The Behaviour of Sal'nikov's Reaction, $P \rightarrow A \rightarrow B$, in a Spherical Batch Reactor with the Diffusion of Heat and Matter

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Abstract

The behaviour of a simple chemical reaction, occurring with the release of heat in a closed batch reactor, is considered for the situation when matter and heat are transported only by diffusive processes; thus, the reacting fluid has negligible velocity, so that heat transfer is by thermal conduction. The reaction is Sal'nikov's, which consists of two, consecutive first-order steps, producing 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 to be thermoneutral, with zero activation energy, whilst the second is exothermic, with an appreciable activation energy. These features make Sal'nikov's reaction the simplest to display thermokinetic oscillations such as characterise many, more complex schemes, *e.g.* cool flames in hydrocarbon combustion. This study involves identifying the regions of parameter space, in which these oscillations in the temperature and the concentration of the intermediate A occur, by means of numerical simulation. These regions are compared with previous analytical stability analyses in one-dimensional systems. It was found that oscillations occur over a much larger range of conditions in the case considered here, *i.e.* a reactor with spherical symmetry, than in the simple 1-D case, previously studied by Gray and Scott. In addition, approximate analytical solutions for the temperature and concentration of A are presented for two limiting cases of non-oscillatory behaviour. These analytical solutions have been verified by comparison with full numerical solutions of the governing equations.

1. Introduction

When even simple exothermic reactions proceed in a closed vessel, complex behaviour can ensue. An example of this is the thermokinetic oscillations which typify cool flames¹⁻³, which are a feature of the low-temperature combustion of hydrocarbon vapour. This work examines the behaviour of Sal'nikov's reaction⁴, which is the simplest reaction to exhibit such oscillations. It should be noted, of course, that Sal'nikov's reaction is a considerable simplification of the mechanism governing cool flames, which includes chemical feedback through chain branching in addition to the thermal feedback present in Sal'nikov's model⁵. Nevertheless, Sal'nikov's reaction can provide useful insights into the interaction of thermokinetic oscillations and various transport mechanisms. Sal'nikov's reaction has received extensive analysis in the limit of perfect mixing⁶⁻¹⁰, when its behaviour is now well understood. In recent years, focus has switched to two other regimes of behaviour, away from this idealised state. At terrestrial conditions, in an unstirred vessel, the temperature gradients induced by the exothermic reaction can be sufficiently large to cause the buoyancy forces to move the gas, *i.e.* natural convection is induced. This convection can significantly alter the behaviour within the reactor whilst the reaction proceeds; these effects have been studied numerically recently¹¹⁻¹⁵. The other case to consider is that when convection is eliminated from the unstirred vessel, so that diffusion is the only mode of heat and mass transfer in the reactor. This corresponds to reaction occurring in microgravity as studied experimentally by Pearlman¹⁶, for n-butane and oxygen cool flames. Alternatively, a gaseous system at sufficiently low pressures can have negligible natural convection. Theoretical and numerical studies of this diffusion-reaction system have focussed primarily on either temporal oscillations or the formation of stable spatial patterns under the so-called 'pool chemical approximation', where the effects of the decay of the concentration of the precursor P are ignored. Gray and Scott¹⁷ studied, analytically, both the temporal and spatial stability of a simplified rectangular geometry in which diffusion occurs in only one dimension. Forbes studied the formation of spatial patterns in a similar rectangular, pseudo-one-dimensional geometry¹⁸, and in circular geometry¹⁹. This situation corresponds to the experimentally observed formation of target and spiral

patterns in uniformly propagating planar flames²⁰⁻²² and indeed Scott *et al.*²³ have used Sal'nikov's reaction as a model to simulate these phenomena in pre-mixed flames. Numerical studies^{24, 25} of Sal'nikov's reaction in a purely diffusive system have considered some aspects of the temporal development of oscillations when the reaction occurs in a spherical vessel, with a fixed wall temperature; that situation is similar to the experimental configuration described by Pearlman¹⁶.

This study considers Sal'nikov's reaction occurring in a spherical vessel, with slow disappearance of the precursor, P, included. Regions in parameter space where temporal oscillations occur are sought, and the nature of the non-oscillatory solutions is also studied. This work expands on the numerical studies of Fairlie and Griffiths^{24, 25}.

2. Governing Equations

Sal'nikov's reaction consists of two, consecutive first-order steps in:

where the precursor P is converted to the final 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 $q_2 > 0$. This work considers initially pure P, reacting to form the product B in a closed spherical vessel of radius L , whose wall is held at a constant temperature, T_0 , throughout the course of the reaction (*N.B.* all symbols are defined in the nomenclature section following the conclusions). The only transport mechanism considered is diffusion, as *e.g.* would be the case if the reaction were carried out in microgravity. The equation governing the conservation of the intermediate A can therefore be stated as:

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

It is assumed in the derivation of this equation that the precursor P is initially distributed uniformly within the reactor, and remains so equal to $p_0 \exp(-k_1 t)$, throughout the course of the reaction. This assumption, of course, depends on k_1 being independent of temperature (because $E_1 = 0$). The conservation of energy can be expressed as:

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

where ρ_0 is the density of the fluid at the temperature of the wall, T_0 , which is assumed to remain constant throughout. The assumption of constant density is, of course, a considerable simplification and this should be borne in mind when interpreting the results; however, previous analytical¹⁷⁻¹⁹ and numerical studies^{24, 25} of Sal'nikov's reaction occurring in the presence of purely diffusive transport processes have made the same assumption. The adoption of such an assumption also allows easier comparison with the results of numerical studies in the presence of natural convection, which have applied the Boussinesq approximation¹¹⁻¹⁵, *i.e.* when the density is only allowed to vary in the buoyancy term of the Navier-Stokes equations. Comment should also be made on the inclusion of C_P , the heat capacity at constant pressure, in what is a constant volume system. Its inclusion arises from the standard definition of the thermal diffusivity, $\kappa = k_T / (\rho C_P)$. The thermal diffusivity has been defined thus to enable comparison between the results in a purely diffusive system, with one in which convection plays a role¹¹⁻¹⁵. To achieve the required form of κ , each term in Eq. (2) is accordingly divided by $\rho_0 C_P$.

Initially the fluid in the reactor is held at a constant temperature, T_0 , which is the fixed wall temperature. It is assumed that there is no motion of the fluid in the reactor. A no-flux condition is applied to all the chemical species at the wall, implying that surface chemistry has not been taken into account. In addition, it is assumed that the thermal conductivity, κ , also remains constant. Because the temperature of the wall of the reactor is fixed, heat can be removed from the system at the wall. This boundary condition differs from that in the previous 1-D studies^{17, 18}, which assumed zero heat flux at the boundary of the region studied. The conditions used in this study are however the same as those studied by Fairlie and Griffiths^{24, 25}. The boundary conditions used are therefore:

$$t = 0: \quad p = p_0; \quad a = 0; \quad T = T_0; \quad \forall \underline{r}$$

$$\text{At the wall:} \quad \underline{n} \cdot \nabla p = \underline{n} \cdot \nabla a = 0; \quad T = T_0, \quad (3)$$

where $\underline{n}$ is a unit vector perpendicular to the wall of the vessel.

Equations (1) and (2) can be made dimensionless by introducing the following five dimensionless variables:

$$a' = \frac{a}{a_0}; \quad p' = \frac{p}{p_0}; \quad T' = \frac{T - T_0}{\Delta T_s}; \quad r' = \frac{r}{L} \quad \text{and} \quad t' = \frac{\kappa t}{L^2}, \quad (4 \text{ a - e})$$

where L is the radius of the reactor, p_0 is the initial concentration of the precursor P, and the scales for the characteristic concentration of the intermediate A, a_0 , and the temperature rise, ΔT_s , are of the form defined by Campbell *et al.*¹³, *i.e.*

$$a_0 \sim \frac{k_1}{k_{2,0}} p_0; \quad \Delta T_s \sim \frac{q_2 k_1 L^2}{C_P \kappa}. \quad (5 \text{ a, b})$$

This approach differs somewhat from that used in previous studies of the well-mixed or diffusive systems, which have chosen other dimensionless groups from thermal explosion theory to reduce the governing equations. Such analyses, with some small variations, have been presented by Gray and Scott^{10, 17} and by Fairlie and Griffiths^{24, 25}. In particular, Gray and Scott presented their results in both the well-mixed¹⁰ and diffusive¹⁷ regimes in terms of the parameter-space coordinates $\mu_G \& S = k_1 t_{cooling} p / c_{ref}$, which is a dimensionless measure of the concentration of the precursor, and $\kappa_G \& S = k_2 t_{cooling}$, which is a measure of the dimensionless rate of step 2 of reaction (I). In the well-mixed system $t_{cooling}$ was taken to be the Newtonian cooling time, and in the diffusive system it was taken as the Fourier timescale. The reference concentration, c_{ref} , is a large group containing kinetic terms as well as terms describing heat transfer between the system and its surroundings. The analysis presented by Gray and Scott^{10, 17} is powerful, but due to the nature of the dimensionless groups used, it is difficult to interpret the physical significance of their results. By using the simple dimensionless variables in Eqs. (4) and (5), physical interpretation of the results should be straightforward.

It is also useful at this stage to define the three characteristic timescales:

$$\tau_{step1} = \frac{1}{k_1}; \quad \tau_{step2} = \frac{1}{k_{2,0}}; \quad \tau_{diffusion} = \frac{L^2}{\kappa}, \quad (6 \text{ a - c})$$

for both steps of reaction (I), and also the diffusion of heat. Here, $k_{2,0}$ is k_2 evaluated at the wall temperature. Using the scales defined in Eq. (5) and the timescales defined in Eq. (6), the dimensionless governing equations can be written as:

$$\frac{\partial a'}{\partial t'} = \frac{1}{Le} \nabla'^2 a' + \frac{\tau_{diffusion}}{\tau_{step 2}} \exp\left(-t' \frac{\tau_{diffusion}}{\tau_{step 1}}\right) - \frac{\tau_{diffusion}}{\tau_{step 2}} \exp\left(\frac{\phi \frac{\tau_{diffusion}}{\tau_{step 1}} T'}{1 + \frac{q_2}{C_P T_0} \frac{\tau_{diffusion}}{\tau_{step 1}} T'}\right) a', \quad (7)$$

$$\frac{1}{\gamma} \frac{\partial T'}{\partial t'} = \nabla'^2 T' + \exp\left(\frac{\phi \frac{\tau_{diffusion}}{\tau_{step 1}} T'}{1 + \frac{q_2}{C_P T_0} \frac{\tau_{diffusion}}{\tau_{step 1}} T'}\right) a', \quad (8)$$

where ∇' is the dimensionless Laplacian operator and

$$\phi = \frac{E_2 q_2}{RT_0^2 C_P}. \quad (9)$$

It is clear from the form of these equations that the behaviour of a given chemical system depends only on the two groups:

$$\frac{\tau_{step 2}}{\tau_{diffusion}} \quad \text{and} \quad \frac{\tau_{step 2}}{\tau_{step 1}}, \quad (10)$$

which correspond to two of the axes on the three-dimensional regime diagram proposed by Cardoso *et al.*¹², shown in Fig. 1. A general system, in which natural convection and diffusion both play a role, can be represented as a point (C) on this regime diagram. The present work is concerned solely with the vertical plane on this diagram, defined by the axes $\tau_{step 2} / \tau_{diffusion}$ and $(\tau_{step 2} / \tau_{step 1}) p'$, which corresponds to the reaction occurring in a purely diffusive system *e.g.* in microgravity. Inspection of Eq. (7) shows that p' , the dimensionless concentration of the precursor P, is given by:

$$\exp\left(-t' \frac{\tau_{diffusion}}{\tau_{step 1}}\right) = \exp\left(-t' \frac{\tau_{diffusion}}{\tau_{step 2}} \frac{\tau_{step 2}}{\tau_{step 1}}\right). \quad (11)$$

Thus, for the case in which the precursor P is initially distributed uniformly within the reactor, p' is a function of the two groups in Eq. (10) and can therefore be eliminated from the axis of the regime diagram. It is clear that the two groups in Eq. (10), which can be used as parameter-space coordinates, are simple and have a well-defined physical meaning. In this regard, the approach used in this work is an attractive alternative to the method of Gray and Scott^{10, 17} described above.

3. Numerical Method

Equations (1), (2) and (3) were solved numerically for a spherical batch reactor using the PDE solver Fastflo²⁶. The algorithm employed uses the finite element method and is the same as that described elsewhere¹². For the numerical simulations, the thermal decomposition of gaseous di-*t*-butyl peroxide was considered, because this has been shown to behave like Sal'nikov's reaction under certain conditions^{27, 28}. These experimental studies used a semi-batch reactor, with the slow admission of the reactant into the vessel mimicking the effect of step 1 of Sal'nikov's reaction. This arrangement is suitable for studying Sal'nikov's reaction in the well-mixed limit; however, it is not suitable for cases that are not spatially uniform. This reaction has also been studied numerically in the well mixed and zero gravity extremes^{24, 25} as well as when natural convection is present¹¹⁻¹⁵. The reaction between hydrogen and chlorine, using similar experimental techniques, has also been used as a model of Sal'nikov's reaction²⁴. The following parameters were chosen to match those used in previous numerical studies of the di-*t*-butyl peroxide reaction¹¹⁻¹⁵. 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 value of k_1 was varied over a range of $0.0035 - 0.0375 \text{ s}^{-1}$, corresponding to a range of $\tau_{\text{step } 1}$ of $\sim 26 - 285$ s. Variation of this parameter corresponds to changes in the feed rate to the semi-batch reactor described above. The value of $k_2 = Z_2 \exp(-E_2 / R T)$ was taken to be that for the decomposition of di-*t*-butyl peroxide, with $Z_2 = 2 \times 10^{15} \text{ s}^{-1}$ and $E_2 / R = 18280$ K. These values give $k_{2,0} = 0.265 \text{ s}^{-1}$, and hence $\tau_{\text{step } 2} \sim 4$ s, which is at least an order of magnitude faster than step 1. The analysis described in the previous section indicates that the behaviour of the system is defined by the ratio of the kinetic timescales (Eq. (10)). To test this hypothesis $\tau_{\text{step } 2}$ was also varied. This is, of course, a purely hypothetical action, conducted to validate the results in section 2. The value of $k_{2,0}$ was varied by altering the pre-exponential factor Z_2 over the range $6.3 \times 10^{13} - 2 \times 10^{15} \text{ s}^{-1}$, with E_2 / R held constant at 18280 K. This corresponds to $\tau_{\text{step } 2} \sim 4 - 120$ s. Furthermore, the simplifying assumption

that the Lewis number was unity was made. This implies that $\kappa = D_A$, i.e. the diffusivities of heat and chemical species were considered to be equal. This is approximately true for a gas, but not a liquid. For example, for an ionic reaction in water $Le \sim 100$. Throughout this study, the values of the diffusivities were held constant at $\kappa = D_A = 1 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$. The value of $\tau_{diffusion}$ was therefore altered by changing the radius of the reactor, L . We note that a similar variation in $\tau_{diffusion}$ could alternatively be achieved by maintaining a constant vessel radius, and altering the diffusivity, as was done by Fairlie and Griffiths²⁵, who considered reaction occurring in a vessel of radius 0.0492 m with diffusivities of 3×10^{-4} and $6 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$.

4. Region of Temporal Oscillations

4.1 Previous Analytical Work on a Pseudo-1-D System

An understanding of how the system behaves in different regions of parameter space is clearly very important. Principally, the region in which temporal oscillations are observed needs to be defined. Gray and Scott¹⁷ performed a linear stability analysis on Sal'nikov's reaction occurring in a box, in which diffusion was the only transport mechanism operating. The system they studied is shown in Fig. 2, with the reactants contained in a long and very thin box. At either end of the box ($x = 0, L$) there is perfect insulation so no heat can leave the system there. It is also assumed that there is no surface reaction, or other loss of chemical species from the system at these walls. Therefore, there are no-flux conditions, for both chemical species and heat, applied at the right- and left-hand ends of the box. It is also assumed that the horizontal boundaries at $y = 0, l_0$ are impermeable to the chemical species contained in the box, *i.e.* there is no flux of any chemical species across these boundaries. Heat can however be lost from the horizontal boundaries to the surroundings, under the control of a heat transfer coefficient. The box is also considered to be sufficiently thin in the y -direction so that concentration and temperature variations only occur in the x -direction. This means that diffusion, of either heat or mass, can occur in only one dimension, parallel to the x axis. In this system, the

oscillations can arise from thermokinetic effects, *i.e.* due to variations in the production of heat *via* the exothermic reaction and heat loss to the surroundings, and oscillations can also result from the diffusion of heat and mass along the thin box destabilising the system. As the authors¹⁷ themselves point out, this situation bears little resemblance to any real situation; however, it does allow analytical solutions to be derived. It should also be said that the spherical reactor studied in this work is much more relevant to ‘real’ systems.

Whilst the spherical geometry and boundary conditions discussed below are different from those studied by Gray and Scott¹⁷, their analytical work does provide an excellent point of reference for the numerical results described below. In the course of their stability analysis, Gray and Scott¹⁷ were able to define a closed region in parameter space, within which the steady state solution (which can be achieved if the pool chemical approximation is applied) is unstable. In practice, this corresponds to a region where sustained temporal oscillations of the temperature and concentration of A are observed. The behaviour of the system described by Gray and Scott¹⁷ depends on four dimensionless parameters: $\beta_{G \& S}$, $\mu_{G \& S}$, $\kappa_{G \& S}$, and $\gamma_{G \& S}$. These dimensionless numbers can be transformed to yield expressions in terms of the ratios of timescales defined in Eq. (10). This transformation allows the region of instability to be plotted on the appropriate vertical plane of the regime diagram in Fig. 1, whilst also making the results of Gray and Scott¹⁷ easier to interpret physically. There is however a complication in this transformation of coordinates. Gray and Scott’s work¹⁷ includes a heat transfer coefficient in the derivation of the aforementioned dimensionless groups. The spherical system considered in the present work does not describe heat transfer using a transfer coefficient, and the timescales defined in Eq. (6) do not allow for this. To overcome this difficulty, the heat transfer coefficient is defined in terms of a Nusselt number, *i.e.*

$$h = Nu k_T / L. \quad (12)$$

This definition can be substituted into the definitions of the dimensionless groups in Gray and Scott’s work¹⁷, yielding:

$$\begin{aligned}
\beta_{G \& S} &= 1/(Le \gamma); \\
\gamma_{G \& S} &= Nu L/l_0; \\
\mu_{G \& S} &= \frac{\phi}{\gamma \gamma_{G \& S}^2} \left(\frac{\tau_{diffusion}}{\tau_{step 2}} \right)^2 \frac{\tau_{step 2}}{\tau_{step 1}} p' \quad \text{and} \\
\kappa_{G \& S} &= \frac{1}{\gamma \gamma_{G \& S}} \frac{\tau_{diffusion}}{\tau_{step 2}}
\end{aligned} \tag{13 a – d}$$

The region of instability identified by Gray and Scott¹⁷ was expressed in terms of the coordinates $\mu_{G \& S}$ and $\kappa_{G \& S}$, and hence can be plotted on the regime diagram of Fig. 1 using the relations derived in Eq. (13 c, d). It was noted that if the axes $\tau_{step 2} / \tau_{diffusion}$ and $\tau_{step 2} / \tau_{step 1}$ are used on the regime diagram, as defined by Cardoso *et al.*¹², the closed region of instability defined by Gray and Scott¹⁷ becomes open because the values of the boundaries between stable and unstable solutions tend to infinity. This problem can of course be remedied by simply plotting the reciprocal of the two coordinates, *i.e.* $\tau_{diffusion} / \tau_{step 2}$ versus $\tau_{step 1} / \tau_{step 2}$. Plotted in Fig. 3 is the region of instability identified by Gray and Scott¹⁷ for their pseudo-1-D system on the regime diagram with these inverted coordinates. The other two variables, $\gamma_{G \& S}$ and $\beta_{G \& S}$, represent adjustable parameters, which vary the size of the unstable region. The effect of varying $\gamma_{G \& S}$ is shown in Fig. 3. Increasing $\gamma_{G \& S}$, by having a larger Nusselt number for lateral heat transfer, or increasing the length of the box, L , or by decreasing the width, l_0 , in Fig. 2 increases the value of the ordinate of the boundary, whilst the abscissa remains constant. The value of $\beta_{G \& S}$ is fixed at ~ 1 by the physical parameters defined in section 3. When $\beta_{G \& S}$ is increased, the region of instability grows in the direction of both the ordinate and abscissa. An increase in $\beta_{G \& S}$ corresponds to a decrease in Le , the Lewis number, which indicates that there is a much larger area of instability if the molecular diffusion coefficient (D_A) is much larger than the thermal diffusivity (κ). Realistically, the Lewis number is likely to be larger than 1, therefore the region of instability will be smaller. This observation is supported by the work of Fairlie and Griffiths²⁵, who looked at $Le = 1, 2$ and 6 for a given set of kinetic parameters. Their results showed that at the conditions chosen, increasing the Lewis number increased the rate at which the oscillations in temperature damped away.

4.2 Regions of Oscillation in a Spherical Reactor

A series of numerical simulations was carried out in order to identify regions on the regime diagram in which temporal oscillations in the temperature and concentration of the intermediate A occur in a spherical vessel of radius L . The approximate regions identified by performing many simulations are shown in Fig. 4. As was the case with Gray and Scott's pseudo-1-D system¹⁷, closed regions of oscillations were found. The results presented in Fig. 4 are for a system with the dimensionless groups γ , Le , ϕ and $q_2 / C_P T_0$ held constant (see Eqs. (7) – (9)). Variation of these groups would result in a different region of oscillations. It should also be noted that because the Lewis number is assumed to be unity, it is likely that the oscillations observed in the simulations are a result of thermokinetic effects, that is to say the instabilities are driven by differences in local rates of heat production and loss. At low values (< 3) of $\tau_{step\ 1} / \tau_{step\ 2}$, the numerical scheme used in the simulations breaks down due to the appearance of large temperature spikes; even so, it seems reasonable to suggest that the boundaries (in Fig. 4) identified through the simulations (for step 2 much faster than step 1) extend back towards the origin, as is the case in the pseudo-1-D geometry in Fig. 3. The section of the boundary which is dashed indicates the expected behaviour in the region where the numerics break down. These could be confirmed by use of a different modelling technique which is able to handle temperature spikes, *e.g.* a finite volume approach could be used. It should be noted that Fig. 4 shows regions of damped oscillations, as well as sustained temporal oscillations, whereas Gray and Scott¹⁷ identified a region of instability, which would correspond solely to sustained temporal oscillations (Fig. 3). If the region of sustained oscillations in Fig. 4 is compared with the region of instability in the pseudo-1-D system in Fig. 3, it can clearly be seen that in the spherical system, the region is more extensive by an order of magnitude (on both axes). There are many factors which can contribute to this difference, the most obvious of which is, of course, the different geometry. The change from the pseudo-1-D system with linear geometry to one with spherical symmetry can have a dramatic impact on the progress of the reaction. There is also the difference in heat transfer to consider. The lateral heat loss, characterised by a heat transfer coefficient in the pseudo-1-D system of Gray and Scott¹⁷, contrasts with the spherical system, inside which heat can only be transferred by conduction. One further difference is in the

boundary conditions. The pseudo-1-D system considers there to be no heat or mass flux at the side walls, whereas in the spherical system, heat is removed from the system at the wall because of the constant temperature condition. These effects seem to combine to ensure that the spherical system is much more unstable to temporal disturbances, and hence has a larger region in which sustained temporal oscillations are observed.

The much larger region of damped oscillations in Fig. 4 corresponds to steady state solutions which are stable. However, they would be focal in character, if a stability analysis were performed on a system with the pool chemical approximation assumed. This results in relatively small scale oscillations, which decay away very rapidly (in many cases only one oscillatory cycle is seen before a steady decay in temperature and the concentration of A is observed). The results presented here, *i.e.* a relatively small region of sustained oscillations surrounded by a larger region of damped oscillations, are similar to those found by Gray and Scott¹⁰ in the well-mixed regime. Indeed, those authors found a region of sustained oscillations surrounded by a region of damped oscillations which was approximately an order of magnitude larger.

The regions of oscillation can also be compared with the numerical results of Fairlie and Griffiths²⁵, who studied numerically the effect of varying k_I when $L = 0.0492$ m for the cases when the diffusivities of heat and mass were first $3 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$ and then $6 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$. The results they presented are reproduced on Fig. 5, as are the nature of the temporal development of the temperature at the centre of the reactor. Their results are clearly in good agreement with the region defined by the present work. It is also interesting to observe how a point representing a given system moves in the regime diagram when the physical parameters are altered. For example, when $k_I = 0.025 \text{ s}^{-1}$, $k_{2,0} = 0.264 \text{ s}^{-1}$ (as it would be for the decomposition of di-*t*-butyl peroxide), $L = 0.0492$ and $k = D_A = 3 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$, the values of the coordinates are $\tau_{diffusion} / \tau_{step\ 2} = 2.14$ and $\tau_{step\ 1} / \tau_{step\ 2} = 10.6$. This corresponds to the top left filled square in Fig. 5, which is non-oscillatory. In order to move the system into an oscillatory state there are three possibilities (assuming the chemistry of step 2 is to remain unchanged): the precursor supply rate k_I can be decreased (this corresponds to the system point moving horizontally to the right on Fig. 5), the reactor size can be decreased or the diffusivity can be increased (through the addition of a diluent for example). The last two options correspond to the

system point moving vertically downwards. By decreasing k_I to $\sim 0.02 \text{ s}^{-1}$ the system will move into a region of the regime diagram in which damped oscillations occur. If k_I is decreased below $\sim 0.0052 \text{ s}^{-1}$ then the system will again become non-oscillatory. It can be seen in Fig. 5 that sustained oscillations cannot be achieved for any value of k_I , only damped oscillations occur. In order to exhibit sustained oscillations either the radius of the reactor or the diffusivity must be altered. Considering again the case where $k_I = 0.025 \text{ s}^{-1}$, if the radius of the reactor is reduced to $\sim 0.046 \text{ m}$ the system moves vertically downwards into a region of damped oscillatory behaviour. If the radius is reduced further, to $\sim 0.0385 \text{ m}$, sustained oscillations emerge. These sustained oscillations continue until the radius of the reactor is reduced below $\sim 0.028 \text{ m}$, when the behaviour reverts to damped oscillations. For a reactor of radius less than $\sim 0.023 \text{ m}$ there are no oscillations. Because the behaviour of the system is governed by the ratio $\tau_{diffusion} / \tau_{step 2}$, similar effects to reducing the radius could be achieved by increasing the diffusivity. Thus, for a vessel with $L = 0.0492 \text{ m}$ and $k_I = 0.025 \text{ s}^{-1}$, damped oscillations emerge when the diffusivity is increased to $\sim 3.5 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$, sustained oscillations emerge when the diffusivity reaches $\sim 4.9 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$, these revert to damped oscillations when the diffusivity is $\sim 9.3 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$ and the system becomes non-oscillatory when the diffusivity is greater than $\sim 1.4 \times 10^{-3} \text{ m}^2 \text{ s}^{-1}$.

5. Analytical Non-Oscillatory Solutions

Whilst it is important to identify regions in parameter space where oscillations occur, inspection of Fig. 4 shows that over the vast majority of this space, no oscillations are observed. The behaviour of the system in these regions with no oscillation also merits further study. It was noted by Campbell *et al.*^{13, 14} that three distinct types of temporal behaviour are exhibited by this system. These are presented in Fig. 6, which shows the development of the temperature and the concentration of A at the centre of the reactor. For ‘slow’ reactions, which occur close to the $\tau_{step 1} / \tau_{step 2}$ axis (*i.e.* $\tau_{diffusion} / \tau_{step 2}$ is small) of the regime diagram of Fig. 4, there is a slow growth and subsequent decay of the temperature and the concentration of A, as shown in Fig. 6(a). The magnitude of the

increase in temperature is very small (~ 8 K). It is observed that the concentration in the reactor is virtually spatially uniform at any time throughout the course of the reaction. Upon moving vertically upwards in Fig. 4 (*i.e.* increasing $\tau_{diffusion} / \tau_{step\ 2}$), a region of instability is entered resulting in oscillations. Shown in Fig. 6(b) is a solution exhibiting sustained oscillations, as would be expected if the steady state of the corresponding pool chemical system were unstable. For values of $\tau_{diffusion} / \tau_{step\ 2}$ above the region of oscillations in Fig. 4, a third type of behaviour is seen. This is shown by Fig. 6(c); there is an initial increase in the concentration of A, which then rapidly decays to almost zero. The temperature increases quickly initially, followed by a period of slower increase after the concentration has fallen to virtually zero. The temperatures reached in this region are considerably higher (~ 110 K in Fig. 6(c)) than those seen for ‘slower’ reactions. This is not surprising, because this region of behaviour corresponds to larger reactors, with higher ratios of volume to surface area, so more heat can accumulate in the system.

The region of oscillatory behaviour, characterised by Fig. 6(b), was identified in the previous section. The two other cases are now considered, and through appropriate simplification of the governing equations, approximate analytical solutions are sought for these two non-oscillatory cases.

5.1 Non-Oscillatory, Low Temperature Rise Solution: Small $\tau_{diffusion} / \tau_{step\ 2}$

As discussed above, the solution for small values of $\tau_{diffusion} / \tau_{step\ 2}$ takes the form of a slow growth and decay of the temperature and concentration of A. It was also noted that, with diffusion faster than reaction, the concentration of A was virtually uniform throughout the whole reactor. This means that the diffusive term in the governing equation, Eq. (7), is small and can therefore be ignored. Also, because the temperatures reached in the reactor are relatively small (< 10 K increase generally), the exponential term in Eqs. (7) and (8), representing the Arrhenius temperature dependence of step 2 of reaction (I), can be simplified:

$$\exp \left(\frac{\phi \frac{\tau_{diffusion} T'}{\tau_{step1}}}{1 + \frac{q_2}{C_P T_0} \frac{\tau_{diffusion} T'}{\tau_{step1}}} \right) \approx 1 \quad , \text{ since } T' \ll 1 \quad (14)$$

The governing equations, assuming spherical symmetry therefore become in this situation:

$$\frac{\partial a'}{\partial t'} = \frac{\tau_{diffusion}}{\tau_{step 2}} \exp\left(-t' \frac{\tau_{diffusion}}{\tau_{step 1}}\right) - \frac{\tau_{diffusion}}{\tau_{step 2}} a', \quad (15)$$

$$\frac{1}{\gamma} \frac{\partial T'}{\partial t'} = \frac{1}{r'^2} \frac{\partial}{\partial r'} \left(r'^2 \frac{\partial T'}{\partial r'} \right) + a'. \quad (16)$$

Equation (15) can be rewritten in terms of an ordinary derivative and solved to give an expression for the evolution of the concentration within the reactor:

$$a' = \frac{\tau_{step 1}}{\tau_{step 1} - \tau_{step 2}} \left(\exp\left(-t' \frac{\tau_{diffusion}}{\tau_{step 1}}\right) - \exp\left(-t' \frac{\tau_{diffusion}}{\tau_{step 2}}\right) \right). \quad (17)$$

Equation (17) can then be substituted into Eq. (16) to obtain a solution for the evolution of the temperature within the reactor:

$$\begin{aligned} T' = & \sum_{n=1}^{\infty} \frac{2 \tau_{step 1} \gamma \exp\left(- (n\pi)^2 t' \gamma\right) \cos(n\pi) \sin(n\pi r')}{n\pi r' (\tau_{step 1} - \tau_{step 2}) ((n\pi)^2 \gamma \tau_{step 1} - \tau_{diffusion}) ((n\pi)^2 \gamma \tau_{step 2} - \tau_{diffusion})} \times \\ & \left\{ \left[1 - \exp\left(- (n\pi)^2 \gamma t' - t' \frac{\tau_{diffusion}}{\tau_{step 2}}\right) \right] \tau_{step 2} \tau_{diffusion} \right. \\ & \left. + \tau_{step 1} \left[\exp\left(- (n\pi)^2 \gamma t'\right) \left((n\pi)^2 \gamma \tau_{step 2} \exp\left(-t' \frac{\tau_{diffusion}}{\tau_{step 2}}\right) + (\tau_{diffusion} - (n\pi)^2 \gamma \tau_{step 2}) \exp\left(-t' \frac{\tau_{diffusion}}{\tau_{step 1}}\right) \right) - \tau_{diffusion} \right] \right\} \end{aligned} \quad (18)$$

The expressions above for the dimensionless concentration of A and the dimensionless temperature rise are now compared to the results of numerical simulations. Such a comparison is made in Figs. 7(a) for the concentration, and 7(b) for the temperature rise, at the centre of the reactor for increasing time. These results are for a system with $\tau_{diffusion} / \tau_{step 2} = 0.017$ and $\tau_{step 1} / \tau_{step 2} = 10.6$. There is excellent agreement between the analytical and numerical solutions in both cases. A comparison is made of the spatial form of the solutions in Eqs. (17) and (18) in Fig. 8 with the numerically derived spatial solutions at two values of t' . Once again there is excellent agreement between the analytical and numerical results with the discrepancy between the two being $\sim 1\%$. The forms found in Eqs. (17) and (18) prove to be good approximations to the full solution of the governing equations when $\tau_{diffusion} / \tau_{step 2} < \sim 0.1$. When the value increases much beyond this limit, the temperature rise in the reactor is such that the approximation in Eq. (14) breaks down.

5.2 Non-Oscillatory, High Temperature Rise Solution: Large $\tau_{diffusion} / \tau_{step\ 2}$

At larger values of $\tau_{diffusion} / \tau_{step\ 2}$, the simple approximations used in the previous section are not valid, because the exponential term in the Arrhenius equation becomes highly significant due to the much larger temperature rise; also the concentration of A in the reactor deviates from the approximate spatial uniformity seen in section 5.1. The form of the temporal solution seen in Fig. 6(c) is also more complex, with an initial rapid increase in the concentration of A, followed by a sharp decline to almost zero. After this time, the concentration remains at approximately zero at the centre of the reactor. There are therefore two distinct temporal regions of behaviour, which can also be seen in the evolution of the temperature. There is an initial fast rise in temperature, whilst the concentration of A in the reactor is significant; however, when the concentration falls to virtually zero, there is a distinct change of slope in the plot of temperature against time in Fig. 6(c). Given that there are two regions of behaviour, the first of which is a ‘temporal boundary layer’, and that solutions are sought for extreme values of $\tau_{diffusion} / \tau_{step\ 2}$, this problem takes the form of a singular perturbation problem (see *e.g.* Varma and Morbidelli²⁹). This method involves asymptotic expansion of the dependent variables, *i.e.*

$$a'(r', t') = \sum_{n=0}^{\infty} \varepsilon^n a'_n(r', t') = a'_0 + \varepsilon a'_1 + O(\varepsilon^2), \text{ and} \quad (19)$$

$$T'(r', t') = \sum_{n=0}^{\infty} \varepsilon^n T'_n(r', t') = T'_0 + \varepsilon T'_1 + O(\varepsilon^2), \quad (20)$$

where ε is a small parameter determined from inspecting the governing equations (7) and (8). These were rewritten in terms of the two coordinates of the regime diagram, namely $\tau_{diffusion} / \tau_{step\ 2}$ and $\tau_{step\ 1} / \tau_{step\ 2}$, by making the substitution:

$$\frac{\tau_{diffusion}}{\tau_{step\ 1}} = \frac{\tau_{diffusion}}{\tau_{step\ 2}} \frac{\tau_{step\ 2}}{\tau_{step\ 1}}. \quad (21)$$

Solutions are sought when $\tau_{diffusion} / \tau_{step\ 2}$ tends to infinity, so the small parameter, ε , is therefore defined as:

$$\varepsilon \equiv \tau_{step\ 2} / \tau_{diffusion} \quad (22)$$

Given the values of $\tau_{step\ 1} / \tau_{step\ 2}$ over which oscillations occur (shown in Fig. 4) the following definition

$$\tau_{step2} / \tau_{step1} = k\varepsilon, \quad (23)$$

where k is of order unity, was also made.

The singular perturbation method involves substituting the expansions in Eqs. (19) and (20) into the governing equations and then collecting terms of similar order, with respect to the small parameter ε . These sub-problems can then be solved for each term in the asymptotic expansion. This method is useful in handling systems in which there are boundary layers. In this case there is a temporal boundary layer at $t' = 0$. The method involves considering an outer solution, corresponding to the conditions away from the boundary layer, and an inner solution, which deals with the boundary layer. A composite solution is then found by matching the two solutions at the edge of the boundary layer. The present work is only concerned with finding the $O(\varepsilon^0)$ terms, *i.e.* a'_0 and T'_0 , in Eqs. (19) and (20); all higher order terms are neglected.

5.2.1 Outer solution.

Equations (19) – (23) were substituted into Eqs. (7) and (8) in order to find the outer solution. Furthermore, the simplifying assumption that

$$\exp\left(\frac{\phi k T'}{1 + \frac{q_2}{C_P T_0} k T'}\right) \approx \exp(\phi k T'), \quad (24)$$

was made, because in general $\frac{q_2}{C_P T_0} k T' \ll 1$. Solving for concentration yields a'_0 for the outer solution as:

$$a'^o_0 = \frac{\exp(-k t')}{\exp(\phi k T'^o_0)}. \quad (25)$$

The expression derived in Eq. (25) was found without the application of the no-flux boundary condition at the wall of the vessel. This indicates that there is a concentration boundary layer at the wall. This has been ignored in the present analysis, so the solution

will be valid in the middle region of the reactor, but not in the thin boundary layer at the wall. Equation (8) for the temperature reduces to:

$$\frac{1}{\gamma} \frac{\partial T_0''}{\partial t'} = \frac{1}{r'^2} \frac{\partial}{\partial r'} \left(r'^2 \frac{\partial T_0''}{\partial r'} \right) + \exp(-kt'), \quad (26)$$

with the boundary conditions

$$\begin{aligned} \frac{\partial T_0''}{\partial r'}(0, t') &= 0 \\ T_0''(1, t') &= 0 \end{aligned} \quad (27)$$

The initial condition depends on a matching of the inner and outer solutions and so is unknown at this stage.

5.2.2 Inner solution.

For the inner expansion a stretching transformation is applied, *i.e.* the substitution

$$\omega = t' / \varepsilon, \quad (28)$$

is made in the governing equations. Considering first the concentration equation, the equation for $O(\varepsilon^0)$ gives:

$$\begin{aligned} \frac{\partial a_0^i}{\partial \omega} &= 1 - a_0^i \exp(\phi k T_0^i), \\ a_0^i(r', 0) &= 0 \end{aligned} \quad (29)$$

A similar analysis for the temperature reveals that $T_0^i = 0$. This result can be substituted back into Eq. (29) yielding the inner solution for concentration:

$$a_0^i = 1 - \exp(-\omega). \quad (30)$$

Equations (7), (8), (19), (20) and (28) suggest that the non-dimensional boundary layer thickness is of the order ε . Hence:

$$t_{\text{boundarylayer}} = t'_{\text{boundarylayer}} \tau_{\text{diffusion}} = \frac{\tau_{\text{step2}}}{\tau_{\text{diffusion}}} \tau_{\text{diffusion}} = \tau_{\text{step2}}. \quad (31)$$

5.2.3 Composite solution.

In order to produce a solution which is valid across the whole region of interest, the inner and outer solutions must be combined. In general, this is done by adding the two

solutions together and subtracting the common part in the overlapping region. This common part is defined as:

$$\lim_{\omega \rightarrow \infty}(\text{inner solution}) = \lim_{\varepsilon \rightarrow 0}(\text{outer solution}), \quad (32)$$

where this constraint also ensures that the solutions match at the edge of the boundary layer. This rule can most easily be applied to the composite solution for temperature. Because the inner solution for the temperature is zero, this implies that the missing initial condition in Eq. (27) is simply $T_0'' = 0$ at $t' = 0$. Using this additional condition, Eqs. (26) and (27) can be solved giving

$$T_0'^c = T_0'' = \sum_{n=1}^{\infty} \frac{2\gamma \cos(n\pi) \sin(n\pi t') \exp(-kt') (\exp(t' [k - (n\pi)^2 \gamma]) - 1)}{r' ((n\pi)^3 \gamma - kn\pi)}, \quad (33)$$

where k , as defined by Eqs. (22) and (23), is

$$k = \tau_{diffusion} / \tau_{step1}. \quad (34)$$

The solution for T' is therefore

$$T' = T_0'^c + O(\varepsilon). \quad (35)$$

It is interesting to note that the sole dimensionless group influencing the behaviour of the temperature dependence is the ratio of the timescales for diffusion and step 1 of the reaction. This is in general agreement with the scaling work presented by Campbell *et al.*¹³, where this ratio was found to determine the maximum temperature rise within the reactor. Similarly, the composite solution for the concentration of A can be found to be:

$$a_0'^c = \frac{\exp(-kt')}{\exp(\phi k T_0'')} + \left(1 - \exp\left(-\frac{t'}{\varepsilon}\right)\right) - 1 = \frac{\exp(-kt')}{\exp(\phi k T_0'')} - \exp\left(-\frac{t'}{\varepsilon}\right). \quad (36)$$

As in Eq. (35) for temperature, it can be said that

$$a' = a_0'^c + O(\varepsilon). \quad (37)$$

The predictions of the analytical expressions derived above can be compared with the results of numerical simulations. The comparisons are presented in Figs. 9 and 10. The simulations were performed for a value of $\varepsilon (= \tau_{step2} / \tau_{diffusion})$ of 0.0052, and $k = 0.57$. Shown in Fig. 9 is a comparison of the temporal development of (a) the temperature, and (b) the concentration of A at the centre of the reactor. There is excellent agreement between the analytical form for the temperature presented in Eq. (33) and the

result of simulations. The largest discrepancy between the analytical and numerical solutions is at the start of the reaction, within the temporal boundary layer. This discrepancy would probably be remedied by the inclusion of higher order terms. Figure 9(b) shows a comparison of Eq. (36) for the concentration of A and the results from simulation. Once again, it is clear that for large values of time, beyond the temporal boundary layer, the agreement between the analytical and numerical solutions is excellent. Within the boundary layer, however, there is again a significant difference between the two solutions. The higher order terms, neglected in the analysis above, are clearly important within the temporal boundary layer. The calculation of these higher order terms is not trivial, and has therefore not been included in the present work.

Comparison can also be made of the spatial forms predicted by the analytical solutions above. Such a comparison is made in Fig. 10 for five increasing values of t' . For small time, $t' < t'_{boundarylayer}$, the discrepancy between the analytical and numerical forms of both the temperature and the concentration is evident. The overall shape of the temperature profile predicted by Eq. (33) is correct, but the magnitudes of numerical and analytical predictions differ. The simulations show that the concentration is approximately constant over the whole of the reactor. The analytical solution (Eq. (36)) predicts a much larger spatial variation within the reactor with the concentration at the wall being roughly double that at the centre of the reactor. For larger times, when $t' \sim t'_{boundarylayer}$, the analytical and numerical solutions begin to show better agreement, and for $t' > t'_{boundarylayer}$, in the region corresponding to the outer solution, the agreement is excellent. However, there is disparity between the analytical and numerical solutions for large times at the wall, where the prediction of the concentration from the analytical solution is clearly wrong. The form predicted by Eq. (36) violates the no-flux boundary condition at the wall as expected. This implies that a further spatial concentration boundary layer is present at the wall. The work described above could therefore be extended to take account of this additional boundary layer; however, the form predicted by Eq. (36) is valid over the majority of the vessel ($r' < 0.95$), so this has not been considered in the present work.

The above comparison is, of course, for a very small value of $\varepsilon (= 0.0052)$, which corresponds to large values of $\tau_{diffusion} / \tau_{step\ 2}$ (~ 200) in the regime diagram of Fig. 4. This is obviously a considerable way from the region of oscillations. For that reason, a comparison with a simulation much closer to the region of oscillations was also made. The agreement is inevitably poorer, because when $\tau_{diffusion} / \tau_{step\ 2}$ is decreased, ε is increased and hence the higher order terms in Eqs. (35) and (37) are likely to play a much more significant role. The simulation used for comparison had $\varepsilon (= \tau_{step\ 2} / \tau_{diffusion}) = 0.15$, and $k = 0.63$ and is presented in Fig. 11. This case is much closer to the region of oscillations identified in Fig.4. It is unsurprising that in the temporal boundary layer, the analytical expression for concentration in Eq. (36) does not agree with the simulated results. Even when ε is two orders of magnitude smaller, the higher order terms are significant. Beyond the temporal boundary layer, Eq. (36) does provide a reasonable representation of the results of the simulation. Figure 11 shows a comparison of the analytical and numerical solutions for the temperature. The agreement is clearly not as good as in the case for smaller ε , but the analytical expression is still reasonable; there is, for example, only $\sim 10\%$ difference between the analytically derived maximum temperature, and that found by simulation. The largest apparent discrepancy is once again within the temporal boundary layer. The shape of the two curves is clearly different, but the temperature increase within the boundary layer is the same in both cases. Once again, the inclusion of higher order terms would probably correct the shape of the analytical solution in this region.

5.3 Oscillatory Solutions

The region in which oscillations are found falls at the transition between the two non-oscillatory cases discussed in sections 5.1 and 5.2. Whilst no analytical approximations have been sought in this region, it is possible to make some general observations. For example, it is interesting to note that the oscillatory solutions display characteristics of both the low temperature and high temperature reactions described in the previous sections. Figure 12 shows the radial concentration profiles for the first peak and trough of an oscillatory solution. At the first peak, the concentration is virtually

uniform spatially. This is similar to the behaviour discussed in section 5.1 for the non-oscillatory, low temperature reaction, as characterised by Fig. 8. At the first trough, the concentration in the central portion of the reactor is virtually zero; however, it does increase near the wall. This behaviour is similar to that seen in Fig. 10 and discussed in section 5.2 for the non-oscillatory, high temperature reaction. The oscillatory solutions occur at the transition between the two forms of non-oscillatory solutions discussed above, but show features of both of them.

6. Conclusions

The behaviour of Sal'nikov's reaction occurring batchwise in the gas-phase ($Le \sim 1$) in a spherical batch reactor in microgravity (where diffusion is the only active method of heat and mass transport) has been investigated using a combination of numerical simulations and analytical methods. Regions of the regime diagram where oscillations occur have been identified through numerical simulation. These results were compared with previous analytical results for a one-dimensional system. It was found that in this case with spherical symmetry, the region of parameter space in which sustained oscillations occurs is considerably larger than in the 1-D case. This was attributed to the differing geometries of the systems considered, as well as the differing modes of heat transfer considered in each case. In addition to identifying the region of parameter space in which oscillations occur, approximate analytical solutions were sought for two limiting types of non-oscillatory behaviour. The predictions of the new solutions were compared with the results of full numerical solutions, and the comparisons were favourable in each case. It was also observed that the oscillatory solutions exist at the transition between these two, non-oscillatory, cases and that the oscillatory solutions exhibit characteristics of both of these limiting cases.

7. Acknowledgements

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8. Nomenclature

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
h	heat transfer coefficient
k	constant of order unity
k_i	rate constant of step i of the reaction
$k_{2,0}$	rate constant of step 2 evaluated at $T = T_0$
k_T	thermal conductivity
L	characteristic length (radius) of the reactor
Le	Lewis number = κ / D_A
l_0	width of 1-D box considered by Gray and Scott ¹⁷
Nu	Nusselt number = $h L / k_T$
p	concentration of precursor P

p'	dimensionless concentration of P, $p' = p / p_0$
p_0	initial concentration of P
q_i	exothermicity of step i of the reaction
$\underline{r}$	spatial coordinates
$\underline{r}'$	dimensionless spatial coordinates, $\underline{r}' = \underline{r} / L$
R	universal gas constant
t	time
t'	dimensionless time, $t' = \kappa t / L^2$
T	temperature
T'	dimensionless rise in temperature, $T' = (T - T_0) / \Delta T_s$
T_0	constant wall temperature
Z_2	pre-exponential factor in Arrhenius expression for k_2
$\beta_{G \& S}$	Gray and Scott dimensionless parameter
γ	ratio of principal specific heats
$\gamma_{G \& S}$	Gray and Scott dimensionless parameter
ΔT_s	scale for temperature increase
ε	small parameter in perturbation analysis
ϕ	dimensionless activation energy for step 2, $\phi = E_2 q_2 / R T_0^2 C_P$
κ	thermal diffusivity $= k_T / \rho_0 C_P$
$\kappa_{G \& S}$	Gray and Scott dimensionless parameter
$\mu_{G \& S}$	Gray and Scott dimensionless parameter
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	stretching coordinate, $\omega = t' / \varepsilon$

Superscripts

c	composite solution
i	inner solution
o	outer solution

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Figure Captions

Fig. 1 The general three-dimensional regime diagram describing the system when both natural convection and diffusion play roles. The axes represent ratios of the characteristic timescales for reaction, diffusion and convection. A line of constant Rayleigh number (Ra) is shown.

Fig. 2 Schematic representation of the one-dimensional system considered in the analytical work of Gray and Scott¹⁷. There is no flux of either heat or mass from the left and right hand ends. There is also no mass flux from the horizontal boundaries, however heat is lost to the surroundings, with the rate governed by h , the heat transfer coefficient.

Fig. 3 The analytically derived region of instability presented by Gray and Scott¹⁷ for $\beta_{G \& S} = 0.96$. In this region, sustained oscillations occur. The effect of varying the dimensionless parameter $\gamma_{G \& S}$ on the region of instability is indicated by the three different curves.

Fig. 4 Regime diagram showing the approximate regions of oscillations, identified through numerical simulation, in the case of a spherical batch reactor. The dashed lines represent extensions of the boundaries in the region where the numerical scheme broke down.

Fig. 5 Regime diagram showing the regions of oscillations identified in Fig. 4, and the numerical results of Fairlie and Griffiths²⁵, for the case when $L = 0.0492$ m, $k_{2,0} = 0.264$ s⁻¹. The filled symbols represent the cases where the diffusivity was 3×10^{-4} m² s⁻¹, and the open symbols the cases where the diffusivity was 6×10^{-4} m² s⁻¹. In both cases the squares represent non-oscillatory solutions, the triangles represent damped oscillations and the circles sustained oscillations.

Fig. 6 The simulated temperature (solid line) and concentration of A (dashed line) at the centre of the reactor, plotted against time. Each plot is typical of one of the three types of temporal behaviour observed. In each case $\kappa = 1 \times 10^{-4}$ m² s⁻¹, $k_I = 0.025$ s⁻¹ and $k_{2,0} = 0.264$ s⁻¹ corresponding to $\tau_{step 1} = 40$ s and $\tau_{step 2} = 3.77$ s. (a) $L = 10$ mm; $\tau_{diffusion} = 1$ s, (b) $L = 20$ mm; $\tau_{diffusion} = 4$ s and (c) $L = 30$ mm; $\tau_{diffusion} = 9$ s.

Fig. 7 Comparison of the analytical (dashed line) and numerical (solid line) solutions for (a) the dimensionless concentration of A, and (b) the dimensionless temperature rise, at the centre of the reactor for the case where $\tau_{diffusion} / \tau_{step 2} = 0.017$ and $\tau_{step 1} / \tau_{step 2} = 10.6$. In the numerical solution $L = 0.0025$ m, $\kappa = 1 \times 10^{-4}$ m² s⁻¹, $k_I = 0.025$ s⁻¹ and $k_{2,0} = 0.264$ s⁻¹.

Fig. 8 Comparison of the dimensionless spatial temperature and concentration profiles when $\tau_{diffusion} / \tau_{step 2} = 0.017$ and $\tau_{step 1} / \tau_{step 2} = 10.6$, at two distinct times: (a) $t' = 40$ and

(b) $t' = 152$. The solid line represents the numerical solution and the dashed line the analytical solution. The conditions for the numerical solution are the same as in Fig. 7.

Fig. 9 Comparison of the analytical (dashed line) and numerical (solid line) solutions for (a) the dimensionless temperature rise, and (b) the dimensionless concentration of A, at the centre of the reactor for the case where $\varepsilon (= \tau_{step\ 2} / \tau_{diffusion})$ of 0.0052, and $k (= \tau_{diffusion} / \tau_{step\ 2}) = 0.57$. In the numerical solution $L = 0.085$ m, $\kappa = 1 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$, $k_I = 0.000795 \text{ s}^{-1}$ and $k_{2,0} = 0.264 \text{ s}^{-1}$.

Fig. 10 Comparison of the dimensionless spatial temperature and concentration profiles when $\varepsilon (= \tau_{step\ 2} / \tau_{diffusion})$ of 0.0052, and $k (= \tau_{diffusion} / \tau_{step\ 2}) = 0.57$ for increasing values of t' . These values appear at the top of each plot. The solid line represents the numerical solution and the dashed line the analytical solution. The conditions for the numerical solution are the same as for Fig. 9.

Fig. 11 Comparison of the analytical (solid line) and numerical (dashed line) solutions for the temperature at the centre of the reactor when $\varepsilon = 0.15$, and $k = 0.63$. In the numerical solution $L = 0.05$ m, $\kappa = 1 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$, $k_I = 0.025 \text{ s}^{-1}$ and $k_{2,0} = 0.264 \text{ s}^{-1}$.

Fig. 12 Spatial concentration profiles near the first peak and the first trough of an oscillatory cycle in temperature. In this case $L = 0.02$ m, $\kappa = 1 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$, $k_I = 0.025 \text{ s}^{-1}$ and $k_{2,0} = 0.264 \text{ s}^{-1}$. The concentration profile for the temperature peak occurring at $t = 3.1$ s is shown as the solid line, and the concentration profile at the temperature trough at $t = 5.1$ s is shown as a dashed line.