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# АРМЕНИЯ

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# A SCALING AND NUMERICAL ANALYSIS OF THE EFFECTS OF NATURAL CONVECTION WHEN SAL'NIKOV'S REACTION: $P \rightarrow A \rightarrow B$ OCCURS, TOGETHER WITH DIFFUSION AND HEAT TRANSFER IN A SPHERICAL BATCH REACTOR

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#### Abstract

Sal'nikov's reaction:  $P \rightarrow A \rightarrow B$  involves a precursor, P, in two consecutive, first-order chemical reactions, yielding a final product B via an intermediate A. Partly as an academic exercise, but partly because of its relationship with cool flames, the situation is considered where the second step is faster than the first one, which is taken to be thermoneutral without an activation energy. The second step is assumed to have a significant activation energy, although it is exothermic. The reaction proceeds batchwise inside a spherical reactor, whose walls are held at a constant temperature, but do not participate chemically. Natural convection becomes important, once the temperature is high enough for the Rayleigh number (Ra) to reach ~  $10^3$ . The subsequent behaviour of the system depends on the interaction between convection, diffusion of heat and mass, and chemical kinetics. By examining the governing equations, we develop and evaluate scales for the characteristic velocity, the concentration of the intermediate A and the temperature rise during the progress of the reaction, for the two extreme cases when transport is dominated, in turn, by diffusion and then by natural convection. These scales depend on the characteristic timescales for the interacting phenomena of chemical reaction, diffusion and natural convection. Typically, the characteristic velocity in a relatively small reactor of radius 0.27 m is as large as 0.3 m s<sup>-1</sup>, when the temperature rise is  $\approx 100$  K near the centre of the vessel. These theoretical predictions from scaling are verified by full numerical simulations. Oscillations of both the temperature and the concentration of the intermediate, A, can occur and the conditions for their appearance are identified. Any accompanying flow field proves to be toroidal, with the fluid ascending close to the reactor's axis, but descending adjacent to its walls. In addition, the effects of variables, such as the initial temperature of the batch reactor and its contents, the pressure and also the size of the reactor are all assessed, together with a consideration of what happens when the reaction proceeds in the liquid phase. In this case, because of the different physical properties of a liquid and a gas, natural convection is more intense than in the gas-phase and is quite likely to lead to turbulence and good mixing.

# NOMENCLATURE

a	concentration of intermediate A
<i>a'</i>	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>i</i> of Sal'nikov's reaction (I)
8	acceleration due to gravity
$k_i$	rate constant of step <i>i</i> of the reaction
$k_{2,0}$	rate constant of step 2 evaluated at $T = T_0$
L	characteristic length of the reactor
Le	Lewis number = $\kappa / D_A$
р	concentration of precursor P
p'	dimensionless concentration of P, $p' = p / p_0$
$p_0$	initial concentration of P
$\mathcal{P}$	pressure in the reactor
$\mathscr{P}'$	dimensionless pressure, $\mathcal{P}' = (\mathcal{P} - \mathcal{P}_0) / \rho_0 U^2$
$\mathcal{P}_0$	initial pressure
Pr	Prandtl Number, $Pr = \nu / \kappa$
$q_i$	exothermicity of step <i>i</i> of the reaction
R	universal gas constant
Ra	Rayleigh number, $Ra = \beta g \Delta T L^3 / (\kappa v)$
t	time
ť	dimensionless time, $t' = U t / L$
Т	temperature
T'	dimensionless temperature, $T' = (T - T_0) / \Delta T$
$T_0$	constant wall temperature
<u>u</u>	velocity vector
<u>u</u> '	dimensionless velocity vector, $\underline{u}' = \underline{u} / U$
U	scale for velocity
<u>x</u>	spatial coordinates
<u>x</u> '	dimensionless spatial coordinates, $\underline{x}' = \underline{x} / L$

pre-exponential factor in Arrhenius expression for $k_2$
coefficient of thermal expansion, $\beta = 1 / T$
ratio of specific heats = $C_p / C_v$
scale for temperature increase
adiabatic temperature increase, $\Delta T_{ad} = q_2 / C_V$
thermal diffusivity
kinematic viscosity
density
density at $T = T_0$
timescale for convection
timescale for diffusion of species A
timescale for diffusion of heat
timescale for step $i$ of reaction (I)

#### 1. Introduction

During any exothermic reaction in a batch reactor, spatial temperature gradients develop. If these gradients are sufficiently large, natural convection occurs. The intensity of the flow resulting from natural convection is determined by the Rayleigh number,  $Ra = \beta g L^3 \Delta T / \kappa v$ . In general, the overall behaviour of the system will be determined by the interaction of three of its basic properties: chemical reaction, diffusion (of both heat and matter) and natural convection. Several exothermic reactions exhibit oscillations in both the local temperature and concentration of intermediates (Gray & Scott, 1990). One example is a 'cool flame', as displayed by a mixture of a paraffin and oxygen, in which the temperature and concentration of an intermediate display sustained oscillations.



Fig. 1. Cool flame of butane + oxygen in (a) micro- and (b) terrestrial gravity. From http://www.grc.nasa.gov/WWW/RT1999/6000/6711wu.html

Figure 1(a) shows the development of a real cool flame in a mixture of butane and oxygen without natural convection, as achieved under microgravity. If this is compared with Fig. 1(b), which shows

the equivalent cool flame under full gravity, we can see that natural convection removes the spherical symmetry. Instead, a horizontal 'flat' flame moves vertically downwards through the mixture of reactants. This is seen below to depend on the interaction of chemical kinetics, diffusion of both heat and matter, and also natural convection. These interactions have attracted the attention of Professor Merzhanov (Merzhanov & Shtessel, 1973). This contribution is offered as a tribute to Merzhanov, as well as to celebrate his 75<sup>th</sup> birthday and wish him "Many Happy Returns".

# 2. Sal'nikov's Reaction

Interestingly, Sal'nikov's reaction (1949) is probably the simplest way of modelling the chemical reactions in a cool flame (Bardwell & Hinshelwood, 1951). Of course, it fails to describe all the complexities (Griffiths & Barnard, 1995), but it facilitates an exploration of the interaction between chemical reaction, diffusion (of both heat and matter) and natural convection. The reaction consists of two, consecutive first-order steps:

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

This scheme is the simplest to display thermokinetic oscillations and so is investigated here in some detail. The first step of the reaction is assumed here to be thermoneutral (*i.e.*  $E_1$  and  $q_1$ , the activation energy and exothermicity of the reaction are both zero). Step 2 is exothermic with  $E_2$  and  $q_2 > 0$ . Oscillations occur due to the nonlinear thermal feedback arising from the Arrhenius temperature dependence of the rate of step 2.

#### **3.** Governing Equations

We consider, initially pure, gaseous P undergoing Sal'nikov's reaction in a closed spherical vessel of radius L, whose wall is held at a constant temperature,  $T_0$ . The equation for a, the concentration of the active intermediate A, is

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

where  $p_0$  is the initial concentration of P. 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. The conservation of energy is:

$$\frac{C_V}{C_P}\frac{\partial T}{\partial t} + \underline{u}.\nabla T = \kappa \nabla^2 T + \frac{q_2 k_2}{\rho_0 C_P}a,$$
(2)

where  $\rho_0$  is the density at the initial temperature  $T_0$ . The Navier-Stokes equations describe the conservation of momentum in:

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

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where  $\mathcal{P}_0$  is the initial pressure in the reactor. The conventional Boussinesq approximation is adopted, *i.e.* it is assumed that the density only varies in the buoyancy term of the Navier-Stokes equations. In this term the density varies as  $\rho = \rho_0 [1 - \beta (T - T_0)]$ , where  $\beta$  is the coefficient of thermal expansion. 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.*  $\nabla \underline{u} = 0$  (4)

Initially the gas is pure P at a temperature  $T_0$ , and is motionless. The wall of the reaction vessel is held at  $T_0$  throughout, and the usual no-slip condition applies. There is also assumed to be no flux of any species at the wall, where no heterogeneous reactions occur. However, there is of course heat transfer to the wall.

#### 4. Scaling Analysis

In order to make equations (1) - (4) dimensionless, the following seven dimensionless variables can be defined:

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

where  $a_0$  is a characteristic value of the concentration of species A,  $\Delta T$  is the characteristic temperature rise and U is the characteristic velocity. At this stage, these three scales are unknown, whereas  $p_0$  and L (the radius of the reactor) are defined for a given system. It is also useful at this stage to define five characteristic timescales:

$$\tau_{step 1} = \frac{1}{k_1}; \ \tau_{step 2} = \frac{1}{k_{2,0}}; \ \tau_{diffusion H} = \frac{L^2}{\kappa}; \ \tau_{diffusion A} = \frac{L^2}{D_A} \text{ and } \tau_{convection} = \frac{L}{U}, \ (6 \text{ a} - \text{e})$$

for the various interacting phenomena in the system, namely the two steps of reaction (I), diffusion of both heat and the intermediate A and finally convection. Here  $k_{2,0}$  is  $k_2$  evaluated at the wall's temperature,  $T_0$ . The relative values of these timescales will determine the behaviour of the system. For a gas  $\tau_{diffusion A} = \tau_{diffusion H}$ . This implies that  $\kappa = D_A$  or the Lewis number  $Le = \kappa / D_A$  is unity. This leaves four characteristic timescales. In fact, it can be shown (Campbell et al., 2005a,b) that if the initial temperature,  $T_0$ , is fixed, together with the variables:  $C_p$ ,  $C_v$ ,  $D_A$ ,  $\kappa$ ; v, and  $q_2$ , the behaviour of the system is totally defined by the three dimensionless groups:

$$\frac{\tau_{step2}}{\tau_{step1}} p' = \frac{k_1}{k_{2,0}} \frac{p}{p_0}; \quad \frac{\tau_{step2}}{\tau_{diffusion}} = \frac{\kappa}{k_{2,0}L^2}; \quad \frac{\tau_{step2}}{\tau_{convection}} = \frac{U}{k_{2,0}L}$$
(7)

Thus it turns out that in general the behaviour of the system is determined by the position of a point on Fig. 2, the regime diagram. This plots ratios of the above four time constants, as indicated by Eq. (7). On Fig. 2 a straight line is drawn in the vertical plane defined by the axes :  $\tau_{step 2} / \tau_{diffusion}$  and  $\tau_{step 2} / \tau_{convection}$ . This line passes through the origin of Fig. 2 and can be shown to have a slope of  $1/(RaPr)^{1/2}$ . The line is accordingly the locus of constant *Ra*.



**Fig. 2.** The general 3-D regime diagram describing the system, when both natural convection and diffusion are important. The axes represent ratios of the characteristic timescales for the two chemical steps, as well as of diffusion and convection. A line of constant Rayleigh number (Ra) is shown.

Figure 3 is a plot derived from Fig. 2 for constant  $(\tau_{step 2}/\tau_{step 1}) p'$ . It shows the available space divided by the lines for  $Ra = 10^3$  and  $10^6$ . Thus for Ra <<  $10^3$  no natural convection is expected, for  $10^3 < Ra < 10^6$  natural convection will be laminar, but will be turbulent for  $Ra > 10^6$ .



**Fig. 3.** Simplified 2-D regime diagram, showing (for a fixed  $\tau_{step 2}/\tau_{step 1}p'$ ) two lines of constant *Ra*, and the nature of the flow in each region.

Of course, transport can be controlled by either diffusion or convection, and the form of the unknown scales  $(a_0, \Delta T, U)$  will depend on which mechanism dominates. We examine each case, in turn, in order to determine the most appropriate scales in that case. It is important to note that in Fig. 3, a straight line through the origin has a slope  $1/(RaPr)^{1/2}$ , with  $Pr \sim 1$  for a gas, but Pr = 6.6 for liquid water at 22°C.

#### 4.1 Transport Controlled by Diffusion

For Rayleigh numbers less than a threshold value (of  $\approx 10^3$ ) (Tyler, 1966; Turner, 1979), natural convection will be unimportant, so that diffusion will be the dominant mechanism for the transfer of mass. Likewise, heat transfer is by thermal conduction, *i.e.* the diffusion of heat. When diffusion dominates transport, the temperature and concentration fields are approximately spherically symmetric, with the maximum temperature occurring close to the centre of the reactor. In this case, the characteristic velocity, *U*, is given by D / L, where *D* is either the thermal or the molecular diffusivity. We firstly assume that Eq. (1) for species A is dominated by the kinetic terms. This yields a scale for the characteristic concentration of species A:

$$a_0 \sim \frac{k_1}{k_{2,0}} p_0 = \frac{\tau_{step\,2}}{\tau_{step\,1}} p_0, \tag{8}$$

*i.e.* the steady state hypothesis. If we similarly assume that the diffusion and generation terms dominate in the dimensionless version of the energy balance (2), we can derive a scale for  $\Delta T$  as:

$$\Delta T \sim \frac{q_2 k_1 L^2}{C_P \kappa} = \frac{\Delta T_{ad}}{\gamma} \frac{\tau_{diffusion H}}{\tau_{step 1}}, \qquad (9)$$

where  $\Delta T_{ad}$  is the adiabatic temperature increase (=  $q_2 / C_V$ ) and  $\gamma$  is the ratio of specific heats ( $C_P / C_V$ ). This scaling assumes that  $\tau_{convection} \gg \tau_{diffusion} \gg \tau_{step 2}$ , *i.e.* the working point in Fig. 3 is to be found in the region of low *Ra*.

### 4.2 Transport Controlled by Convection

When the Rayleigh number becomes sufficiently large, natural convection becomes the dominant transport mechanism. Thus for  $10^3 < \text{Ra} < 10^6$ , the convective flow is expected (Turner, 1979) to be laminar. Natural convection distorts the spherical symmetry observed when diffusion dominates transport; it also leads to the formation of a hot zone above the centre of the reactor (Cardoso *et al.*, 2004a, b). If we assume that the convective and buoyancy terms dominate in the Navier-Stokes Eqs. (3), we can define an appropriate scale for the characteristic velocity as

$$U \sim \left[\beta_{\mathcal{B}} L(\Delta T)\right]^{1/2}.$$
(10)

Similarly, if we assume that the chemical kinetic terms dominate Eq. (1) (as in the previous section) and that convection and the generation of heat dominate the thermal balance (2), we can define a scale for  $\Delta T$  as:

$$\Delta T \sim \left(\frac{q_2}{C_P}\right)^{2/3} \left(\frac{k_1^2 L}{\beta g}\right)^{1/3} = \frac{\Delta T_{ad}}{\gamma} \frac{\tau_{convection}}{\tau_{step \, 1}} \,. \tag{11}$$

This scaling for  $\Delta T$  assumes that  $\tau_{diffusion} >> \tau_{convection} >> \tau_{step 2}$ . Interestingly, by assuming that convection and the generation of A in step 1 dominate Eq. (1) one obtains:

$$a_0 \sim \frac{\kappa_1 p_0 L}{U} = \frac{\tau_{convection}}{\tau_{step1}} p_0.$$
(12)

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This is for the working point being located on Fig. 3 in a region of medium *Ra*. In the next section we compare these scales to the results of a full numerical solution of all the governing equations, for the two separate cases where either diffusion or natural convection is the dominant mode of transport.

#### 5. Numerical Solution

Equations (1) – (4) were solved numerically for a spherical batch reactor with a fixed wall temperature,  $T_0$ , containing initially pure gas P, which then undergoes Sal'nikov's reaction. The equations were solved using *Fastflo* (Fastflo Tutorial Guide, 2000), which is a PDE solver utilising the finite element method. The algorithm used was the same as that outlined by Cardoso *et al.* (2004b).

For the purpose of the numerical simulations, we take physical and chemical data for the thermal decomposition of di-t-butyl peroxide in a spherical reactor. This reaction was chosen, because it can be shown to behave like Sal'nikov's reaction under certain conditions (Griffiths et al., 1988; Gray and Griffiths, 1989); thus experimental studies using a semi-batch reactor with the slow admission of reactant mimics the effect of step 1 in Sal'nikov's reaction. Such an arrangement is suitable for investigating Sal'nikov's reaction in the well-mixed limit; however, it is not suitable for cases which are not spatially uniform. Sal'nikov's reaction has been studied numerically by Fairlie and Griffiths (2002) in both the well-mixed and zero-gravity extremes, as well as by Cardoso et al. (2004a, b) when natural convection is important. The following constants were chosen to match those used by Cardoso et al. (2004a, b). The temperature of the wall of the spherical reactor,  $T_0$ , was held constant at 500 K and the physicochemical properties used were as follows: the initial molar density  $\rho_0$  = 8.2 mol m<sup>-3</sup> (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,  $q_2 = 400 \text{ kJ mol}^{-1}$ . We define the base case chemistry such that the rate constant  $k_1 = 0.025 \text{ s}^{-1}$ , corresponding to  $\tau_{step 1} = 40 \text{ s}$ , and  $k_2 = Z_2 \exp(-1)$  $E_2 / R T$ ) with  $Z_2 = 2 \times 10^{15} \text{ s}^{-1}$  and  $E_2 / R = 18280 \text{ K}$ . These values give  $k_{2,0} = 0.265 \text{ s}^{-1}$ , and hence  $\tau_{step 2} = 3.77$  s, which is thus approximately an order of magnitude faster than step 1. Furthermore, the simplifying assumption that the Lewis and Prandtl numbers are unity was made. Computations were done for reactors of different sizes at several values of Ra, both in the region where diffusion controls transport and when convection dominates. To further verify the scales developed, the kinetic rate constants were also varied. Given that the two scales for  $\Delta T$  (Eqs. (9) and (11)) depend on  $k_1$  only, a range of values for  $k_1$  was considered. The pre-exponential factor in  $k_2$  was hypothetically halved to confirm that  $\Delta T$  is indeed independent of  $k_2$ .

#### 6. NUMERICAL RESULTS

#### 6.1 Diffusive Regime

We begin by exploring all the cases when diffusion controls transport by considering in detail the cases Ra = 0 and  $Ra \sim 600$ . This means that as far as Fig. 3 is concerned, we are only considering systems on, or very near, the vertical axis (so  $g \sim 0$ ),



**Fig. 4.** Plots of the temperature (*T*) and concentration (*a*) of the intermediate A at the centre of the reactor against time, when diffusion controls transport for: (a)  $\tau_{diffusion} = 1$  s; L = 10 mm (b)  $\tau_{diffusion} = 4$  s; L = 20 mm (c)  $\tau_{diffusion} = 9$  s; L = 30 mm, all for the base-case chemistry with g = 0 m s<sup>-2</sup> and  $\kappa = 1 \times 10^{-4}$  m<sup>2</sup> s<sup>-1</sup>.

where only diffusion and reaction occur. Another example of *Ra* being low is a gaseous system at a low pressure; in this context it is noted below that *Ra* is proportional to the square of the pressure. Nevertheless, it turns out that there are three identifiable regions, where the system behaves differently, as shown more clearly in Fig. 4(a – c). The temporal development of the temperature and the concentration of A at the centre of the reactor for three different values of  $\tau_{diffusion}$  are plotted. In the three cases presented, the chemistry is that of the base case, *i.e.*  $\tau_{step 1} = 40$  s and  $\tau_{step 2} = 3.77$  s at

500 K, and  $\tau_{diffusion}$  has been varied by changing the radius, L, of the reactor (in this case the graphs represent L = 10, 20 and 30 mm, respectively). For a small reactor (L < 0.01 m), the working point is on the vertical axis of Fig. 3, far away from the origin. For this case, Fig. 4(a) shows slow growths and decays of both the temperature and the concentration of A with time. In addition, there is only a relatively small increase in temperature (of  $\sim 8 \text{ K}$ ) to the maximum at the centre of the reactor, so the system behaves almost isothermally. For these cases with a small  $\tau_{diffusion}$ , we would expect the temperature and concentration fields to be in effect spatially uniform, with the exception of the thermal and concentration boundary layers at the wall. This approximate spatial uniformity decreases the magnitude of the convective and diffusive terms in Eq. (1) relative to that of the reaction terms. Therefore, we expect  $\Delta T$  to have the form of Eq. (9), *i.e.* there is a dependence on  $k_1$ , but not  $k_2$ . Indeed, the concentration and temperature fields obtained numerically were virtually uniform in these cases. The temperature and concentration only change by ~ 1%, on moving from the wall to the centre of the reactor. This small variation in temperature and concentration leads us to describing the system as approximately spatially uniform. Additionally our numerical results show that the decay in temperature and concentration (as shown by Fig. 4(a)) is proportional to  $\exp(-k_I t)$ , thus lending support to the hypothesis that  $k_1$  is the dominant kinetic parameter in this system. In all three cases plotted in Fig. 4(a-c), the fields of temperature and of the concentration of the intermediate A were in fact spherically symmetric.

When we increase the size of the reactor, we move into a region of instability, where the temperature and the concentration of A exhibit temporal oscillations, as shown in Fig. 4(b) for the centre of the reactor. In fact, the concentration of A oscillates in anti-phase with the temperature, as has been shown previously (Cardoso *et al.* 2004a, b). It was found that oscillations only occurred for values of the reactor's radius, *L*, in a narrow band, whose location depended on the physical and kinetic parameters used. It seems that (see below), when diffusion is the dominant transport mechanism, the range of *L*, over which oscillatory behaviour is observed, corresponds to the region where the characteristic timescales for diffusion and reaction in step 2 are of similar magnitude, *i.e.*  $\tau_{diffusion} \approx \tau_{step 2}$ .

For L > 0.03 m, the working point moves along the vertical axis of Fig. 3 closer to the origin. Now the temporal evolutions of temperature and the concentration of A at the centre of the reactor are shown by Fig. 4(c). Instead of the oscillations, there is now an initial peak in the concentration curve, which then rapidly decays to almost zero. The temperature now rises by ~ 100 K, because of heat removal from a larger vessel being slower. The plot in Fig. 4(c) shows an initially fast rise in temperature and then there is a distinct 'kink' in the curve (at ~ 2 s), when the concentration of the intermediate reaches a steady value, close to zero. The 'kink' in the temperature curve can be explained by examining Eq. (2) for the conservation of energy. When the concentration of A falls rapidly to virtually zero, the heat generation term in Eq. (2) effectively disappears. It is this swift change in the form of the governing equation that causes the observed change in the temporal development of the temperature.

The plot in Fig. 5 checks Eq. (9) by showing the computed values of  $\gamma (\Delta T / \Delta T_{ad})$  plotted against  $(\tau_{diffusion} / \tau_{step l})$  for when diffusion is the dominant transport mechanism. The temperature rise was

taken to be that at the centre of the reactor, because this is where  $\Delta T$  is at its maximum value, due to the spherical symmetry. Figure 5 evidently reveals three regimes. There is linearity for high and very low ( $\tau_{diffusion} / \tau_{step l}$ ); the region between them is where oscillations occur. Equation (9) suggests that there should be a linear plot in Fig. 5. Therefore our scale, Eq. (9), for  $\Delta T$  is of the correct form. When  $\tau_{diffusion} / \tau_{step l} > 0.1$ , Eq. (13) can be modified by adding a constant factor, which can be found from Fig. 5 by the least squares method. Thus the characteristic temperature rise is given by:

$$\gamma \frac{\Delta T}{\Delta T_{ad}} = \left(0.141 \pm 0.002\right) \frac{\tau_{diffusion}}{\tau_{step1}}, \left(\frac{\tau_{diffusion}}{\tau_{step1}} < 0.04\right)$$
(13)  
and  $\gamma \frac{\Delta T}{\Delta T_{ad}} = \left(0.100 \pm 0.003\right) \frac{\tau_{diffusion}}{\tau_{step1}} + \left(0.030 \pm 0.002\right), \left(\frac{\tau_{diffusion}}{\tau_{step1}} > 0.1\right).$ (14)

In the narrow region between these two linear regimes, where oscillations occur, the 'error bars' in Fig. 5 show the range of the oscillations, measured from the first peak to the first trough. Oscillations were only observed in this narrow band, where  $\tau_{diffusion} \sim \tau_{step 2}$ , as noted above.



**Fig. 5.** Plot of  $\gamma(\Delta T/\Delta T_{ad})$  against  $\tau_{diffusion} / \tau_{step 1}$  in the diffusive regime. The line shown corresponds to Eq. (14). ( $\blacklozenge k_1 = 0.025 \text{ s}^{-1}, k_{2,0} = 0.265 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.0125 \text{ s}^{-1}, k_{2,0} = 0.265 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.0375 \text{ s}^{-1}, k_{2,0} = 0.265 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.025 \text{ s}^{-1}, k_{2,0} = 0.265 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.025 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.025 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.025 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.025 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.025 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.025 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.025 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.025 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.025 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.025 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.025 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.025 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.025 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.025 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.025 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.025 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.025 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.025 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.025 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.025 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.025 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.025 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.025 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.025 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.025 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.025 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.025 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.025 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.025 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.025 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.025 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.025 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.025 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.025 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.025 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.025 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.025 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.025 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.025 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.025 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.025 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.025 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.025 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.025 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.025 \text{ s}^{-1}, Ra = 0$ ;  $\blacksquare k_1 = 0.025 \text{ s}^{-1}, R$ 

#### 6.2 Oscillations in Microgravity

A region of oscillations was identified by performing very many simulations for when diffusion is the only transport mechanism, as in microgravity, but for different  $\tau_{step 1}/\tau_{step 2}$ . Figure 6 shows the approximate regions defined through simulations for g = 0 and different  $\tau_{step 1}/\tau_{step 2}$ . The axes of the regime diagram in Fig. 6 are the reciprocal of those in Fig. 2. This is to ensure that the region of oscillations is closed. Also, p' has been omitted from the abscissa, because it is a function of the two quantities being plotted in Fig. 6, when the precursor P is uniformly distributed throughout the reactor. Regions of sustained and damped oscillations were found. These areas in Fig. 6 are an order of magnitude larger than the region of oscillations defined analytically for a pseudo-1-D system by Gray and Scott (1990). An example of a sustained oscillation was seen in Fig. 4(a). Interestingly, these sustained oscillations disappear when  $Ra > 10^3$  and the oscillations become noticeably damped. The dotted lines shown in Fig. 6 correspond to areas where the numerical scheme broke down. As an aside, one of our initial assumptions was that  $\tau_{step 2} < \tau_{step 1}$ , which partly explains the dotted lines in Fig. 6. The oscillations occur in the region defined approximately by 0.04  $\tau_{step l} < \tau_{diffusion} < 0.2 \tau_{step l}$ , subject to the constraint that  $\tau_{diffusion} < 4 \tau_{step 2}$ . Before, for  $Ra < 10^3$  it was decided that  $\tau_{diffusion} \sim \tau_{step 2}$ for oscillations to occur. Figure 6 for Ra = 0 broadens that criterion by also considering the importance of  $\tau_{step} \ _{2} / \tau_{step}$  ]. In addition to the region of oscillations, two distinct types of nonoscillatory behaviour are shown in Fig. 6. These correspond to a slow reaction with a low temperature rise, and a rapid reaction with a large temperature rise. This situation is very similar to the conditions for the occurrence of cool flames, which on an ignition diagram are found to lie between those for a rapid thermal explosion and a very slow reaction.



**Fig. 6.** A 2-D regime diagram showing the approximate region of oscillations for zero-gravity, as identified after many simulations. The dashed lines are extrapolations of the boundaries into regions where the numerical scheme and model broke down.

#### 6.3 Convective Regime

The behaviour of the system when convection is more important than diffusional transport was investigated by again examining full numerical solutions, but for  $Ra \sim 5000$  and 21500. The convective flow in both these cases should be laminar. The flow-field is such that the gas rises vertically along the axis of symmetry and falls downwards close to the cooler walls, thus forming a toroidal vortex. Figure 7(a) plots the streamlines computed for the flow induced by natural convection. In outline, the system behaves as follows. The walls of the reactor are held at a constant

temperature. Whilst reaction proceeds, heat is released and consequently the temperature of the gas rises. Because the gas becomes hotter than 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). Figure 7(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. 7 refers not just to Sal'nikov's mechanism, but to any exothermic reaction proceeding in a similar vessel.



**Fig. 7.** (a) Streamlines of the flow due to natural convection in a vertical cross section through the axis of the reactor. The toroidal vortex typifying 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.

As mentioned previously, the spherical symmetry of the temperature and concentration fields seen in the diffusive regime is disrupted by the convective flow. Because of the 'hot zone' above the

centre of the reactor (Cardoso *et al.*, 2004a, b), we examine below, the temperature rise,  $\Delta T$ , at a point L/2 above the centre of the reactor (*i.e.* a point three quarters of the way up the vertical axis), instead of at the centre, to give a better indication of the maximum value of  $\Delta T$  within the reactor. Oscillations were observed over a much wider range of values than in the diffusive regime, and in fact, virtually every case studied when convection was significant exhibited oscillations.

Figure 8 shows a plot of the computed maximum vertical velocity at the centre of the reactor against  $(g L^2)^{1/3}$ , which arises from substituting Eq. (11) into (10). The 'error bars' show the range of the observed oscillations in the velocity. The linear form of this plot indicates that our scale, Eq. (10), is of the correct form. It is interesting to note that for a 10 cm diameter vessel undergoing a reaction in terrestrial conditions (*i.e.*  $g = 9.81 \text{ m s}^{-2}$ ), velocities of ~ 10 cm s<sup>-1</sup> were observed. Velocities of up to 30 cm s<sup>-1</sup> were computed for similarly sized vessels for larger values of  $g (= 30 \text{ m s}^{-2})$ . The characteristic velocity, U, can therefore be expressed as:

$$U = (0.31 \pm 0.02) [\beta_g L(\Delta T)]^{1/2}.$$
 (15)

This equation contains  $\Delta T$ . To check its magnitude, Fig. 9 shows  $\gamma (\Delta T / \Delta T_{ad})$  plotted against  $\tau_{convection} / \tau_{step l}$ ; as predicted by Eq. (11), there is a clear linear relationship. In fact, the characteristic temperature rise when convection dominates transport can be expressed as:

$$\gamma \frac{\Delta T}{\Delta T_{ad}} = \left(4.00 \pm 0.08\right) \frac{\tau_{convection}}{\tau_{step 1}}.$$
(16)

Thus our numerical simulations have confirmed the form of the scales developed above, when diffusion and convection are, respectively, the dominant transport mechanism. These scales allow the general behaviour of any given system to be predicted. It should be noted, however, that these scales were developed for a system where  $\tau_{step 1}$  is the dominant kinetic timescale. Thus, the behaviour may well change if  $\tau_{step 1}$  and  $\tau_{step 2}$  are of similar magnitude.



**Fig. 8.** Plot of the maximum vertical velocity of the gas at the centre of the reactor, versus  $(g L^2)^{1/3}$ . The line shown corresponds to Eq (15),  $Ra \sim 21500$ . ( $\oint g = 9.81 \text{ m s}^{-2}$ ,  $k_1 = 0.025 \text{ s}^{-1}$ ,  $k_{2,0} = 0.265 \text{ s}^{-1}$ ;  $\oint g = 4.9 \text{ m s}^{-2}$ ,  $k_1 = 0.025 \text{ s}^{-1}$ ,  $k_{2,0} = 0.265 \text{ s}^{-1}$ ;  $\blacksquare g = 30 \text{ m s}^{-2}$ ,  $k_1 = 0.025 \text{ s}^{-1}$ ,  $k_{2,0} = 0.265 \text{ s}^{-1}$ ).



Fig. 9. Plot of  $\gamma(\Delta T/\Delta T_{ad})$  versus  $\tau_{convection} / \tau_{step l}$  in the laminar convection regime. The line shown corresponds to Eq. (16). 'Error bars' showing the range of oscillations have been suppressed for clarity. (♦  $g = 9.81 \text{ m s}^{-2}$ ,  $k_1 = 0.025 \text{ s}^{-1}$ ,  $k_{2,0} = 0.265 \text{ s}^{-1}$ ,  $Ra \sim 21500$ ; ▲  $g = 4.9 \text{ m s}^{-2}$ ,  $k_1 = 0.025 \text{ s}^{-1}$ ,  $k_{2,0} = 0.265 \text{ s}^{-1}$ ,  $Ra \sim 21500$ ; ■  $g = 30 \text{ m s}^{-2}$ ,  $k_1 = 0.025 \text{ s}^{-1}$ ,  $k_{2,0} = 0.265 \text{ s}^{-1}$ ,  $Ra \sim 21500$ ; ×  $g = 9.81 \text{ m s}^{-2}$ ,  $k_1 = 0.0125 \text{ s}^{-1}$ ,  $k_{2,0} = 0.265 \text{ s}^{-1}$ ,  $Ra \sim 21500$ ; ×  $g = 9.81 \text{ m s}^{-2}$ ,  $k_1 = 0.0375 \text{ s}^{-1}$ ,  $k_{2,0} = 0.265 \text{ s}^{-1}$ ,  $Ra \sim 21500$ ; ×  $g = 9.81 \text{ m s}^{-2}$ ,  $k_1 = 0.0375 \text{ s}^{-1}$ ,  $k_{2,0} = 0.265 \text{ s}^{-1}$ ,  $Ra \sim 21500$ ; ○  $g = 9.81 \text{ m s}^{-2}$ ,  $k_1 = 0.025 \text{ s}^{-1}$ ,  $Ra \sim 21500$ ; ○  $g = 9.81 \text{ m s}^{-2}$ ,  $k_1 = 0.025 \text{ s}^{-1}$ ,  $Ra \sim 21500$ ; ○  $g = 9.81 \text{ m s}^{-2}$ ,  $k_1 = 0.025 \text{ s}^{-1}$ ,  $Ra \sim 21500$ ; ○  $g = 9.81 \text{ m s}^{-2}$ ,  $k_1 = 0.025 \text{ s}^{-1}$ ,  $Ra \sim 21500$ ; ○  $g = 9.81 \text{ m s}^{-2}$ ,  $k_1 = 0.025 \text{ s}^{-1}$ ,  $Ra \sim 21500$ ; ○  $g = 9.81 \text{ m s}^{-2}$ ,  $k_1 = 0.025 \text{ s}^{-1}$ ,  $Ra \sim 21500$ ; ○  $g = 9.81 \text{ m s}^{-2}$ ,  $k_1 = 0.025 \text{ s}^{-1}$ ,  $Ra \sim 21500$ ; ○  $g = 9.81 \text{ m s}^{-2}$ ,  $k_1 = 0.025 \text{ s}^{-1}$ ,  $Ra \sim 5000$ ).

#### 7. Oscillations

The oscillations of *a* and *T* in the above systems result from the interaction between chemical kinetics and heat transfer. This truth is not just restricted to Sal'nikov's reaction (Gray and Scott, 1990), but consideration of Sal'nikov's system indicates how more complex mechanisms might behave. 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 observed oscillations are sustained, but in fact are slightly damped (as in Fig. 4(a)), because the precursor, P, is continually consumed during the course of the reaction, so the production of A follows an exponential decay arising from 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. Interestingly, oscillations with *T* and *a* in phase can occur; they are discussed elsewhere by Campbell *et al.* (2005b). The entire region of Fig. 3 where oscillations occur has been found by performing very many simulations and is shown approximately in Fig. 10. There are two distinct parts to the oscillatory region. For  $Ra < 10^3$ , the boundaries between the oscillatory and non-

oscillatory zones are approximately constant, and are very similar to those seen in the purely diffusive case. For  $Ra > 10^3$ , natural convection dominates over diffusion of heat and mass. Oscillations are observed over a much wider range of parameters when natural convection is important. As Ra increases, the oscillatory region also widens.



**Fig. 10.** Regime diagram showing the effect (on the position of the working point in Fig. 3) of increasing the gas pressure, increasing the reactor's size, and the effect of performing the reaction in the liquid-phase. The area in grey denotes approximately where the concentration of the intermediate and the temperature oscillate.

#### 8. The Effect of Varying Parameters

Examination of the form of the scales developed in the previous sections, along with the expression for the Rayleigh number allows us to predict how the system will respond to variations in certain parameters. In particular, it is important to reveal the effects of pressure, the size of the reactor and the phase of the system (*i.e.* gas or liquid) on the intensity of convection in the reactor. Let us first consider the effect of increasing the pressure in a gas-phase reaction. The kinetic theory of gases indicates that v and  $\kappa$ ; the momentum and thermal diffusivities, are both inversely proportional to pressure. This means that the Rayleigh number is proportional to  $\sigma^2$ . Thus, increasing the pressure increases the Rayleigh number and therefore the intensity of the convective flow. A system represented by a point on the regime diagram of Fig. 10 actually moves vertically downwards, when the pressure is increased, because the terms in the abscissa are independent of pressure. The system could accordingly move from a situation of negligible convection at low pressure, through one of laminar flow, to eventually turbulent convection, when the pressure is increased.

The effect of increasing the reactor's size is shown by the solid curved line in Fig. 10. (*n.b.*  $\tau_{step\,2}/\tau_{diffusion} \propto 1/L^2$ ;  $\tau_{step\,2}/\tau_{convection} \propto 1/L^{1/3}$ ). It is clear from this plot that making the reactor smaller significantly reduces the Rayleigh number, thereby making diffusive processes more

significant. Figure 10 shows that when small reactors are considered, even relatively small increases in their size can significantly alter the Rayleigh number, which *ex hypothesi* has an explicit dependence on  $L^3$ . There is also a dependence of  $\Delta T$  on L via Eq. (9) or (11).

As for the effect of temperature on Ra, for a purely gaseous system in the convective regime, Ra turns out to be inversely proportional to  $T_0^{11/3}$ , according to the simplest version of the kinetic theory of gases. Otherwise, the main effect of temperature on the location of the working point in Fig. 10 is *via* the exponential in the Arrhenius function for  $k_2$ . Consequently any increase in temperature reduces  $\tau_{step 2}$  and so moves the working point towards the origin of Fig. 10, whose abscissa and ordinate are both proportional to  $\tau_{step 2}$ .

The final effect highlighted on Fig. 10 is the effect of moving from a reaction in the gas-phase to one in the liquid-phase. Comparing the relative magnitudes of the terms in the Rayleigh number for typical gases and liquids indicates that Rayleigh numbers will be at least an order of magnitude higher for liquid-phase systems, for similar increases,  $\Delta T$ , in temperature and identical values of L. Thus comparing Ra for reactions with the same  $\Delta T$ , g and L in water and air at normal temperature and pressure indicates that Ra with water is some 240 times Ra with air. In fact,  $\Delta T$  for a reaction in the liquid-phase is likely to be only  $\sim 10\%$  larger than for a reaction with the same kinetic parameters  $(q_2, k_1, k_2,...)$  in the gas-phase. The overall result is that gaseous and liquid systems occupy quite different areas of Fig. 10. In a liquid-phase reaction, natural convection is therefore likely to be more vigorous and important than in a gas-phase reaction with similar kinetic parameters. Certainly Fig. 10 indicates that natural convection is likely to be most important (i.e. turbulent) in reactors on an industrial scale, because of the dependence on  $L^3$ . Whenever natural convection is stronger, Fig. 10 makes it clear that there is a greater likelihood of oscillations in the reactor. This is because of the quite different portions of the two axes (of Fig. 10) occupied by the region wherein oscillations occur. Thus on the vertical axis, the region for oscillations roughly extends over  $0.5 < \tau_{\text{step 2}} / \tau_{\text{diffusion}} < 2$ , whereas along the horizontal axis, oscillations occur over approximately  $5 < \tau_{step 2} / \tau_{convection} < 90$ , *i.e.* a change by a factor of 18. No attempt has been made to investigate what happens when  $Ra > 10^6$  and turbulence occurs.

#### 9. Conclusions

Scales have been developed for the characteristic concentration of intermediate A, temperature rise and velocity when Sal'nikov's reaction occurs in a closed spherical vessel, both for the case where diffusion is the dominant transport mechanism, and when convection dominates. In both cases the characteristic concentration of the intermediate A was determined purely by the kinetics and the temperature rise was shown to be proportional to the ratio of the characteristic timescales for the dominant transport mechanism and the rate-controlling step of the reaction. It should be noted that this behaviour may differ if the relative magnitudes of the kinetic parameters are significantly altered. Using these scales, along with order of magnitude arguments, predictions have been made as to how the system will respond to changes in parameters, such as gas pressure, the size of reactor and if the reaction is conducted in the liquid-phase. It has been shown that natural convection is favoured by a high pressure in gas-phase reactions, and by a larger reactor. Because liquids have different physical

properties, reactions in the liquid-phase develop more intense convection than gas-phase reactions with similar kinetic parameters. The above analysis reveals when oscillations are possible.

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