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Traveling Waves in the Iodate–Sulfite and Bromate–Sulfite Systems

Andrea Keresztessy,^{†,‡} Istvan P. Nagy,^{†,‡} György Bazsa,[‡] and John A. Pojman^{*,†}

Department of Chemistry and Biochemistry, University of Southern Mississippi, Hattiesburg, Mississippi 39406-5043, and Department of Physical Chemistry, Kossuth Lajos University, Debrecen, Hungary H-4010

Received: November 4, 1994; In Final Form: January 3, 1995[©]

We investigated traveling fronts of the oxidation of sulfite by iodate and by bromate. Isothermal density changes ($\Delta\rho_c$) and enthalpies were determined, the latter being negative in both cases. The $\Delta\rho_c$ is negative in the iodate–sulfite system but positive in the bromate–sulfite system. Double-diffusive convection was expected in the bromate system and was observed. The effect of tube diameter and the orientation of the tube on the wave velocity and wave shape were studied, and a gravitational anisotropy was found in both systems. According to the Pojman–Epstein model, only simple convection should have occurred in the iodate–sulfite system. In fact, curved descending fronts with velocities greater than the ascending ones and “fingering” were observed. Several explanations were considered, including the possibility that the current model must be expanded to explicitly treat the effect of a moving interface on the stability of the fluid.

Introduction

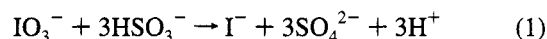
As a front propagates, concentration and thermal gradients are formed that alter the density of the solution, often causing convection.^{1–8} Pojman and Epstein⁹ have classified the types of convection that can occur in traveling fronts. If the reaction is exothermic ($\Delta H < 0$) and the products' solution is less dense than the reactants' ($\Delta V_{\text{rxn}} > 0$), then simple convection can occur, depending on the constraints of the container geometry. If the signs are the same, then multicomponent (double-diffusive) convection may occur, even though the overall density gradient may appear to be stable. In a descending front, double-diffusive convection manifests itself as “salt fingers”, so called because of their discovery in ocean layer mixing.

Modeling and analysis have been performed on fronts that exhibit simple convection.^{4,10–14} No modeling work has been done to date on double-diffusive convection and fronts nor on fronts with complex chemical kinetics.

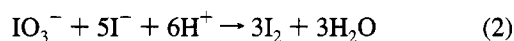
In an earlier work we studied fronts of the chlorate oxidation of sulfite¹⁵ and found double-diffusive convection. In a recent study of fronts in the iodide–nitric acid reaction we extended the Pojman–Epstein model to include the case in which $\Delta\rho_c$ is negative but with two species having significantly different diffusion coefficients.¹⁶ The triiodide–starch complex had a lower diffusion coefficient than other species. In that work we also studied for the first time the shape of the front as a function of concentration and tube orientation and proposed a mechanism for the angular dependence of front velocities based on the Boycott effect.^{17,18} We wished to test our interpretation by studying fronts of sulfite oxidation by bromate and by iodate.

The study of this family of chemical reactions has a long history, originating from the last century. The peculiar kinetic behavior of the iodate–sulfite system, that is, that iodine formation takes place abruptly in the solution after a rather long time lag, was observed by Landolt.¹⁹ Rabai and Beck^{20,21} observed large amplitude hydrogen ion concentration oscillations in the iodate–thiosulfate–sulfite system under closed conditions. They explained that the iodate–sulfite subsystem produces excess hydrogen ion and performs the direct oxidation

of sulfite to sulfate when the pH of the solution does not decrease below 4:



In their analysis they explain the possibilities and limitations of a parallel occurrence of the Dushman reaction, depending on the pH range under which the reaction is performed:



Edblom et al. studied the kinetics and mechanism of the oscillatory bromate–sulfite–ferrocyanide reaction, and they proposed a mechanism to describe the complex behavior of the system under batch and CSTR conditions including a theoretical description of phase diagrams yielded during their examinations.²² Luo and Epstein later gave a general explanation of pH oscillators observed in this branch of chemical reactions.²³ Closely related systems can produce chemical waves that are strongly affected by convection.^{15,24}

Experimental Section

Chemicals and Apparatus. Reactant solutions were prepared with analytical grade chemicals that were used as received: Na_2SO_3 , NaHSO_3 from REANAL; H_2SO_4 , Na_2SO_3 , NaHSO_3 from Fisher, bromophenol blue; NaBrO_3 from Aldrich; KIO_3 from Baker & Adamson Chem. Co.; and deionized water.

Wave experiments were carried out using pipets, glass tubes, and graduated cylinders with inner diameters 0.014 to 5.95 cm. (All tube dimensions indicated refer to inner diameters.) Bromophenol blue indicator was added to the reaction mixture so the front propagation could be observed. Wave position was read from a millimeter scale attached to the wall of the tube. Determinations of reaction enthalpies were carried out using a Dewar flask and a Beckman differential thermometer. The isothermal density change of the reaction solution was determined by measuring the densities of the initial and final solutions with a 25 cm³ pycnometer at 25.0 ± 0.1 °C.

Wave Velocity Measurements. Standard stock solutions and distilled water were pipetted in appropriate volumes to give reaction mixtures of desired concentrations. Capillary tubes were carefully cleaned and dried. To minimize the mixing effect

[†] University of Southern Mississippi.

[‡] Kossuth Lajos University.

[©] Abstract published in *Advance ACS Abstracts*, March 1, 1995.

TABLE 1: Front Shapes and Stabilities in Tubes of Various Inside Diameters, in the Iodate–Sulfite^a and Bromate–Sulfite^b Systems

inside diameter	IO ₃ ⁻ –SO ₃ ²⁻ system		BrO ₃ ⁻ –SO ₃ ²⁻ system	
	ascending front	descending front	ascending front	descending front
0.140 cm	flat/stable	flat/stable	flat/stable	flat/stable
0.260 cm	parabolic/slightly unstable	parabolic/slightly unstable	parabolic/slightly unstable	parabolic/slightly unstable
0.390 cm	parabolic/slightly unstable	parabolic/slightly unstable	parabolic/slightly unstable	parabolic/slightly unstable
0.800 cm	unstable	unstable	unstable/faster than descending one	unstable
1.800 cm	very unstable	unstable	very unstable/faster than descending one	unstable
2.250 cm	very unstable	very unstable	very unstable	very unstable/very fast fingering
5.950 cm		fingering		

^a [KIO₃]₀ = 0.01 M, [Na₂SO₃]₀ = 0.015 M, [NaHSO₃]₀ = 0.016 M, [bromophenol blue]₀ = 0.32 w/v %; *T* = 22.5 ± 0.5 °C. ^b [NaBrO₃]₀ = 0.03 M, [Na₂SO₃]₀ = 0.045 M, [NaHSO₃]₀ = 0.049 M, [bromophenol blue]₀ = 0.32 w/v %; *T* = 22.5 ± 0.5 °C.

from the density difference of the reaction mixture and the initiating acid solution, a filter paper ring was partly immersed under the top of the solution and was carefully impregnated with the acid solution; waves were initiated in a reproducible way. Wave shapes were captured by a digital image processing system that consisted of an IBM 80-486 compatible PC, an LFS-AT 8 bit black and white frame grabber board (LEUTRON AG, Switzerland), and an SDT 4500 monochrome CCD solid state camera (Steiner Datatechnik GmbH, Germany) and the necessary optics (25 mm focal length TOKINA lenses, Japan).

Determination of the Reaction Heat and the Isothermal Density Change. With the iodate–sulfite system appropriate volumes of stock solutions were combined to give a 200.0 cm³ reaction mixture that was poured into a Dewar flask, and the temperature was monitored for 8 min. The reaction was started by adding a small amount of 0.1 M sulfuric acid solution to the reaction mixture. The temperature increase was measured while the solution turned yellow. The temperature change using 0.010 M initial iodate concentration was 0.75–1.05 °C, and the reaction heat was $\Delta H = -560 \pm 120$ kJ/mol. The poor reproducibility is caused by the long time scale of the reaction and lack of sufficient thermal isolation.

With the bromate–sulfite system we had to measure the initial part of the calorimetric curve in a solution containing only sulfite, bisulfite, and distilled water because the first step of the reaction takes place without any initiation with acid and produces a large amount of heat. Bromate was added to the reaction mixture after 2 min. The temperature increase caused by the first reaction step was measured for 15 min, and then a small amount of 0.1 M sulfuric acid solution was dropped into the mixture, which turned yellow. By using 0.015 M initial bromate concentration the temperature change in the total reaction was $\Delta T = 2.67$ – 2.70 °C, and the reaction heat was $\Delta H = -1070 \pm 10$ kJ/mol. The temperature increase in the pH change stage of the reaction was $\Delta T = 1.44$ – 1.46 °C, and the reaction heat was $\Delta H = -580 \pm 10$ kJ/mol.

The isothermal density change was determined under the same conditions as the wave velocity experiments using a 25 cm³ nominal volume pycnometer. The isothermal density change in the iodate–sulfite system was found to be $\Delta \rho_c = -4.67 \times 10^{-4}$ g/cm³. The isothermal density change in the bromate–sulfite system was $\Delta \rho_c = 2.40 \times 10^{-4}$ g/cm³.

Results

Effect of Tube Diameter on Front Shape. Iodate–sulfite System. Using the reaction mixture of [KIO₃]₀ = 0.01 M, [Na₂SO₃]₀ = 0.015 M, [NaHSO₃]₀ = 0.016 M, and [bromophenol blue]₀ = 0.32 w/v %, we performed experiments in vertical tubes having inner diameters of 0.140, 0.260, 0.390, 0.800, 1.800, 2.250, and 5.950 cm. In a 0.140 cm tube both the ascending and descending fronts were flat. In 0.260, and in 0.390 cm tubes the ascending front had a slightly parabolic shape, and

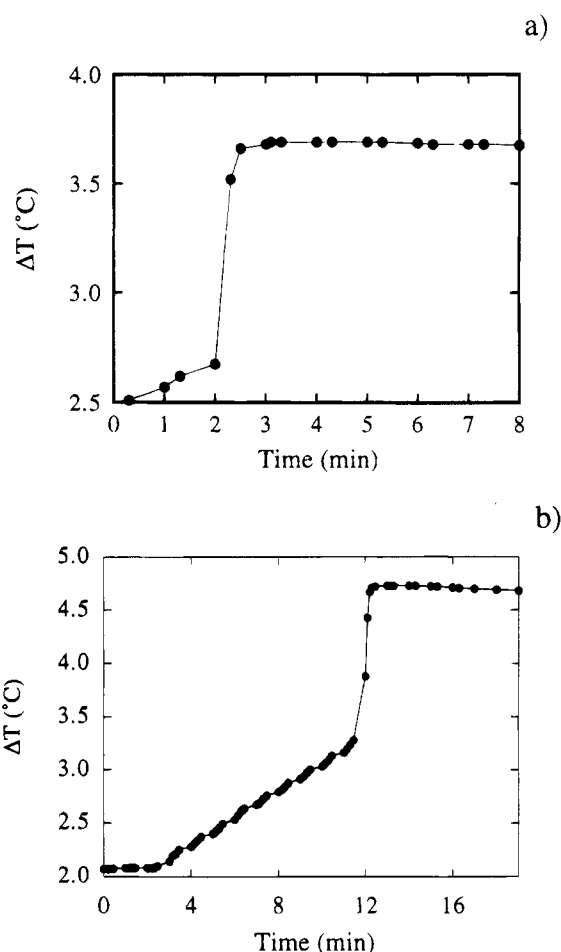


Figure 1. Calorimetric curves: (a) Iodate–sulfite system, [KIO₃]₀ = 0.01 M, [Na₂SO₃]₀ = 0.015 M, [NaHSO₃]₀ = 0.016 M, [bromophenol blue]₀ = 0.32 w/v %; and (b) bromate–sulfite system, [NaBrO₃]₀ = 0.015 M, [Na₂SO₃]₀ = 0.023 M, [NaHSO₃]₀ = 0.025 M, [bromophenol blue]₀ = 0.32 w/v %. The “staircase” is an artifact of the digitization.

the descending front was found have a parabolic shape but more curved. In the case of larger diameters, shapes of both descending and ascending fronts were distorted by time-dependent convection, i.e., the fronts were unstable. The ascending front was slightly faster than the descending one. In a 5.95 cm tube, after initiation of a descending front, fingering could be observed. Table 1 lists the shapes of ascending and descending fronts found in tubes of various inside diameters. Representative wave shapes in small and large diameter tubes are shown in Figure 2.

Bromate–Sulfite System. Using a reaction mixture of [NaBrO₃]₀ = 0.03 M, [Na₂SO₃]₀ = 0.045 M, [NaHSO₃]₀ = 0.049 M, [bromophenol blue] = 0.32 w/v %, we carried out experiments in vertical tubes with inner diameters of 0.140,

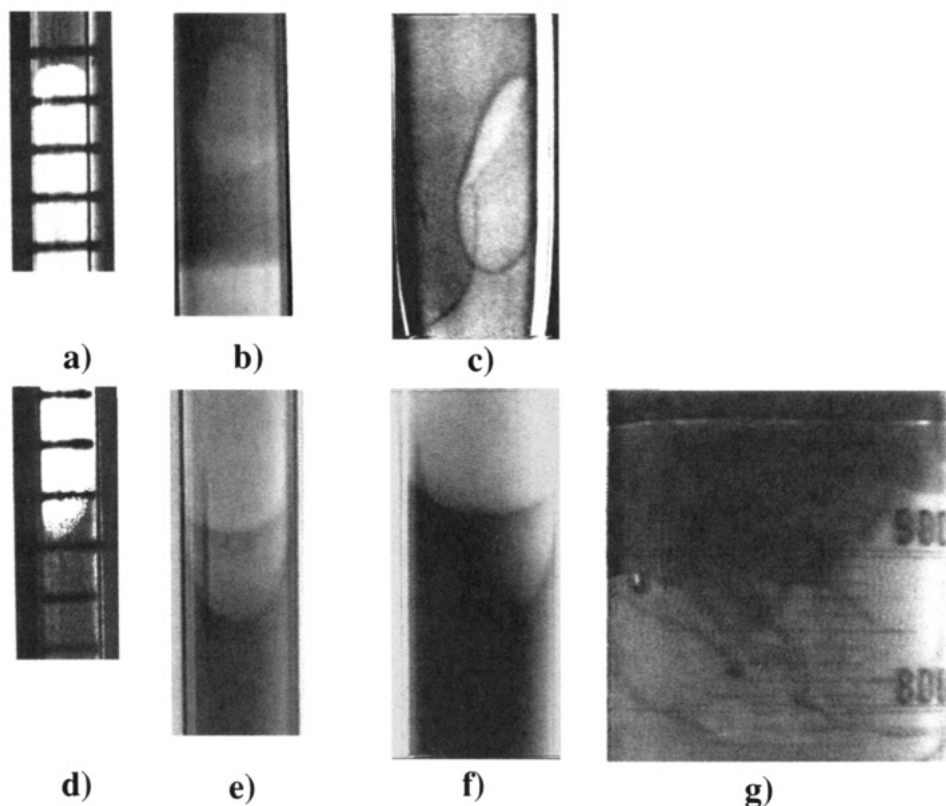


Figure 2. Diameter dependence of the wave shapes in the iodate-sulfite system: (ascending wave) (a) inside diameter = 0.260 cm; (b) inside diameter = 0.800 cm; (c) inside diameter = 1.800 cm; (descending wave) (d) inside diameter = 0.260 cm; (e) inside diameter = 0.800 cm; (f) inside diameter = 1.800 cm; (g) inside diameter = 5.95 cm. Initial concentrations are given in the text of Table 1.

TABLE 2: Reaction Mechanism for the Bromate-Sulfite Reaction²²

	reaction	rate constant
R1	$\text{BrO}_3^- + \text{HSO}_3^- \rightarrow \text{HBrO}_2 + \text{SO}_4^{2-}$	$8.0 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$
R2	$\text{HBrO}_2 + \text{Br}^- + \text{H}^+ \rightarrow 2 \text{HOBr}$	$9.5 \times 10^6 \text{ M}^{-2} \text{ s}^{-1}$
R3	$\text{HOBr} + \text{Br}^- + \text{H}^+ \rightarrow \text{Br}_2 + \text{H}_2\text{O}$	$1.6 \times 10^{10} \text{ M}^{-2} \text{ s}^{-1}$
R4	$\text{Br}_2 + \text{H}_2\text{O} \rightarrow \text{HOBr} + \text{Br}^- + \text{H}^+$	$1.1 \times 10^1 \text{ s}^{-1}$
R5	$2\text{HOBr}_2 \rightarrow \text{BrO}_3^- + \text{HOBr} + \text{H}^+$	$3.0 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$
R6	$\text{Br}_2 + \text{HSO}_3^- + \text{H}_2\text{O} \rightarrow 2\text{Br}^- + \text{SO}_4^{2-} + 3\text{H}^+$	$1.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$
R7	$\text{H}^+ + \text{SO}_3^{2-} \rightarrow \text{HSO}_3^-$	$5.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$
R8	$\text{HSO}_3^- \rightarrow \text{H}^+ + \text{SO}_3^{2-}$	$3.0 \times 10^3 \text{ s}^{-1}$

0.260, 0.390, 0.800, 1.800, 2.250, and 5.950 cm. The 0.140 cm tube supported a flat front in both directions. In a 0.260 cm tube, the ascending front was found to be slightly curved, and the descending front had a significant parabolic shape. In tubes having larger inner diameter, convection distorted the shape of the front, which was unstable in both directions. In the case of the 5.95 cm tube, the descending front showed fingering. (See Table 1) In this system, however, the ascending front traveled at a larger velocity than the descending one. Figure 3 shows the representative wave shapes in small and large diameter tubes.

Effect of Tube Orientation on Front Shape and Wave Velocity. Using a 0.260 cm tube, we observed in both systems the gravitational anisotropy of front velocities first discovered and described by Bazsa and Epstein⁸ and seen in the chlorate-thiosulfite⁷ and iodide-nitric acid systems.¹⁶ Figure 4 shows the results at different orientations in a 0.260 cm tube in the iodate-sulfite and bromate-sulfite systems. We captured pictures of the ascending and descending wave shapes at five orientations, which are shown in Figures 5. Fronts in both systems exhibited a maximum velocity at 150°, which is consistent with the results in the iodide-nitric acid system.¹⁶

Discussion

Edblom et al.²² studied the kinetics and mechanism of the oscillatory bromate-sulfite-ferrocyanide reaction, and they proposed the mechanism shown in Table 2. During their experiments they used the following concentrations: $[\text{BrO}_3^-]_0 = 6.5 \times 10^{-2} \text{ M}$, $[\text{Na}_2\text{SO}_3]_0 = 5.0 \times 10^{-2} \text{ M}$, which are very close to the concentrations in our experiments; they carried out the experiments at a pH of approximately 6. The pH in our reaction mixture was between 6 and 7 during the initial part of the reaction. We therefore assumed the same reaction mechanism for our system.

According to this mechanism, we propose an explanation for the two stage temperature profile shown in Figure 1. A reaction begins as soon as the reactants are mixed that releases large but the bromophenol blue indicator shows no pH change. This first step of the reaction may be described by R1 in Table 2 because it is slow in comparison to the other steps in the mechanism, and no pH change occurs during this reaction. Reaction steps R2 and R3 are fast, and they consume protons; R4 and R5 are slower than the previous two steps and generate protons. The main proton producing step is the R6, so this is responsible for the pH change during the overall reaction.

Iodate-Sulfite System. The thermal density change ($\Delta\varrho_T < 0$) and the isothermal density changes ($\Delta\varrho_c < 0$) have the same sign. According to the Pojman-Epstein model, simple convection should occur as in the iodate-arsenous acid system,² i.e., the ascending front should be curved, and the descending front should be flat. (The shape of the ascending front depends on the tube diameter.¹⁴) The velocity of the descending front should be equal to that of the pure reaction-diffusion front, and the ascending front should travel faster than the descending one. However, the shapes of both of the ascending and descending fronts were parabolic in the 0.260 cm tube, and the

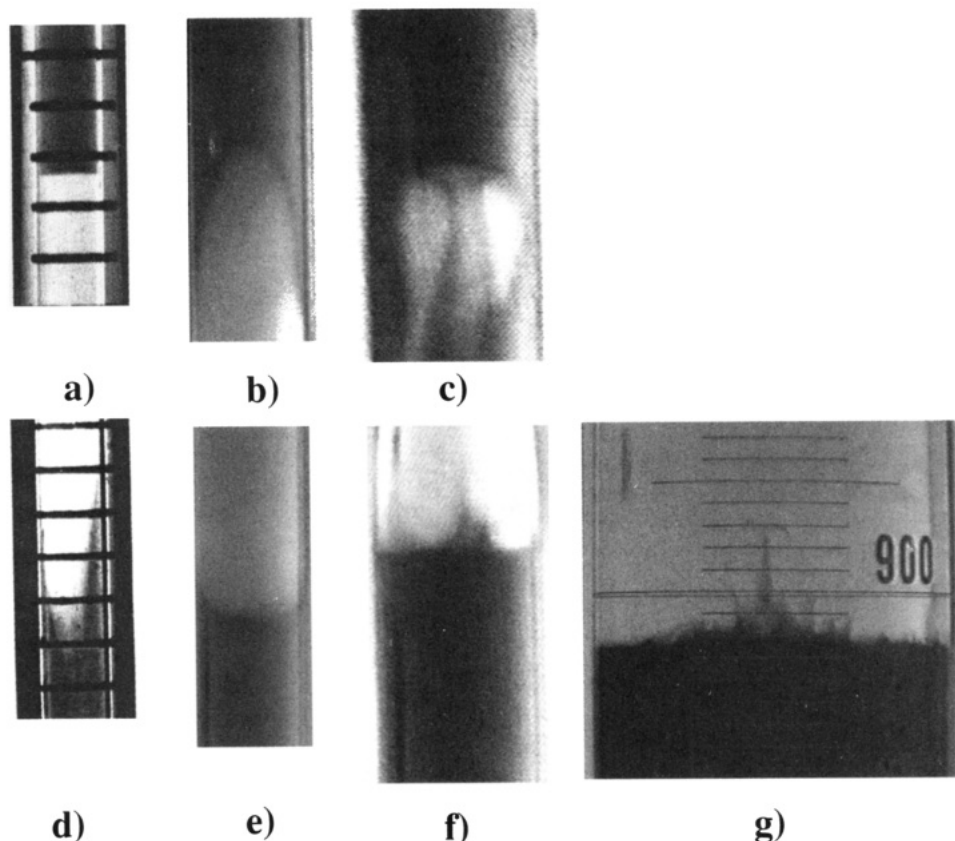


Figure 3. Diameter dependence of the wave shapes in the bromate-sulfite system: (ascending wave) (a) inside diameter = 0.260 cm; (b) inside diameter = 0.800 cm; (c) inside diameter = 1.800 cm; descending wave: (d) inside diameter = 0.260 cm; (e) inside diameter = 0.800 cm; (f) inside diameter = 1.800 cm; (g) inside diameter = 5.95 cm. Initial concentrations are given in Table 1.

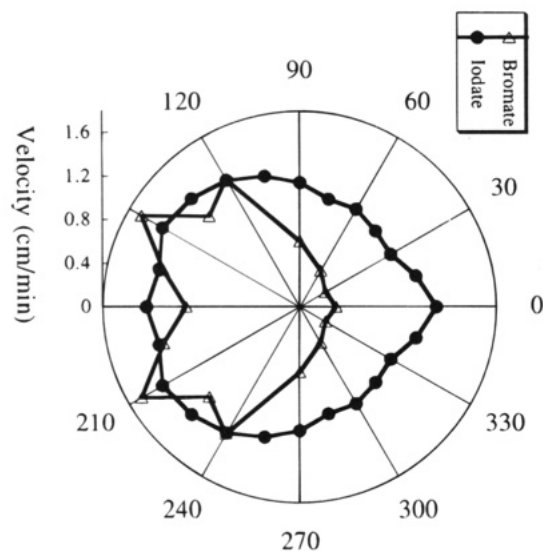


Figure 4. Polar coordinate plots of the front velocities versus tube orientations in the 0.26 cm tube. Iodate-sulfite system (\bullet): $T = 23.5 \pm 0.5$ °C, $[\text{KIO}_3]_0 = 0.01$ M, $[\text{Na}_2\text{SO}_3]_0 = 0.015$ M, $[\text{NaHSO}_3]_0 = 0.016$ M, $[\text{bromophenol blue}]_0 = 0.32$ w/v %; 0° indicates the vertical ascending direction, and 180° is the vertical descending direction. Bromate-sulfite system (Δ): $T = 23.5 \pm 0.5$ °C, $[\text{NaBrO}_3]_0 = 0.03$ M, $[\text{Na}_2\text{SO}_3]_0 = 0.045$ M, $[\text{NaHSO}_3]_0 = 0.049$ M, $[\text{bromophenol blue}]_0 = 0.32$ w/v %; 0° indicates the vertical ascending direction, and 180° is the vertical descending direction.

descending front was *faster* (1.40 cm/min) than the ascending one (1.25 cm/min). The descending fronts observed in larger tubes were unstable. In a 5.95 cm tube fingering was observed. Attempts to prepare convection-free fronts by the addition of silica gel or alumina were unsuccessful; homogeneous reactions occurred.

These observations directly contradict the Pojman-Epstein model and require serious consideration. We have considered three possibilities:

(1) Convection caused by temperature differences in tubes above the front, caused by the mild heat release, is the cause of the anisotropy. This cannot explain the appearance of fingering in large tubes nor the curved shape of the descending fronts in small tubes. Moreover, the ΔT is very close to the iodate-arsenous acid system, which does follow the model.^{2,14}

(2) The Pojman-Epstein analysis is flawed because it is based on a static system of two layers and not upon a moving interface with chemical reaction. Vasquez et al. studied the onset of convection for reaction fronts and found that neglecting the velocity of the front did not significantly affect the stability.⁴ However, systems that are susceptible to double-diffusive convection are not well understood. For example, the original analysis did not predict the curvature of descending fronts in the iodide-nitric acid system.¹⁶

(3) There are species in the product solution that have significantly different diffusion coefficients from reactant species. In an earlier work, we showed that the small diffusion coefficient of the triiodide-starch complex in the iodide-nitric acid system leads to double-diffusive convection even though $\Delta Q_c < 0$.¹⁶ It is possible, but rather unlikely, that high molecular weight sulfur species are produced, which have smaller diffusion coefficients than the ionic reactants. Turner determined that a factor of three difference in diffusion coefficients is all that is required for a double-diffusive instability.²⁵ However, no precipitation of colloidal sulfur was observed, and the reacted solutions did not exhibit the Tyndall effect.

Bromate-Sulfite System. The thermal density change ($\Delta Q_T < 0$) and the isothermal density changes ($\Delta Q_c > 0$) have the opposite sign. According to the Pojman-Epstein model,

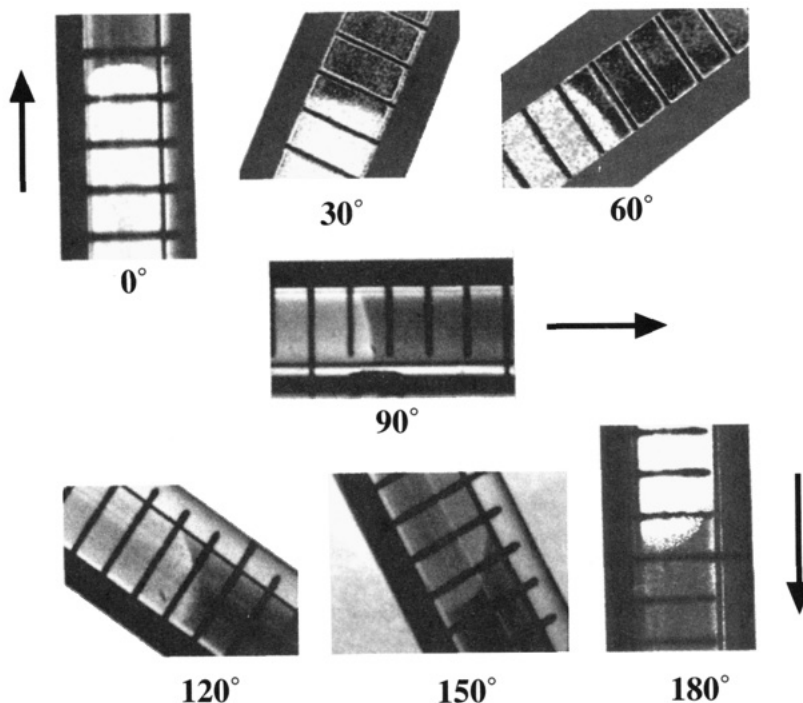


Figure 5. Shapes of propagating fronts in the iodate-sulfite system at seven different orientations to the gravitational field. A vertical ascending wave is at 0° ; vertical descending is at 180° . Initial conditions are the same as in Figure 4. The arrow indicates the direction of propagation.

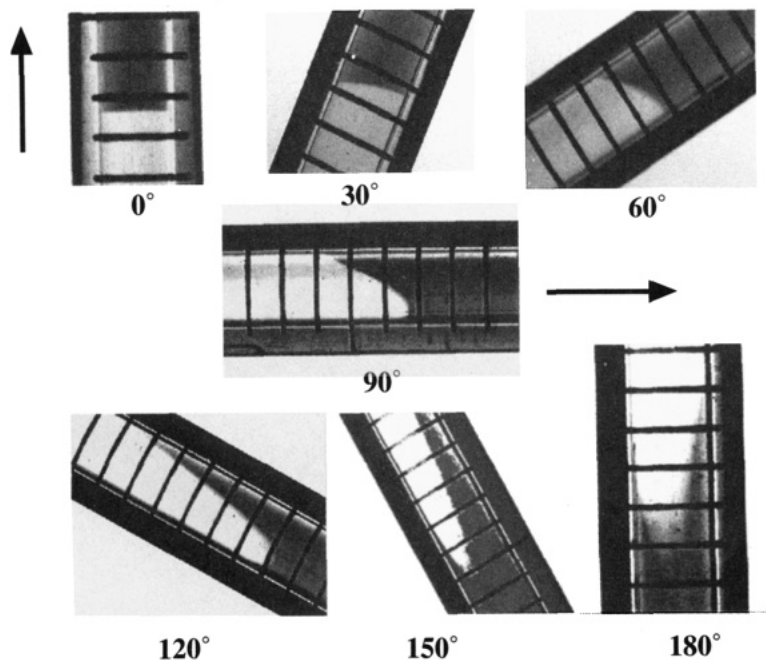


Figure 6. Shapes of propagating fronts in the bromate-sulfite system at five different orientations to the gravitational field. A vertical ascending wave is at 0° ; vertical descending is at 180° . Initial conditions are the same as in Figure 4. The arrow indicates the direction of propagation.

double-diffusive convection should occur as in the iron-nitric acid system,¹ that is, both the ascending and descending fronts propagate faster than a pure reaction-diffusion front. As seen in Table 1, the ascending front is slightly curved in a 0.260 cm tube, and the descending one has a significant parabolic shape. In larger tubes, however, the front is unstable in both directions.

As seen in Figure 4, the descending front travels faster than the ascending one in the 0.260 cm tube (0.33 cm/min compared to 1.04 cm/min). In the case of larger tubes, however, we observed that the ascending front was much faster than the descending front. We believe that this behavior is a result of higher temperature in the large tube. A lower surface area to volume ratio reduces the heat loss to the surroundings. The

higher temperature suppresses the formation of fingers, as Pojman and Epstein had predicted.⁹

We have also observed an interesting phenomenon with the bromate-sulfite system when an initial pH gradient exists. Periodic convection, a "jumping front", appears. We describe this behavior in an accompanying article.

Acknowledgment. This work was supported by the U.S.-Hungarian Science and Technology Joint Fund (Grant J. F. No. 247/92a), the National Scientific Research Fund of Hungary (OTKA Grant No. F-4024), the Ministry of Education of the Hungarian Government (MKM Grant Number 9/94), the National Science Foundation's Mississippi EPSCoR Program,

and NASA's Microgravity Materials Science Program (NAG8-973). We thank Reuben Simoyi, Cordelia Chinake, Marcus Hauser, and Desederio Vasquez for critical readings of the manuscript.

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JP943001K