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Let's make a chemical clock

Info sheet 1: Some historical notes

The discovery of chemical clocks involved many unusual circumstances.[1,2] Chemists were initially sceptical about the existence of oscillatory phenomena, considering them inconsistent with the second law of thermodynamics. However, empirical evidence has been accumulated, especially regarding intermediates and catalysts in biochemical systems. Ilya Prigogine (1917–2003), winner of the 1977 Nobel Prize in Chemistry, succeeded in demonstrating that such behaviours are possible for systems far from equilibrium. To understand the concept of deviation from equilibrium, it can help to compare the oscillatory mechanism of a chemical reaction with the way a beer mug oscillates before it falls. Once it falls, the spillage of beer corresponds to the achievement of a stable state, and similarly, the reaction reaches stability (i.e., equilibrium) when the products are formed. A beer mug that doesn't oscillate before falling corresponds to a classic chemical reaction, in which the products are formed from the reactants without undergoing the autocatalytic and/or self-inhibitory mechanisms that cause intermediate oscillations (figure 1).

Figure 1: Chemical oscillators can be compared to a beer mug that oscillates before falling. AI-generated with Google Gemini

In the 1950s, Soviet chemist Boris Pavlovich Belousov (1893–1970) became interested in oscillatory reactions while studying the Krebs cycle, the heart of cellular metabolism. His articles were repeatedly rejected by scientific journals. After several failed publication attempts, Belousov abandoned his research.

However, the procedure for developing the oscillatory reaction that he discovered was circulated among universities in Soviet Russia. In 1961, it was used by a young biophysicist named Anatol Markovich Zhabotinsky (1938-2008).

During an interview, Zhabotinsky stated:

"...my main research interest was not to study clock reactions per se, but rather to use them to model analogous biological processes. The topic that most attracted me was the propagation of excitation waves in the heart. Everyone knows that normal heart function is controlled by very long excitation waves propagating from the sinoatrial node. There was [...] a theory that attributed the most harmful cardiac arrhythmias to the onset of short spiral excitation waves in the myocardium. Few believed this theory. We began to study chemical waves in thin layers of oscillating mixtures and observed the formation of spiral waves similar to those that would arise in the myocardium."

In his first paper, published in 1962, Zhabotinsky reproduced Belousov's results (who had meanwhile sent him his unpublished manuscripts) and made some experimental modifications, clarifying some steps in the mechanism of what has since been referred to as the 'Belousov-Zhabotinsky reaction', or simply the 'BZ reaction'.

Zhabotinsky kept Belousov constantly informed about his research progress through correspondence. Despite Zhabotinsky's repeated attempts to arrange a meeting, the two never spoke in person; they communicated only by letter (Belousov always declined, offering various excuses).

Although the BZ reaction is the best-known and most studied oscillating reaction, the first evidence of oscillating chemical systems dates back to 1921, when the American chemists W. C. Bray and A. L. Caulkins studied the dual role of hydrogen peroxide in both oxidizing iodine to iodate ion and reducing iodate ion to iodine.

The dual function of hydrogen peroxide is evident in the following reactions:

$5\ H_2O_2 + I_2 \rightarrow 2\ IO_3^- + 2H^+ + 4\ H_2O$ (1)

$5\ H_2O_2 + 2\ IO_3^- + 2H^+ \rightarrow I_2 + 5O_2 + 6\ H_2O$ (2)

These reactions were examined with the aim of finding a catalyst for the decomposition of hydrogen peroxide:

$H_2O_2 \rightarrow H_2O + ½\ O_2$ (3)

Note that the sum of reactions (1) and (2) is 10 times that of (3). In short, it was found that reaction (1) was very fast and autocatalytic. it was evident that the reaction proceeded particularly quickly in the presence of iodate and hydrogen ions. Reaction (2), in contrast, proceeded relatively slowly even under conditions favourable to increasing the rate. Furthermore, in every tested reaction condition, more hydrogen peroxide disappeared than could be explained by reactions (1) and (2), proving that these must have been accompanied by the catalytic decomposition of hydrogen peroxide via reaction (3).

Studying these reactions, the chemists realised that the concentration of molecular iodine was oscillating, as demonstrated by the following photo from Bray's original work:

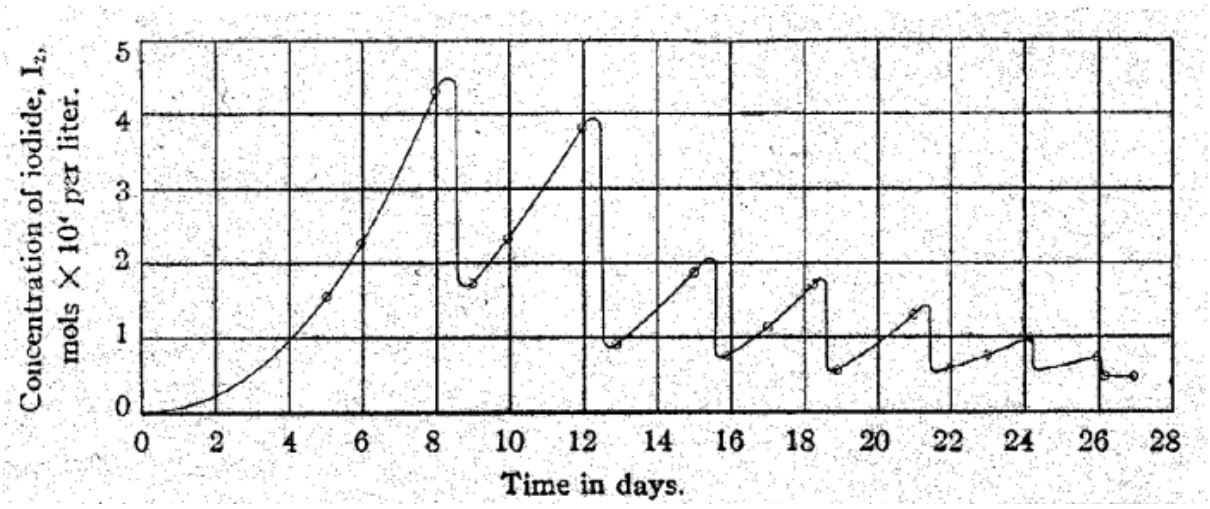

Figure 2: Trend of I_2 concentration (mol· L^{-1} x 10^4) over time (days). Image taken from Ref. [3]

The mechanism of the hydrogen peroxide decomposition reaction, which is very complex, was only clarified in the 1970s. Meanwhile, other chemical clocks have been realised in the laboratories or discovered in nature.

As for the alleged disagreement with the second law of thermodynamics (one of the reasons why Belousov's papers were not accepted by scientific journals), it has been shown that it is only apparent. The initially disputed decrease in entropy only occurs during certain oscillatory mechanisms. In other related mechanisms, the opposite occurs, resulting in an overall increase in entropy.

Reference

[1] Cervellati R (1999) Preistoria e storia delle reazioni chimiche oscillanti. *Chim. Sc.* **2**: 40-46. ISSN: 0392-5912

[2] Cervellati, R. (2009) Anatol M. Zhabotinsky. *Chim. Nella Scuola* **31**: 1-2.

[3] Bray WC (1921) A Periodic Reaction in Homogeneous Solution and its Relation to Catalysis. *J. Am. Chem. Soc.* **43**: 1262-1267. doi: 10.1021/ja01439a007