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CHEMICAL SMOKE RINGS: THE EVOLUTION OF UNCONFINED, BUOYANT, CHEMICAL PLUMES

by Michael C. Rogers and Stephen W. Morris

In chemical systems that exhibit some form of kinetic feedback such as autocatalysis, diffusion can interact with chemical reaction to produce chemical waves, as is the case in the iodate - arsenous acid (IAA) reaction [1]. In a thin horizontal layer of reactant material, the IAA reaction occurs as a propagating front that travels by means of a reaction-diffusion process. A small amount of heat is produced during the reaction, as the reaction is exothermic. In addition, there is also an isothermal density difference between the reactant and product solutions: the product left in the wake of the front is lighter than the reactant [2]. The isothermal density change, along with the exothermicity of the reaction, causes the traveling front to leave behind a product solution that is less dense than the reactant solution.

When the medium for the traveling front is a thin horizontal layer, the density drop across the front does not assist in the transport of reacted fluid. However, a front propagating from below reactant solution creates a buoyant wake, which may drive convection, adding mass transport to the reaction-diffusion system. The coupling between reaction-diffusion and buoyancy driven convection can be studied in a quasi two-dimensional configuration by placing reactant in a vertically oriented slot (Hele-Shaw cell) and initiating the reaction along the entire length of the cell [3-5]. Results from these investigations have shown that the buoyancy driven instability causes an initially flat front to break up into fingers. The fingers arise from the competition between convection, which acts to extend the fingers, and diffusion, which acts to smooth the front. In vertically oriented capillary tubes, convection can assist the propagation of ascending fronts, provided the tube diameter is greater than a critical minimum size [2].

In capillary tubes, the shape of the ascending IAA front remains constant, reducing the study of the system to a one-dimensional problem. In thin vertical slots, the front behavior is two-dimensional. Naturally, this leads one to inquire about how the IAA front behaves in three dimensions, where convection effects are no longer constrained by the viscous interaction with nearby solid boundaries. We set

out to determine the phenomenology of the reaction-driven flow behavior for an essentially unbounded solution of reactant.

Since the discovery of fire, humankind has been captivated by hydrodynamic flows driven by chemical reactions. We examine a new system in which an autocatalytic reaction front yields laminar plumes and vortex rings analogous to rising smoke rings.

In order to get a feel for what one might expect to observe when the buoyant product solution ascends through and reacts with the surrounding reactant solution, we should recall the various types of conventional buoyant convection from isolated sources. A *plume* is a continuous region of buoyancy supplied by a point source. A particular type of plume, known as a *starting plume*, has a well-defined, advancing head. A *thermal*, on the other hand, is a freely evolving buoyant object confined to a limited amount of fluid,

which loses connection with the source that produced it. Thermals may take the form of *vortex rings*, which have overturning internal flow, analogous to smoke rings. These types of flow are abundant in nature, and can be produced in the laboratory by pumping buoyant fluid from a source into a larger volume.

EXPERIMENT

To study the IAA reaction in three-dimensions, we constructed the apparatus shown in Fig. 1. The reaction vessel was a large glass cylinder sealed at both

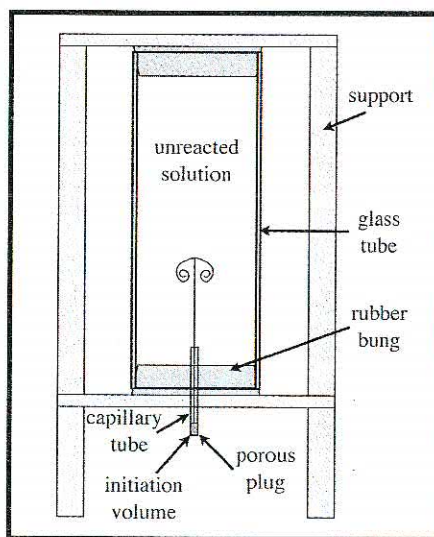


Fig. 1 A schematic of the apparatus. The main volume is a cylinder 32 cm long with an inner diameter of 8.9 cm. The capillary tube has an inner diameter of 2.7 mm.

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ends with rubber stoppers. A capillary tube entered the vessel through a hole in the bottom stopper. The outside end of the capillary tube was sealed with a short rubber tube clamped at one end which formed the initiation volume. The rubber tube was filled with porous plug in order to quench any flow introduced by the initiation of a reaction. Reactions were initiated by inserting a thin needle into the porous plug and injecting a tiny amount of catalyst into the plug. Upon reaction initiation, a reaction will move up the capillary tube until it escapes into the larger tank. The apparatus was illuminated from behind and still images of the front were captured using a digital camera.

For all experimental runs reported here, the reactant fluid contained $[\text{IO}_3^-]=0.005 \text{ M}$ and $[\text{As}_2\text{O}_3]=0.020 \text{ M}$. The front was made visible to the naked eye by introducing an acid base indicator into the reactant solution called congo red. Since the product solution is more acidic than the reactant solution, it induces a color change in the reacted solution, turning it deep blue, which is easily identifiable in the red reactant solution. In addition, various amounts of glycerol were added to the solution to increase its viscosity.

OBSERVATIONS

For all experimental runs carried out with a viscosity close to that of water, long lasting symmetrical plume heads were not observed. These plumes ascend quickly to the upper boundaries of any tank of manageable size. For this reason, glycerol was introduced into the system to allow for an effectively longer evolution time within the experimental tank. We therefore explored the reaction in

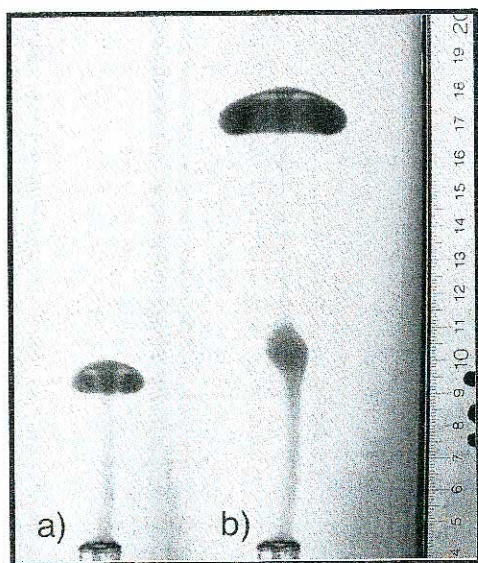


Fig. 2 Pictures of two stages in the evolution of the plume structure, showing (a) a starting plume and (b) a thermal in the form of a vortex ring. A centimeter ruler is on the right side of the figure to illustrate the scale of the structures.

systems with various water-glycerol ratios. The experimental results discussed here are for water-glycerol solutions containing no more than 40% glycerol by volume, which have a kinematic viscosity of $(3.81 \pm 0.04) \cdot 10^{-2} \text{ cm}^2/\text{s}$.

For water-glycerol solutions with 30% by volume glycerol or higher, both starting plumes and thermals were observed, as shown in Fig. 2. In a typical experimental run, the development of these flow structures unfolds as follows [6,7].

Initially, a thin plume rises out of the capillary tube and its head remains roughly spherical and grows slowly. There is very little entrainment of reactant fluid into the plume head during this initial stage. Entrainment of reactant material into the plume head sets in when the familiar mushroom shaped head of a starting plume develops, as shown in Fig. 2a). Here the surrounding fluid is being drawn into the head by a single overturning vortex ring. Once the entraining plume head reaches a certain width, the plume head begins to pinch off from the upwelling conduit. A bottle-neck develops at the site of pinch off which then swells as it fills with rising product solution. While this swelling occurs, what was formerly the plume head becomes an essentially free vortex ring. The vortex ring detaches from the conduit, and is eventually only connected to a very thin filament of product solution, as shown in Fig. 2b). The swelling in the conduit develops into a new, second-generation plume head, which will again repeat the pinch off process. Up to four generations of free vortex rings, or "chemical smoke rings", are formed during a typical experimental run.

From the digital images of plume head evolution, we measured the height and width of the chemical plume head as it evolved. Analysis of a typical experimental run in a 40% glycerol by volume solution is shown in Fig. 3. Figure 3(a) shows that the head accelerates during its ascent. The acceleration of the plume head continues once it has pinched and become a thermal, even though it is almost entirely disconnected from the conduit. Figure 3(b) shows that the width of the plume goes through three distinct regions of approximately linear growth. The slowest growth rate occurs in the early stages of plume head evolution before any obvious entrainment sets in. Entrainment plays a more prominent role once the plume head forms and a second, increased growth rate occurs. The third, and fastest rate of growth commences once the plume head detaches and becomes a thermal.

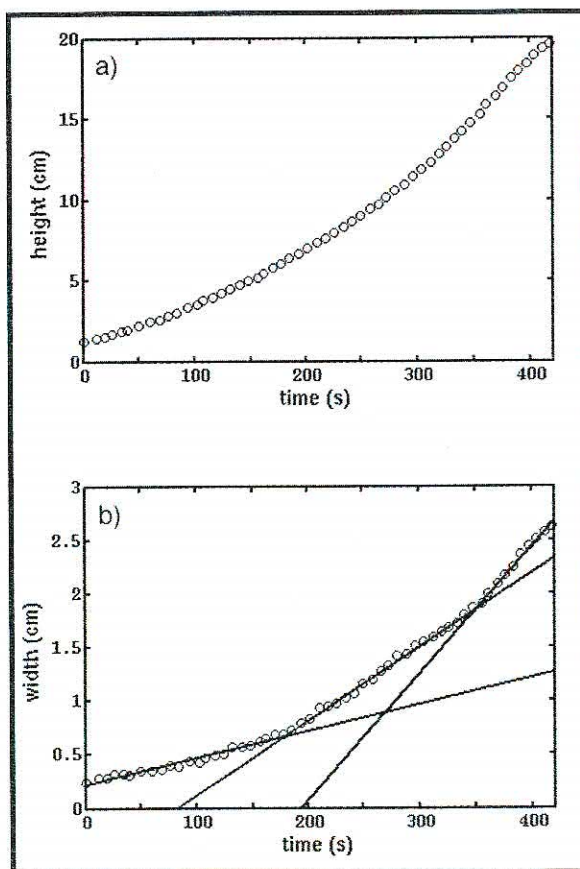


Fig. 3 The growth of a plume as a function of time in a 40% glycerol solution, showing (a) the height of the head, and (b) its width. Lines of best fit in (b) show the three regions of nearly linear growth of the width.)

DISCUSSION

Similar to our autocatalytic chemical plumes, conventional starting plumes can have symmetrical plume heads [8]. Additionally, these heads can pinch off to form buoyant thermals in the form of vortex rings. This type of vortex ring formation in conventional systems has been the subject of both theoretical and experimental interest [9-12]. Despite the fact that discrete thermals form in both conventional and autocatalytic systems, there is a critical difference in their respective behavior. The difference is due entirely to the autocatalytic reaction used to drive buoyancy in the IAA system. Whether or not the source of buoyancy is conventional or an autocatalytic reaction, as a plume head or vortex ring rises, it entrains surrounding fluid, stirring and mixing it into the structure. In the case of autocatalytic plumes, the surrounding fluid is a reactant solution. The delivery of fresh reactant solution assists the buoyancy of the rising vortical structure as it becomes mixed into its interior, and causes it to accelerate both before and after pinch off has occurred. Such behavior is in contrast to the constant ascent velocity previously observed in conventional plumes [13]. The continued acceleration of the head once it pinches off and becomes a thermal is also unique to our autocatalytic system; conventional vortex rings expand and slow down after they have pinched off [14].

CONCLUSION

We have described a study of buoyant, three-dimensional plumes driven by buoyancy induced by the IAA reaction. We have found that when the viscosity of a typical IAA reactant solution is increased with the addition of glycerol, a rising plume with a well-defined head is formed. The plume head subsequently detaches from the upwelling conduit, forming a buoyant vortex ring. The entrainment of reactant solution into the autocatalytic chemical plume and subsequent vortex ring produces additional buoyancy, leading to an acceleration of the vortex ring. This behavior reverses the usual role of entrainment, which normally acts to reduce buoyancy in conventional plumes and thermals.

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