Oscillations, Patterns and Chaos in Deterministic Chemical Systems: an analysis of the Belousov-Zhabotinsky reaction

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Abstract

From the very onset of consciousness, humanity has always wondered about its origin. As we attempt to answer some of our deepest questions, we find that the natural world is very unpredictable, showing complex and erratic behavior. And within complexity, patterns too arise. I begin this project with a brief history about the non-linear dynamics of chemical systems and the dawn of patterns and chaos in them. Furthermore I analyze the mechanism, spatio-temporal patterns and the kinetics of the Belousov-Zhabotinsky reaction.

1 History

The natural world is really one great blooming, buzzing confusion. It is mess of quirky shapes and blotches. The patterns in it are never quite regular and never seem to repeat exactly. The idea that all this mayhem and chaos is underpinned and indeed determined by deep mathematical rules and that we can work out what those rules might be, once countered the most dearly held intuitions of all mainstream scientists.

So, not very surprisingly, the first man to take over the momentous task of unraveling nature's mysterious mathematics had an unusual mind. He was not only a scientist but also a tragic hero - Alan Turing. In 1952, he published a paper on morphogenesis[1] that describes mathematically, how a soup of identical cells with no central coordination, self-organize to form various patterns in different parts of the body. Turing's mathematical equations show that both pattern and chaos arise from very simple deterministic dynamical system with no inherent randomness.

Around the same time another bizarre discovery came from a war-soldier and a chemist from Russia - Boris Pavlovich Belousov. During his research on the Krebs cycle, he discovered that a solution of citric acid in water (with acidied bromate as oxidant and yellow ceric ions as catalyst) turned colorless and then back to yellow and oscillated for an hour while effervescing carbon dioxide. The study of oscillating reactions was born. In 1951, Belousov wrote a paper

[1]The differentiation of embryonic cells into tissues and organs

describing this reaction, but his article was rejected. During that time, chemists believed that oscillations in closed homogeneous systems were impossible because that would imply that the reaction did not go to thermodynamic equilibrium smoothly. Frustrated, the 64-year-old Belousov vowed never to publish again.
In 1961, a young graduate student at Moscow State University named A M Zhabotinsky, while working with Belousov's chemicals found out that, when a homogenous layer of the solution was left undisturbed, fascinating geometric patterns such as concentric circles and Archemedian spirals propagated across the medium. Over the years others scientists have worked on this and have simplified the original reaction.

2 Patterns

Patterns are regular repetitions of a sequence of distinct constituents over space or time. The constituents of patterns can be distinguished by a number of characteristics such as color, shape, size, arrangement, formation and design. In patterns, the constituents basically vary as follows:

1. variation over time at a fixed location
2. variation over space, independent of time
3. variation over both space and time[2]

3 The BZ reaction

The Belousov-Zhabotinsky reaction is a *non-equilibrium thermodynamic reaction*. The reaction remains far from thermodynamic equilibrium for significant time. The reaction proceeds through a very complex mechanism. And, the point of completion oscillates, due to variation in the concentration of an intermediate and its oxidation state. That is, as the reaction moves to one end point, the backward reaction is favored, and when the backward reaction nears completion, the forward reaction is favored. Hence it is an *oscillatory chemical reaction*. To be precise it is a *damped oscillator*.

The reaction has *self-catalytic* properties where the products of the forward reaction acts as catalysts which favor the backward reaction. It uses metal-ion catalyzed oxidation of an easily brominated organic substrate to make molecular bromine from bromate and bromide ions in a strongly acidic medium.

3.1 Chemicals and Apparatus Required

The chemicals required are given in Table 1. Apart from these, a surfactant like Triton X-100 would be required. The apparatus needed are a magnetic stirrer, conical flasks, beakers and petri dishes.

[2]Hence, they are called spatio-temporal patterns

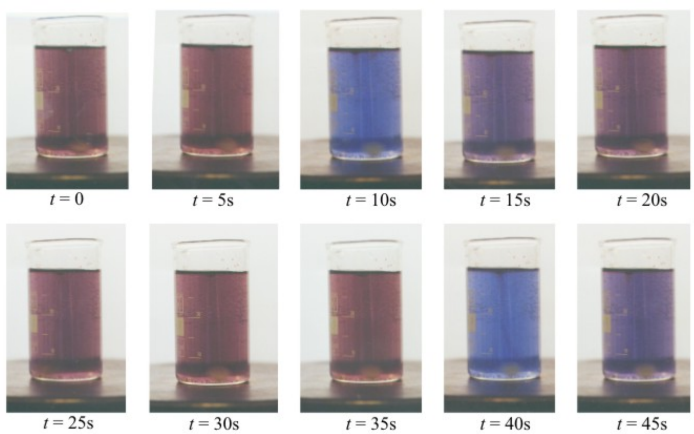
Table 1: Chemicals required

Species	Concentration
Potassium Bromate	0.3M
Potassium Bromide	0.3M
Malonic Acid	0.2M
Sulphuric Acid	0.3M
Ferroin Sulphate	0.005M

3.2 The Experiment and Observations

The original reaction by Belousov was performed in a conical flask and consisted of a solution of potassium bromate, citric acid, sulphuric acid and cerium(IV) sulphate. The ratio of concentration of the Ce^{4+} and Ce^{3+} ions oscillated, causing the color of the solution to oscillate between a yellow solution and a colorless solution. This is because the Ce^{4+} ions get reduced by citric acid to Ce^{3+} ions, which are then oxidized back to Ce^{4+} ions by bromate ions.

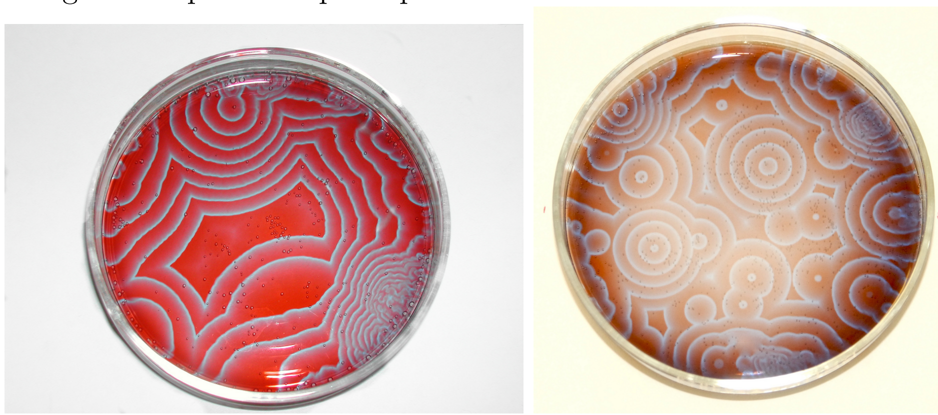
Figure 1: Oscillations observed in the BZ reactions



Zhabotinsky's version had a homogeneous layer of the solution (with contents in Table 1) spread out and left undisturbed in a petri dish. The initial red color of the solution, later began forming blue colored concentric circles and Archemedean spirals which propagated. The surfactant ensured the distribution of ions at a certain range throughout the solution. Otherwise, patterns wold not have formed.

The characterization of the BZ reaction is the change in color. The color change in the patterns formed vary over both space and time. Hence they are *spatio-temporal patterns*. A closer look at the patterns would reveal that the blue color waves, show a *destructive* type of interference. This is an important observation because most waves that we see, like ocean waves, are constructive and never destructive.

Figure 2: Spatio-temporal patterns observed in the BZ reactions



3.3 The Mechanism

The mechanism of this reaction requires the knowledge of *activators* and *inhibitors*. Activators and inhibitors co-exist in the same environment. The activators allow the growth of both themselves and that of the inhibitors. While inhibitors, as the name implies, inhibit the growth of the activators. Any growth in the activator results in a corresponding increase in the inhibitor, which in turn controls the increase of the activator.

The mechanism of the BZ reaction is very complicated: a recent improved model for the Ce^{4+}/Ce^{3+}-catalyzed reaction contains 80 elementary steps and 26 variable species concentrations. However, in a sequence of landmark papers, Field, Körös, and Noyes formulated a model for the most important parts of the kinetic mechanism that gives rise to oscillations in the BZ reaction. This is often referred to as the FKN mechanism and is summarized in Table 2.

Table 2: Elementary steps

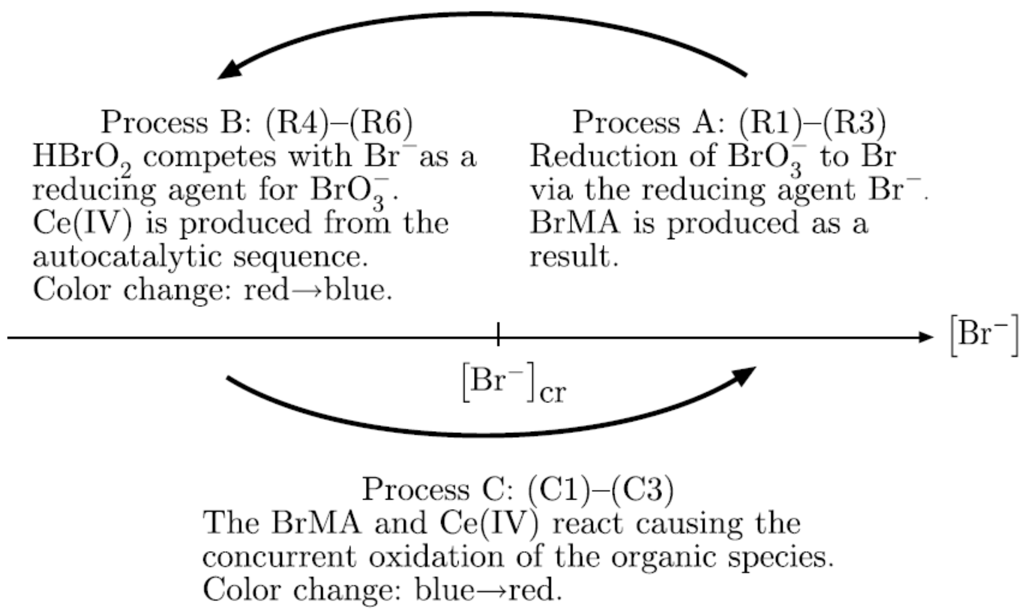
	Reaction
(R1)	$Br^- + HOBr + H^+ \rightarrow Br_2 + H_2O$
(R2)	$HBrO_2 + Br^- + H^+ \rightarrow 2HOBr$
(R3)	$BrO_3^- + Br^- + 2H^+ \rightarrow HBrO_2 + HOBr$
(R4)	$2HBrO_2 \rightarrow BrO_3^-$
(R5)	$BrO_3^- + HBrO_2 + H^+ \rightarrow 2Br\dot{O}_2 + H_2O$
(R6)	$Br\dot{O}_2 + Ce^{3+} + H^+ \rightarrow HBrO_2 + Ce^{4+}$
(C1)	$CH_2(COOH)_2 \rightleftharpoons (HO)_2C{=}CHCOOH$
(C2)	$(HO)_2C{=}CHCOOH + Br_2 \rightarrow BrCH(COOH)_2 + H^+ + Br^-$
(C3)	$10Ce^{4+} + CH_2(COOH)_2 + BrCH(COOH)_2 + 4H_2O$
	$\rightarrow 10Ce^{3+} + f Br^- + 11H^+ + 2HCOOH + 4CO_2$

The FKN mechanism for the BZ reaction can be described as three concurrent (and at times competing) processes.

- Process A: The three step reduction of bromate to bromine.
- Process B: The introduction of bromous acid to compete as a reducing agent for bromate.
- Process C: The reduction of the catalyst formed from Processes A and B.

In Process A, we have the reduction of bromate (BrO_3^-) to bromine (Br_2) by the reducing agent bromide (Br^-). This three-step process makes up (R1) to (R3). As a result, the bromate is reduced, bromomalonic acid (BrMA) is produced, and the concentration of bromide eventually falls below some critical level $[Br^-]_{cr}$. It is at this point that Process B begins to dominate Process A: the bromous acid ($HBrO_2$) begins to compete with the bromide to reduce the bromate. Reactions (R5) and (R6) constitute a two-step autocatalytic sequence. As a result, the amount of bromous acid increases at an accelerating rate and Ce^{4+} is produced. This causes the solution to change suddenly from red to blue (in the presence of a ferroin indicator).

Figure 3: Three subreactions which comprise the BZ reaction.



As Processes A and B cycle back and forth depending on whether $[Br^-]$ is above or below $[Br^-]_{cr}$, the products of these processes, BrMA and Ce^{4+},react. The concurrent oxidation of the organic species in (C3) reduces the cerium catalyst Ce^{4+} to Ce^{3+} causing a color change from blue to red (in the presence of a ferroin indicator). This change is gradual since there is no autocatalysis here. We are then back to Process A and the whole cycle repeats itself as outlined in Figure 3.

3.4 Chemical Kinetics

The mathematical analysis of the BZ reaction is done using the *Oregonator scheme.*The conventional notation used, is shown in Table 3.

Table 3: Notation

X = [$HBrO_2$]	(Bromous acid)
Y = [Br^-]	(Bromide)
Z = [Ce^{4+}]	(Cerium-IV)
A = [BrO_3^-]	(Bromate)
B = [Org]	(Organic species)
P = [HOBr]	(Hypobromous acid)

The Oregonator scheme is outlined in Table 4. Note the correspondence between the Oregonator scheme and the FKN mechanism in Table 4: (O1) is equivalent to reaction (R3); (O2) is equivalent to reaction (R2); (O4) is equivalent to reaction (R4); (O5) represents the organic species in Process C. The autocatalytic sequence is given by (R5) + 2(R6) and can be consolidated into the single reaction (O3).

Table 4: The Oregonator Scheme

	Reaction	Rate
O1	A + Y $\rightarrow$ X+ P	$k_3 = k_{R3}[H^+]^2AY$
O2	X + Y $\rightarrow$ 2P	$k_2 = k_{R2}[H^+]XY$
O3	A + X $\rightarrow$ 2X + 2Z	$k_5 = k_{R5}[H^+]5AX$
O4	2X $\rightarrow$ A + P	$k_4 = k_{R4}X^2$
O5	B + Z $\rightarrow \frac{1}{2}f$Y	k_0BZ

Our goal is to consolidate (O1) to (O5) into a corresponding system of rate equations. The Law of Mass Action is the tool we need here. It states that the rate of a reaction is proportional to the product of the reactant concentrations. Since a reaction may very well involve m molecules of one of the reactants, in this case the concentration of that reactant is raised to the mth power in the corresponding rate equation. See for several examples of how to write the rate equations for various systems. The Law of Mass Action yields the following rate equations for (O1)to(O5) as a 3 X 3 system of nonlinear ordinary differential equations.

$$\frac{dX}{dt} = k_3AY - k_2XY + k_5AX - 2k_4X^2,$$
$$\frac{dY}{dt} = -k_3AY - k_2XY + \frac{1}{2}fk_0BZ,$$
$$\frac{dZ}{dt} = 2k_5AX - k_0BZ.$$

On solving the differential equations we see that the concentrations, X, Y and Z actually oscillate in time.

3.5 Chaos

One of the defining features of *chaos*[3] in a deterministic dynamical system is its exponential sensitivity to initial condition. That is, the state of the system in ant given instant t depends on the initial state and an error in the initial state would amplify in time leading to bizarre results.

The BZ reaction is a deterministic chemical system that is chaotic, in the sense that, depending upon the initial concentration of the constituents, the patterns observed would be entirely different. This is because the rate equations for some elementary reactions are non-linear.

3.6 Thermodynamics

It is a common misconception that in such oscillating chemical reactions, the second law of thermodynamics is violated. The second law of thermodynamics,in simple terms, states that, the disorder or the entropy of a system and its surroundings must increase with time. However, it must be noted here that the BZ reaction is exothermic in nature and that the system and surroundings are taken into consideration in the second law of thermodynamics. The increase in the orderliness of the system, in most cases, is outweighed by an even greater increase in the disorder of the surroundings.

The thermodynamics of the reaction is again quite complex. This is based on the *Helmholtz Free Energy* which is a thermodynamic potential that measures the useful work done, which can be obtained from a closed system under constant volume and temperature. Mathematically, it is represented as,

$$F = U - TS$$

where, F is the Helmholtz Free Energy, U is the internal energy of the system, T is the temperature and S is the entropy. So, in order to minimize F, the value of S should be increased to greater positive values and that's precisely what happens during the reaction.

4 Conclusions

The Belousov-Zhabotinsky reaction is a classical chemical oscillator, which obeys non-linear rate equations and also exhibits chaos. During the course of studying this reaction other hybrid oscillatory reactions like, the Bray-Liebhafsky(BL) and the Briggs-Rausher(BR) have

[3]It is important to note that chaos and entropy are not the same. Entropy is the disorderliness in a system and depends on the number of degrees of freedom of its variables. But chaos the error amplification caused because the system is exponentially sensitive to initial conditions

come up. The complicated behavior of these reactions has been well studies and different mathematical models have been proposed. Hence, such oscillatory reactions are of great theoretical interest. Apart from this, the BZ reaction models some mysterious biological phenomena like morphogenesis. That is why it has been studied in the first place. It is now speculated that, patterns formed in a embryo during growth, that differentiates into tissue and organs, are due to chemical interactions like ones in the BZ reaction.

So, to conclude, the patterns observed in nature are simply beautiful, stunning and possess a grand and intricate design in them: the mysterious hand of chaos. The oscillatory reactions are a clock set by nature. Further examination would reveal some of truths of nature and pave way for a better understanding of it.

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