

Title:

Bulk Thermal Stability Characterization via the SBAT Apparatus

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Abstract:

The temperature at which a substance ignites is a key parameter for safety and design. That temperature, often called the auto-ignition temperature, is not an intrinsic property but depends on the environment in which the substance is found. Energetic substances are unstable and decompose at increasing rates with increasing temperature. Heat is generated by the decomposition of the substance and that heat can then be lost to the surroundings.

An energetic substance can rapidly decompose beginning when the rate of heat generation exceeds the rate of heat loss. The temperature at which the onset of ignition occurs depends on the rate of heat loss which is a strong function of its surroundings. The auto-ignition temperature can be found for conditions where heat loss from the sample is high (e.g. using a Differential Scanning Calorimeter or DSC) or when the heat loss is low (e.g. using an Accelerating Rate Calorimeter or ARC). The auto-ignition temperature can differ by more than 50°C for these two conditions.

Both the amount of insulation and the heating rate can affect the auto-ignition temperature with higher heating rates or less insulation yielding a higher observed temperature of auto-ignition. The Simulated Bulk Auto-Ignition Test (SBAT) apparatus has a high degree of insulation and a low heating rate that yields onset ignition temperatures very close to the accurate heat-wait-search method used by the extremely well insulated ARC apparatus with several advantages. This paper discusses those advantages (including cost, sampling time, and ability to test multiple samples) and use of the SBAT to determine critical temperatures and material compatibility. Work completed at Safety Management Services, Inc. in collaboration with the Tooele Army Depot and ATK.

Presenter's Biography:

Clint Guymon is an engineer at Safety Management Services, Inc. with a doctorate degree in chemical engineering from Brigham Young University. He has experience in

molecular dynamics, heat transfer and kinetics modeling, process hazards analysis, and energetic materials testing and classification.

Technical Session Paper:

Introduction

The auto-ignition temperature (AIT) of a substance is not an intrinsic property. A substance can have many different auto-ignition temperatures depending on the environment in which it is found. Specifically, the kinetic parameters (intrinsic properties of the substance) couple with the heat transfer characteristics (defined by the environment or substance configuration) resulting in non-ignition, ignition after a period of time has elapsed, or immediate ignition.

The AIT is frequently used to assess the thermal stability of a substance. From this value, storage and transportation assessments are often made. Many different types of devices have been used to determine an auto-ignition temperature of energetic materials including Differential Scanning Calorimeter (DSC), Thermal Gravimetric Analyzer (TGA), Accelerating Rate Calorimeter (ARC), and Simulated Bulk Auto-Ignition Test Apparatus (SBAT). Each of these possesses different heat transfer characteristics and confinement conditions and thus gives different AIT values.

This paper discusses the principles that determine the auto-ignition temperature including level of sample insulation, heating rate, confinement, and sample size. We present a simple theoretical model that shows the effects of heating rate, heat transfer, and confinement on the AIT and the time to ignition at a given static temperature. Recent results are also presented comparing the auto-ignition temperature for multiple substances found using the DSC, SBAT, and ARC. We first discuss the principles that govern the AIT, then the experimental results, and lastly highlight the advantages of the SBAT piece of equipment.

Principles Reflected in the Auto-Ignition Temperature

Energetic substances are unstable and react with increasing violence as the temperature and pressure are increased. The temperature and pressure are determined by the transfer of heat to and away from the sample and the level of confinement. The transfer of heat can affect the sample temperature resulting in a response in the rate of reaction; likewise, the level of confinement determines the pressure under which the sample reacts. Most energetic materials have a rate of reaction that is strongly dependent on the pressure.

The auto-ignition temperature is typically found by placing a sample in a test cell and then raising that temperature while recording the temperature the sample produces significant amounts of heat. As mentioned in the introduction, several variables can significantly affect the value of the auto-ignition temperature. As will be shown (experimentally and theoretically) increasing the heat rate, increasing the level of heat

transfer (heat is easily lost from the substance), or reducing the confinement (pressure around sample doesn't increase during testing) can each result in the increased value of the observed AIT. The sample size affects the level of heat transferred from the substance in that a smaller sample allows for greater heat loss (the resistance to heat loss is reduced).

A simple model can be used to easily and independently change the variables mentioned previously and observe the effects. The model is of a sample in a constant volume container (isochoric) where heat can flow into and out of the sample container. The sample reacts according to the Arrhenius equation with a pressure power function. The energy and mass balance equations are given below. Equations are dimensionless to allow for simple comparisons. Parameters used for de-dimensioning are standard temperature, T^θ , for temperature, total mass, m , for mass, and $(C_v \cdot m)/h$ for time (ratio of the product of the constant volume heat capacity and mass to the heat transfer coefficient). Simplifying assumptions were made including constant mass (where one gram of sample reacts to form one gram of gas), sample and gas have the same heat capacity, gas is ideal, and immediate thermal equilibrium exist between sample and gas.

$$\frac{dT^*}{dt^*} = -\frac{\Delta U}{T^\theta \cdot C_v} \cdot \frac{dm_s^*}{dt^*} - (T^* - T_{amb}^*); \quad (\text{Eq.1a})$$

$$-\frac{dm_s^*}{dt^*} = \frac{dm_g^*}{dt^*} = \frac{C_v \cdot k_o}{h} \cdot (P^*)^\alpha \cdot e^{-E_a / (R \cdot T^* \cdot T^\theta)}; \quad (\text{Eq.1b})$$

where T is temperature of the sample and gas, t is time, m is mass, R is the gas constant, P is pressure inside the sample container, α is the pressure exponent, ΔU is the energy of reaction, k_o is the pre-exponention factor of the Arrhenius equation, E_a is the activation energy, subscript amb indicates ambient, and subscripts s and g represent sample and gas, respectively. Dimensionless variables are indicated with an asterisk, all other parameters are constant. The dimensionless pressure is equivalent to the product of the dimensionless temperature and the ratio of the mass of gas to the original mass of gas.

The above equations were integrated to yield the temperature of the sample using the Midpoint Method (a second-order Runge-Kutta method) [1]. Two cases were investigated with the model: (1) the ambient temperature is increased until the sample is consumed, or (2) the ambient temperature is held at a given value and the time required for the sample to be consumed is recorded. Figure 1 shows the temperature traces for different conditions; increasing the heat loss, increasing the heating rate, or decreasing confinement increases the value of the AIT. Figure 2 shows the elapsed time prior to sample consumption for different conditions; the time to consumption

decreases dramatically as the heat loss is reduced or the sample is confined. The base case referenced in each figure is where the grouping of constants in Eq. 1a is 40, the grouping of constants in Eq. 1b is 5, the grouping of constants in the exponential in Eq. 1b is 11, the initial dimensionless ambient temperature is 0.5 (for Figure 1 only, for Figure 2 this varies), the dimensionless ambient heating rate is 5E-04 (for Figure 1 only, for Figure 2 this is zero), the dimensionless initial mass of gas is 0.01, the dimensionless time step is 0.2, and the pressure exponent, α , is 0.

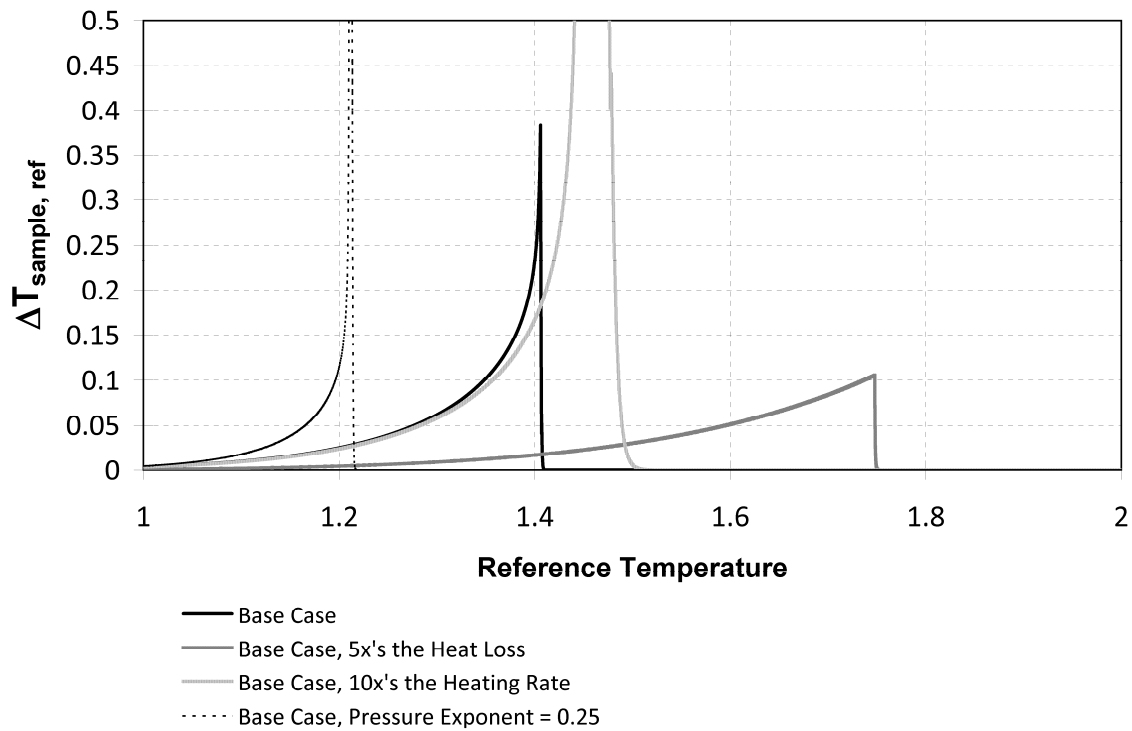


Figure 1 Exotherm plots for different conditions. Results show that increasing the heat loss, increasing the heating rate, or decreasing confinement increases the value of the AIT. The reference temperature is the temperature of a non-reacting equivalent system. The ordinate is the difference between the temperature of the sample and reference with a positive value indicating an exotherm. Temperatures are dimensionless (see text).

In both Figure 1 and 2, the effects of confinement were approximated by varying the pressure exponent, α , from zero (no confinement) to 0.25 (sample is confined). When α is zero, pressure is not a factor in the rate equation (see Eq. 1). If the gasses generated during sample combustion escape the sample compartment (or gasses aren't produced during combustion) then the rate of reaction is based primarily on the sample's temperature, whereas if the gasses don't escape, the pressure builds and the rate of reaction can drastically increase (as the rate of reaction for most energetic materials is strongly dependent on the pressure).

The different heights of the exothermal peaks in Figure 1 are a function of the heat transfer rate to and from the sample. In each case shown, the same amount of mass reacts giving off the same amount of energy; however, the amount of energy transferred into or out of the sample varies depending on the heat transfer which is reflected in the observed sample temperature.

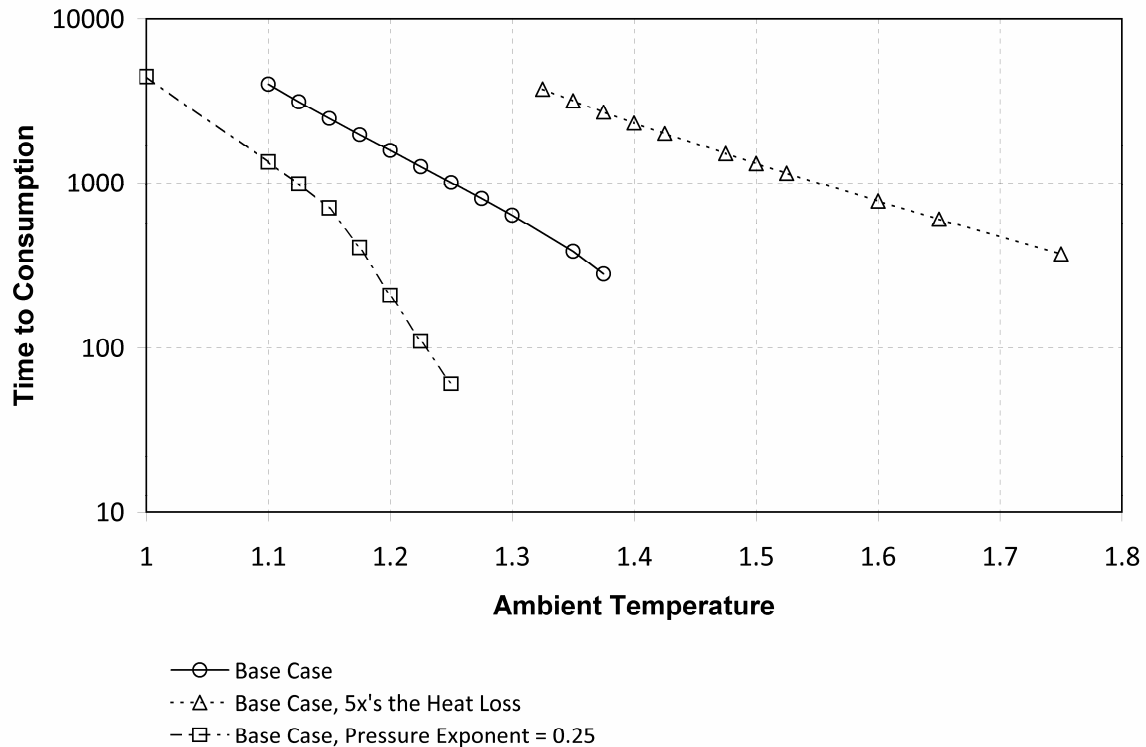


Figure 2 Time to sample consumption for different conditions. Results show that the time prior to sample consumption decreases dramatically as the heat loss is reduced or the sample is confined. Ambient temperature and time to consumption are dimensionless (see text).

The effects detailed using this simple model are invaluable in understanding the applicability of AIT values found from different pieces of equipment as each method used to determine an AIT value or time to initiation can be categorized by the level of heat loss (or insulation value), heating rate, and confinement. This understanding can also be used in determining storage configurations and safety measures to put in place to prevent a large scale cook-off event.

Experimental Comparison of the AIT with Different Equipment

The previous section showed with a simple model the effects of heat transfer, heating rate, and confinement on the value of the AIT and the sample's time to ignition. This section reviews the characteristics of three methods used to determine the AIT and time to ignition. The three pieces of equipment are the DSC, SBAT, and ARC. Table 1 shows the characteristic differences between the three pieces of equipment.

Table 1 Characteristic differences between the DSC, SBAT, and ARC.

Test	Sample Size, grams	Heat Rate, °C/min	Insulation, level	Confinement, level	Temperature Sense Position*
DSC	0.001 – 0.03	20	Low	Medium	External
SBAT	2.0 – 5.0	0.2	High	Low	Internal
ARC	0.3 – 3.0	0.1	High	High	External

*Relative to sample

As seen in Table 1, the ARC has the lowest heating rate, the highest level of insulation and confinement. The ARC is expected to give the most conservative value for the AIT and the shortest time to ignition. Since the DSC has the highest heat transfer rate (lowest level of insulation and smallest sample size), and the highest heat rate, the AIT determined with the DSC is significantly higher than the ARC or SBAT. A thermogravimetric analyzer (TGA) would be expected to give a similar AIT value to that of a DSC due to the similar levels of heat loss and heating rate.

Table 2 shows the results for multiple energetic samples that were tested on a DSC, SBAT, and ARC. The DSC temperatures ranged from 29°C to 74°C (91°C for BKNO₃ at a heating rate of 20°C/min) above the AIT temperature determined by the ARC. The SBAT temperatures varied from those found by the ARC by -1°C to 15°C. The average deviation from the ARC was +8.6°C and +57°C for the SBAT and DSC respectively [2].

The agreement between the ARC and SBAT AIT temperatures is very close. It's expected that the difference between the two would be nearly identical if the sample in the SBAT could be confined, although some substances are not pressure sensitive for which the AIT values would better agree. Confining gram quantities of energetic material presents an operational and safety challenge. When that large of a sample in the ARC is run, the sample temperature and pressure is monitored very closely and active cooling begins immediately once self heating begins; otherwise damage to the equipment occurs.

Although not presented here, several different substances have been tested by the ARC, SBAT, and DSC to determine the time to ignition at temperatures below the AIT value [2]. Determination of the time to ignition at temperatures below the AIT can indicate the safe storage time at a given temperature. Unfortunately, the lower the temperature, the time required for testing increases dramatically. Thermal testing for extended periods can present unreasonable challenges.

For some substances, using the DSC and SBAT were less successful in determining a time to ignition at temperatures below the AIT value than using the ARC due in part to the long sampling times required. The confinement of the sample in the ARC apparatus aids in sensing a rise in the pressure upon reaction. The confinement of the sample

increases the rate of reaction and thus the time to ignition or time to sample consumption is reduced, as shown by the model results in Figure 2.

Table 2 Exotherm Temperatures (°C) from ATK Study [2]

Material	ARC	SBAT	DSC
Nitroglycerine Sample	115	124	178
Liquid Nitrate Ester Sample	115	117	171
Double Base Propellant Sample	120	131	184
Sample Liquid Containing Both Nitramine and Nitrate Ester Groups	125	135	185
Nitrate Ester Propellant Sample	125	136	171
Nitrate Ester Polyether Propellant Sample	125	135	169
Nitrate Ester Polyether Propellant Sample	126	135	168
Organic Azide Sample	150	164	224
Aliphatic Nitrocompound Sample	165	172	225
AP Composite Propellant Sample	180	195	248
Pyrotechnic Sample	185	184	231
RDX Sample	189	195	218
BKNO ₃ Sample	277	-	368*

*20°C/min ramp rate

Note: the temperature at which the SBAT exotherm is reported is when the temperature deviated by greater than 1.1°C above the baseline; the DSC temperature reported is the onset temperature (point of intersection of a line drawn tangent to the steepest slope of the curve with the baseline). The ARC temperatures were determined using a “heat-wait-search” scheme while heating at an approximate rate of 0.1°C/min. The DSC and SBAT samples were heated at a constant 10°C/min and 0.22°C/min, respectively. Average deviation from ARC for SBAT and DSC is +8.6°C and +57°C respectively.

Advantages and Application of the SBAT

Although the ARC is likely to give the most conservative AIT value, simulating the thermal response of a large mass of energetic material, there are some disadvantages to its use. Some of those include its high operating cost, long sampling time, and slow turnaround. The SBAT apparatus was developed at Thiokol (now ATK) by David Smith [6] to drastically reduce the sampling time, sample turnaround, and cost while still maintaining an accurate determination of bulk material behavior. The SBAT can test 5 samples simultaneously and the experimental AIT temperature found is only approximately 9°C above the AIT value of the ARC. The SBAT has a lower operating cost than the ARC, is more robust, and can test multiple samples simultaneously.

The SBAT apparatus consists of an aluminum block with 5 highly insulated ports for sample testing (1 port is used as a reference). Three 600 W cartridge heaters located in the center of the aluminum block heat the samples. Thermocouples sense the temperature of the heated SBAT block, the reference sample, and each test sample.

Each individual sample compartment is highly insulated. Thermocouples are inserted into the center of the 3-5 gram test and reference samples. The temperatures are tracked and used to identify exothermic or endothermic activity of the sample. The reference sample is typically silicone. An insulating cap covers the sample compartment to limit the heat lost to the surroundings.

Figure 3 shows an SBAT trace for RDX. The exotherm temperature of 384 °F (195°C) is taken where the exotherm begins to move above the baseline. The reason that the sample temperature isn't exactly equal to the reference temperature during times of purely sensible heating of the sample is due in part to differences in the heat capacity and heat transfer coefficients between the sample and reference materials.

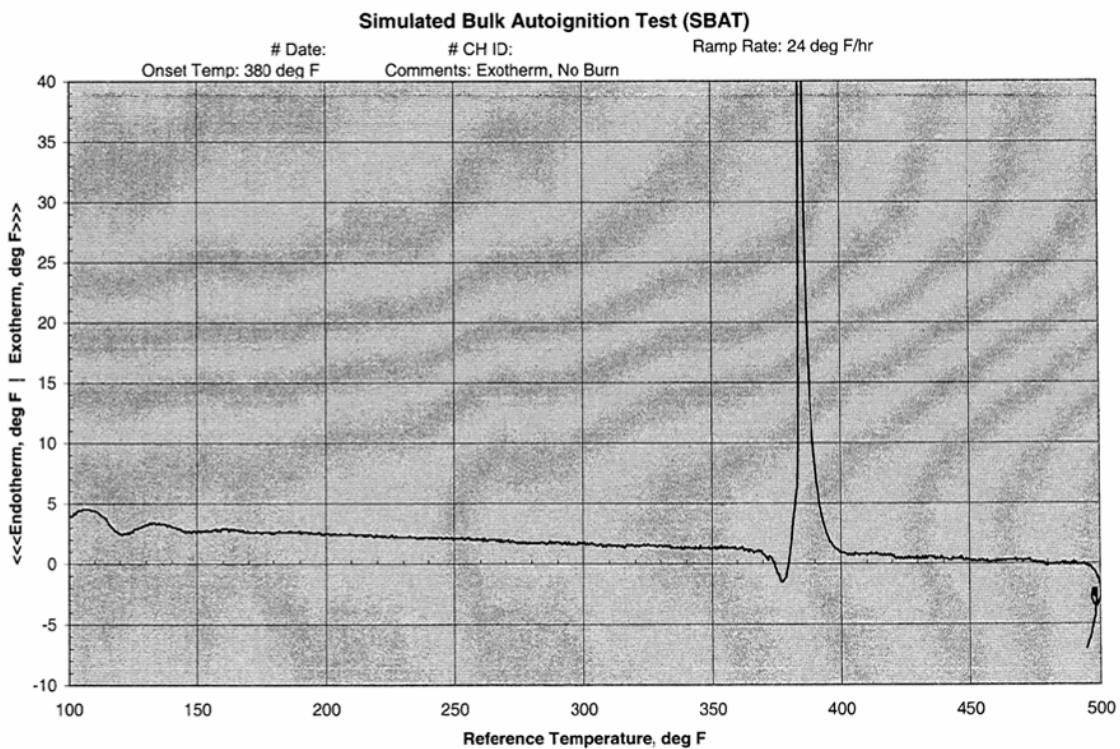


Figure 3 Example RDX scan with the SBAT. The ordinate is the difference between the sample temperature and the reference. Positive values indicate exothermic activity.

In addition to determining an AIT value that represents how a bulk mass of material could be expected to respond to a thermal impetus, the SBAT can be used to determine the expected time to ignition at a given temperature for a given substance. Isothermal SBAT runs are performed at values near (but slightly lower than) the determined AIT. The time to ignition for each tested temperature can be used to estimate the time to ignition at a different temperature; multiple methods exist to extrapolate the ignition time for a different temperature [2-5].

Compatibility of multiple substances with an energetic material can readily be studied with the SBAT due to its multiple sampling ports. A compatible material would be one where the bulk AIT found with the SBAT or the time to ignition is not significantly changed.

Summary and Conclusions

The auto-ignition temperature of a substance is not an intrinsic property. The auto-ignition temperature and time to ignition at a given temperature are strong functions of the heat transfer rate to and from the sample as well as the confinement of the sample. Well insulated substances have lower auto-ignition temperatures than those that are not (they also have a shorter time to ignition at a given temperature). Confinement of the sample can also lower the auto-ignition temperature (and reduce the time to ignition). Rapid heating rates that may be used to determine the auto-ignition temperature can result in observing a higher auto-ignition temperature over that found with slower heating rates.

Auto-ignition temperatures of multiple energetic substances of different chemical types show that the DSC gives an auto-ignition temperature that is 57°C elevated over that determined by the ARC (where in the ARC the sample is well insulated and confined with a slow heating rate). Using an auto-ignition temperature determined by a DSC may be appropriate for conditions where the mass is small and not thermally isolated; however using that temperature to determine bulk storage conditions and safeguards may present unforeseen hazards.

The SBAT apparatus has many advantages over other pieces of equipment typically used to determine an auto-ignition temperature. The number of sampling ports allows for rapid processing and the high level of insulation and slow heating rate yield an AIT that matches well the temperature determined by the more time intensive and sensitive ARC. The SBAT matches the ARC within an average deviation of only +9°C. The SBAT is also not as readily susceptible to damage.

References

- [1] D. V. Griffiths and I. M. Smith, *Numerical Methods for Engineers: a Programming Approach*. (CRC Press, Boca Raton, 1991), pp. 218.
- [2] M. W. Lesley, "Shelf Life Prediction Model Development," ATK Doc. No. TR028565 (2010).
- [3] M. L. Hobbs, W. B. Wentz, and M. J. Kaneshige, "PETN Ignition Experiments and Models," *Journal of Physical Chemistry A* **114** (16), 5306-19 (2010).
- [4] J. Selesovsky, "Thermal Loading of Explosives – Finite Difference Method with Time Step Reduction," *Journal of Hazardous Materials* **174** (1-3), 289-294 (2010).
- [5] K. S. Jaw, and J. S. Lee, "Thermal Behaviors of PETN Base Polymer Bonded Explosives," *Journal of Thermal Analysis and Calorimetry* **93** (3), 953-957 (2008).
- [6] L. D. Smith, "Easily Test Thermal Stability and Detonability," *Chemical Engineering Progress* **90** (9), 67-72 (1994).

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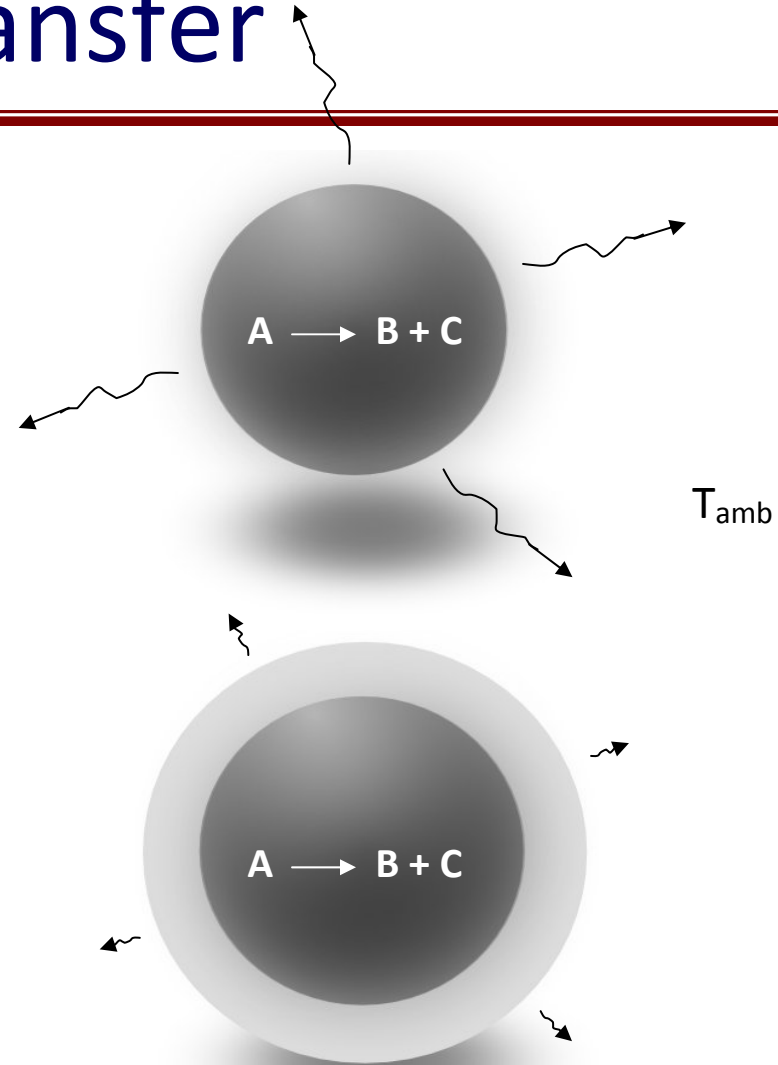
Bob Ford, President

Auto-Ignition Temperature (AIT)

- Used to characterize thermal stability
- Higher AIT can indicate increased thermal stability
- Many methods available: DSC, TGA, SBAT, ARC
- AIT not intrinsic property, function of
 - Heat transfer to/away from substance
 - Confinement
 - Heating rate

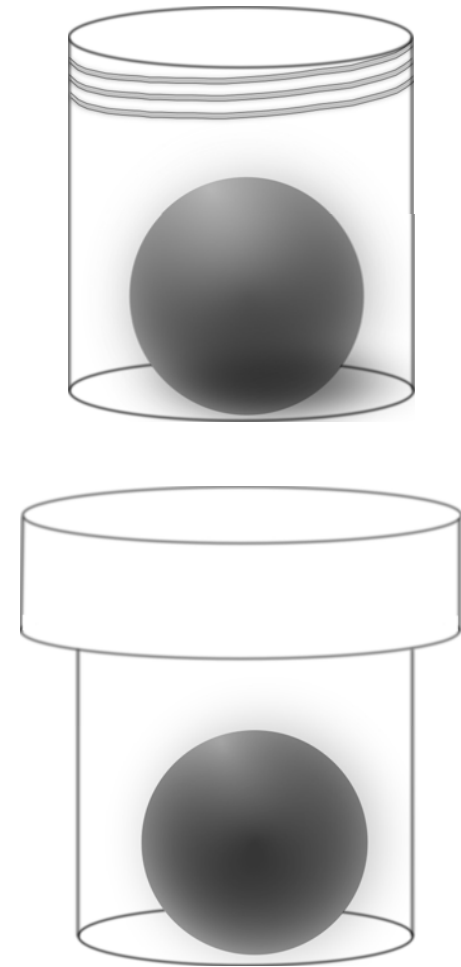
Heat Transfer

- Heat generated inside due to reaction
- Heat generation rate depends on temperature
- Heat leaves/enters the substance depending on surrounding conditions
- Greater insulation = lower AIT value and shorter time to ignition

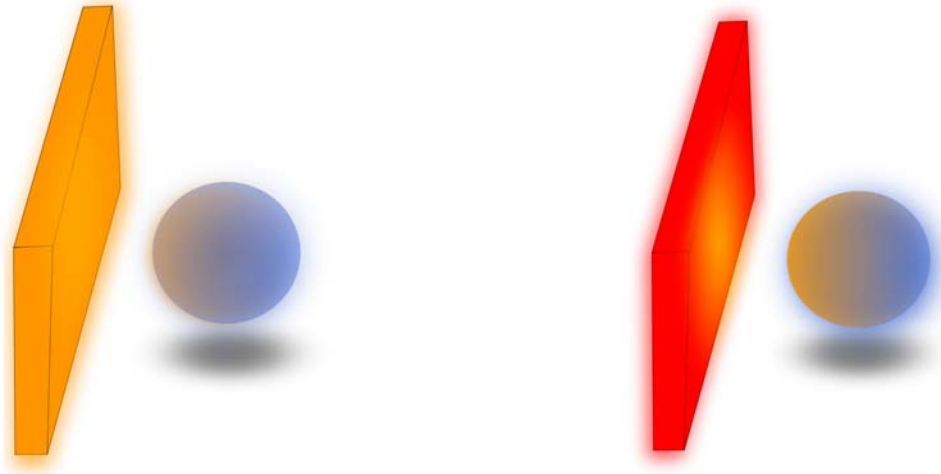


Confinement

- Rate of reaction for most energetic substances is strong function of pressure
- $r = k \cdot \exp(-E/RT) \cdot P^\alpha$
- Increased confinement = increased rate of reaction = lower AIT value, shorter time to ignition



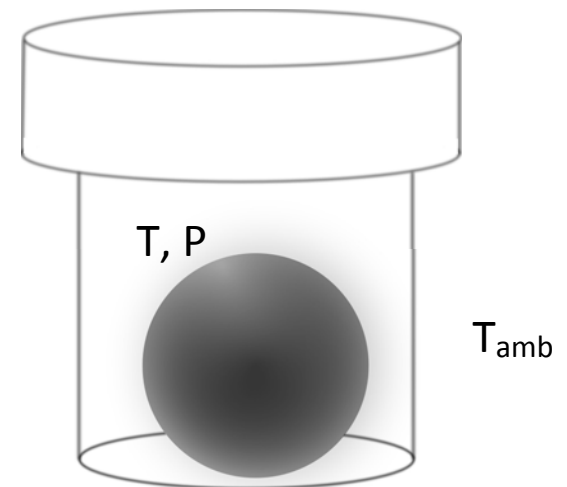
Heating Rate



- Increased rate of heating = higher observed AIT
- External temperature observed to be higher than internal temp. upon ignition
- Time not allotted for heat generation at given temp.

Simple Theoretical Model

- Model of constant volume container (isochoric)
- Heat flows into and out of container
- Sample reacts according to Arrhenius equation with pressure power function
- Pressure sensitivity, heat transfer, heating rate can be independently varied



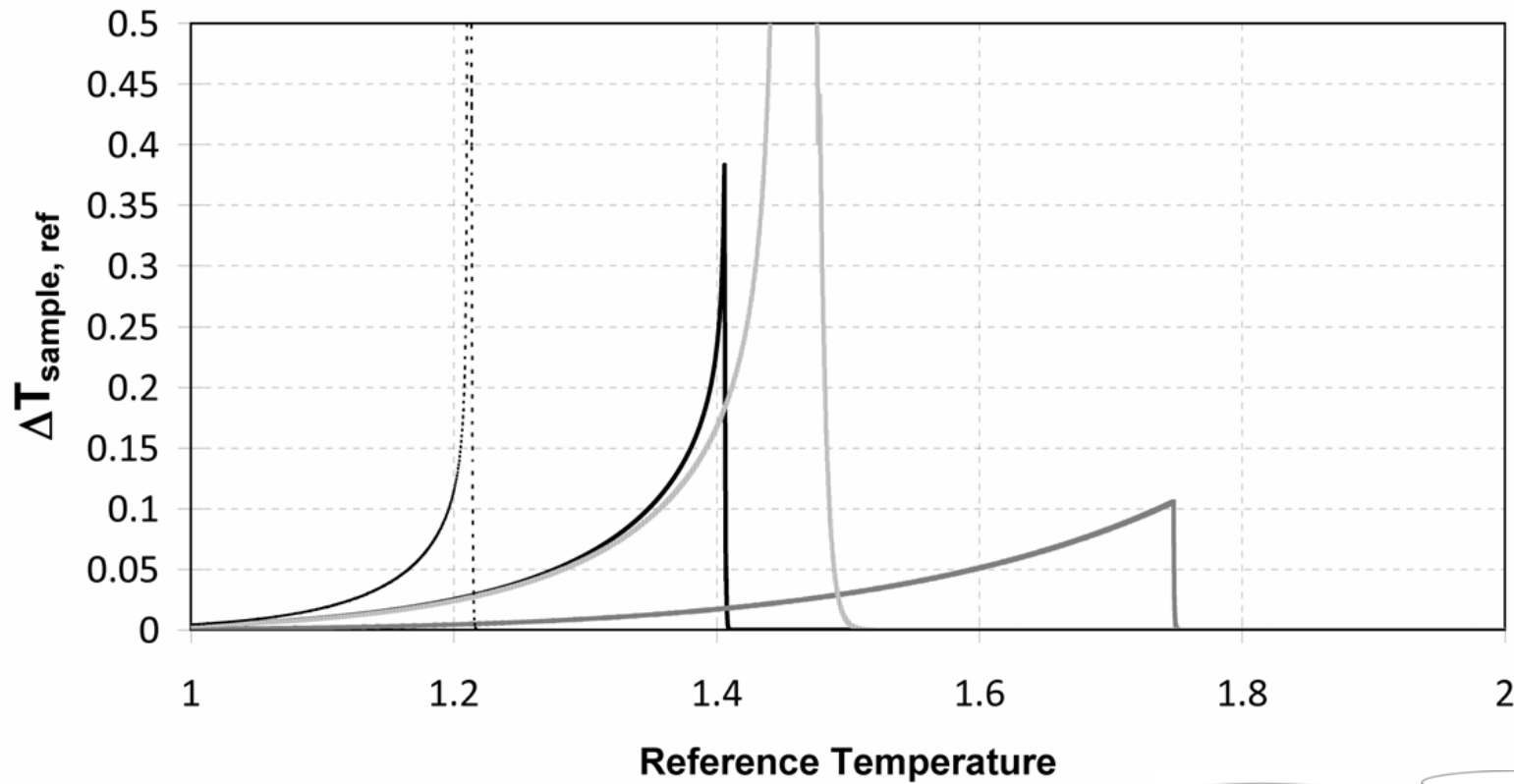
Energy and Mass Balance Equations

$$\frac{dT^*}{dt^*} = -\frac{\Delta U}{T^\vartheta \cdot C_v} \cdot \frac{dm_s^*}{dt^*} - (T^* - T_{amb}^*); \quad (\text{Eq.1a})$$

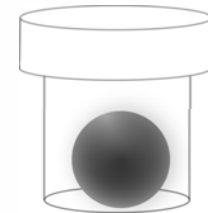
$$-\frac{dm_s^*}{dt^*} = \frac{dm_g^*}{dt^*} = \frac{C_v \cdot k_o}{h} \cdot (P^*)^\alpha \cdot e^{-E_a / (R \cdot T^* \cdot T^\vartheta)}; \quad (\text{Eq.1b})$$

- Constant mass: 1 mass of substance reacts to form 1 mass of gas
- Other assumptions: constant and equivalent heat capacity for substance and gas, ideal gas, immediate thermal equilibrium between substance and gas
- Equations integrated with Midpoint Method

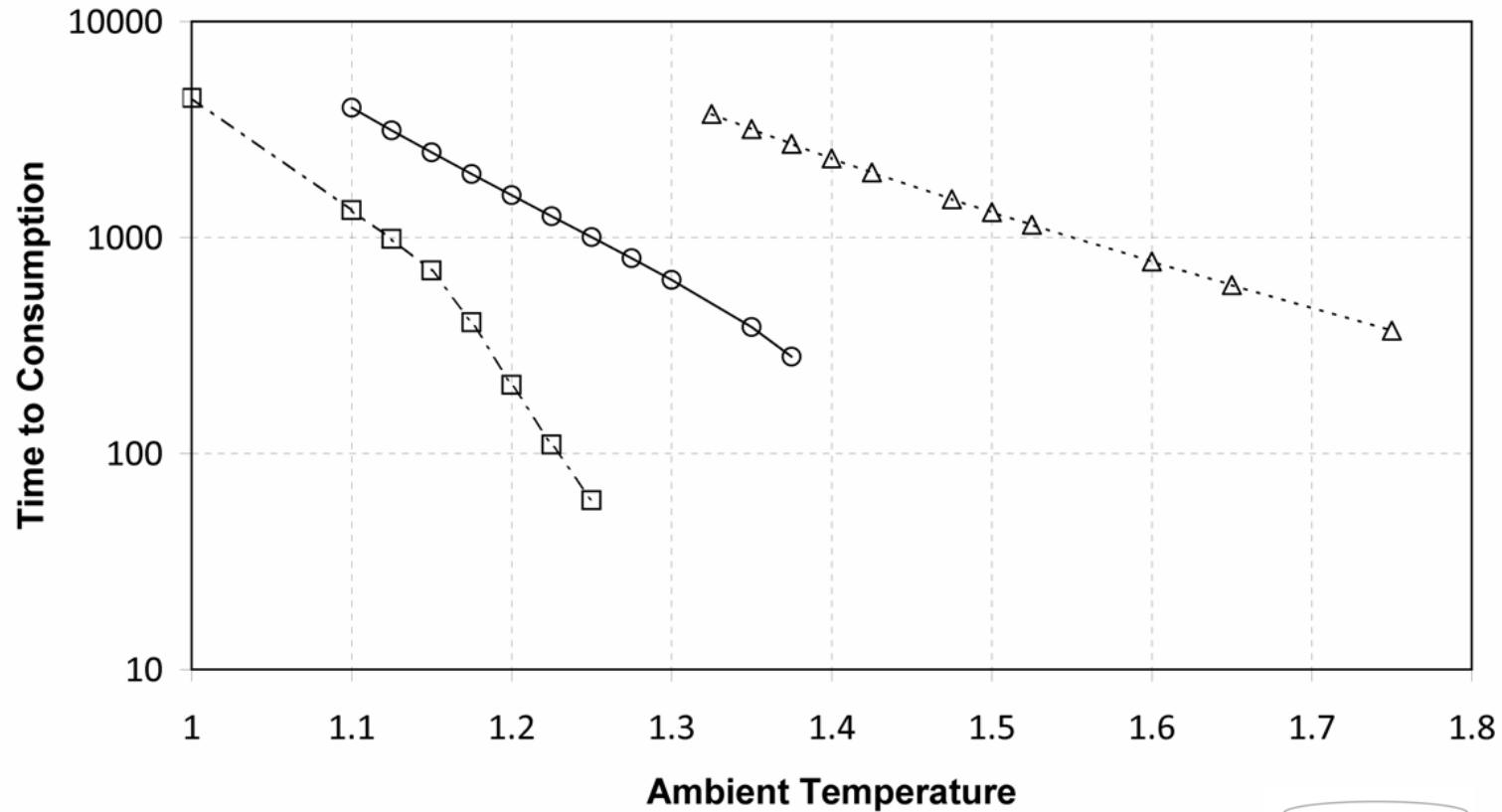
Model Results



- Base Case
- Base Case, 5x's the Heat Loss
- Base Case, 10x's the Heating Rate
- Base Case, Pressure Exponent = 0.25



Model Results Cont.



- Base Case
- △·- Base Case, 5x's the Heat Loss
- Base Case, Pressure Exponent = 0.25



DSC, SBAT, and ARC Comparison

Table 1 Characteristic differences between the DSC, SBAT, and ARC.

Test	Sample Size, grams	Heat Rate, °C/min	Insulation, level	Confinement, level	Temperature Sense Position*
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SBAT	2.0 – 5.0	0.2	High	Low	Internal
ARC	0.3 – 3.0	0.1	High	High	External

*Relative to sample

- Multiple substances of different chemical makeup show DSC varies by +57°C whereas the SBAT varies significantly less at +9°C above ARC

DSC, SBAT, and ARC AIT Temperatures

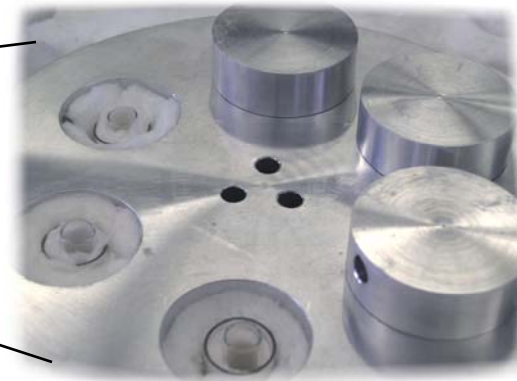
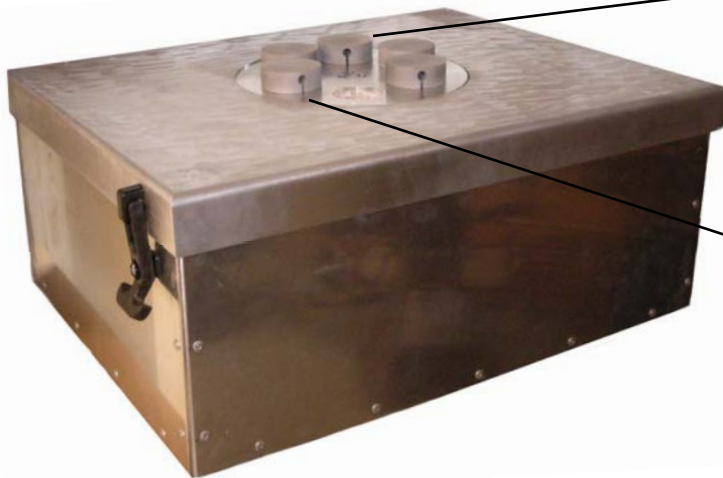
Table 2 Exotherm Temperatures (°C) from ATK Study [Lesley, MW; Shelf Life Prediction Model Development; Doc. No. TR028565, ATK, 2010.]

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BKNO3 Sample	277	-	368*

*20°C/min ramp rate

Advantages of SBAT

- Multiple robust sampling ports
- Low cost, easy setup/cleanup
- Large sample sizes
- Sample temperature directly measured
- Conservative determination of reaction temperatures



SBAT Applications

- Determination of conservative auto-ignition temperature (bulk AIT value)
- Determination of time to ignition at temperatures just below AIT (isothermal run mode)
- Conservative compatibility testing

Summary

- Auto-ignition temperature function of
 - Heat transfer
 - Confinement
 - Heating rate
- AIT values determined by SBAT approximate well bulk material's thermal response
- SBAT has many advantages including cost, sample size, and multiple sampling ports

END

