Characterizing an Oscillating Reaction

Introduction

In the first experiment 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 reactants decreasing and the concentrations of products increasing. In an oscillating reaction, however, some of species participate in two distinct sets of reactions: in one set the concentrations of these species decrease and in the other set their concentrations increase. Which set of reactions is most important at any 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

$$2H^+(aq) + 2BrO_3^-(aq) + 3CH_2(COOH)_2(aq) \longrightarrow 2BrCH(COOH)_2(aq) + 4H_2O(l) + 3CO_2(g)$$

Although the concentrations of malonic acid and bromate decrease throughout the reaction, the concentration of some intermediate species—those present only during the reaction—and the oxidation state of the cerium catalyst undergo oscillations that continue until the reaction's limiting reagent is depleted.

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 an introduction that provides a background to your work and 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 changes color, we can follow its progress by monitoring its absorbance as a function of time. Properties 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 are prepared for you. For this lab, the standard run is 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 $Fe(o\text{-phenanthroline})_3^{2+}$. 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. If the absorbance exceeds 1.0, dilute your working solution and reacquire the spectrum.

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 and dilute each to volume using deionized water. Measure the absorbance of these additional solutions at your previously selected wavelength. Verify Beer's law by constructing a plot of absorbance vs. the concentration of ferroin; you should have a total of five points on this graph, one for each standard. Because you do not know the concentration of the original stock solution of ferroin, treat your *working solution* as having a concentration of 1—unit concentration—and calculate the concentrations of your other ferroin solutions relative to this.

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.

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. For your introduction, use the following prompt:

It is 1967, and although the scientific community now accepts the B-Z reaction, its mechanism remains controversial. You believe the oscillating colors are due to Ce(IV), and the oxidized and reduced forms of ferroin, $\text{Fe}(o\text{-phenanthroline})_3^{3+}$ and $\text{Fe}(o\text{-phenanthroline})_3^{2+}$, and decide to study this spectrophotometrically.

Limit your introduction to two pages of double-spaced text and include a minimum of three references. Your introduction should review the history B-Z reaction—Winfree, A. T., "The Prehistory of the Belousov-Zhabotisky Oscillator," *J. Chem. Educ.* **1984**, *61*, 661-663—and explain how your work will advance understanding of the chemistry occuring in this reaction. Be sure to review the guidelines for preparing reports and the sample report, both available on the course's website.

Working together, prepare a draft of your report and then, after receiving feedback on this draft, prepare a final report. Deadlines are listed on the course's website. When you submit your final report, please append two well-constructed figures, one that shows the calibration curve for $\text{Fe}(o\text{-phenanthroline})_3^{2+}$ and one that shows the reaction's oscillations as a function of time.