Oscillating Reactions: Two Analogies

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Abstract

Oscillating chemical reactions are truly spectacular phenomena, and demonstrations are always appreciated by the class. However, explaining such reactions to high school or first-year university students is problematic, because it may seem that no acceptable explanation is possible unless the students have profound knowledge of both physical chemistry and mathematics. Two analogies are therefore offered in the belief that they are useful aids for facilitating some basic understanding of oscillating chemical reactions but without any mention of somewhat technical terms like "systems far from equilibrium," "self-organization," or "consecutive chemical reactions," and with no use of calculus (differential equations).

Introduction

Oscillating chemical reactions have been known for more than 80 years. Bray (1921) first informed about this peculiar behaviour in the system containing an aqueous solution of KIO_3 and H_2O_2. According to Bray, the concentrations of iodine were subject to periodic changes, and were explained in line with Lotka's (1910) (hypothetical) mechanism based on autocatalysis. Other investigators of that period were suspicious about the very possibility of the existence of "periodic reactions" and tried to offer alternative explanations (Rice & Reiff, 1927).

It was not until 1950 that another chemist, Boris Belousov, rediscovered the phenomenon, although his chemical system was completely different. It was more complex, and was based on cerium sulfate, citric acid, sulfuric acid, and potassium bromate (Winfree, 1984). This time, editors of science journals were highly reluctant to publish the submitted manuscript and suggested the need for much additional work. It was even argued that such reactions would clearly violate the second law of thermodynamics (Scott, 1995). After several years of very hard work on the issue, and another refusal of the heavily-updated manuscript, Belousov gave up attempting to publish his unique results. The phenomenon was recognized, practically for the first time, through the publications of Zhabotinsky (see Zaikin & Zhabotinsky, 1970, and the references therein), both because a decent and detailed explanation was offered and the experimental results could be easily reproduced. The oscillating reaction became world-famous and known as the Belousov-Zhabotinsky (BZ) reaction (Zhabotinsky, 1991). It might be worth noting that apart from the mentioned temporal oscillations, spatial oscillations are also possible (Walker & Winfree, 1978).

From a purely educational point of view, the BZ reaction is indeed an easy-to-perform demonstration and definitely a very attractive one (Scott, 1995; Shakhashiri, 1985; Summerlin & Ealy, 1988). All that are needed is a few grams of malonic or citric acid, potassium bromate, manganese(II) sulfate or cerium(III) sulfate, and some dilute sulfuric acid. After preparation (see Appendix A for details), the class may enjoy no less than about 100 oscillations before the chemicals are exhausted. The system oscillates between two states; the one containing Mn(IV) is brown, while the other one, containing Mn(II), is colourless (Figure 1). To some high school or first-year university students, this may look like "a kind of magic."

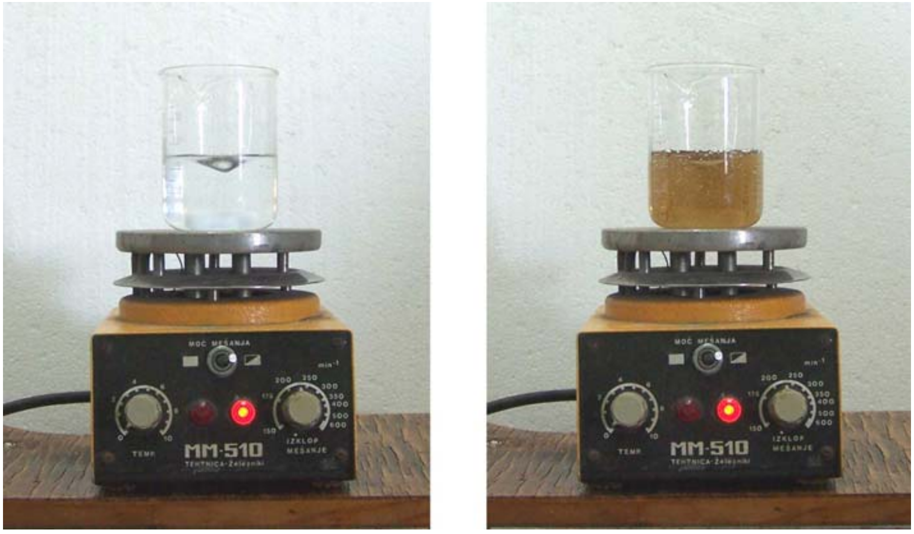

Figure 1. Colourless-to-brown oscillations of the system during the BZ reaction.

Chemistry, though, is not supposed to rely on magic; an explanation must be offered. From a pedagogical point of view, the explanation needs to be appropriate, meaning that it should be understood by the majority of the class. It might be simplified, but it must also be true. In thinking about this, we decided to offer the following two analogies.

Two Analogies

The instructor emphasizes that, in principle, in chemical reactions there exists some equilibrium mixture of reactants and products. Often, however, in the beginning only reactants are present in the system, and in the end only products remain. Such an "ordinary" reaction can be visualized by holding a sticky polymer ball 30–40 cm above a glass panel (or by using some alternative, non-bouncing combination of materials). The instant the instructor drops the ball denotes the start of the chemical reaction. When the ball reaches the glass panel and sticks to it (a fraction of a second after it was dropped), the instructor explains that the reaction has ceased. The practically instantaneous reaction of aqueous solutions of silver nitrate and sodium chloride is a good example.

The instructor further explains another type of reaction called a periodic, or oscillating, reaction. These reactions can be visualized by dropping a rubber ball, from the same height, onto a glass panel (or the floor) and noting that the ball oscillates up and down many times.

After this introduction, the instructor performs the Belousov–Zhabotinsky reaction (Summerlin & Ealy, 1988; Shakhashiri, 1985). Information is given about the chemicals used (e.g. malonic acid, $MnSO_4$, $KBrO_3$, and dilute H_2SO_4). After watching the reaction with the class for several minutes, one possible way to continue with the explanation is as follows:

> It is obvious that there are periodic changes in the system--the liquid in the beaker. Let us see, in a simplified way, what the role of each chemical is. Sulfuric acid is used to adjust the pH value (many reactions are possible only within a limited range of pH values). Potassium bromate is an oxidizing agent, and malonic acid is a reducing agent. Manganese sulfate is a catalyst. The catalyst oscillates between two states, the colourless Mn(II) and the brown Mn(IV).

The system is homogeneous (i.e., all constituents are in solution, in the same liquid phase). At the beginning of the experiment, the composition of the system is very simple (five compounds including water), but with time it becomes a rather complex one. In essence, the process taking place is a catalysed oxidation of malonic acid with potassium bromate. Since it is known that in a homogeneous system, the catalyst usually acts through formation of intermediate compounds, the brown Mn(IV) species might be identified as the intermediate. However, one still must answer the basic question: From where do the oscillations come?

To get an insight into what happens in the system, we can use a pendulum wall clock as an analogy. The wall clock is composed of a load, a pendulum, and some mechanism that enables the gravitational potential energy of the load to be transformed to the energy of the oscillating pendulum. In the case of our BZ reaction, the malonic acid–potassium bromate couple (the reactants) is equivalent to the load, the manganese (present as sulfate) catalyst acts as the pendulum, and the complex solution in the beaker is analogous to the mechanism that transforms the gravitational potential energy into energy of oscillations.

Note that the oscillations of the clock's pendulum all have the same period, while the period of the colour oscillations in the BZ reaction increases with time (with the oscillations eventually ceasing when the chemicals become exhausted). This is so because we have studied a closed system, in which the concentrations of malonic acid and potassium bromate are depleted. If we were to study the same reaction in an open system (allowing for the above concentrations to be kept constant by a continuous influx of fresh quantities of both chemicals), the BZ oscillations would also have a constant period. In this respect, the analogy with the bouncing rubber ball is an excellent one, as the energy dissipation in the case of the ball is analogous to the exhaustion of the chemicals.

When using analogies, one needs to be cautious not to extend too far the drawn conclusions. Analogies are only similarities. For a much deeper understanding of the issue, one needs a profound knowledge of both mathematics and the parts of physical chemistry called thermodynamics and chemical kinetics.

Advantages and Disadvantages of the Analogies

From our experience, this approach is a useful one for achieving a low-level understanding of the phenomenon. On a few occasions, it has proven to be a very stimulating one indeed, with several students claiming later to have decided to graduate in this field owing to the demonstration performed and the explanations offered.

The analogies provide a somewhat simplified explanation, which is why the instructor must warn the students not to make far-reaching conclusions. Instructors also often rely on a simplified approach to start lessons on the structure of the atom, for example, with first-year students. However, it is important to note that when something is oversimplified, this limitation must be pointed out in order to avoid the development of potential misconceptions.

Numerous studies (e.g., Harrison & de Jong, 2005; Orgill & Bodner, 2004; Treagust, Harrison, & Venville, 1998) have shown the usefulness of the use of analogies, stressing both their positive and negative sides. Analogies are sometimes referred to as a "two-edged sword." They help students to understand difficult scientific concepts, but if not used properly they can generate alternative conceptions. When multiple analogies are used (as in our case), the likes are strengthened and the unlikes, as a rule, weakened (as there is considerably less chance that both

analogies used would lead to the same faulty conclusion). Appendix B contains a guide to help those who may decide to adopt the offered analogies and incorporate them as a tool while teaching oscillating reactions to high school or first-year university students. For those curious about the nature of the chemical changes in the system and eager to learn more of the chemistry that is behind the demonstration, the complete set of chemical equations leading to the BZ oscillating reaction is given in Appendix C.

One reviewer of the original manuscript pointed to another excellent analogy; a ball bouncing down a stair-case! In this case, each bounce brings the ball closer to the final state of rest, as in the chemical system. (One fault of both the proposed bouncing ball and the pendulum is that they pass through the equilibrium point, whereas the system subject to an oscillating reaction never passes through equilibrium.)

Acknowledgements

The authors wish to thank reviewers Richard K. Coll and Giacomo Torzo for the many valuable suggestions that have increased the quality of this paper.

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Appendix A

Experimental Procedure for the BZ Reaction

Needed. 200 mL dilute (1 mol/L) sulfuric acid, 5 g solid $KBrO_3$, 4 g solid malonic acid, and 0.5 g $MnSO_4{\cdot}H_2O$.

First, the beaker containing the dilute sulfuric acid is placed on an electromagnetic stirrer and the $KBrO_3$ and malonic acid are dissolved in the acid. Once these are completely dissolved (the dissolution of $KBrO_3$ may take some 5 minutes), the manganese salt is added. The solution immediately turns brown and soon (after about 1 minute--the so-called "induction period") begins to oscillate.

Safety hazard and disposal. Sulfuric acid is a highly corrosive chemical. When performing the demonstration, safety goggles should be worn at all times. Small quantities of dilute sulfuric acid can be flushed down the sink with a large volume of water.

Appendix B

A Guide for Teaching With the Analogies

FOCUS	**Concept**	Periodic or oscillating reactions. These may occur even in simple reaction systems and result from a series of consecutive autocatalytic reactions. The precondition is that the system is far from equilibrium, in the thermodynamic sense of the word. The changes in the composition can often be monitored visually.
	Students	Students (even those of first-year university level) are not prepared to understand the mechanism of periodic reactions, due to a lack of knowledge in both calculus and physical chemistry. They are familiar with the properties of both sticky and elastic polymer balls, and do understand the way a wall clock works, including the transformation of gravitational potential energy into oscillatory motion of the pendulum.
	Analogy 1	A sticky polymer ball is used to demonstrate the reactants (ball held in hand) and products (ball dropped on a glass surface) in an ordinary chemical reaction. An elastic rubber ball dropped on the same surface goes up and down many times, resembling an oscillating reaction.
	Analogy 2	A wall clock with a pendulum is used to demonstrate the oscillations in a chemical system. The left-to-right periodic oscillations resemble the brown-to-clear color changes during an oscillating reaction.
ACTION	**LIKES - Mapping the analogy to the target**	
	Analogy 1: Sticky & elastic balls	**Target: Periodic reactions (closed system)**
	Sticky ball held in hand	Reactants: $NaCl(aq)$ and $AgNO_3(aq)$
	Sticky ball falling (fast process)	Reaction (instantaneous)
	Sticky ball dropped on glass surface	Products: $NaNO_3(aq)$ and $AgCl(s)$
	Elastic ball held in hand	Reactants: $KBrO_3$ and malonic acid
	Elastic ball bouncing	Oscillating reaction
	Ball up	Mn^{2+}
	Ball down	Mn^{4+}
	The ball itself	Catalyst (manganese)
	Ball at rest	Chemicals exhausted (oscillations cease)
	UNLIKES - Where the analogy breaks down	
	• The bouncing ball touches the ground (equilibrium position), unlike the oscillating reactions that never pass through equilibrium.	
	• The period between successive bounces of the ball decreases (a consequence of energy dissipations). The period of an oscillating reaction (in a closed system) increases (a consequence of decreasing concentration of reactants).	
	LIKES - Mapping the analogy to the target	
	Analogy 2: Wall clock	**Target: Periodic reactions (closed system)**
	Pendulum oscillates	Oscillating chemical reaction
	The pendulum itself	Catalyst (manganese)
	Pendulum left/pendulum right	Colour of medium: Colourless/brown
	Pendulum left/pendulum right	Mn^{2+}/Mn^{4+}
	Load	Reactants: $KBrO_3$ and malonic acid
	Load is up	High concentration of reactants
	Load is down	Low concentration of reactants
	Load touches the ground	Chemicals exhausted (oscillations cease)

UNLIKES - Where the analogy breaks down
• The pendulum of the wall-clock passes through equilibrium point, unlike the oscillating reactions that never pass through equilibrium. • Pendulum moves symmetrically. No symmetry exists in the colour change. • The clock pendulum has a constant period. The period of an oscillating reaction (in a closed system) increases (a consequence of decreasing concentration of reactants).

Appendix C

Chemical Reactions for the BZ Oscillations

The system, which is initially composed of a few chemical constituents only (i.e., $KBrO_3$, H_2SO_4, $MnSO_4$, malonic acid, and water), evolves with time. The following chemical equations represent the 18 steps in the BZ reaction (Petruševski & Najdoski, 2000). The hydrated proton is consistently written as H_3O^+.

1. $2H_3O^+ + Br^- + BrO_3^- \rightleftharpoons HOBr + HBrO_2 + 2H_2O$
2. $H_3O^+ + HBrO_2 + Br^- \rightleftharpoons 2HOBr + H_2O$
3. $HOBr + Br^- + H_3O^+ \rightleftharpoons Br_2 + 2H_2O$
4. $CH_2(COOH)_2 \rightleftharpoons (OH)_2C{=}CHCOOH$
5. $Br_2 + H_2O + (OH)_2C{=}CHCOOH \rightleftharpoons H_3O^+ + Br^- + CHBr(COOH)_2$
6. $HBrO_2 + BrO_3^- + H_3O^+ \rightleftharpoons 2BrO_2 + 2H_2O$
7. $2BrO_2 + Mn^{2+} + 2H_3O^+ \rightleftharpoons Mn^{4+} + 2HBrO_2 + 2H_2O$
8. $Mn^{4+} + 2BrO_2 + 6H_2O \rightleftharpoons 2BrO_3^- + Mn^{2+} + 4H_3O^+$
9. $2HBrO_2 + H_2O \rightleftharpoons HOBr + BrO_3^- + H_3O^+$
10. $Mn^{4+} + 2H_2O + 2CH_2(COOH)_2 \rightleftharpoons 2CH(COOH)_2 + Mn^{2+} + 2H_3O^+$
11. $CH(COOH)_2 + CHBr(COOH)_2 + 2H_2O \rightleftharpoons Br^- + CH_2(COOH)_2 + HOC(COOH)_2 + H_3O^+$
12. $Mn^{4+} + 6H_2O + 2CHBr(COOH)_2 \rightleftharpoons 2Br^- + 2HOC(COOH)_2 + Mn^{2+} + 4H_3O^+$
13. $2HOC(COOH)_2 \rightleftharpoons HOCH(COOH)_2 + O{=}CHCOOH + CO_2$
14. $Mn^{4+} + 2HOCH(COOH)_2 + 2H_2O \rightleftharpoons 2HOC(COOH)_2 + Mn^{2+} + 2H_3O^+$
15. $Mn^{4+} + 2O{=}CHCOOH + 2H_2O \rightleftharpoons 2O{=}CCOOH + Mn^{2+} + 2H_3O^+$
16. $2O{=}CCOOH + H_2O \rightleftharpoons O{=}CHCOOH + HCOOH + CO_2$
17. $Br_2 + HCOOH + 2H_2O \rightleftharpoons 2Br^- + CO_2 + 2H_3O^+$
18. $2CH(COOH)_2 + H_2O \rightleftharpoons CH_2(COOH)_2 + HOCH(COOH)_2$

Readers' Forum

The Investigation Question: The Key to Successful Inquiry-Based Science?

When trying to teach using an inquiry approach, we often find that teachers and student teachers run into considerable difficulty because of the lack of a clear, single question that students are to answer. As a result, the rest of the inquiry process falls apart. We believe that often teachers confuse the making of an investigation question with the general questioning used in class, a problem confounded by textbooks, and see the need for an increased emphasis to be placed on developing appropriate investigation questions.

It is important to identify what makes a good investigation question and what doesn't. An investigation question should aim to answer one specific, easily answered question. There is no value in having students trying to answer questions by needing to discover general theories such as natural selection or relativity!