SHILLY-SHALLY SOLUTIONS

Researchers report the first systematically, deliberately designed family of oscillating chemical systems

BY LINDA GARMON

Brown, then clear, then brown, then clear. Normally when several chemicals are thoroughly mixed, the mixture achieves a single, uniform color. But the solution in this beaker can't seem to make up its mind: It keeps changing color from brown to clear and back again. It's the sort of thing that belongs in a believe-it-or-not museum of chemistry. It is an oscillating chemical system, and its designers — Irving R. Epstein and colleagues of Brandeis University in Waltham, Mass.—say it is the first systematically, deliberately developed system of its kind.

Epstein and colleagues began at the drawing board where they listed as many factors as they could theorize might be necessary for a chemical solution to display a fascinating oscillation of color. The Brandeis researchers then set out to engineer one system — reported in the April 22 JOURNAL OF THE AMERICAN CHEMICAL SOCIETY — and later a whole family of oscillators — described in the Aug. 27 NATURE — based on their list of criteria. This attempt is a milestone in the history of chemical systems that oscillate: Previous systems have been loans from nature, only modifications of those known biological systems or serendipitous discoveries.

One of the most famous of the fortuitous finds was a colorless-to-yellow oscillation stumbled upon in 1958 by the Russian chemist B.P. Belousov. Later, drawing on some fundamental oscillation research conducted by Richard C. Thompson of the University of Missouri at Columbia, Richard M. Noyes of the University of Oregon at Eugene — one of the oscillation field's founding fathers — detailed the chemical reactions responsible for the Belousov oscillation. Arthur T. Winfree of Purdue University in Lafayette, Ind., then got into the oscillating act by modifying this same system to obtain a solution whose color rhythmically swings between red and blue.

As is true for all chemical oscillators, the oscillating colors in Winfree's system represent the dramatic rise and fall of the concentrations of at least one of the system's components. In this particular case, the concentrations of ferrous (red) and ferric (blue) dye oscillate; the original Belousov reaction involves a ceric-cerium oscillation; and the Brandeis solution swings between high (brown) and low (clear) concentrations of iodine.

And therein lies the fascination of these systems: They swing back and forth and back and forth, instead of smoothly proceeding to some end point that has been predetermined on the basis of thermodynamic laws. "These are very counter-intuitive types of systems," says Epstein. "Chemists have been trained to expect systems to approach equilibrium without detours along the way. These systems run very much counter to that." As a result, "Idle curiosity is probably what attracts most people to the field," Epstein says.

But the significance of chemical systems that oscillate extends far beyond their ability to wow chemists. "These systems that we look at are simplified models, in a sense, of the temporal behavior of a lot of biological systems," Epstein explains. "They are analogs of all kinds of processes in living systems — heart beat, circadian rhythms ... even leaves turning color on trees and menstrual periods," he says.

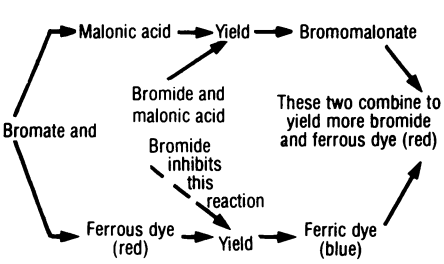
To ensure that their system would more closely parallel such natural processes, Epstein and colleagues decided to conduct their experiments in a continuous flow stirred tank reactor (CSTR) that "pumps in unreacted chemicals and takes out reacted stuff." (Without the help of a CSTR, chemical oscillators eventually reach an equilibrium state, and the color swings cease.) The second step in their systematic approach was to search for a particular type of autocatalytic reaction, or one whose rate increases with increasing concentrations of the reaction product — a phenomenon "somewhat unusual for chemical reactions," Epstein says. Their search ended when they found the reaction $3H_3AsO_3$ (arsenite) + IO_3^- (iodate) → $3H_3AsO_4 + I^-$ (iodide ion). In this reaction, iodide ion is the autocatalyst.

Next, the Brandeis team needed to determine precisely how much arsenite and iodate to add to give rise to a bistable system — one with two different, stable steady states. Once the bistable system was established, the researchers then had to find a suitable agitator that would perturb the system's stability, causing it to oscillate between the two now "psuedo-steady" states. Such an agitator is chlorite ion (ClO_2^-), which reacts with the iodide ion formed in the first reaction: $4H^+ + ClO_2^- + 4I^- \rightarrow 2H_2O + Cl^- + 2I_2$. This reaction is autocatalyzed by the iodine (I_2). Together, the two separate autocatalytic reactions generate a system that oscillates between high (brown) and low (clear) iodide-iodine concentrations.

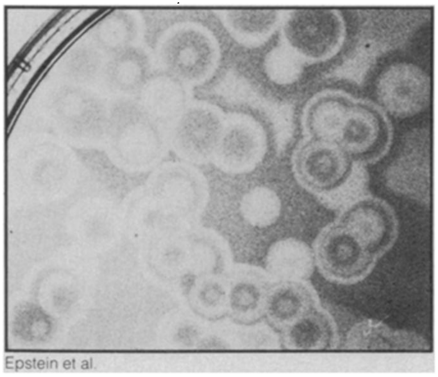
This system now is the father of an entire family of chemical oscillators. Epstein and colleagues found they could replace arsenite with a variety of other reducing agents — or compounds that lose electrons in a reaction. The suitable agents, they discovered, all have redox potentials (a measure of the ability to give electrons to other substances) within a certain defined range.

But, "The acid test will be whether they [Epstein and colleagues] can produce a second such family," Thompson says. This will determine whether this systematic approach is general enough to serve as a tool for constructing other chemical oscillators. "There is no question — they did generate this system on their own," says Thompson. "The critical thing to fortify their approach, though, will be generating a second system. Otherwise," he explains, "their existing system could also be classified as a serendipitous find." ☐

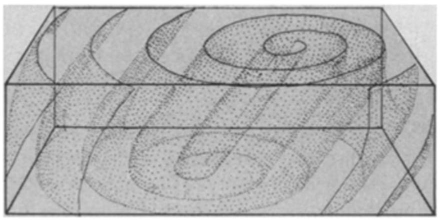
Instructions for Winfree's oscillator are detailed in the May 1980 CHEMTECH.



In certain oscillating systems, chemical — not hydrodynamic — waves can be formed. The waves can be in the shape of bull's eyes.


Epstein et al.

Oscillating waves also can be in the shape of rotating spirals. Again, these are not hydrodynamic waves: The fluid is motionless.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