Chemistry

Chemically generated spatial structures

from Irving R. Epstein

It might seem self-evident that a pattern formed by inhomogeneities in a liquid will eventually blur and disappear through the action of diffusion and that a liquid that is homogeneous will remain so. But recent work in nonlinear chemical dynamics is providing a set of extraordinary examples that do not conform to the intuitively attractive notion that spatial structures tend to decay rather than grow. These phenomena and the models proposed to describe them are beginning to have an impact not only in chemistry but in biology and geology as well, though some of the models are still highly controversial.

Probably the most venerable spatial structures seen in solutions are the Liesegang rings, known since the turn of the century¹. Two solutions containing a pair of ions, such as silver and dichromate, which form a sparingly soluble compound, are placed at opposite ends of a tube containing a gel. As the ions diffuse towards one another, precipitate appears not, as one might expect, uniformly, but in a series of sharp nearly periodically spaced rings. Theories recently developed by Ross², Ortoleva³ and co-workers challenge a 60-year old view⁴ that the phenomenon results from the build-up and release of supersaturation. These new theories successfully explain Liesegang's as well as newer and more puzzling experiments by invoking the competitive autocatalytic growth of different sizes of colloid particles coupled to diffusion of the reactants. Ortoleva⁵, by applying similar ideas, but on much larger scales of time and length, is able to explain the development of textural patterns in initially unbanded metamorphic rock — although the approach has met with some resistance from geologists.

Particularly exciting visually is the spontaneous development of trigger wave or bull's eye patterns (see the figure) in an initially homogeneous disc of reactant liquid. Winfree⁶ has developed recipes and techniques for producing spirals and scroll waves as well as the simpler patterns, and Krinsky⁷ has been able to generate multi-armed vortices (see the figure). A recent paper in *Nature* describes how to add a third dimension to these structures⁸, while in this issue (p.717), Avnir and Kagan describe structures generated at membrane surfaces. Early studies of these phenomena were limited to a single chemical system, the Belousov-Zhabotinsky (BZ) oscillator, but De Kepper *et al.*⁹ have shown that the same patterns may be observed in systems with quite different chemistry. The resemblance between these chemical

structures and those seen in the aggregating slime mold *Dictyostelium discoideum*¹⁰ are striking.

These patterns may be understood in a general sense as the result of a dynamic instability arising from the coupling of a chemically excitable system with diffusive transport and a recent computer simulation based on a two-parameter model¹¹ yields patterns remarkably like those found in the BZ reaction. However, a convincing calculation that predicts the wave pattern from a plausible chemical mechanism for a system as complicated as the BZ reaction has yet to appear. A first step in that direction has been taken by Showalter and colleagues¹², who treat a simpler phenomenon, the propagation of a single concentration wave in the arsenite-iodate reaction, by adding one-dimensional diffusion terms to a plausible model for the chemistry. Both the shape and the velocity of the wave are accurately predicted.

One rather controversial class of spatial phenomena is generated photochemically when initially homogeneous solutions are illuminated. Two recent papers^{13,14} have refuted earlier claims of periodic temporal oscillation in the light emitted by certain photochemical systems subject to constant illumination. Instead, the observed

behaviour is shown to result from spatial oscillations generated by convective motion of the fluid in response to temperature gradients set up by the illumination. (A related controversy involves the report published in *Nature* a few months ago¹⁵ that previously published photochemically generated spatial structures^{13,16}, too, result from convection rather than photochemistry.)

Although the study of spatial pattern formation in chemical systems is still in its infancy, it is progressing rapidly. Answers to the questions raised by some of these beautiful and often counterintuitive phenomena promise important insights not only into chemical dynamics but into such biologically significant problems as morphogenesis as well. □

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Left, spatial wave pattern arising spontaneously in an initially homogeneous mixture of sodium iodide, sodium chlorite, malonic acid, sulphuric acid and starch indicator. Right, wave movement in two- and three-armed vortices (from ref. 7).