Chemistry and Mathematics of the Belousov−Zhabotinsky Reaction in a School Laboratory

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ABSTRACT: Chemical reactions far from equilibrium can exhibit oscillatory behavior. Full understanding of this phenomenon is outside of the school curriculum. However, the importance of such processes in life sciences and peculiar spatial and temporal patterns accompanying the reactions can attract the attention of IB Diploma science students. They will have studied chemical kinetics and received sufficient background knowledge in ordinary differential equations in order to be able to appreciate how sceptical the scientific community was when chemical oscillations were first reported. In this article, the famous Belousov−Zhabotinsky (BZ) reaction is investigated, which involves oxidation of malonic acid to carbon dioxide by bromate ions in the presence of a transition metal catalyst. Cerium(IV) and Manganese(II) catalysts at different initial concentrations are used with the research goal of determining the influence of the catalyst on the way the oscillatory stage is established and on the properties of oscillations. Convincing evidence of oscillatory behavior is observed and quantified by digital video processing. The BZ reaction mechanism is reviewed on the basis of the Field, Körös, and Noyes (FKN) model in reduced Oregonator form. The resulting system of nonlinear differential rate equations is solved numerically, and a remarkable agreement of the theoretically predicted oscillation period with an experiment for a Cerium(IV) catalyst is achieved.

KEYWORDS: *High School/Introductory Chemistry, First-Year Undergraduate/General, Physical Chemistry, Computer-Based Learning, Hands-On Learning/Manipulatives, Catalysis, Kinetics, Oxidation/Reduction, Mechanisms of Reactions, Mathematics/Symbolic Mathematics*

■ INTRODUCTION

In the early 1950s, Boris Belousov discovered that a solution of citric acid, potassium bromate, and cerium(IV) sulfate in dilute sulfuric acid did not react directly to equilibrium but rather turned colorless and then back to yellow for a significant period of time. He attempted publication in peer-reviewed journals since 1951 but was rejected because the reviewers felt that his findings violated the principle of thermodynamic equilibrium. They saw chemical oscillations as being analogous to a physical pendulum, which swings through equilibrium multiple times, therefore contradicting the Second Law of Thermodynamics. Belousov's work finally appeared in a conference proceeding some eight years later.[1] In 1961, a graduate student Anatol Zhabotinsky, under supervision of Professor Schnoll, investigated the reaction in detail and was able to publish his results.[2] In particular, he replaced citric acid with malonic acid and demonstrated that the oscillations in the solution color were due to oscillations in the concentration of Ce^{4+}. Since then, there has been an enormous interest in this complex chemical system and related systems.[3−8] In the obituary of Zhabotinsky, Epstein wrote that the discovery of oscillating reactions revolutionized the way that scientists thought about chemical dynamics.[9] Ilya Prigogine, the 1977 Nobel Prize Winner in Chemistry, regarded the BZ reaction as the most important scientific discovery of the twentieth century, surpassing quantum theory and relativity.

Shakhashiri et al. noted[10] that a more appropriate physical model of chemical oscillation phenomenon is a grandfather clock. While the hands of the clock undergo periodic motion, the potential energy stored in the elevated weights gradually decreases toward equilibrium. It is the decrease in the potential energy that drives the oscillations. The energy landscape of a complex reaction is not as smooth as one would envisage from a textbook diagram. It may well present barriers on the way down, so it may well be more energetically favorable for the reaction to choose a serpentine path. Behind all chemical oscillations, there is always a slow energy releasing reaction. The cycle typically consists of the production and consumption pathways of certain intermediates, which are triggered sequentially by a certain threshold concentration of the species. A mathematical model of this kind of predator−prey behavior was proposed by Alfred Lotka in 1910 to describe autocatalytic reactions.[11] The corresponding system of differential equations is called the Lotka−Volterra equations.

The original 1951 manuscript by Belousov was reproduced after the world finally recognized the importance of the discovery.[12] It can be shocking for students to realize that the path of original discoveries in science can be as difficult in
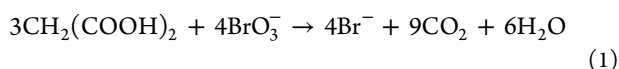
modern times as it was centuries ago. This fact alone would stimulate natural curiosity. But the BZ reaction itself is so visually spectacular, displaying fascinating colorful patterns in space and time, that it would immediately inspire anyone to repeat it and to try and understand its mechanism.[10] Methodologies have been designed to help students observe oscillatory chemical reactions and quantify their findings.[13−15] However, even demonstration of the BZ reaction is rarely performed at school. The main reason is risk, as concentrated sulfuric acid solution is involved. Quantitative measurements would also be difficult in a school laboratory as spectrophotometers or redox meters are usually unavailable. In addition, analysis of the reaction mechanism is considered to be rather complicated as it involves solving a system of nonlinear differential equations, which requires a higher level of mathematical knowledge. IB Diploma students, however, have all the prerequisites. They do study chemical kinetics on one hand and ordinary differential equations on the other. In this article, it is shown that, with proper supervision, the experiment can be conducted and oscillatory behavior can be observed. Quantitative analysis of experimental data is also possible with the help of a MATLAB program digitally analyzing a mobile video recording and extracting 24 bit RGB components, a light version of spectrophotometry. Comparison of experimental data against theoretical prediction of the Oregonator model can be performed with MATLAB functions using a standard Runge−Kutta routine to solve the system of rate equations.[16] This setup makes the world of oscillatory reactions accessible to IB Diploma science students.

■ REVIEW OF THEORY

The principle of detailed balance forbids any oscillations in the vicinity of thermodynamic equilibrium.[17] As a result, many chemists also assumed that oscillations in all homogeneous, closed chemical systems are impossible.[8] In fact, oscillations are quite possible when the system is sufficiently far from the state of thermodynamic equilibrium,[17] as proven by the discovery of the BZ reaction, but the mechanism is rather complex.
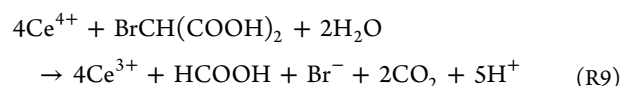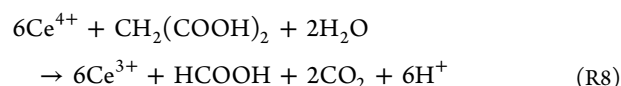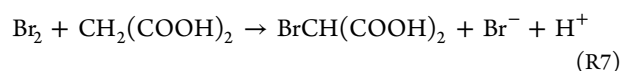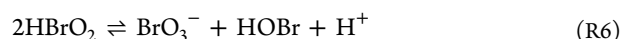
The overall reaction equation is given by

$$3CH_2(COOH)_2 + 4BrO_3^- \rightarrow 4Br^- + 9CO_2 + 6H_2O \tag{1}$$

where cerium (or manganese) works as a catalyst. Zhabotinsky established that oxidation of Ce^{3+} by $HBrO_3$ is an autocatalytic reaction, and self-sustained oscillations of Ce^{4+} concentration arise after accumulation of bromomalonic acid during the induction period.[2,7,8] Ce^{4+} reduction is accompanied by the production of Br^- from the bromoderivatives of the malonic acid. Br^- is a strong inhibitor of the autocatalytic oxidation of Ce^{3+} because of its rapid reaction with the autocatalyst, $HBrO_2$. Field, Körös, and Noyes (FKN) performed detailed thermodynamic and kinetic analysis of the basic chemical processes involved in the BZ reaction and suggested a mechanism responsible for oscillations.[3,4] Györgi, Turányi, and Field went further and introduced a 80-reaction and 26-species mechanistic model for the BZ system.[5] New reaction pathways are still being added upon collection of new experimental evidence.

FKN Model

The 10 key processes according to the landmark FKN mechanism are as follows[3]

$$BrO_3^- + 2H^+ + Br^- \rightleftharpoons HBrO_2 + HOBr \tag{R1}$$

$$HBrO_2 + H^+ + Br^- \rightleftharpoons 2HOBr \tag{R2}$$

$$HOBr + H^+ + Br^- \rightleftharpoons Br_2 + H_2O \tag{R3}$$

$$BrO_3^- + HBrO_2 + H^+ \rightleftharpoons 2BrO_2^\bullet + H_2O \tag{R4}$$

$$BrO_2^\bullet + Ce^{3+} + H^+ \rightleftharpoons HBrO_2 + Ce^{4+} \tag{R5}$$

$$2HBrO_2 \rightleftharpoons BrO_3^- + HOBr + H^+ \tag{R6}$$

$$Br_2 + CH_2(COOH)_2 \rightarrow BrCH(COOH)_2 + Br^- + H^+ \tag{R7}$$

$$6Ce^{4+} + CH_2(COOH)_2 + 2H_2O$$
$$\rightarrow 6Ce^{3+} + HCOOH + 2CO_2 + 6H^+ \tag{R8}$$

$$4Ce^{4+} + BrCH(COOH)_2 + 2H_2O$$
$$\rightarrow 4Ce^{3+} + HCOOH + Br^- + 2CO_2 + 5H^+ \tag{R9}$$

$$Br_2 + HCOOH \rightarrow 2Br^- + CO_2 + 2H^+ \tag{R10}$$

Reaction numbering is changed from the original reference in order to enhance the clarity of explanation. Here, Br^- is bromide ion, BrO_3^- is bromate ion, $HBrO_2$ is bromous acid (O=Br—OH), HOBr is hypobromous acid, $BrCH(COOH)_2$ is bromomalonic acid, and HCOOH is methanoic acid. A similar scheme can be written for manganese.

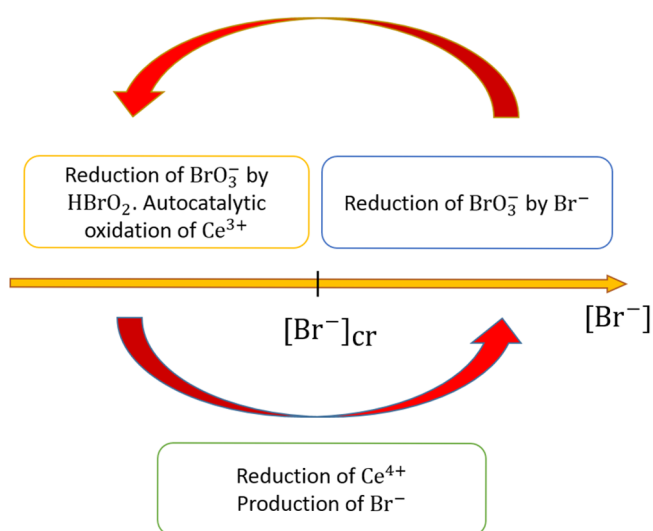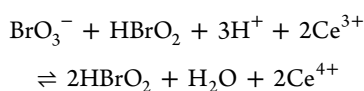The reaction occurs in a cycle of three stages, as illustrated in Figure 1:

Figure 1. Schematic illustration of the three cyclic stages of BZ reaction as described in the text.

- In processes R1−R3, the bromate ion is reduced to bromine via bromous and hypobromous acids by the reducing agent bromide. As a result, the concentration of bromide ion decreases.
- When the bromide ion concentration falls below a certain critical level $[Br^-]_{cr}$, the bromous acid begins to compete with the bromide to reduce the bromate in R4. Autocatalytic production of bromous acid in R4 and R5 is accompanied by the oxidation of the metal ion catalyst in R5, which leads to an observed sudden color change (from pale yellow to dark yellow for cerium). Reaction R6

prevents exponential growth of bromous acid concentration. Indeed one can notice by adding R4 and 2 R5 that

$$BrO_3^- + HBrO_2 + 3H^+ + 2Ce^{3+}$$
$$\rightleftharpoons 2HBrO_2 + H_2O + 2Ce^{4+}$$

and thus one extra molecule of $HBrO_2$ is produced per single reaction. R6 removes $HBrO_2$ and thus allows for a steady state concentration of bromous acid to be established.

- Processes R7−R10 close the feedback loop by reduction of the catalyst and production of the bromide ions. This stage is gradual, with a slow color change (from dark yellow to pale yellow for cerium).

Oregonator

A reduced FKN model received special attention under the name of Oregonator (taking its origin from the University of Oregon), which is still very popular as it is the simplest qualitative model describing oscillations in the BZ reaction.[4,18] The reduction of the model is based on the steady state approximation for certain reaction components. In particular, BrO_3^-, HOBr, $BrCH(COOH)_2$, Ce^{3+}, H^+, and H_2O are present in excess and their concentrations do not change significantly over the course of a few cycles. On the contrary, the concentrations of $HBrO_2$, Br^-, and Ce^{4+} do change significantly and thus their rate equations are of dominant importance for the overall reaction kinetics.

The Oregonator model is composed of the five coupled stoichiometries, as shown in Table 1. Species identifications with

Table 1. Oregonator Reaction Scheme

Step	Reaction	Rate Constant
(O1)	$A + Y \rightarrow X + P$	$k_1 = k_{R1}[H^+]^2$
(O2)	$X + Y \rightarrow 2P$	$k_2 = k_{R2}[H^+]$
(O3)	$A + X \rightarrow 2X + 2Z$	$k_3 = k_{R4}[H^+]$
(O4)	$2X \rightarrow A + P$	$k_4 = k_{R6}[H^+]$
(O5)	$B + Z \rightarrow \frac{1}{2}fY$	k_5

respect to the FKN mechanism are $X = HBrO_2$, $Y = Br^-$, $Z = Ce^{4+}$, $A = BrO_3^-$, $B = CH_2(COOH)_2$, and $P = HOBr$ (or $BrCH(COOH)_2$), and the rate constants are defined in terms of the corresponding FKN rate constants. Step (O5) is a net process of the third stage with an adjustable stoichiometric factor f and an adjustable rate parameter k_5. The model can be improved by explicitly considering the effect of temperature.[15]

Field−Noyes Equations

The Law of Mass Action in a homogeneous (well-stirred) system yields a system of three nonlinear ordinary differential

rate equations for X, Y, and Z.[18] They can be put into a more convenient dimensionless form

$$\epsilon \frac{dx}{d\tau} = qy - xy + x(1 - x) \tag{2}$$

$$\delta \frac{dy}{d\tau} = -qy - xy + fz \tag{3}$$

$$\frac{dz}{d\tau} = x - z \tag{4}$$

by change of variables

$$x = X/X_0, \quad y = Y/Y_0, \quad z = Z/Z_0, \quad \tau = t/T \tag{5}$$

where

$$X_0 = \frac{k_3 A}{2k_4}, \quad Y_0 = \frac{k_3 A}{k_2}, \quad Z_0 = \frac{(k_3 A)^2}{k_4 k_5 B}, \quad T = \frac{1}{k_5 B} \tag{6}$$

and

$$\epsilon = \frac{k_5 B}{k_3 A}, \quad \delta = \frac{2k_4 k_5 B}{k_2 k_3 A}, \quad q = \frac{2k_1 k_4}{k_2 k_3} \tag{7}$$

Equations 2−4 are sometimes referred to as the Field−Noyes equations. Dimensionless parameters describe the relationship between different stages of the BZ cycle. For example, ϵ describes the relative strength of the feedback stage of the recovery of bromide ions with respect to the autocatalytic production of bromous acid. The time scale of the reaction is defined in terms of the inverse rate of decomposition of malonic acid, $T = (k_5 B)^{-1}$.

Let us derive eq 2. The Mass Action Law for X (bromous acid) can be written from eqs O1−O4 as follows:

$$\frac{dX}{dt} = k_1 AY - k_2 XY + k_3 AX - 2k_4 X^2 \tag{8}$$

By substituting the normalized variables of eq 5 we obtain

$$\frac{X_0}{T} \frac{dx}{d\tau} = k_1 AyY_0 - k_2 xyX_0 Y_0 + k_3 AxX_0 - 2k_4 x^2 X_0^2 \tag{9}$$

Recall that A and B are considered to be quasi-stationary. By substituting expressions for X_0, Y_0, and T from eq 6, one can transform eq 9 into

$$\frac{k_5 B}{k_3 A} \frac{dx}{d\tau} = \frac{2k_1 k_4}{k_2 k_3} y - xy + x(1 - x) \tag{10}$$

Equation 2 is an immediate consequence with ϵ and q defined in eq 7. Equation 3 can obtained by a similar chain of transformations starting from the Mass Action Law for Y based

Table 2. Components of the BZ Reaction

Chemical[a]	Molecular Formula	Molar Mass (g · mol^{-1})	Concentration (mol · dm^{-3})	Mass[b] (g)
Sulfuric acid	H_2SO_4	98.08	1.68	32.95
Malonic acid	$CH_2(COOH)_2$	104.06	0.105	2.18
Potassium bromate	$KBrO_3$	167	0.058	1.94
Manganese(II) sulfate	$MnSO_4 \cdot H_2O$	169	0.013	0.44
Cerium(IV) sulfate	$Ce(SO_4)_2 \cdot 4H_2O$	404.3	0.012	0.96

[a]Sulfuric acid was diluted in distilled water from concentrated solution, as described in the text. Only one catalyst, manganese(II) sulfate or cerium(IV) sulfate, was used in a single experimental run. [b]Mass is given per 200 cm^3 of solution.
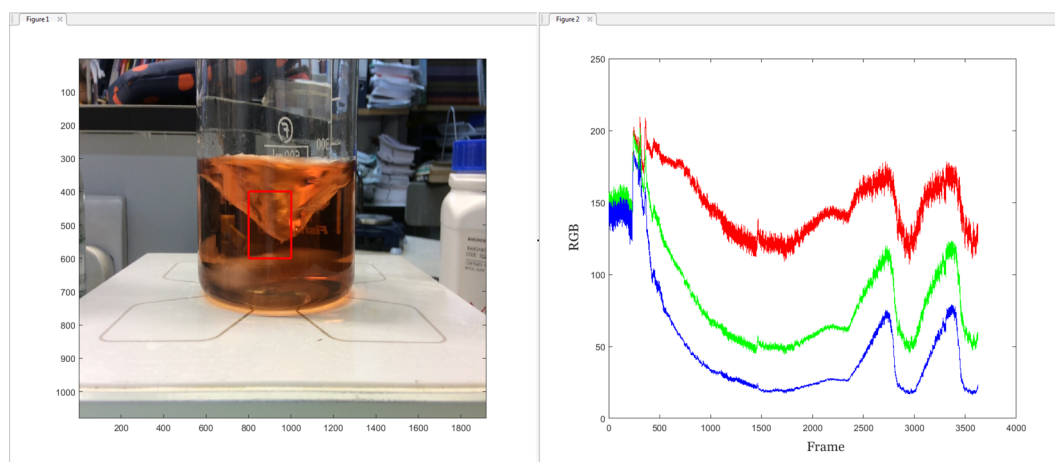
Figure 2. Video processing routine. Left panel represents an image corresponding to a single video frame. Red rectangle shows the area of focus. Twenty-four bit RGB color values extracted in this area are averaged and displayed in the right panel as a function of frame number.

on eqs O1, O2, and O5. Equation 4 is a normalized consequence of eq O5.

EXPERIMENT

Materials and Equipment

Jahnke and Winfree have compiled all the major recipes for the BZ reaction.[19] Herein, the experimental setup followed the general recipe outlined by the Nuffield Foundation and the Royal Society of Chemistry.[20] In this BZ reaction, bromate ions oxidize malonic acid to carbon dioxide, catalyzed by either manganese(II) or cerium(IV) ions.

Equipment

The equipment required for this experiment includes:

- tall plastic 250 cm^3 measuring cylinder (± 1 cm^3)
- glass 600 cm^3 cylinder beaker
- magnetic stirrer
- weighting paper
- balance (± 0.01 g)
- video camera (30 frames per second)
- protection (goggles and gloves)

Materials

Chemicals are listed in Table 2, along with the base composition of the initial solution. Bulk volume of sulfuric acid diluted in distilled water was prepared in advance. According to ref 20, 75 cm^3 of concentrated H$_2$SO$_4$ was added to 750 cm^3 of water. Concentrated solution was 95% (w/w) H$_2$SO$_4$ of density 1.834 g·cm^{-3}. After mixing with 750 cm^3 of water, the solution became 17.3% H$_2$SO$_4$ with a density 1.12 g·cm^{-3} according to ref 21. Therefore, the final volume of solution was $(1.834 \cdot 75 + 750)/1.12 = 792$ cm^3, and the resulting concentration was [H$_2$SO$_4$] = 1.68 mol·dm^{-3}. Two cubic decimeters of stock solution was prepared in this way.

Procedure

Each experimental run was carried out under the following procedure:

- H$_2$SO$_4$ solution (200 cm^3, 1.68 mol·dm^{-3}) was measured using the measuring cylinder and poured into the large glass beaker (reaction container) placed on a stirrer.
- Each of the reactants was weighed out separately on pieces of paper. The balance was zeroed with the paper before adding chemicals. Then, all solid reactants were mixed on a separate piece of paper.
- Magnetic stirrer was switched on, along with the video recording.
- Solid reactant mixture was added to stirred H$_2$SO$_4$ solution.
- Video was recorded until at least five oscillations of color were detected.

The concentration of malonic acid and potassium bromate was the same in all experiments. Either manganese(II) sulfate or cerium(IV) sulfate was chosen as a catalyst, and experiments were performed for concentrations in multiples of 2, 1, 0.5, 0.25, and 0.125 of the base concentration given in Table 2, namely, 0.026, 0.013, 0.0065, 0.0033, and 0.0016 mol·dm^{-3} for manganese(II) and 0.024, 0.012, 0.006, 0.003, and 0.0015 mol·dm^{-3} for cerium(IV).

In order to analyze the video recordings, a program was written in MATLAB,[22] which was reading the video, frame by frame, and extracting the average 24 bit RGB (red, green, and blue) values within a small rectangle focusing on the mixture, as shown in Figure 2. Color components were plotted during video processing as a function of frame number and saved for further analysis after converting frames to real time (a 30 frames per second camera was used). It was noticed that the blue component was the most responsive to color changes. Therefore, the analysis of all the experimental results was done with the blue component.

Risk Assessment

Concentrated sulfuric acid is highly corrosive. Malonic acid, manganese(II) sulfate, and cerium(IV) sulfate are classified as harmful, potassium bromate is classified as toxic and oxidizing.[20] Extreme care should be taken when dealing with these compounds. Protective goggles and gloves need to be worn at all times.

RESULTS

Figure 3 illustrates a single reaction trajectory extracted from a video of a BZ reaction with [Mn(II)]$_0$ = 0.026 mol·dm^{-3}, the highest catalyst concentration used. Similar results were obtained for Cerium(IV). Color changes primarily originated from changes in transition metal ion concentration. Although experimental equipment was rather basic, the results look consistent with those obtained using professional electro-
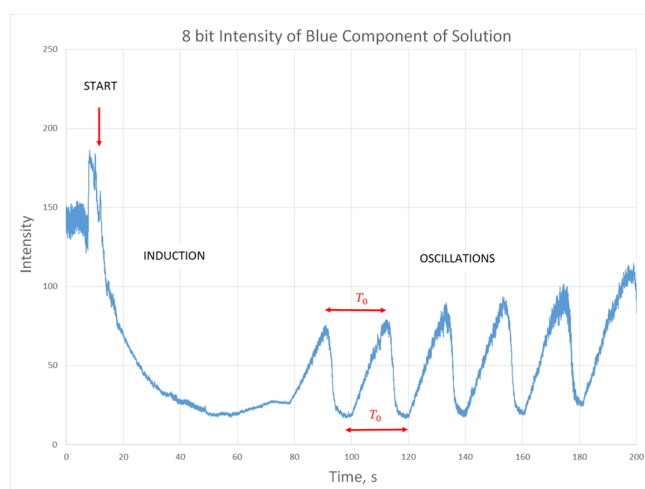
Figure 3. Average 8 bit (0−255) intensity of the blue component of BZ solution color as a function of time for $[Mn(II)]_0 = 0.026$ mol·dm^{-3}. Solid reactants were added to 200 cm^3 of stirred 1.68 M H_2SO_4 solution at the start time. After the induction period, oscillations of color were observed.

chemical methodology.[3] There is a well-defined induction period, which also includes the time during which the reactants actually dissolved—solutions stayed opaque for about 20 s. The induction is also partly due to bromination of malonic acid, as discussed in more detail in the preceding section. At the end of the induction period, one may assume that the reaction is actually over as the signal becomes stable, but this is exactly when the oscillations start with a clear seesaw pattern. The shape of each tooth is very similar to the one observed by a number of authors for a given catalyst concentration.[3,5]

In further analysis, the induction period is defined as the time difference between the start of the reaction and the peak in the first oscillation. The oscillation period is determined as the average distance between consecutive peaks and consecutive troughs, for five patterns in a row.

Figure 4 shows the dependence of the oscillation period T_0 on catalyst concentration for both Ce(IV) and Mn(II). The error
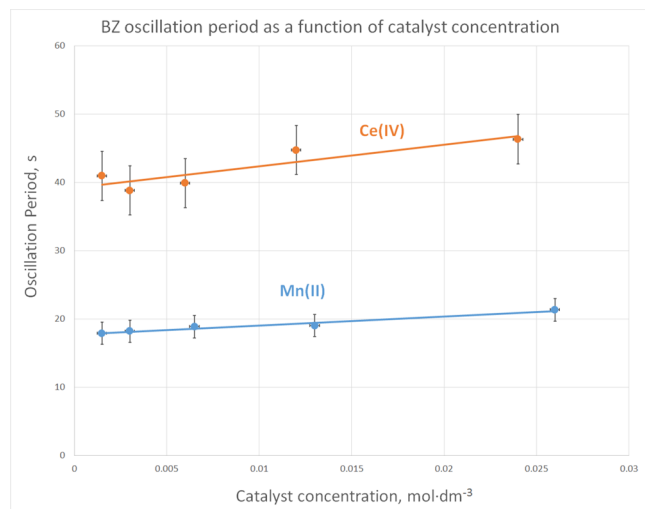

Figure 4. Oscillation period T_0 as a function of catalyst concentration c with Ce(IV) (orange) and Mn(II) (blue) as catalyst.s Linear best fit lines are $T_0 = 320c + 40$ for Ce(IV) and $T_0 = 130c + 20$ for Mn(II).

bars on concentration are derived from the accuracy of mass measurements. Indeed, volume measurements are at 1/200 cm^3 or 0.5% accuracy, while mass measurements for the lowest concentration of Mn (II) are at 0.005/0.055 g or 9%. The accuracy of determination of Mn(II) concentration is $\pm 0.005 \times (1000/200)/169 = \pm 1.5 \times 10^{-4}$ mol·dm^{-3}. Similarly for Ce (IV), $\pm 6 \times 10^{-5}$ mol·dm^{-3}. The accuracy of oscillation period measurements is not determined by frame duration; it is much larger due to visible noise in the pattern. We determined the accuracy as the average half-width of the peak (trough) at the minimal signal. For example, when we look at the peak, we take the minimum visible reading of intensity and look at the width of the peak at this level. Values of 2 s was obtained for Mn(II) and 4 s for Ce(IV), or about 10%, which turned out to be consistent with the standard deviation of oscillation periods calculated from different peaks (troughs) within one experimental run. The accuracy of the induction period is rather vague despite easiness of determination. First of all, the solution remained opaque for some time after mixing. Thus, part of induction period is actually dissolution. Second, the onset of oscillations was not always entirely obvious. Therefore, a reasonable assumption is to set the oscillation period as the accuracy of the induction period. No additional experiments were conducted due to time and resource constraints.

A slight increase of T_0 with increasing catalyst concentration was observed, which can be modeled by a linear dependence (parameters in figure caption). This is consistent with observations reported in the literature,[23] where the dependence is also weak. The authors did not focus on the precise functional dependence, in part because they derived this dependence from complex numerical model calculations and in part because their experimental results were very scattered, emphasizing how sensitive the BZ reaction is to the initial conditions.

The observed oscillation period was considerably longer for Ce(IV) than it was for Mn(II). This result is also in agreement with findings in the literature,[24] as can be understood by considering the electronic structure. Mn^{2+} electron configuration is [Ar]3d^5. It is stable due to symmetry of a half-filled d-orbital. However, Ce^{4+} has the electronic configuration of Xe and is thus even more stable.

Figure 5 displays the variation of the observed induction period T_i as a function of catalyst concentration. In agreement with the experiments reported in the literature,[25] the induction period increases dramatically as the catalyst concentration is decreased. A power law dependence fits the data well within the experimental error (parameters in figure caption). Qualitatively, the overall dependence can be understood as acceleration of reaction with added catalyst. At high concentrations, the catalyst becomes in excess and its influence no longer varies. The induction period for Ce(IV) is longer than that for Mn(II), which is consistent with the reactivity consideration as discussed above for the oscillation period.

Numerical Solution of the Oregonator Model

It is interesting to compare experimental results against even the simplest theory provided by the Oregonator model. The required rate constants are available in the literature for cerium:[23] $k_{R1} = 2$ mol^{-3}·dm^9 s^{-1}, $k_{R2} = 1.8 \times 10^6$ mol^{-2}·dm^6 s^{-1}, $k_{R4} = 48$ mol^{-2}·dm^6 s^{-1}, $k_{R6} = 3 \times 10^3$ mol^{-1}·dm^3 s^{-1}. In our experiment, $[H^+] = 1.68$ mol·dm^{-3}, $A = [BrO_3^-] = 0.058$ mol·dm^{-3}, and $B = [CH_2(COOH)_2] = 0.105$ mol·dm^{-3}. In line with Fields,[18] it is assumed that $k_5 = 1.6$ mol^{-1}·dm^3 s^{-1} and $f = 1$.
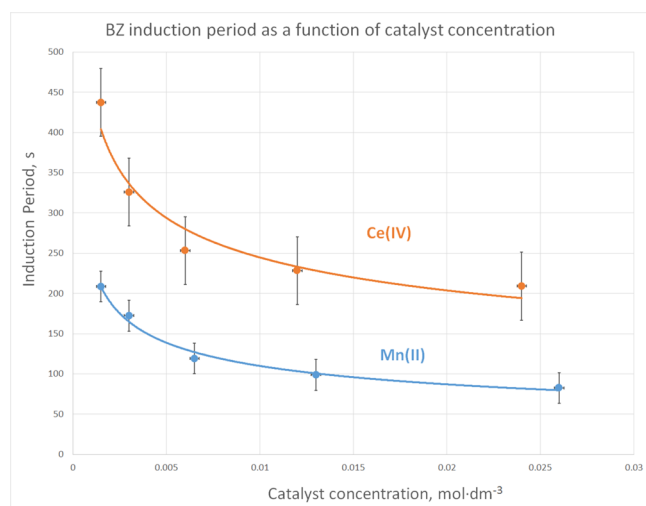
Figure 5. Induction period T_i as a function of catalyst concentration c with Ce(IV) (orange) and Mn(II) (blue) as catalysts. Power law best fit lines are $T_i = 70c^{-0.26}$ for Ce(IV) and $T_i = 20c^{-0.35}$ for Mn(II).

Thus we obtain for dimensionless parameters from eq 7: $\epsilon = 3.6 \times 10^{-2}$, $\delta = 1.2 \times 10^{-4}$ and $q = 2.4 \times 10^{-4}$. Characteristic time scale is $T = (k_5 B)^{-1} = 5.95$ s, according to eq 6. The system of Field−Noyes eqs 2−4 was solved numerically in MATLAB using standard ode45 solver.[22]

The results presented in Figure 6 display pronounced oscillations in concentration of bromous acid, bromide, and
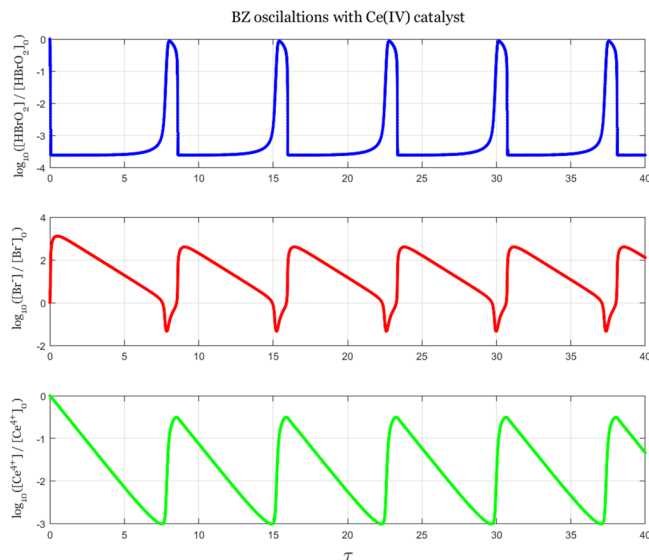

Figure 6. Time dependence of BZ reactant concentrations calculated using the Oregonator model by solving numerically the Field−Noyes equations with the parameter values defined in the text.

cerium ions. The obtained period of oscillations (trough to trough distance $\tau_0 = 7.4$) converted back to dimensional time is $T_0 = \tau_0 T = 44$ s, which is in remarkable agreement with experimental results in this study. The Oregonator model cannot explain the dependence of the oscillation period on catalyst concentration nor can it properly describe the induction period. One has to resort to a more detailed formulation for quantitative analysis,[5,23] which can be solved numerically using modern software packages such as Comsol Multiphysics. The focus of the Oregonator model was on oscillations, and the

theoretical prediction of the period of oscillations agrees very well with experiment.

Limit Cycle

Although the numerical solution clearly shows oscillations taking place in the system, it is instructive to understand the mathematical reasoning and possibly derive the oscillation period. Following Tyson,[26] we noticed that $\delta \ll 1$, and thus, the left-hand side of eq 3 is approximately zero forcing $y = fz/(x + q)$, i.e., y is quasi-stationary and can be eliminated, bringing the Oregonator system to a more tractable two-variable form,

$$\epsilon \frac{\mathrm{d}x}{\mathrm{d}\tau} = x(1 - x) - fz \frac{x - q}{x + q} \tag{11}$$

$$\frac{\mathrm{d}z}{\mathrm{d}\tau} = x - z \tag{12}$$

Recall that x (HBrO$_2$) acts as the autocatalytic (or the activator) species and z (Ce^{4+}) as the consuming (inhibitor) species. The nullclines of the system correspond to zero time derivatives,

$$z = \frac{x(1 - x)(x + q)}{f(x - q)} \tag{13}$$

$$z = x \tag{14}$$

The nontrivial equilibrium point lies at their intersection

$$x^* = z^* = \frac{1}{2}(1 - f - q + \sqrt{(1 - f - q)^2 + 4q(1 + f)}) \tag{15}$$

The nullclines are illustrated in Figure 7 for the parameters presented earlier in this section.

Since $\epsilon \ll 1$, the right-hand side of eq 11 will stay close to 0, and thus, the system will tend to move along the nullcline of eq 13 where possible. If we perturb the system from the equilibrium point upward along the nullcline of eq 13, we see that it will be to the right of the other nullcline or in the region of $\mathrm{d}z/\mathrm{d}\tau > 0$. In other words, the system will tend to move further upward.

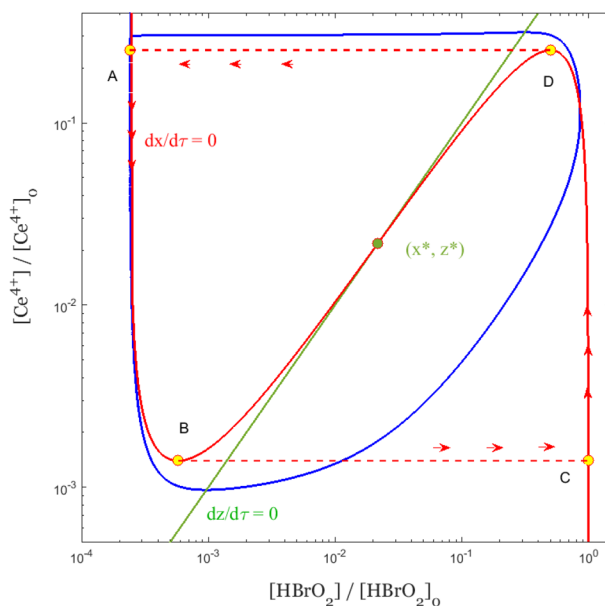**Figure 7.** $x − z$ phase plot of the Oregonator model: limit cycle of the original model (blue), nullclines of the reduced Oregonator ($\mathrm{d}z/\mathrm{d}\tau = 0$, green), and ($\mathrm{d}x/\mathrm{d}\tau = 0$, red); equilibrium point (x^*, z^*).

Similarly, if we perturb the system downward, it will tend to move further downward, i.e., away from equilibrium, indicating that the equilibrium point is unstable. Instead of reaching the equilibrium, the system will travel along the $dx/d\tau = 0$ nullcline from A to B, then rapidly jump to C because it cannot further move along $dx/d\tau = 0$ toward equilibrium while in the region of $dz/d\tau < 0$. From C it will move to D and then jump again to A because it cannot further move along $dx/d\tau = 0$ toward equilibrium while in the region of $dz/d\tau > 0$. ABCD is the limit cycle, which is not very far off the limit cycle produced by the original Oregonator, as shown in Figure 7. This kind of oscillatory behavior arises in systems of ODE with complex eigenvalues. General analysis of stability and the locus of unstable points in parameter space can be found elsewhere.[18]

In order to estimate the oscillation period, we assumed that jumps BC and DA are instantaneous and focused on time spent on moving along the nullcline of eq 13. From now on we set $f = 1$. During AB stage $x \approx q$, and eq 12 simplifies into $dz/d\tau = q - z$. This stage is clearly visible in Figure 6 as a flat period in $HBrO_2$ concentration. The time spent on AB can be found by integration

$$T_{AB} = \int_{z_A}^{z_B} \frac{dz}{z - q} = -\log q - 3 \log 2 - \log(1 + \sqrt{2}) \tag{16}$$

Here, $z_A = \frac{1}{4} + q$ and $z_B = (1 + \sqrt{2})^2 q$ are extrema of the nullcline. During CD stage $x \gg q$ and thus $z = x(1 - x)$. By substituting this result into eq 12 and integrating we find

$$T_{CD} = \int_{x_C}^{x_D} \frac{1 - 2x}{x^2} dx = 2 \log 2 - 1 \tag{17}$$

Finally, the estimation for the total period of oscillations is given by

$$T = -\log q - 1 - \log 2 - \log(1 + \sqrt{2}) \approx 5.76 \tag{18}$$

This is within 30% of the numerical solution of the full three-variable Oregonator, which is not bad given qualitative nature of the discussion.

CONCLUDING REMARKS

This study was focused on the demonstration in the school laboratory of the ability of the BZ reactions to exhibit oscillatory behavior. The reaction is known to be very sensitive to initial conditions and even to the purity of water used. Therefore, just to be able to observe it was an exciting achievement. The experiment was successful with cerium(IV) sulfate and manganese(II) sulfate as catalysts. Observations were very clear due to significant color differences between Ce^{4+} (dark yellow) and Ce^{3+} (pale yellow), Mn^{3+} (dark brown-red), and Mn^{2+} (pale pink). The induction period was found to be strongly decreasing with increasing catalyst concentration before saturating at higher concentrations. Manganese(II) showed a shorter induction period as a catalyst with stronger reactivity, in agreement with similar studies in the literature. The oscillation period displayed only a weak dependence on catalyst concentration but was very sensitive to the choice of catalyst, again in agreement with the results reported in the literature.

The mechanism of the BZ reaction was reviewed on the basis of the Field, Körös, and Noyes (FKN) model, which involves three concurrent cyclic stages: reduction of bromate by bromide, autocatalytic production of bromous acid accompanied by the oxidation of the metal ion catalyst and the reduction of the catalyst, and regeneration of bromide ions. The model was further investigated in reduced Oregonator form by numerically solving the Field−Noyes equations. By taking the rate constants of the processes involved from the literature and substituting the conditions of the present study, it was possible to achieve a remarkable agreement of the theoretically predicted oscillation period with an experiment for cerium(IV) as a catalyst.

Due to restricted resources, all experiments were performed on a single trial basis. Although one can estimate the error of measuring the period of oscillations by comparing different waves, it is not by any means a full measure of real experimental error. Sensitivity of BZ reactions to initial conditions demands one to use multiple trials for rigorous quantitative measurements. Therefore, although good agreement with the literature that was observed in the results of the present study can only be classified as qualitative. The experimental accuracy could also be improved by preparing buffer solutions of reactants. All dry reactants in measured quantities were added to a sulfuric acid solution at the start, and it was visible that they did not dissolve immediately as the solution stayed opaque for a few seconds. This adds uncertainty to the determination of the induction period as it is hard to judge when the reaction actually starts. By mixing buffer solutions, it would be possible to avoid this problem. There is a significant demand on the accuracy of the color signal, which is a proxy of the oxidized metal concentration. Manual video recording was used, and thus, the image of the beaker was slowly drifting within the frame. This effect was dealt with by averaging the signal over a certain area of the image. The accuracy of measurements would be improved by using a professional fixed camera or a color sensor driven by Arduino.

BZ reactions are fascinating and rich in their displayed behavior, so extension of the present study would be rewarding. Research on other catalysts, such as Fe(II) or Ru(II), different counterions, and varying initial concentrations of potassium bromate and malonic acid would complement the understanding of the effect of initial conditions. Another interesting project for a school laboratory is to investigate the reaction without stirring, to see and analyze theoretically how chemical waves propagate in space, forming beautiful dynamic patterns.

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Notes

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