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Analysis of a competitive exothermic-endothermic reaction scheme

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Abstract: We consider the propagation of an exothermic reaction front subject to possible heat loss through a competitive endothermic reaction. Such reaction schemes are of considerable practical importance to industry, where they arise in connection with ammonium nitrate based explosives and explosive gas combustion in underground mines, for example. In particular, competitive endothermic-exothermic reaction schemes are appropriate for the study of the burning of ammonium nitrate (NH_4NO_3) in the context of emulsion explosives, which finds abundant application in mining and other industries. It is common to represent the chemistry of ammonium nitrate combustion as two competitive reactions — one exothermic and one endothermic:

$$\begin{array}{lcll} NH_4NO_3 & \rightarrow & NH_3 + HNO_3 & \text{(endothermic)} \\ NH_4NO_3 & \rightarrow & N_2O + 2H_2O & \text{(exothermic)} \end{array}$$

Properties of the reaction fronts, which are modelled as travelling wave solutions of a corresponding reaction-diffusion system, are derived numerically over a range of different parameter values, such as those describing the relative enthalpies, rates and activation energies of the endothermic and exothermic reactions. These properties include the speed of the reaction front and the peak temperature produced by the reaction. Unique reaction front solutions have been shown to exist for each distinct combination of the parameter values. The stability of the reaction fronts are of particular interest and it has been shown that when the activation energy of the endothermic reaction is twice that of the exothermic reaction, stable and oscillatory unstable reaction regimes exist. In this case, if the heat released from the exothermic reaction is sufficiently large in proportion to the heat absorbed by the endothermic reaction, the reaction fronts are stable, while if the relative heat released by the exothermic reaction is not sufficiently large the reaction fronts are oscillatory unstable.

The analyses presented in the current paper, however, indicate that the assumption of the endothermic activation energy being twice that of the exothermic reaction implies that the endothermic reaction is essentially deactivated. As such, and as shown by Sharples et al. (2011), the behaviour of the reaction front is not all that different to that seen in a single-step exothermic reaction. The analyses reveal a range of parameter values where behaviour of the reaction front could be expected to depart significantly from a single-step exothermic reaction. We present some preliminary numerical results for parameter values in this range and indicate some directions for future work, particularly in regards to the stability of the reaction fronts.

Keywords: Combustion, reaction-diffusion, travelling waves, competitive reaction, endothermic reaction, flame front speed

1 INTRODUCTION

This work concerns the existence and propagation of reaction fronts through reactive media where diffusive processes are present and where a main exothermic reaction is accompanied by an endothermic reaction as well. A number of authors have addressed problems where an independent endothermic process affects the progress of a combustion front (Gray et al. 2002, Please et al. 2003, Simon et al. 2003, 2004); our concern in this paper is with the possibility of competitive endothermic and exothermic reactions, where the same reactive material provides the feed for both reactive steps (Hmaidi et al. 2010).

Though most observed physico-chemical phenomena are a consequence of several, often numerous, concurrent or consecutive endothermic and exothermic reactive processes, much useful understanding can often be gained by considering much simpler "lumped" models which reproduce the essential phenomenology. In some cases, notably when thermal effects are prominent in the process, the simplest useful model comprises a pair of reactions, one exothermic and one endothermic, characterised by different chemical kinetics. These reactions may feed on the same unique reactant material, so-called competitive reactions, or each reaction may independently consume a different reactant, so-called parallel reactions (Ball et al. 1999). In the parallel case the coupling between the reactions is solely thermal, whereas in the competitive case there is a second coupling through the reactant consumption.

In contrast to the case of parallel reactions, which has been widely studied, competitive reactions have received little attention. This situation is less that desirable given the appropriateness of competitive schemes in modelling decomposition or pyrolysis processes (Antal and Varhegyi 1995, Wu et al. 1994) and their applicability to ammonium nitrate based explosives (Sinditskii et al. 2005). An exception to this observation is the study by Clavin et al. (1987) which established the existence of combustion wave multiplicity in the case of competing exothermic reactions. Whereas, in the parallel case, the net enthalpy production by complete consumption of both reactants is uniquely determined, this is not true for competitive reactions, where the net production depends on the full time history of the process; if the temperature is kept relatively low, by thermal diffusion or other extraneous effects e.g. Newtonian or radiative cooling, the net production may be, counter-intuitively, actually increased.

Hmaidi et al. (2010) investigated the existence and stability of travelling one-dimensional reaction fronts propagating through a solid reactive slab (infinite Lewis number), effectively extending the work of Matkowsky and Sivashinsky (1978) to the case where heat is lost through a competitive endothermic reaction term. The behaviour of the competitive system was modelled by regarding the endothermic reaction as a perturbation to an exothermic reaction. This necessitated some restrictions on the ordering of the kinetic parameters of the endothermic step. Specifically, the endothermic reaction was assumed to have twice the activation energy of the exothermic reaction and a pre-exponential frequency term much greater than that for the exothermic reaction. In the present paper we scrutinise the consequences of these assumptions, particularly with reference to the relative magnitudes of the activation energies. Moreover, we modify the ratio of activation energies so that the endothermic reaction plays a greater part in the overall reaction scheme and examine the behaviour of the reaction fronts that result.

The work reported here therefore extends the work of Hmaidi et al. (2010) and our previous work (Sharples et al. 2011) to consider a more comprehensive range of parameter values. We again consider propagation of a reaction front in which the driving exothermic reaction competes with an endothermic reaction that consumes both reactant and heat within the system. As mentioned, the parameter values we assume permit a stronger contribution from the endothermic reaction. Following Hmaidi et al. (2010), we assume adiabatic conditions, though unlike Hmaidi et al. (2010) we allow for the diffusion of reactant as well as heat (Sharples et al. 2011). We also lift the restriction of large activation energies and pre-exponential frequency of the endothermic reaction.

2 MATHEMATICAL MODEL

It is assumed that the, possibly non-solid, reactant undergoes two competitive reactions: one exothermic and one endothermic, and that the reaction products are chemically inert and have no effect on physical properties such as the diffusivity of the reaction surroundings. Arrhenius kinetics are assumed for both reactions with the endothermic reaction kinetics characterised by the activation energy E_1, the pre-exponential factor A_1 and heat release $Q_1 < 0$. The exothermic reaction drives the combustion and is characterised by the activation energy E_2, the pre-exponential constant A_2, and heat release $Q_2 > 0$. To summarise, we may represent the reaction scheme as the two competing reactions:

$$\begin{array}{lll} R & \rightarrow & P_1 + Q_1, \quad k_1(T) = A_1 \exp(-E_1/RT) \quad \text{(endothermic reaction)} \\ R & \rightarrow & P_2 + Q_2, \quad k_2(T) = A_2 \exp(-E_2/RT) \quad \text{(exothermic reaction)} \end{array}$$

where T is temperature and $k_1(T)$ and $k_2(T)$ are the temperature-dependent reaction rates of the endothermic and exothermic reactions, respectively. The reactant is common to both reactions and is represented by R, with the two different reaction products represented by P_1 and P_2.

The governing equations for the system described are then the heat and mass balance equations accounting for the reaction and diffusion of heat and reactant (e.g. Weber et al. (1997)):

$$\rho \mathrm{c_p} \frac{\partial T}{\partial t'} = k \frac{\partial^2 T}{\partial x'^2} + \rho \left(-Q_1 A_1 e^{-E_1/RT} + Q_2 A_2 e^{-E_2/RT} \right) C \tag{1}$$

$$\rho \frac{\partial C}{\partial t'} = \rho D \frac{\partial^2 C}{\partial x'^2} - \rho \left(A_1 e^{-E_1/RT} + A_2 e^{-E_2/RT} \right) C \tag{2}$$

Here C denotes the reactant mass fraction. Time and space coordinates (in the laboratory frame) are denoted by t' and x', ρ is the density (assumed constant), k is the thermal conductivity, D is the coefficient of mass diffusion, R is the universal gas constant and $\mathrm{c_p}$ is the heat capacity at constant pressure of the reactant.

Introducing the dimensionless temperature and space and time coordinates:

$$u = \frac{RT}{E_2}, \quad x = \sqrt{\frac{\rho Q_2 A_2 R}{k E_2}} x', \quad t = \frac{Q_2 A_2 R}{\mathrm{c_p} E_2} t', \tag{3}$$

the system (1, 2) can be written in non-dimensional form as

$$\frac{\partial u}{\partial t} = \frac{\partial^2 u}{\partial x^2} + C e^{-1/u} - q r C e^{-f/u} \tag{4}$$

$$\frac{\partial C}{\partial t} = \frac{1}{\mathrm{Le}} \frac{\partial^2 C}{\partial x^2} - \Theta C e^{-1/u} - \Theta C r e^{-f/u}, \tag{5}$$

where the new parameters are defined as follows:

$$\Theta = \frac{\mathrm{c_p} E_2}{R Q_2}, \quad q = \frac{Q_1}{Q_2}, \quad f = \frac{E_1}{E_2}, \quad r = \frac{A_1}{A_2}, \quad \mathrm{Le} = \frac{k}{\rho \mathrm{c_p} D} \tag{6}$$

For the sake of the present analysis we will consider travelling wave solutions to the system (4, 5). To this end we express the system in terms of the coordinate frame defined by $\xi = x - vt$, which moves with the reaction front at a constant speed v. Rewriting the system in terms of ξ yields the system of ordinary differential equations:

$$u_{\xi\xi} + v u_\xi + C \left(e^{-1/u} - q r \, e^{-f/u} \right) = 0 \tag{7}$$

$$\mathrm{Le}^{-1} C_{\xi\xi} + v C_\xi - C \Theta \left(e^{-1/u} + r \, e^{-f/u} \right) = 0 \tag{8}$$

Solutions to the system (7, 8) are obtained using shooting and relaxation techniques. The reader is referred to Gubernov et al. (2003) for further details on the numerical solution scheme.

3 ASYMPTOTIC RESULTS

In this section we present some results pertaining to the effect of varying the parameter f. Asymptotic results are available in two parameter ranges, the first corresponding to $f \gg 1$ for which the exothermal reaction dominates, and the second corresponding to $f \to 1$ so that the activation energies of the two reactions are closely matched.

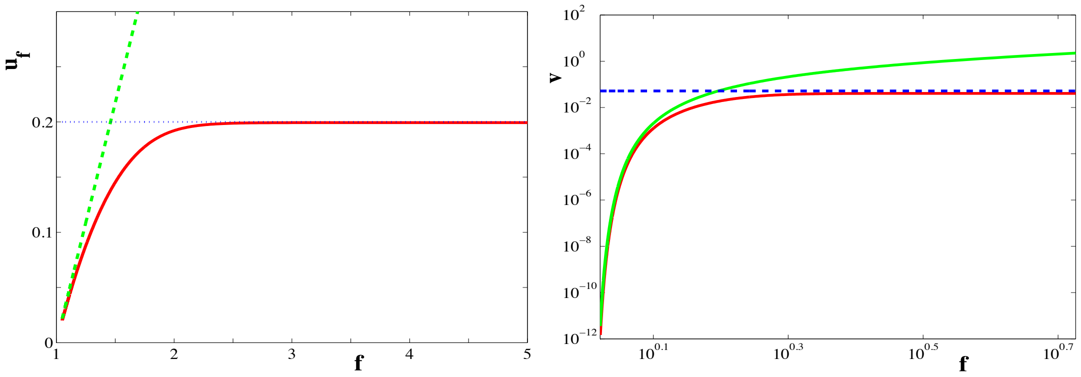

Figure 1. (a) Dependence of the reaction temperature, u_f, on f, and (b) Dependence of the wave speed v on f, for $\mathrm{Le} = 1$, $\Theta = 5$, $q = 5$, $r = 2$. The green curves are plotted according to asymptotic formulae (10) for $0 < f - 1 \ll 1$. The blue curves correspond to the AEA ($\Theta \gg 1$) asymptotic formulae (9) for the one-step model. The red curves show the numerical results.

3.1 Asymptotic results for when the exothermic reaction dominates

Assuming $f \gg 1$ the second (endothermic) reaction is effectively deactivated and a single-step reaction model can be considered. In the case of asymptotically large Θ a perturbation analysis gives the well known formulas for front speed and reaction temperature

$$u_f \to u_b = \Theta^{-1}, \qquad v = \sqrt{\frac{2\,\mathrm{Le}}{\Theta}} \exp\left(-\frac{\Theta}{2}\right). \tag{9}$$

3.2 Asymptotic results for when the activation energies are closely matched

We consider f approaching unity (from above), so that $f-1$ can be treated as a small (positive) parameter. Varying f in this way has the effect of reducing the relative magnitude of the activation energy of the endothermic reaction, thereby increasing the endothermic effect in the reaction scheme.

Taking $f - 1 \to 0$ and treating it as a small parameter permits asymptotic analysis. Taking the other parameters as fixed and $O(1)$ the following expression for the reaction front speed and temperature u_f in the product zone is obtained

$$u_f \to u^*, \qquad v = \sqrt{\frac{\Theta\,\mathrm{Le}(1+q^{-1})}{\Omega}}\, u^* \exp\left(-\frac{1+u_0 u^*}{2u^*}\right), \qquad u^* = \frac{f-1}{\ln(qr)} \tag{10}$$

where u^* is the crossover temperature at which the rates of the endothermic and exothermic reactions are equal; Ω and u_0 are constants of the order of $O(1)$ which do not depend of f.

Whilst the expression for v is singular at $f = 1$, it does indicate that the front speed reduces to zero as $f \to 1$ (providing $qr > 1$).

3.3 Numerical results

Figure 1 shows how the asymptotic formulae fit with values of the flame temperature and wave speed derived numerically for $\mathrm{Le} = 1$, $\Theta = 5$, $q = 5$, $r = 2$ and $1 < f \leq 5$. It can be seen that the limits indicated above are realised at least for the parameter ranges so far considered. Furthermore, the figures indicate that there are three front propagation regimes. Figure 1a shows that for $f > 2$ the endothermic reaction is almost completely frozen, the reaction temperature is equal to the adiabatic reaction temperature u_b that arises in the corresponding one-step model ($r \to 0$). As f becomes smaller there is an intermediate reaction regime between approximately $f = 1.2$ and $f = 2.0$ where the endothermic reaction becomes important and the temperature diverges from u_b. As $f \to 1$ the influence of the endothermic reaction as a heat sink increases in significance and the reaction temperature converges to u^*.

In Figure 1b the dependence of speed of the reaction front v on f is plotted. It is seen to exhibit the same type of behaviour as the reaction temperature. For large f the speed is constant and is equal to the reaction speed for the one-step model. The asymptotic equation (9) gives a higher value which is not surprising since $\Theta = 5$ is too small to expect good quantitative agreement. As $f \to 1$ the increasing significance of the endothermic reaction is observed, as described by equations (10). In particular, there is good agreement between the numerical results and the asymptotic formula for v as $f \to 1$.

4 PARAMETRIC ANALYSIS

Recalling the definition of the crossover temperature u^* (equation (10)) we can identify four distinct regions of parameter space:

1. $u^* < 0$: $f > 1, qr < 1$
2. $u^* < 0$: $f < 1, qr > 1$
3. $u^* > 0$: $f > 1, qr > 1$
4. $u^* > 0$: $f < 1, qr < 1$

If $u^* < 0$, then for any physically feasible reaction temperature the rates of heat release and consumption cannot be equal i.e. one always dominates the other. If $f > 1$, $rq < 1$ (case 1) the exothermic reaction always releases more heat than can be consumed by the endothermic reaction. Therefore the solution could theoretically exist. On the other hand, if $f < 1$, $rq > 1$ (case 2) the heat balance is in favour of heat consumption and the rate of heat reduction by the endothermic reaction is always greater. It is thus not possible for the reaction front to continue propagation once the temperature falls below the activation temperature.

For parameter values with $u^* > 0$, $u^* \to \infty$ as $qr \to 1$. The limit $f \to 1$ is also distinguished, since $u^* \to 0$ and changes sign as the line in parameter space described by $f = 1$ is crossed. In fact, for $f = 1$ the competitive reaction scheme reduces to the following one-step combustion scheme (Gubernov et al. (2003)):

$$\begin{aligned} u_{\xi\xi} + vu_\xi + C(1 - rq)e^{-1/u} &= 0, \qquad (11)\\ \mathrm{Le}^{-1} C_{\xi\xi} + vC_\xi - C\Theta(1 + r)e^{-f/u} &= 0. \qquad (12) \end{aligned}$$

Obviously, if $qr > 1$ then the heat release is negative in (11) and no solutions can exist. This again supports the notion that for $f < 1$ and $qr > 1$ the reaction exhibits extinction. If $qr < 1$, then changing the variables to $z = \sqrt{1 - qr}\,\xi$, yields

$$\begin{aligned} u_{zz} + v'u_z + Ce^{-1/u} &= 0, \qquad (13)\\ \mathrm{Le}^{-1} C_{zz} + v'C_z - C\beta e^{-1/u} &= 0. \qquad (14) \end{aligned}$$

where

$$\beta = \frac{\Theta(1 + r)}{(1 - qr)}, \qquad v' = \frac{v}{\sqrt{1 - qr}}. \qquad (15)$$

In the large β limit this gives the following formula for flame speed v' and flame temperature u_b:

$$v' = \sqrt{2\,\mathrm{Le}\,\beta^{-1}}e^{-\beta/2} \qquad u_b = \beta^{-1}. \qquad (16)$$

Note that $\beta \to \infty$ as $qr \to 1$, and so the above expressions (16) for speed and temperature should be accurate. In the original variables we have

$$v = \sqrt{\frac{2\,\mathrm{Le}(1 - qr)^2}{(1 + r)\Theta}} \exp\left(-\frac{\Theta(1 + r)}{2(1 - qr)}\right), \qquad u_b = \frac{1 - qr}{\Theta(1 + r)}. \qquad (17)$$

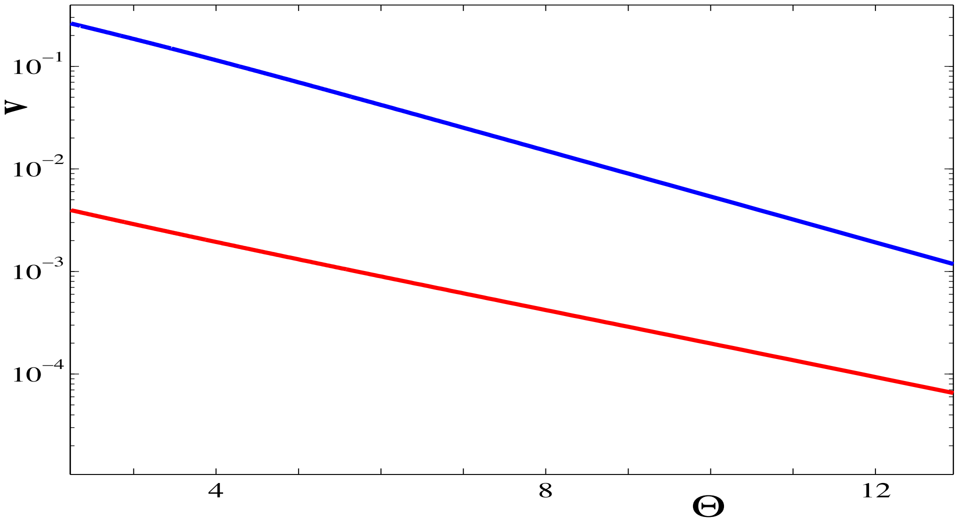

Figure 2. Dependence of the wave speed v on Θ for $\mathrm{Le} = 1$.The red curve shows the speed for $f = 1.156$ while the blue curve shows the speed for $f = 2$.

Thus according to (17) as $qr \to 1$ the speed approaches zero in a very sharp way and the reaction temperature vanishes. This again supports the argument that extinction should occur in this limit. Moreover, note that if $f = qr = 1$ then the system (7, 8) degenerates to one whose only solution is $u = 0$ and $C =$ constant.

5 DISCUSSION AND CONCLUSION

We have presented an analysis of a competitive endothermic-exothermic reaction scheme, which despite their application have received only fleeting attention in the literature. Based on consideration of the parameter f, which describes the relative magnitude of the activation energies of the endothermic and exothermic reactions, three regimes of reaction behaviour were identified. For $f > 2$ the exothermic reaction dominates and reaction properties are thus close to those obtained through consideration of a single step exothermic reaction. Indeed, the reaction wave characteristics and stability properties for $f = 2$ discussed by Sharples et al. (2011) bear a strong resemblance to those obtained in the single-step exothermic reaction case (Gubernov et al. (2003)). The wave characteristics and stability results obtained by Sharples et al. (2011) for $f = 2$ should therefore be considered as quite distinct from what might arise as $f \to 1$. For $f \to 1$ the endothermic reaction has a stronger influence on the competitive reaction scheme: the reaction temperature approaches the crossover temperature and the reaction front speed is well approximated by an analytical formula. In the intermediate region $1 < f < 2$ the behaviour of the reaction should be more interesting and will form the focus of future work. Figure 2 shows how the reaction front speed differs with varying f. Two cases corresponding to $f = 2$ and $f = 1.156$ are shown, with the smaller f value corresponding to a lower overall speed.

It will be particularly interesting to investigate the effect that the endothermic reaction has on the stability of the reaction wave as its influence becomes stronger. One would expect to find pulsating solutions for certain combinations of the parameter values but the exact nature of these pulsations as the endothermic effect starts to dominate is yet to be understood.

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