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, $\tau_{Step\ 2}$, and natural convection, $\tau_{Convection}$. When $\tau_{Step\ 2} / \tau_{Convection} < 10$, the temperature and the concentration oscillate in anti-phase, but when $\tau_{Step\ 2} / \tau_{Convection}$ 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:

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 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 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 $(\tau_{Step\ 2} / \tau_{Convection})$ and $(\tau_{Step\ 2} / \tau_{Step\ 1}) p'$, where p' is the dimensionless concentration of the precursor P, corresponds to the well-mixed case, whereas the vertical plane defined by the axes $(\tau_{Step\ 2} / \tau_{Diffusion})$ and $(\tau_{Step\ 2} / \tau_{Step\ 1}) p'$ 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 $(\tau_{Step\ 2} / \tau_{Convection})$ and $(\tau_{Step\ 2} / \tau_{Diffusion})$ (for any fixed $(\tau_{Step\ 2} / \tau_{Step\ 1}) p'$) represents a constant value of the Rayleigh number.

Campbell et al. (2005) studied the behaviour of this system for the case when $\tau_{Step\ 1} \gg \tau_{Step\ 2}$. A range of kinetic parameters was investigated, when diffusion and natural convection were in turn the dominant transport mechanism. The impact of their scaling analysis for $\tau_{Step\ 1} \gg \tau_{Step\ 2}$ on Fig. 2 is discussed further in section 2 of this paper. The numerical results showed temporal oscillations of both the temperature and the concentration of the intermediate A, for a range of conditions. These oscillations result

from the interaction between chemical kinetics and heat transfer. Previous work in the well-mixed region (e.g. Gray and Scott, 1990) has shown that oscillations in the temperature and the concentration of the intermediate A occur in anti-phase. The physical basis of these anti-phase oscillations for the well-mixed limit can be easily explained. The reactor initially contains pure precursor P, with no intermediate. When reaction (I) proceeds, the intermediate, A, is produced by step 1 and so begins to accumulate. Step 2 of reaction (I) consumes A and generates heat because of its exothermicity. The temperature within the system therefore rises. Because step 2 of the reaction has an Arrhenius temperature dependence, it is self-accelerating. Once the temperature is such that the rate of depletion of A in step 2 exceeds the rate of production of A in step 1, the concentration of A begins to decline. The rate of heat generation, however, is still greater than the rate of heat loss to the walls; consequently the temperature continues to increase. The concentration of A decreases to a point where the rate of heat generation in step 2 is less than the rate of heat loss, causing the temperature to decrease. With the temperature falling, the rate of depletion of A in step 2 also drops, until once again the rate of production of A is greater than the rate of its destruction in step 2. At this point the cycle begins again. The observed oscillations are damped because the precursor is continually consumed during the course of the reaction, so the production of A follows an exponential decay because of the kinetics of step 1. This oscillatory behaviour is due to the interaction of the highly non-linear thermal feedback, due to the Arrhenius temperature dependence of step 2, the timescales of steps 1 and 2 of reaction (I) and the nature of heat transfer from the reactor. The inclusion of natural convection significantly

alters the removal of heat from the system and can therefore potentially influence the nature of any observed oscillatory behaviour.

One intriguing effect highlighted by Cardoso et al. (2004b) and Campbell et al. (2005), is the phase relationship between the temporal developments of the temperature and the concentration of the intermediate A at the centre of the reactor when oscillations are observed. Cardoso et al. (2004b) presented four case studies in detail, two of which exhibited temporal oscillations in the fields of the temperature and concentration of the intermediate A. They showed that when $Ra \sim 605$, the temperature and concentration of A oscillated in anti-phase; this is similar to the previously described behaviour in the well-mixed regime. However, when $Ra \sim 10^5$, natural convection is more significant and the oscillations in the temperature and concentration observed at the centre of the reactor were seen to be in-phase. The present work aims to investigate this shift in phase difference by means of a full numerical solution of the governing equations.

2. Theory

The equation describing the conservation of the active intermediate A is

$$\frac{\partial a}{\partial t} + \underline{u} \cdot \nabla a = D_A \nabla^2 a + k_1 p_0 \exp(-k_1 t) - k_2 a. \quad (1)$$

It is assumed in this equation that the concentration of P in the reactor is initially uniform, and that it remains so, equal to $p_0 \exp(-k_1 t)$, throughout the course of the reaction. This assumption depends on k_1 being independent of temperature (because $E_1 = 0$) and holds only for relatively small increases in temperature, as discussed below. The conservation of energy is described by

$$\frac{C_v}{C_p} \frac{\partial T}{\partial t} + \underline{u} \cdot \nabla T = \kappa \nabla^2 T + \frac{q_2 k_2}{\rho_0 C_p} a, \quad (2)$$

where ρ_0 is the density at the initial temperature T_0 . The familiar Navier-Stokes equations

$$\frac{\partial \underline{u}}{\partial t} + \underline{u} \cdot \nabla \underline{u} = -\frac{1}{\rho_0} \nabla (\mathcal{P} - \mathcal{P}_0) + \nu \nabla^2 \underline{u} + \frac{\rho - \rho_0}{\rho_0} \underline{g}, \quad (3)$$

describe the conservation of momentum. The Boussinesq approximation is adopted, i.e. it is assumed that the density only varies in the buoyancy term of Eq. (3), where the density varies as $\rho = \rho_0[1 - \beta(T - T_0)]$ for β being the coefficient of thermal expansion. The Boussinesq approximation requires that the characteristic temperature rise ΔT is such that $\Delta T / T_0 \ll 1$; otherwise full compressibility needs to be taken into account. That $\Delta T \ll T_0$ further justifies Eq. (1), because the assumption that P remains uniformly distributed throughout the reactor requires that there be no significant change in temperature or density. The final equation required is the continuity equation. The adoption of the Boussinesq approximation allows the continuity equation to be written in its incompressible form, i.e.

$$\nabla \cdot \underline{u} = 0 \quad (4)$$

Initially, the gas in the reactor is considered to be pure P , at temperature T_0 . There is no initial motion in the gas. Throughout the reaction, the temperature of the wall is held constant at T_0 . This, of course, means that heat will be removed from the system at the wall. It is also assumed that the no-slip condition holds at the wall, and that there is no flux of any species at the wall. Any effects of surface chemistry are therefore neglected.

The above four governing equations are made dimensionless by introducing the following seven dimensionless groups:

$$a' = \frac{a}{a_0}; \quad p' = \frac{p}{p_0}; \quad T' = \frac{T - T_0}{\Delta T}; \quad \underline{u}' = \frac{\underline{u}}{U}; \quad \mathcal{P}' = \frac{\mathcal{P} - \mathcal{P}_0}{\rho_0 U^2}; \quad \underline{x}' = \frac{\underline{x}}{L} \quad \text{and} \quad t' = \frac{Ut}{L}, \quad (5 \text{ a - g})$$

where L is a characteristic length of the reactor (taken to be the radius in the present work), p_0 is the initial concentration of the precursor P, and the scales for the characteristic intermediate concentration, a_0 , for the velocity due to convection, U , and for the temperature rise, ΔT , are of the form defined by Campbell et al. (2005), i.e.

$$a_0 \sim \frac{k_I}{k_{2,0}} p_0; \quad U \sim [\beta g L (\Delta T)]^{1/2}; \quad \Delta T \sim \frac{q_2 k_I L}{C_P U} = \left(\frac{q_2}{C_P} \right)^{2/3} \left(\frac{k_I^2 L}{\beta g} \right)^{1/3}. \quad (6 \text{ a - c})$$

It is worth noting that the characteristic velocity, U , for natural convection is proportional to $\Delta T^{1/2}$.

At this stage it is also useful to define the four characteristic timescales:

$$\tau_{Step1} = \frac{1}{k_I}; \quad \tau_{Step2} = \frac{1}{k_{2,0}}; \quad \tau_{Diffusion} = \frac{L^2}{\kappa}; \quad \tau_{Convection} = \frac{L}{U}, \quad (7 \text{ a - e})$$

for the two steps of reaction (I), diffusion, and finally natural convection. Using the scales defined in Eq. (6) and the timescales in Eq. (7), the dimensionless governing equations can be written as:

$$\frac{\partial a'}{\partial t'} + \underbrace{\underline{u}' \cdot \nabla' a'}_{convection} = \underbrace{\frac{1}{Le} \frac{\tau_{Convection}}{\tau_{Diffusion}} \nabla'^2 a'}_{diffusion} + \underbrace{\frac{\tau_{Convection}}{\tau_{Step2}} p' - \frac{\tau_{Convection}}{\tau_{Step2}} \exp\left(\frac{\phi T'}{1 + \eta T'}\right) a'}_{reaction}, \quad (8)$$

$$\frac{1}{\gamma} \frac{\partial T'}{\partial t'} + \underbrace{\underline{u}' \cdot \nabla' T'}_{convection} = \underbrace{\frac{\tau_{Convection}}{\tau_{Diffusion}} \nabla'^2 T'}_{diffusion} + \underbrace{\exp\left(\frac{\phi T'}{1 + \eta T'}\right) a'}_{reaction}, \quad (9)$$

$$\frac{\partial \underline{u}'}{\partial t'} + \underline{u}' \cdot \nabla' \underline{u}' = -\nabla' \mathcal{P}' + Pr \frac{\tau_{Convection}}{\tau_{Diffusion}} \nabla'^2 \underline{u}' - \frac{g}{g} T', \quad (10)$$

$$\nabla' \cdot \underline{u}' = 0, \quad (11)$$

where $k_{2,0}$ is k_2 evaluated at the wall temperature, T_0 , and

$$\eta = \frac{\Delta T}{T_0} \text{ and } \phi = \frac{E_2 \Delta T}{RT_0^2}. \quad (12)$$

For a given chemical system therefore, the behaviour is defined by the three dimensionless groups:

$$\frac{\tau_{Step\ 2}}{\tau_{Convection}}; \frac{\tau_{Step\ 2}}{\tau_{Diffusion}} \text{ and } p'. \quad (13)$$

This differs from the general case, considered in Fig. 2, as derived by Cardoso et al. (2004b), whose third group was $(\tau_{Step\ 2} / \tau_{Step\ 1}) p'$. This difference is due to the form of the scales used in this analysis for the specific case where $\tau_{Step\ 1} \gg \tau_{Step\ 2}$. Thus, it is interesting to note that $\tau_{Step\ 1}$ does not appear explicitly in Eqs. (9) – (12). However, inspection of Eq. (6c) shows that $\Delta T \propto (\tau_{Step\ 1})^{-2/3}$, so the value of $\tau_{Convection}$ depends on $\tau_{Step\ 1}$, as of course does p' . For this specific case, therefore the third axis on the 3-D diagram of Fig. 2 can be changed from $(\tau_{Step\ 2} / \tau_{Step\ 1}) p'$ to simply $p' = \exp(-t / \tau_{Step\ 1})$. In this work $\tau_{Step\ 1} \sim 40$ s and the reaction is considered over a period of 10 s. There is therefore only a relatively small variation in p' during the time period considered, so a two-dimensional representation of the regime diagram is sufficient. This 2-D diagram is shown in Fig. 3.

3. Numerical Method

Eqs. (1) – (4) were solved numerically for a spherical batch reactor using the PDE solver *Fastflo* (Fastflo Tutorial Guide, 2000). The algorithm employed utilises the finite element method and is the same as that outlined by Cardoso et al. (2004b). For the purposes of the numerical simulations, the thermal decomposition of di-*t*-butyl peroxide

was considered, because this has been shown to behave like Sal'nikov's reaction under certain conditions (Griffiths et al., 1988; Gray and Griffiths, 1989). The following parameters were chosen to match those used by Cardoso et al. (2004a, b) and Campbell et al. (2005). The temperature of the wall of the spherical reactor was held constant at $T_0 = 500$ K and the physicochemical properties used were as follows: the initial molar density $\rho_0 = 8.2 \text{ mol m}^{-3}$ (corresponding to a pressure of 0.34 bar at 500 K), the heat capacity at constant volume $C_V = 190 \text{ J mol}^{-1} \text{ K}^{-1}$, and the exothermicity of step 2, $q_2 = 400 \text{ kJ mol}^{-1}$. The chemistry is defined such that the rate constant $k_1 = 0.025 \text{ s}^{-1}$, corresponding to $\tau_{\text{Step } 1} = 40 \text{ s}$, and $k_2 = Z_2 \exp(-E_2 / R T)$ with $Z_2 = 2 \times 10^{15} \text{ s}^{-1}$ and $E_2 = 152 \text{ kJ mol}^{-1}$. These values give $k_2 = k_{2,0} = 0.265 \text{ s}^{-1}$ at 500 K, and $\tau_{\text{Step } 2} \sim 4 \text{ s}$, i.e. step 2 is an order of magnitude faster than step 1 in reaction (I). In the present work, the effect of altering the values of these rate parameters is not considered. Furthermore, the simplifying assumption that both the Lewis and Prandtl numbers were unity was made. This implies that $\nu = \kappa = D_A$, i.e. the diffusivities of momentum, heat and chemical species were considered to be equal.

Runs were carried out in those regions of the regime diagram (highlighted on Fig. 3) found by Campbell et al. (2005) to exhibit oscillations in the temperature and the concentration of A. The radius of the reactor, L , was varied, as were the values of g and the diffusivity D . Table 1 shows the values used in each of the sixteen runs considered; cases 2 and 16 correspond, respectively, to cases B and D presented by Cardoso et al. (2004b). Estimates of Ra and the values of $\tau_{\text{Step } 2} / \tau_{\text{Convection}}$ and $\tau_{\text{Step } 2} / \tau_{\text{Diffusion}}$ are shown in Table 1. The characteristic velocity and temperature rise were calculated using the

expressions in Eq. (6b, c); the Rayleigh number was calculated using the numerical coefficient calculated by Campbell et al. (2005), i.e.

$$Ra = 5.40 \frac{(\tau_{Step\ 2} / \tau_{Convection})^2}{(\tau_{Step\ 2} / \tau_{Diffusion})^2} . \quad (14)$$

4. Results and Discussion

All the cases in Table 1 exhibited temporal oscillations in the temperature and the concentration of the intermediate. Three of these cases are discussed in detail below; their behaviour is typical of that of the other 13 cases studied, which are summarised later. The cases presented in detail are case 2, which is in the region of the regime diagram where diffusion controls transport, and cases 3 and 14, which are in the region where laminar convection is the controlling mechanism. Of these three cases, case 14 typifies the region in which oscillations at the top of the reactor are anti-phase, whereas at the bottom they are in-phase; consequently, it is considered in the greatest detail. In each case, plots of the temperature and the concentration of A, whilst the reaction proceeds, are shown (in Figs. 4, 6, 7) at five points in the reactor. These plots provide a profile of the reactor along its vertical and horizontal axes and were chosen as follows: on the vertical axis the points are at distances $y = 0.5 L$, L (i.e. the centre of the reactor) and $1.5 L$ from the bottom of the reactor. On the horizontal axis the points are located a distance of $x = 0.25 L$, and $0.75 L$ from the vertical axis. The coordinates of each point appear in the top right corners of the plots, relative to the origin, which is defined as being on the vertical axis of the reactor, at the very bottom. For cases 2 and 14, i.e. the cases displaying anti-phase oscillations throughout the reactor, and in-phase behaviour in the bottom of the reactor respectively, a term by term analysis of the governing equations is also presented.

(i) Case 2

The Rayleigh number is 680 and hence diffusion controls transport in this case. Fig. 4 shows the temporal development of the temperature and the concentration of A (a) at the five points within the reactor. It is clear that the temperature and concentration are oscillating out-of-phase, as discussed above, with the concentration leading the temperature. This, almost anti-phase oscillation throughout the reactor, is similar to that seen in the well-mixed case (Gray and Scott, 1990). It is interesting to note that although diffusion is the dominant mode of transport, the effects of the very weak convective motion can still be seen in Fig. 4. The top portion of the reactor is clearly hotter than the bottom section. This is in contrast to what is seen when diffusion is the only transport mechanism (i.e. in microgravity), where the temperature field is spherically symmetric. The weak convection present in case 2 has caused the hot zone in the reactor to be shifted above the centre, thus disrupting the spherical symmetry.

The rates of chemical reaction and transport of species A, as well as the generation and transport of heat, into and out of a local elemental control volume are now considered in detail. This is done by analysing the magnitudes of the convective, diffusive and reactive terms in the equations for the conservation of chemical species A and thermal energy, as a function of time. Fig. 5(a) shows each of the terms in Eq. (8) for the non-dimensional concentration of A; Fig. 5(b) shows each of the terms in the energy equation, Eq. (9).

At the top of the reactor, the convective and diffusive terms in the concentration equation are positive, while the net reactive term, which combines steps 1 and 2 of the reaction, is negative. This means that species A is transported into the control volume by

diffusion and transported out by convection; these two transport mechanisms result in a net inflow of intermediate A. It should be recalled that A is generated in step 1 and consumed in step 2 of the chemical reaction; thus a negative reactive term means that there is a net depletion of A. It can be concluded therefore, that at the top of the reactor, transport by both diffusion and convection supplies species A, which is consumed by chemical reaction. The magnitudes of the terms in the temperature equation show that the heat generated by this chemical reaction is transported out of the control volume by diffusion.

At the bottom of the reactor, diffusion, of both species A and heat, has a small role after the first oscillation. Species A is transported by convection into the control volume and consumed by chemical reaction. The heat generated locally is removed mainly by convection.

(ii) Case 3

For case 3, the value of g was increased to 30 m s^{-2} (see Table 1), thus increasing the Rayleigh number to 1445; the effects of natural convection are now significant, due to the higher value of Ra (see Fig. 3). Plots of the temperature and concentration of A at the five specified points in the reactor are shown in Fig. 6. It can be seen that the behaviour at the top of the reactor is similar to that shown in case 2, i.e. the concentration of A and the temperature are oscillating approximately in anti-phase. However, in the bottom section of the reactor, the difference in phase (measured arbitrarily between the second peaks in both curves) is 0.6 s compared with 1.2 s at the

top of the reactor. Clearly, the phase difference in this case depends on the position in the reactor.

(iii) Case 14

The final case presented in detail (case 14) has a Rayleigh number of $\sim 2.6 \times 10^4$, i.e. it is well within the region where laminar convection is the dominant transport mechanism (see Fig. 3). Like cases 2 and 3, in the hot zone in the top section of the reactor, the temperature and concentration of A oscillate almost in anti-phase, as shown in Fig. 7. At the centre of the reactor, the phase difference is 0.2 s compared with 1 s in the top section. In the bottom of the reactor the temperature and the concentration of A are oscillating in-phase, but with relatively small amplitudes. This behaviour mirrors that observed by Cardoso et al. (2004b) in their case D (case 16 in Table 1). What is also interesting to note is how the phase difference behaves with increasing radial position along the horizontal axis. Thus, Fig. 7 shows that at the centre of the reactor, the temperature and the concentration of A oscillate, virtually, in-phase. However, when the radius is increased, the concentration and temperature plots become out-of-phase. At a radius of $0.75 L$, the temperature lags the concentration by 0.9 s. The temperature plots at all points along the horizontal axis are nearly identical. Thus, the magnitude of the temperature varies significantly in the vertical direction, but very little in the horizontal direction. Such stratification is expected in systems with moderate convection, because it corresponds to maximum gravitational stability. This temperature stratification can also be seen in Fig. 8, which shows the concentration of A, and the temperature on a vertical cross section through the axis of the reactor at 0.4 s intervals, whilst the reaction proceeds.

Fig. 8 clearly shows the two distinct regions of behaviour observed previously in Fig. 7. At the top of the reactor the anti-phase oscillations in concentration and temperature are evident. It is also apparent that the temperature in this region is considerably higher than in the bottom of the reactor at all times and that the amplitude of the oscillations is larger. In the bottom section of the reactor, where the temperatures are relatively low, the in-phase oscillations cannot be seen clearly due to their relatively small magnitude; however, it is clear that the concentration of A in this bottom section of the reactor is significantly higher, and the temperature significantly lower, than at the top, throughout the course of the reaction. It is also noticeable from Fig. 8 that, whilst the cold fluid descends at the wall, there is a significant increase in the concentration of the intermediate A. This effect is highlighted more clearly in Fig. 9. Fig. 9(a) shows how the temperature and concentration of A vary in a notional element of gas, whilst it is circulating in the flow. Fig. 9(b) shows the vertical coordinate, y , of the fluid element; it should be recalled that y is the vertical distance from the bottom of the reactor. In this case the element is initially stationary at a position $(0.3 L, L)$, i.e. it is on the horizontal axis of the reactor, and slightly removed from the vertical axis. Fig. 9(b) allows the duration of each complete flow loop to be estimated by looking at the time when the element moves upwards past its initial y coordinate. The end points of these circuits are shown as the broken vertical lines in Fig. 9(a). There are three such loops shown. Initially, the element moves slowly upwards, and the temperature increases only very slightly. This results in the production of A in step 1 of reaction (I) being favoured over its destruction in step 2. A small peak in temperature is observed at ~ 1.2 s as the element moves through the hottest point in the reactor (at the top). The fluid then descends at the wall and remains at a low temperature,

with A accumulating. When the element begins to rise, near the vertical axis, the temperature increases rapidly and, conversely, the concentration decreases, because step 2 now dominates at this higher temperature. Once through the hot zone, the fluid cools to near the wall temperature and, once more, significant accumulation of A is observed, whilst this cooler fluid descends. It is interesting to note that the difference in temperature between the hot zone at the top of the reactor, and the cool regions at the wall and at the bottom is very large (as seen in Fig. 8), and also that the fluid element spends only a small amount of time under the influence of the hot zone. Fig. 9(a) also clearly shows the effect of the large temperature oscillations at the top of the reactor. The first major temperature peak at ~ 2.4 s reaches ~ 590 K, whereas the second major peak (corresponding to the third time the particle passes through the hot zone) at ~ 4.1 s only reaches ~ 540 K. What is interesting is the effect this has on the concentration of A when the element reaches the bottom of the reactor. After passing through the much hotter first peak, the concentration of A in the element is $\sim 0.19 \text{ mol m}^{-3}$ at the bottom of the reactor, whereas after passing through the hot zone during the next cycle, now at a lower temperature, the concentration at the bottom is $\sim 0.24 \text{ mol m}^{-3}$. It should be noted that the difference between these values is of similar magnitude to that of the oscillations in the bottom section of the reactor.

The magnitudes of the convective, diffusive and reactive terms in Eq. (8) for the conservation of chemical species A and in Eq. (9) for energy, as a function of time, are now analysed. Fig. 10(a) shows each of the terms in Eq. (8); Fig. 10(b) shows each of the terms in Eq. (9).

At the top of the reactor, the transport of both species A and heat by diffusion is much smaller than by convection. It is concluded that convection supplies A, which reacts locally in step 2. The heat generated by this chemical reaction is removed by convection. This situation is similar to that already described for case 2: the transport processes (diffusion, convection or both) combine to locally supply A for chemical reaction and remove the heat released by reaction.

At the bottom of the reactor, the behaviour is strikingly different from that found in case 2. The reactive term is now positive, almost at all times, instead of negative. This means that species A is locally generated, rather than being depleted by chemical reaction. This generation of species A by chemical reaction, as well as its transport by convection into the control volume, are balanced by diffusion of A out of the control volume. The heat generated by chemical reaction is transported away by convection, because the term for the diffusion of heat is relatively very small in Eq. (9) for the temperature.

(iv) General Trends

Some general trends are apparent from comparing the above three cases. It is interesting to note that the frequency of the oscillations in each case is similar, which may be seen in Figs. 4, 6, and 7. Gray and Scott (1990) showed that in the well-mixed case, the frequency of oscillations is given by $\omega_0 = (\phi - 1)^{1/2}$. Inserting the relevant parameters for cases 2, 3 and 14 into this expression leads to a predicted oscillatory frequency of $\sim 2 \text{ rad s}^{-1}$, which is in reasonable agreement with that observed in our study. Of course, this is only a very approximate calculation given that cases 2, 3 and 14 are not well-mixed. It

is also clear from Figs. 4, 6 and 7 that the phase of the temporal development of temperature is almost independent of position in the reactor, i.e. the peaks and troughs in the temperature occur at approximately the same times throughout the reactor. However, the phase of the oscillations in the concentration of A does depend on position in the reactor. This implies that the changing phase difference between the concentration and temperature curves is due to the concentration curve shifting. This should be a result of a change in the balance of the terms in the concentration equation, from point to point within the reactor. If the ‘anti-phase’ oscillations in each case are compared (i.e. the whole of case 2 and the top sections of the reactor in cases 3 and 14), it is clear that these oscillations occur at higher temperatures and have a greater amplitude than the ‘in-phase’ oscillations. At all points considered in case 2 (see Fig. 4), the temperature peaks at ~ 590 K, and the peak-to-peak change of the first oscillation (measured from the first peak to the first trough) is ~ 60 K. Similar ranges are found in the hot zones in the top section of the reactor in cases 3 and 14. Lower down the reactor in cases 3 and 14, however, the temperatures are considerably lower. For example, in the bottom section of the reactor in case 3 (Fig. 6), the temperature reaches a peak value of only ~ 525 K, with the peak-to-peak range of the first oscillation being ~ 12 K. This is seen again in case 14 (Fig. 7), where the bottom section of the reactor is relatively cool and only exhibits small oscillations in the temperature and the concentration of A. Therefore there is a change in behaviour, from case 2, where the whole reactor is ‘hot’ and the temperature and concentration oscillate out-of-phase, through a transitional stage (case 3), to a situation as in case 14, where the reactor can, in effect, be split into a ‘hot’ zone at the top of the reactor, in which temperature and concentration oscillate out-of-phase, and a ‘cold’ zone

at the bottom, where the smaller oscillations are in-phase. These ‘hot’ and ‘cold’ zones can be easily identified in Fig. 8, showing the evolution of temperature and concentration of A for case 14.

In order to understand this transition, complete computations for all sixteen cases presented in Table 1 were done to characterise fully the observed oscillations. Fig. 11 shows these sixteen points plotted on the regime diagram in Fig. 3. The closed diamonds represent the cases where the oscillations in the temperature and the concentration of A are out-of-phase at all points in the reactor (as typified by case 2). At the other extreme, the open diamonds show the cases where the observed oscillations were in-phase in the bottom half of the reactor (e.g. case 14). The open squares represent the transition between these two extremes, i.e. there is some shift in the phase difference between the temperature and concentration plots, but the oscillations cannot be described as being in-phase (e.g. case 3). Fig. 11 clearly shows that the transition from out-of-phase oscillations everywhere, to oscillations in-phase in the bottom half of the reactor depends on the value of $\tau_{\text{Step 2}} / \tau_{\text{Convection}}$ (but not on $\tau_{\text{Step 2}} / \tau_{\text{Diffusion}}$), with the transition occurring at a value of $\sim 10 - 15$. In other words, in-phase oscillations are observed when the characteristic timescale for convection is an order of magnitude faster than the timescale for step 2 of Sal’nikov’s reaction (I).

The in-phase oscillatory behaviour above is a result of a complex interaction between chemical kinetics, and the transport of heat and mass by convection and diffusion. It occurs when the oscillations in temperature have relatively small amplitude, so that the supply of A by step 1 dominates the depletion of A in step 2 throughout the whole cycle of an oscillation in temperature. The reactive term in Eq. (8) is then always

positive, as is the case for the reactive term in Eq. (9) for the temperature. The evolution of the concentration of intermediate and temperature during one cycle of such an oscillation can be followed. Whilst the intermediate A is produced in step 1, its concentration rises. Species A is then consumed in step 2, which is exothermic, so the temperature rises. Because this second step has an Arrhenius temperature-dependence, it is self-propagating. While the temperature increases, the convective velocity also increases according to Eq. (6b). The rate of generation of A then slows down due to the rate of step 2 increasing, and hence the rate of heat generation also slows down. The temperature accordingly begins to fall when the rate of heat removal by convection exceeds the rate of generation in the second step of the reaction. When the temperature falls, removal of intermediate A by diffusion overtakes the supply by convection and chemical reaction. When the temperature becomes so low that the rate at which heat is convected away is less than the rate of heat generation by chemical reaction, the temperature starts to increase. As the temperature increases, the supply of A by convection increases, beginning the cycle again.

Also noted in case 14 was the fact that the oscillations appeared to become out-of-phase at locations farther from the centre of the reactor. This is due to the flow patterns within the reactor. Away from the centre of the reactor, the flow is less influenced by the axial up-flow of cool, intermediate-rich gas around the vertical axis of the reactor and more influenced by the relatively hot gas, with a low concentration of A, which moves from the top half of the reactor into the boundary layer. It is therefore unsurprising that the in-phase oscillations, which typify the former, are less evident on moving further away from the axis. The effect of the flow in the boundary layer can clearly be seen in

plots of concentration in Fig. 8. At the top of the reactor, a horse-shoe shaped region of similar concentration can be seen at all times. This particular shape occurs due to the influence of the flow at the walls.

5. Conclusion

The phase relationship between oscillations in the temperature and in the concentration of intermediate A for a gas undergoing Sal'nikov's reaction (I) in a closed spherical vessel has been studied at various points inside the reactor, through full numerical solutions of the governing equations. It was found that these oscillations could either effectively be in anti-phase throughout the reactor, or the reactor could be divided into two regions, with a hot zone at the top of the reactor, where oscillations occurred in anti-phase, and a cool zone in the bottom of the reactor, where these oscillations were in-phase. Which of these possibilities occurs depends on the relative values of the characteristic timescales for step 2 of Sal'nikov's reaction (I) and natural convection. When $\tau_{Step\ 2} / \tau_{Convection} < 10$, the oscillations are in anti-phase throughout the reactor, and when $\tau_{Step\ 2} / \tau_{Convection}$ is increased beyond 15, the phase difference between the plots of temperature and the concentration of A against time disappears. It was also seen that the in-phase oscillations were confined to a region around the vertical axis in the lower half of the reactor and that away from the vertical axis, the oscillations once again become out-of-phase. It is believed that these differences in phase at various points inside the reactor are due to a complex interaction of the convective flow, the kinetics of Sal'nikov's reaction, and the diffusion of both heat and the intermediate species. This

study has provided a criterion for determining the nature of any observed oscillations when reaction (I) occurs in a closed spherical vessel.

Notation

a	concentration of intermediate A
a'	dimensionless concentration of A, $a' = a / a_0$
a_0	scale for concentration of A
C_P	specific heat at constant pressure
C_V	specific heat at constant volume
D_A	diffusion coefficient of species A
E_i	activation energy of step i of Sal'nikov's reaction
g	acceleration due to gravity
k_i	rate constant of step i of the reaction
$k_{2,0}$	rate constant of step 2 evaluated at $T = T_0$
L	characteristic length (radius) of the reactor
p	concentration of precursor P
p'	dimensionless concentration of P, $p' = p / p_0$
p_0	initial concentration of P
$\mathcal{P}$	pressure
$\mathcal{P}'$	dimensionless rise in pressure, $\mathcal{P}' = (\mathcal{P} - \mathcal{P}_0) / \rho_0 U^2$
$\mathcal{P}_0$	initial pressure
Pr	Prandtl number
q_i	exothermicity of step i of the reaction

R	universal gas constant
Ra	Rayleigh number, $Ra = \beta g \Delta T L^3 / \kappa \nu$
t	time
t'	dimensionless time, $t' = U t / L$
T	temperature
T'	dimensionless rise in temperature, $T' = (T - T_0) / \Delta T$
T_0	constant wall temperature
$\underline{u}$	velocity vector
$\underline{u}'$	dimensionless velocity vector, $\underline{u}' = \underline{u} / U$
U	scale for velocity
x	coordinate measuring the horizontal distance from the centre of the reactor
$\underline{x}$	spatial coordinates
$\underline{x}'$	dimensionless spatial coordinates, $\underline{x}' = \underline{x} / L$
y	coordinate measuring the vertical distance from the bottom of the reactor
Z_2	pre-exponential factor in Arrhenius expression for k_2
β	coefficient of thermal expansion, $\beta = 1 / T$
γ	ratio of principal specific heats
ΔT	scale for temperature increase
ϕ	dimensionless activation energy for step 2, $\phi = E_2 \Delta T / R T_0^2$
η	parameter in dimensionless Arrhenius expression, $\eta = \Delta T / T_0$
κ	thermal diffusivity
ν	kinematic viscosity

ρ	density
ρ_0	density at $T = T_0$
$\tau_{Convection}$	timescale for convection
$\tau_{Diffusion}$	timescale for diffusion of heat
$\tau_{Step\ i}$	timescale for step i of the reaction
ω_0	angular frequency

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Figure Captions

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.

Fig. 2. The general three-dimensional regime diagram describing the system, where the axes represent ratios of the characteristic timescales for reaction, diffusion and convection.

Fig. 3. Two-dimensional regime diagram. The plane defined by the axes ($\tau_{Step\ 2} / \tau_{Convection}$) and ($\tau_{Step\ 2} / \tau_{Diffusion}$) is sufficient to describe the system when $\tau_{Step\ 1} \gg \tau_{Step\ 2}$. Shown on this plane are two lines of constant Rayleigh number, $Ra = 10^3$ and 10^6 . Also shown is the nature of the flow in each region and the locations of cases 2, 3 and 14, which are discussed in detail below. The shaded area shows the approximate region in which oscillations have been found to occur.

Fig. 4. Plots of the temperature and concentration of A at five locations within the reactor as a function of time, for case 2. The numbers in the top right corner of each plot are the coordinates of the location considered, relative to the origin which is defined to be at the bottom of the reactor, on the vertical axis. The plots are arranged schematically to indicate their relative positions in the reactor.

Fig. 5. Temporal evolution of the convective, diffusive and reactive terms in (a) the concentration equation, Eq. (8), and in (b) the energy equation, Eq. (9), for case 2. Note that time is dimensional for ease of comparison.

Fig. 6. Plots of the temperature and concentration of A at the specified five points within the reactor for case 3.

Fig. 7. Plots of the temperature and concentration of A at the specified five points within the reactor for case 14.

Fig. 8. Evolution of the concentration of A (top) and temperature (bottom) in the reactor, for case 14. The frames occur at regular intervals of 0.4 s, over the course of 8 s.

Fig. 9. (a) The evolution of the temperature and the concentration of A within a notional fluid element as it is tracked through the flow field generated by natural convection in case 14. The element begins at a location $(0.3 L, L)$. The broken lines indicate the time taken for the element to return to its starting point.

(b) The y coordinate of the fluid element as it moves around the reactor.

Fig. 10. Temporal evolution of the convective, diffusive and reactive terms in (a) the concentration Eq. (8), and in (b) the energy Eq. (9), for case 14. Note that time is dimensional for ease of comparison.

Fig. 11. Regime diagram showing the sixteen cases considered. The closed diamonds represent the case where oscillations always occurred out-of-phase; the open diamonds represent those cases where in-phase oscillations were observed at some point in the reactor; and the open squares represent the transitional cases where a shift in the phase difference was observed.

Table Caption

Table 1. Details of the 16 cases considered. The highlighted entries show the cases discussed in detail.