

# Studies of the Thermal Stability and Sensitiveness of Sulfur/Chlorate Mixtures — Part 5: Application of Self-Heating Theory to the Prediction of Ignition Temperatures

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## ABSTRACT

*The self-heating models of Frank-Kamenetskii and Thomas have been applied to predict self-ignition temperatures for sulfur-chlorate mixtures in spherical and cylindrical geometries of varying size. The models were validated by comparison to experimental cardboard tube test data previously reported. It was found that the Frank-Kamenetskii model, combined with kinetic data from differential scanning calorimetry, gave the best agreement with the experimental results. However, careful selection of the kinetic parameters proved critical and, in this study, DSC data provided more relevant predictions than ARC data. By appropriate selection of size and geometry, the models could be further applied to predict self-ignition temperatures for other mixtures and geometries or systems that can be related to actual fireworks.*

**Keywords:** sulfur, chlorate, fireworks, thermal stability, self-heating, Frank-Kamenetskii, Thomas

## Introduction

Previously reported work in this series<sup>[1-4]</sup> has examined the thermal stability of sulfur/potassium chlorate mixtures in cardboard tubes when heated using a heated-block apparatus. The test samples were either heated at a constant rate or held at a constant elevated temperature until an ignition was observed. The thermal stability of the mixtures was reported in terms of the lowest temperature at which spontaneous ignition was observed, referred to as the (self) ignition temperature. Sulfur-chlorate mixtures have been shown to have low thermal stability and ignition temperatures as low as

383 K have been reported<sup>[2]</sup> for stoichiometric mixtures held in cardboard tubes.

The self-ignition temperature of a material depends upon the rate at which heat is generated inside the material through internal chemical reaction balanced against the rate at which heat is dissipated to the surroundings. If the rate of heat generation exceeds the rate of heat loss, then the material will self-heat and spontaneous ignition may occur. The self-ignition temperature is defined as the lowest temperature, to which a sample must be heated, under prescribed conditions, for self heating, leading to spontaneous ignition, to occur. Under bulk conditions or conditions favourable to heat retention, sulfur/chlorate mixtures are liable to self-heating, giving rise to spontaneous ignitions.

Part 5 of this series applies the self-heating theories of Frank-Kamenetskii and Thomas to predict the ignition temperatures of sulfur/chlorate mixtures. The predicted temperatures are compared to those observed in previously reported experiments.

## Self-Heating Theory

Theoretical models of self-heating are based upon the mathematical interpretation of the balance between the rates of heat generation and heat dissipation. For a system in thermal equilibrium the temperature distribution,  $T$ , as a function of time,  $t$ , can be described by

$$\rho_b c \frac{\partial T}{\partial t} = \lambda \nabla^2 T + Q \rho_b A \exp\left(-\frac{E}{RT}\right) \quad (1)$$

where

$\rho_b$  = density,

$c$  = heat capacity of the material,

- $\lambda$  = thermal conductivity of the material,
- $Q$  = heat of reaction per unit mass,
- $A$  = Arrhenius pre-exponential factor,
- $E$  = activation energy,
- $R$  = universal gas constant  
(8.314 J mol<sup>-1</sup> K<sup>-1</sup>), and
- $\nabla^2$  = Laplacian operator.

A zero-order Arrhenius type rate of heat generation is assumed and heat transfer is by conduction only.

A general solution to equation 1 would include two constants of integration derived from the boundary or storage conditions under consideration. Because of the exponential term, an exact analytical solution of the heat balance equation has so far not been achieved. However, models for self-heating have been proposed that find approximate solutions for the heat balance equation and differ from each other only in the assumptions made.

Semenov<sup>[5]</sup> proposed a solution where the temperature distribution of the reacting body is uniform and resistance to heat transfer occurs solely through thermal resistance at its boundary (i.e., the wall of the containment vessel). This model is most readily applied to gases and turbulent liquids, where the principal heat transfer mechanism is convection, and is of less relevance to solids, where other models are more appropriate.

Frank-Kamenetskii<sup>[6]</sup> proposed a solution in which all the resistance to heat transfer is within the reacting mass and that its boundary acts as an isothermal heat sink (i.e., remains at the same temperature as the environment). This model is most suited to solid systems, in contrast to Semenov's model. Frank-Kamenetskii gives an approximate solution to the heat balance equation, describing the steady-state temperature distribution in a reacting body in terms of the Frank-Kamenetskii (FK) parameter,  $\delta$ , defined as

$$\delta = \frac{Er^2 Q \rho_b}{\lambda R T_a^2} A \exp\left(-\frac{E}{RT_a}\right) \quad (2)$$

where

$T_a$  = environment temperature and

$r$  = characteristic length of a geometric shape: half-thickness of a slab or radius of a sphere or cylinder.

Frank-Kamenetskii showed that solutions of the heat-balance equation (eq. 1), for a steady-state temperature distribution, are possible only when the FK parameter  $\delta$ , is less than or equal to a critical value,  $\delta_c$ . If  $\delta > \delta_c$ , no stationary state temperature distribution exists, and the sample temperature will continue to rise, by self-heating, resulting in a thermal explosion. Frank-Kamenetskii calculated  $\delta_c$  for  $m = 0$  (an infinite slab) analytically and for  $m = 1$  (an infinitely long cylinder) and  $m = 2$  (a sphere) numerically. The calculated values of  $\delta_c$  are given in Table 1 for each shape factor  $m$ .

**Table 1. Critical Values of  $\delta_c$  Derived by Frank-Kamenetskii.**

Shape Factor, $m$	$\delta_c$
0, infinite slab	0.88
1, infinite cylinder	2
2, sphere	3.32

Thomas<sup>[7]</sup> refined the Frank-Kamenetskii model by allowing for thermal resistance and dissipation of heat through the boundary, effectively amalgamating the Semenov and Frank-Kamenetskii models. Thomas proposed an approximate solution to equation 1 that allowed for Newtonian cooling through a finite heat transfer co-efficient,  $H$ , at the interface between the reacting mass and its surroundings (the self-heating material may be contained within a vessel or may be enclosed in a second solid material of different thermal properties, generating no heat).

Thomas defined the Biot number,  $\alpha$ , as:

$$\alpha = \frac{H \times r}{\lambda} \quad (3)$$

where

- $\alpha$  = Biot number,
- $r$  = the length parameter, and
- $H$  = overall heat transfer co-efficient.

For each of the three geometries in Table 1, Thomas calculated the critical parameter  $\delta_c$  in

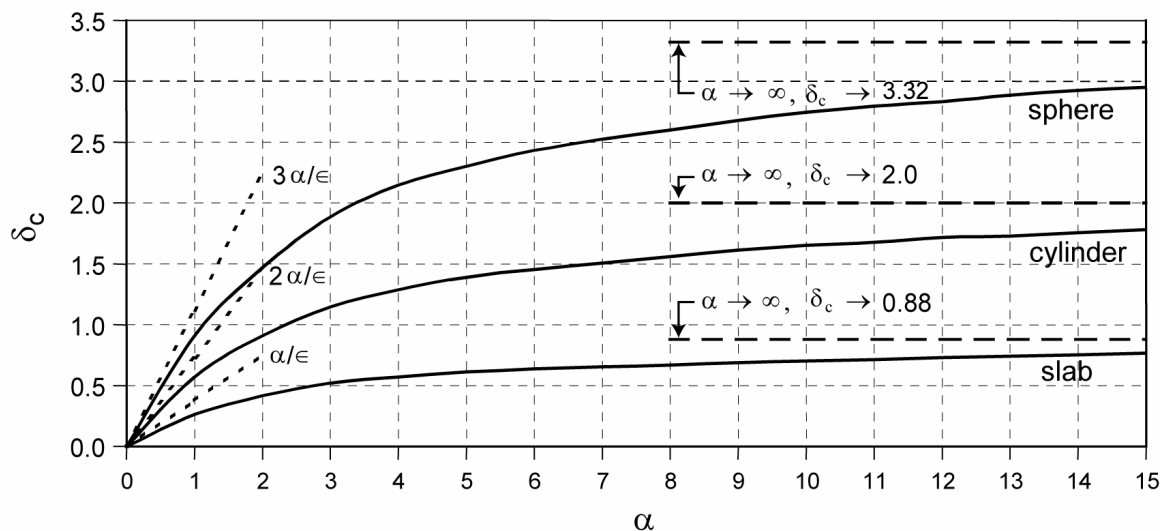


Figure 1.  $\delta_c$  as a function of  $\alpha$  for a slab, cylinder and sphere.

terms of  $\alpha$ . The plot in Figure 1 shows calculated values for  $\delta_c$ .

It can be seen from Figure 1 that as  $\alpha \rightarrow \infty$ , the values of  $\delta_c$  for a slab, cylinder and sphere approach the limiting values calculated by Frank-Kamenetskii (0.88, 2 and 3.32 respectively). As  $\alpha \rightarrow 0$ ,  $\delta_c$  approaches limiting values given by  $(m + 1) \alpha/\epsilon$ , which is in fact the Semenov condition.<sup>[5]</sup> Therefore, the Thomas model successfully combines the Semenov and Frank-Kamenetskii models giving the same results as these models at the extreme limits of  $\alpha$ .

The existence of a critical value of  $\delta$ , for a given system, infers that there is also a critical (environment) temperature  $T_c$ , above which the system is thermally unstable and will undergo self-heating.

To calculate  $T_c$ , it is first necessary to calculate the Biot number,  $\alpha$ , for the geometry under consideration (eq. 3). Once  $\alpha$  is known, the critical value of the Frank-Kamenetskii number  $\delta_c$  can be calculated either mathematically from the equations of Thomas or graphically from Figure 1. For a purely Frank-Kamenetskii approach ( $H = \infty$  and hence  $\alpha = \infty$ ) values for  $\delta_c$  can be taken from Figure 1. The critical temperature,  $T_c$ , can then be determined from equation 2, provided the necessary parameters are known. Alternatively, a critical value for the

characteristic length of the required geometry can be calculated, for a given environment temperature.

For this work on sulfur/chlorate mixtures, where the onset of self-heating leads rapidly to spontaneous ignition of the material, the theoretical critical temperatures predicted by the Frank-Kamenetskii and Thomas models are considered to be equivalent to the experimentally determined (self) ignition temperature of the mixtures.

While the infinite slab geometry is of limited practical use, the cylindrical and spherical geometric models can be applied to fireworks. The spherical geometry could be used to predict  $T_c$  for individual fireworks components such as stars, typically of 10 to 20 mm diameter. On a larger scale, the Frank-Kamenetskii and Thomas models (with an appropriate value for  $H$ ), could be applied to a complete firework such as a simple shell typically with diameters up to 300 mm, although 75 to 150 mm is more common. Although this is an over-simplification, since variations in internal compositions or components would need to be ignored, it would give a worst-case situation.

Similarly, the infinitely long cylinder geometry could be used to model a fountain type firework, provided its length was much greater than its radius. This latter situation could be

applied to the previous thermal studies for compositions contained within cardboard fireworks tubes.

## Experimental

Application of the Frank-Kamenetskii and Thomas models requires knowledge of certain properties of the material and system being studied. These properties fall into three categories; the chemical thermodynamic and kinetic properties ( $E$ ,  $A$ ,  $Q$ ), physical properties ( $c$ ,  $\lambda$ ,  $\rho_b$ ) and geometric properties ( $m$ ,  $r$ ,  $H$ ). Where possible, values for these parameters were obtained from the literature. In the absence of suitable literature data, values were determined by experiment.

Previous work has examined many mixtures with widely varying compositions. However, for this study, it was decided to focus on three specific mixtures; the compositions are listed in Table 2. Mixture 1 is an approximately stoichiometric composition according to Tanner's equation<sup>[8]</sup> and has been previously extensively studied. Mixture 2 was chosen because previous work<sup>[3]</sup> identified the 5:95 mixtures as the least stable (i.e., having the lowest ignition temperature). Mixture 3, more representative of a typical fireworks composition, was obtained by replacing half of the sulfur in Mixture 1 with charcoal.

**Table 2. Composition of Test Mixtures.**

Component	Mixture		
	1	2	3
Flowers of sulfur	30	5	15
Potassium chlorate (AnalaR)	70	95	70
Charcoal	0	0	15

### Chemical Properties

Literature data<sup>[9]</sup> for sulfur/chlorate mixtures were limited and there was insufficient or incomplete information available for the three selected mixtures. In addition, the acidity of the sulfur, in mixtures where data were reported,

differs from that of the sulfur used here. Since previous work in this series has shown sulfur acidity to have an effect on thermal stability, such literature data are not applicable for this work. Therefore, thermodynamic and kinetic data were obtained for the three mixtures by experiment. The techniques of differential scanning calorimetry (DSC) and accelerating rate calorimetry (ARC) were employed to determine values for the parameters  $E$ ,  $A$  and  $Q$ .

DSC data were obtained using a Mettler-Toledo TA4000/DSC25 heat-flux calorimeter following the procedure described in ASTM Test Method No. E698-79.<sup>[10]</sup> Isothermal ageing tests were performed, following the same procedure, to check the validity of the calculated kinetic parameters.

ARC data were obtained using a Columbia Scientific ARC2000 calorimeter. Kinetic data were calculated using ArcWin computer software V1.5, following the methodology described by Townsend and Tou.<sup>[11]</sup>

The thermodynamic and kinetic data obtained are listed in Table 3.

### Physical Properties

The heat capacities of the three mixtures were derived from the fractional sum of the heat capacities of the components in the mixture. Heat capacity data for the components were obtained from the literature<sup>[12]</sup> and showed little variation over the temperature range of interest, from ambient (293 K) up to typical ignition temperatures of 393 K.

Thermal conductivity of the mixtures was determined by experiment, using an electrical version of the Lee's disk method.<sup>[13]</sup> Disks of each test material were made by compressing 8 g of loose material in a hand-operated hydraulic press, to a pressure of 1000 kg (1 tonne). By applying 7, 8 and 9 volts, the thermal conductivity of each disk was determined over a range of temperatures. However, little difference was seen as a function of temperature and the reported results are averaged over the three voltage settings.

**Table 3. Thermo-Kinetic Parameters Determined by DSC and ARC.**

Method/Parameter (units)	Mixture 1 30% sulfur (flowers) 70% potassium chlorate	Mixture 2 5% sulfur (flowers) 95% potassium chlorate	Mixture 3 15% sulfur (flowers) 15% charcoal 70% potassium chlorate
<b>DSC</b>			
Activation energy, $E$ ( $\text{J mol}^{-1}$ )	$1.47 \times 10^5$	$1.40 \times 10^5$	$4.40 \times 10^5$
Arrhenius factor, $A$ ( $\text{s}^{-1}$ )	$1.67 \times 10^{16}$	$1.33 \times 10^{15}$	$1.67 \times 10^{50}$
Heat of reaction, $Q$ ( $\text{J g}^{-1}$ )	2350	1410	2380
<b>Isothermal Ageing</b>			
Half life/temperature	63 min. @ 380 K	62 min. @ 386 K	68 min. @ 423 K
Heat of reaction of aged sample ( $\text{J g}^{-1}$ )	1319	1080	No exotherm observed
<b>ARC</b>			
Activation energy, $E$ ( $\text{J mol}^{-1}$ )	$2.32 \times 10^5$	$1.66 \times 10^5$	$5.73 \times 10^5$
Arrhenius factor, $A$ ( $\text{s}^{-1}$ )	$6.7 \times 10^{36}$	$6.5 \times 10^{20}$	$3.7 \times 10^{70}$
Heat of reaction, $Q$ ( $\text{J g}^{-1}$ )	1055	807	1595

Bulk density data, obtained from the physical measurement of each disk, were in the range of 1.4–1.69  $\text{g cm}^{-3}$ . Previously reported work in this series examining the thermal stability of mixtures pressed into the shape of cylindrical stars (diameter 9 mm, length 10 mm and mass 1.0 g) gave a density of 1.6  $\text{g cm}^{-3}$ . The physical properties of the three mixtures are summarised in Table 4.

#### Geometric Parameters

The physical dimensions of ten cardboard tubes identical to those used in previous work were measured and average values obtained.

$$\begin{aligned} \text{Length} &= 140 \pm 0.2 \text{ mm} \\ \text{Internal diameter} &= 10.0 \pm 0.2 \text{ mm} \end{aligned}$$

$$\begin{aligned} \text{External diameter} &= 14 \pm 0.1 \text{ mm} \\ \text{Mass} &= 6.4 \pm 0.1 \text{ g} \end{aligned}$$

The overall heat transfer coefficient,  $H$ , of the system (material inside the cardboard tubes) was evaluated<sup>[14,15]</sup> by recording a cooling curve for a cardboard tube—closed at one end with a clay plug—filled with boiling water and closed at the upper end with a tissue plug. Over the period of the measurements, the sealed tubes remained intact; no absorption of water into the cardboard was observed and the appearance of the outer surface of the tubes remained dry. A plot of  $\ln(T - T_a)$  versus time should be linear, allowing  $H$  to be calculated from the gradient (the reciprocal of the gradient gives the Newtonian cooling time,  $t_N = Vc_p/SH$ , where  $V$  = volume and  $S$  = surface area).

**Table 4. Physical Properties of Sulfur/Chlorate Mixtures.**

Parameter (units)	Mixture 1 30% sulfur (flowers) 70% potassium chlorate	Mixture 2 5% sulfur (flowers) 95% potassium chlorate	Mixture 3 15% sulfur (flowers) 15% charcoal 70% potassium chlorate
Heat capacity, $c$ ( $\text{J g}^{-1} \text{K}^{-1}$ )	0.84	0.88	0.88
Thermal conductivity, $\lambda$ ( $\text{W m}^{-1} \text{K}^{-1}$ )	0.337	0.402	0.292
Bulk density, $\rho_b$ ( $\text{g cm}^{-3}$ )	1.50	1.69	1.40

The average overall heat transfer coefficient of four tubes was calculated to be:

$$H = 16.8 \pm 1.0 \text{ W m}^{-2} \text{ K}^{-1}$$

## Application of Models

The data obtained for the three mixtures were used in the Frank-Kamenetskii model. Theoretical (self) ignition temperatures were calculated for an infinitely long cylinder and a sphere for a range of characteristic lengths (radii). The results are given in Tables 5 and 6 and shown graphically in Figure 2. Critical temperatures were calculated twice, using thermodynamic and kinetic data from both the DSC and the ARC.

**Table 5. Ignition Temperature of an Infinitely Long Cylinder of Sulfur/Chlorate Mixture, Calculated as a Function of its Characteristic Length (Radius), Using the F-K Model.**

Characteristic Length: Radius of infinite cylinder (mm)	Ignition Temperature (K)					
	Mixture 1 30% sulfur (flowers) 70% potassium chlorate		Mixture 2 5% sulfur (flowers) 95% potassium chlorate		Mixture 3 15% sulfur (flowers) 15% charcoal 70% potassium chlorate	
	DSC	ARC	DSC	ARC	DSC	ARC
5	376	295	384	352	419	398
10	365	291	372	343	414	395
20	354	286	360	335	410	392
50	341	281	346	325	404	387
100	332	276	336	317	400	385
200	323	273	327	310	396	382

**Table 6. Ignition Temperature of a Sphere of Sulfur/Chlorate Mixture, Calculated as a Function of its Characteristic Length (Radius), Using the F-K Model.**

Characteristic Length: Radius of sphere (mm)	Ignition Temperature (K)					
	Mixture 1 30% sulfur (flowers) 70% potassium chlorate		Mixture 2 5% sulfur (flowers) 95% potassium chlorate		Mixture 3 15% sulfur (flowers) 15% charcoal 70% potassium chlorate	
	DSC	ARC	DSC	ARC	DSC	ARC
5	380	296	389	355	421	400
10	369	292	376	346	416	396
20	358	288	365	338	411	393
50	344	282	350	327	406	389
100	335	278	339	320	401	386
200	326	275	330	313	397	383

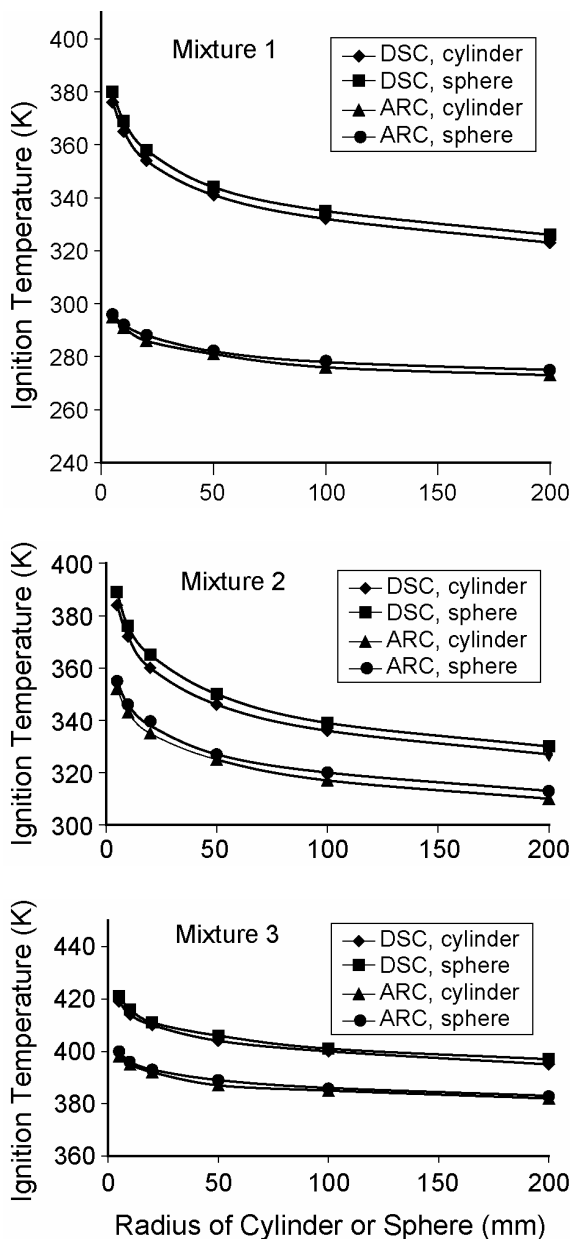


Figure 2. Predicted ignition temperatures for Mixtures 1 to 3 calculated using the F-K model.

The characteristic lengths for which the ignition temperatures were calculated were chosen to be representative of typical sizes of fireworks and/or firework components. The larger lengths (20, 50 and 100 mm) relate to typical sizes of firework shells that are commonly available, while the smaller lengths (5 and 10 mm) are typical of individual fireworks components (e.g., stars). The 5 mm characteristic length, combined with infinitely long cylinder geometry, approximately describes the experimental arrangement of cardboard fireworks tubes used in previous work.

The collected parameters were applied to the Thomas model, using the cylinder geometry with a radius of 5 mm, to predict ignition temperatures of cardboard firework tubes containing test mixtures. The data used and the calculated results are given in Table 7.

### Comparison with Experimental Tube Test Data

**Mixture 1.** The calculated ignition temperatures, following Frank-Kamenetskii, for Mixture 1 contained in 5 mm radius, infinitely long cylinders are 376 K using DSC derived kinetic parameters and 295 K using ARC derived data. The equivalent values, following Thomas, are 357 and 287 K for DSC and ARC, respectively. The Thomas values are lower than their equivalent Frank-Kamenetskii values, which is to be expected since Thomas allows for thermal resistance at the boundary (insulation) so more heat is retained in the system. Stoichiometric mixtures of flowers of sulfur with AnalaR potassium chlorate, equivalent to Mixture 1, have been studied isothermally, within 5 mm radius

Table 7. Ignition Temperatures ( $T_c$ ) of Sulfur/Chlorate Mixtures Contained within Cardboard Firework Tubes, Calculated from DSC and ARC Data Using the Thomas Model.

Parameter	Mixture 1	Mixture 2	Mixture 3
$H$	$16.8 \text{ W m}^{-2} \text{ K}^{-1}$	$16.8 \text{ W m}^{-2} \text{ K}^{-1}$	$16.8 \text{ W m}^{-2} \text{ K}^{-1}$
$r$	5 mm	5 mm	5 mm
$\lambda$	$0.337 \text{ W m}^{-1} \text{ K}^{-1}$	$0.402 \text{ W m}^{-1} \text{ K}^{-1}$	$0.292 \text{ W m}^{-1} \text{ K}^{-1}$
$\alpha (H \times r / \lambda)$	0.249	0.209	0.287
$\delta_c$	0.18	0.15	0.21
$T_c$ (ARC)	287 K	336 K	393 K
$T_c$ (DSC)	357 K	362 K	412 K

cardboard firework tubes, under conditions of elevated temperature. It was found that at a temperature of 383 K, mixtures ignited after 250–260 minutes, while, at 373 K, no ignitions were observed after 23 days. This suggests that the critical temperature lies within the range 373–383 K. The ignition temperature, calculated using the DSC data (376 K), gives good agreement with the experimental results when the Frank-Kamenetskii model is used. With the Thomas model however, the calculated value is lower (by 15–20 K) than that observed by experiment. This difference may be due to the time period of the tube experiments (i.e., an exotherm, leading to ignition, may occur at lower temperatures than actually observed, if the induction or observation period was much longer) or it may be attributed to an incorrect choice for the overall heat transfer coefficient for the experimental conditions. The ignition temperatures calculated using ARC data (295 K, Frank-Kamenetskii) are significantly lower than actually observed and are approaching typical ambient temperatures.

**Mixture 2.** Calculated ignition temperatures, for a cylinder with a 5 mm radius, using the Frank-Kamenetskii model, are 384 K with DSC data and 352 K with ARC data. Applying the Thomas model, the calculated ignition temperatures are 362 and 336 K with DSC and ARC data, respectively. Experimental tube test data indicated that the ignition temperature was in the range of 373–383 K (ignitions as low as 383.7 K, after 330 minutes, were observed). For this mixture, as with Mixture 1, the ignition temperature predicted by the Frank-Kamenetskii model, combined with DSC data, most closely resembles the experimental results, giving a good correlation. Calculated values using ARC data and/or the Thomas model were again significantly lower than that observed by experiment.

**Mixture 3.** Calculated ignition temperatures are 419 and 398 K by Frank-Kamenetskii with DSC and ARC data, respectively and, 412 and 393 K by Thomas with DSC and ARC data. Again, experimental tube tests gave ignitions as low as 383 K (after 365 minutes). None of the models predicted an ignition temperature in agreement with the experimental results.

## Discussion

From the information above, it can be seen that the Frank-Kamenetskii model, combined with DSC chemical data, correctly predicts, to a reasonable degree of certainty, the ignition temperatures of Mixtures 1 and 2. Predictions with the same model, using ARC data, are consistently lower than are actually observed and approach typical ambient temperatures. For example, the predicted ignition temperature for Mixture 1, in a 5 mm radius infinitely long cylinder, using the Frank-Kamenetskii model with ARC data is 295 K. This difference between ARC and DSC can be explained in terms of how the kinetic parameters are derived by each technique.

The ASTM method used for the DSC, calculates kinetic data by measuring the temperature at which the reaction maximum occurs. Therefore, it is influenced mainly by the actual ignition reaction of the bulk material. The ‘fine detail’ of the reaction (i.e., the early reaction stages) is of less significance. In contrast, the pseudo-rate constant analysis used by the ARC considers the finer detail, and kinetic parameters are calculated primarily with data from the early stages of the reaction. In the case of sulfur/chlorate mixtures, the ARC identifies small pre-ignition exotherms which, in the adiabatic environment of the ARC, lead to ignition of the bulk material. The calculated kinetic parameters (and hence predicted ignition temperatures) are influenced mainly by these early exotherms. In practice, however, sulfur/chlorate mixtures in cardboard tubes are not adiabatic, heat is lost to the environment and the small exotherms do not cause ignition, which occurs at much higher temperatures. The ignition temperatures predicted using ARC kinetic data are therefore lower than actually observed. The ignition temperatures predicted using DSC kinetic parameters give better agreement with experimental data since the kinetic parameters better reflect the behaviour of the bulk material in a non-adiabatic environment.

The failure of the Frank-Kamenetskii model for Mixture 3 may be attributed to an incorrect choice for the kinetic parameters. This is confirmed for DSC data by the failure of the isothermal ageing test. For Mixture 3, the iso-aged



sample showed no reaction suggesting that it had ignited during the ageing process and that the calculated kinetic values are too high. This is reflected in the calculated ignition temperatures, which are much higher than the experimental ignition temperatures.

The failure of ARC and DSC to obtain correct kinetic data for Mixture 3 may be because of the complex nature of the chemical reaction. The ARC pseudo-rate constant analysis and DSC ASTM method are applicable to reactions whose behaviour can be described by the Arrhenius equation and the general rate law. They are not applicable to reactions that are partially inhibited or processes that include simultaneous or step reactions, and may not be applicable to materials that undergo phase transitions if the reaction rate is significant at the transition temperature. It has been suggested that the ignition of a sulfur/chlorate mixture may be triggered by the generation of sulfur dioxide. In the case of Mixture 3, the charcoal present in the mixture would tend to absorb any sulfur dioxide present, thus inhibiting the reaction.

It is already known that the addition of certain materials has a stabilising effect on the sulfur/chlorate mixture. Robertson<sup>[6]</sup> found that the addition of kieselguhr (diatomite), charcoal and calcium chloride dihydrate increased thermal stability while sodium sulfate decahydrate had no effect. In general, any material that has the ability to absorb either the active species (sulfur dioxide) or water or to prevent formation of acidic species will have a stabilising effect on the mixture.

The predicted ignition temperatures calculated by the F-K models have been compared to, and show agreement with, a single experimental data point (i.e., a long cylinder of diameter 5 mm). The trends predicted by the model have not been verified since the collection of additional experimental data points was outside the scope of this study. Verification would require data points for larger diameter geometries (e.g., 20, 50 or even 100 mm). However, with larger diameters there is an increase in hazard potential.

## Conclusions

The Frank-Kamenetskii model has been shown to give the best agreement with the experimental results, predicting, to a reasonable degree of certainty, the ignition temperatures of sulfur/chlorate mixtures in cardboard tubes. However, careful selection of the kinetic parameters is critical and, in this study, DSC data provided more relevant predictions than ARC data. This model could be further applied to predict ignition temperatures for other mixtures and geometries or systems that can be related to actual fireworks.

When a third component is added to the mixture, the predicted results differ from those measured due to the complexity of the reaction. The experimental techniques used to derive kinetic data for the model assume standard Arrhenius kinetics. The failure of the model to correctly describe a sulfur/chlorate composition containing charcoal is attributed to experimental problems of obtaining accurate chemical kinetic data.

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