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The influence of natural convection on the temporal development of the temperature and concentration fields for Sal’nikov’s reaction, $P \rightarrow A \rightarrow B$, occurring batchwise in the gas phase in a closed vessel

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Abstract

Sal’nikov’s chemical reaction is very simple; it consists of two consecutive first-order steps, yielding a product B from a precursor P via an active intermediate A, in $P \rightarrow A \rightarrow B$. The first of these steps is assumed here to be thermoneutral, with zero activation energy, whilst the second step is taken to be exothermic with a positive activation energy. These properties make this reaction one of the simplest to display thermokinetic oscillations, such as characterise cool flames. This study considers Sal’nikov’s reaction occurring batchwise in the gas-phase in a closed spherical reactor, whose wall is held at a constant temperature. Natural convection becomes significant once the temperature in the reactor has risen sufficiently for the Rayleigh number to reach $\sim 10^3$. The behaviour of the system is governed by the interaction between three phenomena: natural convection, diffusion of both heat and matter, and chemical reaction. Recent studies of such a system revealed that when natural convection is significant, the oscillations in the temperature are not always in anti-phase with those in the local concentration of the intermediate A, as was previously thought. Instead, the phase difference between the oscillations in the temperature and the concentration of A depends on the position and conditions in the reactor. The shift of this phase difference is studied here using a full numerical solution of the governing equations for a system in which the first step of the reaction is much slower than the second. The phase behaviour is found to depend on the ratio of the characteristic timescales for step 2 of the reaction, $\tau_{\text{Step 2}}$, and natural convection, $\tau_{\text{Convection}}$. When $\tau_{\text{Step 2}}/\tau_{\text{Convection}} < 10$, the temperature and the concentration oscillate in anti-phase, but when $\tau_{\text{Step 2}}/\tau_{\text{Convection}}$ is increased above ~ 15, i.e., when natural convection is relatively fast, there is, near the axis in the bottom of the reactor, no phase difference between these oscillations. This shift in the phase difference results from a surprisingly complex interaction between chemical kinetics and heat and mass transport, by both natural convection and diffusion.

Keywords: Natural convection; Cool flame; Kinetics; Modelling; Oscillations; Sal’nikov’s reaction

1. Introduction

Natural convection can be induced in a fluid by an exothermic reaction once the temperature has risen sufficiently that the Rayleigh number, $Ra = (\beta g L^3 \Delta T)/(\kappa \nu)$, reaches $\sim 10^3$ (Turner, 1979). The interaction of chemical reaction, diffusion of both heat and matter, and natural convection determines the behaviour of the system considered below i.e., an initially pure gas undergoing Sal’nikov’s reaction (1949). This reaction is the simplest to display thermokinetic oscillations, such as characterise cool flames (Gray, 1975; Griffiths and Barnard, 1995; Knox, 1967). The reaction consists of two consecutive first-order steps:

$$P \xrightarrow{1} A \xrightarrow{2} B \tag{I}$$

where a precursor P is converted to a product B via an active intermediate A. The first step is assumed to be thermoneutral, with E_1, its activation energy, and q_1, the exothermicity of step 1, both equal to zero. Step 2 is considered to be

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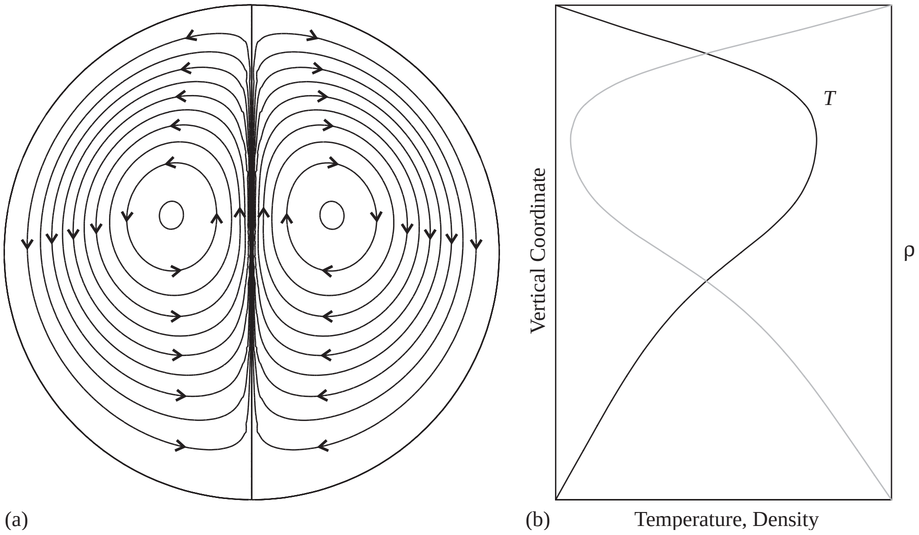

Fig. 1. (a) Streamlines of the flow due to natural convection in a vertical cross section through the axis of the reactor. The torroidal vortex which typifies the flow (upwards near the axis, downwards near the wall) is shown. (b) Temperature and density profiles along the vertical axis of the reactor, showing the unstable density distribution in the top half of the reactor, which drives flow, and the stable density distribution in the bottom half of the reactor, where flow is driven by conditions in the boundary layers.

exothermic, with $E_2 > 0$ and $q_2 > 0$. Reaction (I) has been extensively studied in the well-mixed limit (Forbes, 1990; Gray et al., 1988; Gray and Roberts, 1988; Gray and Scott, 1990; Kay and Scott, 1988), where the effects of diffusion can be neglected. Work has also been carried out on another limiting case, where the transport of heat and mass is purely diffusive (Gray and Scott, 1990). This diffusive limit corresponds to reaction occurring in microgravity, as studied experimentally by Pearlman (2000) and numerically by Fairlie and Griffiths (2001, 2002). More recently, numerical studies have investigated the influence of natural convection on Sal'nikov's reaction. Cardoso et al. (2004a) reported some preliminary results on the development of natural convection in a spherical vessel containing a gas undergoing Sal'nikov's reaction.

In outline, the system behaves as follows. The walls of the reactor are kept at a constant temperature. Whilst reaction proceeds, heat is released and consequently the temperature of the gas rises. Because the temperature of the gas rises above that of the walls, heat is removed from the system at the walls. This coupling of heat generation and loss causes a hot zone to form at the centre of the reactor. This in turn results in a gravitationally unstable density distribution in the top section of the reactor and so leads to the development of the familiar Rayleigh–Bénard convection (Turner, 1979). This is shown schematically in Fig. 1; part (a) shows the streamlines of the induced flow, and part (b) plots the temperature and density along the vertical axis of the reactor. The hot gas near the centre of the reactor rises quickly initially and moves into the hottest part of the reactor (in the top half). However, it slows as it passes through the hot zone, due to the decreased density difference. The hot gas then contacts the relatively cold walls, where it cools and descends relatively rapidly due to the large density differential. In the lower half of the reactor the density distribution is intrinsically stable, with the flow being induced by the descending, cooler gas at the wall. This downward flow of cool gas results in a relatively slow upward flow (around the centreline of the reactor) of gas displaced from the bottom of the reactor. Whilst this gas rises, it heats up and hence accelerates. The situation in Fig. 1 refers not just to Sal'nikov's mechanism, but to any exothermic reaction in a batch reactor.

The development of convection was considered in greater detail by Cardoso et al. (2004b), who showed through appropriate scaling of the governing equations that the behaviour of this system depends on three non-dimensional groups, each of which can be expressed as the ratio of the timescales of two of the three interacting phenomena, namely chemical reaction, diffusion and convection. A system undergoing Sal'nikov's reaction can therefore be represented as a point on the three-dimensional (3-D) diagram in Fig. 2. The axes of this diagram correspond to each non-dimensional group. The horizontal plane in this diagram, described by the axes $(\tau_{\mathrm{Step}\ 2}/\tau_{\mathrm{Convection}})$ and $(\tau_{\mathrm{Step}\ 2}/\tau_{\mathrm{Step}\ 1})\ p'$, where p' is the dimensionless concentration of the precursor P, corresponds to the well-mixed case, whereas the vertical plane defined by the axes $(\tau_{\mathrm{Step}\ 2}/\tau_{\mathrm{Diffusion}})$ and $(\tau_{\mathrm{Step}\ 2}/\tau_{\mathrm{Step}\ 1})\ p'$ corresponds to the purely diffusive case. In a general Sal'nikov system (point C in Fig. 2), both diffusion and natural convection will play a role. A straight line through the origin of the plane described by the axes $(\tau_{\mathrm{Step}\ 2}/\tau_{\mathrm{Convection}})$ and $(\tau_{\mathrm{Step}\ 2}/\tau_{\mathrm{Diffusion}})$ (for any fixed $(\tau_{\mathrm{Step}\ 2}/\tau_{\mathrm{Step}\ 1})\ p'$) represents a constant value of the Rayleigh number.

Campbell et al. (2005) studied the behaviour of this system for the case when $\tau_{\mathrm{Step}\ 1} \gg \tau_{\mathrm{Step}\ 2}$. A range of kinetic