DETERMINATION OF THE SELF-ACCELERATING DECOMPOSITION TEMPERATURE (S.A.D.T.) FROM THERMAL STABILITY DATA GENERATED USING ACCELERATING RATE CALORIMETRY.

Stelios Mores, Philip F. Nolan and Gerrard O,Brien
Chemical Engineering Research Center, South Bank University, London SE1 0AA, UK.

The Accelerating Rate Calorimeter (A.R.C.$_{TM}$) is used extensively in the assessment of thermal stability hazards. The established means of determining the self accelerating decomposition temperatures (S.A.D.T.s) for material-equipment (M.E) systems has been heavily based on the United Nations S.A.D.T. test, with which data from the A.R.C.$_{TM}$, analysed through the use of the Semenov self-heating model, has been shown to agree closely. An alternative means of analysis of the A.R.C.$_{TM}$ data has been adopted by the authors, using the Frank-Kamenetskii and Thomas models describing criticality. This has brought to light evidence which questions the validity of U.N. S.A.D.T. data that has on occasion been extrapolated from test conditions to those of larger scales.

Key Words : *Accelerating Rate Calorimetery, Thermal Stability Hazards, Self-accelerating Decomposition Temperture, Crash-cooling Safety Temperature Limit.*

Introduction

The need for the establishment of techniques for the prediction of potential thermal hazards involved with the handling of materials in the chemical and allied industries, has led to the development of a number of instruments and experimental techniques dedicated to the determination of safety limits associated with materials and material-equipment (M.E.) systems. Both destructive and non-destructive techniques are in common use, each providing data that indicate the scale of the potential hazard, and possibly a recommended limit that should be adhered to, if this hazard is to be avoided. A comparison of various thermal hazard assessment techniques is given by a number of workers(1,2).

Self-Accelerating Decomposition Temperature Test

The self-accelerating decomposition temperature (S.A.D.T.) test(3) is used in the determination of the lowest temperature at which a sample undergoes auto-accelerative decomposition, and is the method prescribed by the United Nations (U.N.) for the determination of safety parameters associated with the packaging and transportation of materials. The U.N. S.A.D.T. test comprises of a well insulated test chamber, in which the M.E. system being tested is supported. The temperature of this is controlled to within a limit of $\pm$ 1.5°C by force circulating air around the M.E. system under test, creating a thermostatically controlled environment. During operation, the temperature of the air bath is maintained constant over a period of seven days, or until such time as auto-accelerative decomposition occurs. Various set temperatures (usually in 6.0°C steps) need

to be used so as to establish the minimum temperature of self-acceleration. The S.A.D.T. test is limited to the assessment of actual M.E. systems, and can handle system volumes of up to 220 litres (referred to usually as the U.S. S.A.D.T. test), with possible reactions to destruction.

Accelerating Rate Calorimetry

The Accelerating Rate Calorimeter ($A.R.C._{TM}$) is a computer controlled adiabatic calorimeter, capable of detecting exothermic activity at sensitivities of up to 0.02°C min^{-1}. In principle, it consists of an insulated, heater-maintained adiabatic environment, in which the sample (up to 8ml in volume) and test-cell are suspended. Heating in a step-wise fashion determines the temperature at which self-heating is observed. Having established an onset temperature, the reaction is allowed to proceed adiabatically whilst temperature, temperature-rate, pressure and time data are logged. A facility exists for the capture of a further temperature input. In comparison to other thermal stability assessment techniques it has proved to be the most sensitive, detecting self-heating behaviour at temperatures below most other instruments[1]. In general, application of the $A.R.C._{TM}$ provides a more detailed evaluation of the scale of the potential hazard, whose presence has already been verified using techniques such as differential thermal analysis (D.T.A.) and differential scanning calorimetry (D.S.C.) as screening tools. The data gathered is both in terms of pressure rise and temperature rise, providing indicators for both thermal and explosive hazards. Initially, use of the generated data is in the derivation of kinetic parameters associated with the sample chemistry[4,5,6,7]. These parameters are essential in the detailed understanding of the behaviour of the material and the possible M.E. systems being considered, whilst being invaluable in the calculation of safety limits[4,7,8,9].

Kinetic Considerations

Analysis of $A.R.C._{TM}$ generated data is based on a number of chemical kinetic models[4,5,6,9], based on classical combustion and chemical reaction theory. The methodology proposed by Townsend and Tou[4] is adopted in the established methods for the determination of S.A.D.T.s. This is based on the single-step decomposition model,

$$A \rightarrow B$$

Use is made of the Arrhenius equation

$$k = A \exp\left(-E/RT\right) \qquad \qquad ...(1)$$

to describe the variation of reaction rate constant with temperature. The rate of depletion of reactant for a single-step reaction mechanism is given by

$$\frac{dC}{dt} = -kC^{n} \qquad \qquad ...(2)$$

A number of workers[4,5,8] have shown that the time to maximum rate for a single-step decomposition reaction under adiabatic conditions is given by the relationship,

$$t_{m} = \frac{RT^{2}}{E\frac{dT}{dt}} \qquad \qquad ...(3)$$

The activation energy E, is determined from a Wilson plot, whereby a linear plot of the logarithm of the pseudo-rate constant k^*, versus the reciprocal of temperature is obtained at the correct order of reaction. The pseudo-rate constant is determined from,

$$k^* = kC_O^{n-1} = \frac{(T_F - T)^{n-1} \frac{dT}{dt}}{(T_F - T_O)} \qquad ...(4)$$

and equations 1 and 2 combine to give,

$$k^* = AC_O^{n-1} \exp\left(-E/RT\right) \qquad ...(5)$$

It has been further shown(4,8) that there exists a temperature for a particular M.E. system, beyond which heat generated is not completely dissipated to the environment. This inevitably leads to self-acceleration in decomposition rates, increased self-heating and a runaway scenario. This temperature is referred to as the temperature of no return T_{NR}, and is obtained from the point of tangency between the heat generation rate and the equipment heat transfer line. ie.

$$mC_p AC_O^{n-1}(T_F - T_O)\exp\left(-E/RT\right) = US(T_O - T_A) \qquad ...(6)$$

In addition, it is possible to approximate a zero-order reaction to the initial stage of a reaction of any order(4,8,10). Wilberforce(8) has used this in conjunction with the T_{NR} to determine the S.A.D.T. for an M.E. system. The time line for the equipment can be evaluated from the slope of the cooling curve, determined from the Newtonian cooling of the system from an elevated temperature. ie.

$$\frac{dT_{EQUIPMENT}}{dt} = \frac{US\left(T_{EQUIPMENT} - T_A\right)}{mC_P} \qquad ...(7)$$

Having established the value for the time line. ie.

$$t_{EQUIPMENT} = \frac{US}{mC_{P(EQUIPMENT)}} \qquad ...(8)$$

it is possible to determine the temperature T^* at the point of equality with the time to maximum rate. The S.A.D.T. is then obtained from the relationship,

$$S.A.D.T. = T^* - \frac{RT_{NR}^2}{E} \qquad ...(9)$$

The approach adopted by Wilberforce(8) has proven to be successful in the determination of S.A.D.T. values for a number of M.E. systems, resulting in close agreement with those determined using the U.N. S.A.D.T. procedure. An inspection of the above methodology reveals that the basis for solution is the Semenov model(11,12) for an isothermal self-heating system with the resistance to heat transfer at the boundary layers. A number of workers(9,13,14,15) have described the use of this model in S.A.D.T. determination, using data from A.R.C.$_{TM}$ tests.

Apart from the Semenov model, it was suspected that use of a further two self-heat models, those proposed by Frank-Kamenetskii(7,12,16,17) and Thomas(12,18) could provide an alternative mathematical interpretation of M.E. systems under investigation.

The Semenov, Frank-Kamenetskii and Thomas Self-heat Models

The case of a solid slab of thickness 2r is to be considered (figure 1), in which a steady non-uniform temperature distribution has been established as a result of self-heating. The heat generation for an elemental volume can be described by the relationship,

$$q = -K\frac{d^2T}{dx^2} \qquad ...(10)$$

and with reference to equation 1, the rate of heat generation is given by,

$$q = Q\rho A \exp\left(-E/RT\right) \qquad ...(11)$$

The reactants are considered to be unlimited so that a zero-order is maintained (ie. the rate of reaction is forever increasing). A further assumption is that the reaction is independent of diffusion control effects.

A temperature symmetry is expected to occur about the centre point, assuming both sides of the slab are subjected to an identical temperature. Hence at the centre point (ie. at x = 0),

$$\frac{dT}{dt} \simeq 0 \qquad ...(12)$$

Finally, consideration of heat transfer limitations at the outer surface, relate the finite conductive heat transfer in the slab to the heat dissipated to the environment. ie.

$$\pm K\frac{dT}{dt} = U\left(T_s - T_A\right) \qquad ...(13)$$

for x = ± r.

If a Frank-Kamenetskii expansion(12) is considered about the temperature of the surroundings T_A, then the following approximation holds,

$$-\frac{E}{RT} = -\frac{E}{RT_A} + \frac{\Theta}{1 + \varepsilon_A\Theta} \qquad ...(14)$$

where E/RT » 1. Also,

$$\Theta = \frac{E(T - T_A)}{RT_A^2} \qquad ...(15)$$

and,

$$\varepsilon_A = \frac{RT_A}{E} \qquad ...(16)$$

Equation 14 can be simplified further to,

$$-\frac{E}{RT} \approx -\frac{E}{RT_A} + \Theta \qquad ...(17)$$

assuming that the parameter ε_A « 1, and the dimensionless characteristic temperature difference Θ is not large. Further, with the introduction of the dimensionless length,

$$y = x/r \qquad ...(18)$$

equations 10, 11, 17 and 18 can be combined to give the second-order differential relationship,

$$\frac{d^2\Theta}{dy^2} = -\delta\exp(\Theta) \qquad ...(19)$$

where the dimensionless constant δ is given by

$$\delta = \frac{E}{RT_A}\frac{r^2 Q\rho A}{K}\exp\left(-E/RT_A\right) \qquad ...(20)$$

Introducing the dimensionless parameters into equations 12 and 13 results in the relationships,

$$\frac{d\Theta}{dy} = 0 \qquad (y=0) \qquad ...(21)$$

and

$$-\frac{d\Theta}{dy} = \alpha\Theta_s \qquad (y=\pm1) \qquad ...(22)$$

where the Biot number α is given by,

$$\alpha = \frac{Ur}{K} \qquad ...(23)$$

and where Θ_s is the characteristic temperature at the surface (ie. $\Theta_s = \Theta(T_s)$).

It has been shown by Thomas[18] that equation 19 can be solved to give the following relationship,

$$\ln(\delta) = \ln\left(\frac{2D^2}{\cosh^2(D)}\right) - \frac{2D\tanh(D)}{\alpha} \qquad ...(24)$$

This is known as the Thomas model of criticality for thermal explosion of the first kind, where

$$D = \sqrt{\frac{\delta}{2}\exp(\Theta_o)} \qquad ...(25)$$

and $\Theta_o = \Theta(T_o)$.

The Thomas model describes the conditions that prevail in the most general case. However, two extreme cases can exist. In the first case, the effects of conductivity can be considered negligible, and it is assumed that the body of reacting material remains isothermal, whilst all the resistance to heat transfer lies within the boundary layer. This is the case originally described by Semenov[11], and it can be shown[16] that at the limit $\Theta_o \to \Theta_s$, where both $\delta \to 0$ and $\alpha \to 0$,

$$\frac{E}{RT_A^2}\frac{Q\rho A}{rK}\exp\left(-E/RT_A\right) = \exp(-1) \qquad ...(26)$$

The second extreme describes the case where no resistance to heat transfer exists at the surface boundary, but instead, a temperature gradient is established within the body of the reacting mass. In this instance, $\alpha = 0$, so that equation 24 reduces to,

$$\delta = \frac{2D^2}{\cosh^2(D)} \qquad ...(27)$$

This is the Frank-Kamenetskii equation for criticality.

Critical Temperatures From A.R.C.$_{TM}$ Data.

The time, temperature, temperature-rate and pressure data acquired during an A.R.C.$_{TM}$ test can be used to visualise the magnitude of a thermal stability problem. Limits are imposed on the handling of M.E. systems in the light of both mechanical and economical considerations. Decomposition with a high rate of gas generation might necessitate strict control of temperature in one particular case, whilst similar control might be required in a second, as a means of preventing degradation of the material during storage.

The Semenov, Frank-Kamenetskii and Thomas equations for criticality are to be incorporated in corresponding models that allow the interpretation of A.R.C.$_{TM}$ data in terms of critical temperatures for specific M.E. systems. These temperatures are equivalent to critical heat balance temperatures (C.H.B.T.) whose peaks (single plateau in the Semenov case) define S.A.D.T. limits(8,13).

Although the case of the slab of thickness r may be considered, a more general interpretation includes the cases of the sphere and cylinder by introducing the concept of surface area to volume ratio. It can be shown that,

$$r = \frac{\tau V}{S} \qquad \qquad ...(28)$$

where τ = 1, 2, 3 for a slab, a cylinder and a sphere respectively.

Incorporating equation 28 into equations 23 and 25 gives,

$$\alpha = \frac{\tau V U}{SK} \qquad \qquad ...(29)$$

and,

$$\delta = \frac{E}{RT_A^2} \frac{\tau^2 V^2}{S^2} \frac{\rho}{K} QA \exp\left(-E / RT_A\right) \qquad \qquad ...(30)$$

Substitution of equations 15, 29 and 30 into 25 results in,

$$D = \left[\frac{E}{2RT_A^2} \frac{\tau^2 V^2}{S^2} \frac{\rho}{K} QA \exp\left(\frac{E}{RT_A^2}(T_o - 2T_A)\right)\right]^{1/2} \qquad \qquad ...(31)$$

Equation 11 gives the heat generation per unit volume as a function of temperature. This can be determined directly from the self-heat rate r_t ie.

$$q = r_t \rho C_p$$

The thermal inertia factor(4) ϕ is introduced at this stage to correct for any thermal dilution effects that the sample cell has on the absolute temperature rate. Hence,

$$q = \phi r_o \rho C_p \qquad \qquad ...(32)$$

Combining equations 11 and 32 gives,

$$QA = C_p \phi r_o \exp\left(E / RT_o\right) \qquad \qquad ...(33)$$

Substitution of equation 33 into 31 results in,

$$D = \left[\frac{E}{2RT_A^2} \frac{\tau V^2}{S^2} \frac{\rho}{K} C_P \phi r_\phi \exp\left(\frac{E(T_O - T_A)^2}{RT_A^2 T_O} \right) \right]^{1/2} \quad ..(34)$$

and is independent of the heat of reaction and the Arrhenius frequency factor.

Incorporating equations 29, 30 and 33 into 24 gives the C.H.B.T.s of the M.E. system thus,

$$T_A = \left\{ \frac{1}{T_O} + \frac{R}{E}\left[\ln\left(\frac{E}{RT_A^2} \frac{\tau V^2}{S^2} \frac{\rho}{K} C_P \phi r_\phi \right) - \ln\left(\frac{2D^2}{\cosh^2(D)} \right) + \frac{2S}{\tau V} \frac{K}{U} D \tanh(D) \right] \right\}^{-1} \quad ...(35)$$

Equation 35 is solved iteratively, providing a quasi steady-state solution for the system under consideration. An initial approximation for temperature may be taken at $T_A = T_0$, where

$$T_{AO} = \left\{ \frac{1}{T_O} + \frac{R}{E}\left[\ln\left(\frac{E}{RT_O^2} \frac{\tau V^2}{S^2} \frac{\rho}{K} C_P \phi r_\phi \right) - \ln\left(\frac{2D_O^2}{\cosh^2(D_O)} \right) + \frac{2S}{\tau V} \frac{K}{U} D_O \tanh(D_O) \right] \right\}^{-1} \quad ...(36)$$

and,

$$D_O = \left[\frac{E}{2RT_O^2} \frac{\tau V^2}{S^2} \frac{\rho}{K} C_P \phi r_\phi \right]^{1/2} \quad ..(37)$$

A very similar relationship can be obtained based on the Frank-Kamenetskii model for criticality (ie. equation 27). A parallel approach results in the derivation of the following relationship for the critical temperature,

$$T_A = \left\{ \frac{1}{T_O} + \frac{R}{E}\left[\ln\left(\frac{E}{RT_A^2} \frac{\tau V^2}{S^2} \frac{\rho}{K} C_P \phi r_\phi \right) - \ln\left(\frac{2D^2}{\cosh^2(D)} \right) \right] \right\}^{-1} \quad ...(38)$$

where the parameter D is identical to that of equation 34.

As with equation 35, equation 38 is solved iteratively, using the initial approximations of D_0 and

$$T_{AO} = \left\{ \frac{1}{T_O} + \frac{R}{E}\left[\ln\left(\frac{E}{RT_O^2} \frac{\tau V^2}{S^2} \frac{\rho}{K} C_P \phi r_\phi \right) - \ln\left(\frac{2D_O^2}{\cosh^2(D_O)} \right) \right] \right\}^{-1} \quad ...(39)$$

The determination of the critical temperature based on the Semenov equation is different. Substitution of equations 28 and 33 into 26 results in,

$$T_A = \left\{ \frac{1}{T_O} + \frac{R}{E}\left[1 + \ln\left(\frac{E}{RT_A^2} \frac{\tau V}{S} \frac{\rho}{U} C_P \phi r_\phi \right) \right] \right\}^{-1} \quad ...(40)$$

Once again the temperature T_A is determined iteratively. An initial estimate for T_A can be obtained from,

$$T_{AO} = \left\{ \frac{1}{T_O} + \frac{R}{E} \left[1 + \ln\left(\frac{E}{RT_O^2} \frac{\tau I'}{S} \frac{\rho}{U} C_p \phi r_\phi \right) \right] \right\}^{-1} \qquad ...(41)$$

Equations 34, 35, 38 and 40 can be used to determine a C.B.H.T. profile, corresponding to the temperature in the self-heat rate relationship.

S.A.D.T. Determination For Di-tert Butyl Peroxide

A.R.C.$_{-TM}$ data obtained from the decomposition of di-tert butyl peroxide (D.T.B.P.) is to be used to illustrate the application of equations 35, 38 and 40. A pure sample of D.T.B.P. was used for comparison with the literature. The test loading data are summarised in table 1.

Thermal Dilution Factor (ϕ)	7.749
Sample Mass (g)	2.1542

Table 1 _ Loading summary for the D.T.B.P. test.

Note that the use of a system with a high thermal inertia (ϕ) is unavoidable due to the anticipated high pressure rise which requires the use of a heavy hastelloy-B high-pressure test cell (rated at 650 bar).

A standard heat-wait-search sequence with 3.0°C temperature steps and a self-heat rate sensitivity of 0.02°C min^{-1} commencing at a start temperature of 80°C was conducted. The results are illustrated in figure 2. Kinetic data from the subsequent analysis is given in table 2.

Order of Reaction	1
Activation Energy (kJ kmol^{-1})	155519
Frequency Factor (s^{-1})	5.95E+16
Heat of Reaction (kJ kg^{-1})	1219

Table 2 _ Relevant kinetic parameters derived from the D.T.B.P. test data.

The activation energy was used in the subsequent S.A.D.T. analysis, in conjunction with the non-depletory (zero order) relationship,

$$r_t = \phi r_\phi = \frac{Q M_{RMM}}{C_p \rho} A \exp\left(-E/RT \right) \qquad ...(42)$$

describing the worst case scenario.

Equations 34, 35, 38 and 40 were used to determine S.A.D.T. values for a number of geometries. The M.E. system thermal properties were obtained from standard literature sources(20,21) and are given in table 3.

Throughout the investigation, an attempt is made to replicate conditions similar to those experienced by a sample during a U.N. S.A.D.T.(5) test. Deviations from these conditions are to be used to illustrate possible circumstances which a material might experience under normal handling.

Density of D.T.B.P. $\left(kg\ m^{-3} \right)$	704.0
Thermal Conductivity of D.T.B.P. (kW m⁻¹ K⁻¹)	0.00921
Specific Heat Capacity of D.T.B.P. (kJ kg⁻¹ K⁻¹)	2.0939
Heat Transfer Coefficient for 35.5 litre Container (U.S. S.A.D.T. test)(22) $\left(kW\ m^{-2}K^{-1} \right)$	0.0028
Heat Transfer Coefficient for 220 litre Container (U.S. S.A.D.T. test)(22) $\left(kW\ m^{-2}K^{-1} \right)$	0.011

Table 3 _ Thermal properties of the M.E. system.

Solutions of Equations

Iterative solutions of equations 35, 38 and 40 are obtained at the point of equality between the ambient temperature T_A and the temperature dependent function. The solution of interest as regards the C.H.B.T. is the upper-most value obtained from the intercept. This represents the ambient temperature that needs to be maintained to prevent a rise in the temperature and temperature rate at the centre of the packaged material. A peak in the C.H.B.T. profile is established in the Frank-Kamenetskii and Thomas model based cases, corresponding to the S.A.D.T. for the system. Further, for various M.E. system configurations there exists a single tangential intercept. This condition illustrates the occurrence of a limit with regards to the existence of a temperature at which the system will not self-heat. This is in effect a crash-cooling self-heat rate limit and corresponds to the crash-cooling temperature limit (C.C.S.T.L.). Figure 3 shows a case, in which the volume has been raised from 50 litres to 1500 litres whilst the height to radius (L / R) ratio is maintained constant (ie. the intrinsic geometry of the system remains unchanged). If the system is increased in volume further, it is found that there is no solution for equation 35. The model based on the Thomas equation for criticality indicates the presence of a self-heating scenario irrespective of the ambient temperature T_A. Similar results can be obtained from the Frank-Kamenetskii based solutions of equation 38. In the Smenov model case, a single C.H.B.T. value is obtained which corresponds to the S.A.D.T., consequently the presence of a C.C.S.T.L. is transparent.

It is possible to attribute the conditions for non-solution of equations 35 and 38 to the temperature gradients within the system body, described by both the Frank-Kamenetskii and Thomas models for criticality. Indeed, it is this temperature profile alone that provides the resistance to heat loss in the former case. Conditions can therefore arise in which thermal gradients are sheer enough to prevent sufficient heat loss to the environment, irrespective of the value of T_A.

Solutions for S.A.D.T. values for the full range of self-heat rates and temperatures have been determined for a selection of M.E. system configurations. Figures 4 and 5 illustrate how the Thomas, Frank-Kamenetskii and Semenov models evaluate S.A.D.T.s. (curve peaks). Different orders are assumed based on variations in the system volume.

Figure 6 gives an insight into the role played by the system shape, as an increase in its ability to dissipate heat (ie. surface area to volume ratio) results in a rise in the values set for the S.A.D.T. The effects of volume change under the restriction of a constant l/r ratio have already been considered. Figure 3 shows this comparison for a cylindrical system. Finally the effects resulting from changes in the relative dimensions of the cylindrical system (ie. height and radius) but maintaining a constant volume of 220 litres are examined (figure 7).

System Volume (l)	System Geometry	R/L Ratio	Equation Used	S.A.D.T. (K)	C.C.S.T.L. (K)
220	Slab	0.265	40	358.4	---
220	Slab	0.265	38	379.1	401
220	Slab	0.265	35	358.2	373
220	Cylinder	0.265	40	353.0	---
220	Cylinder	0.265	38	367.6	388
220	Cylinder	0.265	45	352.5	368
220	Sphere	---	40	350.7	---
220	Sphere	---	38	362.5	383
220	Sphere	---	35	349.7	366
50	Cylinder	0.265	40	356.6	---
50	Cylinder	0.265	38	375.2	397
50	Cylinder	0.265	35	356.1	372
700	Cylinder	0.265	40	350.4	---
700	Cylinder	0.265	38	361.8	382
700	Cylinder	0.265	35	349.6	366
1500	Cylinder	0.265	40	348.7	---
1500	Cylinder	0.265	38	358.3	378
1500	Cylinder	0.265	35	347.5	364
10000	Cylinder	0.265	40	344.5	---
10000	Cylinder	0.265	38	349.5	368
10000	Cylinder	0.265	35	342.2	359
50000	Cylinder	0.265	40	341.0	---
50000	Cylinder	0.265	38	342.3	360
50000	Cylinder	0.265	35	337.5	355
220	Cylinder	0.066	40	356.3	---
220	Cylinder	0.066	38	374.7	396
220	Cylinder	0.066	35	355.9	371
220	Cylinder	0.132	40	354.7	---
220	Cylinder	0.132	38	371.1	392
220	Cylinder	0.132	35	354.3	369
220	Cylinder	0.794	40	350.6	---
220	Cylinder	0.794	38	362.3	381
220	Cylinder	0.794	35	349.8	366
220	Cylinder	1.232	40	349.4	---
220	Cylinder	1.232	38	359.7	380
220	Cylinder	1.232	35	348.1	365

Table 5 _ Predicted S.A.D.T. and C.C.S.T.L. values for the D.T.B.P. sample, as a function of the influences of volume and geometry.

Finally, it should be stressed that use of C.H.B.T.s based on equation 40 (and hence the Semenov model), do not predict the presence of C.C.S.T.L.s. Consequently, systems that will self-heat auto-acceleratively irrespective of the environmental temperature are not detected. Use of

which seem to play a major role in the determination of a system's thermal stability. It should be noted at this stage, that the incorporation of an experimentally derived equipment time line (equation 7) for use with equations 35 and 40 would provide improved S.A.D.T. estimates by these equations.

Ref.2 U.S. S.A.D.T (K)	Ref.8. U.S. S.A.D.T (K)	Ref.8. Method (K)	Ref.22 U.S. S.A.D.T (K)	Ref.22 Method of Ref.8. (K)	Eq.35 (K)	Eq.38 (K)	Eq.40 (K)
366	363	361	363	357	356	396	356

Table 4 _ A comparison of S.A.D.T. values determined from various techniques, for D.T.B.P. in a 35.5 litre cylinder suspended in an isothermal air-bath.

Table 5 reflects the diverse range of S.A.D.T. values that can result from variations in volume, shape and relative geometry. Results span a complete spectrum, from a maximum predicted by the Frank-Kamenetskii based model (ie. equation 38) at 103.1°C for a slab of 220 litres, to a minimum solution of 61.0°C predicted for a cylinder of the same volume by the Thomas based equation 35.

Conclusion

A detailed study of the determination of S.A.D.T. values based on various experimental and mathematical techniques has resulted in evidence indicating the possible oversimplification of the M.E. systems being assessed. The U.N. S.A.D.T. test can determine directly S.A.D.T. values for a particular system by definition. Care must be taken when adhering to values determined by this test, with regards to its use in other systems. A good correlation has been shown to exist between the experimental values determined directly and the values determined through the use of A.R.C.$_{TM}$ data, so long as the volume to surface-area ratio remains the same. In the case of the cylinder used with the 220 litre U.N. S.A.D.T. test, it is necessary to adhere to the use of identical radii. All mathematical models indicate changes in S.A.D.T. as a function of equipment parameters, and in the light of this, can provide a better understanding of the potential hazard.

Use of the Wilberforce[8] methodology for the prediction of S.A.D.T.s is similar to that of equation 40, in which the Semenov thermal model for criticality is adhered to. Although this interpretation does give a certain amount of variation in S.A.D.T., it fails to describe the situation entirely. Use of equation 38 on the other hand, based on the Frank-Kamenetskii description, improves understanding of the prevailing conditions that limit heat flow from the reacting medium, but fails to predict the overall effects successfully when large surface-area to volume ratios are involved. Predictions of S.A.D.T. made through the use of equation 35, using the Thomas criticality criterion, will always give the results with the greatest safety margin. One main failing of all three criticality models lies with their solid system bases. It has been shown however[23,24] that the thermal behaviour of a number of liquid systems approximate those of a solid. In any case, the consequence for the neglection of convective and radiative effects present in the liquid systems, is a lowering of the estimated S.A.D.T., providing improved safety limits. It is recommended that equation 35 be used in the determination of S.A.D.T. in all solid systems and most liquid systems. Equations 38 and 40 applied respectively to the cases of, systems with large surface-area to volume ratios, and well stirred low viscosity liquid systems.

System Volume (l)	System Geometry	R/L Ratio	Equation Used	S.A.D.T. (K)	C.C.S.T.L. (K)
220	Slab	0.265	40	358.4	---
220	Slab	0.265	38	379.1	401
220	Slab	0.265	35	358.2	373
220	Cylinder	0.265	40	353.0	---
220	Cylinder	0.265	38	367.6	388
220	Cylinder	0.265	45	352.5	368
220	Sphere	---	40	350.7	---
220	Sphere	---	38	362.5	383
220	Sphere	---	35	349.7	366
50	Cylinder	0.265	40	356.6	---
50	Cylinder	0.265	38	375.2	397
50	Cylinder	0.265	35	356.1	372
700	Cylinder	0.265	40	350.4	---
700	Cylinder	0.265	38	361.8	382
700	Cylinder	0.265	35	349.6	366
1500	Cylinder	0.265	40	348.7	---
1500	Cylinder	0.265	38	358.3	378
1500	Cylinder	0.265	35	347.5	364
10000	Cylinder	0.265	40	344.5	---
10000	Cylinder	0.265	38	349.5	368
10000	Cylinder	0.265	35	342.2	359
50000	Cylinder	0.265	40	341.0	---
50000	Cylinder	0.265	38	342.3	360
50000	Cylinder	0.265	35	337.5	355
220	Cylinder	0.066	40	356.3	---
220	Cylinder	0.066	38	374.7	396
220	Cylinder	0.066	35	355.9	371
220	Cylinder	0.132	40	354.7	---
220	Cylinder	0.132	38	371.1	392
220	Cylinder	0.132	35	354.3	369
220	Cylinder	0.794	40	350.6	---
220	Cylinder	0.794	38	362.3	381
220	Cylinder	0.794	35	349.8	366
220	Cylinder	1.232	40	349.4	---
220	Cylinder	1.232	38	359.7	380
220	Cylinder	1.232	35	348.1	365

Table 5 _ Predicted S.A.D.T. and C.C.S.T.L. values for the D.T.B.P. sample, as a function of the influences of volume and geometry.

Finally, it should be stressed that use of C.H.B.T.s based on equation 40 (and hence the Semenov model), do not predict the presence of C.C.S.T.L.s. Consequently, systems that will self-heat auto-acceleratively irrespective of the environmental temperature are not detected. Use of

equations 35 and 38 provides such limits, with information on possible evasive action that in certain cases can bring about the control of an exothermic runaway scenario.

Nomenclature

A   Arrhenius frequency factor

C   Concentration of sample

C_0 Initial concentration of sample

C_P Specific heat capacity at constant pressure

C_V Specific heat capacity at constant volume

D   Dimensionless factor

D_0 Initial estimate of D

E   Activation energy

K   Thermal conductivity of sample

k   Reaction rate constant

k^* Pseudo-rate constant

l   Height / width of vessel geometry

m   Sample mass

M_{RMM} Relative molecular mass

n   Reaction order

Q   Enthalpy of reaction per unit mass

q   Power per unit volume

R   Universal gas constant

r   Radius / thickness of vessel geometry

r_t Self-heat rate

r_ϕ Self-heat rate _not_ corrected for thermal inertia

S   Surface area available for heat transfer for vessel

T   Absolute temperature

T^* Time line / T.M.R. line intersection temperature

T_0 Central temperature for vessel / Onset temperature of A.R.C. data.

T_A Ambient / environment temperature equivalent to S.A.D.T.

T_{A0} Initial estimate for T_A

T_F Final temperature of A.R.C. data.

T_I Temperature determined by r_{tI}

T_L Temperature determined by r_{tL}

T_{NR} Temperature of no return

T_S Surface temperature of vessel

t   Time

t_m Time to maximum rate

U   System heat transfer coefficient

V   Vessel volume

x   Distance from centre of mass

y   Dimensionless length

Greek Symbols

α Biot number for M.E. system

τ Shape factor for vessel

δ Frank-Kamenetskii number

ε_4 Dimensionless Frank-Kamenetskii constant

Θ Dimensionless temperature rise

Θ_0 Θ at centre of mass

Θ_x Θ at surface of vessel

ρ Density of sample

ϕ Thermal inertia factor

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Figures
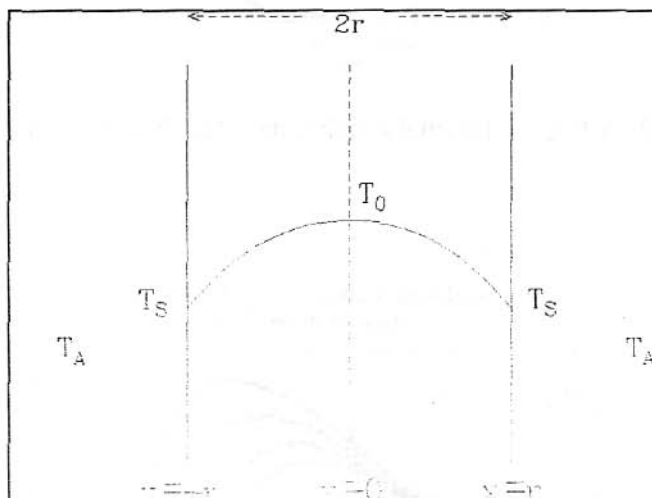
Fig 1. Temperature distribution in a self-heating slab.

Thermal Stability Test Data
Di-tert Butyl Peroxide
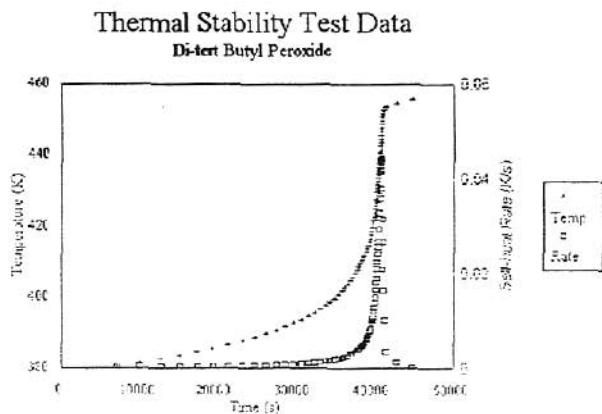
Fig 2. A.R.C.$_{TM}$ thermal stability data for di-tert butyl peroxide.

Ambient Temp. - System Temp.
Thomas Criticality Model
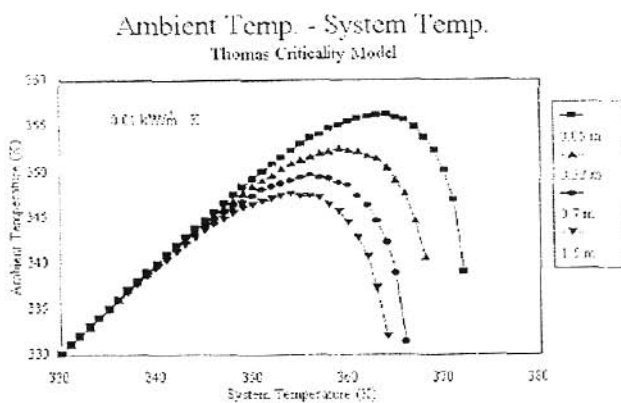
Fig.3. CHBT profiles and SADTs for different cylindrical volumes.
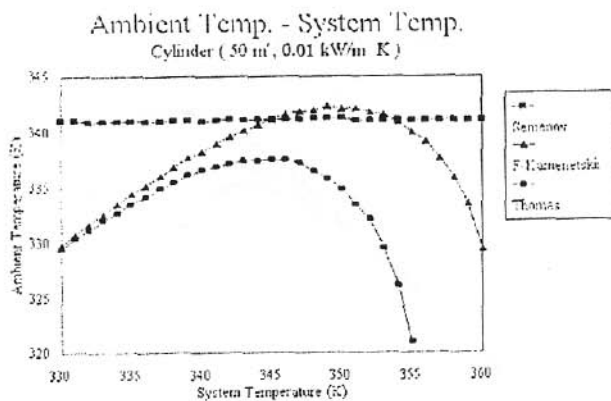
Fig.4. Differences in CHBT profiles and SADTs on the basis of criticality model.
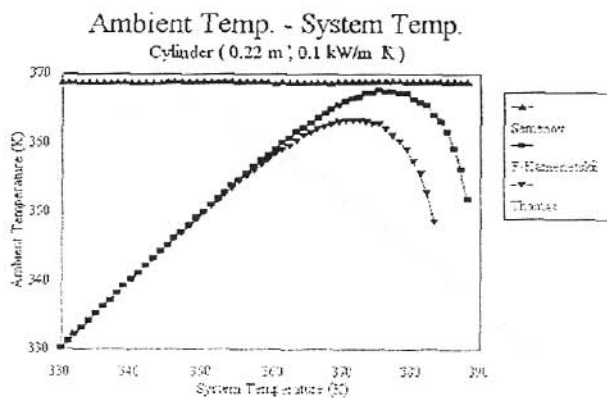

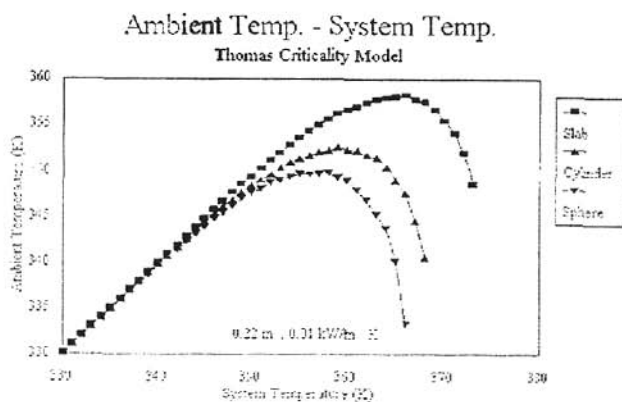Fig.5. Differences in CHBT profiles and SADTs as a result of criticality model.

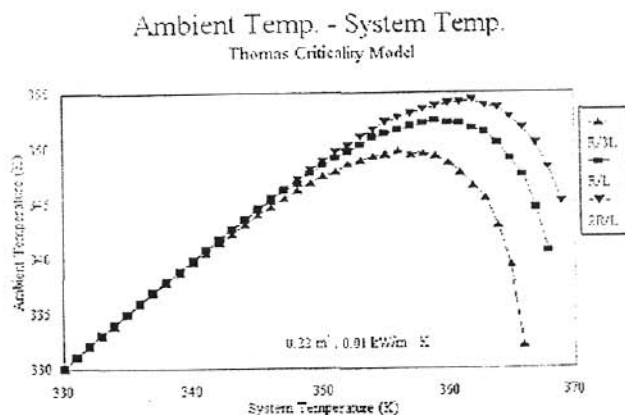Fig.6. CBHT profile and SADT prediction for various geometries.

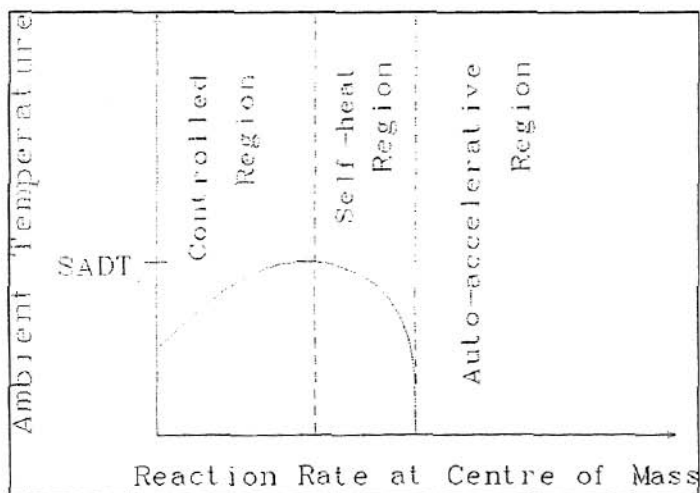
Fig.7. CHBT profile and SADT prediction for various R/L ratios.

Fig.8. F-Kamenetskii and Thomas criticality model predictions summary.