

if one looks at 0° or 180° azimuth to the sun, an oil film will appear brighter than water, but at 90° azimuth most of the energy will be of the parallel polarization component and, as shown in Fig. 1, a crossover in contrast can occur near 53° in the direction of downward view.

To illustrate the advantage of viewing one polarization component in preference to another, we took photographs (Fig. 2) of an oil spill with two cameras having polarizers rotated 90° with respect to each other. We used Kodak infrared aerographic film 2424 with a Wratten No. 25 red-transmitting filter. The scene is an oil spill contained by a barrier. In the center is a thin film of oil, exact thickness unknown, and toward the bottom, within the barrier, is a thicker pool of oil. Figure 2A was taken with a polarizer oriented to transmit the parallel component, and for Fig. 2B we used a polarizer which transmitted the perpendicular component. Although this particular day was partially overcast, the advantage of the perpendicular technique is readily seen. The thin slick stands out vividly, as shown in Fig. 2B.

On the basis of these photographs, it appears that enhancement in contrast can be obtained by a difference technique. Figure 2A contains information primarily from light backscattered from beneath the water surface (background information). Figure 2B contains information from both backscattered plus reflected light (background plus signal). By subtracting one image from the other, the thin oil slick should stand out vividly. This differencing of images forms the basis of an airborne oil-spill detection system presently under development.

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4. We thank B. G. Pongeggi for taking the photographs in Fig. 2. We thank Commander R. N. Abrahams, Office of Research and Development, U.S. Coast Guard, for his cooperation in coordinating our overflight of the photographed oil-spill area.

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Horizontal Bands in the Belousov Reaction

Abstract. *The formation and propagation of spatial patterns in the presence of an initial gradient in temperature or the concentration of one or more of the reactants is explained kinematically. Experimental verification of this mechanism is given, showing that diffusion plays a very minor role in the formation of the bands.*

Belousov (1) reported that a solution containing bromate ions, malonic acid, sulfuric acid, and a small amount of cerous ion will undergo temporal oscillations. If the oxidation-reduction indicator tris(1,10-phenanthroline) ferrous complex (ferroin) is added, the stirred solution turns alternately from reddish purple to clear blue and back again. The chemical mechanism and kinetics of this reaction have been extensively investigated, particularly by Noyes *et al.* (2); see also (3, 4).

Various authors have reported the ability of this solution to form spatial patterns when the fluid is not stirred. Busse (5) noticed horizontal bands forming when the fluid was allowed to sit undisturbed in a vertical tube, and Zaikin and Zhabotinskii (6) reported that if the fluid is placed in a thin layer (about 2 mm), patterns of outwardly propagating concentric rings form. These spatial patterns are also discussed in (7). Some of the authors do not attempt an explanation of the origin of the patterns; those who do, appear to assume that the same mechanisms are at work in producing both kinds of spatial structure. In general it has been supposed that diffusion plays an important role, although only qualitative reasoning has been used to support this conjecture.

We believe that the bands noticed by Busse are formed for reasons qualitatively different from those responsible for the "target patterns" of Zaikin and Zhabotinskii (6) reported form in the presence of an externally

imposed gradient of concentration (or temperature). The purpose of this report is to show that under such conditions bands form and propagate for strictly kinematic reasons; that is, the oscillations occurring at different places in the fluid are independent of one another and the macroscopic spatial pattern arises from spatial variations in the frequency of these independent oscillators. In particular, diffusion is of negligible importance. We shall cite some experimental evidence in support of this hypothesis. Details of these experiments and some mathematical arguments are presented more fully in (8). This kinematic mechanism does not work for the target patterns, which form without any externally imposed gradient. We discuss elsewhere (9) how diffusion can interact with the chemical kinetics to form the target patterns.

Concentration gradients can be formed by mixing together all but one component, and then adding the last one without thorough mixing. If H_2SO_4 is added last it tends to sink; if cerium is added last it tends to float. Thus, there is a density gradient associated with the concentration gradient. In each of these two situations bands form and propagate upward. As time goes on there appear to be more and more bands, and they move more and more slowly through the fluid (which is not itself in motion).

The frequency of oscillation of this reaction (in homogeneous circumstances) is quite sensitive to many

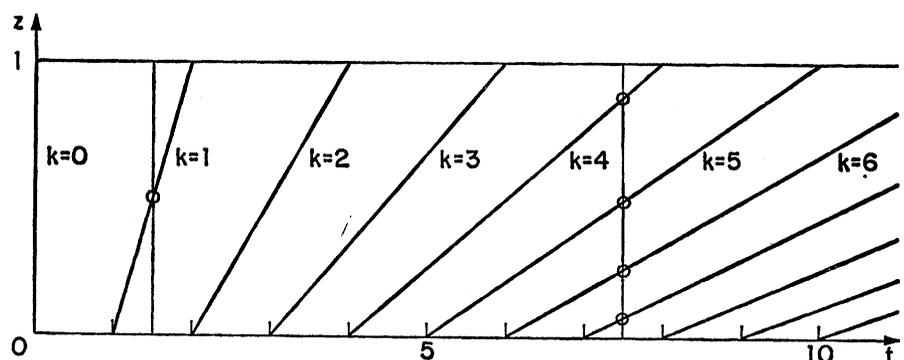


Fig. 1. Space-time graph of "crests," $\phi = 2\pi k$, for period variation $T(z) = 1 + z$ and initial phase zero throughout $0 \leq z \leq 1$. Note that at $t = 1.5$ there is just one crest in the interval, but at $t = 7.5$ there are four.

things: the initial concentrations, the temperature, how recently the ingredients have been mixed together, and even the rate of stirring. Here we report only that, within the range of concentrations we were using, increasing the cerous concentration decreases the frequency, whereas increasing the sulfuric acid concentration or raising the temperature increases it (4, 8). The effects of stirring are discussed in some detail in (8).

The dependence of the frequency on initial concentrations suggests that if there is a concentration gradient in the fluid, it will be accompanied by a gradient in the period of oscillation. It is this period gradient that we believe to be responsible for producing the bands. Whenever one has a family of uncoupled oscillators whose period $T(z)$ varies with a position coordinate z , a pattern of propagating kinematic waves will develop with a spatial scale that gets finer and finer as time goes on. This can be seen by imagining the "state" (for instance the color) of the oscillator to be specified by some 2π -periodic function of a phase ϕ given by $\phi(z,t) = \psi(z,t) + \phi_0(z)$. Here $\phi_0(z)$ is the initial distribution of phases [so that $\psi(z,0) = 0$] and $\psi(z,t)$ increases by 2π if time t is increased by $T(z)$. Let $\bar{t}(z)$ be the time at which the phase is zero at position z , so $\psi(z,\bar{t}) + \phi_0(z) = 0$. Then at time $t = \bar{t} + kT(z)$, for any integer k , $\phi = \psi(z,\bar{t} + kT) + \phi_0 = 2\pi k + \psi(z,\bar{t}) + \phi_0(z) = 2\pi k$. Thus, the space-time points (z,t) corresponding to phase $2\pi k$ lie on the curve $t = kT(z) + \bar{t}(z)$. For definiteness, assume that we are concerned with the interval $0 \leq z \leq 1$ and that $T(z)$ is monotonically increasing there. If $\phi_0(z) = 0$, $\bar{t} = 0$ also, and the phase $2\pi k$ is always reached first at $z = 0$ and last passed at $z = 1$. The k th "crest" (where $\phi = 2\pi k$) enters the interval of interest at $z = 0$ and leaves it at $z = 1$, after propagating through with speed $1/kT'(z)$, which is at each point z slower by a factor of k^{-1} than the speed of the $k = 1$ crest. As time goes on there will be more and more crests in the interval since they enter at $z = 0$ more frequently than they depart at $z = 1$; at time t there are approximately $t[1/T(0) - 1/T(1)]$ points in the interval $0 \leq z \leq 1$ with phases that are integral multiples of 2π . [See Fig. 1 for the graphs of these crests in the case $T(z) = 1 + z$ and $\Phi(z) = 2\pi t/T(z)$.] If $\Phi_0(z) \neq 0$ the above statements are asymptotically correct, as one sees from $T(z) = [t - \bar{t}(z)]/k \sim t/k$ for large t .

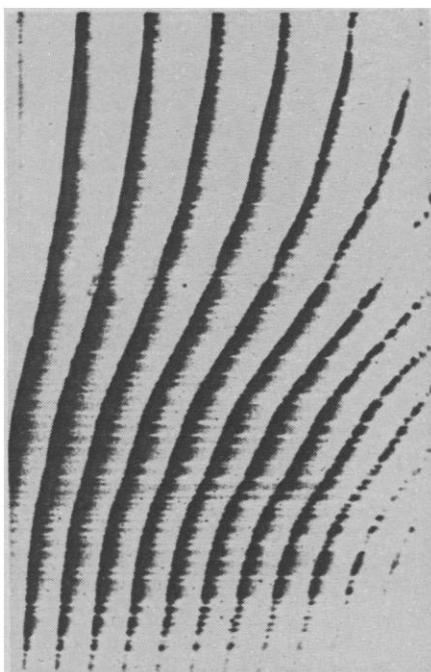


Fig. 2. Space-time picture showing the vertical propagation of horizontal bands and the development of increasingly small-scale structure in the Belousov reaction with a vertical sulfuric acid gradient. The horizontal axis in the picture corresponds to time, increasing to the right; the vertical axis corresponds to vertical position, up being up. The total time lapse of the picture is about 7 minutes; the vertical range is about 20 cm. Note the uniform horizontal (temporal) spacing of the fronts at each level. The picture is a negative.

We believe that the formation and evolution of the horizontal bands seen when the Belousov reaction is carried out with a vertical gradient is due to just such a kinematic mechanism. This means that we think that under these conditions the reaction at each level is oscillating periodically, the oscillators at different levels being essentially independent.

To test this hypothesis experimentally, we filled a tall rectangular cell with the reaction mixture (10) in such a way that there was a vertical gradient in the sulfuric acid concentration alone, the lower fluid having a greater sulfuric acid concentration than that higher up. The front surface of the cell was covered except for a thin vertical slit, and the cell was illuminated from the back. A camera focused on the slit was placed on a carriage permitting it to be moved horizontally so that the image of the slit would sweep across the film in about 10 minutes. Such a time-lapse picture provides a space-time graph of lines of constant phase, since the bright blue color appears rather suddenly and makes a sharp edge on the film.

Mild, mainly horizontal stirring with a vertical rod was done just before opening the shutter; this more or less homogenized the phase throughout the fluid without destroying the gradient, so that the experiment could be done with $\Phi_0(z) \cong 0$. The resulting picture (see Fig. 2) shows that the oscillation is indeed periodic at each height and that the higher frequency is at the bottom, as would be expected if it were determined just by the sulfuric acid concentration. This picture shows rather clearly the evolution of smaller and smaller scales in the manner described above.

According to the kinematic model the essential element in the band formation is the period gradient, irrespective of what produces it. To further test this model we repeated the experiment with a temperature gradient, the upper fluid being hotter. Since the period decreases with increasing temperature, the upper fluid had a higher frequency and we obtained bands that moved downward. The space-time pictures were similar to Fig. 2 (upside down). We also did experiments with a gradient in cerium. Since the concentration of cerous ions is small, it is possible to produce a cerium gradient that is not coupled to a density gradient. Thus, we could produce gradients with a higher or lower cerous concentration at the top; as predicted by the kinematic model, we obtained bands propagating downward if the concentration was lower at the top, and upward otherwise.

The experiments described above show that the reaction is oscillating periodically at each level, with a period gradient associated with the imposed concentration gradient. They also show that the period at each level does not change as the scale becomes finer, which suggests that different levels are oscillating independently (that is, diffusion is not an important factor). To further rule out the importance of diffusion we repeated the experiment with a thermal gradient, this time completely separating the top half of the fluid from the bottom; a Plexiglas partition was inserted horizontally just after the initial stirring. The resulting photograph showed the space-time fronts as before.

To get a quantitative check on this model we attempted to compare the periods at the different levels in the cell with those of homogeneous solutions having the same initial concentrations, temperature, and age. It was most con-

venient to do this using the thermal gradient. It is difficult, however, to measure the period definitively in the homogeneous case, primarily because of its sensitivity to the rate of stirring. This appears to be due to the effect of stirring on the transfer of gases (such as Br_2 , O_2) across the free surface (8). Another complicating factor is that the period changes slowly with age in a manner that appears to depend on the temperature, gas transfer, and so forth throughout the previous evolution of the reaction. Nevertheless, on the whole, such measurements of the period at different temperatures seemed to agree with what one deduces from pictures like Fig. 2 in the thermally stratified case.

As the scale of the bands becomes finer it must be expected that eventually diffusion will begin to play a role. One can construct mathematical models which show that diffusion can counter the imposed period gradient to stop the formation of an ever-finer scale structure and lead to a situation in which the frequency is uniform (even though the basic concentration gradient remains). However, we estimated that, within our concentration ranges, this would take an amount of time on the order of the lifetime of the overall reaction (8). (It takes far longer—approximately a month—for the basic concentration gradient to diffuse away.) Hence we do not have any experimental evidence of the role of diffusion in the band patterns.

The kinematic model also predicts some other effects that are observed. For example, if there is a gradient of H_2SO_4 (so that propagation is upward), the bands tend to curve downward near the walls. The kinematic mechanism says that even if the phases are a function not only of height, z , but also of some horizontal coordinate y , the fronts $\Phi(z,x,t) = 2\pi k$ will approach the horizontal as long as the period is just a function of height. For then $\Phi(z,x,t) = \Psi(z,t) + \Phi_0(z,x,t)$, where Ψ is as before and Φ_0 is the initial distribution of phases. As before, the initial conditions wash out. In general, the bands tend toward the shape of the surfaces of constant period. If the only factor affecting the period is concentration and if this is tied to density, these constant-period surfaces will be horizontal. However, the period of the Belousov oscillation is also affected by temperature. Since the reaction is exothermic, the fluid near the walls of the container is somewhat cooler, and so it

oscillates more slowly. Hence the surfaces of constant period tend to curve downward near the walls. From the hydrodynamic equations it is possible to estimate the size of this effect and show it to be approximately what one observes in the downward curving of the bands (8). The exothermicity alone, without the period gradient, cannot cause the propagation of the bands or keep them horizontal (8); indeed the pulses of heat given off by the reaction cause very little fluid motion, and whatever there is tends to increase rather than decrease any perturbation of the bands from the horizontal.

Another effect partially due to kinematic mechanisms is the rapid loss of all temporal or spatial structure in the solution when it is placed in a beaker with no external gradient and not stirred. Our experiments show that in this situation the reaction is still oscillating at each point in the fluid, but at somewhat different frequencies (possibly because of temperature fluctuations), so that the phases are random. Also, in the absence of the external density gradient, temperature differences due to the heating from the reaction and cooling along the boundaries are enough to drive irregular convective motion of the fluid. Patterns formed in this situation by kinematic mechanisms are irregular because of the random fluctuations in temperature, and they are further convoluted by the convective motion. Hence, after a short time, there is no visible structure.

The horizontal bands described here are quite stable, and a visible structure remains for some time. In this case

there is, in general, a density gradient as well as a period gradient. The period gradient dominates irregular variations so that the constant-period surfaces remain nearly horizontal. The density gradient prevents convective motion. Hence, the horizontal bands due to, say, a sulfuric acid gradient may be expected to be stable. When there is no associated density gradient (for example, with a cerium gradient) the bands are much less stable.

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10. The mixture consisted of 0.3M malonic acid, 0.08M potassium bromate, 0.002M cerous sulfate, 0.75 to 2.2M sulfuric acid, and 0.0006M ferroin. The temperature was 25°C.
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Al-Khwarizmi: A New-Found Basin on the Lunar Far Side

Abstract. *Apollo 16 and Apollo 17 photographs of the far side of the moon reveal a double-ringed basin 500 kilometers in diameter centered at 1°N, 112°E. The structure is very old and subdued; it is probably Pre-Nectarian in age and appears to have been filled and modified by younger events. The heights of the basin's rings are based on laser altimeter data from Apollo missions 15 through 17; these data suggest a third outer ring, approximately 1000 kilometers in diameter. Laser measurements also indicate that the filled basin separates the relatively low terrain on the eastern limb of the moon from the higher, more rugged highlands to the east.*

In the course of planning orbital photography and visual observations on Apollo missions 15 through 17, the astronauts and I studied the interesting crater King and its environs (1). The pilots of the command modules of the three missions took photographs and made visual observations of features in

this region of the farside highlands. They described the King crater area, previously labeled the "Soviet Mountains" (2), as a plateau, a gentle rise which they compared to another rise around the crater Saenger (4.5°N, 102.5°E).

Study of the Apollo photographic