration of each species. These reactions may be very complex.

Excitability

An excitable system is one that is quiescent until sufficiently perturbed. Then it proceeds through a range of states until returning to its initial quiescent state. A nerve cell is excitable as are heart cells.

In an excitable system, the behavior is more interesting than the simple case of a traveling front because after the reaction passes through a point, the reactants are regenerated (almost, because some other material slowly reacts to replenish the needed species). Consider a grass fire. After the fire passes, the grass can regrow and then another fire can spread. But how frequently fires pass through a specific region depends on how fast the grass grows. So if you looked from a satellite over a long period, you could observe fire “waves” spreading through the prairie. The slower the grass grows, the wider the distance between the rings of fire.



Waves in the BZ system propagate as rings of oxidation, called “trigger waves” which form “target patterns”. Initially a solution is homogeneous. Then, a small excess of $HBrO_2$ is formed. It is not clear if this occurs because of a spontaneous concentration fluctuation or via a heterogeneous reaction (perhaps on a dust particle). The excess $HBrO_2$ catalyzes more of its own production. As the increasing concentration of $HBrO_2$ diffuses into neighboring regions, $HBrO_2$ production is stimulated there as well. A front of reaction propagates out from the initial perturbation. If the target pattern is disturbed, it is possible to observe spiral waves that look like pinwheels.

In the BZ system, the autocatalytic species is $HBrO_2$, and its rate law is given by the equation below:

$$\frac{d[HBrO_2]}{dt} = k\,[H^+][BrO_3^-][HBrO_2]$$

We would like to determine this rate constant. However, measuring it directly is difficult because we can not run an experiment in a beaker in which we mix bromate and $HBrO_2$ in acid solution. $HBrO_2$ not a stable species. However, in the BZ system, the formation of $HBrO_2$ is accompanied by the oxidation of the metal ion. Therefore, as a traveling wave of oxidation propagates, we will be able to observe the color change in the ferroin.

Velocity = $2(k[H^+][BrO_3^-]D)^{1/2}$ where D is the diffusion coefficient of $HBrO_2$ (2×10^{-5} cm^2/s).

In this experiment, you will test this model by determining the sensitivity of the front velocity to the concentration of the metal catalyst, $[BrO_3^-]_0$, and $[H^+]_0$. Using this data, you will calculate the value of k.

Procedure

1) The following solutions do not have to be prepared by you:

Label	**Solution**

C) 25 mM Ferroin

2) The following solutions must be prepared by you:

Label	**Solution**
A)	100 mL 0.8 M $NaBrO_3$ / 0.8 M H_2SO_4
B)	40 mL 0.48 M Malonic Acid
D)	0.97 M NaBr (1g/10 mL)

Procedure

Into a small Erlenmeyer flask, introduce 7 mL of (A), 3.5 mL (B) and 1 mL of (D). **Stopper and allow to stir on magnetic stirrer. (It is essential that you stopper the flask to prevent the loss of the volatile bromine.)**

The brown color is bromine which forms from the oxidation of bromide by bromate. {The bromine color may not appear. If this happens, don't worry, just allow the solution to stir for about five minutes.} The bromine slowly disappears as it reacts with the malonic acid to form bromomalonic acid. When the solution has cleared, add 0.5 mL of the ferroin solution and stir.

The reaction may oscillate between red and blue. Ignore it. Use a pipette to transfer sufficient solution to a clean petri dish and mix in Cabosil (fine silica gel). You want the gel to form a thin, viscous layer. Cover the dish and wait.

You will notice small rings of blue forming in the red solution. At this point, focus the camera on the reaction and adjust the lighting. Once this is done, proceed with video taping. Place a ruler in the video picture for reference.

Once the video taping is completed, you will use Image software and the video tape to measure the distance a wave travels in a specific amount of time. Measure the change in the radial distance from the center of a target pattern as a function of time. The slope of the line drawn through this data will provide the wave speed. Also measure the wavelength (the distance between fronts).

Repeat this experiment using the following:

(2) 6 mL of A, 3.5 mL of B 1 mL of D, 1 mL of distilled water
(3) 5 mL of A, 3.5 mL of B 1 mL of D, 2 mL of distilled water
(4) 4 mL of A, 3.5 mL of B 1 mL of D, 3 mL of distilled water
(5) 3 mL of A, 3.5 mL of B 1 mL of D, 4 mL of distilled water

Videotape each experiment. It might be a good idea to place a label of what experiment you are doing in the video picture.

Be certain that you have observed your reactions long enough to complete the data analysis. If you do not, then you will need to repeat reactions to obtain the necessary data. It is up to the student to determine how long taping should continue.

Notes:

If too many form to see the waves clearly, swirl the dish around. New waves will form.
To make a spiral, slowly move a pipette through the center of a target pattern.
Waves should appear within fifteen minutes of the start of the reaction.

Cautions

Cabosil is a lung irritant and should not be breathed. Mix Cabosil only in the hoods.

Data Analysis

As you will have a video tape of the reaction, you may need to refer back to the tape several times to gather enough information of complete the following analysis. Be sure, then, that you do not destroy you tape until you have completed this lab and are satisfied with your grade.

TO determine the wave velocity, plot the position of the front as a function of time. The slope of the best fit line is the velocity.

In the homogenous BZ, you should have seen a change in the oscillation frequency with time. Does the wave velocity change as the reaction ages, and what does this observation tell you about the reaction? A plot of the wave velocity versus time may be of use. Is this similar to the oscillations in the stirred BZ?

Plot the wave velocity as a function of the product of $[H^+]$ and $[BrO_3^-]$. You should use the velocity the same time after pouring in the reagents. Fit a line. Using the slope and the diffusion coefficient of $HBrO_2$ (2×10^{-5} cm^2/s), calculate the rate constant of the autocatalysis reaction. Compare your calculated value to the reported value of 20 M^{-2} s^{-1}.

Calculate the length of time it would take for a molecule to diffuse one centimeter given the diffusion coefficient, $D = 10^{-5}$ cm^2/s, and the distance traveled by a molecule diffusing is equal to $(Dt)^{1/2}$), where t = time, D = the diffusion coefficient, and the distance is in cm. Can diffusion explain the occurrence and velocity of the observed waves? What does this tell you about the reaction?

How do the waves behave in general? What happens when they encounter a barrier? What happens when they collide? Do they behave as water waves would? Explain these observations in terms of the reaction-diffusion model presented in the introduction to this experiment.

What are the bubbles that form in the reaction?

What is the Cabosil used for? Does this material affect the reaction? Does the thickness of the reaction media seem to have an effect? How could you test this?