

- of **1b** to give a substrate concentration of 330 to 2000 μM , and the reaction mixture was immediately brought to 1000 rpm. Initial linear rates were measured at <5% consumption of **1b**. Thus, in a typical analysis, the organic phase was removed from the reaction vial and stripped of solvent in vacuo. The residue was diluted with 100 μL of a stock solution (5×10^{-4} M) of the standard in hexane-isopropanol (97/3) and analyzed.
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Transient Turing Structures in a Gradient-Free Closed System

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Transient, symmetry-breaking, spatial patterns were obtained in a closed, gradient-free, aqueous medium containing chlorine dioxide, iodine, malonic acid, and starch at 4° to 5°C. The conditions under which these Turing-type structures appear can be accurately predicted from a simple mathematical model of the system. The patterns, which consist of spots, stripes, or both spots and stripes, require about 25 minutes to form and remain stationary for 10 to 30 minutes.

The symmetry-breaking, stable, stationary structures predicted by Turing (1) in 1952 to result from coupling diffusion with a set of appropriate chemical reactions have attracted considerable attention as a mechanism for morphogenesis, not only in biology (2, 3) but also in such diverse fields as astrophysics (4) and economics (5). The first unambiguous evidence of Turing structures emerged only recently, 38 years after Turing's remarkable theoretical work, in experiments (6) on the chlorite-iodide-malonic acid (CIMA) reaction in an open gel reactor. These and subsequent experiments (7, 8) have used an experimental configuration in which different reactants are fed into the system from opposite ends of the reactor, producing concentration gradients. Turing's model (1) envisions a system without imposed gradients in which the key reactants are maintained at uniform concentrations throughout the medium. In fact, nearly all mathematical analysis of Turing structures is based on such a picture, although for practical reasons all experiments to date have used imposed gradients. We report a set of experiments in which

Turing-type structures have been generated in a closed system without externally imposed gradients. Because the system is closed, the patterns are necessarily transient.

Mechanistic investigation of the CIMA system (9) led to the discovery that chlorine dioxide (ClO_2) and iodine (I_2) play key roles in the dynamical behavior of this reaction and that Turing structures can also be obtained in a system containing these two species and malonic acid (MA) (10). The behavior is well described by a simple two-variable mathematical model (9). Analysis of this model and of more general models shows that it is possible to calculate the position and depth of quasi-two-dimensional Turing structures in the usual experimental configuration by taking into account the gradient, thereby making the model parameters position-dependent (11). The success of this approach suggests that, just as one can treat imposed gradients by allowing the concentrations of "constant" reagents to vary in space, one should be able to predict the emergence of transient Turing structures in a gradient-free, closed system from knowledge of the concentrations at which a Turing instability occurs in a gradient-containing open system.

In Fig. 1A we show for an open system the spatial dependence of the concentrations of the reactants, where $x = 0$ is the boundary at which ClO_2 and MA enter the gel and I_2 enters at $x = 1$. The starch

(Fisher, soluble) concentration is uniform throughout the gel. The range of Turing instability, which occurs whenever the functions of concentration K' , H_1 , and H_2 are related by $K' > H_1 > H_2 > 0$ (12), is shown in Fig. 1B. Turing structures appear only in a narrow range along the spatial coordinate. Initial concentrations in this range should be capable of generating Turing patterns in a batch reactor. In earlier open-system experiments, polyacrylamide gel was used to provide a convection-free medium. However, its presence is not essential. Agladze *et al.* (13) obtained Turing structures without gel in the presence of starch an open capillary tube reactor.

In an open spatial reactor, Turing structures in the ClO_2 - I_2 -MA reaction develop over several hours. During their development, their qualitative appearance (hexagons or stripes or both) does not change, but they move in the medium. Eventually, their motion stops, and they remain stationary until the concentration of input reactants leaves the region of Turing behavior. Structures can develop more rapidly in a batch system, because it is not necessary to wait until a stationary concentration gradient is established. In a closed system, zero flux boundary conditions apply, because there is no mass exchange at the boundaries. The structures, however, cannot be truly stationary, because the reactants are consumed.

Several other factors are crucial for gen-

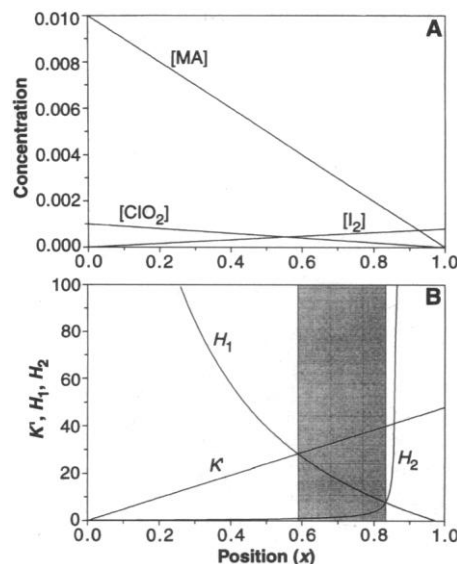


Fig. 1. (A) Concentration gradients imposed by the boundary conditions and (B) the range of Turing instability in the presence of this gradient. $[\text{ClO}_2]_0 = 1 \times 10^{-3}$ M, $[\text{I}_2]_0 = 8 \times 10^{-4}$ M, $[\text{MA}]_0 = 1 \times 10^{-2}$ M, rate constants (9): $k_1 = 6.2 \times 10^{-4} \text{ s}^{-1}$, $k_2 = 9.0 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$, $k_3 = 9.2 \times 10^{-5} \text{ s}^{-1}$, $h = 10^{-14} \text{ M}^2$, $D_u = 7.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, $D_v = 7.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, $K'[\text{S}] = [\text{S}]_3/([\text{I}][\text{I}_2]) = 6.0 \times 10^4 \text{ M}^{-1}$ at 4°C.

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erating and observing Turing-type structures in a batch system. The thickness of the layer is one important parameter. It should be smaller than or comparable with the characteristic wavelength of the structures, a few tenths of a millimeter. If this condition is violated, the structures are three-dimensional, which precludes their unambiguous identification with the use of standard systems built for detecting two-dimensional structures. The temperature is also crucial; we found it necessary to carry out all of the open system experiments at 4° to 5°C. The concentrations must be precise, because the structures appear only in a very narrow range of initial concentrations.

For the experiments, ClO₂ was prepared and purified as described previously (9). A saturated I₂ stock solution (in 30% acetic acid at 4°C) was used. Malonic acid (Aldrich) was used without further purification. The reaction mixture was poured into a dish of height 0.5 mm, and a glass plate was immediately slid over the mixture to prevent the evaporation of ClO₂ and I₂. The experiments were run in a cold room at 4°C to ensure that all of the stock solutions and equipment were at the same temperature. Comparatively small temperature differences cause significant effects on the structures. At higher temperatures, waves appear. If the dish is not at a uniform temperature, the structures are inhomogeneous, with waves in some regions and Turing-type structures in others. The time development

of the structures was recorded on a video cassette recorder and later analyzed with an image analysis system.

In Fig. 2, we show two basic types of structures that appear in a batch reactor; similar patterns are found in an open spatial gel reactor. The pattern in Fig. 2A is a mixture of spots and stripes, as seen more clearly in the Fourier spectrum, which consists of a hexagon of spots in which two spots at opposite ends are much darker than the other four. The pattern in Fig. 2B has a cell network-like structure. The wavelengths we have observed lie between 0.15 and 0.4 mm, with the cell network-like patterns generally at the longer end of the range.

The concentration of ClO₂ cannot be varied significantly because only a narrow range of [ClO₂] leads to Turing structures. The system is relatively insensitive to the concentration of starch between 0.5 and 2%. The I₂ concentration cannot be increased because precipitation occurs, nor can it be decreased significantly because of the resulting poor contrast. The MA concentration was varied in the range 1 × 10⁻³ to 4 × 10⁻³ M. Below this concentration range no structures appear, whereas above it periodic traveling waves occur. The structures require less than 25 min to develop; they then remain stationary for 10 to 30 min. These times are quite sensitive to the concentration of MA. The structures form rapidly at high MA concentrations (~4 ×

10⁻³ M) and require much more time at the low MA limit (~1 × 10⁻³ M).

To simulate the experiments, we used a model developed (14) to take into account the effect of starch in this system. The differential equations that describe the temporal and spatial development of the ClO₂-I₂-MA reaction system are

$$u_t = a - u - 4 \left(\frac{uw}{1 + u^2} \right) = u_{xx} + u_{yy} \quad (1a)$$

$$v_t = (1 + K') \left[b \left(u - \frac{uw}{1 + u^2} \right) + c(v_{xx} + v_{yy}) \right] \quad (1b)$$

where t is time, x and y are the spatial variables, u and v are the dimensionless concentrations of iodide and chlorite ion, respectively, a and b are kinetic parameters; K' is the effective equilibrium constant of the starch-triiodide complex, and c is the ratio of the diffusion coefficients of chlorite and iodide ions. The parameters were calculated with our experimental concentrations and rate constants from (15).

In the calculations we used an explicit method of successive approximation with Chebyshev acceleration and odd-even ordering (16). The calculations were started with randomly distributed inhomogeneous perturbations of amplitude ≤0.1% around the steady state. The zero flux boundary conditions have significant effects on the structures, which "sense" the shape of the boundaries. This effect is decreased with the use of periodic boundary conditions. In the experiments, we had zero flux at the boundaries, but the system was about 500 times longer in extent than the characteristic wavelength; consequently, the boundaries have a significantly smaller effect. In Fig. 3 we show calculated patterns and their Fourier transform. The patterns here are interacting hexagons.

The existence of transient Turing-type structures should greatly facilitate the study of this fascinating phenomenon. Although constructing an open gel reactor requires considerable expertise and success has been reported to date by only three groups, carrying out reactions in a closed system of the type described here is a straightforward task. Of equal or greater significance is the fact that, if patterns in developing embryos do arise by Turing bifurcation (17), it is likely to be through a scenario similar to the one we have used in this work rather than one in which different reactants enter from opposite ends of the embryo. One may imagine that patterns arise transiently in the embryo from nearly uniform concentrations and then evolve during the course of development. Instead of passing all the way through the interval of pattern stability, as occurs in our experiments, the developing

Fig. 2. (A) Mixed spots and stripes and (B) network-like structures in a batch reactor. The wavelength is 0.25 mm in (A) and 0.3 mm in (B). [ClO₂]₀ = 5 × 10⁻⁴ M, [I₂]₀ = 8 × 10⁻⁴ M, [MA]₀ = 1 × 10⁻³ M in (A) and 3 × 10⁻³ M in (B), [starch] = 1 g per 100 ml, and [acetic acid] = 10%.

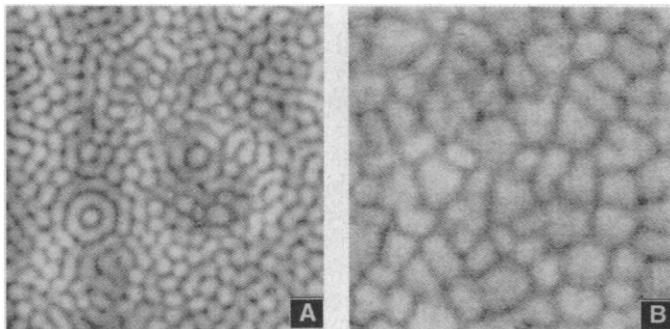
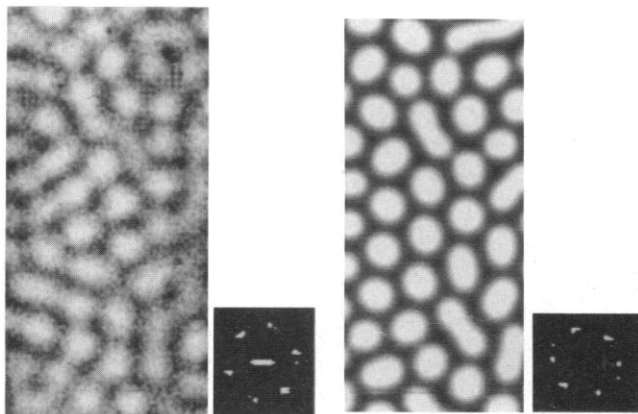


Fig. 3. Comparison of experimental (left) and calculated (right) patterns using differential Eq. 1 in the ClO₂-I₂-MA-starch reaction system. [ClO₂]₀ = 4 × 10⁻⁴ M, [I₂]₀ = 8 × 10⁻⁴ M, [MA]₀ = 1 × 10⁻³ M, and $K[S] = 3 \times 10^4 \text{ M}^{-1}$; rate constants are the same as in Fig. 1.



system can "freeze in" the pattern as the result of developmentally determined changes in its chemical environment.

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$$H_1 = -\frac{a_{11}}{a_{22}} - 1$$

$$H_2 = \frac{-a_{11}}{2\sqrt{c(a_{11}a_{22} - a_{12}a_{21}) - ca_{11}}} - 1$$
 where a_{ij} are the elements of the Jacobian matrix of the complex-free system and K' is the stability constant of the complex that binds the activator species.
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A Cationic Cesium Continuum in Zeolite X

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A cesium continuum that fills the channels and cavities of zeolite X has been prepared, and its structure has been determined by single-crystal x-ray crystallography. The three-dimensional continuum is cationic to balance the negative charge of the zeolite framework. Its valence electrons, only 0.3 per Cs^+ ion, are widely delocalized over 95 percent of the cesium ions in the crystal. The continuum has a unit cell formula of $(\text{Cs}_{122})^{86+}$ and contains Cs_{13} and Cs_{14} clusters (one per supercage) arranged like the atoms in diamond, with one Cs_2 appendix (in the sodalite cavity) per cluster.

Zeolites with guest species incorporated in their nanometer-dimension windows, channels, and cavities can have novel optical and electronic properties (1, 2). An interesting subclass of such materials could be produced by filling zeolites with metals. If the guest metal were the same element as the extraframework cations already present in the zeolite, it might be stabilized within the zeolite by electron delocalization. The result would be an arrangement of metal atoms, different from that of the metal itself, containing far less than a stoichiometric number of electrons.

Zeolite X (3) (of idealized composition NaSiAlO_4) has an aluminosilicate frame-

work that may be viewed as an assemblage of sodalite cavities, cubo-octahedra of composition $(\text{Si}_{12}\text{Al}_{12}\text{O}_{48})^{12-}$ (Fig. 1A), which are arranged in space (Fig. 1B) like the carbon atoms in diamond. They are joined at alternating 6-oxygen rings by six bridging oxygen atoms, not shown in Fig. 1A, one bound to each vertex of Fig. 1A to complete a tetrahedron. This leads to the existence of small double 6-ring cavities and

large supercages (Fig. 1B). The extraframework cations that compensate for the negative charge of the framework occupy the various positions indicated in Fig. 1B by Roman numerals.

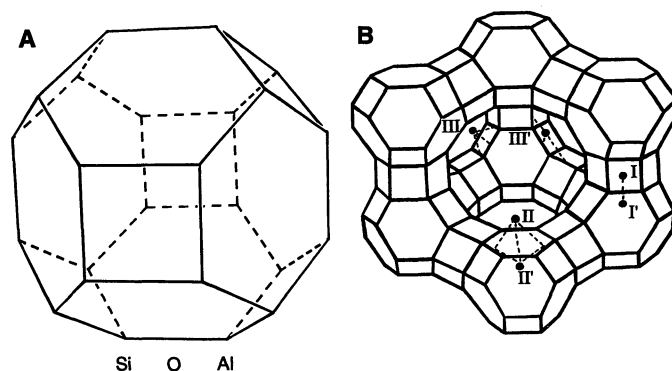
Earlier work has shown that zeolites exposed to alkali metal vapor can absorb extra alkali metal atoms into their cavities to form clusters. By using the electron spin resonance (ESR) technique, Kasai and Rabo (4-7), Edwards *et al.* (8-11), Martens *et al.* (12-14), Xu and Kevan (15, 16), and Smeulders *et al.* (17, 18) were able to detect paramagnetic clusters in zeolites A, X, and Y and sodalite. The cationic clusters Na_6^{5+} , Na_5^{4+} , Na_4^{3+} , K_4^{3+} , and K_3^{2+} were found in sodalite cavities. Metallic particles were also found in the supercages of zeolites X and Y, but the ESR method is ineffective at describing them. In general, no attempt was made to control stoichiometry or to achieve high loadings. Recently, K_{n+4}^{n+} was reported in zeolite A (19).

We studied the products of the reactions of zeolite A with Cs and Rb vapor by single-crystal x-ray diffraction (20-26). The triangular cluster Rb_3^{n+} [$n = 1$ (20) or 2 (21)], synthesized by exposing dehydrated zeolite A to Rb vapor, was found crystallographically in the sodalite unit of zeolite A; Rb_3^{n+} is stabilized by coordination to between one and three Rb^+ cations. The linear Cs_4^{3+} cluster, which extends from a large cavity through a sodalite unit into another large cavity, was found in zeolite A (22-26).

This study was initiated with the hope that fully Cs^+ -exchanged zeolite X could be prepared from Na-zeolite X (Na-X) by redox reaction with Cs gas, as had been done with zeolite A (22-26). Full exchange of Cs for Na has not been achievable by conventional aqueous methods of ion exchange (27-29). In addition, it was hoped that excess Cs atoms would be sorbed to form Cs clusters, as had occurred in zeolite A (22-26).

Large single crystals of Na-X with the stoichiometry $\text{Na}_{92}\text{Al}_{92}\text{Si}_{100}\text{O}_{384}$ were prepared in St. Petersburg, Russia (30). One of these, a colorless octahedron ~0.25 mm on an edge, was lodged in a

Fig. 1. Framework structures of a sodalite cavity (A) and of zeolite X (B). Extraframework cation positions are labeled with Roman numerals.



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