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SENSITIVITY OF PROPELLANTS:
THE ADIABATIC SELF - HEATING OF AHH, ARCITE 358 AND ANP 2639AF (C)

15 JANUARY 1959
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SENSITIVITY OF PROPELLANTS:
THE ADIABATIC SELF-HEATING OF AHH, ARCITE 358 AND ANP 2639AF

Prepared by:
Adolph B. Amster

ABSTRACT: The study of the stability and sensitivity of propellants to
detonation requires a knowledge of the energy of activation and the frequency
factor of the chemical reactions involved.

The method chosen by this Laboratory to perform such studies involves
the observation of temperature (as a function of time) in a sample which is
allowed to self-heat adiabatically (3, 8). Dr. A. Robertson and Mr. D. Gross,
of the National Bureau of Standards, under contract to this Laboratory, have
made such measurements on AHH, Arcite 358, and ANP 2639AF. From the data
obtained, and values for the heat capacity and thermal conductivity, they have
calculated not only the aforementioned kinetic data but also, for any tempera-
ture, that size sphere of the material for which the rate of heat evolution
within the sample becomes greater than that lost to the environment, leading
to inevitable explosion.

Results, including anomalous behavior of ANP 2639AF, have been evaluated
at this Laboratory and are reported and discussed herein.
This investigation was conducted under Task NOL-323, Polaris Program on the Sensitivity of Solid Propellants. NavOrd 3906, Key Problems in Explosives Research and Development, Part I, cites tests for sensitivity as Key Problem 7 under section 7.7. This investigation had two objectives: first, to determine thermal and kinetic properties needed for theoretical treatments of sensitivity; second, to obtain some idea of the critical size of propellant grains. Above the critical size the propellant grain is susceptible to spontaneous combustion.

MELL A. PETERSON
Captain, USN
Commander

[Signature]

for

ALBERT LIGHTBODY
By direction
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SYMBOLS

\( B_c \) = critical explosion radius of a sphere
\( c \) = heat capacity per unit mass
\( E \) = energy of activation of reaction
\( \Delta H \) = molar heat of decomposition
\( K \) = reaction rate = \( Ze^{-E/RT} \)
\( \lambda \) = thermal conductivity
\( M \) = molecular weight
\( Q \) = heat produced per mole per unit time
\( q \) = \( Q/M \)
\( \rho \) = density
\( T \) = absolute temperature (\(^\circ\)K)
\( T_c \) = critical temperature
\( T_e \) = environment temperature
\( T_i \) = initial temperature
\( T_s \) = surface temperature
\( t \) = time
\( t_e \) = time to explosion
\( Z \) = "collision" factor
INTRODUCTION

The study of the hazards involved in the handling of propellants inevitably leads to a requirement for the thermal and thermochemical properties of the systems involved. Such data find application to studies of the mechanism of thermal decomposition and of the transition from deflagration to detonation and to evaluation of the hazards associated with the storage and use of propellant systems.

The application of these data to thermal decomposition studies is obvious and needs no discussion here. Problems associated with the transition from deflagration to detonation require for their solution reasonably accurate values for rates of chemical reactions under various severe conditions of temperature and pressure. Given sufficient information it now appears from the work of Macek and Gipson (1, 2) that the appearance of the shock wave associated with this transition can be predicted with reasonable success. Finally, the kinetic data are immediately applicable to problems of major concern to the missile industry: storage and use. It is to this aspect of sensitivity that this paper is directed. A review of the principles involved is in order.

THERMAL PROPERTIES
AND THEIR RELATION TO STORAGE PROBLEMS (3)

The temperature of any system will rise when the heat lost through its surface is less than that being transmitted to it or generated within it. In the case of a system, such as an explosive or propellant which undergoes spontaneous exothermic decomposition the situation can get rapidly out of hand because of the nature of the decomposition rate equation in which the heat produced per unit time, \( Q \), bears the familiar Van't Hoff relation to the temperature:

\[
Q = (\Delta H) Z e^{-E/RT}
\]

It is seen that a rising temperature causes an exponential increase in the rate of reaction and, hence, in the heat produced per unit time. Inasmuch as the heat lost is, in general, determined by Newtonian (linear) cooling laws, the temperature rise within the sample soon proceeds at a dramatic rate, leading very rapidly to explosion. For a given system there exists some critical temperature above which this self-heating, as it is termed, will proceed spontaneously, and the time required \( (\tau_e) \) for explosion to occur will be determined by the difference between the environment temperature \( (T_e) \) and this critical temperature \( (T_c) \). For \( T_e < T_c \) there will, of course, be no
exploration; for $T_e > T_c$, $T_e$ will decrease with increasing values of $T_e - T_c$.

In order to predict the behavior of a sample one needs to know the rate at which heat will be lost from the system and the rate at which heat is produced within. The balance between these two factors is expressed in the generalized heat equation:

$$-\lambda \nabla^2 T + \rho c \frac{dT}{dt} = \rho Q K$$  \hspace{1cm} (1)

If the system can be made adiabatic, the heat loss term $-\lambda \nabla^2 T = 0$ and the temperature rise becomes a function of fewer factors. The adiabatic requirement is well satisfied if the reaction rate is high, for then there is insufficient time for heat to flow into or out of the reacting element. It is also satisfied inside of an infinitely large sample of explosive, near the center of a massive piece or when the explosive is placed in a thermostat whose temperature is continuously changed so as to follow precisely the rising temperature of the sample. In this adiabatic case (and when $RT/E \ll 1$ which is a restriction generally applicable):

$$c \frac{dT}{dt} = \rho K = QZ e^{-E/RT}$$  \hspace{1cm} (2)

or

$$\frac{dT}{dt} = \frac{QZ}{c} e^{-E/RT}$$  \hspace{1cm} (2a)

and

$$\ln \frac{dT}{dt} = \ln \frac{QZ}{c} - \frac{E}{R} \frac{1}{T}$$  \hspace{1cm} (3)

Hence, given sufficient data one may obtain values for $\frac{QZ}{c}$ and $E$ from one experiment and $T_e$ may be evaluated without the necessity of carrying the process to completion (i.e., explosion) since:

$$T_e = \frac{cRT_o^2}{QZ} e^{-E/RT_o}$$

Now let us consider the case of a finite sized piece of explosive in a constant temperature environment. The thermal state of the sample will depend upon the rate of chemical reaction and, hence, heat evolution within it and, unlike the previous case, the rate at which heat is transferred to the

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environment. Depending upon the ratio of surface to volume and bulk of the sample, explosion may or may not occur. Above some critical value of the ambient temperature the rate of heat evolution within the sample will become greater than the heat loss and the temperature will continue to rise. Below this critical temperature solution of the generalized heat equation (1) leads to a steady state, i.e., at any point within the sample

$$\frac{\partial T}{\partial t} = 0.$$  

Integration of equation (1) has been performed numerically by Enig, Shanks, and Southworth at the Naval Ordnance Laboratory (4) and by others (5, 6) for all reasonable values of $T_0$ and $E$ for $\frac{RT_0}{E} < 0.1$. By this process critical conditions of explosion can be found and, for any particular set of parameters $Z$, $T_s$, $E$, $\rho$, $Q$, and $\lambda$, the critical dimensions for explosion of a sphere, an infinite cylinder, and a semi-infinite slab can be determined. These critical values are expressed in terms of a parameter

$$\delta = \frac{N_s}{\theta_s}^2 - \frac{1}{\theta_s^2},$$

where

$$N_s = \left( \frac{\rho Q Z R}{\lambda E} \right)^{1/2}$$

$$b = \text{half-thickness (or radius) of the combustible}$$

$$\theta_s = \frac{RT_s}{E} = \text{dimensionless temperature}$$
The critical values are found to be (5):

\[ \delta_{sl} = 0.88 \text{ for the slab} \]

\[ \delta_{cyl} = 2.00 \text{ for the cylinder} \]

\[ \delta_{sph} = 3.32 \text{ for the sphere} \]

It is seen, therefore, that the results of the adiabatic self-heating experiment plus values for thermal conductivity and heat capacity can be used to predict critical size and temperature for self-ignition.

EXPERIMENTAL PROCEDURE AND RESULTS

At the request of the Naval Ordnance Laboratory, personnel of the National Bureau of Standards (J. J. Loftus and D. Gross under the direction of Dr. Alexander Robertson) undertook to determine the thermal and kinetic properties of three propellants: AHH, Arcite 358, and Aerojet ANP 2639AF. Formulations of these propellants are given in Table I.
TABLE I
Propellant Compositions

<table>
<thead>
<tr>
<th>Component</th>
<th>Wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrocellulose (12.6% N)</td>
<td>54.63</td>
</tr>
<tr>
<td>Nitroglycerine</td>
<td>32.08</td>
</tr>
<tr>
<td>Triacetin</td>
<td>7.83</td>
</tr>
<tr>
<td>2-nitro-diphenylamine</td>
<td>0.93</td>
</tr>
<tr>
<td>Lead salicylate</td>
<td>1.67</td>
</tr>
<tr>
<td>L-26</td>
<td>1.19</td>
</tr>
<tr>
<td>Other extractables</td>
<td>1.67</td>
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</tbody>
</table>

Arcite 358

<table>
<thead>
<tr>
<th>Component</th>
<th>Wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium perchlorate</td>
<td>58.90</td>
</tr>
<tr>
<td>QTIV (Polyvinylchloride)</td>
<td>8.62</td>
</tr>
<tr>
<td>Plasticizer-Adipol 2EH (Chio Apex)</td>
<td>10.79</td>
</tr>
<tr>
<td>Detergent mixture</td>
<td>0.25</td>
</tr>
<tr>
<td>1 part Aerosol OT</td>
<td></td>
</tr>
<tr>
<td>1 part glyceryl mono-oleate</td>
<td></td>
</tr>
<tr>
<td>1 part pentaerythritol dioleate</td>
<td></td>
</tr>
<tr>
<td>Aluminum powder (Alcoa 123)</td>
<td>21.10</td>
</tr>
<tr>
<td>Stabilizer</td>
<td></td>
</tr>
<tr>
<td>1 part XE-82</td>
<td>0.17</td>
</tr>
<tr>
<td>1 part X23-7</td>
<td>0.17</td>
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</table>

ANP 2639AF

<table>
<thead>
<tr>
<th>Component</th>
<th>Wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium perchlorate</td>
<td>60.00</td>
</tr>
<tr>
<td>Aluminum</td>
<td>15.00</td>
</tr>
<tr>
<td>Copper chromite</td>
<td>0.40</td>
</tr>
<tr>
<td>Carbon black (P-33)</td>
<td>0.50</td>
</tr>
<tr>
<td>Polyurethane</td>
<td>2.10</td>
</tr>
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</table>

A. Thermal Conductivity Measurements

For these measurements, a heat-flow meter type of thermal conductivity apparatus (9) was used. In operation, two slabs each 10 by 10 by 1-in., comprising a sample pair of the specimen under test are placed one on each side of a heat-flow meter and then the faces of a hot plate and of a cold plate are brought together to make intimate contact with the specimen. At steady state, the heat flowing through the meter from the hot plate maintained at 32.8°C (91°F) to the cold plate maintained at 13.3°C (56°F) produces an emf proportional to the temperature gradient through the meter. The coefficient of thermal conductivity for each specimen was determined from the heat-flow meter output, the thickness of the specimen and the temperature drop in the specimen as measured by thermocouples. The heat-flow meter was calibrated by tests made on two materials of known conductivities as previously determined using a guarded hot plate (ASTM C 177-45). Two tests, one "forward" and one "reverse", were performed on AHH and Arcite 358. Since only one 10 by 10 by
1-in. specimen of ANP 2639AF was available for test, this propellant was tested in only one direction.

The results are summarized in Table II.

**TABLE II**

<table>
<thead>
<tr>
<th>Material</th>
<th>Density g/cm³</th>
<th>Mean Temperature °C</th>
<th>Thermal Conductivity c²ft²/sec-cm-deg C</th>
</tr>
</thead>
<tbody>
<tr>
<td>AHH</td>
<td>1.621</td>
<td>23.1</td>
<td>0.0005253 0.0005315 0.000527 ± 1%</td>
</tr>
<tr>
<td>Arcite 358</td>
<td>1.786</td>
<td>23.1</td>
<td>0.001322 0.001329 0.001326 ± 0.5%</td>
</tr>
<tr>
<td>ANP 2639AF</td>
<td>1.634</td>
<td>31.0</td>
<td>0.001002 ± 1%</td>
</tr>
</tbody>
</table>

**B. Specific Heat Measurements**

For these measurements, each propellant sample measured 1 by 2 by 2-1/2-in. To eliminate the possibility of interaction between the propellants and the water bath of the calorimeter, the AHH and Arcite 358 were sealed in individual plastic envelopes while the ANP 2639AF was spray-coated with a plastic film for test. The specific heats of the samples were measured by substituting them, separately, for 100 g of water in a calorimeter normally containing 600 g, and measuring the energy equivalent of the calorimeter and contents electrically. From the value obtained for the calorimeter with 600 g of water and the values obtained when the propellants were tested, the specific heats of the propellants including their plastic envelopes were obtained. The specific heat of the propellant was determined using a value of 0.69 cal/g-deg C for the specific heat of the plastic envelope. The specific heat of water was taken as 0.99921 cal/g at 22.5°C. Measurements were made over a 3 to 4 deg C range between 20 and 25°C. This method of measurement groups all the errors of measurement into the value obtained for the specific heat of the propellant. Two duplicate tests on the same sample were performed and the results are summarized in Table III.
TABLE III

Specific Heat Measurements

<table>
<thead>
<tr>
<th>Material</th>
<th>Sample Weight g</th>
<th>Envelope Weight g</th>
<th>Temp. Rise deg C</th>
<th>Mean Temp. °C</th>
<th>Specific Heat cal/g-deg C</th>
</tr>
</thead>
<tbody>
<tr>
<td>AHH</td>
<td>134.1903</td>
<td>1.8603</td>
<td>3.337</td>
<td>23.2</td>
<td>0.3906</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.325</td>
<td>22.3</td>
<td>0.3731 0.38 ± 0.01</td>
</tr>
<tr>
<td>Arcite 358</td>
<td>145.5787</td>
<td>1.7949</td>
<td>3.841</td>
<td>22.9</td>
<td>0.2827</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.500</td>
<td>23.0</td>
<td>0.3026 0.29 ± 0.01</td>
</tr>
<tr>
<td>ANP 2639AF</td>
<td>140.9178</td>
<td>4.3152*</td>
<td>3.163</td>
<td>23.4</td>
<td>0.3124</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.234</td>
<td>23.5</td>
<td>0.2925 0.30 ± 0.01</td>
</tr>
</tbody>
</table>

*sprayed-on plastic film

C. Kinetic Measurements

For these measurements, two pre-cut wafers 2-in. in diameter by 1-in. thick as furnished were placed together to form a cylindrical specimen 2-in. in diameter by 2-in. long. The specimen was assembled and mounted within a furnace designed for self-heating studies (8). During the initial heating period, the thermostatically controlled furnace air temperature was gradually increased by small temperature intervals. At a temperature at which an indication of self-heating was obtained according to the signal from a differential thermopile, the control system was actuated to provide "adiabatic" or compensating temperature rise control. The differential thermopile was composed of four (4) 28 ga. (B and S) chromel-alumel thermocouples in series to indicate the mean temperature difference between the specimen and the furnace atmosphere. The electrical signal from the differential thermopile was applied to an amplifier and servo control system so as to automatically compensate for any temperature rise within the specimen. Under these conditions, the specimen temperature remains uniform throughout its mass.

Continuous records of the specimen and furnace air temperatures were obtained on an automatic recorder from the signals of 24 ga. (B and S) chromel-alumel thermocouples. Sections of one such record are shown in Figure 1. Measurements were made of the slope of the curve, dT/dt, at a number of temperatures over the self-heating range. By taking logarithms and plotting ln dT/dt versus 1/T, the resultant line has a slope of -E/R, and intercepts the ln dT/dt axis at ln QZ/c (see equation (3)). At least two tests for each propellant were performed and the results from one test for each propellant are shown in Figure 2 together with those from similar tests on nitrocellulose plastic, wood fiberboard and purified cotton linters.
The plotted points approximate straight lines very closely and show the rate of temperature rise due to self-heating for each material under negligible heat loss conditions. Within the range shown, the displacement of a line toward higher values of reciprocal temperature indicates self-heating at relatively lower temperatures. Comparative rates of self-heating at any temperature may be read directly from the graph as illustrated in Table IV.

**TABLE IV**

Comparative Rates of Self-Heating

<table>
<thead>
<tr>
<th>Material</th>
<th>Rate of self-heating, deg C/min</th>
<th>Temperature: 135°C (1/T = 0.002450)</th>
<th>Temperature: 209°C (1/T = 0.002075)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AHH</td>
<td>1.15</td>
<td></td>
<td>c</td>
</tr>
<tr>
<td>Arcite 358</td>
<td>a</td>
<td></td>
<td>0.84</td>
</tr>
<tr>
<td>ANP 2639AF</td>
<td>0.07</td>
<td></td>
<td>1.58</td>
</tr>
<tr>
<td>Nitrocellulose plastic</td>
<td>0.225</td>
<td></td>
<td>c</td>
</tr>
<tr>
<td>Wood fiberboard</td>
<td>0.025</td>
<td></td>
<td>2.3</td>
</tr>
<tr>
<td>Cotton liners</td>
<td>b</td>
<td></td>
<td>0.067</td>
</tr>
</tbody>
</table>

a. No appreciable self-heating until 190°C  
b. No appreciable self-heating until 180°C  
c. Specimen consumed

At 135°C, the AHH exhibited self-heating at a rate of 1.15 deg C/min, while the Arcite 358 exhibited no appreciable self-heating at temperatures below 190°C. At this same temperature ANP 2639AF self-heated at a rate of 0.07 deg C/min. At 209°C, the AHH had been entirely consumed while the Arcite 358 exhibited self-heating at a rate of 0.84 deg C/min, and ANP 2639AF showed self-heating at a rate of 1.58 deg C/min.

The values of the kinetic constants determined from the lines in Figure 2 are listed in Table V for the applicable temperature ranges.
In the tests with Arcite 358 and ANP 2639AF, a (nearly) constant temperature phase was observed at a temperature of about 240°C, corresponding to a change in the crystal structure of NH₄C10₄.

In the tests with ANP 2639AF, melting, softening or slumping of the propellant was observed at a temperature of about 140 to 160°C. For the purposes of this analysis, it was assumed that the self-heating characteristics of the melted or slumped propellant were the same as those of the original solid.

Due to the unexpected behavior of the ANP 2639AF in the first few tests, a total of six tests were performed on specimens of this material and details of each of the tests are described below.

Test No. 1

At an initial temperature setting of 114°C, no appreciable self-heating was observed. After 38 minutes at this temperature, the temperature was raised to 155°C. The specimen self-heated to 213°C in 65 minutes and remained at this temperature for about 2 minutes. After this short constant-temperature phase, very rapid combustion set in and the specimen was consumed. Based upon the data from this test, an activation energy of about 55 kcal/mole was computed.
Test No. 2

At an initial temperature setting of 141°C, very little self-heating was observed. After 136 minutes at this temperature, the temperature was raised to 149°C. The specimen self-heated to 162°C in 135 minutes at which time the adiabatic control operation and consequently the temperature measurements became erratic. It is interesting to note the behavior of this test specimen after the furnace temperature was increased in an effort to destroy the specimen. At a temperature of about 195°C, this decision was reconsidered and the furnace heater was turned off. The specimen continued to heat reaching a temperature of 225°C before it started to cool. It had cooled down to 215°C and was continuing to cool when recording was discontinued for the day. It was found on the next day that the specimen had been consumed.

Test No. 3

After 25 minutes at a temperature setting of 82°C, the furnace temperature was raised to 142°C. After 15 minutes, the adiabatic control operation became erratic as in Test No. 2. The test was discontinued after approximately 90 minutes during which period the maximum recorded specimen temperature was 147°C. The furnace and specimen were allowed to cool overnight. Inspection of the furnace chamber the following day showed that the specimen had melted away from its holder and from the recording and controlling thermocouples and was found resolidified at the bottom of the furnace chamber.

On the basis of this finding, it was assumed that softening or melting had occurred in each of the previous tests. It is speculated that in Test No. 1 a small quantity of propellant material had remained in contact with the control thermopile to permit adiabatic control operation whereas in Test Nos. 2 and 3, complete separation had occurred. For all succeeding tests, the cylindrical propellant specimens were placed in a 2-in. diameter by 2-in. high stainless steel wire basket consisting of 40 mesh, 0.010-in. diameter wires. This basket served to support the softened or melting propellant specimen in position during the self-heating process.

Test No. 4

From an initial temperature of 130°C, the specimen self-heated to 238°C in about 15 hours. After a short pause at this temperature, very rapid combustion occurred and the specimen was consumed. The data on the rate of temperature rise versus reciprocal temperature for this test was best approximated by two straight lines yielding an activation energy of 38.1 kcal/mole for the temperature range 180 to 200°C and an activation energy of 19.9 kcal/mole for the temperature range 200 to 235°C.
Test No. 5

From an initial temperature of 130°C, the specimen self-heated to 238°C in about 12 hours. After a short delay at this temperature, very rapid combustion occurred and the specimen was consumed. Analysis of the data yielded an activation energy of 24.1 kcal/mole for this test.

Test No. 6

From an initial temperature of 131°C, the specimen self-heated to 236°C in about 10 hours. Following the characteristic pause at almost constant temperature, very rapid combustion occurred and the specimen was consumed. The activation energy for this test was calculated at 28.6 kcal/mole and is the value reported in the tables.

**CALCULATION OF CRITICAL SIZE**

In order to estimate the critical size for ignition of a mass of self-heating material, the analysis presented by Enig, Shanks and Southworth (4) was used.

The assumption was made that the kinetic properties measured over higher temperature ranges may be applied to the temperature range of practical interest for ordinary storage (20 - 100°C). It was further assumed that the measured thermal properties may be applied over the whole temperature range. Critical radius determinations for a sphere have been made for each propellant and, for comparison, for three other common materials known, on occasion, to self-ignite. These are listed in Table VI and shown graphically in Figure 3. It may be noted from the previous discussion that for a given surface temperature, the critical radius for a cylinder and the critical half thickness for a semi-infinite slab are given very closely by 0.775 B and 0.514 B, respectively, where B is the critical radius for the sphere.
TABLE VI
Critical Size Calculations

<table>
<thead>
<tr>
<th>Material</th>
<th>Surface Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20°C (68°F)</td>
</tr>
<tr>
<td>AHH</td>
<td>9800 cm</td>
</tr>
<tr>
<td></td>
<td>320 ft</td>
</tr>
<tr>
<td>Arcite 358</td>
<td>2.4x10^7</td>
</tr>
<tr>
<td></td>
<td>7.9x10^5</td>
</tr>
<tr>
<td>ANP 2639AF</td>
<td>1.9x10^4</td>
</tr>
<tr>
<td></td>
<td>633</td>
</tr>
<tr>
<td>Nitrocellulose plastic</td>
<td>7.7x10^4</td>
</tr>
<tr>
<td></td>
<td>2500</td>
</tr>
<tr>
<td>Wood fiberboard</td>
<td>4500</td>
</tr>
<tr>
<td></td>
<td>150</td>
</tr>
<tr>
<td>Cotton linters</td>
<td>4.2x10^6</td>
</tr>
<tr>
<td></td>
<td>1.4x10^5</td>
</tr>
</tbody>
</table>

SUMMARY

An analysis is given of the relation between thermodynamic properties and storage hazards.

Measurements of the specific heat, thermal conductivity and kinetic properties of 3 propellants have been made.

In the self-heating experiments, AHH self-heated from an initial temperature of 100°C to a temperature of 170°C in 10 hours. At this temperature, very rapid combustion occurred and the sample was consumed. The activation energy over this temperature range was 38.8 kcal/mole. Arcite 358 self-heated in 2-1/2 hours from an initial temperature of 190°C to a temperature of 242°C, at which temperature very rapid combustion occurred and the sample was consumed. The activation energy over this temperature range was 8.3 kcal/mole. ANP 2639AF self-heated in 10 hours from an initial temperature of 131°C to a temperature of 236°C at which temperature very rapid combustion occurred and the sample was consumed. The activation energy over this temperature range was 28.6 kcal/mole.
A comparison of critical radius determinations, under the given assumptions, is presented in Table VI and Figure 3. Size limitations on the storage of bulk quantities of these propellants and careful control of temperature and ventilation conditions seem justified on the basis of these calculations.

In particular, attention must be directed to the very small critical diameter of spheres of AHH for which, as a consequence, one is restricted at 180°F to storage of slabs having a thickness of less than 1.24 feet.

Results obtained are encouraging in that they lend support to the previously reported indications (10) that shock test results may be a better guide to overall handling and use requirements. Thus, as seen in Table VII, whereas double base propellants are more sensitive to impact than are composites, the reverse situation maintains as regards shock sensitivity. The self-heating results reported herein give the same relative order of sensitivity as do the shock measurements.

The relation between the results of self-heating experiments and other measures of sensitivity is under continuing investigation. Data for several additional propellants and explosives are required and plans are currently being formulated to continue this work at the National Bureau of Standards.
**ACKNOWLEDGMENT**

The author is grateful to personnel of the National Bureau of Standards who performed all of the experimental work and computed the results thereof reported herein and wrote the sections entitled, "Experimental Procedures and Results" and "Calculations of Critical Size".
FIGURE 1

Initial and Final Sections of a Typical Specimen vs Temperature Record
FIGURE 2

Rate of Temperature Rise for Propellants and Other Materials
FIGURE 3

Critical Explosion Radium for Spheres of Propellants and Other Materials
REFERENCES

(1) Macek, A. and Gipson, R. W., "Sensitivity of Explosives V, Transition from Slow Burning to Detonation in Cast Pentolite" 
NavOrd 5758, 1 November 1957.

(2) Macek, A., "Sensitivity of Explosives VII, Transition from Slow Burning to Detonation: A Model for Shock Formation in a Deflagrating Solid" 

(3) Gamov, G. and Finkelstein, R. J., "Theory of the Detonation Process" 

NavOrd Report 4377, 7 November 1956.

(5) Frank-Kamenetskii, D. A. 
   a. Diffusion and Heat Exchange in Chemical Kinetics  
      Princeton University Press (1955)
   c. J. Phys. Chem. (USSR) 13, 735 (1939)

(6) Chambre, P. L., "On the Solution of the Poisson-Boltzmann Equation with Applications to the Theory of Thermal Explosions" 

(7) Loftus, J. J. and Gross, D., "Thermal and Self-Ignition Properties of Three Solid Propellants" 


(9) Lang, D. L., "A Quick Thermal Conductivity Test on Insulating Materials" 