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Thermochimica Acta 392–393 (2002) 37–40

thermochimica
acta

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Critical Ignition Temperature

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Received 15 November 2000; accepted 28 September 2001

Abstract

Critical ignition temperature (T_I) is the minimum temperature for which an explosive, propellant, or pyrotechnic charge of specified size, shape, and boundary constraint must be heated in order to induce thermal runaway. Methods of thermal analysis such as differential scanning calorimetry (DSC) are uniquely suited for evaluating the thermokinetic parameters required to calculate T_I. Small scale independent testing is a necessary prerequisite for scaling T_I for systems with equivalent heat-transfer characteristics to larger radii. Valid calculations and reliable scaling require accurate thermokinetic parameters. This presentation addresses a practical approach for prediction and validation of T_I data.

Keywords: Critical ignition temperature; Activation energy; Conductive heat flow; Calorimetric technique

1. Introduction

The critical ignition temperature (T_I) an important parameter required to insure safe storage and process operations involving explosives, propellants, and pyrotechnics. It is defined as the lowest temperature to which a specific charge may be heated without undergoing thermal runaway [1,2]. T_I may be calculated from inflammation theory and appropriate thermokinetic parameters, namely the activation energy (E), the pre-exponential factor (A), and the heat of reaction (Q). Thermal methods such as isothermal and scanning calorimetry provide a variety of methods to evaluate A, E, and Q. This paper addresses the validation of T_I data calculated from thermokinetic parameters measured with common calorimetric techniques.

1.1. Critical conditions

Eqs. (1) and (2) define the net heat flow for the systems governed by convective- and conductive-heat flow [3].

$$\rho C_p \frac{dT}{dt} = \rho Q A\, e^{-E/RT} - \frac{hS}{V}(T - T_0) \qquad (1)$$

$$\rho C_p \frac{dT}{dt} = \rho Q A\, e^{-E/RT} + \lambda \nabla^2 T \qquad (2)$$

In these equations, ρ is density, C_p the heat capacity, T the reactant temperature, T_0 the ambient temperature, t the time, Q the total heat, A the pre-exponential factor, E the activation energy, R the ideal gas law constant, h the heat-transfer coefficient, λ the thermal conductivity, S the surface area, and V the volume. Classical steady state solutions to Eqs. (1) and (2) derived by Semenov and Frank–Kamenetskii are given by Eqs. (3) and (4) [3,4]. Zinn and Mader [5] obtained a numerical solution for the

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PII: S0040-6031(02)00068-0

case of conductive-heat transfer.

$$\frac{\rho r^2 QAE\,\mathrm{e}^{-E/RT}}{\lambda RT^2} = \delta \tag{3}$$

$$\frac{\rho VQAE\,\mathrm{e}^{-E/RT}}{hSRT^2} = \mathrm{e}^{-1} \tag{4}$$

In Eq. (3) δ, is a shape parameter with values of 0.88, 2.0, and 3.32 for an infinite slab, cylinder, and sphere, respectively. Eqs. (3) and (4) are critical conditions. If the left-hand side of Eq. (3) exceeds 1/e or Eq. (4) exceeds δ, the potential for thermal runaway exists. In general, Semenov conditions are applicable to a homogenous fluid while the Frank–Kamenteskii relation is used for viscous materials and solids. For each mode of heat-transfer T_I may be calculated by iteration.

Eqs. (3) and (4) assume zero-order kinetics. For significant reactant depletion [4] and autocatalysis [3,6], Eqs. (3) and (4) require correction with a depletion function ($f(\alpha)$) evaluated at the maximum rate. Autocatalytic reactions may be expressed empirically with Eq. (5)

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(\alpha_0 + \alpha)^x (1-\alpha)^y \tag{5}$$

where k is the rate coefficient, α_0 and α the extents of reaction when t is 0 and greater than 0, respectively and x and y are reaction orders [6]. The depletion function is $f(\alpha) = (\alpha_0 + \alpha)^x (1+\alpha)^y$. At the maximum rate $\alpha_\mathrm{m} = (x - \alpha_0 y)/(x+y)$ and $f(\alpha_\mathrm{m}) = (1+\alpha_0)^{x+y}(x/(x+y))^x (y/(x+y))^y$. The corrected critical parameters are $\delta/f(\alpha_\mathrm{m})$ and $\mathrm{e}^{-1}/f(\alpha_\mathrm{m})$ for conduction and convection, respectively.

1.2. Critical ignition temperature validation

Rearrangement of Eqs. (3) and (4) yields Eqs. (6) and (7) [3]. These relations provide eloquent methods to determine the activation energy for a specific charge with a defined boundary constraint. The ignition temperature is determined by trial and error for a series of charges with a defined radius, r and boundary constraint. When data are plotted with coordinates, $\{\delta(T_\mathrm{I}/r)^2$, $1/T_\mathrm{I}\}$ for conduction or $\{hST_\mathrm{I}^2/(\rho V)$, $1/T_\mathrm{I}\}$ for convection, the slope of the line yields E. If the plots of Eqs. (6) and (7) are linear, the data may be scaled with reasonable confidence. Deviations from a straight line are an indication of reaction complexity.

$$\ln\left(\frac{\delta T_\mathrm{I}^2}{r^2}\right) = -\frac{E}{R}\left(\frac{1}{T_\mathrm{I}}\right) + \ln\left(\frac{\rho AEQ}{\lambda R}\right) \tag{6}$$

$$\ln\left(\frac{hST_\mathrm{I}^2}{\rho V}\right) = -\frac{E}{R}\left(\frac{1}{T_\mathrm{I}}\right) + \ln\left(\frac{\mathrm{e}AEQ}{R}\right) \tag{7}$$

2. Example

2.1. Ignition temperature for pentaerythritol tetranitrate (PETN)

Valid predictions for T_I require reliable data for A, E, and Q. It is emphasized that a single set of kinetic parameters do not necessarily exist for explosives.The reason is that the variations in impurities or traces of residual solvents can influence the apparent kinetic parameters; small perturbations may have a significant influence upon the T_I. While A and E may be determined from scanning calorimetry by a variety of methods, isothermal methods usually provide the best data. Fig. 1 illustrates T_I data for charges of PETN calculated with the following parameters: $A = 6.3\times10^{19}$, $E = 47.0\ \mathrm{kcal\ mol^{-1}}$, $Q = 300\ \mathrm{cal\ g^{-1}}$, $\rho = 1.74\ \mathrm{g\ ml^{-1}}$, and $\lambda = 6.0\times10^{-4}\ \mathrm{cal\ ^\circ C^{-1}\ cm^{-1}\ s^{-1}}$ [1,7]. These kinetic parameters were validated by Rodgers for small slabs of PETN [1]. An analogous plot for charges enclosed within a defined heat transfer surface may be constructed with Eq. (4).

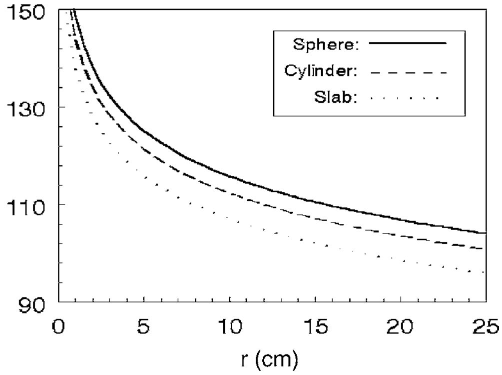

Fig. 1. Critical ignition temperature vs. charge radius conductive-heat flow for PETN.

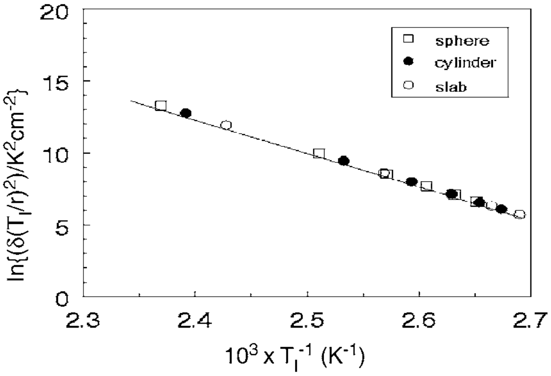

Fig. 2. Inverse critical ignition temperature plot conductive-heat flow for PETN.

Fig. 2 shows the graphical representation of Eq. (7) calculated with the kinetic parameters for PETN. It is noted that the points for different charge shapes with different radii fall on the same line. If one were to measure T_I for each of the geometric shapes, then the linearity of the plot is a confirmation of the kinetic data. An assessment of the radial dependence of the T_I is the preferred method for critical temperature validation; however, the amount of work involved is usually prohibitive. Charges with selected radii (r) may be used to verify the calculated values of the ignition temperature. If valid kinetic parameters are determined by thermal methods, then reasonably safe extrapolations may be made with Eqs. (3) and (4). Validity of the kinetic parameters and the ignition data calculated for small charges may be determined with a variety of related tests such as the Henkin test [8], the adiabatic storage test [9], and the cook-off test.

2.2. *Smokeless propellant cook-off*

Fig. 3 shows a schematic arrangement for a generic apparatus that is useful for validation of the ignition temperature. It is constructed with either small or large cylindrical chambers. A large chamber has a volume of 60 l; it is useful for ignition studies on small charges and component measurements such as airbag inflators. Smaller chambers with a volume of 300 ml are used for cook-off testing. Chamber temperatures are monitored with three thermocouples attached to the bottom, side, and top of a cylindrical vessel. A separate internal thermocouple monitors the actual temperature of the explosive or pyrotechnic charge. Temperature, pressure, and time are monitored with a fast Fourier transform data acquisition system. Fig. 4 shows representative cook-off data obtained for a commercial smokeless propellant. A 3 in. × 0.25 in. metal cylinder loaded with 0.6 g of commercial propellant was subjected to a constant temperature ramp. The internal

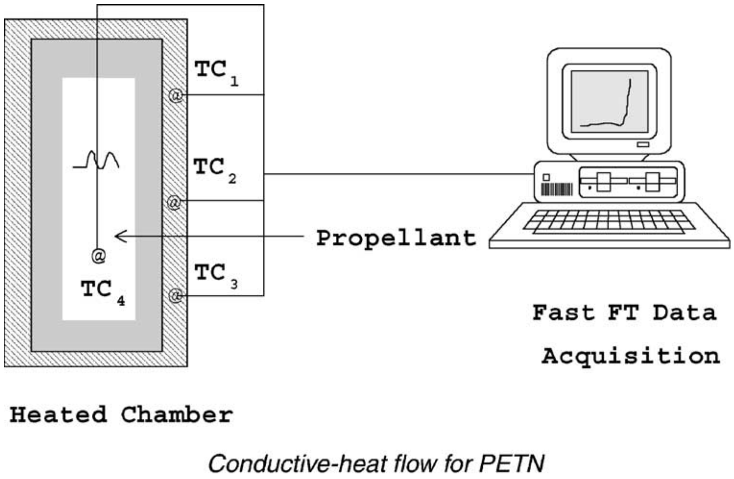

Fig. 3. Apparatus for validation of critical ignition temperature.

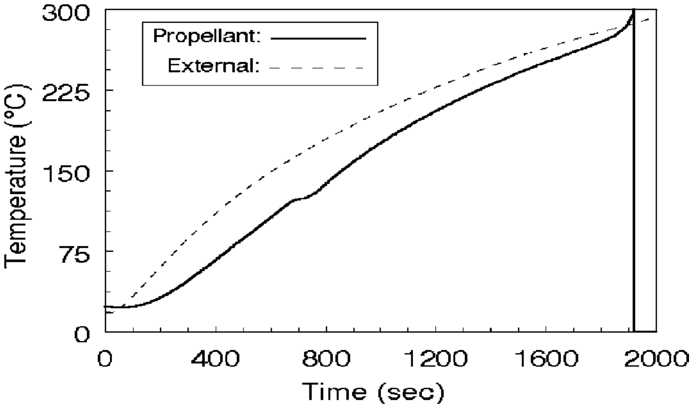

Fig. 4. Cook-off for a smokeless propellant.

temperature data shown in Fig. 4, revealed that the charge experienced a small endotherm at 150 °C, self-heating commenced at 255 °C, and explosion occurred at 300 °C.

3. Conclusion

A systematic approach is necessary for reliable evaluation of T_I and subsequent extrapolation for charges with larger radii. Ignition temperatures calculated from steady state inflammation conditions require accurate data for the thermokinetic parameters, A, E, and Q. Values of T_I calculated with kinetic parameters obtained with thermal methods require independent validation.

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