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Explosives, Mixtures, and Plastic-Bonded
Explosives Determined Experimentally**

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Specific Heat and Thermal Conductivity of Explosives, Mixtures, and Plastic-Bonded Explosives Determined Experimentally

John F. Baytos



SPECIFIC HEAT AND THERMAL CONDUCTIVITY OF EXPLOSIVES, MIXTURES,
AND PLASTIC-BONDED EXPLOSIVES DETERMINED EXPERIMENTALLY

by

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ABSTRACT

The specific heat and thermal conductivity of explosives and plastic-bonded explosives of interest to WX operations, determined experimentally, are reported in three tables. Specific heat was determined by differential scanning calorimetry against sapphire standards. Thermal conductivity was determined by two means: the guarded hot-plate method or the differential scanning calorimeter comparative method on miniature samples.

I. INTRODUCTION

As new explosives, plastic-bonded explosives, and mixtures are developed and phased into WX-Division operations, the thermal properties are determined. This report summarizes the specific heat and thermal conductivity values for explosives experimentally determined at Group WX-3. Previously published values were used to check our work.

This report also describes the methods used to determine specific heat and thermal conductivity. Details are given of innovations that made the determinations easier to make with safety. The values determined experimentally are presented in three tables.

II. DISCUSSION

Specific heat was determined through the use of a Perkin-Elmer DSC-1B Differential Scanning Calorimeter (DSC) by the method of O'Neill.^{1,2} Actual operating directions in the manual³ supplied with the instrument were followed.

The DSC was used to make a direct comparison of an unknown sample with a standard sapphire disc at the temperature of interest. The NBS⁴ value for the specific heat of sapphire was used for the calculation in cgs units (cal/g°C). For SI-derived units⁵ (J/kg K), the cgs value is multiplied by 4184.0.

Specific heat values determined in this way are presented in linear equation form as a function of temperature in Table I, along with the temperature range of the experiments. The standard deviation was calculated from the least-squares fit at midrange.

Thermal conductivity was determined by two methods, the guarded hot-plate (GHP), ASTM C-177,⁶ and a comparative method adapted for the DSC.⁷

The GHP method is primarily a method for measuring the thermal conductivity of insulation board, but has been used for other materials provided that they can be formed into the required sample size. A serious disadvantage of the method for

measurements on explosives is the use of large samples, which makes it a hazardous operation requiring extraordinary safety precautions. Furthermore, the standard geometry requires that two large-size samples, 8-in. square by 1-in. high, be matched pairs and that the surfaces be plane and parallel. This requirement is especially difficult when the supply of sample material is limited. Another disadvantage of the method is the long equilibration time, usually overnight. Furthermore, temperature and power measurements must be taken until a period of two hours is passed without change, according to the ASTM specifications. For these reasons, only a few samples of explosives were measured in accordance with the ASTM C-177 GHP method. These values are reported in Table II, in cgs units and in SI-derived units⁵ (W/m·K), along with temperature data. SI-derived units are obtained by multiplying cgs units by 418.4. The values are based on our calibration against Teflon [6.02 x 10⁻⁴ cal/s cm² (°C/cm)] at several temperatures that agree with the values reported by Eierman.⁸

Because sample size and the associated safety hazards were a problem, we looked for a method that uses smaller samples. A comparative method meeting these requirements was reported by Brennan, Miller, and Whitwell,⁷ who describe the use of the DSC for making thermal conductivity measurements. The method uses the DSC to regulate the heat flow entering two samples resting on separate heating platens, mounted side by side,⁹ to which are attached resistance thermometers. The thermometers sense the temperature of the hot surface, and a servo amplifier monitors the power to maintain each heater at the designated test temperature. The output signal of

the DSC control unit is a voltage proportional to the power needed to keep the system isothermal. The cold surface temperature readings come from thermocouples in a cold sink resting on top of the samples in the test cell. When the experiment comes to steady-state, the temperature gradient, equal for both the sample and the reference, is measured as is the difference in power input to the two heaters. These data, the sample dimensions, and known value of the reference permitted us to calculate the thermal conductivity of the unknown sample on a comparative basis.

The thermal conductivities of explosives determined by this method are presented in Table III; the temperature data and results are in cgs units and SI-derived units. The DSC apparatus was calibrated with samples made from sample slabs whose thermal conductivity was measured by the GHP method. Teflon samples cut from a GHP test sample were generally used as the reference. To determine the calorimeter constant, Teflon and other samples of known thermal conductivity were used. The closer the reference value was to the value of the unknown, the less error there was in the experimental result. Because the values measured by using the DSC method agreed well with those from the GHP method, we were able to make measurements on small, readily available samples in much less time.

III. SPECIFIC HEAT MEASUREMENTS BY DIFFERENTIAL SCANNING CALORIMETER

Because the method used is detailed in the instrument manufacturer's instructions, only exceptions to the procedure are described here.

For measurements on monolithic materials, 6-mm-diam samples were cut from a

cast or pressed wafer 0.5-mm thick and then encapsulated in a sample pan. For powdered materials, samples 20-30 mg in weight and encapsulated into pans were an optimum size for satisfactory measurements.

The DSC was calibrated with materials of known specific heat, that is, sapphire, benzoic acid, and triple-recrystallized succinic acid. The differences between our measured and published values were within the error reported by O'Neill¹ in his calibration.

At each temperature of interest, the specific heat of the unknown was calculated, after making the corrections for the aluminum encapsulation pans containing the unknown and the sapphire samples, by the equation given in the DSC manual.

The specific heat of the unknown was calculated at temperatures up to the melting point or to the onset of decomposition of the unknown. When all the data pairs were acquired, a statistical least-squares equation was computed for the specific heat of the unknown sample as a function of temperature, along with the standard deviation at the midrange temperature.

IV. GUARDED HOT-PLATE METHOD FOR THERMAL CONDUCTIVITY MEASUREMENTS

The guarded hot-plate apparatus includes the heating plate, cold sinks, edge insulation, metered power supply for the heaters, thermostated circulator for the cold sinks, and thermocouple and power measurement recording system. The ASTM C-177 method presents general instructions, and only improvements for optimum operation of the apparatus are discussed here.

Because commercially manufactured plates were unavailable, a metal-surfaced hot plate was fabricated in our shops to the specifications of ASTM C-177-71. The

plate was an 8-in. square by 1/4-in. thick laminated assembly with a resistance heater etched on a nickel-clad printed circuit board, covered with a clear board, and bonded on both sides with brass plates. The central and guard heaters were located in the center of the laminate so that heat flowed equally to each surface of the plate, with minimum loss to the sides. Temperatures of the surfaces of the plate were sensed by eight thermocouples welded to the surfaces. Their leads were imbedded in channels in the metal surface.

The cold plates were 8-in. square by 1-in. high hollow brass chambers into which thermostated liquid was circulated from a controlled temperature circulator.

In operation, a test stack was assembled in the following order: the bottom cold plate, the bottom sample, the metal-surfaced heating plate, the top sample, and finally the top cold plate. This aligned stack was clamped in a fixture with wing nuts while a load of 11.5 kg was applied to ensure contact of all surfaces. This stacked assembly was placed in a foamed plastic chamber to which vermiculite insulation was added to insulate the stack.

After all the electrical and plumbing connections were made to the power supply, to readout instruments, and to the temperature controlled circulator, the system was turned on and allowed to reach steady state. By using a data logger with a digital microvoltmeter and printer, rather than a manual potentiometer, it became apparent that materials of low thermal conductivity required a long time, usually overnight, to come to the steady-state conditions required by ASTM C-177. After the test reached steady state and the temperature conditions were in compliance with ASTM-C-177 specifications, the data was then processed. Thermal conductivity

values were computed, the results were treated statistically, and the averages were compared according to the requirements of the ASTM C-177 method.

The thermal conductivity of samples was calculated by the following equation:

$$k = \frac{q L}{2A(T_1 - T_2)} \quad (1)$$

where

k = thermal conductivity, cal/s cm^2 ($^{\circ}\text{C}/\text{cm}$),

q = DC volts times amperes times conversion factor (0.2389), cal,

L = thickness of each specimen, cm,

A = area of central portion of heated surface, cm^2 ,

T_1 = temperature of hot surface, $^{\circ}\text{C}$, and

T_2 = temperature of cold surface, $^{\circ}\text{C}$.

V. DIFFERENTIAL SCANNING CALORIMETER COMPARATIVE METHOD FOR THERMAL CONDUCTIVITY MEASUREMENTS

To adapt the DSC for making thermal conductivity measurements as described by Brennan, accessories were machined and modifications were made to the base of the removable assembly cover. This was necessary to align and press the unknown and reference samples to assure good contact with the heating and cooling surfaces. A radiation shield ring surrounded the sample and reference. A cold sink was machined of copper with two circular surfaces aligned to fit on top of the sample and the reference. Thermocouples were inserted into wells of the reference and unknown contact surfaces for measuring the sample cold surface temperatures. A button heater was fastened to the top of the cold sink for producing temperatures higher than ambient. A small spring inserted between the top of the cold sink and a cross bar built on the removable

assembly cover gave sufficient pressure for good contact between the samples and the heater and cold sink. Heater and thermocouple wires from the cold sink were sealed through outlets in the removable assembly cover, and a seamless canopy of aluminum, fitted over O-rings on the removable assembly cover, sealed the samples in a still atmosphere, or one into which inert gas could be passed by using the DSC system. The cold temperature of the temperature gradient, read on a digital microvoltmeter, was determined from these thermocouples.

The determination of the calibration constant of the instrument also required that the temperature of the heat platens, the hot temperature of the temperature gradient, in an isothermal condition be known accurately. As there was no direct way to fasten thermocouples when the samples were in place, the temperature counter on the DSC control unit was used to indicate the heat platen temperature and was related to the actual temperature by calibration. For heat platen calibration, fine thermocouples were attached to the surface of the platens, and the DSC average, differential, and slope controls were adjusted until there was a relationship between the temperature counter and the temperature of the sample and reference heat platens, both of which were at the same temperature. After calibration at several operating temperatures, a regression line was calculated for the actual temperature of the heat platen as a function of the temperature counter value. This was the high value of the temperature gradient.

With the temperature of the heat platens established, the calorimeter constant at the test temperature, in terms of microcalories per microvolt, was determined by comparing samples of known thermal conductivity. The optimum sample

cylinder size was determined experimentally to be 6.0-mm diam by 7.5-mm high. A further requirement was that the height of the unknown and reference be within 0.002 mm so that the cold sink made total contact on the top surfaces. Because each heater assembly of the DSC has small differences in geometry, resistance, and heat transfer properties, and because each heater platen can be used as a reference, the samples were run twice to cancel these small errors. When the sample was on the left platen and the reference on the right, this was normal mode. When specimens were reversed, this was considered reverse mode. The results so determined were then averaged.

To make a measurement, four steps were required. To null the instrument, duplicate reference samples (usually Teflon) were set on the heater platens at the temperature conditions of the test, and the DSC zero control was adjusted for null output. In the second step, the calorimeter constant was checked by substituting a calibration sample for Teflon on the left heat platen. Next, the unknown sample was substituted for the calibration sample in the left platen (normal mode) and a value determined. In the fourth step, the unknown was run on the right platen (reverse mode) and its thermal conductivity again calculated. The mean of the two values was reported as the thermal conductivity of the unknown.

To determine when the experiment was at steady state and to make the calculations in real time, the output of the DSC and the output of the thermocouples were input to a digital microvoltmeter data logger and then transferred to a programmable calculator and printer. With fixed data in the calculator memory and variable data from the DSC, the calculator computed the thermal conductivity of the sample. It was thus possible to determine the

thermal conductivity at steady state in a minimum of time.

The equation for calculating thermal conductivity was revised to account for the area-to-height ratio of both the unknown and reference samples. When the unknown is in the reverse position, the polarity in the equation needs to be specified. The calculator program was written for either normal or reverse mode when specified at the start of a test. Thermal conductivity was calculated from the following revised equation:

$$k_x = k_r \frac{R_r}{R_x} - \frac{(\mu v)(C_c)}{(R_x)(T_h - T_c)} \quad (2)$$

where

k_x = thermal conductivity of unknown, cal/s cm^2 ($^{\circ}\text{C}/\text{cm}$),

k_r = thermal conductivity of reference,

R_r = ratio of area of reference sample to height, cm^2/cm ,

R_x = ratio of area of unknown sample to height, cm^2/cm ,

μv = output of digital voltmeter, μV ,

C_c = calorimeter constant, $\mu\text{cal}/\mu\text{V}$,

T_h = temperature of hot platen converted from DSC counter, $^{\circ}\text{C}$, and

T_c = temperature of cold sink surfaces from thermocouples, $^{\circ}\text{C}$.

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TABLE I
EXPERIMENTAL VALUES OF SPECIFIC HEAT OF EXPLOSIVES
BY DIFFERENTIAL SCANNING CALORIMETER

Name Composition/Description Source/Lot	Density (g/cm ³)	Temperature Range (°C)	Specific Heat (cal/g°C)	Std Dev at Midrange (cal/g°C)
Ammonium picrate Commercial grade, CTT 215C WX-2	1.730	37 to 207	0.287 + 0.00068T	0.010
Comp B-3 RDX 60%/TNT 40% (below melt point) Holston, Lot 37-16 (6018)	1.725	7 to 67	0.234 + 0.00103T	0.006
Comp B-3 RDX 60%/TNT 40% (above melt point) Holston, Lot 37-16 (6018)	*	97 to 157	0.137 + 0.00209T	0.009
HMX Grade 2, Class D Holston, Lot SR-22A65 (0306-00)	1.900	37 to 167	0.231 + 0.00055T	0.004
NQ (Nitroguanidine) High bulk density Lot 62-071-21	1.689	37 to 167	0.269 + 0.00070T	0.006
NQ (Nitroguanidine) Low bulk density Lot CCL-10-621	1.651	37 to 167	0.242 + 0.00111T	0.009
PETN (Pentaerythritol- tetranitrate) Superfine DuPont, Lot 12-9 (0601-02)	1.770	32 to 127	0.239 + 0.00080T	0.005
Picric acid Commercial grade, MP 122C WX-2	1.760	37 to 117	0.235 + 0.00073T	0.013
Potassium picrate Commercial grade, CTT 255C WX-2	1.930	37 to 237	0.267 + 0.00030T	0.011
PBX 9010-02 RDX 90%/Kel-F 3700 10% Lot 16	1.785	37 to 167	0.247 + 0.00064T	0.007
PBX 9011-02 HMX 90%/Estane 5740 10% Lot 91-21	1.772	17 to 167	0.259 + 0.00063T	0.007
PBX 9404-03 HMX 94%/NC 3%/CEF 3% Lot 37	1.845	7 to 147	0.224 + 0.00070T	0.005
PBX 9407 RDX 94%/Exon 6% Lot 24-59 Batch 8	1.660	37 to 167	0.241 + 0.00077T	0.006
PBX 9501-01 HMX 95%/Estane 2.5%/BDNPA-F 2.5% Blend 72-015, PO 33187, (X-0242)	1.835	50 to 175	0.238 + 0.00079T	0.002

*Not determined

TABLE I (cont)

Name Composition/Description Source/Lot	Density (g/cm ³)	Temperature Range (°C)	Specific Heat (cal/g°C)	Std Dev at Midrange (cal/g°C)
PBX 9502 TATB 95%/Kel-F 800 5% LASL WX-3 (X-0290)	1.900	37 to 177	0.249 + 0.00059T	0.007
RDX Type B, Class E Holston, Lot SR 40-57 (0201-00)	1.804	37 to 167	0.232 + 0.00072T	0.004
TATB (Triaminotrinitrobenzene) Production grade Pantex 75-09-10/Cordova 1B034052	1.938	37 to 137	0.243 + 0.00063T	0.002
TNT Below melt point (M.P. 80.5°C) Lot WLG 3083, (0101-00)	1.654	17 to 67	0.254 + 0.00075T	0.007
TNT Above melt point (M.P. 80.5°C) Lot WLG 3083, (0101-00)	*	97 to 157	0.329 + 0.00055T	0.002
X-0217 HMX 94%/DNPA 2.5%/ BDNPA-F 2.5%/Wax 1% 94-01-75	1.867	27 to 147	0.239 + 0.00071T	0.005
X-0219 TATB 90%/Kel-F 800 10% Batch 16639-49, PO 32580	1.907	50 to 275	0.222 + 0.00070T	0.008
X-0228 NQ 95%/Estane 5% Blend 76-27, PO 37162	1.686	37 to 167	0.293 + 0.00066T	0.005
X-0280 RDX 95%/Estane 5% Blend 7438, PO 35514	1.720	50 to 150	0.221 + 0.00071T	0.003
X-0290 TATB 95%/Kel-F 800 5% Pantex/Cordova	1.900	37 to 177	0.249 + 0.00059T	0.007
X-0309 TNT 74.5%/D-2 4.5%/ Acetylene black 2%/Al 19% Destex, PO 37887	1.707	37 to 67	0.199 + 0.00232T	0.007
XTX 8003-00 PETN 80%/Sylgard 182 20% Batch 2716	1.557	37 to 127	0.252 + 0.00085T	0.008
XTX 8004 RDX 80%/Sylgard 182 20% Batch 4875 (X-0208)	1.538	25 to 187	0.247 + 0.00062T	0.006

*Not determined

TABLE II
EXPERIMENTAL VALUES OF THERMAL CONDUCTIVITY OF EXPLOSIVES
BY GUARDED HOT PLATE METHOD ASTM C-177

Name Composition/Description Source/Lot	Density (g/cm ³)	Mean Temperature (°C)	Temperature Difference (°C)	$\frac{k}{s \text{ cm}^2 (\text{°C/cm})}$	$\frac{k}{\text{W} \cdot \text{K}}$
Comp B-3 RDX 60%/TNT 40% PO 21749 (6018)	1.730	46.3	22.6	5.23×10^{-4}	0.219
Cyclotol RDX 75%/TNT 25% PO 21750 (7506)	1.760	45.9	21.8	5.41×10^{-4}	0.227
PBX 9010 RDX 90%/Kel-F 3700 10% PO 21705	1.875	48.8	27.4	5.14×10^{-4}	0.215
PBX 9011* HMX 90%/Estane 5740X2 10% PO 21706	1.772	43.4	23.4	9.08×10^{-4}	0.379
PBX 9404 HMX 94%/NC 3%/CEF 3% PO 21751	1.845	46.2	22.0	9.20×10^{-4}	0.385
PBX 9501-01-02 HMX 95%/Estane 5703 F-1 2.5%/BDNPA-F 2.5% LASL WX-3 PO 32580	1.847	55.0	9.8	10.84×10^{-4}	0.454
X-0219-00-00-10 TATB 90%/Kel-F 800 10% LASL WX-3 PO 32580	1.907	45.5	9.3	13.23×10^{-4}	0.553
X-0226* RDX 89.5%/Estane 5740X2 10.5% LASL WX-3 PO 26010	1.697	48.6	26.8	5.18×10^{-4}	0.217

*Volume match for comparison of HMX and RDX thermal conductivity.

TABLE III
EXPERIMENTAL VALUES OF THERMAL CONDUCTIVITY OF EXPLOSIVES
BY DSC-1B COMPARATIVE METHOD

Name Composition/Description Source/Lot	Density (g/cm ³)	Mean Temperature (°C)	Temperature Difference (°C)	$\frac{k}{(s \text{ cm}^2 (\text{°C}/\text{cm}))}$	$\frac{k}{(\text{W} \cdot \text{K})}$
NQ (Nitroguanidine) Low bulk density Lot CCL 10-629	1.651	41.3	22.7	10.14×10^{-4}	0.424
NQ (Nitroguanidine) High bulk density Lot 62-071-21	1.689	41.3	22.6	9.85×10^{-4}	0.412
PBX 9502 TATB 95% Kel-F 800 5% Pantex TATB Lot 75-09/10 (X-0290)	1.893	38.0	13.0	13.20×10^{-4}	0.553
TATB (Triaminotrinitrobenzene) Pressed into cylinder TATB 100% Pantex Lot, Blend 75-09/10 PO 37378	1.891	38.0	13.0	12.80×10^{-4}	0.536
XTX 8004 RDX 80% Sylgard 182 20% Batch 4875 (X-0208)	1.540	39.8	25.5	3.42×10^{-4}	0.143
X-0228 NQ 95% Estane 5% LASL Blend 76-27	1.694	42.1	21.7	10.83×10^{-4}	0.453
X-0309 TNT 74.5% D-2 4.5%/ Acetylene black 2% Al 19% Destex, PO 37887	1.700	40.9	23.5	8.06×10^{-4}	0.337
X-0280 RDX 95% Estane 5% LASL PO 35514, Blend 74-38	1.720	43.1	19.0	4.14×10^{-4}	0.173

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