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THEN & NOW

Chaos and beauty in a beaker: The early history of the Belousov-Zhabotinsky reaction**

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Discovered in 1950 by Belousov in the Soviet Union and further investigated by Zhabotinsky and his research group in the 1960s, the Belousov-Zhabotinsky reaction soon came to the wider attention of scientists on both sides of the Iron Curtain and made an important contribution to consolidating Prigogine's theory of nonequilibrium thermodynamics. Allowing scientists to study chaotic behavior in the laboratory, it also paved the way for further investigations of self-organizing systems in biology and played an important part in the formation of the field of nonlinear science. Focusing on the period between 1950 and 1975, this paper explores the early history of this enigmatic reaction.

Figure 1 Boris P. Belousov around 1930 (private collection of Prof Simon E. Shnoll).[1]

Introduction

When investigating the reaction mechanism of the citric acid cycle at Moscow's All-Union Institute of Sanitation and Chemistry in 1950, Soviet scientist Boris P. Belousov (Fig. 1) discovered a chemical solution capable of oscillations in the form of periodic color changes in time. The reaction was further investigated by Anatoly M. Zhabotinsky (Fig. 2) and his research group in the 1960s. During the 1970s, the Belousov-Zhabotinsky reaction (BZ reaction hereafter) came to the wider attention of scientists on both sides of the Iron Curtain. Through the combined efforts of various research groups across the globe, the reaction's mechanism and kinetic properties were gradually uncovered and explained. While Soviet scientists had been well aware of the origins and early history of the BZ reaction since the 1960s, researchers outside the Soviet Union began to learn more about the rich history of Belousov's discovery only during the 1980s [1].

The Belousov-Zhabotinsky reaction

The Belousov-Zhabotinsky reaction is described as an autocatalytic oxidation of an organic acid (originally

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[1] Also available in the public domain at https://commons.wikimedia.org/wiki/File:Boris_Pavlovich_Belousov_2.jpg.

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Figure 2 Anatoly M. Zhabotinsky, Rostock 1977 (Courtesy of Prof Werner Ebeling).

Figure 3 Target patterns in a petri dish. Image by Prof Stephen W. Morris.[2]

malonic acid) by potassium bromate. Oscillations can be generated by means of different experimental conditions and reagents, such as the use of cerium or manganese ions or ferroin as catalysts. When performed in a stirred container, the solution will exhibit a periodic change of color (temporal oscillations). The use of ferroin yields the most impressive color changes (bright red and blue). The reaction is also capable of pattern formation in space and time when performed in a shallow petri dish filled with a thin layer of unstirred BZ reagent. Two types of colored oxidation waves will appear around pacemakers and propagate through the medium at a constant velocity (spatiotemporal oscillations). While waves of the first type, known as target patterns, will form concentric rings expanding away from the pacemaker (Fig. 3), second-type spiral waves will rotate around their center and exhibit a dynamic pattern. It is known today that the BZ reaction comprises a multitude of individual reactions, and that its behavior is subject to the principles of nonlinear kinetics due to complex feedback mechanisms. To date, more than eighty elementary reactions have been identified [2]. A standard composition of reagents (potassium bromate, malonic acid and sulphuric acid) was introduced by Richard J. Field, Endre Körös and Richard M. Noyes in 1972 [3].

Today, it is well established that chemical oscillations in closed systems can only occur far from the thermodynamic equilibrium for a limited period of time. In an open system, sustained oscillations will appear in certain thermodynamically stable states far from the equilibrium if a continuous inflow of reagents and an outflow of reaction products is provided. This behavior is explained by the laws of nonequilibrium thermodynamics, elaborated by Ilya Prigogine, Grégoire Nicolis, Paul Glansdorff and other members of the Brussels School of thermodynamics over the course of the 1950s and 1960s. Yet when the reaction was first discovered in the early 1950s, this knowledge did not belong to the scientific mainstream. It was only by the mid-1970s that a full theoretical understanding of the reaction's thermodynamic and kinetic properties was finally achieved.

History of the Belousov-Zhabotinsky reaction, 1950–1975

Boris Belousov was not the first scientist to investigate oscillatory phenomena in chemical systems. Gustav T. Fechner's description of an electrochemical cell producing an oscillating current was published in 1828, and Raphael E. Liesegang's discovery of his "Liesegang Rings" appeared in 1896. Wilhelm Ostwald studied electrochemical oscillations during the late 1890s and early 1900s, and Georg Bredig published his observations of the catalytic decomposition of hydrogen peroxide in 1903 [4]. Alfred J. Lotka and William Bray are often named as Belousov's immediate precursors [5]. Lotka proposed several kinetic models of an idealized chemical oscillation in homogeneous phase [6]. Lotka's models were received by William Bray, who discovered the first genuine oscillatory reaction in homogeneous phase in 1921 [7], later known as the "Bray-Liebhafsky reaction". Yet Bray's interpretation of his discovery was challenged by many of his contemporaries and thus had little impact on the

[2] Belousov–Zhabotinsky reaction, © Stephen W. Morris, published at www.flickr.com/photos/nonlin/4297013382 under CC BY 2.0 License, creativecommons.org/licenses/by/2.0.

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scientific world of his time [8]. It was only in the 1960s that oscillatory chemical reactions came to the attention of scientists again.

Historical sources on Belousov's career are extremely scarce. Belousov was born in Moscow in 1893, but moved to Switzerland with his parents in 1908. He trained as a chemist at ETH Zurich and graduated in 1915, albeit without obtaining a formal diploma. He returned to Moscow in 1916 and began a career as a chemistry teacher. From the early 1920s onwards, Belousov was employed both as a teacher and researcher with military institutions such as the Higher Military Chemical School and the School for Advanced Training of Officers of the Red Army. In 1935, Belousov became senior researcher at the All-Union Institute of Sanitation and Chemistry. During the Great Patriotic War (1941–1945), he was working on projects in radiation and chemical warfare protection. Through his investigation of methods to remove toxic agents from the human body, Belousov developed a strong interest in the role of biochemical cycles within living organisms. After the war, part of Belousov's work included the reaction mechanism of the citric acid cycle (also known as Krebs cycle). It was eventually in connection with this research that Belousov made the accidental discovery of periodic concentration oscillations in 1950. Towards the end of his working life, Belousov directed several other research projects in radiation protection at the Institute of Biophysics of the USSR Ministry of Health (formed in 1952) until his retirement in 1966. He died on 12 June 1970 in Moscow [9].

While trying to recreate the autocatalytic processes of the Krebs cycle in his laboratory in 1950, Belousov observed that a solution of citric acid in water, bromate and cerium ions displayed periodic color changes which continued for almost an hour. After some theoretical reflection on the reaction's mechanisms, Belousov submitted a short paper to the Soviet periodical *Zhurnal obshchey khimii (Journal of General Chemistry)* in 1951. However, his article was almost instantly rejected on the grounds that the suggested mechanism contradicted the Second Law of Thermodynamics. Apparently, the editors stated that Belousov's discovery was theoretically impossible and would be published only if he could prove that the existing theory was flawed. Having intensified his research and revised his first paper, Belousov attempted a second submission to the journal *Kinetika i kataliz (Kinetics and Catalysis)* in 1955, but was rejected again for the same reason [10]. It was only in 1958 that a strongly abbreviated paper under Belousov's name appeared in an edited volume titled *Collection of Abstracts on Radiation Medicine* [11]. Due to the publication's unfavorable publicity, however, the report went mostly unnoticed and Belousov's discovery was soon forgotten. It was only three years after the publication of this report that Anatoly Zhabotinsky, a young and aspiring biophysicist, became finally aware of the reaction's scientific importance.

After graduating from the Physics Institute of the Moscow State University with a degree in biophysics in 1961, young Zhabotinsky decided to do a postgraduate research degree on biorhythms, the periodic processes in living organisms [12]. When looking for a suitable research project, Zhabotinsky was recommended to investigate Belousov's reaction by his supervisor Simon E. Shnoll, professor of biochemistry at Moscow State University and one of the few scientists familiar with Belousov's previous work at that time [13]. During his postgraduate years, Zhabotinsky was employed at a cancer research institute of the All-Union Institute of Experimental Medicine in Moscow, where he could find enough spare time to pursue his research project as Shnoll's doctoral student. During the period 1961–1964, Zhabotinsky focused on deciphering the reaction's mechanism by trying to identify those elementary reactions which constituted the system's complex chemical behavior. By 1964, the young researcher had cleared up the reaction scheme of the system's first oscillatory cycle. In addition, Zhabotinsky improved Belousov's original recipe by replacing the citric acid with malonic acid. Unlike Belousov, however, Zhabotinsky was not faced with any difficulties when publishing two papers with his preliminary results in 1964. A possible explanation of this surprising turn was recently put forward by the historian of Soviet science István Hargittai: unlike Belousov, Zhabotinsky did not publish his results in a chemical or physical journal, but opted for a biological periodical and the interdisciplinary *Proceedings of the USSR Academy of Sciences* (*Doklady Akademii Nauk SSSR*) [14]. Hargittai claims that the editors of these journals were much less concerned with the thermodynamic consequences of Zhabotinsky's reaction scheme than the editors of *Zhurnal obshchey khimii* and *Kinetika i kataliz* in Belousov's case [15].

After being awarded his PhD diploma (degree of "kandidat nauk"), Zhabotinsky managed to secure a position as a junior research associate at the Institute of Biophysics of the USSR Academy of Sciences in Pushchino in 1964. Other young researchers such as Albert Zaikin, Genrikh Ivanitsky, and Valentin Krinskym joined Zhabotinsky at the Institute in the same year, thus forming a highly productive interdisciplinary research group consisting of mathematicians, biophysicists and biochemists. Between 1964 and 1967, their research focused on detailed experimental studies of the reaction rates of elementary reactions and the chemical processes of self-sustained propagations of chemical waves. The group was also able to provide the long-expected experimental proof that the reaction takes place in a chemically homogeneous phase, and that chemical self-oscillations can occur in a closed homogeneous system [16]. The work of Zhabotinsky's research group culminated in a first pan-Soviet conference on chemical and biological oscillators in Pushchino in 1966 [17]. Yet until the late 1960s, very few scientists outside of the Soviet Union had been aware of these results. It was only at the first international conference on biological and biochemical oscillators held in Prague from 19th to 21st of July 1968 that Soviet research on oscillatory reactions came to the attention of scientists from the other side of the Iron Curtain [18].

Oscillatory reactions in homogeneous phase were also investigated in the United States during the early 1960s. Occurring simultaneously to Soviet investigations of the BZ system, Britton Chance and his co-workers Joseph Higgins, Amal Ghosh, and E. Kendall Pye, among others, were undertaking research on self-sustained oscillations of the glycolytic pathway at University of Pennsylvania's School of Medicine. The reaction was discovered in Philadelphia in 1964, and is described as an oscillatory process taking place in the glycolytic enzyme system [19]. This reaction forms a substantial part of the metabolism of every living cell and is accountable for the decomposition of long-chain glucose molecules into smaller pyruvic acid molecules. Most of the research work between the mid-1960s and the early-1970s was spent on determining the feedback mechanisms which generated oscillatory behavior. Yet again, it was only during the conference in Prague that Soviet and American research groups learned about each other.

In the years following the Prague conference, a dramatic rise in research activity took place as new collaborations and major research groups were established in USA, Germany, Hungary, India, and Switzerland to study the BZ system or to research new reactions in chemistry and biochemistry [20]. Investigation of oscillatory chemical reactions in the United States was led by Irving R. Epstein at Brandeis University, where Arthur T. Winfree and Steven Jacobs were among the first members of the growing research group. Epstein's Nonlinear Dynamic Group at Brandeis continues to produce pioneering research in nonlinear chemistry to the present day. In Germany, rigorous experimental studies of the BZ reaction were performed by Lothar Bornmann, Heinrich Busse, and Benno Hess at the Max-Planck-Institut für Ernährungsphysiologie in Dortmund [21]. In Hungary, two separate research groups engaged in further investigations of the BZ mechanism and its kinetic properties, with a large collective established by Körös at the Institute of Inorganic and Analytical Chemistry of Eötvös Loránd University in Budapest [22], and a smaller group formed by Mihály T. Beck and Zoltan Váradi at the Institute of Physical Chemistry of Lajos Kossuth University in Debrecen [23]. Using the data from their researches, both groups also sought to create entirely new oscillatory reactions. New variants of the BZ reaction were also investigated in India by Raghunath P. Rastogi and K. D. S. Yadava at Gorakhpur University and J. Sreekantha Babu and Kotra Srinivasulu at Vikram University in Ujjain, as well as by Désimir Janjic, Philippe Stroot, and Ulrich Burger at the University of Geneva in Switzerland [24]. Lothar Kuhnert and Hartmut Linde were able to develop a new oscillatory chemical reaction in a solution of aryldiazonium salt, bromate and sulphuric acid at the Zentralinstitut für Physikalische Chemie (ZIPC) of the GDR Academy of Sciences in 1977 [25]. Altogether, the 1970s witnessed major advances in the field of self-organizing systems. The Continuous Flow Stirred-Tank Reactor (CSTR) came into wide use by 1975. This piece of equipment constitutes a container with a continuous inflow of reagents and a drainage of reaction products, thus establishing a permanent and adjustable exchange of matter. In addition, the technology allows for the precise control of such experimental conditions as temperature and pressure of the reaction. Patrick De Kepper, Kenneth Kustin, and Irving Epstein were among the first researchers to employ the CSTR technology for the systematic development of new oscillatory chemical reactions during the late 1970s and early 1980s [26]. It has been already mentioned that a comprehensive reaction mechanism of the entire BZ system was for the first time described by Field, Körös, and Noyes in 1972. Field and Noyes also suggested an accurate kinetic model of the BZ reaction, known as the "Oregonator", in 1974 [27]. While a similar model had been developed by the Brussels School in 1967, it was not based on empirical evidence. Instead, the so-called "Brusselator" was meant to simulate nonlinear behavior of a hypothetical periodic reaction according to the principles of nonequilibrium thermodynamics [28]. In contrast, the "Oregonator" combined the existing model of the Brussels school with the most recent results from experimental research. By the mid-1970s, a comprehensive understanding of the BZ reaction was finally achieved.

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Conclusions

The Belousov-Zhabotinsky reaction represents the first chemical system whose complex nonlinear behavior was sufficiently explained in experimental and theoretical terms. In retrospect, we can see that the BZ reaction played an essential role in the development and consolidation of the theory of nonequilibrium thermodynamics by Ilya Prigogine and members of the Brussels Schools of Thermodynamics during the late 1960s and early 1970s. Prigogine and his colleagues later stated on several occasions that the BZ reaction was the very first piece of empirical evidence for their thermodynamic hypotheses [29]. In addition, the study of self-organization processes and spatial effects in the BZ system resulted in a deeper theoretical understanding of nonlinear processes in biological systems of a much higher degree of complexity, as well as providing significant insights into the thermodynamics of evolution. Self-organization and nonlinear behavior of chemical, biological, sociological, and economic systems remain important research subjects until today.

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