Characterizing an Oscillating Reaction

Introduction

In the first week of lab you prepared three solutions, combined them with a fourth solution, and observed the resulting reaction. This reaction, which is known as the cerium-catalyzed Belousov-Zhabotinsky reaction, is one of a class of reactions that oscillate between different chemical states.

Chemical reactions usually proceed smoothly from reactants-to-products with the concentrations of all reactants decreasing and the concentrations of all products increasing. In an oscillating system of reactions, however, some (but not all) of the species in the reaction participate in two distinct sets of reactions: in one set of reactions the concentrations of these species decrease and in the other set of reactions their concentrations increase. Which system of reactions is most important at any point in time depends on the relative concentrations of these species.

The cerium-catalyzed Belousov-Zhabotinsky reaction is complex, consisting of as many as 80 individual steps that involve 26 different species! At its simplest level, the net reaction is the bromination of malonic acid; thus, the reaction's overall stoichiometry is

$$2\mathrm{H}^+(aq) + 2\mathrm{BrO}_3^-(aq) + 3\mathrm{CH}_2(\mathrm{COOH})_2(aq) \rightarrow 2\mathrm{BrCH}(\mathrm{COOH})_2(aq) + 4\mathrm{H}_2\mathrm{O}(l) + 3\mathrm{CO}_2(g)$$

Although the concentrations of malonic acid and bromate decrease steadily, the concentration of intermediate species—those species present only during the reaction—and the form of the cerium catalyst undergo oscillations, which continue until the reaction's limiting reagent is used up.

Skills Emphasized In This Lab

By completing this lab you will become more comfortable with:

- using a spectrometer
- preparing a set of calibration standards and verifying Beer's law
- writing a thorough introduction that provides a succinct background to your work and clearly outlines the goals of your work

Preparing for Lab

Before coming to lab, read the essays "Visible Absorbance Spectra and Beer's Law" and "The Mathematical Modeling of Experimental Data," and complete the appropriate sections of your electronic notebook.

Procedure

The goal of this week's lab is to characterize the oscillations in the cerium-catalyzed Belousov-Zhabotinsky reaction using a computer-interfaced spectrometer. Because the reaction mixture is colored, we can follow the reaction's progress by monitoring its absorbance as a function of time. Properties of the oscillating reaction of interest include the magnitude and period of the oscillations and how each changes as the reaction progresses, whether there is a difference in the oscillations at different wavelengths, and the reproducibility of the oscillations from trial-to-trial.

To save time, all solutions have been prepared for you. For this lab, a standard run consists of 25 mL each of solutions A, B, and C, and 1.5 mL of ferroin (Solution D). Use graduated cylinders to measure the appropriate volumes of solutions A, B, and C, and a disposable plastic pipet for solution D. Be sure to follow the correct order for mixing the reagents: first combine solutions A and B and, when the solution is clear, add simultaneously solutions C and D.

Before monitoring the reaction, you will first verify that Beer's law applies to ferroin, which is red due to the presence of Fe(o-phenanthroline)$_3^{2+}$. Begin by adding 1.5 mL of ferroin to 75 mL of deionized water; this working solution has a concentration of ferroin similar to that at the beginning of the reaction. Set up the spectrometer and record the spectrum of your working solution using deionized water as a reference. Adjust the signal acquisition parameters to obtain a reasonably smooth spectrum over the available range of wavelengths. When you are satisfied with your spectrum, select a wavelength where the solution's absorbance is strong, but not noisy, and record the absorbance. Next, prepare a series of standard solutions of ferroin by pipetting 5, 10, 15, and 20 mL of your working solution into separate 25-mL volumetric flasks, diluting each to volume using deionized water. Measure the absorbance of these four solutions at your previously selected wavelength. Verify Beer's law by constructing a plot of absorbance vs. [ferroin]; you should have a total of six points on this graph, one of which is your reference.

After verifying Beer's law for ferroin, initiate the oscillating reaction, transfer a portion of the reaction mixture to a cuvette and follow the reaction's changing colors using the spectrometer. For your first trial, simply observe the changes in the solution's spectrum as the reaction progresses and identify two to four wavelengths where there is an oscillation in absorbance. Try to select wavelengths that correspond to each of the oscillating reaction's most obvious colors.

After selecting your wavelengths, discard the reaction mixture and initiate a new oscillating reaction. This time use the software's kinetics mode to monitor the reaction at the wavelengths identified above. Set the sampling rate to one point per second and monitor the reaction for 15 minutes or until the oscillations stop, whichever is shorter. Repeat for at least one additional trial.

Cautions

There are no cautions for this lab other than the normal respect for chemicals.

Waste Disposal

Pour any remaining solutions together and flush them down the drain with plenty of water.

Lab Report

For this report, focus on the introduction only. Research has a purpose and its context forms the basis for the introduction. Choose one of the following contexts for your introduction:

- After attending a seminar by Boris Belousov in 1956, in which he describes his discovery of an oscillating reaction and its rejection by the scientific community, you decide to gather spectrophotometric evidence to support his discovery.
- It is 1967, and although the scientific community now accepts the B-Z reaction, the reaction's mechanism remains controversial. You believe the oscillating colors are due to Ce(IV), and the oxidized and reduced forms of ferroin, Fe(o-phenanthroline)$_3^{3+}$ and Fe(o-phenanthroline)$_3^{2+}$, and decide to study this spectrophotometrically.
- The scientific community has come to agreement on a mechanism for the B-Z reaction following the publication by Field, Körös, and Noyes in 1972 of a mathematical model that explains the oscillations. Changes in the reaction's oscillations with time, however, have not been studied; you decide to fill this gap.

Limit your introduction to two or three pages of double-spaced text, not counting space used for reactions or equations, and include a minimum of three references. For a history of the B-Z reaction, see Winfree, A. T., "The Prehistory of the Belousov-Zhabotishky Oscillator," *J. Chem. Educ.* **1984**, *61*, 661-663. Be sure to state clearly which prompt you are using—and be true to the prompt by not introducing content not known at the time—and to review the guidelines for preparing reports and the sample report, both available on the course's website.

After discussing your results as a group, choose one group member to prepare an initial draft and, after receiving edits from the other group members, prepare a final draft. The final draft is due by 4:00 pm on Tuesday, February 28th; this is a firm deadline. Comments on your final draft will be shared with you in lab on Thursday, March 2nd. Your final report, which is prepared as a group, is due on Thursday, March 9th.

When you submit your final report, append two neatly prepared figures, one that shows the calibration curves for $Fe(o\text{-phenanthroline})_3^{2+}$ and one that shows the reaction's oscillations.