# Chemical Instability Induced by a Differential Flow

Arkady B. Rovinsky[1],[2] and Michael Menzinger[1]

[1]*Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1*

[2]*Institute of Theoretical and Experimental Biophysics, Puschino, Moscow Region, 142292, Russia*

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A new kind of instability is predicted for a system involving activator and inhibitor kinetics in a reactive flow. It is shown that a differential flow of activator and inhibitor, achievable, e.g., by selectively binding one component to a support, can destabilize the spatially homogeneous state of the system in a similar way as differential diffusivity does in the case of the Turing instability. The differential-flow-induced chemical instability is of the traveling-wave type. It is free from the restrictions of the Turing instability on the diffusion coefficients and can thus be expected to occur in a wide variety of natural and artificial systems.

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Interest in mechanisms of pattern formation has been further stimulated by the experimental discovery of Turing patterns [1] in the chlorite-iodide-malonic-acid system [2]. As Turing predicted [1], a homogeneous and otherwise stable reactive system may lose its stability and form inhomogeneous patterns due to the interaction of diffusion and reaction. The mechanism is believed to be fundamental to morphogenesis in biological systems [3] and it is likely to also be operative in various physical systems like plasmas, solids, solid-liquid interfaces, superconductors, lasers, and hydrodynamics (Ref. [4] and references therein).

The Turing instability can only occur if a system involves an autocatalytic species (as well as an inhibitor) and if the diffusion coefficient of the inhibitor is sufficiently larger than that of the activator [3]. When such a system is kept homogeneous, e.g., by stirring, it settles in a steady state through the balance of activation and inhibition. On the other hand, when a local concentration fluctuation arises in an unstirred system, diffusion comes into play in addition to chemical relaxation. Diffusion tends to remove or replenish species that are locally in excess or depleted, as the case may be. However, this process occurs with different rates for the two species, proportional to their diffusivities. Hence the balance between the activator and the inhibitor that existed in the perfectly stirred system may be broken in such a way as to allow the activator to grow locally [3]. The primary role of diffusion in the instability is, thus, to spatially disengage the counteracting species.

The starting point of this paper is the notion that the key species may be disengaged more generally by their differential transport. We show here that the homogeneous steady state may be destabilized by flows of activator and inhibitor at different flow rates, regardless of which one is faster. This makes the present mechanism free of the rather severe restrictions of the Turing instability on the diffusion coefficients and thus much more general. We refer to the mechanism as the differential-flow-induced chemical instability (DIFICI).

Consider a situation where one of the species, $Y$, is immobilized on a solid support [5] while the $X$ species flows through the one-dimensional reactor with velocity $v$. This system is described by the reaction-flow equations

$$\dot{X}=f(X,Y)+v\frac{\partial X}{\partial r}\,,\qquad \dot{Y}=g(X,Y)\,, \tag{1}$$

where the spatial coordinate axis is chosen to lie in the direction of the flow. We assume that the chemical reaction has a stable steady state $X_0$, $Y_0$ [i.e., $f(X_0,Y_0)=g(X_0,Y_0)=0$] when run in a perfectly stirred vessel. Linearizing the system near the steady state results in

$$\dot{x}=a_{11}x+a_{12}y+v\frac{\partial x}{\partial r}\,,\qquad \dot{y}=a_{21}x+a_{22}y\,, \tag{2}$$

where $X=X_0+x$, $Y=Y_0+y$, and stability requires that $a_{11}+a_{22}<0$ and $\Delta\equiv a_{11}a_{22}-a_{12}a_{21}>0$.

Assume now that our system is either spatially infinite or periodic (a ring). Then we can use the spatial Fourier expansion $x(r,t)=\int x_k(t)e^{ikr}dk$ and obtain the equations for the Fourier components,

$$\dot{x}_k=(a_{11}+ikv)x_k+a_{12}y_k\,,\qquad \dot{y}_k=a_{21}x_k+a_{22}y_k\,. \tag{3}$$

The eigenvalues of system (3) are

$$\lambda_{1,2}=\tfrac{1}{2}\{a_{11}+a_{22}+ikv\pm[(a_{11}+a_{22})^2-4\Delta-k^2v^2+2ikv(a_{11}-a_{22})]^{1/2}\}\,. \tag{4}$$

The real part $R$ of the square root in Eq. (4) is

$$R=(1/\sqrt{2})\{[(Q-k^2v^2)^2+4k^2v^2(a_{11}-a_{22})^2]^{1/2}+Q-k^2v^2\}^{1/2}\,, \tag{5}$$

where $Q=(a_{11}+a_{22})^2-4\Delta$.

It can be shown that the sign of $dR/d(k^2)$ is either always positive (if $a_{12}a_{21}<0$) or negative (if $a_{12}a_{21}>0$) and consequently that $R$ is a monotonic function of $k$. Then, depending on the sign of $dR/d(k^2)$, $\mathrm{Re}\lambda_1(k)$ rises (falls) monotonically from $\mathrm{Re}\lambda_1(0)$ to $\mathrm{Re}\lambda_1(\infty)$ and $\mathrm{Re}\lambda_2(k)$ falls (rises) from $\mathrm{Re}\lambda_2(0)$ to $\mathrm{Re}\lambda_2(\infty)$. It follows that $\mathrm{Re}\lambda_1(\infty)=a_{11}$ and $\mathrm{Re}\lambda_2(\infty)=a_{22}$ if $a_{11}>a_{22}$ and that $\mathrm{Re}\lambda_1(\infty)=a_{22}$ and $\mathrm{Re}\lambda_2(\infty)=a_{11}$ if $a_{11}<a_{22}$.

Let us assume that $a_{11}>a_{22}$. Furthermore, if $a_{11}>0$ and still subject to $a_{11}+a_{22}<0$, then it is clear that $\mathrm{Re}\lambda_1$ becomes positive at sufficiently large $k$ and that the system becomes unstable against short-wavelength perturbations. The critical wave number $k_c$ [i.e., such that $\mathrm{Re}\lambda_1(k_c)=0$] is

$$k_c=-\frac{a_{11}+a_{22}}{v}\left(-\frac{\Delta}{a_{11}a_{22}}\right)^{1/2}. \tag{6}$$

Since $\lambda_1$ is always complex for $k>0$, the instability is of the traveling-wave type.

When diffusion is included, the dispersion relation is

$$\mathrm{Re}\lambda_1=\tfrac{1}{2}\{a_{11}+a_{22}-(D_1+D_2)k^2+(1/\sqrt{2})[(q^2+p^2)^{1/2}+q]^{1/2}\}, \tag{7}$$

where $p=2kv[a_{11}-a_{22}-(D_1-D_2)k^2]$ and

$$q=[a_{11}-a_{22}-(D_1-D_2)k^2]^2+4a_{12}a_{21}-k^2v^2.$$

To illustrate this DIFICI case of spatial instability on hand of an experimentally verifiable system, we consider here the Puschinator model [6] of the Belousov-Zhabotinsky reaction,

$$\frac{\partial x}{\partial\tau}=\frac{1}{\epsilon}\left[x(1-x)-\left(2q\alpha\frac{y}{1-y}+\beta\right)\frac{x-\mu}{x+\mu}\right],$$
$$\frac{\partial y}{\partial\tau}=x-\alpha\frac{y}{1-y}, \tag{8}$$

where

$$[\mathrm{Fe(phen)_3}^{3+}]\equiv Y=Cy,\quad [\mathrm{HBrO_2}]\equiv X=\frac{k_1A}{2k_4}x,\quad \epsilon=\frac{k_1A}{k_4C},$$
$$\alpha=\frac{k_4K_8B}{(k_1Ah_0)^2},\quad \mu=\frac{2k_4k_7}{k_1k_5},\quad t=\frac{k_4C}{(k_1A)^2h_0}\tau,\quad \beta=\frac{2k_4k_{13}B}{(k_1A)^2h_0},$$
$$C=[\mathrm{Fe(phen)_3}^{2+}]+[\mathrm{Fe(phen)_3}^{3+}],\quad A=[\mathrm{NaBrO_3}],\quad B=[\mathrm{CHBr(COOH)_2}],$$

$h_0$ is the acidity function, $q$ is the stoichiometric factor, and $k_i$ are the rate constants [6,7]. (Here we use $Y/y$ for $[\mathrm{Fe(phen)_3}^{3+}]$ instead of the traditional notation $Z/z$.) Dispersion curves $\mathrm{Re}\lambda_1(k)$ were calculated in the absence of diffusion as functions of $k$ for different values of the flow rate $v$, as shown in Fig. 1(a). As one can see, for any velocity $v$ there is a critical wave number given by Eq. (6) above which the homogeneous state becomes unstable.

In real systems, diffusion must be considered in addition to flow. Introducing autocatalyst diffusion (the inhibitor is immobilized) through a diffusion term in the first equation in (1) produces the short-wavelength cutoff in the dispersion curves, as shown in Fig. 1(b). This entails the appearance of a threshold flow velocity $v_{\min}$, below which the homogeneous steady state is always stable. This critical velocity as well as the critical wave number $k_c$ are implicitly given by the conditions $\mathrm{Re}\lambda_1(k_c)=0$ and $d[\mathrm{Re}\lambda_1(k_c)]/d(k^2)=0$. The accurate explicit expressions for $k_c$ and $v_{\min}$ are rather cumbersome in this case but a rough estimate is simple: $k_c\sim(|a_{11}+a_{22}|/D)^{1/2}$ and $v_{\min}$ can be evaluated through Eq. (6) as $v_{\min}\sim[(a_{11}+a_{22})\Delta D/a_{11}a_{22}]^{1/2}$. It is also worth noting that the dispersion curves at constant diffusion ratio $\delta=D_{\mathrm{inh}}/D_{\mathrm{act}}$ parametrized by $v$ resemble closely those of the Turing case parametrized by $\delta$ in the absence of the flow [Fig. 1(c)].

To study the dynamical consequences of the DIFICI we have numerically integrated the reaction-diffusion-flow equations [Eq. (1) supplemented with a diffusive term $D_x\partial^2x/\partial r^2$] for the Puschinator model as described elsewhere [7]. Two configurations of the 1D reactor were studied. One was circular, with periodic boundary conditions. The other corresponded to a semi-infinite tube, fixed in the frame of immobilized ferroin species, that was fed with an input flow containing neither ferroin nor the autocatalyst $\mathrm{HBrO_2}$ (Dirichlet's boundary condition). In the circular reactor, the perturbation of the homogeneous state was imposed as a cosine function of the spatial coordinate with an amplitude equal to 1% of the steady-state value. In the tubular reactor, the boundary condition itself acted as the perturbation. In both configurations the perturbations evolved into pulses that traveled along the tube like ordinary pulses in excitable media as long as the flow velocity exceeded the minimum value. Otherwise they decayed to the stationary homogeneous state in the opposite case. The evolution and asymptotic form of a typical pulse train traveling around the circular reactor are shown in Fig. 2.

The difference between the waves simulated here and ordinary trigger waves [8] lies in their origin. The generation of trigger waves is always associated with a local pacemaker and local inhomogeneity [8] that imposes a finite perturbation (either single, periodic, or multiple aperiodic) on the system and thus locally drives it above the excitation threshold.

The pacemaker emits waves with radial symmetry. If

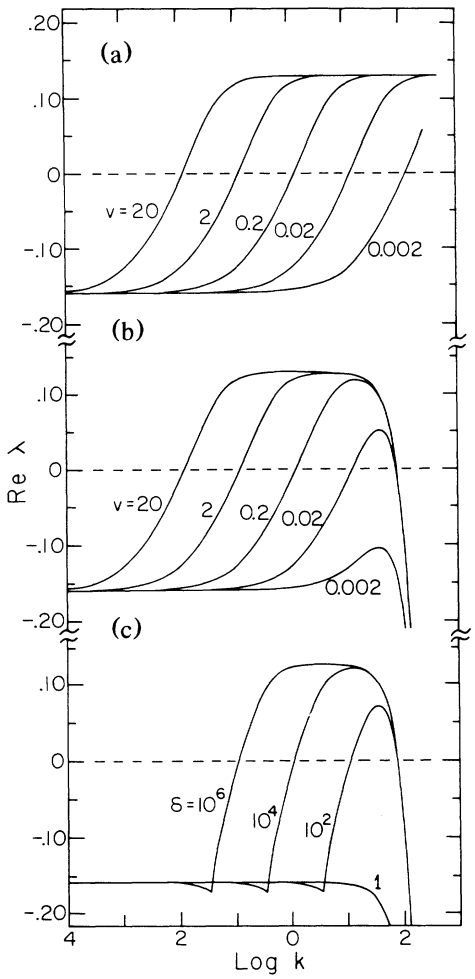


FIG. 1. (a) The real part of the eigenvalue as a function of the wave number for different flow velocities $v$ (cm/sec) (without diffusion); (b) the same with diffusion of $X$ species added, $D_X=2\times10^{-5}$; (c) the real part of the eigenvalue for different diffusion ratios $\delta$ and zero flow velocity. Parameters of the Puschinator model are $A=0.125$, $B=0.2$, $C=0.0003$, $h_0=0.03$.

the perturbation is smaller than the threshold trigger waves do not appear and the system remains stable and homogeneous. In the present case, due to the instability, the waves develop all over the system from infinitesimally small perturbations and are asymmetric: They propagate only in the direction of the flow.

This DIFICI resembles the Kelvin-Helmholtz instability of inviscid shear flow in hydrodynamics [9,10], except for one significant difference. Since the Kelvin-Helmholtz instability occurs in a conservative system (as long as viscosity is neglected), such a system may be destabilized by a flow of arbitrarily low velocity. This is reflected by the linear dispersion relation between Re$\lambda$ and the perturbation wave number $k$ (Fig. 3) and physically by the facts that inviscid shear flow may be destabilized by perturbations at arbitrary $k$, however small it

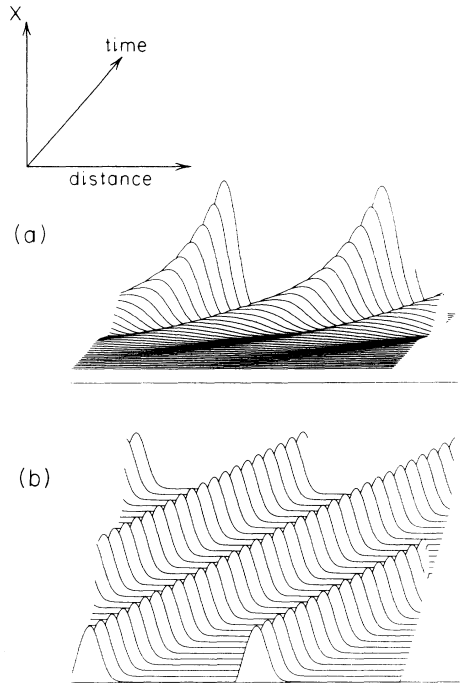


FIG. 2. The evolution of a perturbation in the circular reactor with flow of the $X$ species. (a) The initial stage of the instability; (b) the instability has developed into a pulse train traveling around the medium; $A=0.15$, $v=0.2$, and all the other parameters are as in Fig. 1. The vertical scale in (b) is 10 times as large as in (a).

may be, and that Re$\lambda$ rises to infinity with $k$ (if the surface tension of the interface can be neglected). On the other hand, the asymptotic (at large $k$) growth rate of perturbations in the DIFICI case is determined by $a_{11}$, i.e., by local kinetics, and the local kinetics makes the sys-

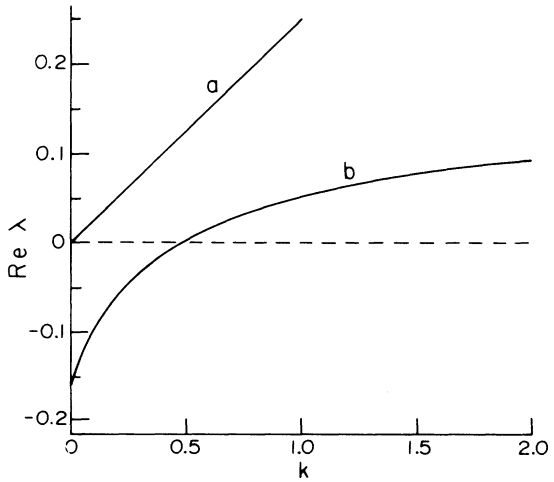


FIG. 3. The real part of the eigenvalue as a function of the wave number, curve $a$, for the Kelvin-Helmholtz instability and, curve $b$, for the DIFICI.

tem stable against smooth perturbations.

The present instability also has much in common with the Turing instability. The obvious analogy is that the necessary condition for both instabilities is the same: $a_{11}$ or $a_{22}$ must be positive, implying the presence of an autocatalytic species. (If a diagonal element, either $a_{11}$ or $a_{22}$, is positive then the corresponding species grows exponentially provided that the concentration of the other species is fixed.) This similarity is illustrated by the dispersion relation illustrated by Figs. 1(b) and 1(c) where the latter represents the Turing case. The same decay rates at $k=0$ and the maximal growth rates of perturbations ($=a_{11}$) for both Turing and differential-flow cases illustrate the fact that the ultimate cause of the instabilities in both cases is the local autocatalytic kinetics of one of the species while the transport, either diffusive or flow, serves merely to disengage the autocatalyst from the inhibitor response.

While the occurrence of the Turing instability depends crucially on the ratio of diffusion coefficients $\delta$ (with $\delta > 1$, a condition that is usually beyond experimental control although theoretically $\delta$ is often treated as the control parameter), the flow-induced instability is determined merely by the magnitude $|v|$ of the relative flow velocity (or rather by the ratio $|v|/\sqrt{D}$ when diffusion is included). Thus it is immaterial which of the two control species is immobilized: Fixing the inhibitor [5] promotes the DIFICI while this would prevent the Turing instability from occurring. Furthermore, the flow rate is easily controlled over a wider range. Therefore, we foresee that this instability occurs in a broad class of experimental systems.

One can expect that the differential-flow-induced chemical (or chemohydrodynamic) instability occurs whenever there is relative motion of activator and inhibitor species of a system. This may be important in many fields ranging from chemistry to physics to biology. An experimental verification of the effect predicted above has been achieved for the Belousov-Zhabotinsky reaction. The results will be published elsewhere.

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