NATIONAL BUREAU OF STANDARDS REPORT

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THERMAL AND SELF-IGNITION PROPERTIES OF SIX EXPLOSIVES

by

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U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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ABSTRACT

Measurements have been made of the specific heat, thermal conductivity and kinetic properties of six explosives. Based upon these measurements, estimates are provided of the self-ignition hazard associated with the use and bulk storage of these explosives.

INTRODUCTION

At the request of the Naval Ordnance Laboratory, determination of the thermal and kinetic properties of a number of propellants and explosives was intiated. This report summarizes the results of measurements on six explosives to supplement the results on three solid propellants reported in NBS Report No. 6111.

From these measurements and an analysis of the self-heating reaction, an estimation may be made of the self-ignition hazard associated with the use and bulk storage of such explosives. These measurements may also be useful for possible intercorrelation and interpretation of sensitivity data.

MATERIALS

The six explosive materials were furnished by the Naval Ordnance Laboratory in the shapes required for test. The designations were those supplied by Naval Ordnance Laboratory.

EXPERIMENTAL WORK

A. Kinetic Measurements

Cylindrical specimens 2-in. in diameter by 2-in. long were prepared by placing together two precut wafers 2-in. in diameter by 1-in. thick as furnished. Thermocouples were placed within the specimen which was assembled, placed in a stainless steel beaker, and mounted within a furnace designed for self-heating studies. The apparatus and method of analysis of the data have been described previously[1, 2].

At least two tests for each explosive were performed in order to establish satisfactory reproducibility between duplicate tests and the results are shown in Figure 1. Straight lines have been drawn through one set of points in each case and the activation energy E determined from the slopes. Comparative rates of self-heating at any temperature may be read directly from the graph by drawing a vertical line at the abscissa point corresponding to the temperature desired. For example, at 165°C (1/T=.002283), the explosives RDX, CYCLOTOL and DINA exhibited self-heating at the rates of 0.015, 0.25, and 7.5 deg C/min, respectively, whereas any self-heating of explosives Q, QR and TNT was below the limit of sensitivity of the apparatus used at this temperature.

The values of the kinetic constants determined from the lines in Figure 1 are listed in Table 1 for the applicable temperature ranges. Test observations and remarks are summarized below:

MATERIAL	OBSERVATIONS
TNT	Specimen melted at about 80°C Adiabatic control initiated at 190°C Very rapid combustion upon reaching 265°C; specimen consumed.
RDX	Adiabatic control initiated at 168°C Short constant temperature phase at about 193°C Very rapid combustion upon reading 200°C; specimen consumed.
Q	Adiabatic control initiated at 247°C Constant temperature phase in range of 271-276°C followed by very rapid combustion upon reaching 295°C; specimen consumed.
QR	Adiabatic control initiated at 200°C Constant temperature phase at about 275°C followed by very rapid combustion. Specimen consumed except for approximately 10 gm of gray, crusty residue of same shape as test specimen (initial weight 180 gm) which remained following test.
DINA	Apparent melting at about 48°C Adiabatic control initiated at 126°C Very rapid combustion upon reaching 204°C; specimen consumed.

MATERIAL	OBSERVATIONS
CYCLOTOL	Apparent melting at about 67°C Adiabatic contol initiated at 151°C Very rapid combustion upon reaching 204°C; specimen consumed.

B. Specific Heat Measurements

Specimens for these measurements consisted of two pieces each 1-7/8 by 2 by 1/2 in. and each piece was sealed into an individual polyethylene plastic envelope. The specific heat of each specimen was measured by substituting it separately for 65.8 g of the initial 177.8 g of Varsol in a half-pint Dewar flask calorimeter, and measuring the energy equivalents of the calorimeter and contents electrically. The calorimeter was so constructed that the two pieces constituting a specimen formed two sides of a channel through which the Varsol was circulated by a centrifugal pump. Storage batteries supplied electrical energy to a submerged cartridge heater, measurements being made of the heater current I, heater resistance R and time of power input t. The energy input was calculated by the equation $E = I^2Rt/4.184$ calories. From the value obtained for the calorimeter and 177.8 g of Varsol and the values obtained when the specimens were tested, the specific heat of each specimen, including the plastic envelopes, were obtained. Varsol was used as the heat transfer fluid because of its low heat capacity, 0.4730 cal/g-deg C as measured over the experimental temperature range. The specific heat of the specimen was determined using a value of 0.55 cal/g-deg C for the specific heat of the polyethylene envelope. After the first run, all measurements were made over the same temperature range. Three tests on each specimen were performed and the results are summarized in Table 2.

Subsequent to the first tests on both TNT and RDX, some disintegration of each specimen due to Varsol leakage through the plastic envelopes was observed. The other four explosives showed very little or no disintegration. Repeat tests on the same specimens indicated that the Varsol attack did not appreciably affect the specific heat determinations.

C. Thermal Conductivity Measurements

Specimens for these measurements consisted of a circular disk of 6-in. diameter and of uniform thickness of approximately 0.5 in.

The thermal conductivity was determined in the conductive disc apparatus* consisting of a circular disc of metal sandwiched between two specimens which in turn are sandwiched between two water-cooled plates all of the same 6-in. diameter. The stainless steel conductive disc was uniformly heated at its edge by means of electrical resistance wire set in an edge groove. The heat generated at the disc edge tends to flow in the disc radially toward its center and also from the disc through the two specimens to two brass cold plates. These plates were maintained at a uniform temperature by circulating cold water through copper tubing soldered to them. Under steady-state conditions, the temperature of the conductive disc decreases toward its center. By measuring the temperature of the conductive disc at its center and at a suitable radius, temperatures Vo and V, respectively, the effective conductance of the specimens can be calculated, if the temperatures of the cold plates and the conductivity and thickness of the disc metal are known.

It was decided to use only one explosive specimen for these measurements and therefore a "dummy" specimen was used in place of a duplicate of the principal specimen. This consisted of a 1-in. thick semirigid glass-fiber insulating board of stable low thermal conductivity (0.348 mw/cm C at 50°C). A thickness of 0.991 in. was maintained during use by three small fiber pegs thrust perpendically through the board. The lower, cold plate of the apparatus, the dummy specimen, and the conductive disc were fastened together with rubber cement to form a subassembly.

The apparatus was calibrated by measurements on six specimens of known thermal conductance in the range 0.3 to 4.4 mw/cm^2 C. The conductances of these specimens and of the dummy specimen were previously determined using the guarded hot plate apparatus (ASTM C177-45). A smooth curve drawn through these six points relates the observed ratio of temperatures V/Vo of the conductive disc to the value of conductance of the specimen. Departures of the experimental calibration points from this calibration curve did not exceed one per cent.

Following calibration, measurements were made on the six explosive specimens. Care was taken to ensure good thermal contact between the specimen and the working surfaces. During the course of the measurements, two check readings were made on one of the six original calibration specimens (1.28 cm thick neoprene). The

* A paper giving a rigorous mathematical analysis of the conductive disc method and details of design and construction is being prepared for publication by H. E. Robinson, D. R. Flynn and T. W. Watson.

conductance of this specimen as determined in the hot plate was 2.494 mw/cm^2 C at 48°C while the check values were 2.50 and 2.56 mx/cm^2 C, respectively. Therefore, a variation in results of 2.4 per cent was observed, to which the results on the explosives must be considered subject. The results are given in Table 3.

The two measurements made on TNT, at 33 and 38°C, indicate a negative temperature coefficient of conductivity. Because of the small difference in test temperatures, however, the uncertainty in this value (α = -0.011 per deg C) is probably large.

To prevent the possibility of melting or softening, the cold plate temperature was maintained at a much lower temperature for those explosives echibiting low temperature melting. This was accomplished by using chilled or ice water as the cold plate coolant. The specimen conductances were corrected to compensate for the change in the conductive disc conductivity when its mean temperature departed from the temperature during calibration (69°C).

D. 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 [3] was used. This related the half-thickness of a material of given thermal and kinetic properties with the temperatures at the center and the surface under critical steady-state conditions. This analysis has been applied to wood fiberboard and cotton linters and fair agreement with experimental results has been obtained [4].

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. These are broad assumptions, particularly for those materials for which the kinetic measurements were made on the liquid phase (DINA, CYCLOTOL and TNT).

Critical radius determinations for a sphere have been made for each explosive and are listed in Table 4, and shown graphically in Figure 2. It may be noted from the tables in reference [3] 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_c and 0.514 B_c respectively, where B_c is the critical radius for the sphere.

SUMMARY

Measurements of the specific heat, thermal conductivity and kinetic properties of six explosives have been made and are summarized in Tables 1 to 3. In the self-heating experiments, initial self-heating was observed at temperatures ranging from 126°C for DINA to 247°C for Q. With one exception, all materials were completely consumed during the experiments; a grey, crusty residue comprising about 5 per cent of the initial weight remained following the burning of QR. Activation energy values as measured by this method ranged from 35.5 to 65.8 kcal/mole.

A comparison of critical radius determinations, under the given assumptions, is presented in Table 4 and Figure 2. Size limitations on the storage of bulk quantities of DINA, CYCLOTOL and TNT and careful control of temperature and ventilation conditions seem justified on the basis of these calculations. Of course, consideration must be given to melting or other phase transformations occurring at relatively low temperatures. In the case of DINA, CYCLOTOL and TNT (apparent) melting occurred at temperatures of about 48°C, 67°C and 80°C respectively. Explosives Q, QR and RDX do not appear likely to present any storage hazard with respect to self-ignition at ordinary storage temperatures.

ACKNOWLEDGMENT

The specific heat measurements were made by E. S. Newman and the thermal conductivity measurements by D. R. Flynn.

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Table 1. Kinetic Measurements

Material	Temperature Range °C	State	Activation Energy E kcal/mole	Heat Generation Coefficient A cal/sec-cm^3
TNT	220-260	Liquid	37.0	7.80×10^{13}
RDX	170-200	Solid	57.2	3.47×10^{24}
Q	250-270	Solid	65.8	7.45×10^{23}
QR	200-275	Solid	38.6	5.43×10^{13}
DINA	130-175	Liquid	35.5	2.72×10^{16}
CYCLOTOL	155-180	Liquid	43.6	1.03×10^{19}

Table 2. Specific Heat Measurements

Material	Sample Weight g	Envelope Weight g	Temp. Rise deg C	Mean Temp. °C	Specific Heat cal/g-deg C	
TNT	98.7262	2.3383	1.68	23.8	0.2592	
			3.31	24.5	0.2742	
			"	"	.2582	0.264
RDX	102.0285	2.7555	"	"	0.2687	
			"	"	.2612	
			"	"	.2633	0.264
Q	112.6514	2.5743	"	"	0.2732	
			"	"	.2586	
			"	"	.2501	0.261
QR	107.1495	1.5606	"	"	0.2575	
			"	"	.2566	
			"	"	.2595	0.258
DINA	99.0307	1.4618	"	"	0.2713	
			"	"	.2732	
			"	"	.2700	0.272
CYCLOTOL	104.3517	1.5324	"	"	0.2537	
			"	"	.2608	
			"	"	.2614	0.259

Table 3. Thermal Conductivity Measurements

Material	Thickness cm	V/Vo	Cold Plate Temp. °C	Disc Temperature Center °C	Disc Temperature At R=5.08cm °C	Disc Temperature Mean °C	Mean Temp. °C	Thermal Conductivity, k mw/cm °C	Thermal Conductivity, k cal/sec cm °C
TNT	1.272	1.1094	24.72	40.18	41.87	41	33	2.04	0.000487
TNT	1.272	1.1029	24.57	50.36	53.01	52	38	1.93	0.000461
RDX	1.281	1.1083	21.97	51.19	54.35	53	37	2.05	0.000490
Q	1.273	1.1354	23.24	47.17	50.42	49	36	2.59	0.000619
QR	1.272	1.1316	18.89	44.25	47.21	46	33	2.50	0.000597
DINA	1.270	1.1275	0.05	12.00	13.52	13	6	2.33	0.000557
CYCLOTOL	1.271	1.1358	6.74	18.17	19.72	19	13	2.15	0.000600

Table 4. Critical Size Calculations

Critical Radius of a Sphere

Material	Surface Temperature 20°C (68°F)	48.9°C (120°F)	82.2°C (180°F)	100°C (212°F)
TNT	6.4×10^5 cm 2.1×10^4 ft	4.0×10^4 cm 1300 ft	3000 cm 97 ft	880 cm 29 ft
RDX	8.0×10^7 2.6×10^6	1.1×10^6 3.5×10^4	1.8×10^4 590	2700 90
Q	3.0×10^{11} 1.0×10^{10}	2.1×10^9 6.9×10^7	1.8×10^7 6.1×10^5	2.1×10^6 6.9×10^4
QR	3.2×10^6 1.1×10^5	1.8×10^5 5900	1.2×10^4 390	3300 110
DINA	9700 320	700 23	57 1.9	18 0.6
CYCLOTOL	5.0×10^5 1.6×10^4	1.9×10^4 620	860 28	210 6.8

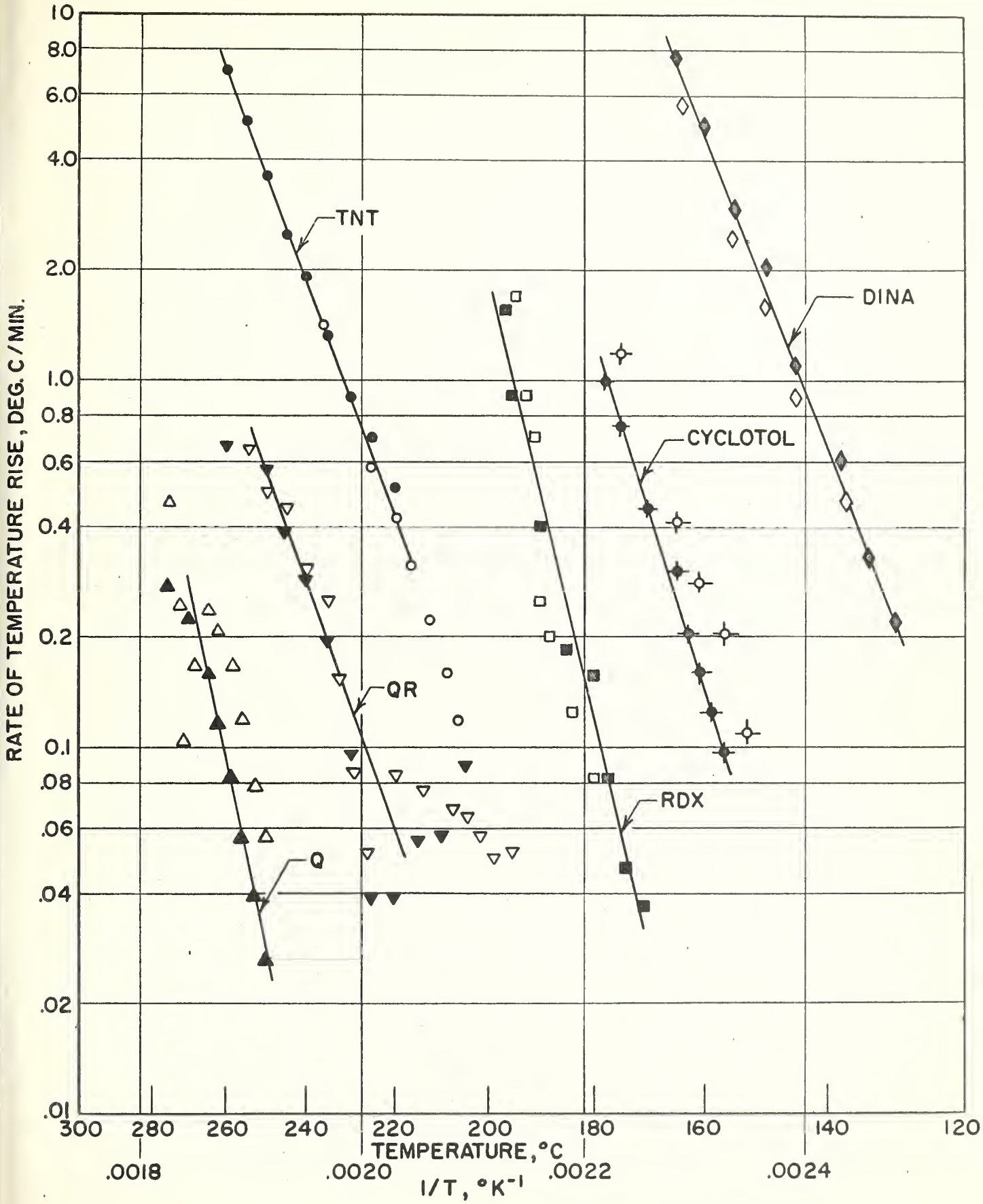

FIG. 1 – ADIABATIC SELF-HEATING DATA FOR SIX EXPLOSIVES

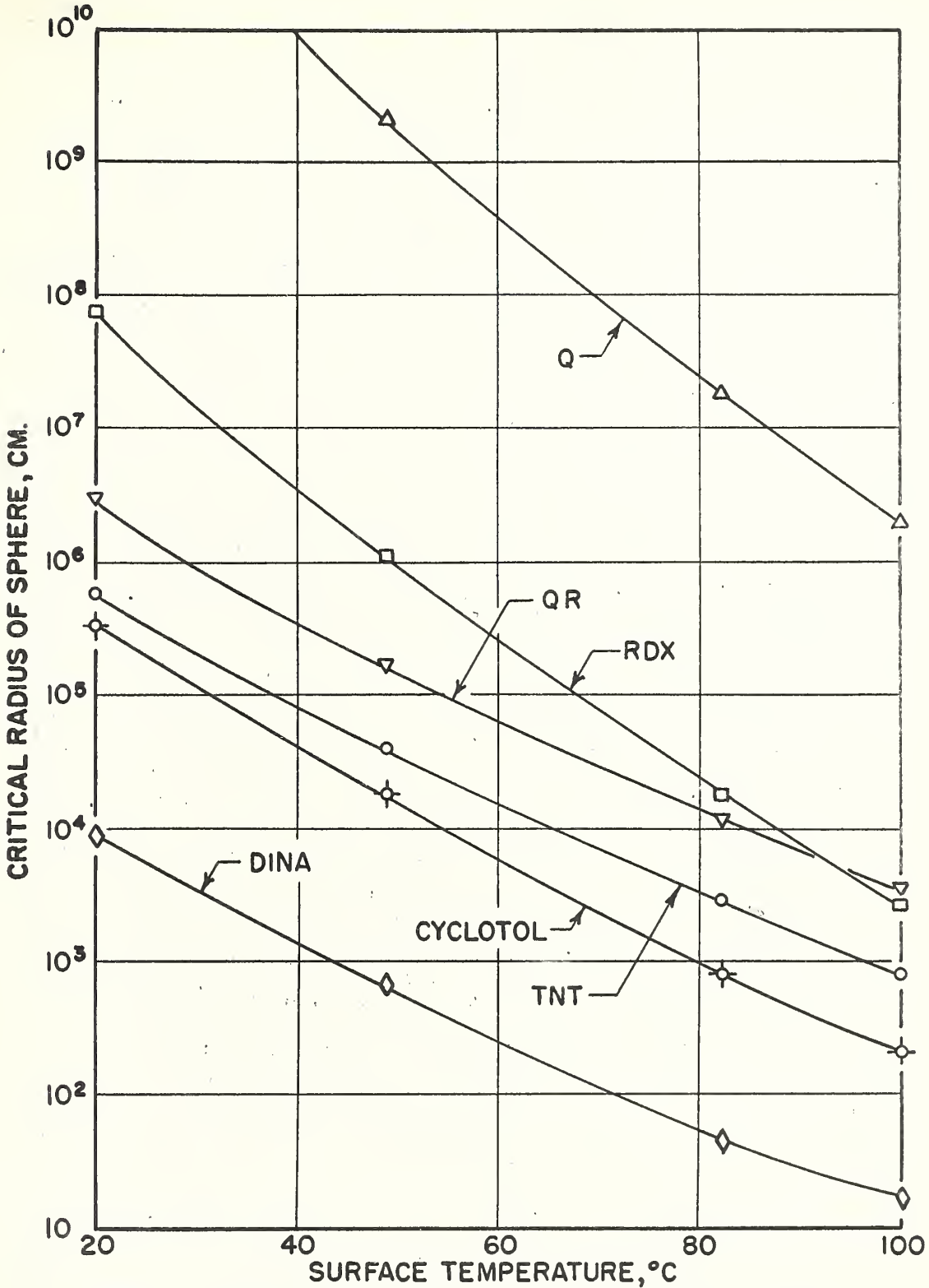

FIG. 2 – COMPUTED CRITICAL RADII AND CRITICAL SURFACE TEMPERATURES FOR SPHERICAL PILES OF SIX EXPLOSIVES

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