Spatial patterns and double diffusion in chemical reactions
(photochemical dissipative structures/chemically driven convection)

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ABSTRACT Spatial ordering has been observed recently during various photochemical reactions. Convoluted concentration bands first appear near the surface of shallow irradiated solutions. They thereafter extend into the bulk, and finger-like structures spontaneously develop. We discuss here the possible role of double-diffusion effects in the onset of this phenomenon. Indeed, chemical reactions occurring near the surface or evaporation of the solvent, or both, induce in the bulk adverse gradients of a pair of properties (concentrations of solute or concentration and temperature) having different diffusivities. This difference can then destabilize the homogeneous solution and trigger the observed patterns.

The competition between nonlinear chemical kinetics and diffusion (Turing mechanism) or other hydrodynamical processes can lead to coherent macroscopic structures in open chemical systems driven far from thermal equilibrium (1). Unfortunately experimental examples of such stationary chemical dissipative structures are scarce and not well characterized (2–5; for a recent review, see ref. 6). Furthermore the detailed mechanism of these complex reactions are still not completely elucidated. However, recently the formation of spatial structures have been reported in a large class of photochemical reactions not only in complex systems such as the photolysis of halogen compounds but also in photosystems exhibiting simple reaction kinetics (7–9) (first- or second-order reaction). It follows that these patterns are not generated by the Turing mechanism. Furthermore, as the characteristic wavelength is not intrinsic and depends on the thickness of the solution (3), one must therefore search for the origin of these structures in the coupling of the chemical processes with hydrodynamics. We want to stress here the importance of double diffusive convection in systems where chemical reactions occur near the surface. Double diffusion mechanisms have indeed been recognized as leading effects inducing instabilities in multicomponent systems (10–12).

For the sake of clarity, we consider the following model. A shallow layer of solution (of thickness L) of a chromogenic compound A of concentration \( \hat{A}_0 \) is irradiated. The photochromic reaction \( \text{A} + h\nu \rightarrow \text{B} \) takes place near the surface in the absorbing layer. This reaction induces in the solution time-dependent nonlinear concentration gradients of A and B, the Laplace transforms of which are of the form:

\[
\partial_z \hat{A}_0(z, \omega) = -\frac{\hat{A}_0}{(\omega \hat{D}_A)^{1/2}} \sinh(\omega/\hat{D}_A)^{1/2} \frac{z}{L} \cosh(\omega/\hat{D}_A)^{1/2} \frac{L}{z}
\]

and

\[
\partial_z \hat{B}_0(z, \omega) = \frac{\hat{A}_0}{(\omega \hat{D}_B)^{1/2}} \sinh(\omega/\hat{D}_B)^{1/2} \frac{z}{L} \cosh(\omega/\hat{D}_B)^{1/2} \frac{L}{z}
\]

\( \hat{D}_A \) and \( \hat{D}_B \) are the diffusion coefficients; \( k \gg \hat{D}_A L^{-2}, \hat{D}_B L^{-2} \);

\( z \) is the vertical coordinate, the solution being confined between \( z = 0 \) and \( z = L \). Because the products of the reaction (B) are often ions in a polar solvent, the diffusion coefficient \( \hat{D}_B \) is expected to be smaller than \( \hat{D}_A \). Hence as A tends to diffuse faster to the surface than B does to the bottom of the reactor, a convective instability may occur leading first to inhomogeneous concentration patterns at the irradiated surface of the solution. The concentration fluctuations \( [a = A - A_0(z, t), b = B - B_0(z, t)] \) are effectively coupled to the vertical component \( W \) of the velocity field. As a consequence, the linear part of the equations of motion may be written (\( g \) is the acceleration of gravity, \( \beta \) is the concentration expansion coefficient where \( \beta_A = \beta_B = \beta \), and \( \nu \) is the kinematic viscosity):

\[
\partial_z \phi(x, y, z, t) = \hat{D}_A \nabla^2 \phi + \frac{\partial \hat{A}_0}{\partial z} \cdot W,
\]

\[
\partial_z b(x, y, z, t) = \hat{D}_B \nabla^2 b + \frac{\partial \hat{B}_0}{\partial z} \cdot W,
\]

and

\[
\partial_z \nabla^2 W(x, y, z, t) = \nu^2 \nabla^2 + g \beta \nabla^2 (a + b),
\]

where

\[
\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2},
\]

\( \nabla^2 \) is the Laplacian in the \( (x, y) \) plane.

The main problem is concerned with the determination of the time of onset for the instability to occur in the presence of the time developing gradients \( \partial_A A_0(z, t) \) and \( \partial_B B_0(z, t) \). A simple method to estimate this time is provided by the quasistationary approximation. It consists in freezing the concentration profile at a given time and determining its stability. Although this approximation is known to yield inaccurate values of the growth rate of the disturbances, it seems in fact to predict the time at which the structuration first develops in the layer accurately (13).

As the concentration gradients are slowly developing in time \( (\hat{D}_A, \hat{B} \sim 10^{-5} \text{ cm}^2 \text{ s}^{-1}) \), their effects can only be felt in a small layer at the top of the solution, the thickness of which is of the order of \( (\hat{D}_A t)^{1/2} (10^{-2} \text{ after } 10 \text{ s}) \). An instability may nevertheless occur as fluctuations periodic in space in the \( (x, y) \) plane start growing in this layer for times such that

\[
t \geq [27 \nu^2 t / 4(1 - \gamma) g \beta \hat{D}_A \hat{D}_B t^{1/2}],
\]

where \( \gamma = \hat{D}_B / \hat{D}_A (\gamma < 1) \). For values of the parameters corresponding to the experimental situations, one finds \( t \sim 10 \text{ s} \), which is of a reasonable order of magnitude. This instability occurs if the difference between the time developing gradients exceeds some threshold value \( 27 \nu^2 t / 16 \beta \). This difference increases with the relative diffusivity \( \hat{D}_A - \hat{D}_B \) but diminishes with time. Hence, if \( \hat{D}_A - \hat{D}_B \) is too small, this threshold may
never be attained, and neither spatial organization nor convection occurs in the system. However, in some experiments the evaporation of the solvent may be sufficiently intense to create a destabilizing temperature gradient able to induce spatial patterns by evaporative cooling of the top surface. Indeed the importance of evaporation has been clearly demonstrated in some photochemical experiments conducted with a volatile solvent (9). Two effects have to be considered in this case.

(i) A weak convection may be established before the illumination of the solution by evaporative cooling. In some experiments, prepatterns have indeed been visualized by using Schlieren photography. In this case the spatial organization of the system no longer is randomly forced as in the situation described above, and the convection can be enhanced by the double diffusion effect when the photochemical reaction starts. For the kind of systems we consider ($L < 1$ cm), the initial velocity field is expected to be constituted by its fundamental harmonic alone $[\sin(\pi z/L)]$. Effectively, the temperature gradient responsible for this convection develops sufficiently rapidly to be felt in the entire solution. Hence after illumination, concentration fluctuations of wavelength $\lambda = 2\sqrt{2L}$ in the $(x,y)$ plane are amplified after an onset time defined by

$$
\frac{27}{4} \left( \frac{\pi}{L} \right)^4 \leq \frac{3}{4\pi c_1 D} \left[ \frac{gA_0}{\gamma} \right] \left[ \frac{1}{c_2} \right] \left[ \frac{1}{c_4} \right]
$$

If the concentration gradients evolve purely diffusively (i.e., isothermal reactions; no thermodiffusive effects), $c_1 = D_i$ and

$$
\tau = \frac{\pi c_1 L}{gA_0 B_0 (1 - \gamma)}
$$

(for realistic values of the parameters, this time is of the order of $10-100$ s).

(ii) The temperature gradient created by the evaporation of the solvent also may induce a concentration gradient of solute through the Soret effect (14, 15). If the thermodiffusion coefficient is positive, there is a tendency for the solute to move towards the coolest regions of the fluid, in this case the top surface. As a consequence, the difference between the gradients induced by the photochemical reactions may be enhanced and their diffusivity may be modified ($c_2 \neq c_4$). Hence, the effective threshold for the instability may be modified, giving onset times that eventually decrease with $L$.

In order to check the relevance of the double diffusion effects described in this note in the formation of photochemical patterns, further experimental and theoretical investigations are needed. From the experimental point of view, the precise knowledge of the diffusion and thermodiffusion coefficients would be desirable as well as refined measurements of the onset times (times at which the fluctuations start growing), critical times (times at which the patterns become well established), and growth rate of the inhomogeneous disturbances and, particularly, the dependence of these quantities on the thickness $L$ of the solution.

From the theoretical point of view, as the basic concentra-
