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NAVORD REPORT 2579

THE SENSITIVITY OF EXPLOSIVES

7 August 1952

U. S. NAVAL ORDNANCE LABORATORY

WHITE OAK, MARYLAND

RESTRICTED

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THE SENSITIVITY OF EXPLOSIVES

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ABSTRACT: A translation of a lecture on "The Sensitivity of Explosives", by Masayoshi Niimi in Japanese is given herein. An abstract of this lecture appeared in Chemical Abstracts, 33, 4423 (1939). This abstract was taken verbatim from the Japanese Journal of Engineering, 16, 62 (1938). The author claims to have proved the accuracy of his calculated theoretical formula for sensitivity of explosives. Therefore, it seemed worthwhile to make the complete English text of his lecture available to those concerned with sensitivity of explosives.

Explosives Research Department
U.S. NAVAL ORDNANCE LABORATORY
WHITE OAK, MARYLAND

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The abstract of Masayoshi Niimi's lecture which appeared in Chemical Abstracts indicated that a fundamental contribution to a theory of sensitivities of explosives had been made. Therefore, a photostatic copy of the Japanese text of the lecture was obtained and has been translated. The assistance of Commander R. W. McNitt, USN, in obtaining the photostat, and in procuring translation are acknowledged with gratitude.

EDWARD L. WOODYARD
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By direction

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THE SENSITIVITY OF EXPLOSIVES*

INTRODUCTION

The article on the Sensitivity of Explosives by Masayoshi Niimi was published in the Journal of the Military Explosives Society 30, No. 2 106-111 (1936). The photostatic copy was obtained by the Department of State. Their Tokyo mission found that a copy of the original journal is filed in the Library of Tokyo University. This was traced through the National Diet Library, who obtained the photostatic copy. It seems probable that this photostat is the only one available in the United States and the translation thereof is the only English translation in existence. The translation follows.

SUMMARY

A formula for the sensitivity of explosives has been derived from the theoretical view of the sensitivity of explosives by adding physical and chemical interpretations to it. We discovered from this formula that the sensitivity of explosives could be analyzed from two factors, chemical and physical. The accuracy of the derived formula has been proved by the sensitivity test made by dropping a hammer on picric acid and on tetryl under various temperatures. Calculating from the test value, the activation energy of the picric acid and tetryl were 75 Kcal/mol and 38 Kcal/mol respectively. Consequently, we will show here that even for those typical explosive compounds the molecule itself is not necessarily unstable.

THEORY

Derivation of the Theoretical Formula

According to the theory of chemical reactions a molecule must acquire more energy than a given quantity E_A for its own decomposition. E_A is the so called activation energy. Now then, the energy within a molecule consists of the energy of vibration of atoms, energy of rotation of the molecule and energy of the electrons. However, in regard to the activation of a solid molecule, it is generally believed that of these energies the vibration energy is the only problem, in other words, E_A consists of only energy of vibration of the atoms within that molecule.

This principle, of course, could also be applied to explosives. Furthermore, it is known, in regard to explosives, that in order to bring about an explosive decomposition of a mass as a whole, a great many neighboring molecules must be decomposed in a limited area simultaneously.(1) In other words, when, by some method, the energy which is necessary for the decomposition of many neighboring molecules is exerted on a limited mass of an explosive compound, a sufficiently large number of neighboring molecules

*Lecture delivered at the Third University Association Meeting by Masayoshi Niimi a Navy Ordnance Lt. (Sr. grade) attached to the Research Section of the Naval Explosive Factory.

are activated by the cooperative action created by the simultaneous decomposition of molecules in that area and thereby an explosive decomposition is created. With this occurrence, the action is propagated to the entire explosive mass by a chain reaction and the entire mass is exploded. Many neighboring molecules such as described above constitute a so called explosive center and their number is represented here by n.

Now, if the average energy possessed by a molecule of an explosive at a given temperature is expressed by E, the average energy which is necessary for the activation of that molecule at that temperature is $E_A - E$. Consequently, the necessary energy to start an explosion of that mass of explosive is $n(E_A - E)$.

When an energy A is exerted on an explosive test material, only 1/s of this energy will be consumed in the formation of an explosive center in the test material. Then, when energy A satisfies the following formula, the explosion will occur, and when it does not satisfy the formula, the explosion will not occur.

$$A/s = n(E_A - E) \quad \text{or} \quad A = sn(E_A - E) \qquad (1)$$

In other words, formula (1) is a theoretical formula which shows the sensitivity.

As stated above in formula (1), the E_A is created from the vibration energy of atoms, and the vibration energy of the atoms is the only energy which affects the specific heat of a solid at ordinary temperature. Therefore, the E in formula (1) can be represented by formula (2):

$$E = \frac{1}{N_A}\int_0^T C_v dT \qquad (2)$$

In the above formula, N_A is Avogadro's number, C_v is the molecular heat at constant volume, and T is the absolute temperature. Since E is known and a function of temperature, formula (1) gives the relation between the temperature and sensitivity; when the E of formula (1) is replaced by formula (2), the formula (3) can be derived:

$$A = sn(E_A - \frac{1}{N_A}\int_0^T C_v dT) \qquad (3)$$

Two Factors of Sensitivity

Looking at formula (1), it is evident that the sensitivity can be attributed to two factors, chemical and physical. In other words, $n(E_A - E)$

is a chemical factor and is the necessary energy to explode a mass of explosive. Consequently, it is peculiar to each explosive and peculiar in each molecule of the compound. Also, s is a physical factor and is related to the ratio of the energy that is consumed in the formation of an effective explosive center out of the total energy exerted on the test material. Consequently, it is determined by the physical properties of the test materials, test conditions, etc. The sensitivity of each explosive, therefore, is characterized by the magnitude of those two factors, and explosives are classified by their sensitivity as in Table 1.

Table 1

Classification of Explosives by Sensitivity

Sensitivity	First Type	Second Type	Third Type	Fourth Type
Chemical Factor	Small	Small	Large	Large
Physical Factor	Small	Large	Small	Large
Sensitivity	Most sensitive	Sensitive to heat but insensitive to such physical actions as shock and friction	Reverse of the second kind	Most insensitive

In discussing the relationship between the sensitivity of explosives, such physical and chemical characteristics as the molecular structure of the explosives, heat of formation, heat of explosion, ignition point, and the activation energy must also be taken into consideration. Also it should be understood that the difference in sensitivity of tested explosives of the same type results from different test methods and is caused by physical factors. For example, the equivalent relation between shock sensitivity and friction sensitivity is expressed as a factor on both tests. While it may be called shock sensitivity or friction sensitivity, in the final analysis it does not concern anything but the difficulty or ease of transmitting mechanical energy exerted on the test material by shock or friction to the explosive as a vibration energy of the atoms which compose the molecules of the explosive.

The A in formula (1) can be determined experimentally, and the value of E corresponding to the test temperature, can be determined from formula (2). Consequently, the activation energy E_A and an can be computed from a set of data obtained from the sensitivity test carried out under various temperature conditions.

EXPERIMENT

A sensitivity test by hammer dropping on picric acid and tetryl was carried out at various temperatures.

Test Samples

(1) Pure crystalline picric acid with a melting point of 121.4 degrees centigrade and tetryl with a melting point of 130.2 degrees centigrade

(2) Test quantity

These samples were carefully weighed in a chemical balance. The amount used was 0.080 grams in the first test and 0.0635 grams in the second test.

(3) Shape, compression and wrapping

Quantitatively weighed picric acid or tetryl was wrapped in two pieces of tinfoil (230 by 300 millimeters weighing 6.00 ~ 6.09 grams) (diameters 15.5 millimeters and 9.5 millimeters for the first test, and diameters 14.5 millimeters and 8.5 millimeters for the second test), and each sample was compressed under a pressure of 25 kilograms per square centimeter, and thereby made into disks of 10 millimeters diameter for the first test and 9 millimeters diameter for the second test. Both were of 1 millimeter thickness.

Hammer Dropping Apparatus

(1) Weight of hammer: 2.178 kilograms

(2) Apparatus for hammer dropping

An electromagnet was used. The mechanism was arranged so that electric current was sent first through the primary coil which demagnetized the core and let the hammer drop by its own weight. In the use of this apparatus, the consistency in the manner of dropping the hammer, the most important factor controlling the accuracy of the sensitivity test, was markedly favorable.

Reading of Temperatures

For the reading of temperatures, a platinum wire sealed thermometer was used in order to decrease the time lag.

Testing Method

The material to be tested was placed on a steel column, 12.7 millimeters in height and 12.7 millimeters in diameter, which in turn was mounted on an anvil. The hammer was dropped on it and the occurrence or absence of an explosion was observed.

Test Results

Test results are shown in Tables 2 through 5, and in Figures 1 and 2.

Table 2

Picric Acid (Test 1)
(Test Weight 0.030 g - Testing Diameter 10 mm)

Test Temperature (°C)	Height of Fall (cm)	Explosion Ratio	Critical Explosion (cm)
25.0	47.2	22/40	46.8
	46.6	19/40	
32.5	46.6	22/40	46.4
	46.0	17/40	
37.0	46.0	19/40	46.2
	45.4	15/40	
46.5	45.8	20/40	45.8
54.5	45.8	22/40	45.4
	45.2	19/40	
62.5	44.6	17/40	44.9
	44.0	11/40	
71.0	44.6	19/40	44.7
	44.0	13/40	

Table 3

Picric Acid (Test 2)
(Test Weight 0.0635 g - Test Diameter 9 mm)

Test Temperature (°C)	Height (cm)	Explosion Ratio	Critical Explosion Point (cm)
19.5	41.9	15/40	42.4
	42.5	21/40	
21.5	41.5	20/40	42.1
	42.5	29/40	
26.5	41.9	19/40	42.2
	42.5	22/40	
31.5	41.5	18/40	41.8
	42.3	23/40	
38.0	41.1	16/40	41.5
	41.7	21/40	
44.0	41.1	18/40	41.4
	41.9	23/40	

Table 4

Tetryl (Test 1)
(Test Weight 0.080 g - Test Diameter 10 mm)

Test Temperature (°C)	Height (cm)	Explosion Ratio	Critical Explosion Point (cm)
22	44.4	23/40	43.65
	43.4	19/50	
27	43.4	22/40	42.9
	42.4	18/40	
32	43.0	22/40	42.5
	42.0	18/40	
37	42.2	21/40	41.7
	41.2	19/40	
42	42.4	23/40	41.65
	41.4	19/40	
47	41.8	24/40	41.0
	40.8	19/40	
52	40.4	21/40	40.2
	39.4	15/40	

Table 5

Tetryl (Test 2)
(Test Weight 0.0635 g - Test Diameter 9 mm)

Test Temperature (°C)	Height (cm)	Explosion Ratio	Critical Explosion Point (cm)
22	39.15	13/40	39.7
	39.95	23/40	
28	38.15	12/40	38.8
	39.15	25/40	
34	38.35	19/40	38.5
	38.95	23/40	
40	37.75	19/40	37.85
	38.75	25/40	
46.5	37.15	19/40	37.25
	38.75	25/40	
52	36.55	18/40	36.75
	37.15	24/40	

FIG. 1

PICRIC ACID

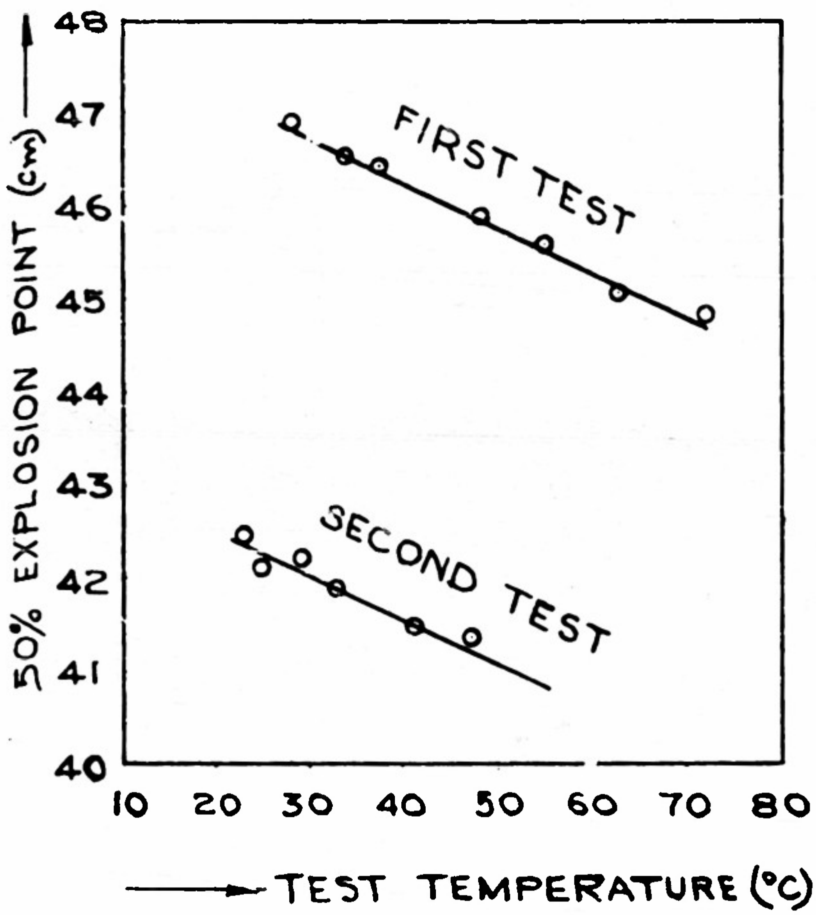
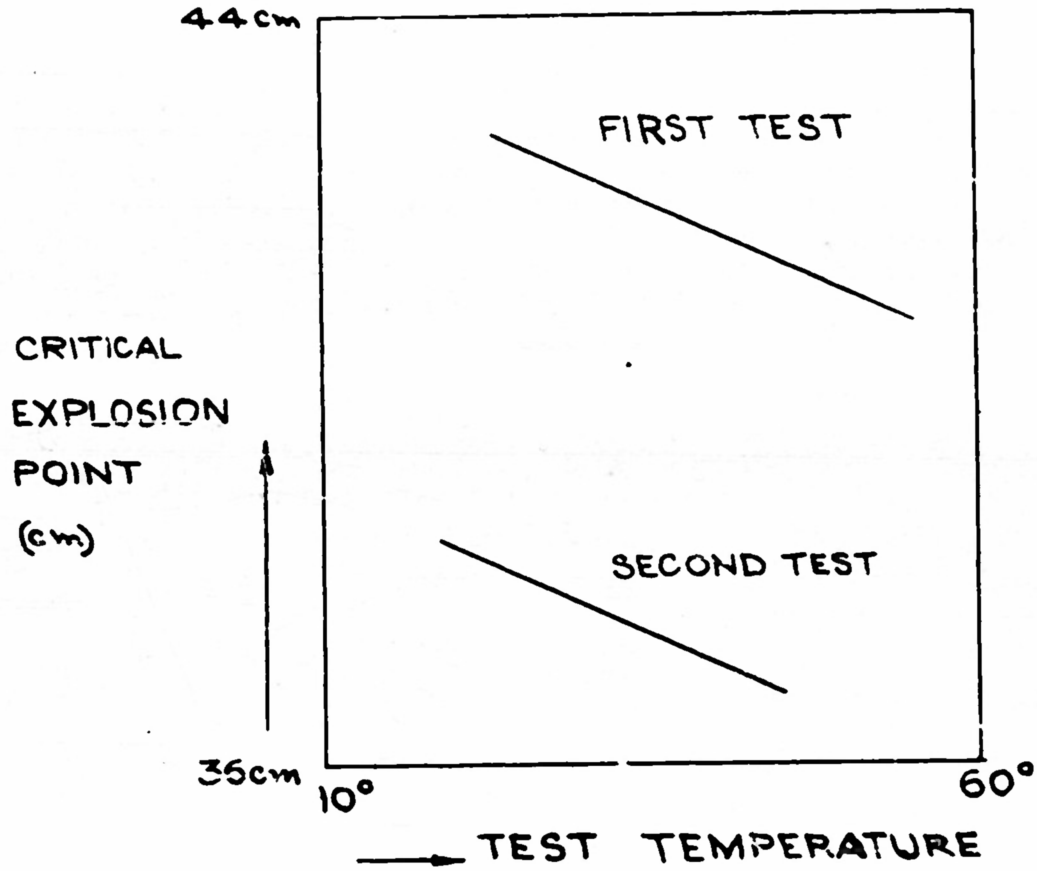


FIG. 2

TETRYL


44cm
35cm
CRITICAL
EXPLOSION
POINT
(cm)
FIRST TEST
SECOND TEST
10°
60°
TEST TEMPERATURE

CALCULATIONS

The value of A at various temperatures was determined by this experiment. In order to use formula (1), it is necessary to know the average energy E which represents the energy of the molecule at a given temperature. Now, the test values of the specific heat of picric acid and of tetryl which have been determined by Taylor and Rinkenback (3) are listed in the first and second columns of Tables 6 and 7.

The following formula is derived from Einstein's theoretical formula for atomic heat of solids as a test formula which shows the average energy of solid molecules.

$$E = \frac{K}{e^{\theta/T} - 1} \quad (4)$$

In this formula, K and Θ are constants. In formula (4), when it is assumed that $K = 2.81 \times 10^{-12}$ and $\Theta = 510$ in the case of picric acid and $K = 1.26 \times 10^{-12}$ and $\Theta = 270$ in the case of tetryl, E appears in ergs; when this value is converted to calories per gram, the result shows a satisfactory agreement with the test value as listed in column 4 of Tables 6 and 7. The test value however, is the molecular heat at constant pressure, and in this case it is assumed that $C \approx C_v$.

Table 6

Specific Heat and Heat Capacity of Picric Acid

Temperature Range (°C)		Average Specific Heat	Heat Capacity (cal/g) Test Value	Computed Value
-182.8	0.0	0.176	31.2	31.9
-182.8	19.0	0.182	36.7	37.0
-182.8	98.1	0.210	59.0	59.8
-182.8	121.5	0.219	66.6	66.7

Table 7

Specific Heat and Heat Capacity of Tetryl

Temperature Range (°C)		Average Specific Heat	Heat Capacity (cal/g) Test Value	Computed Value
-182.8	0	0.188	34.4	34.3
-182.8	22.5	0.191	39.2	39.2
-182.8	97	0.200	56.0	55.8

A and E at various temperatures are thus determined and are shown in the third and fourth columns of Tables 8 through 11.

Table 8

Picric Acid (Test 1)

Test Temperature (°C)	Critical Falling Height (cm)	A (erg)	E (erg/molecule)	sn	E_A (erg/molecule)
25.0	46.8	9.99×10^{7}	6.20×10^{-13}	2.24×10^{19}	5.09×10^{-12}
32.5	46.4	9.90	6.52	"	"
37.0	46.2	9.86	6.72	"	"
46.5	45.8	9.78	7.14	"	"
54.5	45.4	9.69	7.50	"	"
62.5	44.9	9.58	7.87	"	"
71.0	44.7	9.54	8.25	"	"

Table 9

Picric Acid (Test 2)

Test Temperature (°C)	Critical Falling Height (cm)	A (erg)	E (erg/molecule)	sn	E_A (erg/molecule)
19.5	42.4	9.05×10^{7}	5.95×10^{-13}	$1.$[illegible]$\times 10^{19}$	5.25×10^{-12}
21.5	42.1	8.99	6.40	"	"
26.5	42.2	9.01	6.26	"	"
31.5	41.8	8.92	6.48	"	"
38.0	41.5	8.86	6.76	"	"
44.0	41.4	8.84	7.03	"	"

Table 10

Tetryl (Test 1)

Test Temperature (°C)	Critical Falling Height (cm)	A (erg)	E (erg/molecule)	sn	E_A (erg/molecule)
22	43.65	9.32×10^{7}	8.41×10^{-13}	5.20×10^{19}	2.63×10^{-12}
27	42.9	9.16	8.62	"	"
32	42.5	9.07	8.85	"	"
37	41.7	8.90	9.06	"	"
42	41.65	8.89	9.29	"	"
47	41.0	8.75	9.50	"	
52	40.2	8.59	9.72	"	"

Table 11

Tetryl (Test 2)

Test Temperature (°C)	Critical Falling Height (cm)	A (erg)	E (erg/molecule)	sn	E_A (erg/molecule)
22	39.7	8.48×10^{7}	8.41×10^{-13}	4.65×10^{19}	2.66×10^{-12}
28	38.8	8.27	8.67	"	"
34	38.5	8.21	8.94	"	"
40	37.85	8.08	9.20	"	"
46.5	37.25	7.95	9.48	"	"
52	36.75	7.84	9.72	"	"

Plotting the values of Tables 8 through 11, for A~E, a straight line results as is shown in Figures 3 and 4. Consequently, the calculated results from formula (1) are listed in the fifth and sixth columns of Tables 8 through 11. In other words, in case of picric acid, 5.1×10^{-12} ergs per molecule or 74 Kcal/mol was obtained from Test 1 as the activation energy. Also, sn is identical within the test temperature range and Test 1 shows 2.24×10^{19} and Test 2 shows 1.94×10^{19}.

In case of tetryl, 2.6×10^{-12} ergs per molecule or 38 Kcal/mol is the Test 1 and 2.7×10^{-12} ergs per molecule or 38 Kcal/mol for the Test 2 were obtained for the activation energy. Also, within that range of test temperature, sn is constant and is 5.2×10^{19} for Test 1 and 4.6×10^{19} for Test 2.

EXAMINATION OF THE TEST RESULTS

The activation energies of picric acid and tetryl which were obtained from Test 1 and Test 2 (conducted under different experimental conditions) are equal within the range of experimental error and are 75 Kcal/mol and 38 Kcal/mol respectively. In other words, the amount of the activation energy of picric acid and tetryl, which are typical explosive compounds, is the same as such non-explosive compounds as saturated hydrocarbons. This proves that the molecules of the explosive compounds are not necessarily unstable and the reason that explosives as a system (mass) are thought to be unstable is simply because when a limited volume of an

FIG 3
PICRIC ACID

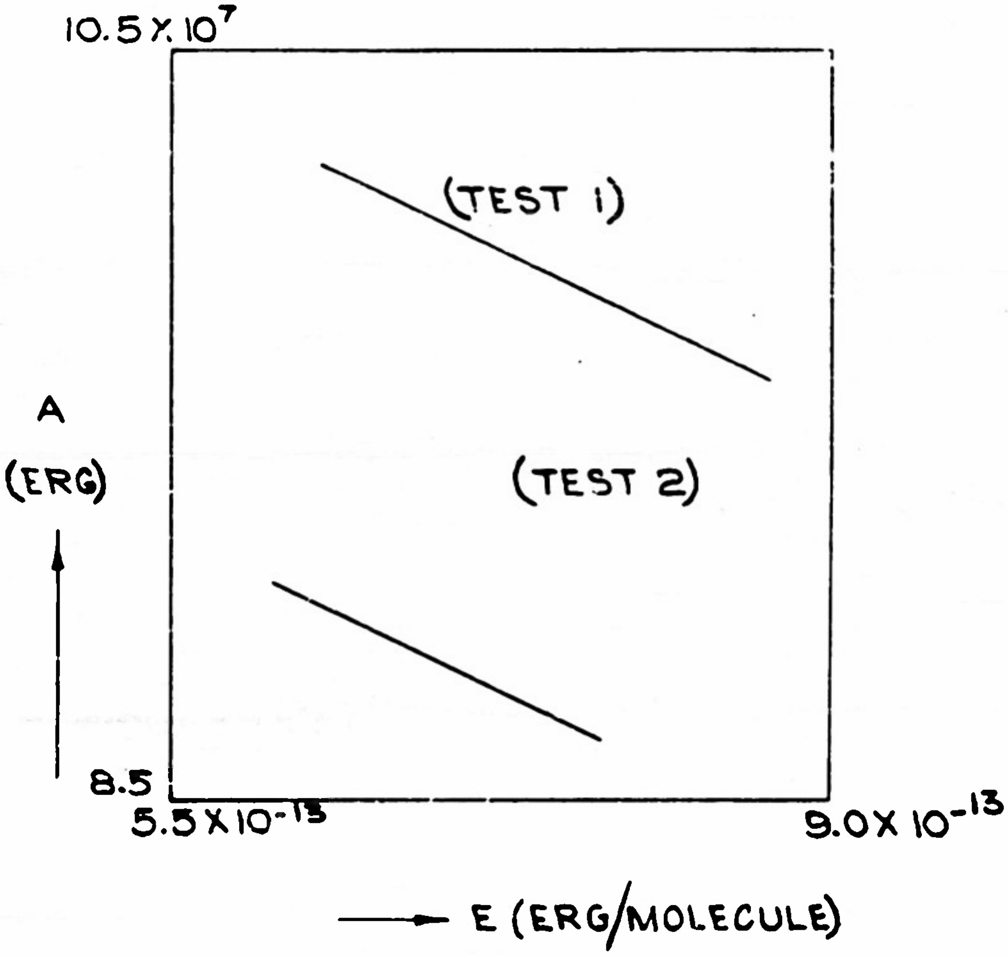
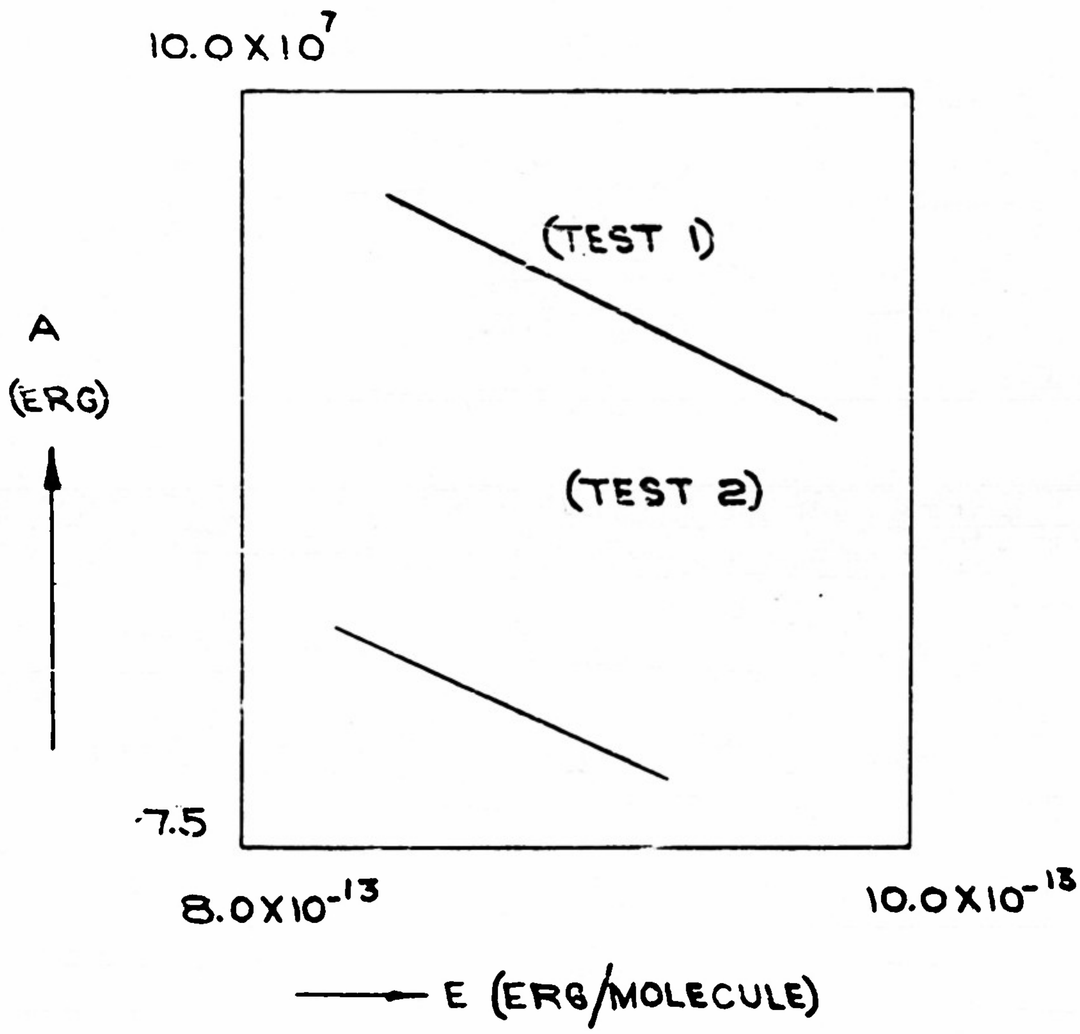


FIG 4
TETRYL


10.0X10^7
(TEST 1)
A
(ERG)
(TEST 2)
7.5
8.0X10^-13
10.0X10^-13
E (ERG/MOLECULE)

explosive mass starts to explode, the entire mass explodes. This action occurs because, when the limited volume explodes, the released energy is great enough to activate large numbers of neighboring molecules. This fact corrects the original idea that the molecules of explosives are especially unstable.

Also, in regard to sn the fact that the same results are obtained from Test 1 and Test 2 of picric acid and of tetryl proves that s, the physical factor, is constant since n is constant in those tests.

This is as can be expected since test conditions are always the same except the physical characteristics of the tested materials and the temperature. Also the fact that the sn is small in Test 2, where the diameters of the tested materials were smaller compared to Test 1, definitely coincides with the results expected from the above theory.

By the results of these tests, the accuracy of the calculated theoretical formula for sensitivity has been proved.

Russell McGill
RUSSELL McGILL

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