Buoyant plumes and vortex rings in an autocatalytic chemical reaction

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Buoyant plumes, evolving free of boundary constraints, may develop well-defined mushroom shaped heads. In conventional plumes, overturning flow in the head entrains less buoyant fluid from the surroundings as the head rises, robbing the plume of its driving force. We consider here a new type of plume in which the source of buoyancy is an autocatalytic chemical reaction. The reaction occurs at a sharp front which separates reactants from less dense products. In this type of autocatalytic plume, entrainment assists the reaction, producing new buoyancy which fuels an accelerating plume head. When the head has grown to a critical size, it detaches from the upwelling conduit, forming an accelerating, buoyant vortex ring. A second-generation head then develops at the point of detachment. Multiple generations of autocatalytic vortex rings can detach from a single triggering event.

Hydrodynamic flows driven by chemical reactions have been studied since the discovery of fire, the oldest technology of humankind [1]. Exothermic combustion reactions produce buoyant flames in the form of rising, reacting plumes and thermals which are often highly turbulent [2]. In this Letter, we examine a much simpler, yet still very rich, new system in which relatively gentle autocatalytic reaction fronts give rise to both laminar starting plumes and thermals in the form of free vortex rings. We call a continuous region of buoyancy supplied by a point source a *plume*. A *starting plume* is a plume with a well-defined, advancing head. These cases of buoyancy driven flow may be distinguished from a *thermal*, which is a freely evolving buoyant object disconnected from its source. Thermals may take the form of *vortex rings*, which have a specific type of overturning internal flow, analogous to smoke rings. Such flows may have the effect of enhancing mixing by entraining the surrounding fluid. Unlike conventional non-reacting plumes and thermals arising from localized heat sources, the flows that we report here have an internal source of buoyancy, an autocatalytic reaction. The reaction is enhanced by subsequent entrainment, which leads to flow acceleration similar to combustion.

In our experiments, buoyancy was produced by the iodate - arsenous acid (IAA) reaction [3]. This reaction exhibits cubic autocatalysis [4]. The short range diffusion of the autocatalyst, here the iodide ion, limits the reaction to a very thin front separating reacted and unreacted solution. The front region of active reaction is typically only a few tens of microns thick, and is by far the smallest lengthscale in the system. Across the front there is a density jump between the reactant and product. This sharp change in density is created both by thermal expansion due to the slight exothermicity of the reaction, and by the partial molal density decrease of the product solution [5]. Under gravity, the density difference across an ascending front is hydrodynamically un-

stable, because less dense products are below more dense unreacted solution [3, 5–13].

In our plume experiments, we increase the viscosity of the water solution by adding glycerol. An ascending front is allowed to escape from a capillary tube into a much larger volume, so that boundaries no longer constrain the shape of the front. In the larger volume, a rising plume with a well-defined head is formed. During the early stages of the evolution of the head, its growth is due to both a volume flux of upwelling product solution and by the entrainment of reactant solution. Later, the plume head detaches and becomes a rising vortex ring, analogous to a chemically reacting smoke ring. The upwelling conduit that is left behind forms a new head which also eventually detaches, leading to generations of accelerating vortex rings. This surprising behaviour is in contrast to conventional buoyant vortex rings, which do not accelerate. It may have application as a laboratory analog of plumes in internally heated fluids, such as the Earth's mantle [14].

The propagation of IAA reaction fronts has enjoyed considerable theoretical and experimental attention. It has been well-studied in capillary tubes [5, 7], in thin slots [8–11], and in the presence of a superposed flow [12, 13]. In sufficiently narrow vertically oriented capillary tubes, convection is suppressed and the sharp reaction front is observed to propagate at constant speed in either direction. If the tube radius a is increased beyond a critical size, the front deforms and upward propagation is accompanied by convection [15]. Within a simple thin front approximation [6], the relative importance of buoyancy is described by a dimensionless quantity

$$S = \frac{\delta g a^3}{\nu D_c},\tag{1}$$

where g is the acceleration due to gravity, ν is the kinematic viscosity, D_c is the diffusion constant of the autocatalyst, and $\delta = (\rho_u/\rho_r) - 1$ is the dimensionless density

jump between the reacted (ρ_r) and unreacted (ρ_u) solutions. The critical tube radius for convection corresponds to a critical value $S_c \sim 90$. At slightly larger values $S > S_c$, a transition to an axisymmetric mode of convection can be identified [5]. In the plume experiments described below, a very large tube was used, corresponding to $S \approx 10^8$.

In all previous studies of the IAA reaction [3, 5, 7–13], convection effects were severely constrained by the viscous interaction with nearby solid boundaries. We set out to find the reaction-driven flow phenomenology for an *unbounded* solution in which the reaction is initiated at a point, as nearly as possible. To achieve this, we allowed an ascending front to escape from a capillary tube into a much larger volume, so that boundaries no longer constrain the shape of the front. In such a scenario, two experimental difficulties immediately arise. For solutions with a viscosity close to that of water, the IAA reaction produces fronts that are sufficiently buoyant that the resulting plumes ascend quickly to the upper boundaries of any tank of managable size. These plumes also had Reynolds numbers, $Re \sim 7$ and therefore had a rather complex internal flow structure. We therefore explored the reaction in a water-glycerol solution in which the kinematic viscosity was increased to $(3.81 \pm 0.04) \times 10^{-2}$ cm^2/s in order to limit the Reynolds number to $Re \sim 0.1$, and to allow for an effectively longer evolution time within the experimental tank. These experiments revealed plumes with well-defined heads which eventually pinched-off to form essentially free vortex rings.

The second difficulty concerns initiating the front at a localized point. When the front is released from a very narrow capillary tube with diameter 0.9 mm into a much larger volume, we found that the front did not propagate. This "front death" phenomenon is due to the requirement of a minimum critical concentration of autocatalyst near the initiation region, which therefore cannot be too small. Such a threshold effect is predicted [16, 17] for cubic autocatalysis in three dimensions. To our knowledge, this effect has not been reported for the IAA reaction before. This constraint is easily overcome by using a large enough capillary tube to launch the reaction into the unbounded region. A diameter of 2.7 mm proved to be sufficient.

Reactant solutions were prepared using reagent grade chemicals and distilled water with 40% glycerol by volume. Iodate stock solutions were prepared by dissolving KIO$_3$ powder in distilled water. Arsenous acid stock solutions were prepared by dissolving As$_2$O$_3$ powder in hot, stirred water. These stock solutions were diluted so that the working solution contained [IO$_3^-$]=0.005M and [As(III)]=0.020M. These concentrations were not varied in the experiments we report here. Congo Red indicator was used to visualize the reaction fronts. It was present in solution at a concentration of 2×10^{-5}M. Congo Red has a pH range of 3.0 to 5.0, where the acid form is blue and the base form is red. The reaction front leaves in
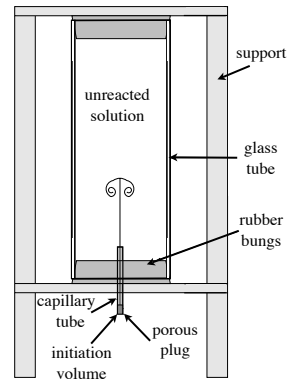

FIG. 1: A schematic of the apparatus. The main volume is a cylinder 32 cm long with an inner diameter of 8.9 cm. The capillary tube has an inner diameter of 2.7 mm.

its wake a product solution with pH of ~ 2.7, so that the upwelling blue products are easily visible within the red unreacted solution. The temperature was constant at $24.0 \pm 0.2°$ C.

The measured dynamic viscosity was 4.24 ± 0.04 Pa s. We measured the density of the reactant and product solutions using a commercial vibrating U-tube densitometer. The density of the reactant solution ρ_r was 1.1124 ± 0.0001 g/cm^3, and the isothermal density difference $\rho_r - \rho_u$ was $(4 \pm 2) \times 10^{-4}$ g/cm^3. This slightly underestimates the density jump across the front, which has an additional positive contribution from the exothermicity of the reaction. The iodate diffusion constant D_c in water is [3] 2.04×10^{-5} cm^2/s; using the Stokes-Einstein relation, we estimate that this is reduced to 4.28×10^{-6} cm^2/s in our glycerol-water mixture. With our large tube of inner radius $a = 4.45$ cm, Eqn. 1 gives $S \approx 10^8$.

The apparatus is shown in Fig. 1. The reaction tank was a large glass cylinder sealed by large rubber stoppers. A capillary tube entered through a hole in the lower 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 by a porous plug made of loosely packed cotton. Reactions were initiated by inserting a thin needle into the rubber tube and then injecting a very small amount of product solution into the plug. The plug served to quench any hydrodynamic disturbance of the reactant solution during reaction initiation. The reaction proceeded up the capillary tube, which is large enough that $S > S_c$ and some convection is already present. It then escapes into the larger tank. The apparatus was illuminated from behind and still images of the evolving front were captured using a digital camera.

The various stages in the evolution of the resulting free autocatalytic plume are shown in Fig. 2. Initially the plume rises out of the capillary tube and its head

remains roughly spherical and grows slowly. This stage of growth is shown in Fig. 2a. In this initial stage, there is essentially no entrainment of reactant solution into the plume head. At a well-defined point, entrainment sets in. Fig. 2b shows a plume head well past the onset of entrainment. This shows the familiar mushroom-shaped head for a plume in which the surrounding fluid is being drawn into the head by a single overturning vortex ring.

Once the entraining autocatalytic plume head reaches a second critical size, the plume head begins to pinch-off from the upwelling conduit. The pinch creates a bottleneck in the conduit which then swells as it fills with rising product solution. During the swelling below the bottleneck, what was formerly the head of a starting plume becomes an essentially free vortex ring. As shown in Fig. 2c, the vortex ring detaches from the conduit, and is eventually connected only by a very thin filament of product solution. The swelling in the conduit develops into a new, second generation plume head. In Fig. 2d, a new pinch-off process has started again below the second generation plume head. Yet another bottleneck is formed when the second generation head pinches-off and becomes a vortex ring. The new bottleneck swells and the process is repeated. We have observed four generations of pinch-off and subsequent vortex ring formation in autocatalytic plumes. The fourth generation plume head eventually reaches the top boundary of the reaction vessel, closing the possibility of further pinch-off [18].

From the digital images of plume evolution, we determined the height and width of the ascending buoyant plume as a function of time. Height was measured from the top of the front to where it exited the capillary tube, and the width refers to the maximum width across the head or vortex ring. It is useful to define the dimensionless ratio $\alpha = w_h/w_c$, where w_h is the width of the head and w_c is the width of the conduit. Only the first generation head and vortex ring were considered in this analysis.

We found that the initial stage of growth ends and entrainment begins once α reaches a critical value of $\alpha_1 = 2.6 \pm 0.1$. Similarly, once the entraining plume head reaches a second critical size, $\alpha_2 = 4.6 \pm 0.1$, the plume head begins to pinch-off from the upwelling conduit.

Typical width and height data for first generation head formation of an autocatalytic plume is shown in Fig. 3. Fig. 3a shows that the width of the plume goes through three distinct regions of approximately linear growth. The initial, and slowest, growth rate obtains when $\alpha < \alpha_1$ and there is no obvious entrainment into the plume head and it remains roughly spherical. A transition to a second, increased growth regime occurs once entrainment begins and $\alpha_1 < \alpha < \alpha_2$. Finally, the third and fastest growth regime commences once $\alpha > \alpha_2$ and the plume head detaches and becomes a thermal. Fig. 3b shows that the head accelerates during its ascent. The acceleration of the plume head continues after
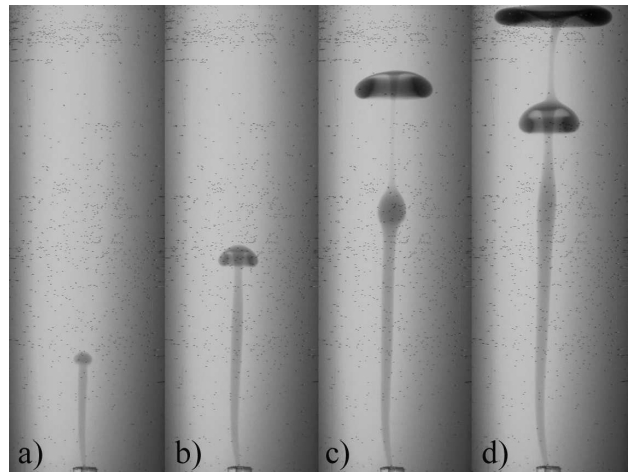

FIG. 2: A sequence of images showing the evolution of the plume structure. (a) 202 s, (b) 328 s, (c) 458 s and (d) 554 s after release.
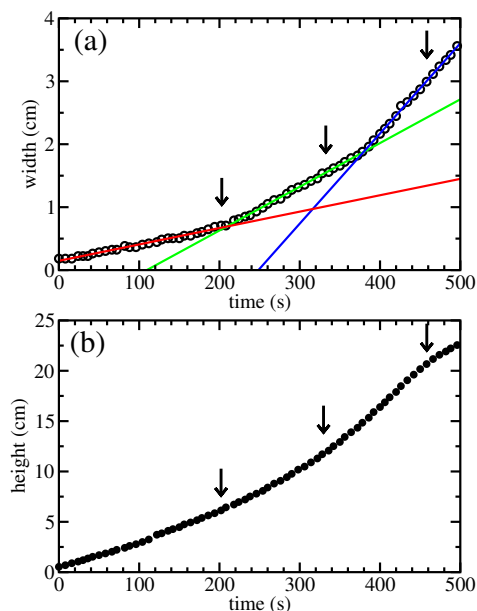

FIG. 3: (Color online) The growth of the plume as a function of time, up to the completion of the first pinch-off, showing (a) the width of the head, and (b) its height. Colored lines in (a) show the nearly linear evolution of the width in the three regimes indicated. Vertical arrows indicate the positions of images (a), (b) and (c) from the previous figure.

it has pinched-off, even though it is almost entirely disconnected from the conduit.

To our knowledge, our experiments mark the first study of buoyant, three-dimensional plumes that are directly driven by an autocatalytic reaction [19]. Of course, conventional buoyant plumes [14, 20–22] and vortex rings [22–24] have been the subjects of extensive previous study.

There is great diversity in past experiments on con-

ventional starting plumes. In typical experiments, conventional starting plumes are formed from buoyant fluid that has been injected into a less-buoyant medium at a point source. The buoyancy may be due to a temperature or composition difference or both. In these cases, all the buoyancy is derived from processes external to the experiment and arrives with the volume of injected fluid. Subsequent stirring and entrainment of less buoyant surrounding fluid can only dilute and reduce this buoyancy. In the case of autocatalytic plumes, the volume of buoyant fluid injected is negligible and all of the buoyancy is generated by the conversion of dense fluid into buoyant fluid at the thin reaction front. The growth rate of the head in conventional starting plumes has been determined [20] to scale with time t as t^β, where $\beta = 0.54 \pm 0.05$. It is clear from Fig. 3a that this is not the case for autocatalytic plumes.

Symmetrical plume heads similar to those observed in our experiment can be found in conventional starting plumes [14]. Moreover, the heads of these starting plumes can be observed to pinch-off to form buoyant thermals in the form of vortex rings. The formation of thermals by pinch-off has been the subject of theoretical and of experimental interest in conventional systems [25–28]. Despite the fact that discrete thermals form in both conventional and autocatalytic systems, there is a critical difference in their respective behavior. This difference is due entirely to the autocatalytic reaction used to drive buoyancy in our system. As a plume head or vortex ring rises, whether or not it is conventional or autocatalytic, it entrains surrounding fluid, stirring it into the structure. In the case of autocatalytic plumes, the surrounding fluid is reactant solution. The delivery of fresh reactant solution feeds the rising vortical structure as it becomes mixed into its interior, and causes it to accelerate both before and after pinch-off has occured. This stirring is laminar, and presumably involves the extreme stretching of the thin reaction front within the vortex ring. The acceleration of autocatalytic plume heads is in contrast to the constant velocity rise behavior previously observed in conventional plumes [20]. 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 [23].

Autocatalytic plumes may have a useful analogy to important geophysical processes. Hotspots due to upwelling from deep in the mantle have been the subject of laboratory analog experiments using conventional plumes [14]. Instabilities in the bottom layer of the mantle are also likely to give rise to thermals which may contain internal sources of buoyancy due to radioactive heating [29]. Autocatalytic thermals could serve as an interesting laboratory analog of these processes.

We have described a study of buoyant, three-dimensional plumes driven by the iodate-arsenous acid reaction. In a water solution that was made more vis-

cous with the addition of glycerol, we found that a rising plume with a well-defined head was formed. The plume head grew to a critical size and subsequently detached from the upwelling conduit to form a buoyant vortex ring. The entrainment of reactant solution into the autocatalytic chemical plume head and subsequent vortex ring produced additional buoyancy by assisting the chemical reaction, 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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