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Employing Complex Kinetic Diagrams to Understand the Belousov- Zhabotinskii Reaction

Scot T. Martin

Division of Engineering and Applied Sciences
Harvard University
Cambridge, MA 02138
smartin@deas.harvard.edu

In contrast to many physical phenomena such as a swinging pendulum, chemical reactions must approach equilibrium monotonically. However, far from equilibrium, concentrations of chemical species can oscillate during the time course of the reaction. This interesting branch of kinetics is exemplified by the Belousov-Zhabotinskii reaction. After an induction period, the color of the solution changes between clear and yellow with a period of two minutes for several hours. In this article, a general, convenient chemical kinetics solver is employed in conjunction with complex kinetic diagrams to understand the coupling of chemical reactions that yield chemical oscillations.

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Chemical kinetics is the discipline concerning the time rate of change of the concentration of chemical species through the course of a chemical reaction. The typical approach to chemical kinetics problems is first to note the elementary steps and then to express the time rate of change of the concentration of each chemical species as a sum of its sources and sinks. The result is a system of coupled, often nonlinear, differential equations. This set of equations is subsequently simplified by appropriate approximations, and the reduced set of equations is solved analytically or numerically, as appropriate. For example, for the reaction $A \rightarrow B$, we can write $\frac{\partial [A]}{\partial t} = -k[A]$ where k is the rate constant. The solution for $A[t]$ readily follows as $A_0 e^{-kt}$ where A_0 is the initial concentration of A.

The chemical kinetics of the reaction $A \rightarrow B$ are thus readily understood, and an analytical solution is easily obtained. Many chemical reactions are much more complex, and an understanding of the coupled differential equations is more difficult. A fascinating chemical reaction is the Belousov-Zhabotinskii reaction, discovered first in 1958 and again in 1964. Prior to its discovery, esteemed chemists argued that oscillating chemical reactions could not occur. In the Belousov-Zhabotinskii reaction, when the proper concentrations of bromate, malonic acid, sulfuric acid, and cerium ions are mixed together, the color of the solution oscillates from yellow to clear with a period of about two minutes for several hours. How can this reaction be understood? Many fundamental chemical measurements have been made over the last three decades to obtain the rate constants of the elementary steps, and twenty-one important steps have been identified. In addition, the resulting system of coupled differential equations has been numerically integrated to reproduce the observed oscillations. However, obtaining an intuitive understanding of this complex system is difficult for the novice. One successful approach in the past has been through chaos theory, invoking an Oregonator model. In this paper, a general chemical kinetics solver for *Mathematica* is introduced. Then, the powerful numerical engine and graphic capabilities of *Mathematica* are employed to understand the Belousov-Zhabotinskii reaction.

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The Belousov-Zhabotinskii Reaction

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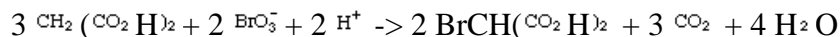
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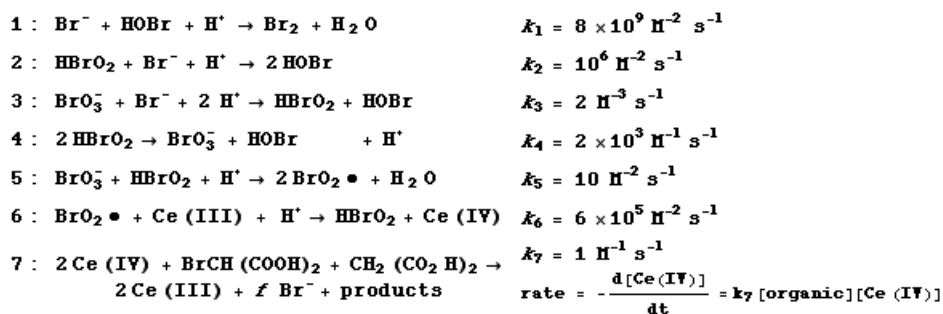
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The reactants include malonic acid, sodium bromate, and sulfuric acid, which are mixed together at initial concentrations far from equilibrium. Energy is released by the oxidation of malonic acid by bromate. The net reaction is as follows:



The direct chemical reaction between bromate and malonic acid is kinetically slow. Thus, cerium ions at much lower concentrations are added to the reaction mixture. The cerium ions catalyze the overall reaction by acting as an electron relay between malonic acid and bromate. During the course of the reaction, the color of the solution oscillates between clear and yellow with a period of about two minutes because the dominant chemical speciation of cerium oscillates between the +3 and +4 oxidation states. The oscillatory reaction can be represented in 21 steps, but the following 6 elementary steps and 1 empirical step retain the essential features of the system [4]:



To simulate this system by numerical methods, we write a rate equation for each reactant. The list of nine reactant species includes: Br^- , HOBr , H^+ , HBrO_2 , BrO_3^- , $\text{BrO}_2 \bullet$, Ce(III) , Ce(IV) , and "organic" (namely malonic acid). We then specify initial conditions and seek a numerical solution.

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Kinetic Equations

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A *Mathematica* notebook accompanying this article, [Kinetics.nb](#), contains the instructions to process the kinetic input and generate the graphs. To translate the chemical equations into a system of coupled differential equations, the user interface proceeds by identifying the chemical species, by providing initial conditions and the integration time, and by specifying each kinetic step. Every place a user should change information to specify the kinetic system is shown in blue. The detailed procedure is as follows.

Names of Species in Kinetic Analysis

```
species =
  {"Br-", "HOBr", "H+", "HBrO2", "BrO3-",
   "BrO2•", "Ce(III)", "Ce(IV)", "organic"};
```

Initial Concentrations (M) of Chemical Species

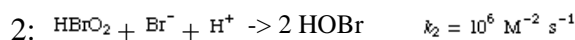
```
conditions = {0.000625, 10-6, 2.
              10-6, 0.0625, 10-6, 10-6, 0.002, 0.275};
```

Length of Time (sec) Over Which to Obtain Kinetic Solution

```
integrationtime = 20*60;
```

Elementary Rate Equation for Each Species

The entry of the kinetic equations is now shown by employing reaction 2 as an example, as follows.



The following entries are made for this elementary step:

```
{2, 4, loss, {4, 1, 3}, 1, 106},
{2, 1, loss, {4, 1, 3}, 1, 106},
{2, 3, loss, {4, 1, 3}, 1, 106},
{2, 2, production, {4, 1, 3}, 2, 106}
```

The first line is interpreted as follows: "In reaction 2, species #4 (i.e., HBrO_2) is lost according to a rate law including species #4 (HBrO_2), #1 (Br^-), and #3 (H^+) with a rate constant of 10^6 ." The corresponding differential equation is as follows:

$$2: \frac{d[\text{HBrO}_2]}{dt} = -10^6 [\text{HBrO}_2] [\text{Br}^-] [\text{H}^+]$$

This entry is one term in the complete expression for $\frac{d[\text{HBrO}_2]}{dt}$. Reactions 3 to 6 also contribute to $\frac{d[\text{HBrO}_2]}{dt}$.

The six entries in each sublist correspond to the following format:

1. reaction number
2. species number for time-derivative
3. "loss" or "production" of species
4. {first species, second species, ... and so on} of kinetic rate equation
5. rate multiplier [account for stoichiometry]
6. rate constant

Reactions that do not fit this mold (e.g., surface reactions) can be manually adjusted in the kinetic equations later.

The complete set of entries corresponding to reactions 1 to 7 of the Belousov-Zhabotinskii chemical mechanism are shown below.

```

rates =
{
  {1. 1. "loss", {1. 2. 3}, 1. 8×109},
    {1. 2. "loss", {1. 2. 3}, 1. 8×109},
    {1. 3. "loss", {1. 2. 3}, 1. 8×109},
    {2. 4. "loss", {4. 1. 3}, 1. 106},
    {2. 1. "loss", {4. 1. 3}, 1. 106},
    {2. 3. "loss", {4. 1. 3}, 1. 106},
    {2. 2. "production", {4. 1. 3}, 2. 106},
    {3. 5. "loss", {5. 1. 3. 3}, 1. 2},
    {3. 1. "loss", {5. 1. 3. 3}, 1. 2},
    {3. 3. "loss", {5. 1. 3. 3}, 2. 2},
    {3. 4.
"production", {5. 1. 3. 3}, 1. 2},
    {3. 2. "production",
{5. 1. 3. 3}, 1. 2},
    {4. 4. "loss", {4. 4}, 1. 2×103},
    {4. 5. "production", {4. 4}, 1. 2×103},
    {4. 2. "production", {4. 4}, 1. 2×103},
    {4. 3. "production", {4. 4}, 1. 2×103},
    {5. 5. "loss", {5. 4. 3}, 1. 10},
    {5. 4. "loss", {5. 4. 3}, 1. 10},
    {5. 3. "loss", {5. 4. 3}, 1. 10},
    {5. 6. "production", {5. 4. 3}, 2. 10},
    {6. 6. "loss", {6. 7. 3}, 1. 6×105},
    {6. 7. "loss", {6. 7. 3}, 1. 6×105},
    {6. 3. "loss", {6. 7. 3}, 1. 6×105},
    {6. 4.
"production", {6. 7. 3}, 1. 6×105},
    {6. 8. "production",
{6. 7. 3}, 1. 6×105},
    {7. 8. "loss", {9. 8}, 1. 1},
    {7. 9. "loss", {9. 8}, 1. 1},
    {7. 7. "production", {9. 8}, 1. 1},
    {7. 1. "production", {9. 8}, 0.5 f 11

```

};

Special Instructions

There is occasionally the need for special instructions to be appended to the elementary rate equations. For example, in the Belousov-Zhabotinskii reaction, there is the parameter f . What value should it take?

```
specialinstructions = {f -> 2};
```

Input Verification

After providing this input to *Mathematica*, the user verifies the interpretation. The species numbers, labels, and initial concentrations are displayed, as follows:

```
Table[{i, species[[i]], conditions[[i]]},
      {i, totalspecies}] // TableForm
```

1	Br ⁻	0.000625
2	HOBr	$\frac{1}{1000000}$
3	H ⁺	2
4	HBrO ₂	$\frac{1}{1000000}$
5	BrO ₃ ⁻	0.0625
6	BrO ₂ •	$\frac{1}{1000000}$
7	Ce(III)	$\frac{1}{1000000}$
8	Ce(IV)	0.002
9	organic	0.275

The individual kinetic terms are also displayed, as shown below for sorting by species. A complete kinetic term for the time rate of change of a species is the sum of the individual terms.

Species

1	d[Br ⁻]/dt =	0.5 f x 1. [organic][Ce(IV)]
1	d[Br ⁻]/dt =	-1.e6 [HBrO ₂] [Br ⁻] [H ⁺]
1	d[Br ⁻]/dt =	-2. [BrO ₃ ⁻] [Br ⁻] [H ⁺] [H ⁺]
1	d[Br ⁻]/dt =	-8.e9 [Br ⁻] [HOBr] [H ⁺]
2	d[HOBr]/dt =	2000. [HBrO ₂] [HBrO ₂]
2	d[HOBr]/dt =	2. [BrO ₃ ⁻] [Br ⁻] [H ⁺] [H ⁺]
2	d[HOBr]/dt =	2 x 1.e6 [HBrO ₂] [Br ⁻] [H ⁺]
2	d[HOBr]/dt =	-8.e9 [Br ⁻] [HOBr] [H ⁺]
3	d[H ⁺]/dt =	-10. [BrO ₃ ⁻] [HBrO ₂] [H ⁺]
3	d[H ⁺]/dt =	-1.e6 [HBrO ₂] [Br ⁻] [H ⁺]
3	d[H ⁺]/dt =	2000. [HBrO ₂] [HBrO ₂]
3	d[H ⁺]/dt =	-2 x 2. [BrO ₃ ⁻] [Br ⁻] [H ⁺] [H ⁺]
3	d[H ⁺]/dt =	-600000. [BrO ₂ •] [Ce(III)] [H ⁺]

$$\begin{aligned}
3 \quad d[\text{H}^+]/dt &= -8. \text{e}9 \quad [\text{Br}^-] [\text{HOBr}] [\text{H}^+] \\
4 \quad d[\text{HBrO}_2]/dt &= -10. \quad [\text{BrO}_3^-] [\text{HBrO}_2] [\text{H}^+] \\
4 \quad d[\text{HBrO}_2]/dt &= -1. \text{e}6 \quad [\text{HBrO}_2] [\text{Br}^-] [\text{H}^+] \\
4 \quad d[\text{HBrO}_2]/dt &= -2000. \quad [\text{HBrO}_2] [\text{HBrO}_2] \\
4 \quad d[\text{HBrO}_2]/dt &= 2. \quad [\text{BrO}_3^-] [\text{Br}^-] [\text{H}^+] [\text{H}^+] \\
4 \quad d[\text{HBrO}_2]/dt &= 600000. \quad [\text{BrO}_2\bullet] [\text{Ce(III)}] [\text{H}^+] \\
5 \quad d[\text{BrO}_3^-]/dt &= -10. \quad [\text{BrO}_3^-] [\text{HBrO}_2] [\text{H}^+] \\
5 \quad d[\text{BrO}_3^-]/dt &= 2000. \quad [\text{HBrO}_2] [\text{HBrO}_2] \\
5 \quad d[\text{BrO}_3^-]/dt &= -2. \quad [\text{BrO}_3^-] [\text{Br}^-] [\text{H}^+] [\text{H}^+] \\
6 \quad d[\text{BrO}_2\bullet]/dt &= 2 \times 10. \quad [\text{BrO}_3^-] [\text{HBrO}_2] [\text{H}^+] \\
6 \quad d[\text{BrO}_2\bullet]/dt &= -600000. \quad [\text{BrO}_2\bullet] [\text{Ce(III)}] [\text{H}^+] \\
7 \quad d[\text{Ce(III)}]/dt &= 1. \quad [\text{organic}] [\text{Ce(IV)}] \\
7 \quad d[\text{Ce(III)}]/dt &= -600000. \quad [\text{BrO}_2\bullet] [\text{Ce(III)}] [\text{H}^+] \\
8 \quad d[\text{Ce(IV)}]/dt &= -1. \quad [\text{organic}] [\text{Ce(IV)}] \\
8 \quad d[\text{Ce(IV)}]/dt &= 600000. \quad [\text{BrO}_2\bullet] [\text{Ce(III)}] [\text{H}^+] \\
9 \quad d[\text{organic}]/dt &= -1. \quad [\text{organic}] [\text{Ce(IV)}]
\end{aligned}$$

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Chemical Oscillations

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After the user enters the chemical system as shown above, the subsequent steps of setting up the differential equations and numerically solving the coupled equations are fully automated. After the numerical engine has finished the computations, the user is presented with graphs of the solutions, as shown in Figures 1 and 2. Following an initial induction period, the oscillatory behavior of chemical intermediates is apparent in Figure 1. In particular, $[\text{Ce(IV)}]$ oscillates from nearly zero to 2 mM, with accompanying changes from clear to yellow. Figure 2 shows that the concentrations of the reactants are much higher than those of the chemical intermediates, and the concentrations monotonically decrease during the course of the reaction. There are some periods when the overall reaction rate is apparently slow (i.e., the nearly flat regions in Figure 2) and other periods when the reaction rate appears to accelerate.

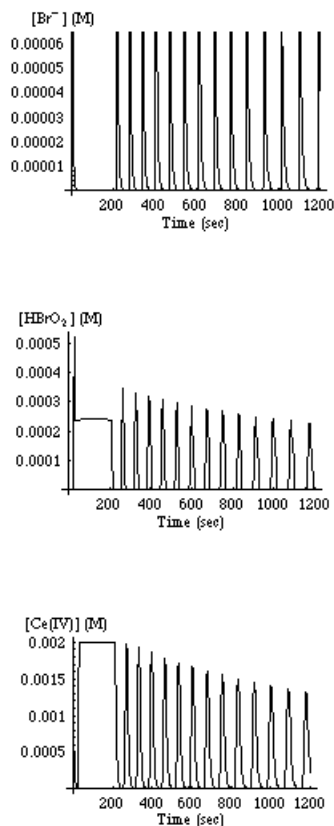


Figure 1. The concentrations of Br^- , HBrO_2 , and Ce(IV) as a function of time from 0 to 1200 sec. After an initial induction period, an oscillatory behavior with a period of about 2 minutes is observed.

The following two conditions must be satisfied for a reaction to oscillate.

1. The concentrations of reactants and products must be far from their equilibrium conditions.
2. There must be chemical feedback in the chemical mechanism (implying a complex kinetic mechanism).

At sufficiently long time periods (i.e., when reactant and product concentrations are sufficiently close to equilibrium), the chemical system reverts to a single mode and all chemical species approach equilibrium concentrations monotonically. Throughout the course of the reaction, the free energy of the system declines as the extent of reaction continues.

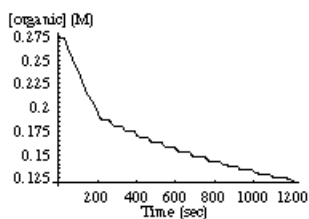
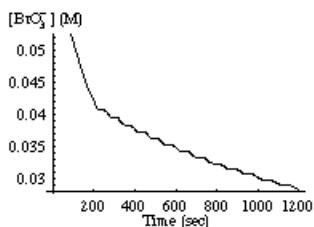
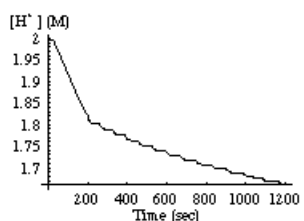


Figure 2. The concentrations of H^+ , BrO_3^- , and organic as a function of time from 0 to 1200 sec. The concentrations of these reactant species decrease monotonically through the course of the reaction, proceeding stepwise through periods of slow and fast reaction rates.

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Complex Kinetic Diagram

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A *complex kinetic diagram* is introduced in Figure 3 to understand the interactions that result in the oscillations shown in Figure 1. The complex kinetic diagram shows a snapshot at 360 sec of the rates of reactions leading to the production of chemical species. The right-hand side of the diagram is a bar chart indicating the percent change in the concentration of the nine chemical species per unit time. On the left-hand side of this diagram, the fastest rate of all seven reactions is shown to be $6.2 \times 10^{-6} \text{ M s}^{-1}$, and that value represents unity. All other rates are scaled to that value. The nine black circles shown each have a radius of 1. The red circles indicate net production of a species while the blue circles indicate a net loss of a species. The rate of loss or production is proportional to the radius of the circle shown (i.e., as a fraction of unity). We can say, for example, that $d[\text{H}^+]/dt$ is being lost at $6.2 \times 10^{-6} \text{ M s}^{-1}$ whereas Ce(III) is being produced at approximately 75% of this rate. The dashed lines show connections between products and reactants. The product side of the line is indicated by the heavy black mark. Thus, in this scheme, BrO_2^\bullet is *potentially* produced from BrO_3^- , HBrO_2 , and H^+ . In turn, BrO_2^\bullet produces Ce(IV) and HBrO_2 . How much BrO_2^\bullet is *actually* being produced? The length of the red line covering the heavy black line indicates the rate at which a species is actually being produced. It is apparent that very little BrO_2^\bullet is being produced. In contrast, Ce(III) is rapidly being produced from organic and Ce(IV) . We can also see that HOBr is being produced rapidly from Br^- , which is likewise being produced rapidly from Ce(IV) . Very little is producing Ce(IV) , and its net loss rate (circle in blue) is seen to be substantial.

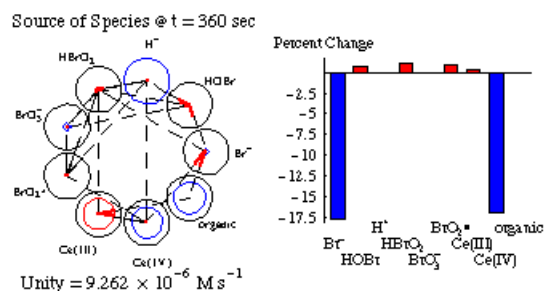


Figure 3. Complex kinetic diagram showing a snapshot of the Belousov-Zhabotinskii reaction at 360 sec. See further explanation in the text.

In Figure 4, the concentrations of Ce(IV) , Br^- , and HBrO_2 are overlaid through several chemical cycles. The drop in $[\text{HBrO}_2]$ is

seen to be followed by a rapid increase in $[\text{Br}^-]$. Similarly, the rise in $[\text{Ce(IV)}]$ is coincident with the rise in the $[\text{HBrO}_2]$. A specific timepoint (e.g., 360 sec) can be selected and analyzed in greater detail, as was done in Figure 3. Timepoints of 309, 325, 332, and 342 sec are also selected and shown as complex kinetic diagrams in Figure 5. Figure 4 shows that these timepoints cover the initiation, peak, and quiescence of one chemical cycle.

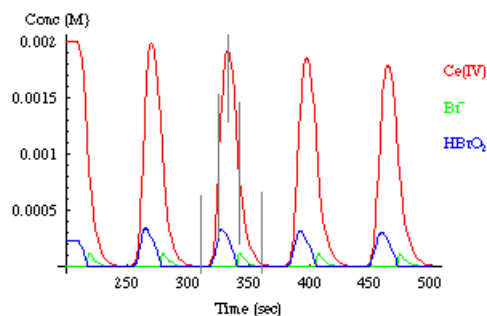


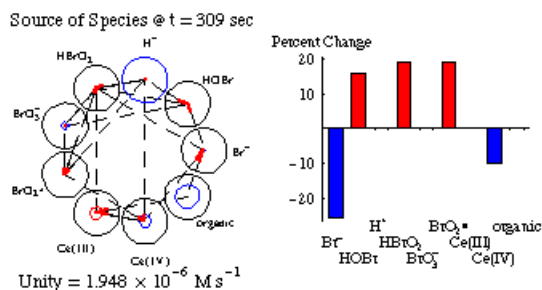
Figure 4. Concentrations of Ce(IV) , Br^- , and HBrO_2 from 200 to 500 sec. The gray bars are shown at timepoints of 309, 325, 332, 342, and 360 sec and correspond to the complex kinetics diagrams shown in Figures 3 and 5.

The *Mathematica* notebook is highly automated. Subsequent to the numerical solutions obtained in Figures 1 and 2, the user can execute the following command to display a complex kinetics diagram at a given time point. The user enters the parameters shown in blue, that is, `drawrates[1, 2, 3, 4, 5]` where the first parameter is the timepoint and the other parameters are options not employed in this article but discussed in the notebook itself.

```
assem = Graphics[
  drawrates[325, 1, True, "production", True],
  TextStyle -> {FontFamily -> "Times",
    FontSize -> 10}, AspectRatio -> 1,
  PlotRange -> {{-r, r}, {-r, r}}];

percentbar = makepercentbar[325];

Show[GraphicsArray[{assem, percentbar}],
  GraphicsSpacing -> 0, ImageSize -> {72 5, 72 3}]
```



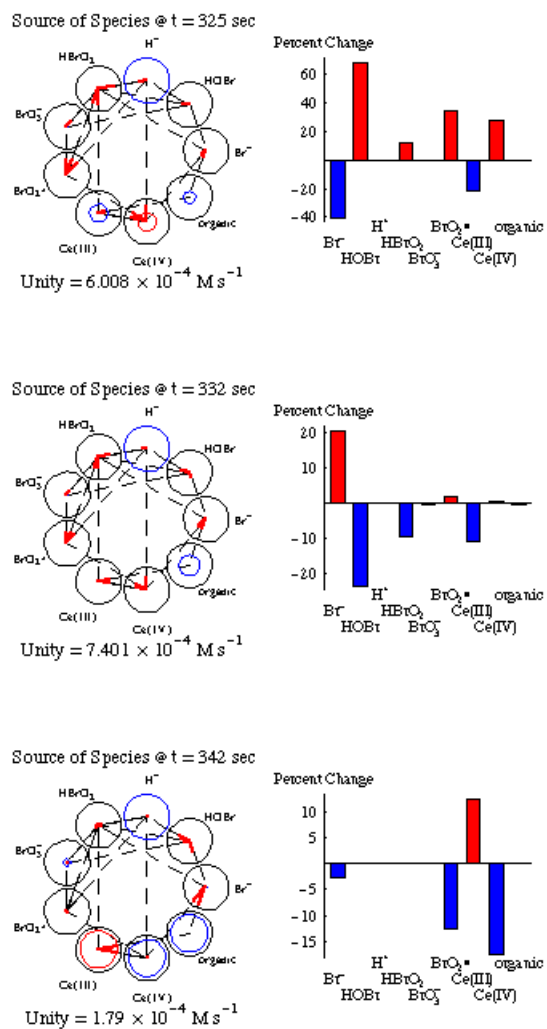


Figure 5. Complex kinetic diagrams of the Belousov-Zhabotinskii reaction at 309, 325, 332, and 342 sec. The timepoint at 360 sec is shown in Figure 3.

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Understanding the Chemical Oscillations

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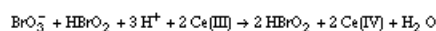
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The complex kinetics diagram can be employed to understand the oscillatory behavior shown in Figure 1. At the beginning of a chemical cycle, $[\text{HBrO}_2]$ and $[\text{Br}^-]$ are low, as shown at 309 sec in Figure 4. Although the overall reaction is slow ($1.9 \times 10^{-6} \text{ M s}^{-1}$ in Figure 5), reactions 5 and 6 together combine to make an autocatalytic sequence for HBrO_2 , as follows.



$[\text{HBrO}_2]$ is thus increasing at an accelerating rate. The production of HBrO_2 from BrO_2^\cdot , H^+ , and Ce(III) (reaction 6) is shown by the red lines surrounding HBrO_2 in Figure 5. In turn, the red lines surrounding BrO_2^\cdot indicate production from BrO_3^- , HBrO_2 , and H^+ (reaction 5). $[\text{HBrO}_2]$ and $[\text{BrO}_2^\cdot]$ are increasing by 20% per second, as shown in the bar chart. By 325 sec, $[\text{HBrO}_2]$ has dramatically increased by the autocatalytic process (Figure 4). Accompanying the increase in $[\text{HBrO}_2]$, $[\text{BrO}_2^\cdot]$ is high enough that reaction 6 is depleting Ce(III) at about 20% per second, as shown in the bar chart. Consequently, Ce(IV) is forming (Figure 4). However, a limit is being approached because the disproportionation reaction (4) limits $[\text{HBrO}_2]$, as indicated by the red line representing production of BrO_3^- from HBrO_2 . The continuing increase of $[\text{Ce(IV)}]$ leads to the formation of Br^- via reaction 7, as shown by the 20% per second increase in $[\text{Br}^-]$ at 332 sec. At this point, the overall reaction rate has increased to $7.4 \times 10^{-4} \text{ M s}^{-1}$. The formation of Br^- leads to the depletion of HBrO_2 via reaction 2. This relationship is apparent in Figure 4 and in the bar chart at 332 sec in Figure 5. The red lines indicate the formation of HOBr from the reactants for reaction 2 (i.e., Br^- , HBrO_2 , and H^+). The removal of HBrO_2 shifts the system away from reactions 5, 6, and 7, as shown by the absence at 342 sec of red lines corresponding to these reactions (cf. 325 sec). $[\text{Ce(IV)}]$ continues to fall (Figures 4 and 5), and the red lines show the accompanying production of Ce(III) and Br^- . Overall, however, $[\text{Br}^-]$ is decreasing via reactions 1 through 3. When Br^- is depleted to trace levels, the overall reaction rate is slow (viz. 360 sec in Figure 3). The low concentration of Br^- keeps reaction 2 slow while allowing HBrO_2 to begin forming via reaction 3. $[\text{HBrO}_2]$ and $[\text{Br}^-]$ are again low (cf. 309 sec), and the chemical cycle then repeats.

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Conclusions

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Reaction 7 is an empirical relationship including a factor, f , which relates the number of Br^- ions released by the reduction of two Ce(IV) ions and the concomitant oxidation of malonic acid and its brominated derivatives. The concentration of brominated derivatives depends on the time course of the reaction via the production of Br_2 in reaction 1. Thus, f also depends on time. To account for this complete mechanism, the seven reactions employed in this paper must be expanded to 21 elementary steps. As employed, however, f plays a pivotal role. If f is much below 2, then an insufficient amount of Br^- is produced to remove HBrO_2 completely. In this case, the steady-state $[\text{HBrO}_2]$ is high and depends upon the competition between an autocatalytic cycle (reactions 5 and 6) and a second-order disproportionation reaction (4). When f is much above 2, then $[\text{Br}^-]$ is sufficient at all times that reaction 2 is important. This sink for HBrO_2 competes with an autocatalytic cycle (reactions 5 and 6). The result is a low steady-state $[\text{HBrO}_2]$. Chemical oscillations occur when f is near 2 because the dominant chemical mode alternates.

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About the Author

Professor Martin earned a B.S. in chemistry from Georgetown University (1991) and a Ph.D. in environmental/physical chemistry from Caltech (1995). He was supported by a Department of Defense National Defense Science and Engineering Graduate Fellowship. After his Ph.D., he completed postdoctoral work at MIT in atmospheric chemistry. During that time, he was supported by a National Oceanic and Atmospheric Administration postdoctoral fellowship in global climate change. He began as Assistant Professor of Aquatic and Atmospheric Chemistry at The University of North Carolina at Chapel Hill in January 1997. In 1998, he was awarded a CAREER grant from the National Science Foundation Atmospheric Chemistry Program, and in 1999 he received a Presidential Early Career Award for Scientists and Engineers (PECASE). He began as an Associate Professor of Environmental Chemistry at Harvard University in July 2000.

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