A Thermokinetic Model for the Combustion of Strobe Composition

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Abstract: *A model chemical reaction scheme, in which a substance undergoes a two-stage decay process, is developed. It is shown that this reaction scheme follows the Shimizu hypothesis for pyrotechnic strobe combustion; both decay stages are temperature dependent with only the second generating a significant quantity of heat. The model is derived from the combustion reaction between ammonium perchlorate and fine magnesium powder although reaction of other strobe compositions is expected to proceed in a similar manner. It will be shown that the effects of additives, such as potassium dichromate as a frequency modifier, can be investigated without explicitly including them in the model. The model is therefore a first step towards a useful design tool for developing compositions with specific strobe characteristics.*

Keywords: *thermokinetic model, strobe composition, Shimizu hypothesis, bifurcation theory, two-stage decay*

Introduction

Pyrotechnic compositions are usually designed and expected to burn at an almost constant linear velocity to produce an effect such as light, sound, heat or smoke. The occurrence of irregularities is usually dismissed as due to variability in manufacture or experimental noise. However, in some instances, it is desirable to deliberately produce fluctuations in an effect. Pyrotechnic strobe compositions burn in an oscillatory manner such that there is a marked variation of emitted light intensity as a function of time. According to Jennings-White[1] it is not necessary for the minimum light intensity to extend to zero but the peaks must be separated by a sufficiently long time interval such that each can be individually identified by an observer.

It is probable that the first pulsating flash composition was discovered by chance. Brock's Fireworks Ltd. documented the first recorded oscillatory pyrotechnic combustion system in 1898 under the heading "Orion Flashing Guns".[2,3] The composition:

51%	Sulfur
25%	Barium nitrate
17%	Fine magnesium powder
7%	Fine aluminium pyroflake

was pressed into hard pellets and it was observed to burn periodically, after ignition, with white flashes. Since then, several mixtures with oscillatory combustion behaviour have been reported in the literature.[1]

It is of interest to understand the mechanisms that give rise to oscillations in pyrotechnic combustion processes so that the desired effects can be optimised and unfavourable conditions such as thermal runaway can be avoided.

A common interpretation of oscillatory strobe combustion, attributed to Shimizu,[4] is that two different kinds of pyrochemistry are involved; one in the light (flash) phase and one in the dark (smouldering) phase. It was suggested by Shimizu,

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with earlier contributions from Wasmann[5] and Krone,[6] that during the dark phase of an oscillation, hot spots develop in the smouldering slag layer. These hot spots grow in size and temperature until a critical point is reached when the flash reaction commences. It was thus conjectured that the dark reaction should have a small activation energy with a relatively low (possibly zero) heat output whilst the flash reaction should have a large activation energy as well as a large heat output. A later experimental study,[7] using scanning electron microscopy to analyse an extinguished strobe star, showed that generation of hot liquid on the surface of the star was necessary for initiation of the flash process.

Feng *et al*.[3] applied a pool chemical approximation to the Gray–Scott model[8] (a cubic autocatalytic model) to mimic experimental observations. The effect of temperature was represented by the autocatalytic step and no temperature dependence was included via the Arrhenius function. However, the model was not investigated in any detail and no attempt was made to relax the pool chemical approximation in accordance with the finite quantities involved in the experimental system.

Here a 'minimal oscillator model' scheme is proposed, which represents the minimum number of chemical steps required to qualitatively reproduce the experimentally observable behaviour.

Combustion of a pyrotechnic strobe composition

The ammonium perchlorate–magnesium composition was chosen, for pedagogical reasons, as a suitable example of the strobe effect but it is anticipated that other strobes function through a similar mechanism. When the pressed composition is ignited the low temperature reactions include the decomposition of ammonium perchlorate as described by:

$$NH_4ClO_4 \rightarrow NH_3 + HClO_4 + 197.81 \text{ kJ mol}^{-1}$$

$$150\ ^\circ\text{C} < T < 300\ ^\circ\text{C} \qquad (1)$$

$$4NH_4ClO_4 \rightarrow 2Cl_2 + 3O_2 + 8H_2O + 2N_2O + 593.02 \text{ kJ mol}^{-1}$$

$$T > 300\ ^\circ\text{C} \qquad (2)$$

Since reaction (2) is exothermic it increases the temperature and hence enhances the rate of decomposition. When the temperature reaches 450 °C, ammonium perchlorate decomposes fully to generate O_2. Potassium dichromate is commonly added to this composition to control the frequency of oscillation. It begins decomposition at 390 °C and decomposes fully at 500 °C absorbing a large amount of heat in the process. It thus has the effect of restraining the increasing rate of reaction. However, potassium dichromate is not included explicitly in the current scheme. The rate-determining step in this smouldering/dark phase is the oxidation of solid magnesium, given by:

$$Mg_{(s)} + \tfrac{1}{2}\, O_{2(g)} \rightarrow MgO_{(s)} + 601.67 \text{ kJ mol}^{-1} \qquad (3)$$

The composition takes on a honeycomb-like structure, comprising solid magnesium covered by magnesium oxide, as the ammonium perchlorate is consumed. This offers a large surface area of magnesium for oxidation. There is a creeping rise in the temperature during the above processes and when 650 °C is reached, the magnesium begins to melt. The magnesium undergoes a second phase change, to the gaseous state, at 1107 °C. The major reactions then become:

$$Mg_{(s)} \rightarrow Mg_{(l)} -9.2 \text{ kJ mol}^{-1} \qquad (4)$$

$$Mg_{(l)} \rightarrow Mg_{(g)} -131.8 \text{ kJ mol}^{-1} \qquad (5)$$

$$Mg_{(l)} + \tfrac{1}{2}O_2 \rightarrow MgO_{(l)} -526.76 \text{ kJ mol}^{-1} \qquad (6)$$

$$Mg_{(g)} + \tfrac{1}{2}O_2 \rightarrow MgO_{(g)} -588.52 \text{ kJ mol}^{-1} \qquad (7)$$

The principal reaction is the gas phase oxidation of magnesium, which liberates large amounts of heat. As the magnesium quickly reaches boiling point, the concentration of vapour phase magnesium increases rapidly. Both the reaction rate and temperature increase suddenly and flash combustion occurs. The extremely high temperatures evaporate the MgO and the honeycomb structure disappears; the duration of the flash event is very short. This results in the majority of heat being transferred to the surroundings and not into the un-reacted composition. In addition, the vapour phase concentration of magnesium decreases rapidly and hence the reaction rate decreases abruptly, returning to the smouldering dark phase.

Problem formulation

From the discussion in the previous section it is clear that oscillatory combustion is caused by the competition between the three phases of

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magnesium for oxygen.

$$Mg_{(s,l)} + \tfrac{1}{2}O_2 \xrightarrow{\bar{k}_1} MgO_{(s,l)} \quad (8a)$$

$$Mg_{(g)} + \tfrac{1}{2}O_2 \xrightarrow{\bar{k}_2} MgO_{(g)} + 588.52 \text{ kJ mol}^{-1} \quad (8b)$$

Where $\bar{k}_i$, i = 1, 2 represents the temperature dependence of the reaction through the Arrhenius function:

$$\bar{k}_i = A_i e^{-E_i/RT} \quad (9)$$

The decomposition of ammonium perchlorate results in a stoichiometric excess of oxygen in the early stages of the smouldering process. Consequently, the concentration of oxygen can be combined with the reaction rate constant. The rate constants for the above reaction steps are:

$$k_1 = \bar{k}_1[O_2] \qquad k_2 = \bar{k}_2[O_2] \quad (10)$$

From previous arguments, it is clear that the reaction scheme adheres to the Shimizu hypothesis that:

$Q_1 \approx 0,\ E_1 > 0$

$Q_2 > 0,\ E_2 > 0 \qquad E_1 < E_2$

where Q_i and E_i are the heat generated by, and the activation energy of, the ith reaction step respectively.

Implementing the above conditions, the model reaction scheme takes the form:

$$P \xrightarrow{k_1} X \xrightarrow{k_2} B + Q_2 \quad (11)$$

Where P is a generalised set of reactants ($Mg_{(s,l)}$ in this case), X represents the intermediate chemical species produced ($Mg_{(g)}$ in this case) and B the final combustion products ($MgO_{(s,l,g)}$ in this case).

This model scheme resembles the simplest example in combustion theory of an oscillatory chemical reaction as studied by Sal'nikov.[9] The Sal'nikov prototype combustion system, developed later by Gray and Roberts[10] and Kay and Scott,[11] only involves the first step of the above scheme but with $Q_1 > 0$.

The dynamical system considered here can be written as a set of mass conservation equations, thus:

$$\frac{d\bar{p}}{dt} = -A_1 e^{-E_1/RT}[O_2]\bar{p} \quad (12)$$

$$\frac{d\bar{a}}{dt} = A_1 e^{-E_1/RT}[O_2]\bar{p} - A_2 e^{-E_2/RT}[O_2]\bar{a} \quad (13)$$

$$\rho c V \frac{d\bar{T}}{dt} = V Q_2 A_2 e^{-E_2/RT}[O_2]\bar{a} - \chi S\left(\bar{T} - \bar{T}_a\right) \quad (14)$$

subject to the following initial conditions:

$$\bar{p}(t=0) = p_0 \qquad \bar{a}(t=0) = 0 \qquad \bar{T}(t=0) = T_{ig} \quad (15)$$

See Nomenclature for a complete list of symbol descriptions.

Let:

$Z_1 = A_1[O_2]$

$Z_2 = A_2[O_2]$

Defining the following quantities:

$$\tau = \frac{tZ_2}{p_o}, \quad a = \frac{\bar{a}QR}{\rho c E_2}, \quad T = \frac{\bar{T}R}{E_2}, \quad Ta = \frac{\bar{T}_a R}{E_2},$$

$$l = \frac{\chi S p_o p_o}{V \rho c Z_2}, \quad p = \frac{A_1 \bar{p} Q_2 R}{A_2 \rho c E_2}, \quad \mu = \frac{E_1}{E_2} \quad (16)$$

the governing equations, (12)–(14) can be re-cast in the following dimensionless form:

$$\frac{dp}{d\tau} = -pe^{-\mu/T} \quad (17)$$

$$\frac{dp}{d\tau} = -pe^{-\mu/T} \quad (18)$$

$$\frac{dT}{dt} = ae^{-1/T} - l\left(T - T_a\right) \quad (19)$$

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The system contains four parameters: μ, l , T_a, p_o. The last three are genuine control parameters in that they can, to a certain extent, be controlled in the laboratory. The first parameter is not, insofar as it is fixed for a given chemistry. This set of equations reduces to the classical Sal'nikov oscillator for $\mu = 0$. Nevertheless, μ is treated here as a parameter and included in a later analysis to determine the effect of changing the reaction chemistry by, for example, changing the reactants.

We will proceed initially by assuming the pool chemical approximation for p:

$$\frac{dp}{dt} = 0, \quad p = p_o \tag{20}$$

We thus have a two variable system with four parameters.

Discussion

To demonstrate the usefulness of this model, we choose to investigate the influence of the heat loss parameter, l, on the combustion behaviour of this particular strobe model. For subsequent calculations, the following parameter values were

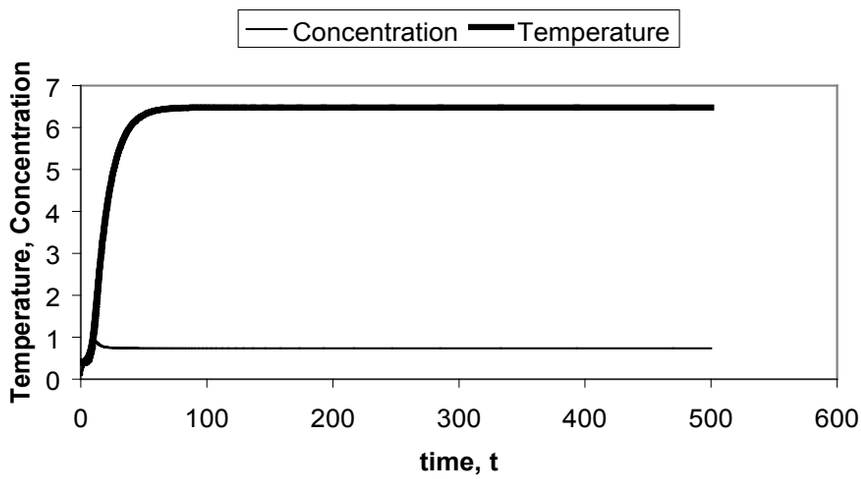

Figure 1. *Temporal concentration and concentration profiles for a reaction with low heat loss (l = 0.1).*

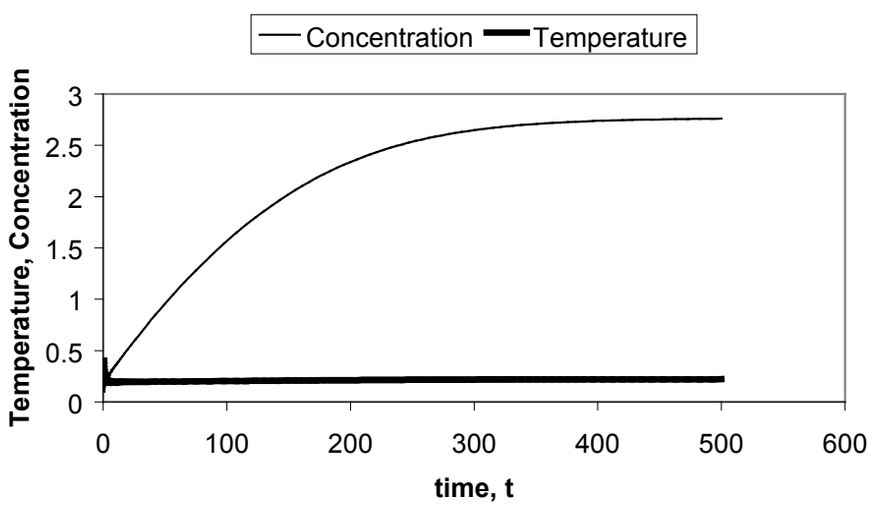

Figure 2. *Temporal concentration and concentration profiles for a reaction with high heat loss (l = 1.0).*

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fixed p_o = 0.7, T_a = 0.19, μ = 0.7. Intuitively, if the rate of heat loss is low (l = 0.1 say), the temperature of the system will increase rapidly thereby increasing the rate of conversion of the intermediate species to final product. The concentration of the intermediate species therefore remains low. This is the "fast burn" (flash) regime (Figure 1). Conversely, a high rate of heat loss (l = 1.0 say) causes the temperature to remain relatively low and conversion of the intermediate species to final product is slow. The intermediate species therefore slowly accumulates in the system. This is the "slow burn" (smoulder) regime (Figure 2).

The question now arises: What happens at intermediate heat loss values? An intensive parametric search could be undertaken by slowly varying the heat loss parameter. However, this is inefficient and instead bifurcation theory is employed.

Bifurcation theory seeks to identify parameter ranges that separate regions of qualitatively different behaviour by defining conditions for the behavioural changes. In this instance, regions of parameter space in which oscillatory combustion phenomena may be observed are identified. The defining conditions for oscillations are:[12]

$$f = g = \mathrm{tr}(J) = 0, \qquad \det(J) > 0 \qquad (21)$$

where $f = \mathrm{d}a/\mathrm{d}t$ (18), $g = \mathrm{d}T/\mathrm{d}t$ (19), and tr(J) and det(J) are the trace and determinant of the Jacobian matrix (J) given by:

$$J = \begin{bmatrix} \mathrm{d}f/\mathrm{d}a & \mathrm{d}f/\mathrm{d}T \\ \mathrm{d}g/\mathrm{d}a & \mathrm{d}g/\mathrm{d}T \end{bmatrix}$$
$$tr(J) = \mathrm{d}f/\mathrm{d}a + \mathrm{d}g/\mathrm{d}T \qquad (22)$$
$$\det(J) = \mathrm{d}f/\mathrm{d}a \; \mathrm{d}g/\mathrm{d}T - \mathrm{d}f/\mathrm{d}T \; \mathrm{d}g/\mathrm{d}a$$

Solving equations (21) defines the oscillatory range to be contained within the limits l = 0.5503, 0.6777. Choosing l = 0.6, the concentration of the intermediate species (a) and the system temperature (T) exhibit temporal oscillations (Figure 3). Figure 4 shows the phase plane plot where the temporal dependence of the variables is removed and the correlation between concentration and temperature is more clearly displayed.

At point A in Figures 3 and 4, the system temperature is high and the cycle is just at the

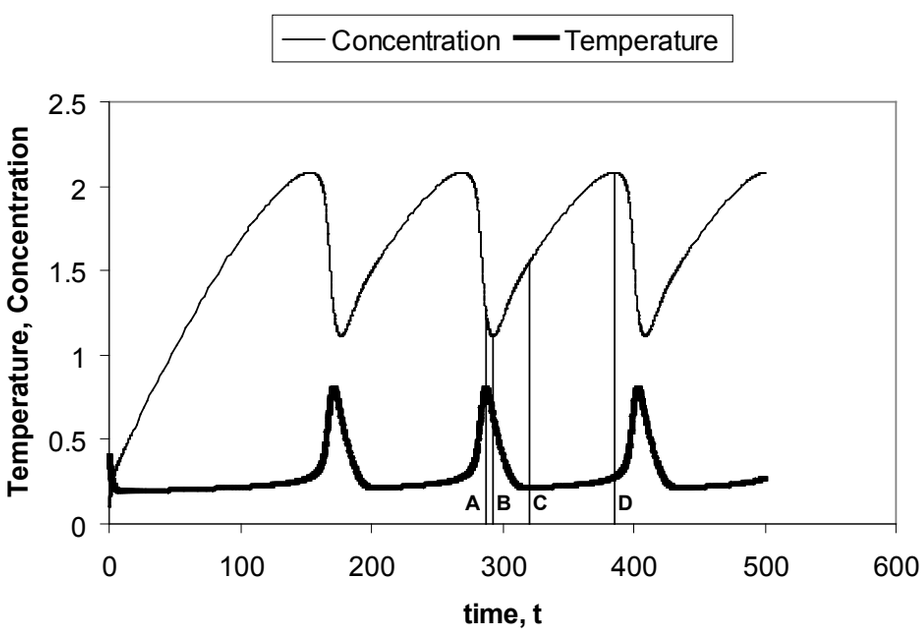

Figure 3. *Self-sustained oscillations in concentration and temperature for an intermediate heat loss value (l = 0.6) showing temporal dependence.*

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end of a flash phase. The system begins to cool but the temperature is still sufficient to convert the intermediate species to product so the concentration continues to decrease towards point B. At point B, the system is still cooling but the temperature has dropped below the critical level required to convert the intermediate species into product (reaction step 2), so the concentration of the intermediate species begins to increase towards point C (reaction step 1 dominates). At point C, the concentration of the intermediate species reaches a level which begins to drive reaction step 2. As reaction step 2 progresses, heat is generated and the temperature is thus increased slowly towards point D. This is the smoulder phase. The increasing temperature causes reaction step 2 to accelerate thereby producing more heat and further enhancing the reaction rate. At point D, the concentration of the intermediate species reaches a critical level and reacts very rapidly producing a large quantity of heat which is observed as a jump in temperature back to point A and a consequent decrease in the intermediate species concentration as it is converted to product. This final (flash) stage completes the cycle.

The simplification made early in the development of the model, namely the pool chemical approximation is now addressed. The generalisation is relaxed so that the concentration of the reactant decays with time. Direct integration of equation (17) yields the result:

$$p = p_o e^{-\mu/T} \tag{23}$$

Substituting (23) into (18) and solving (18) and (19) numerically yields Figure 5.

In Figure 5, a decrease in the system temperature is observed initially as reactant is consumed during reaction step 1 when little or no heat is generated. During this time, the intermediate species concentration increases slowly. Eventually, the concentration of reactant decreases to a critical value; the concentration of intermediate is at a sufficiently high level to cause the temperature to increase rapidly in a flash reaction. The sudden temperature increase causes a rapid conversion of the intermediate species to final product. Rapid consumption of the intermediate causes the temperature to drop and the cycle begins again. As the initial reactant is consumed, the amplitude of

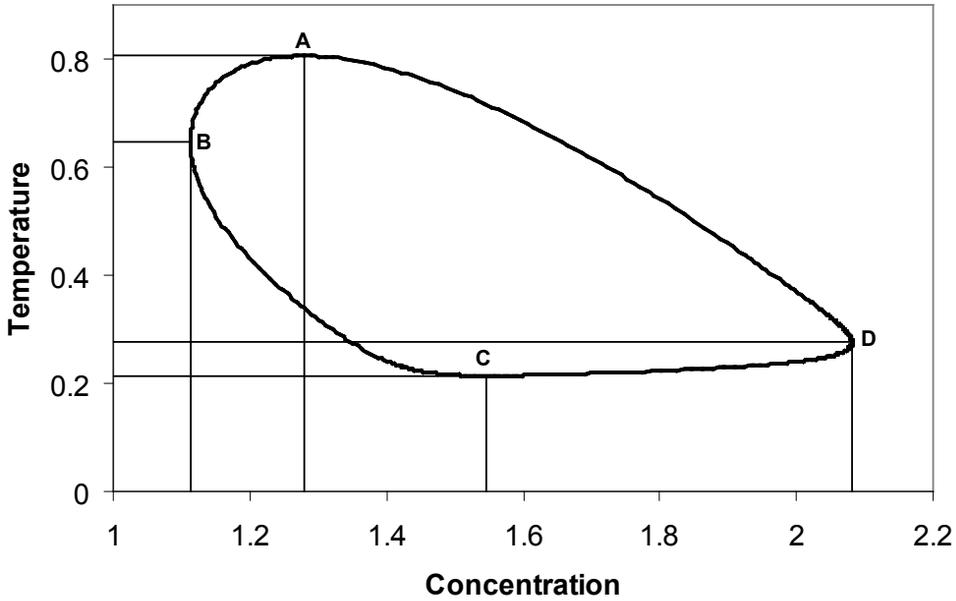

Figure 4. *Self-sustained oscillations in concentration and temperature for an intermediate heat loss value (l = 0.6) showing correlation between concentration and temperature.*

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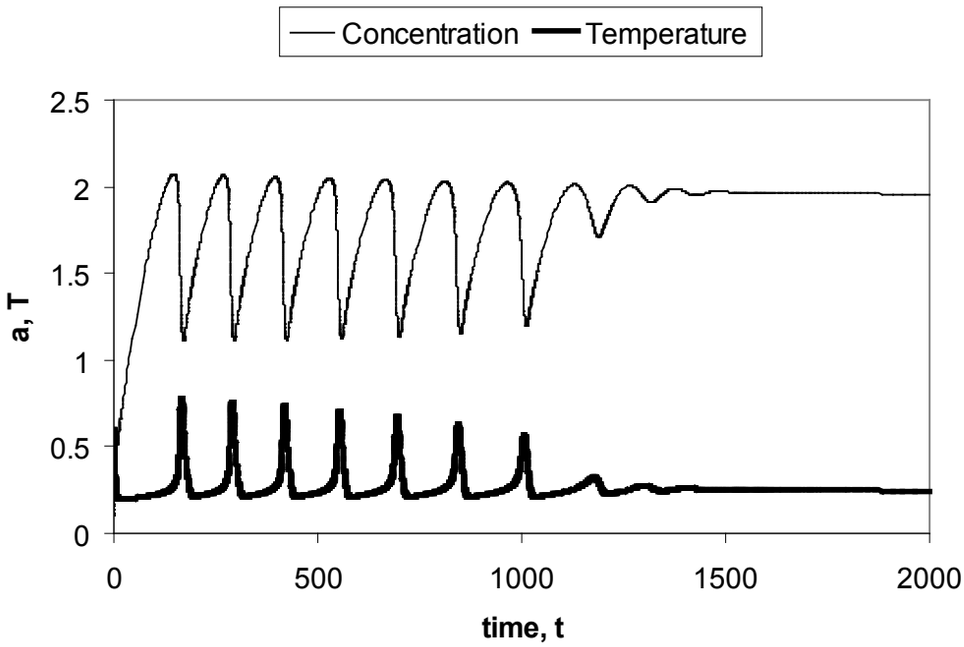

Figure 5. *Transient oscillations in temperature and concentration as a result of precursor decay.*

the oscillations decreases and the period lengthens until eventually the oscillations die out completely and the reactant concentration decays to zero.

Conclusions and further work

A model has been derived, which follows the Shimizu hypothesis for the combustion of pyrotechnic strobe composition. The mechanism dictates that the combustion process takes place in a two-stage decay process; the rates of both steps are affected by temperature. Bifurcation theory has been employed to identify regions of the heat loss parameter space where self-sustained oscillations exist. The theory can be applied to any other parameter to allow suitable design of strobe compositions.

No elaboration on the behaviour of the oscillations has been given. A description of how to determine the frequency and amplitude of the emerging oscillations is deferred to a later paper. It is likely that multiple stationary states exist in this system and that oscillatory behaviour can coexist with steady (slow or fast) burning. In this case, it becomes critical to ensure that the intial conditions are well established in the basin of attraction in which the system is intended to operate. Given the large manufacturing tolerances associated with fireworks, minor deviations in composition can send the system towards the wrong end state with disastrous consequences. This will be discussed further in subsequent articles on the combustion of pyrotechnic strobe composition.

Nomenclature

Symbol	Definition
A	Pre-exponential factor, s^{-1}
B	Final combustion products
E	Activation energy of reaction
P	Generalised set of reactants
Q	Heat generated by reaction
R	Ideal gas constant
S	External surface area of sample
T	Dimensionless system temperature
T_a	Dimensionless ambient temperature
V	Sample volume
X	Intermediate chemical species
Z	Modified pre-exponential parameter
a	Dimensionless concentration of X
c	Heat capacity of material
k	Reaction rate constant
l	Dimensionless heat transfer coefficient
p	Dimensionless concentration of P

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p_o	Initial concentration of P
t	time, s
χ	Heat transfer coefficient
μ	Ratio of activation energies
ρ	Material density
τ	Dimensionless time

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