

and the nature of the system (such as bromate and chlorite oscillators, enzyme reactions, heterogeneous systems, etc.), these classifications are not based on different structures in the reaction mechanisms.

Although all 25 investigated simple oscillators shown in Table I fit into the presented classification scheme, it is quite likely not

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complete. If simple oscillators with different unstable features are discovered, new subcategories may be appropriate and new methods for their distinction have to be found. The operational methods of the present classification scheme require detection and perturbation of chemical species including intermediates.

It is desirable to develop operational methods to distinguish the production of Z in the 1B category and W in the 1CW category by a tangent or an exit reaction, as well as to determine the origin of Z in 1C oscillators. While these distinctions are usually not necessary in order to construct the unstable current, they may be useful if some of the proposed operational methods are not easily applicable in a specific experimental system.

Some ideas on how to extend the classification scheme to nonsimple oscillators and the notion of nonessential species to complex dynamical behavior are given in section 5 of ref 1. There we also discuss possibilities how to get quantitative information about rate constants with methods related to SNA. The extension as well as the experimental application of the proposed classification scheme to various systems will be subject of future studies.

Acknowledgment. We express our deep gratitude to Bruce L. Clarke for his hospitality, a detailed introduction to stoichiometric network analysis, and helpful discussions. This work was supported in part by the Deutsche Forschungsgemeinschaft (DFG), by the National Science Foundation, and by the Air Force Office of Scientific Research.

Convective Effects on Chemical Waves. 2. Simple Convection in the Iodate-Arsenous Acid System

John A. Pojman,^{†,‡} Irving R. Epstein,^{*,†} Terence J. McManus,[§] and Kenneth Showalter^{*,§}

Department of Chemistry, Brandeis University, Waltham, Massachusetts 02254-9110, and Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506-6045 (Received: July 18, 1990)

The convection-induced increase of the wave front velocity in the iodate-arsenous acid system can be explained by considering the convective flow velocity caused by the density gradient in the reaction front. The density is decreased by the exothermicity of the reaction and by the positive volume change of the reaction. Because both effects decrease the density, no complicated mechanism such as double-diffusive convection need be invoked. The wave front velocity may be considered as a superposition of a fluid flow velocity on a reaction-diffusion velocity. We provide a qualitative description of the upward and downward propagating fronts and make predictions of changes in the shape of the upward front at different tube radii. We calculate the increase in front velocity for ascending fronts using results from experiments on flames in vertical tubes. We also calculate the increase in front velocity for waves in a horizontal tube using an asymptotic solution for the fluid velocity in a differentially heated cylinder.

Introduction

Chemical waves may have features that differ significantly from the familiar reaction-diffusion wave when convective mass transport plays a role. For example, wave velocities in the iodate-arsenous acid reaction may depend¹ on the direction of propagation relative to the force of gravity. Bazsa and Epstein² have found anisotropic front velocities in the iron(II)-nitric acid system, and Nagypál et al. reported similar effects in the chlorite-thiosulfate reaction.³ Gravity effects in these systems result from density changes within the front. In a previous work, we have explored the mechanisms of convection in chemical waves.⁴ We considered the stability of density gradients arising both from heat liberated (or absorbed) by chemical reaction and from molar volume differences between reactants and products. The ma-

croscopic motion of fluid that can result from the buoyant forces in a fluid density gradient is called free or natural convection.

Two types of convection can occur, depending on the relative signs of the thermally and chemically induced density changes. In an exothermic reaction, there is a thermal expansion of the reacted solution, causing a density decrease relative to the unreacted region. There may also be an isothermal density change because the reactants and products have different partial molar volumes. In other words, the product solution has a different density than a solution of the reactants. If there is an isothermal expansion (a positive volume of reaction), then the chemically and thermally induced density changes will have the same sign. The resulting density gradient may cause simple convection. This is

[†] Brandeis University.

[‡] Current address: Department of Chemistry, University of Southern Mississippi, Hattiesburg, MS 39406-5043.

[§] West Virginia University.

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the case in the iodate oxidation of arsenous acid.

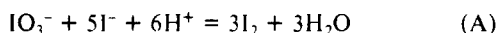
If there is an isothermal contraction competing with the thermal expansion, then a different mode of convection may occur which is called double-diffusive or multicomponent convection. Double-diffusive convection may occur even if the density gradient appears to be statically stable; it can have dramatic effects on the front velocity.² A system exhibiting this behavior will be analyzed in part 3 of this series.⁵

Fronts propagating through iodate-arsenous acid reaction mixtures contained in a vertical glass tube travel faster in the upward direction than in the downward direction, if the tube radius is greater than a critical value. This observation indicates that the density changes caused by the heat and the volume of reaction both result in a decrease in density of the reaction mixture. This density gradient causes free convection.

Fronts propagating in a horizontal tube always travel faster than a descending front in a vertical tube. Any density gradient in a horizontal configuration is unstable and will result in convection.⁴ In this paper, we present experimental results demonstrating the effects of convection on chemical waves in the iodate-arsenous acid system and an explanation of these effects in terms of density changes due to chemical reaction.

Iodate-Arsenous Acid Reaction

The iodate oxidation of arsenous acid is conveniently described in terms of two component processes,^{6,7} process A (the Dushman reaction⁸) and process B (the Roebuck reaction⁹).

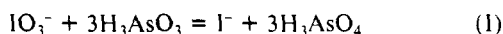


Process A is governed by rate law (α)¹⁰ and process B is governed by rate law (β):^{9,11}

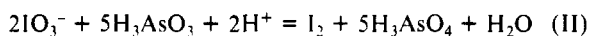
$$R_\alpha = -\frac{1}{5} \frac{d[\text{I}^-]}{dt} = (k_a + k_b[\text{I}^-])[\text{I}^-][\text{IO}_3^-][\text{H}^+]^2 \quad (\alpha)$$

$$R_\beta = \frac{-d[\text{I}_2]}{dt} = \frac{k_c[\text{I}_2][\text{H}_3\text{AsO}_3]}{[\text{I}^-][\text{H}^+]} \quad (\beta)$$

When arsenous acid is in stoichiometric excess ($[\text{As(III)}]_0 > 3[\text{IO}_3^-]_0$), the net reaction is given by



When iodate is in stoichiometric excess ($[\text{As(III)}]_0 < \frac{5}{2}[\text{IO}_3^-]_0$), the net reaction is



Reaction I is obtained by combining (A) + 3(B), and reaction II is given by 2(A) + 5(B). For initial reaction mixtures with $\frac{5}{2}[\text{IO}_3^-]_0 < [\text{As(III)}]_0 < 3[\text{IO}_3^-]_0$, an appropriate linear combination of (I) and (II) describes the stoichiometry of the system.

Factors Affecting Solution Density

The density of a solution is a function of its temperature and composition. We can define coefficients that relate the density ρ to changes in temperature T and composition C

$$\alpha = -\frac{1}{\rho} \frac{\partial \rho}{\partial T} \quad (1)$$

$$\beta_i = \frac{1}{\rho} \frac{\partial \rho}{\partial C_i} \quad (2)$$

where C_i is the molar concentration of the i th species. The total

density of the solution perturbed from a set of reference conditions ρ_0 , T_0 , and C_{0i} is

$$\rho = \rho_0[1 - \alpha(T - T_0) + \sum \beta_i(C - C_0)_i] \quad (3)$$

As the wave front proceeds, the region into which the wave has not yet propagated will be at a different temperature than the region through which it has already passed. This can cause a density gradient, which may result in convection. This source of density gradients has been recognized by several authors.¹²⁻¹⁴ Even if the reaction neither consumes nor generates heat, density gradients can arise if the partial molal volumes of the products differ from those of the reactants, and these gradients may be sufficient to cause convection.

If V_0 is the initial volume of the reaction mixture, the volume of reaction,¹⁵ ΔV , can be related to the change in density caused by the change in chemical composition by

$$\Delta \rho_c = -\frac{\Delta V/V_0}{1 + \Delta V/V_0} \rho_0 \approx -\frac{\Delta V}{V_0} \rho_0 \equiv \beta \Delta C \rho_0 \quad (4)$$

where ρ_0 is the initial density of the solution, ΔC is the change in concentration of the limiting reagent, and β is the mean molar density coefficient. Thus, a positive ΔV corresponds to a decrease in density.

From α (eq 1) and the heat capacity C_p of the reaction solution, we can calculate the density change, $\Delta \rho_T$, caused by the enthalpy change of an adiabatic reaction:

$$\Delta \rho_T = \Delta H \Delta C (1/C_p) \alpha \rho_0 \quad (5)$$

Alternatively, the change in temperature, $(-\Delta H \Delta C)/C_p$, can be measured directly.

The volume change can be calculated a priori from literature data, which are not, however, as extensive as tabulated enthalpy data. Nonetheless, Millero has compiled an impressive set of tables.¹⁶ If the partial molal volumes of the reactants and products are not known, then ΔV must be determined experimentally.

The ΔH° of reaction I is -334 kJ/mol. We assume that α for the dilute reaction mixture is the same as that for distilled water, whose value was measured in a dilatometer at 25 °C to be

$$\alpha = -1.8 \times 10^{-4} \text{ } ^\circ\text{C}^{-1} \quad (6)$$

Using the ΔH° and the heat capacity and density of water, we can calculate from eq 5 $\Delta \rho_T/\Delta[\text{I}^-]$ (the change in density caused by the heat released from a given change in the concentration of iodide).

$$\Delta \rho_T/\Delta[\text{I}^-] = -1.4 \times 10^{-2} \text{ g}/(\text{cm}^3 \text{ M}) \quad (7)$$

As described in the Experimental Section, we measured the volume and temperature changes associated with a 0.0075 M change in $[\text{I}^-]$. We then used our value of α (eq 6) to correct for the thermal expansion (eq 5) to obtain a value for $\Delta \rho_c$, the change in density caused by the change in composition (eq 4):

$$\Delta \rho_c = (\Delta V/V_0) \rho_0 = 1.3 \times 10^{-4} \text{ g}/\text{cm}^3 \quad (8)$$

So

$$\Delta \rho_c/\Delta[\text{I}^-] = -1.7 \times 10^{-2} \text{ g}/(\text{cm}^3 \text{ M})$$

The two factors act in the same direction to decrease the density. If this were not the case, then double-diffusive, and not simple, convection could occur.⁴

Experimental Section

Materials and Apparatus. Reactant solutions were prepared with reagent grade chemicals and doubly distilled water. Arsenous

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TABLE I: Composition of Reaction Mixtures Containing Excess Arsenous Acid

	reactant varied		
	KIO ₃	H ₃ AsO ₃	H ⁺
10 ³ [KIO ₃], M	3.50–5.00	5.00	5.00
10 ² [H ₃ AsO ₃], M	1.49	1.79–4.47	1.68
10 ³ [H ⁺], M	8.71	12.6	3.78–13.8
10 ² (wt % starch)	4.00	4.00	4.00

TABLE II: Composition of Reaction Mixtures Containing Excess Iodate

	reactant varied		
	KIO ₃	H ₃ AsO ₃	H ⁺
10 ³ [KIO ₃], M	6.00–10.0	5.00	5.00
10 ³ [H ₃ AsO ₃], M	14.9	1.49–13.4	4.47
10 ³ [H ⁺], M	8.71	12.6	1.01–11.1
10 ² (wt % starch)	4.00	4.00	4.00

TABLE III: Other Reaction Mixture Compositions

	concentration, mM			
	H ₃ AsO ₃	KIO ₃	H ⁺	I [−]
wave velocities				
reaction mixture A	29.8	5.00	10.0	<0.0001
reaction mixture B	4.96	5.00	5.75	<0.0001
enthalpy of reaction				
reaction mixture C	29.8	5.00	3.71	<0.0001
volume of reaction				
reaction mixture D	29.5	7.50	5.90	<0.001
temperature gradient				
reaction mixture E	44.7	20.0	15.1	<0.001

acid solutions were prepared from NaAsO₂ and H₂SO₄ in a 1:1 mole ratio, and the concentrations were determined iodometrically.

Chemical wave experiments were carried out using water-jacketed 25.0-cm glass capillary tubes with various inside radii. The temperature was maintained at 25.0 ± 0.1 °C. Wave position was read from a millimeter scale attached to the capillary tube. Waves were initiated at Pt electrodes (B&S Gauge No. 26) in each end of the tube. Enthalpy of reaction experiments were carried out using a Dewar flask and an Omega Model 871 digital thermometer. A homemade dilatometer was utilized to measure reaction mixture density changes during the course of reaction.

Wave Velocity Measurements. Standard stock solutions and doubly distilled water were pipetted in appropriate volumes to give reaction mixtures of desired concentrations. The mixture was used to first flush, and then fill, the capillary tube. Wave initiation occurred at a Pt electrode in one end of the tube, negatively biased with respect to another Pt electrode in the other end. (Applied potentials ranged between −1.0 and −5.0 V.) The appearance of blue solution at the electrode signaled wave initiation, at which time the electrode polarity was reversed in order to initiate a wave at the other end of the tube. When a blue region was evident at both ends of the tube, the electrodes were removed and the tube was placed in a vertical position. Measurements were made as each wave traveled about one-fourth the length of the tube. The tube was then placed in a horizontal position for additional measurements. In this manner, wave position as a function of time was recorded for ascending, descending, and horizontal waves. Plots of position vs time in all three cases were linear, allowing velocities to be calculated from least-squares fits of the data.

Studies of front velocity dependence on iodate, arsenous acid, and hydrogen ion concentrations were carried out by varying the concentration of the component of interest while keeping all other reactant concentrations constant. Initial concentrations of reactants are summarized in Tables I–III. The ratio of the initial arsenous acid concentration to the initial iodate concentration, $R = [\text{H}_3\text{AsO}_3]_0/[\text{IO}_3^-]_0$, determines the reaction stoichiometry and the type of chemical wave produced. Initial concentrations for reaction mixtures with $R \geq 3$, corresponding to excess arsenous acid stoichiometry, are given in Table I. Initial concentrations for reaction mixtures with $R < 3$, corresponding to excess iodate

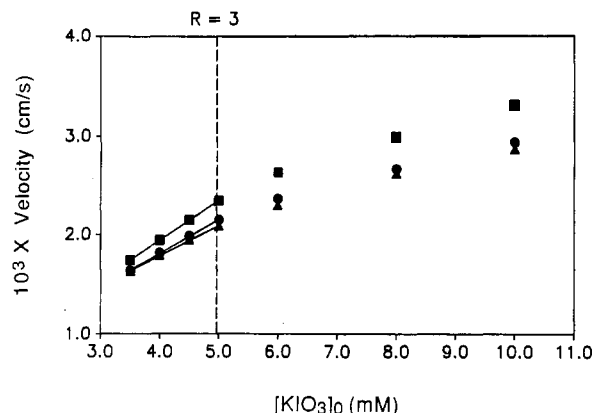


Figure 1. Wave velocity as a function of $[\text{KIO}_3]_0$ for ascending waves (●), descending waves (▲), and horizontal waves (■) in a tube of radius 0.047 cm. Excess arsenous acid waves are to the left of the line labeled $R = 3$; excess iodate waves are to the right. Solution composition in Tables I and II.

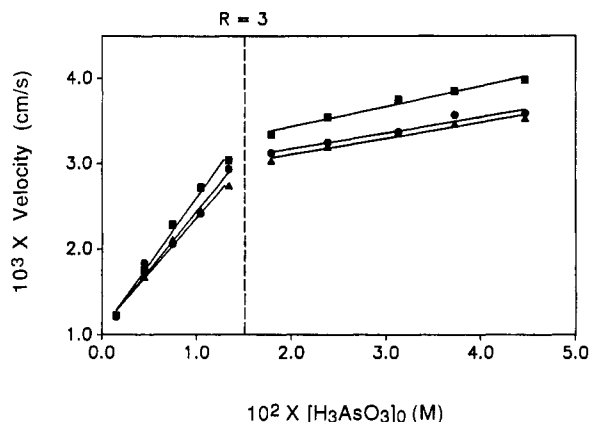


Figure 2. Wave velocity as a function of $[\text{H}_3\text{AsO}_3]_0$ for ascending (●), descending (▲), and horizontal waves (■) in a tube of radius 0.047 cm. Excess arsenous acid waves are to the right of the dashed line labeled $R = 3$; excess iodate waves are to the left. Solution composition in Tables I and II.

stoichiometry, are given in Table II. A constant pH was maintained in the reaction mixture by a NaHSO₄/Na₂SO₄ buffer.

Enthalpy of Reaction. Measurements of reaction enthalpy were performed in a Dewar flask. Appropriate volumes of stock solutions were combined to give a 50.0-mL reaction mixture of composition C in Table III. The heat capacity of the Dewar flask was determined by measuring the final temperature of aliquots of distilled water with different initial temperatures.

Isothermal Volume of Reaction. A homemade dilatometer was used to measure the isothermal volume of reaction. After degassing, two reactant solutions were thermally equilibrated with the dilatometer in a 25.0 °C water bath. The reactants were combined and mixed in the dilatometer, which was equipped with a magnetic stir bar. Temperature and volume were continuously recorded during the course of the reaction. Measurements were made until chemical equilibrium was established and the temperature of the reaction mixture had reequilibrated to that of the water bath.

In separate experiments, the dilatometer was filled with degassed, distilled water to determine the effective isobaric coefficient of thermal expansion α' . The temperature of the water bath was increased, and measurements of volume as a function of temperature were made in order to calibrate the dilatometer.

Experimental Results

Velocity Dependence on Initial Concentrations. Velocities were determined for waves propagating in vertical and horizontal capillary tubes. Figure 1 shows velocities of ascending, descending, and horizontally traveling waves as a function of initial KIO₃ concentration, confirming the reasonably linear dependence on

TABLE IV: Front Velocity Dependence on Tube Radius and Orientation^a

tube radius, cm	10 ³ × velocity, ^b cm/s		
	ascending	descending	horizontal
0.047	2.93 (1.12)	2.94 (1.13)	3.35 (1.16)
0.089	4.82 (1.30)	3.02 (1.27)	4.70 (1.53)
0.12	5.79 (1.68)	2.95 (1.23)	5.83 (1.85)

^a Reaction mixture A (B) in Table III. ^b All values $\pm 0.05 \times 10^{-3}$ cm/s.

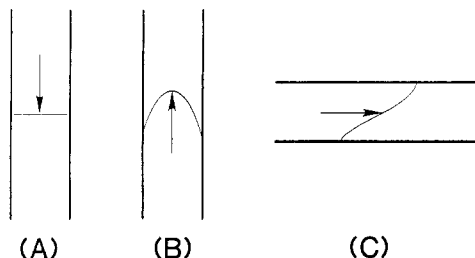


Figure 3. Schematic representation of propagating fronts for different orientations: descending wave (A), ascending wave (B), and horizontal wave (C).

iodate concentration in excess arsenous acid solutions found in earlier studies.⁷ Velocities of ascending, descending, and horizontal waves as a function of initial H_3AsO_3 concentration are shown in Figure 2.

Wave Velocity in Capillary Tubes. Table IV gives velocities of waves propagating through solutions contained in vertical and horizontal glass tubes with varying inner diameters. The reaction mixture designated A contains excess arsenous acid, and reaction mixture B contains excess iodate. Figure 3 illustrates the front shapes for the three configurations. Fronts traveling in horizontal capillary tubes are not flat and perpendicular to the direction of travel but are slanted at approximately 45°. In vertical capillary tubes, descending waves exhibit flat fronts that are perpendicular to the direction of travel, while ascending waves produce fronts that are convex and approximately parabolic in shape.

Enthalpy of Reaction. A temperature rise of 0.3 °C was measured for reaction mixture C in Table III. This temperature rise corresponds to $\Delta H^\circ = -334$ kJ/mol for reaction mixtures of stoichiometry (I). This value compares reasonably well with the standard-state value calculated from thermodynamic data¹⁷ of -305 kJ/mol. For the excess iodate stoichiometry (II), the standard enthalpy of reaction is -606 kJ/mol.

Isothermal Volume of Reaction. The percent change in volume as a function of time for an excess arsenous acid reaction mixture is shown in Figure 4a. In Figure 4b, a plot of temperature as a function of time for the same reaction mixture is shown. The sudden temperature increase from the baseline value of 24.9 °C and the subsequent decrease result from the rapid heat release of the autocatalytic reaction followed by the slower thermal equilibration of the reaction mixture. The isobaric coefficient of thermal expansion α' , defined as

$$\alpha' = (\partial V / \partial T)_P / V \quad (9)$$

gives the relative change in volume with respect to temperature at constant pressure. For water¹⁷ at 20.0 °C, $\alpha' = 2.1 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$, which compares well with our experimentally determined value of $1.8 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$, measured between 25.2 and 25.8 °C. The effective coefficient of thermal expansion for iodate-arsenous acid reaction mixtures was assumed to be the same as the measured value for water. The value of α' equals the inverse of α , the change in density as a function of temperature.

The volume change over the course of reaction shown in Figure 4a can be corrected to isothermal values by subtracting the volume

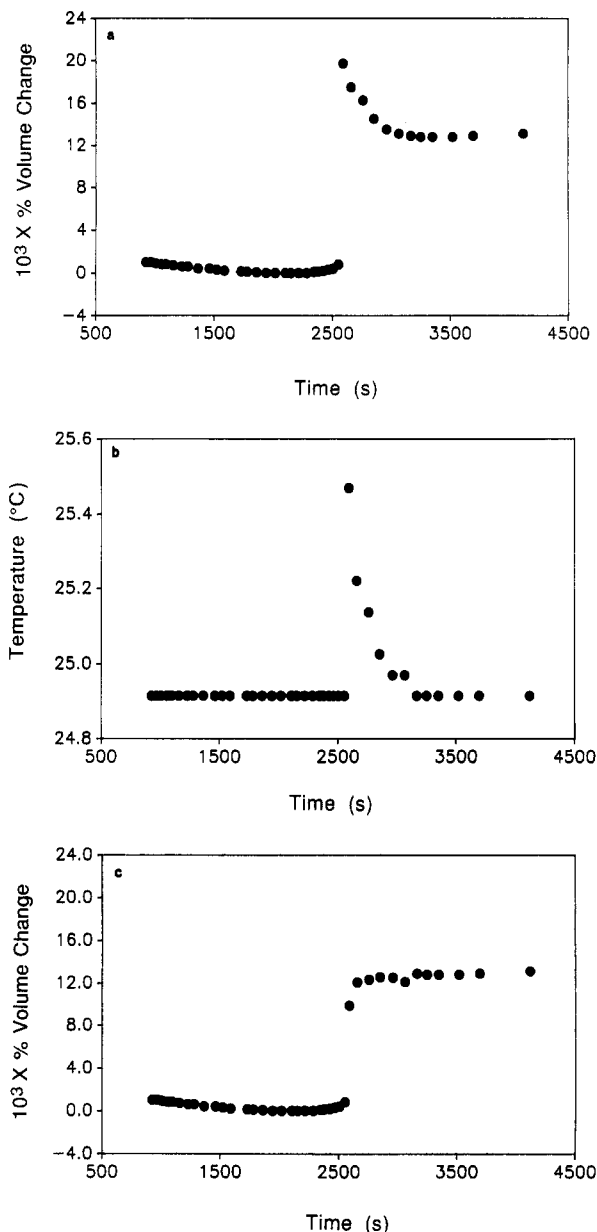


Figure 4. (a) Percent volume change as a function of time for a homogeneous iodate-arsenous acid reaction mixture. Composition D in Table III (excess arsenous acid). (b) Temperature of reaction mixture as a function of time. (c) Percent volume change as a function of time, corrected for volume change due to change in temperature.

change resulting from the variation in temperature. This correction is carried out by reducing the values in Figure 4a by $\alpha(\Delta T)$, where ΔT is the difference between the dilatometer temperature at a particular time and the baseline temperature, given in Figure 4b. The corrected volume change is shown in Figure 4c. The increase in volume corresponds to the decrease in solution density due to differing partial molal volumes of reactant and product species.

Effect of Orientation

From Table IV, we see that the front propagation velocity is a function of the orientation, as well as the radius of the tube. Within the experimental error of $\pm 0.05 \times 10^3$ cm/s, the descending velocity is independent of the tube width. This is consistent with the theory that the descending front in an exothermic reaction with a positive reaction volume (ΔV) is always a pure reaction-diffusion front.⁴ The fact that the ascending front velocity depends strongly on the tube radius, and that there is a radius at which the velocity is the same as that of the descending front, suggests that simple convection occurs. That the horizontal velocity is always greater than the descending velocity is also con-

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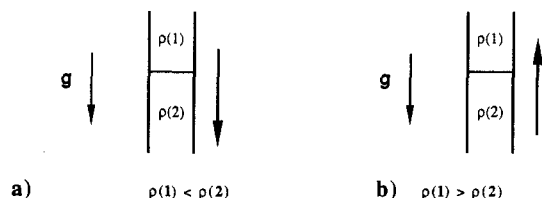


Figure 5. (a) Density gradient induced by a descending wave front. Because $\rho(1) < \rho(2)$, the liquid is stable and no convection will occur. (b) Density gradient induced by an ascending wave front. Because $\rho(1) > \rho(2)$, the liquid may be unstable, depending on the size of the tube and the size of the density difference. The direction of gravitational force is indicated by g . Large arrows show direction of propagation.

sistent. To understand these observations, we must analyze the stability of the density gradient created by a propagating front in each of the three orientations.

Stability Analysis

We now consider the stability of the solution at the wave front in each of the three orientations. First, we use eqs 7 and 8 to calculate the total density difference caused by the temperature change and the change in composition. In an excess arsenous acid solution with an initial iodate concentration of $[\text{IO}_3^-]_0 = 0.005 \text{ M}$

$$\Delta\rho = (0.005 \text{ M}) \left(\frac{\Delta\rho_c}{\Delta[I^-]} + \frac{\Delta\rho_T}{\Delta[I^-]} \right) = -1.6 \times 10^{-4} \text{ g/cm}^3$$

Descending Front. To understand why the descending front is not affected by convection, we must consider the density gradient formed by the reaction front. Figure 5a shows schematically the configuration of the less dense, reacted fluid above the more dense, unreacted solution. This is always stable. Convection cannot arise, and the front velocity is completely determined by the coupling of reaction and diffusion. The descending front provides the value for the pure reaction-diffusion wave. For a given set of reactant concentrations, a velocity greater than that of a descending front must result from convection.

Ascending Front. An ascending front will cause a density gradient in which less dense fluid lies under more dense fluid. This configuration, which may be unstable, is shown in Figure 5b. Several factors affect whether free convection will occur. The greater the density gradient, the less stable the configuration. A narrow tube increases the stability, as does a high viscosity. The final stabilizing factor is the value of the transport coefficient for the property causing the density gradient. For a solute gradient, the diffusion coefficient is relevant, because it is a measure of how rapidly a perturbation in concentration will diffuse away. For a temperature gradient, the thermal diffusivity is the relevant parameter.

The Rayleigh number is a measure of the stability of a system. For a vertical cylinder of radius r , it is given by¹⁹

$$\text{Ra} = \frac{r^4 g}{\mu \text{Tr}} \frac{d\rho}{dz} \quad (10)$$

where Tr is the relevant transport coefficient and μ is the viscosity. Taylor calculated that the maximum value for Ra that does not result in convection is 67.9.²⁰

We might expect the need to calculate two Rayleigh numbers, because both solute and thermal gradients are present. In general this is true, but we may neglect the thermally induced density gradient, because it is about the same size as that caused by the concentration difference, while the mass transport coefficient is 2 orders of magnitude smaller:

$$D_{\text{iodide}} = 2.04 \times 10^{-5} \text{ cm}^2/\text{s} \quad \kappa_{\text{water}} = 1.4 \times 10^{-3} \text{ cm}^2/\text{s}$$

TABLE V: Rayleigh Number Calculated for Reaction Mixture A

tube radius, cm	Ra	convection observed?
0.047	23	no
0.089	295	yes

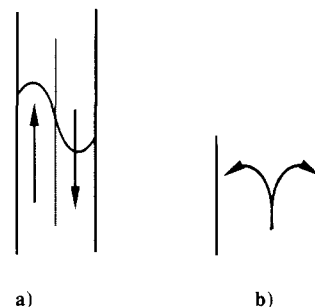


Figure 6. Convective fluid flow and the effect upon the wave form: (a) antisymmetric flow, slightly above the critical Rayleigh number; (b) fluid flow at Rayleigh numbers greatly exceeding the critical value, where axisymmetric flow is expected. The wave form has a parabolic shape. A wider tube increases the Rayleigh number.

(See refs 7 and 19, respectively.) For the solute-induced density gradient, we calculate Ra as follows:

$$\mu = \text{viscosity} = 0.0089 \text{ g/(cm s)} \quad (\text{for water}^{19})$$

$$g = 980 \text{ cm/s}^2$$

$$\Delta\rho_c = 8.5 \times 10^{-5} \text{ g/cm}^3 \quad (\text{from calculation in eq 7})$$

Calculating the density gradient requires that we know the width of the wave front and that we assume the concentration gradient is linear. Hanna et al.⁷ found that

$$\Delta z \approx 0.1 \text{ cm}$$

Thus

$$\text{Ra} = (4.6 \times 10^6 \text{ cm}^{-4}) r^4 \quad (11)$$

In Table V we give the Rayleigh numbers for two tube sizes used in our experiments. We expect that no convection should occur in the smallest tube and the front velocity should be the same for the ascending and descending fronts, which is in agreement with the experiments. The critical value of $\text{Ra} = 67.9$ yields a minimum radius for convection, r_c , of 0.062 cm. This situation is similar to the case of a fluid between two parallel, horizontal plates, the Rayleigh-Bénard experiment.²¹ As the lower plate is heated, a density gradient arises. When the density gradient reaches a critical value, convection ensues. The critical Rayleigh numbers for the two experiments are different because of the different geometries.

Horizontal Front. The horizontal case is very different. It is analogous to a system with fluid between two vertical, differentially heated plates. Such a configuration is always unstable and hence should have no critical radius for the onset of convection. This prediction agrees with the data in Table IV, which show that the horizontally propagating front is always faster than the pure reaction-diffusion front. These results may seem paradoxical. One might expect that to eliminate the effect of gravity on a propagating front the tube should be horizontal. This expectation is not true, because the tube is not one-dimensional; gravity can always influence an inhomogeneous fluid.^{4,13}

Convective Fluid Flow

For an ascending orientation, the front has a parabolic shape, as shown schematically in Figure 3. Such a shape should arise if the fluid flow were axisymmetric as shown in Figure 6b. However, Taylor predicts that the first convective mode to become unstable at the critical Rayleigh number (67.9) is the antisym-

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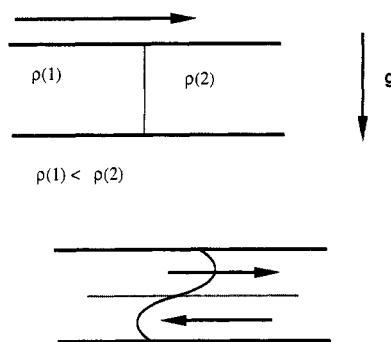


Figure 7. (top) Wave front propagating from left to right in a horizontal tube. (bottom) An antisymmetric fluid flow results which causes a slanted wave front.

metric flow depicted in Figure 6a. This prediction has been confirmed with numerical simulations of water in a vertical cylinder heated from below.²² If the reaction is run in a wider tube, the Rayleigh number increases. Gershuni and Zhukhovitskii²³ have analyzed the modes of convection at higher values of the Rayleigh number. When $Ra = 452.0$, axisymmetric flow occurs with fluid rising in the center of the cylinder and descending along the sides. Such a flow would distort the wave front into a parabolic shape as the less dense, reacted solution rises into the unreacted zone. The front in Figure 3b was observed at a Rayleigh number much greater than 67.9 but less than 452.0.

To understand why axisymmetric fluid flow occurs below a Rayleigh number of 452.0, we must take into account that Taylor's stability analysis is for a density gradient in a nonreactive fluid. If an antisymmetric flow develops in the present situation, then the descending, unreacted fluid enters a region of reacted solution. Diffusion of the autocatalytic species into unreacted solution will cause it to react and to decrease in density. Diffusion will be facilitated by mixing of the moving fluid. The descending fluid is now less dense and will rise. However, our understanding of this process is limited, and further work must be done on how the transition between the different modes of convection occurs in a reacting fluid.

No experiments were performed at the critical Rayleigh number of 67.9. An antisymmetric mode of convection may occur. To perform this experiment, one could vary the reactant concentrations (and thus alter the density gradient) or perform the reaction in a tube with an inner radius near the critical radius of 0.061 cm.

Similarly curved fronts have been observed with ascending flame fronts. Von Lavante and Strehlow²⁴ studied methane-air flames freely propagating up a tube. The photographs of these fronts bear a striking resemblance to those in the iodate-arsenous acid system. Pelcé-Savornin et al. were able to stabilize an ascending flame by flowing the unreacted gases down a tube.²⁵ They also observed curved fronts which they attributed to the effect of buoyancy arising from the difference in density between the reacted and unreacted gases. These experiments were performed at Rayleigh numbers well above 452.0 ($\approx 500\,000$). Pelcé-Savornin et al. observed that the curved front appeared to be self-stabilized by the fluid flow induced by its own buoyancy.

A front propagating in a horizontal tube should cause an antisymmetric fluid flow. The wave front propagating from left to right is shown in Figure 7. The front creates a density gradient analogous to one formed in a horizontal tube with a higher temperature at the left side. An antisymmetric flow results with the shape indicated in Figure 7, which looks like the front depicted in Figure 3c. Similarly shaped fronts have been observed for flames propagating in horizontal tubes.²⁶

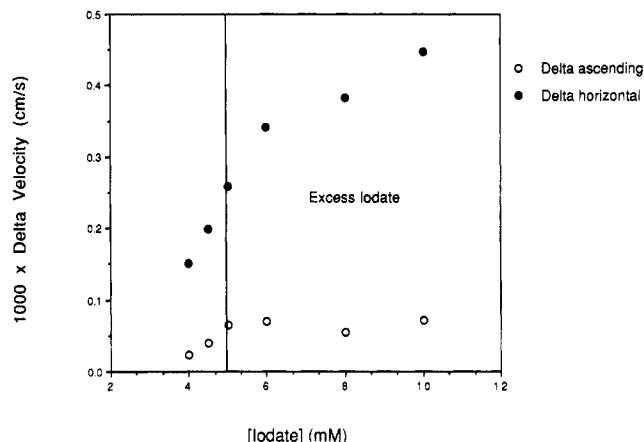


Figure 8. Δv_{exp} for the ascending and horizontally propagating fronts plotted versus $[KIO_3]_0$.

Analytical Model To Calculate Δv_{exp}

We now attempt to explain the increase in wave front velocity due to convection. We call the difference between the observed velocity and the pure reaction-diffusion velocity (taken to be the descending front velocity) Δv_{exp} . We assume that this increase in propagation velocity equals the average flow velocity caused by the density gradients resulting from the concentration and thermal gradients in the front.

$$\Delta v_{\text{exp}} = \langle \text{vel} \rangle \quad (12)$$

Thus, the problem can be considered in a reference frame moving with constant velocity equal to the convection-free rate of propagation.

The wave front velocity as a function of arsenous acid concentration, for a fixed iodate concentration, is shown in Figure 1. Notice that the ascending and horizontally propagating fronts have higher velocities than the descending fronts. The Δv_{exp} as a function of $[KIO_3]_0$ is presented in Figure 8. The left half is the excess arsenous acid region. As the concentration of initial iodate increases, the total density change from thermal and chemical origins increases linearly. Thus, the density gradient increases linearly. If the fluid flow is a linear function of the density gradient, then the flow velocity and Δv_{exp} will also increase in a linear fashion. For the excess iodate region, the total density change should not increase, because the limiting reagent, arsenous acid, is not increasing. However, the rate of reaction will increase, and this will decrease the time over which the heat and products formed may diffuse. The resulting density gradient increases, as well as the resulting convective flow velocity. However, the slope of this line is less than when iodate is the limiting reagent, and Δv_{exp} should approach an asymptotic limit.

Figure 2 shows the wave front velocity as a function of arsenous acid concentration for a fixed concentration of iodate. These experiments were performed in a sufficiently narrow tube that the convection in an ascending front was almost eliminated. Figure 9 shows Δv_{exp} as a function of $[H_3AsO_3]_0$. Not much can be said about the ascending fronts, but the data from the horizontal fronts indicate a linear dependence on the concentration of arsenous acid with a qualitative change between the excess iodate and the excess arsenous acid stoichiometries. This transition occurs because the density gradient in the wave front is different for each stoichiometry. The isothermal density change should be different for each mechanism, although it was not measured, and tables do not provide the data for the partial molal volumes of all the reactants and products.¹⁶ However, the thermally induced density change is definitely different, because the ΔH° of the excess iodate reaction, -606 kJ/mol, is greater than that of the excess arsenous acid reaction. The slope of the curve in the excess iodate region in Figure 9 is greater than the slope in the excess arsenous acid region. Again, the slope decreases when the excess arsenous acid

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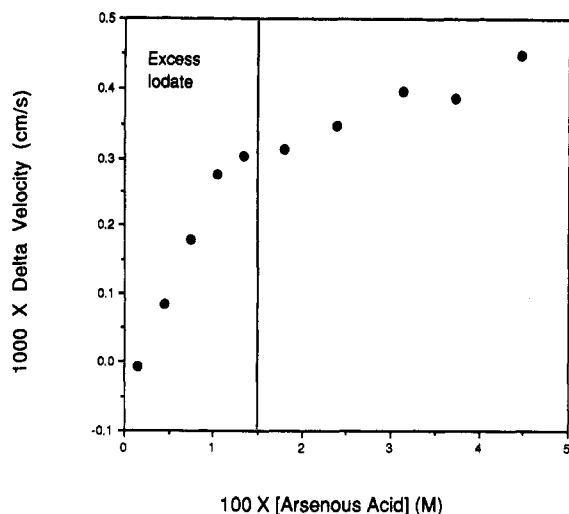


Figure 9. Δv_{exp} for the horizontally propagating fronts plotted versus $[\text{H}_3\text{AsO}_3]_0$.

TABLE VI: Δv_{exp} and Average Calculated Fluid Velocity in a Vertical Cylinder^{a,b}

r_0 , cm	$\langle \text{vel} \rangle$ (eq 12)	Δv_{exp}
0.089	1.7	1.8
0.12	2.0	2.7

^a Reaction mixture A in Table III. ^b All velocities have units of 10^{-3} cm/s.

region is reached because only the rate of reaction and not the net density difference is changing.

Calculating the fluid flow for the ascending wave front is extremely difficult and has not been undertaken in this study. However, work on ascending flames has indicated that the increase in front velocity can be calculated from the velocity of a bubble of hot air (with the same temperature difference as caused by the flame) rising under its own buoyancy.^{24,25} Von Lavante and Strehlow²⁴ successfully calculated the increase in the velocity of an ascending flame compared to a descending one using a relationship derived explicitly for gases and lacking dependence on viscosity. We have modified their expression by scaling with the ratio of the viscosities of air and water because the velocity of free convective, laminar flow in a tube depends inversely on the viscosity of the fluid:²⁷

$$\langle \text{vel} \rangle = [gr_0\Delta\rho(0.492)]^{1/2}(\mu_{\text{air}}/\mu_{\text{water}}) \quad (13)$$

$$\mu_{\text{air}} = 2.0 \times 10^{-4} \text{ g/(cm s)} \quad (\text{at } 25^\circ\text{C}^{28})$$

Calculations of $\langle \text{vel} \rangle$ using a $\Delta\rho = 1.4 \times 10^{-4} \text{ g/cm}^3$ for two tube sizes are compared with the observed Δv_{exp} in Table VI. The values are of the right order of magnitude, but it is not clear whether the velocity scales as $r_0^{1/2}$ as eq 13 predicts. Additional experiments must be performed to test this relationship.

Greater progress has been made on the flow in horizontal orientation. Bontoux et al.²⁹ present an asymptotic solution for the convective flow in the vertical midplane of a horizontal cylinder, with ends held at different temperatures. They calculate the antisymmetric fluid velocity as a function of the scaled distance from the central axis of the cylinder, r

$$\text{vel}(r) = -\frac{1}{8} \frac{L}{2r_0} \text{Ra}(r^2 - 1)r \cos \phi \quad (14)$$

where ϕ is the angle with respect to the midplane of cylinder, r_0 is the radius, and L is the length of cylinder. Using eq 9, we

TABLE VII: Δv_{exp} and Average Calculated Fluid Velocity in a Horizontal Cylinder^{a,b}

r_0 , cm	$\langle \text{vel} \rangle$ (eq 16)	$\langle \text{vel} \rangle$ (eq 17)	Δv_{exp}
0.047	0.15	0.42	0.42
0.089	1.9	1.5	1.8
0.12	6.2	2.7	2.7

^a Reaction mixture A in Table III. ^b All velocities have units of 10^{-3} cm/s.

convert this relation from dimensionless variables into the relevant physical quantities in our system

$$\text{vel}(r) = -\frac{1}{8} \frac{r_0^4 g}{L\mu} \frac{d\rho}{dz}(r^2 - r) \quad (15)$$

where L is the width of the front. Integrating over r provides the average fluid velocity, which is the same in either direction.

$$\langle \text{vel} \rangle = \frac{1}{32} \frac{r_0^4 g}{\mu} \left[\frac{\Delta\rho_c}{L_c^2} + \frac{\Delta\rho_T}{L_{th}^2} \right] \quad (16)$$

$\Delta\rho_{c,T}$ is the density difference caused by the concentration (temperature) difference between reacted and unreacted regions, and $L_{c,T}$ is the physical length over which this difference occurs.

The length scale of the concentration difference is available from Hanna et al.⁷ $L_c \approx 0.1$ cm. From a thermocouple measurement of the temperature change with time as an ascending wave front (reaction mixture E) passes, L_T was found to be approximately 0.6 cm. Using the values of $\Delta\rho_c$ and $\Delta\rho_T$ from eqs 6 and 7, we obtain the following expression for the $\langle \text{vel} \rangle$ as a function of the tube radius:

$$\langle \text{vel} \rangle \text{ (cm/s)} = (30 \text{ cm}^{-3}/\text{s})r_0^4 \quad (17)$$

In Table VII we compare the velocity calculated from eq 17 and the observed Δv_{exp} . The order of magnitude is correct, but the dependence on the tube radius is in error. If we postulate that the width of the front changes linearly with r_0 , and modify eq 17 by adjusting the constant to provide the experimental value at the smallest radius, we obtain reasonably good agreement with experiment (Table VI), using

$$\langle \text{vel} \rangle \text{ (cm/s)} = (0.19 \text{ cm}^{-1}/\text{s})r_0^2 \quad (18)$$

This rescaling might be justified by recalling the large uncertainties in the constants used in eq 17. The width of the concentration profile was estimated from experiments in a Petri dish and not in a horizontal tube. The width of the temperature front was estimated from measurements on an ascending front, not a horizontally propagating front. To test the validity of eq 18, measurements of the width of the temperature and concentration profiles of horizontal fronts for a wide range of tube radii should be performed.

Conclusion

The iodate-arsenous acid system is an exothermic reaction that supports constant-velocity reaction-diffusion fronts. The release of heat decreases the density of the reacted fluid with respect to the unreacted solution. There is also an isothermal decrease in density caused by the positive reaction volume (i.e., the sum of the partial molal volumes of the products is greater than that of the reactants). By analyzing the stability of the density gradient produced in the solution at the front, we conclude the following: (1) The descending front is a pure reaction-diffusion front. (2) For an ascending front, there is a critical tube radius below which no convection can occur. If convection does occur, the ascending front velocity is increased by an amount equal to the average convective fluid flow velocity. This flow velocity is a function of the tube radius and of the density gradient caused by the concentration gradient. The thermal gradient plays little role in destabilizing the fluid, because the reaction is not very exothermic and because heat transfer is much more rapid than diffusion. We predict that the front may have a transient, antisymmetric form

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close to the critical Rayleigh number of 67.9 and an axisymmetric shape for larger Rayleigh numbers, as was observed. (3) There is no critical radius in the horizontal orientation, and convection always increases the wave front velocity. Using the expression for the asymptotic flow velocity of a differentially heated horizontal cylinder, we can predict the order of magnitude of the increase in front velocity caused by convection.

If a wave reaction were endothermic and had a negative reaction volume, then the upward front would be the pure reaction-diffusion one, and the descending front would be affected by convection. The horizontal configuration would show the same behavior as the iodate-arsenous acid system with the angle of the front reversed.

If an exothermic wave reaction has a negative reaction volume, or an endothermic reaction has a positive reaction volume, then a completely different mechanism will affect the front velocity. This scenario requires double-diffusive convection to explain the increase in front velocity, a problem that will be treated in part 3 of this series.

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Convective Effects on Chemical Waves. 3. Multicomponent Convection in the Iron(II)-Nitric Acid System

John A. Pojman,[†] István P. Nagy,[‡] and Irving R. Epstein*

Department of Chemistry, Brandeis University, Waltham, Massachusetts 02254-9110, and Institute of Physical Chemistry, Kossuth Lajos University, H-4010 Debrecen, Hungary (Received: July 18, 1990)

We consider the effects of convection on chemical waves in which density gradients result from the exothermicity as well as from the isothermal volume change of the reaction. The nitric acid oxidation of Fe(II) supports a constant-velocity traveling front which can be followed by observing the brown ring of the intermediate FeNO^{2+} . The front velocity is extremely sensitive to the width of the tube in which the reaction is performed as well as to the orientation with respect to the gravitational vector. Ascending fronts propagate faster than pure reaction-diffusion fronts. Descending fronts propagate with the greatest velocities, as much as 80 times more rapidly than the reaction-diffusion front. Using the theory of multicomponent (double-diffusive) convection, we can explain this behavior in which there is a thermally induced density decrease in the front as well as an isothermal density increase. We qualitatively account for the observed concentration and orientation dependences.

Introduction

In a previous work,¹ we analyzed the stability of density gradients induced by traveling fronts, as well as the mechanisms of free convection, which may greatly affect the front velocity. Density gradients are caused by the heat released or absorbed, a thermal effect. The difference in the partial molal volumes of the reactants and products can also result in an isothermal density change. We determined that there are two different mechanisms by which convection may increase the front velocity, depending on the relative signs of these two effects: simple convection and multicomponent (double-diffusive) convection.

In the preceding work, we have considered simple convection in the iodate-arsenous acid system.² In that system, simple convection increased the propagation velocity for both ascending and horizontal fronts. Descending fronts were unaffected. This type of convection is the cause of smoke rising and the increase in the rate of a burning cigarette held filter side up.³

Bazsa and Epstein⁴ observed in the iron(II)-nitric acid system that in a vertical tube descending fronts propagate more rapidly than ascending ones. What is most surprising is that not only do the descending fronts propagate more rapidly than the ascending ones, and necessarily the pure reaction-diffusion fronts, the ascending fronts also propagate more rapidly than the pure reaction-diffusion fronts. Simple convection is clearly not the operative mechanism. A mode of convection that increases front velocity for both ascending and descending fronts is required, even when the density gradient is statically stable. A type of convection that can occur even with an apparently stable density gradient is called

multicomponent or double-diffusive convection.

In this work, we present the results of experiments on the iron(II)-nitric acid system and, using the theory of multicomponent convection, provide qualitative explanations for the dependence of the velocity on initial concentrations, tube size, and tube orientation.

Chemistry of the Iron(II)-Nitric Acid System

The oxidation of Fe(II) in nitric acid proceeds according to the following reaction:⁵



An intermediate is FeNO^{2+} , which is brown and forms the basis of the brown ring test for the qualitative analysis of nitrates and nitrites.⁶ The kinetics of this reaction have been studied in batch⁷ and in a flow reactor⁵ and found to be autocatalytic in nitrous acid. Bazsa and Epstein⁴ determined that this system can support traveling waves in which a brown ring of FeNO^{2+} propagates in a tube. In convection-free systems, the ring is extremely narrow (≈ 0.1 cm). Póta and Lengyel⁸ obtained an approximate analytical expression for the convection-free front velocity as a function of

[†] Current address: Department of Chemistry, University of Southern Mississippi, Hattiesburg, MS 39406-5043.

[‡] Kossuth Lajos University.

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