

UNCLASSIFIED

AD NUMBER	
ADA800110	
CLASSIFICATION CHANGES	
TO:	unclassified
FROM:	restricted
LIMITATION CHANGES	
TO: Approved for public release; distribution is unlimited.	
FROM: Distribution authorized to DoD only; Test and Evaluation; DEC 1948. Other requests shall be referred to Army Office of the Chief of Research and Development, Pentagon, Washington, DC 20310.	
AUTHORITY	
E.O. 10501, 5 Nov 1953; OCRD ltr, 25 Feb 1970	

THIS PAGE IS UNCLASSIFIED

UNCLASSIFIED

AD _____

DEFENSE DOCUMENTATION CENTER

FOR

SCIENTIFIC AND TECHNICAL INFORMATION

CAMERON STATION ALEXANDRIA, VIRGINIA

DOWNGRADED AT 3 YEAR INTERVALS:
DECLASSIFIED AFTER 12 YEARS
DCD DIR 5200.10



UNCLASSIFIED

**THIS REPORT HAS BEEN DECLASSIFIED
AND CLEARED FOR PUBLIC RELEASE.**

**DISTRIBUTION A
APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION UNLIMITED.**

The Thermal Stability of Nitromethane Project No. TV2-1

51272

(None)

Griffin, Donald N.

California Inst. of Technology, Jet Propulsion Lab., Pasadena, Calif.

PR-9-24

US Army Centr. No. W-04-200-ORD-1482

(None)

Dec '48 Restr. U.S. English 30 photos, tabs, diagrs, graphs

A study has been made of nitromethane as an attempt to establish the temperature limits of the thermal stability of nitromethane as a first step in the development of fundamental data concerning the combustion as well as the thermal decomposition of nitromethane. The thermal decomposition of nitromethane apparently falls into two categories, the first being the normal decomposition which may be assumed to involve a simple breaking down of the nitromethane molecule, followed by oxidation, leading to normal oxidation, or combustion products. The rates of this mechanism of decomposition are measurable, and the temperature limits have been clearly defined. Second, there exists a high-order mechanism by which nitromethane decomposes with detonation violence under certain conditions of heating. This mechanism, as yet unidentified may cause unpredictable and often unexplained explosions. The temperature region in which these detonations occur has also been defined.

Copies of this report obtainable from CADO.

Fuels and Lubricants (12)

Fluid Propellants (7)

(1)

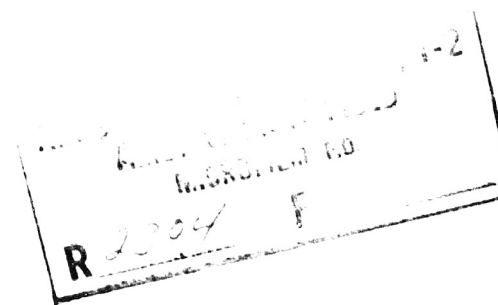
Nitromethan - Propellant properties

(6847); Propellants, Liquid - Physical properties (75456.25);

Propellants, Liquid - Stabilizers (75456.45); Oxidant - Pro-

pellant - Combination (68499)

USA C.N. W-04-200-ORD-1482



*Dup.
Rockets
Propellants*

RESTRICTED

ATI No. 51272

This document contains information affecting the National Defense of the United States within the meaning of the Espionage Act U.S.C. 5031 and 32. Its transmission or the revelation of its contents in any manner to an unauthorized person is prohibited by law.

PROGRESS REPORT No. 9-24

THE THERMAL STABILITY OF NITROMETHANE

DONALD M. GRIFFIN

JET PROPULSION LABORATORY

CALIFORNIA INSTITUTE OF TECHNOLOGY

PASADENA, CALIFORNIA

DECEMBER 8, 1948

RESTRICTED

RESTRICTED

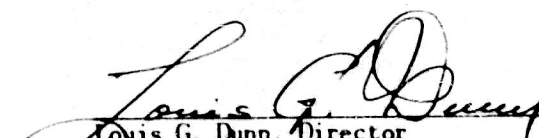
Project No. TU2-1
Contract No. W-04-200-ORD-1482
BASIC RESEARCH ON ROCKET PROPELLANTS

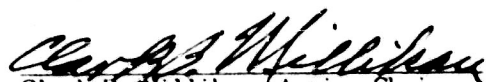
Progress Report No. 9-24

THE THERMAL STABILITY OF NITROMETHANE

Donald N. Griffin


Martin Summerfield, Chief
Rockets and Materials Division


Louis G. Dunn, Director
Jet Propulsion Laboratory


Clark B. Millikan, Acting Chairman
Jet Propulsion Laboratory Board

Copy No. 15

JET PROPULSION LABORATORY
California Institute of Technology
Pasadena, California
December 8, 1948

RESTRICTED

TABLE OF CONTENTS

	Page
I. Introduction and Summary	1
II. Thermal Decomposition Tests	1
A. Bomb Tests	1
B. Capillary-Tube Tests	5
III. Conclusion	7
A. Rapid Thermal Decomposition of Nitromethane	7
B. Thermal Detonation of Nitromethane	7
C. Future Studies	8
Tables	9
Figures	13
References	25

LIST OF TABLES

	Page
I. Thermal Decomposition Bomb Tests with a Heating Block Held at Temperatures Between 450 and 540°C	9
II. Preliminary Series of Thermal Decomposition Bomb Tests, Using a Small-Size Copper Block Heating Apparatus Having a Slower Heating Rate Than the Main Apparatus	10
III. Thermal Decomposition Bomb Tests with a Heating Block Held at Temperatures Between 350 and 400°C	10
IV. Tests Made by Heating Nitromethane in Sealed Glass Capillary Tubes	11

LIST OF FIGURES

	Page
1. Thermal Decomposition Bomb	13
2. Thermal Decomposition Bomb and Copper Heating Block, Disassembled	14
3. Thermal Decomposition Bomb and Copper Heating Block in Operating Position	14
4. Diagram of Thermal Decomposition Apparatus	15
5. Representative Test of Nitromethane in Thermal Decomposition Bomb	16
6. Temperature at Which Rapid Decomposition Occurred vs Temperature of the Heating Block	17
7. Half-Life of Nitromethane vs Temperature	17
8. Vapor Pressure of Nitromethane	18
9. Pressure Effect in the Critical Region of a Sample of Nitromethane Having a Mean Bulk Density Less Than the Critical Density	19
10. Pressure Effect in the Critical Region of a Sample of Nitromethane Having a Mean Bulk Density Greater Than the Critical Density	20
11. Log p vs $1000/T$ for Some of the Samples of Nitromethane Which Detonated	21
12. Brass Heating Block for Glass Capillary-Tube Tests	22
13. Brass Heating Block Enclosed in Shield	22
14. Time before Explosion vs Temperature for Nitromethane Capillary-Tube Tests	22
15. Temperature Scale of Nitromethane	23

I. INTRODUCTION AND SUMMARY

The use of mononitromethane as a rocket fuel, either monopropellant or bi-propellant, has long been recognized as offering distinct advantages with respect to performance, storage and handling, toxicity, etc. Yet after approximately 5 years of developmental research at this Laboratory and elsewhere, no successful nitromethane motor has been placed in service. Test motors have been operated satisfactorily, but their development beyond the test stage has been prevented by (a) problems of combustion which necessitate the use of a motor having a very large L^* and (b) heat and shock sensitivity of nitromethane, which have caused frequent, violent, and unpredictable explosions during motor operations.

This situation indicates the need for considerable fundamental investigation of various phases of nitromethane combustion, combustion catalysis, and its thermal and shock sensitivity. Sufficient information has been obtained concerning the shock sensitivity to permit a reasonably good definition (Cf. Ref. 1) of the limits of safety of handling, etc. However, previous studies of the thermal sensitivity of nitromethane have led to conflicting data by various workers, indicating the dependence of their data on their experimental procedure. No clearly defined limits of thermal stability have been reported.

In the investigation described in the present report, an attempt was made to establish the temperature limits of the thermal stability of nitromethane as a first step in the development of fundamental data concerning the combustion as well as the thermal decomposition of nitromethane. The thermal decomposition of nitromethane apparently falls into two categories, the first being the normal decomposition which may be assumed to involve a simple breaking down of the nitromethane molecule, followed by oxidation, leading to normal oxidation, or combustion products. The rates of this mechanism of decomposition are measurable, and the temperature limits have been clearly defined. Second, there exists a high-order mechanism by which nitromethane decomposes with detonation violence under certain conditions of heating. It is assumed that this second mechanism, as yet unidentified, gives rise to the unpredictable and often unexplained explosions that have hampered the efforts to develop a successful nitromethane motor. The temperature region in which these detonations occur has also been defined.

II. THERMAL DECOMPOSITION TESTS

A. Bomb Tests

Tests were conducted to determine the temperature region where rapid decomposition of nitromethane occurs. Previous workers have reported temperatures varying from 288 to 410°C: Laurence (Cf. Ref. 2), using a thin-walled, stainless-steel tube wound with a nichrome electric heating element, recorded bulk temperatures of 288

$\pm 28^\circ\text{C}$ for the rapid decomposition of nitromethane. Kaplan (Cf. Ref. 1), using a thin-walled, stainless-steel bomb heated with a Bunsen flame, obtained bulk temperatures of $318 \pm 20^\circ\text{C}$. McKittrick (Cf. Ref. 3) reported an explosion temperature of approximately 410°C for nitromethane in a glass capillary tube heated rapidly in a copper block. These variations in the reported temperature of rapid decomposition of nitromethane indicate the apparent dependence of the results on the apparatus and the heating procedure used.

Apparatus and procedure. In the present investigation samples of 1.5 to 2.0 ml of nitromethane, purified by fractional crystallization, were placed in a stainless-steel bomb having an internal volume of approximately 8 ml (Cf. Fig. 1), and were heated by means of an electrically heated copper block into which the bomb fitted (Cf. Figs. 2 and 3). The temperature of the sample was recorded by a thermocouple located within the bomb and attached to a Leeds and Northrup Micromax recorder. The pressure was recorded by a Brown Company Bourdon-type recording gage connected to the bomb by an oil-filled capillary line. The temperature of the copper block was also recorded by the Micromax, and was automatically controlled by a controller unit attached to the Micromax recorder (Cf. Fig. 4). The point of rapid decomposition of the sample was accompanied by a sudden rise in the temperature and pressure of the system (Cf. Fig. 5). The bomb was designed to withstand the maximum pressures developed, therefore the system remained closed during the entire period of a test.

Normal rapid decomposition of nitromethane. A series of thirty tests was made with the block held at constant temperature throughout each test; however, the block temperature was varied between tests from 450 to 540°C (Cf. Table I). An average was made of the results of the tests in which rapid decomposition occurred above 390°C . The average decomposition temperature was 411°C (with an average deviation of $\pm 8^\circ\text{C}$) and corresponded to an average block temperature of 481°C (with an average deviation of $\pm 20^\circ\text{C}$). It was observed that higher block temperatures resulted in slightly lower decomposition temperatures, and this effect was considered to be caused by slight local overheating of the sample at the walls of the bomb. Therefore a plot was made of observed decomposition temperature vs block temperature (Cf. Fig. 6), in order to obtain a straight line representing the average trend of the points, three points were plotted at the following values which represented the average value plus the two points of average deviation:

Block Temperature ($^\circ\text{C}$)	Decomposition Temperature ($^\circ\text{C}$)
481 (average value)	411 (average value)
501 ($481 + 20$)	403 ($411 - 8$)
461 ($481 - 20$)	419 ($411 + 8$)

This line was then extrapolated to the point of zero heat flux in the bomb (i.e., the point at which the temperature of the copper block equals the temperature

of rapid decomposition) in order to eliminate the heating effect. The average deviation of the points about this line was $\pm 4.6^\circ\text{C}$. However, it can be seen that the points tend to converge at the point of zero heat flux, as would be expected if the increase in the amount of scatter of the points at higher block temperatures was attributed to local overheating. This method of interpretation gave 431°C for the approximate temperature at which normal rapid decomposition occurs.* Although the average deviation of the lower half of the points, as plotted about the line, was $\pm 3^\circ\text{C}$, indicating a deviation of even less than this value at the point of zero heat flux, the final value assigned to the temperature of normal rapid decomposition was $431 \pm 5^\circ\text{C}$, inasmuch as this value represents only an approximate upper temperature limit at which these decompositions can occur, not an exact physical point.

When this curve is extrapolated to high block temperatures, it gives qualitative agreement with the temperature reported by Kaplan (Cf. Ref. 1) and Laurence (Cf. Ref. 2) if it is assumed in each case that they had conditions of severe local overheating at the walls of their apparatus to temperatures above their recorded bulk temperatures.

Two tests were then made to determine the effect of additives on the temperature of decomposition. In one test commercial grade nitromethane was used, and in the other nitromethane containing 2½ per cent aniline (a mixture known to be sensitive to detonation by shock). In neither case was the temperature of normal rapid thermal decomposition affected.

In the preceding tests, the rate of heating of the bomb and the time elapsed before decomposition were dependent on the block temperature. In order to determine the effect of the length of time of the test on the temperature of decomposition, the results of these tests were compared with preliminary tests that had been made using a smaller copper block (which gave lower heating rates) and a bomb of approximately 15-ml internal volume (Cf. Table II). The average time elapsed before decomposition in the tests made with the large copper block was approximately 9 minutes. In the tests made with the small block, the average elapsed time was 18 minutes. However, when a plot was made of observed decomposition temperature vs block temperature for the series of tests made with the small block, there was no apparent difference in the temperature of rapid decomposition for a given block temperature as compared with the series of tests made with the large copper block (Cf. Fig. 6).

It is therefore reasonable to assume that the effect of the variations in the length of time of the tests is negligible within the limits of reproducibility of these tests.

On the basis of their studies of the rate of decomposition of nitromethane in the gas phase at low pressures, Taylor and Vesselovsky (Cf. Ref. 4) reported that rapid decomposition occurred in the region from 330 to 420°C . They determined the fractional lives of nitromethane in this temperature range, and reported the energy of activation to be 61,000 calories. From the values for the half-life and energy of activation as

*A rough calculation was made of the wall temperature of the bomb under average conditions, and a temperature difference of approximately 10°C was obtained between the wall temperature and the bulk temperature of the sample. This value is of the same order of magnitude as the amount of correction obtained by the method of extrapolation given above, and therefore lends support to that method.

given by Taylor and Vesselovsky, values of the half-life of nitromethane were calculated for various temperatures using the following form of the Arrhenius-equation:

$$\frac{t_{1/2}(T_1)}{t_{1/2}(T_2)} = e^{\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)}$$

A plot was then made of half-life $t_{1/2}$ vs temperature T (Cf. Fig. 7). The sharp decrease in the half-life at approximately 400°C would indicate rapid thermal decomposition in this region. This effect further lends support to the belief that the mechanism of the decomposition above 400°C observed in these tests is similar to that obtained by Taylor and Vesselovsky and that this mechanism constitutes the normal rapid thermal decomposition of nitromethane.

In roughly 15 to 20 per cent of the tests, a low-temperature decomposition occurred in the region from 280 to 350°C (Cf. Table I and Fig. 6). The reaction was more violent than in other tests, always causing a rupture at some point in the apparatus, and it appeared to be a higher-order reaction resembling a detonation. In the case of normal rapid decomposition, the temperature and pressure rises could be seen to accelerate just before explosion (Cf. Fig. 5), but in all detonations no prior increase in the measured rate of decomposition was observed.

This second reaction appears to be that which initiates the unexplained detonations of nitromethane when it is used as a fuel; hence further work was directed toward establishing the temperature limits of this reaction in order to identify its mechanism, if possible, and to study its suppression or elimination. It was considered that the temperature limits of the first reaction were satisfactorily defined and that the first reaction represents the normal thermal decomposition of nitromethane.

Thermal detonation of nitromethane. In the preceding series of tests, the copper-block heating unit was maintained at temperatures of 450°C or higher. By keeping the temperature of the block below the temperature for normal decomposition (431 ± 5°C), it was hoped that the normal rapid decomposition of nitromethane could be prevented, and that the sample would either decompose slowly according to its normal rate of reaction at that temperature, or would detonate. In this manner it would be possible to isolate the detonation reaction from the normal rapid decomposition reaction. A series of tests was carried out in which the copper block was maintained at a temperature of 400°C or below, and the assumption that was made was found to be true (Cf. Table III). Four tests were made with the block at 400°C. In two of these, after the temperature became constant, the pressure continued to rise gradually, indicating slow decomposition of the sample. After approximately 30 minutes of heating, the pressure also became constant, indicating that the decomposition was completed in both cases. In one of these tests, the temperature of the block and hence of the bomb was then raised gradually to above 450°C, but there was no further evidence of reaction, confirming the fact that decomposition was completed.

In two of the tests with the block at 400°C, the sample detonated with sufficient violence to rupture the pressure connection on the bomb at temperatures of 340 and 360°C after approximately 15 minutes of heating.

Three tests were then made with the block at 350°C. In the first of these the sample was allowed to heat up to 200°C, after which the bomb was removed from the block and allowed to cool for several minutes. The temperature of the sample was recycled several times in this fashion between 150 and 280°C for approximately 1 hour. When the temperature was then raised, the sample detonated at 307°C. In the following two tests, one detonated at 325°C after 16 minutes of heating, and the other decomposed slowly, no violent reaction taking place in over 1 hour of heating.

It was therefore observed that by lowering the block temperature, the normal high-temperature rapid decomposition of nitromethane was prevented, and the frequency of detonations was increased from 15 to 20 per cent to approximately 60 per cent. The upper temperature limit of the nitromethane detonations was also apparently established at approximately 350 to 370°C.

Because of the violence of the detonations, which invariably ruptured the pressure line at some point, the bomb was fitted with a small aluminum blowout disk designed to burst at approximately 2000 psi. It was also decided at this point that no further intentionally induced detonation tests would be made with this apparatus.

The critical point of nitromethane. In all of the tests using the thermal decomposition bomb, it was observed that an irregularity always occurred in the temperature and pressure traces at approximately 300°C. When a plot was made of $\log p$ vs $1/T$ for any of these tests, a straight line was produced, corresponding to the vapor pressure of nitromethane, up to the discontinuity at which point the curve deviated from the straight line, and hence marking the transition from a two-phase to a one-phase system. This value is not necessarily the critical point unless the critical density of the material is taken into account. Tests were made, therefore, using various sizes of samples (1.5 to 3.5 ml) in order to obtain values of the transition point for samples having mean bulk densities both greater and less than the critical density (Cf. Figs. 8, 9, and 10). The critical point of nitromethane was then obtained by plotting the temperature of the points of transition vs mean bulk densities and extrapolating to the critical density from both sides. This work on the critical point of nitromethane has been reported in Reference 5. The critical temperature of nitromethane was found to be 315°C.

Lower temperature limit of detonation of nitromethane. Plots were made of $\log p$ vs $1/T$ for each of the tests in which a detonation occurred (Cf. Fig. 11). In every test the detonation occurred at a temperature above the critical region, in which case the sample was in the single gas phase. From these observations it would appear that the thermal detonations of nitromethane do not occur in the liquid phase or at temperatures below the critical temperature. However, this conclusion does not preclude the possibility of a detonation occurring at a lower temperature if a sample is heated at a lower temperature for a sufficient length of time.

The fact that the plot of $\log p$ vs $1/T$ for each test was a straight line up to the critical point indicated that the pressure measured was only the vapor pressure of the sample, and that there was also no measurable decomposition of nitromethane below the critical temperature.

B. Capillary-Tube Tests

As was just mentioned, it was decided that no further intentionally induced

detonation tests would be made using the thermal decomposition bomb apparatus. Therefore, in order to study the frequency of detonations at various temperatures, and the possible effect of additives on that frequency, the sealed glass capillary-tube technique was used, making possible a large number of tests in a relatively short period of time and without damage to the apparatus when explosions occurred.

Apparatus and procedure. Pyrex glass capillary tubes, approximately 1.0 mm OD, 0.3 mm ID, and 35 mm long, were partially filled with various sizes of samples and sealed. They were then dropped into holes in a small brass block maintained at a fixed temperature by nichrome heating coils which were controlled by a Leeds and Northrup Micromax recording potentiometer and controller unit (Cf. Figs. 12 and 13). The time required before explosion was measured with a stop watch. The upper end of the capillary tube was exposed when resting in the block, and could be observed visually through a safety-glass window during the test.

Over two hundred tests were made at block temperatures varying from 300 to 450°C. The temperature limits for the normal decomposition of nitromethane as determined by the bomb method were substantiated. The critical point as previously determined was also confirmed, for the disappearance of the meniscus in the capillary-tube tests was observed visually to occur at approximately 300°C. However, the method was not satisfactory for studying the frequency of detonations, inasmuch as the evidence for actual detonation, not merely pressure failure of the capillary tube, was inconclusive. An actual detonation was evidenced only by a sharp cracking sound which could be distinguished audibly from a less violent popping noise made in the case of a pressure failure or a normal rapid decomposition explosion. This distinction is on only a qualitative basis; hence it is not conclusive evidence for every individual test.

Upper temperature limit of nitromethane decomposition. The heating time required before explosion was averaged for each temperature (Cf. Table IV), and a plot was made of time of heating vs temperature of heating block (Cf. Fig. 14). A smooth curve was produced with a sharp decrease in time in the region from 380 to 420°C. This curve corresponds, in form, very closely to the plot of half-life of nitromethane vs temperature as given in Figure 7. Hence it is evident that most of the explosions which occurred in the capillary-tube tests were caused by the normal rapid decomposition of nitromethane, not by the detonation mechanism. The upper temperature limit of stability of nitromethane, as determined in the thermal decomposition bomb tests, is also corroborated by this curve.

Lower temperature limit of nitromethane decomposition. In the tests at temperatures of 400°C or higher, as listed in Table IV, an average deviation of 15 to 20 per cent in the average time of explosions was obtained. In contrast with this finding, the average deviation of the tests at temperatures between 330 and 380°C was between 50 and 75 per cent. It may be deduced from this fact that the rate of decomposition at the higher temperatures was so great that actual adiabatic explosion of the nitromethane occurred, and that the time of explosion of the tubes was essentially independent of the variations in the strengths of the various tubes used. At the lower temperatures, normal isothermal decomposition of the nitromethane occurred, causing a uniform rate of pressure rise. In this case the explosion of the tubes resulted from a pressure rupture which was dependent on the variations in the strengths of the

individual tubes, hence giving rise to the marked increase in the average deviations of the time of explosion.

At temperatures below 330°C the rate of decomposition became so slow that the time which elapsed before explosion and the average deviations of that time became too great for the tests to be practicable. The decomposition of the nitromethane in the capillary tubes could be observed visually by the darkening of the color from water-white to brown and ultimately black. At 330°C there was no appreciable coloring of the samples for approximately 4 minutes, after which they began to darken quite rapidly. At 320°C a period of 4 to 10 minutes of heating was required before color appeared, but at 300°C no evidence of color appeared after 15 minutes of heating.

The lower limit of normal decomposition of nitromethane cannot be given as any fixed temperature, but on the basis of all the preceding tests it is evident that the rate of decomposition becomes insignificant in the region of 300 to 320°C, and that the normal handling of nitromethane is apparently safe up to these temperatures.

III. CONCLUSION

A. Rapid Thermal Decomposition of Nitromethane

On the basis of the tests made, it is concluded that the normal thermal decomposition of nitromethane does occur at rates similar to those determined by Taylor and Vesselovsky in their low-pressure, gas-phase studies of nitromethane. At 300°C the half-life of nitromethane is 30 days, according to the data of Taylor and Vesselovsky, and in the tests described in this report there was no evidence of observable decomposition at this temperature. Above 300°C nitromethane decomposes slowly, but the rate does not become appreciable until a temperature of approximately 350°C or above is reached. From 350 to approximately 400°C nitromethane will decompose slowly and completely according to its normal rate of decomposition. Above 400°C the rate of decomposition is high enough to elevate the bulk temperature of the materials because of the heat liberated by the decomposition; hence the decomposition rate becomes auto-accelerating, and the sample will decompose with explosive violence. A temperature of 431°C was found to represent the upper limit at which these normal rapid decompositions of nitromethane could occur. In other words, nitromethane cannot be heated to temperatures above this limit, but will decompose completely, at rates dependent on the temperature and rate of heating, before this temperature is reached.

B. Thermal Detonation of Nitromethane

Between 300 and 360°C nitromethane occasionally detonates. Apparently such detonations occur only in the single gas-phase state above the critical point. Also, no measurable decomposition of the nitromethane takes place before detonations occur. These facts indicate that the detonation mechanism is initiated by the very earliest-formed products of the normal decomposition mechanism. This possibility is further substantiated by the fact that no detonations occurred after appreciable decomposition of the nitromethane had taken place. Therefore, it is proposed that the thermal detonations of nitromethane may be caused by one, or several, of the initial decomposition products or fragments (e.g., free radicals such as CH_3 or NO_2 , etc.) formed in

the temperature regions in which the normal decomposition of nitromethane takes place at a very slow rate, and that at higher temperatures the higher rate of normal decomposition of nitromethane prevents the existence of conditions favorable to the occurrence of detonations.

Figure 15 gives a summary of the effects of various regions of temperature on the state of nitromethane.

C. Future Studies

Further tests will be made to identify, if possible, the substance or substances which initiate the detonation mechanism, and to establish the mechanism itself. If this information can be obtained, a logical approach could then be made toward eliminating or substantially reducing the frequency of detonations, either by mechanical design or by the use of a chemical suppressant.

TABLE I

THERMAL DECOMPOSITION BOMB TESTS WITH A HEATING BLOCK HELD AT TEMPERATURES BETWEEN 450 AND 540°C

Test No.	Sample Size (ml)	Material Used	Temp of Block (°C)	Temp at Which Rapid Decomposition Occurred (°C)	Elapsed Time (min)	Remarks
1	2.0	Purified NM ↓ 2% aniline crude NM	495	398	6.5	possible detonation
2	1.8		474	392	7	
3	2.0		450	---	15	
4	2.0		459	427	12.5	
5	2.0		460	422	11	
6	2.0		454	380	9	
7	2.0		460	418	10.5	detonation detonation
8	1.0		465	---	15	
9	2.0		465	414	8.5	
10	1.5		490	350	6	
11	1.5		464	340	7.5	
12	1.5		465	420	10.5	
13	1.5		468	409	8	
14	1.5		451	422	10	
15	1.5		475	415	9	
16	1.5		516	394	6	
17	1.5		487	407	7.5	detonation detonation detonation
18	1.5		504	410	7.5	
19	1.5		530	393	6	
20	1.5		526	304	4.5	
21	1.5		538	286	4.5	
22	1.5		523	350	5.5	
23	1.5		505	408	7	
24	1.5		524	402	7	
25	1.5		507	414	8	
26	1.5		470	418	9.5	
27	1.5		485	416	8.5	
28	1.5		453	420	10	
29	1.5		461	416	11.5	
30	1.5		478	407	10	

TABLE II

PRELIMINARY SERIES OF THERMAL DECOMPOSITION BOMB TESTS, USING A SMALL-SIZE COPPER BLOCK HEATING APPARATUS HAVING A SLOWER HEATING RATE THAN THE MAIN APPARATUS

Test No.	Sample Size (ml)	Material Used	Temp of Block (°C)	Temp at Which Rapid Decomposition Occurred (°C)	Elapsed Time (min)
1a	5	purified NM ↓	482	412	16
2a	7		471	412	18.5
3a	7		471	408	18.5
4a	7		468	415	18.5
5a	7		460	411	17.5
6a	7		466	404	18
7a	7		482	422	19

TABLE III

THERMAL DECOMPOSITION BOMB TESTS WITH A HEATING BLOCK HELD AT TEMPERATURES BETWEEN 350 AND 400°C

Test No.	Sample Size (ml)	Material Used	Temp of Block (°C)	Temp at Which Rapid Decomposition Occurred (°C)	Elapsed Time (min)	Remarks
31	1.5	purified NM ↓	400	---	50	
32	1.5		400	360	15.5	detonation
33	2.0		400	340	14.5	detonation
34	1.8		400	---	70	
35	2.0		350	307	63	detonation
36	2.0		350	325	15	detonation
37	2.0		357	---	60	

TABLE IV

TESTS MADE BY HEATING NITROMETHANE IN SEALED GLASS CAPILLARY TUBES

Temperature of Block (°C)	Number of Tests	Average Time of Explosion	Average Deviation
431	20	5.7 sec	± 1.0 sec
421	22	6.8 sec	± 1.6 sec
415	10	7.5 sec	± 1.2 sec
410	11	8.6 sec	± 1.6 sec
400	7	10.1 sec	± 1.6 sec
373	18	2.4 min	± 1.8 min
360	10	9.4 min	± 5.6 min
350	20	16 min	± 8 min
340	8	25 min	± 14 min
330	10	35 min	± 12 min

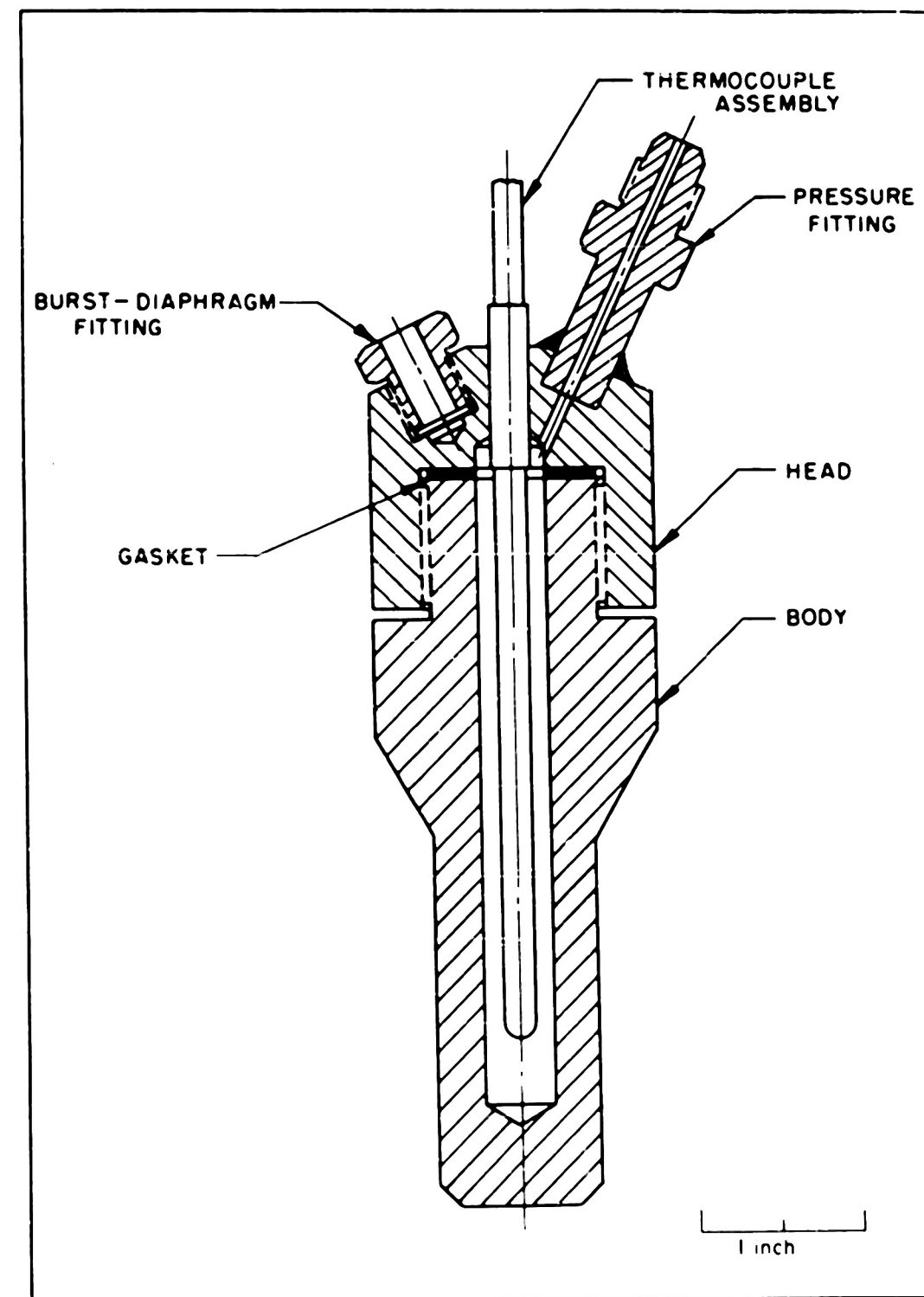


Figure 1. Thermal Decomposition Bomb



Figure 2
Thermal Decomposition Bomb and Copper
Heating Block, Disassembled



Figure 3
Thermal Decomposition Bomb and Copper
Heating Block in Operating Position

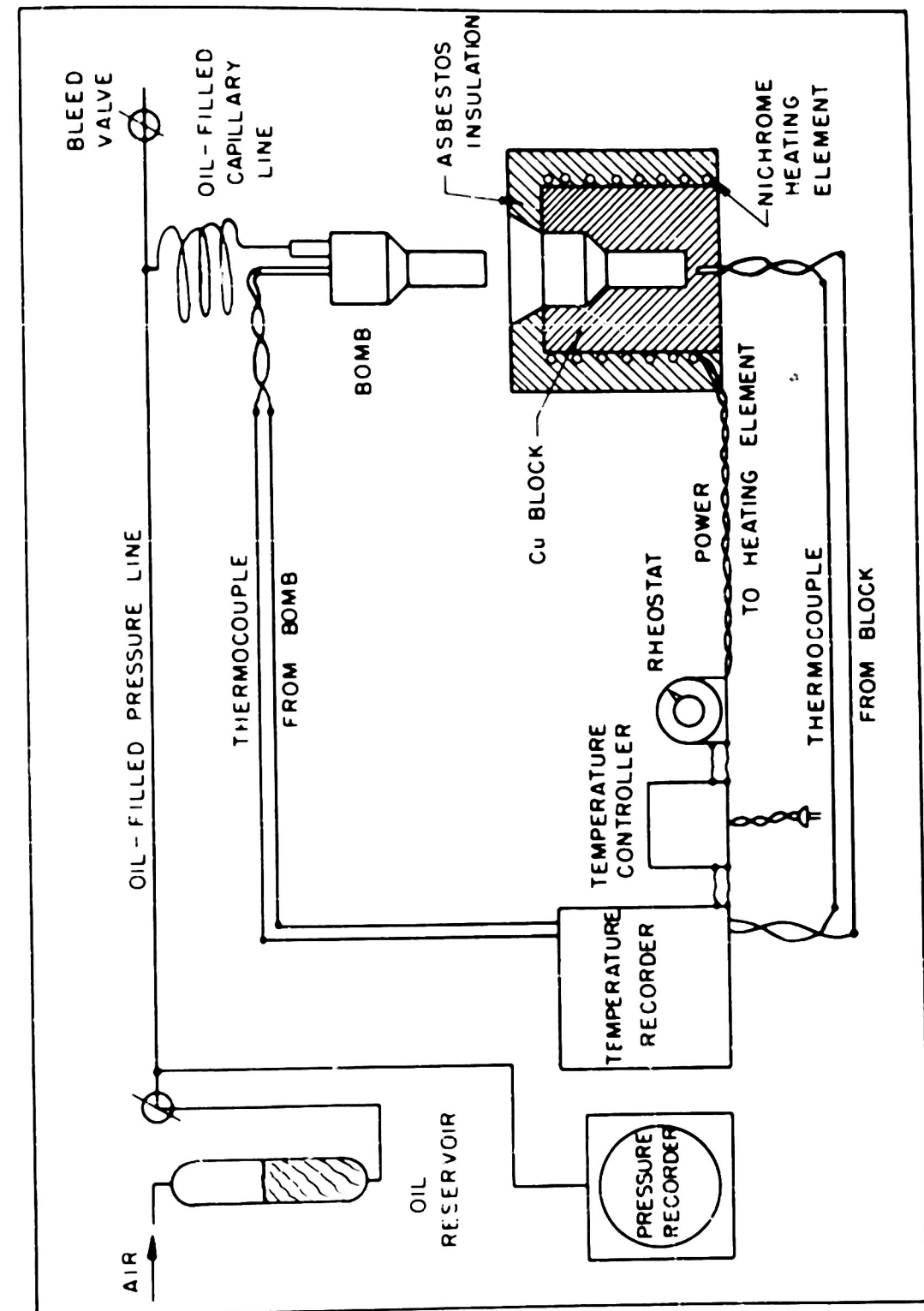


Figure 4. Diagram of Thermal Decomposition Apparatus

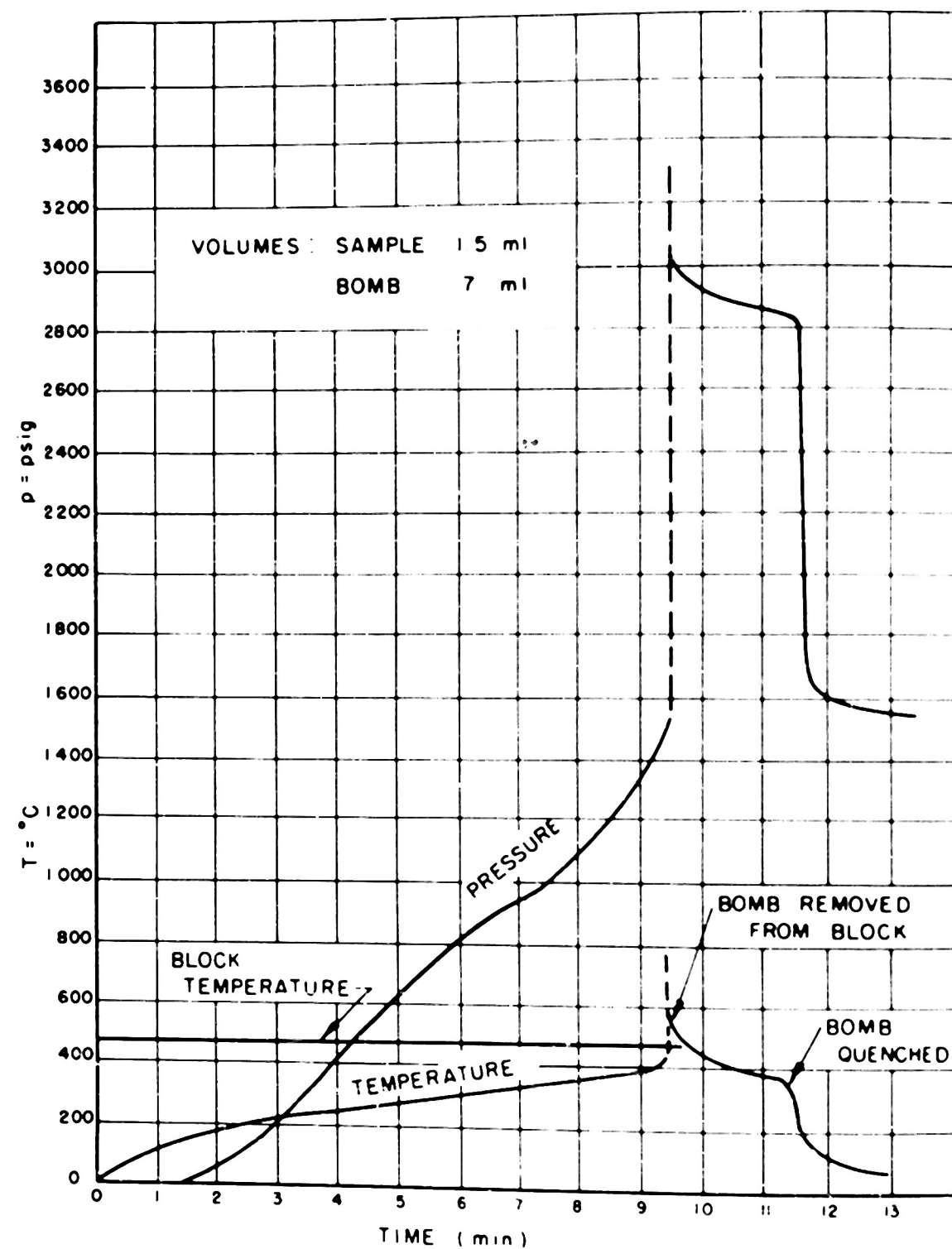


Figure 5. Representative Test of Nitromethane in Thermal Decomposition Bomb.

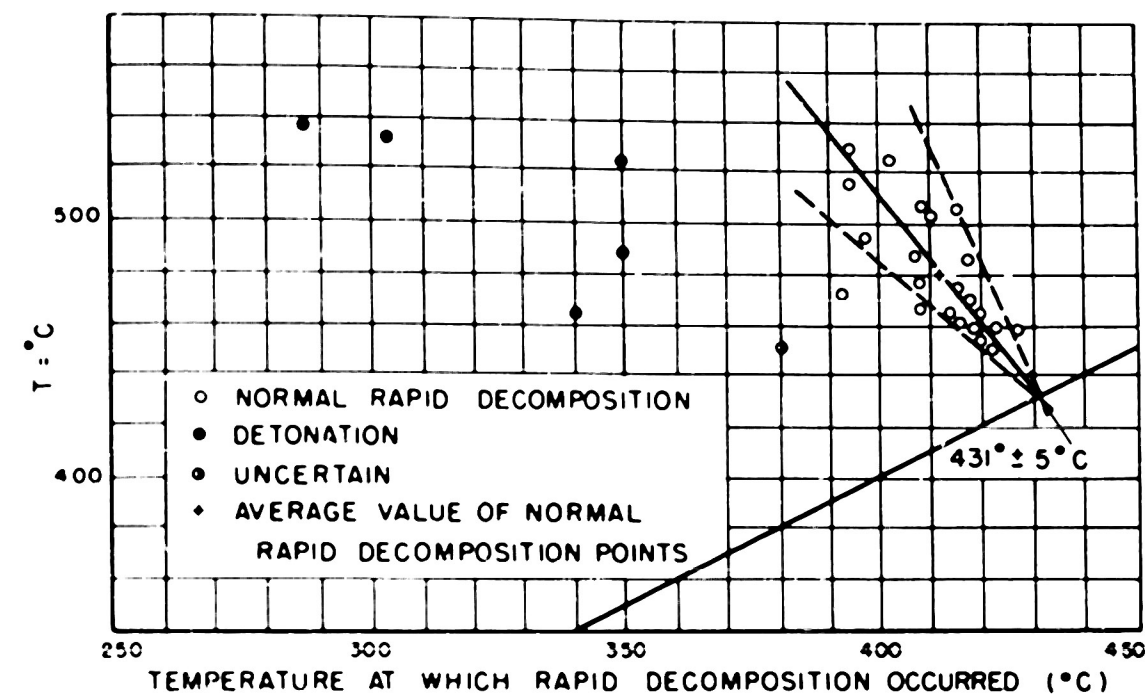


Figure 6. Temperature at Which Rapid Decomposition Occurred vs Temperature of the Heating Block

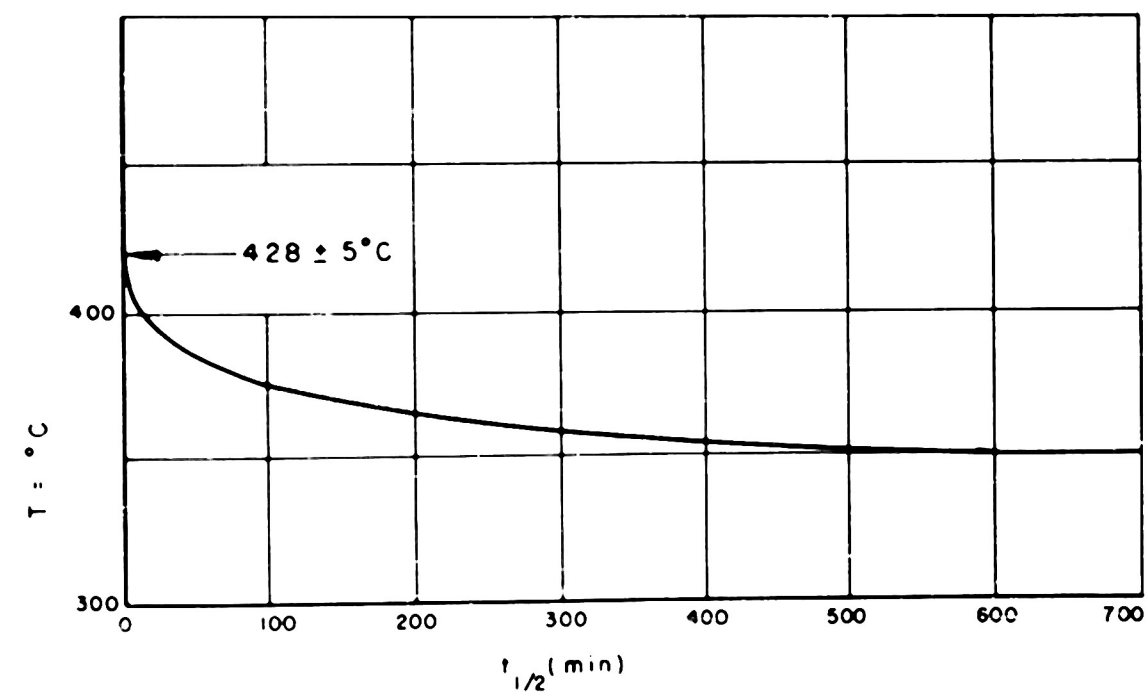


Figure 7. Half-Life of Nitromethane vs Temperature

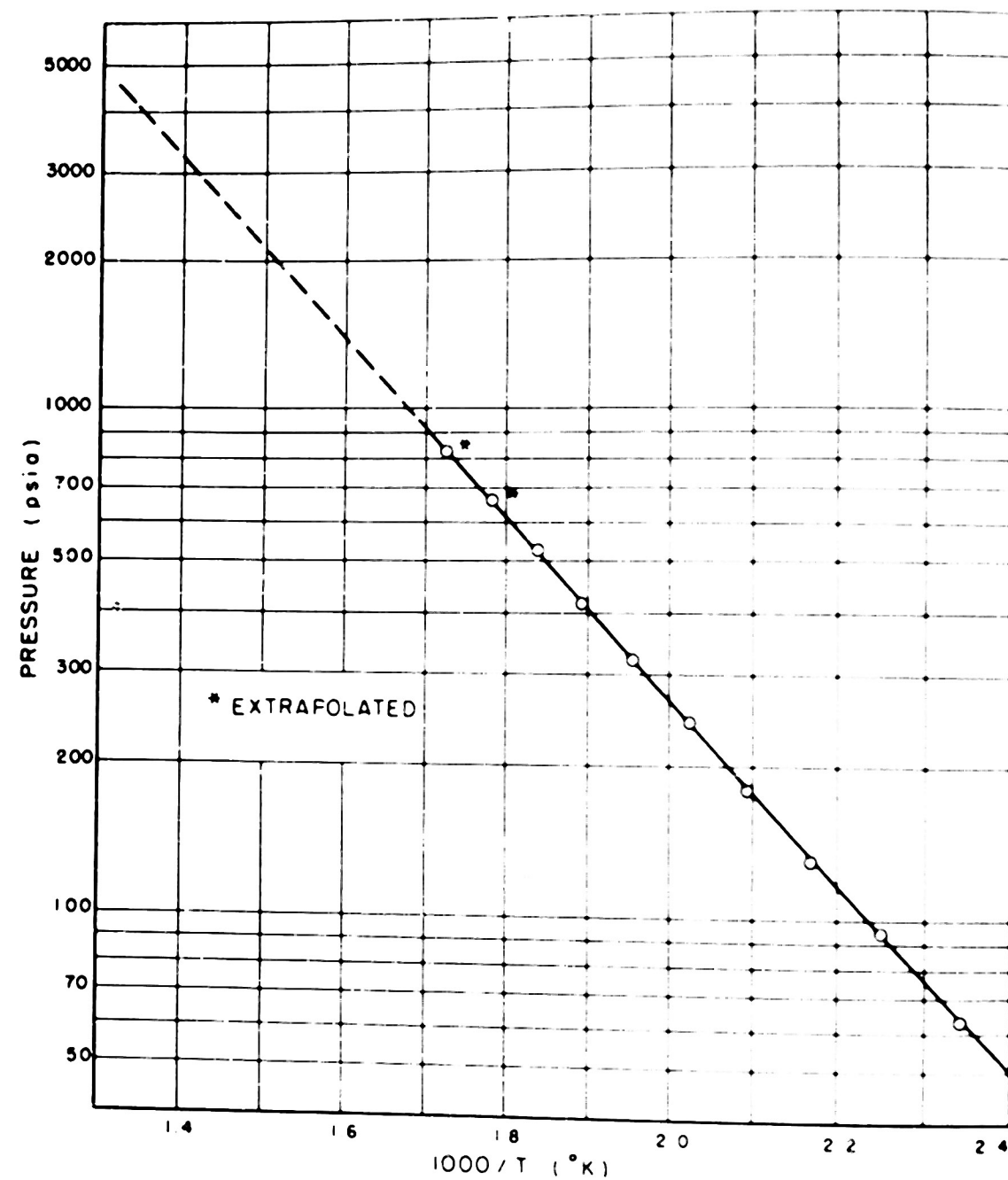


Figure 8. Vapor Pressure of Nitromethane

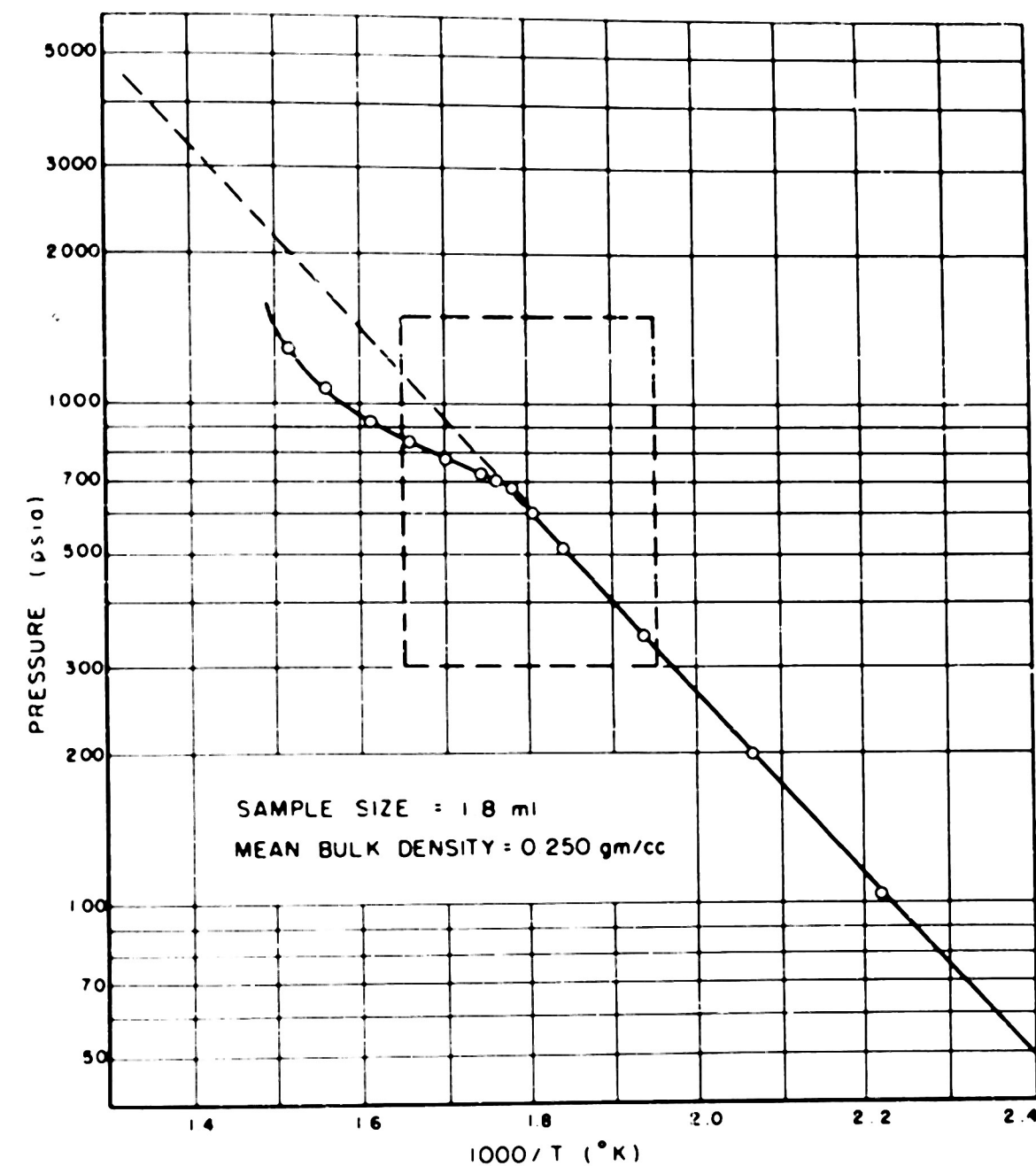


Figure 9. Pressure Effect in the Critical Region of a Sample of Nitromethane Having a Mean Bulk Density less Than the Critical Density

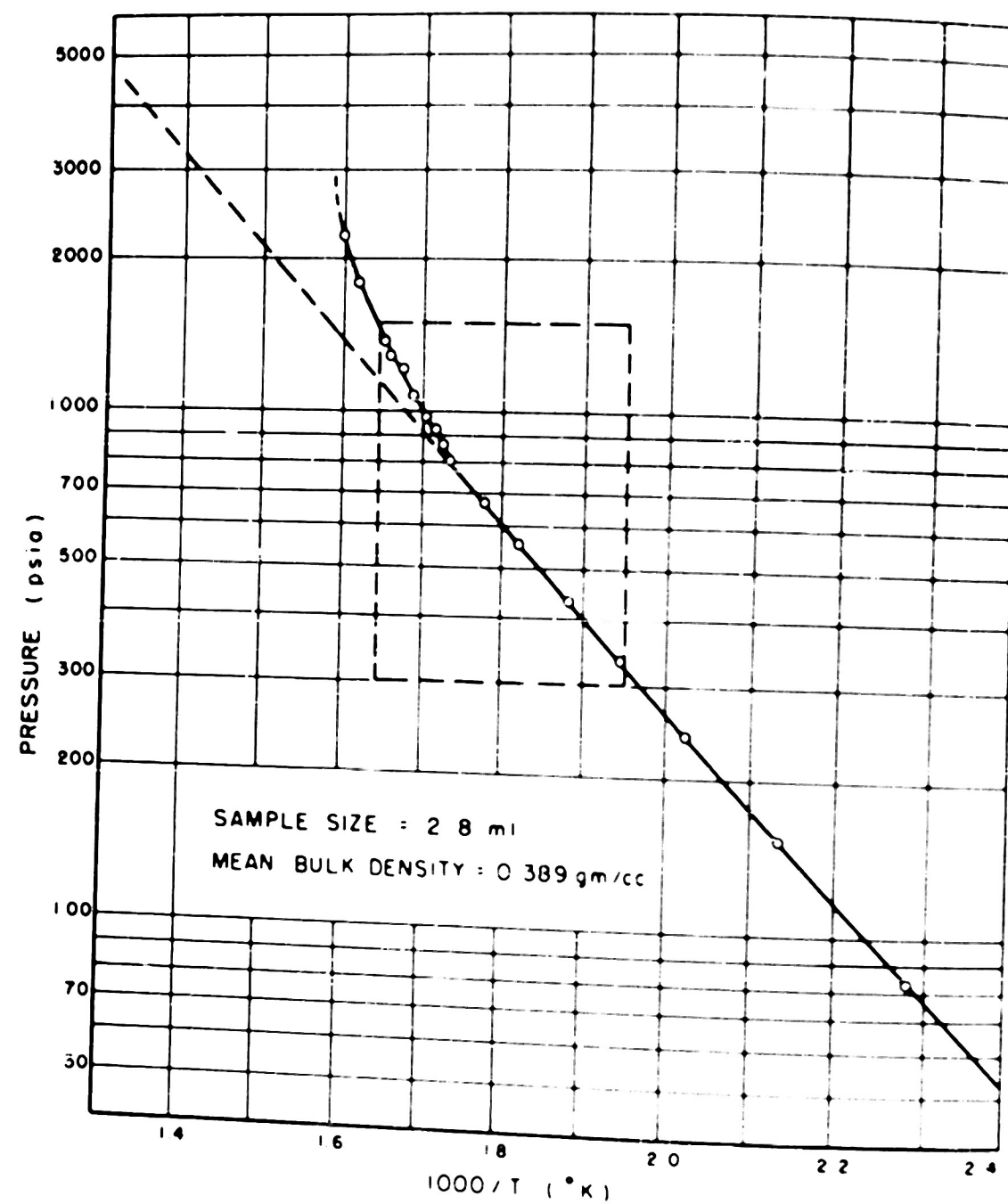


Figure 10. Pressure Effect in the Critical Region of a Sample of Nitromethane Having a Mean Bulk Density Greater Than the Critical Density.

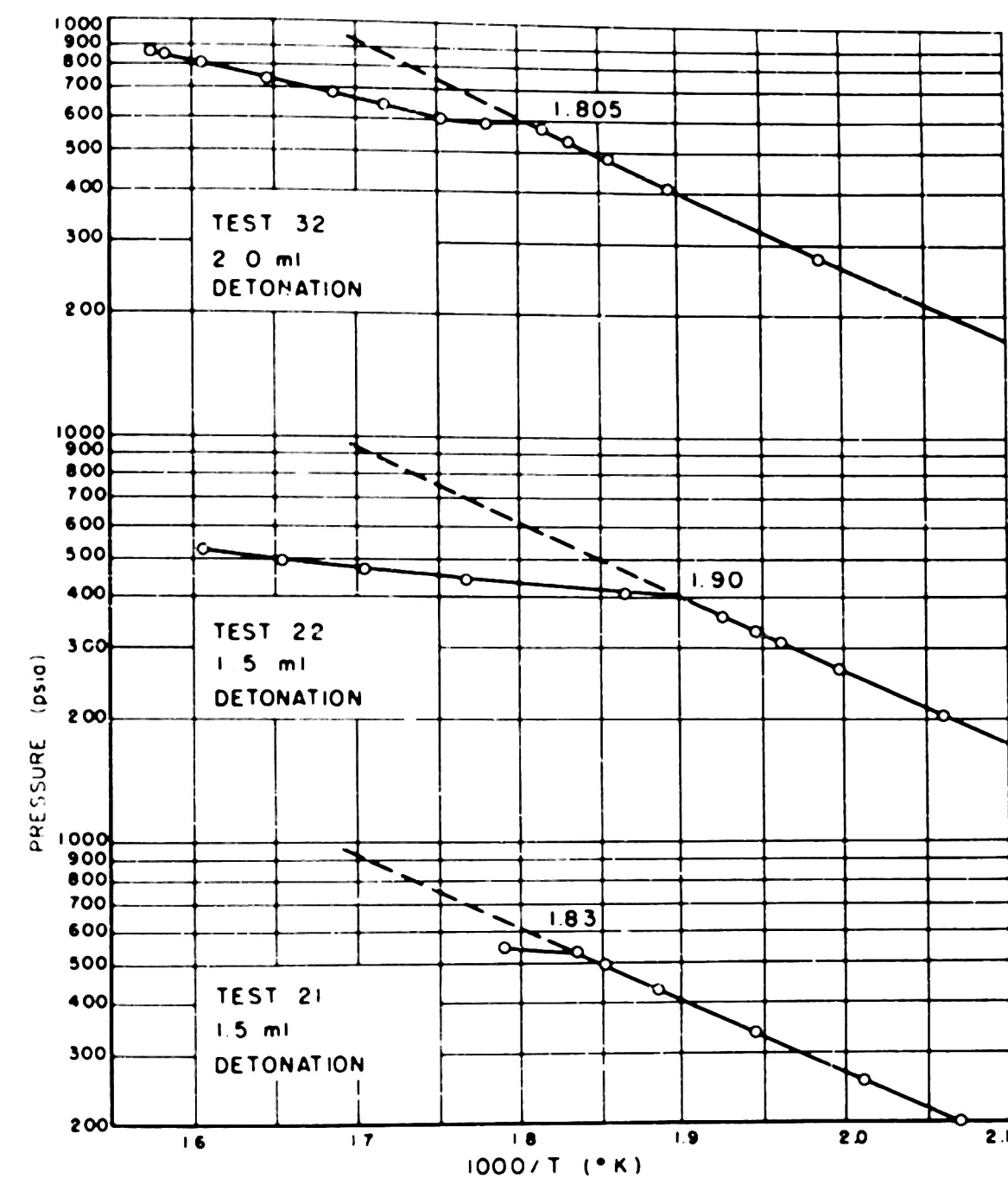


Figure 11. Log p vs $1000/T$ for Some of the Samples of Nitromethane Which Detonated

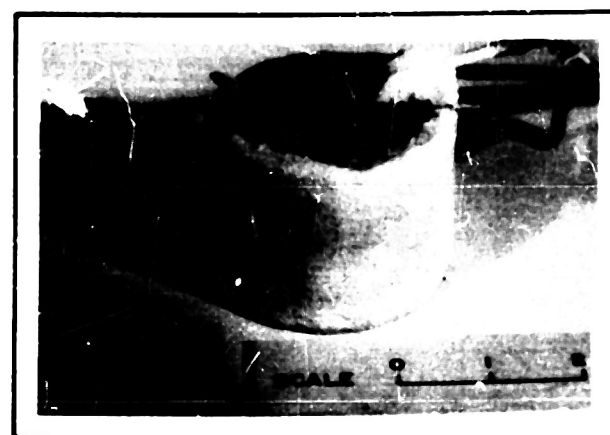


Figure 12
Brass Heating Block for Glass
Capillary-Tube Tests

Figure 13
Brass Heating Block
Enclosed in Shield

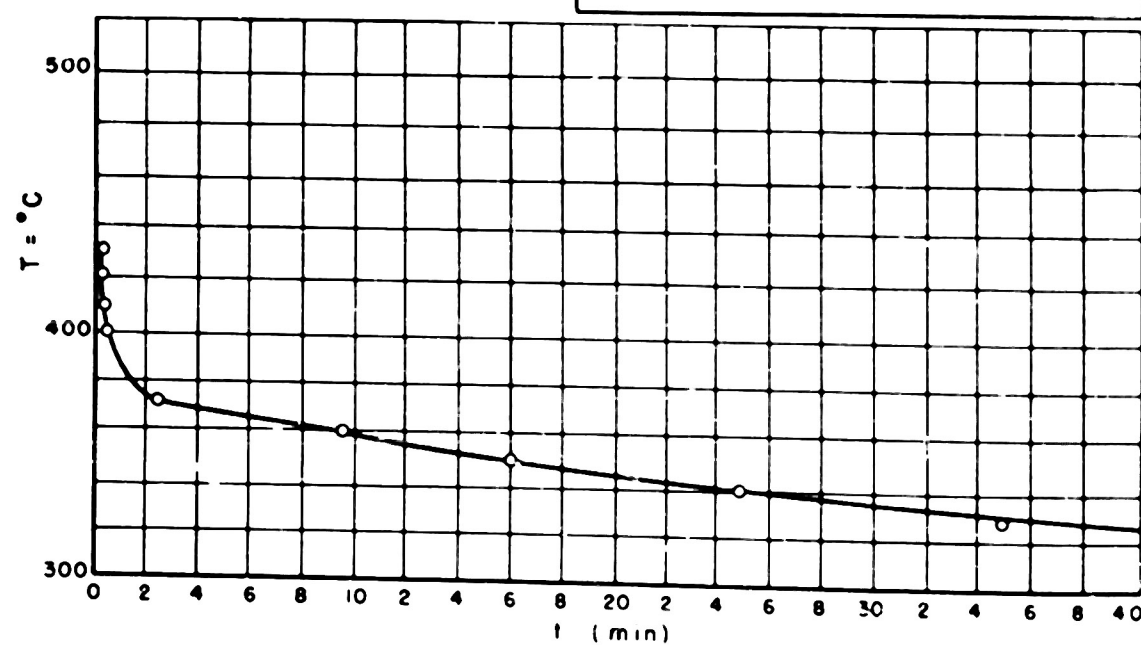
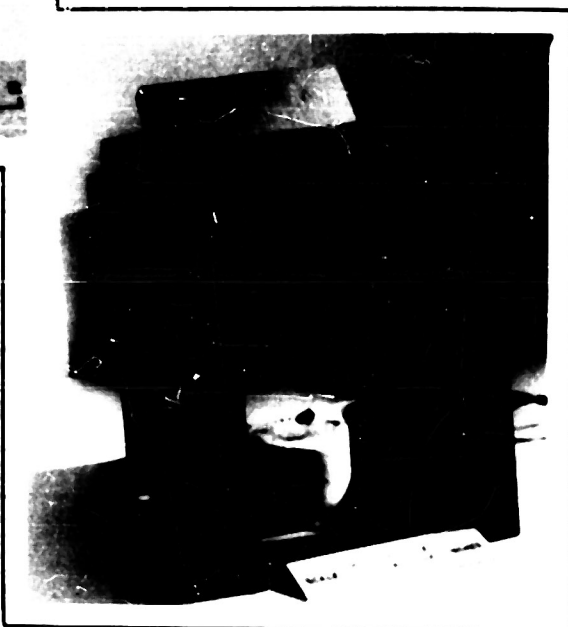


Figure 14. Time Before Explosion vs Temperature for Nitromethane Capillary-Tube Tests

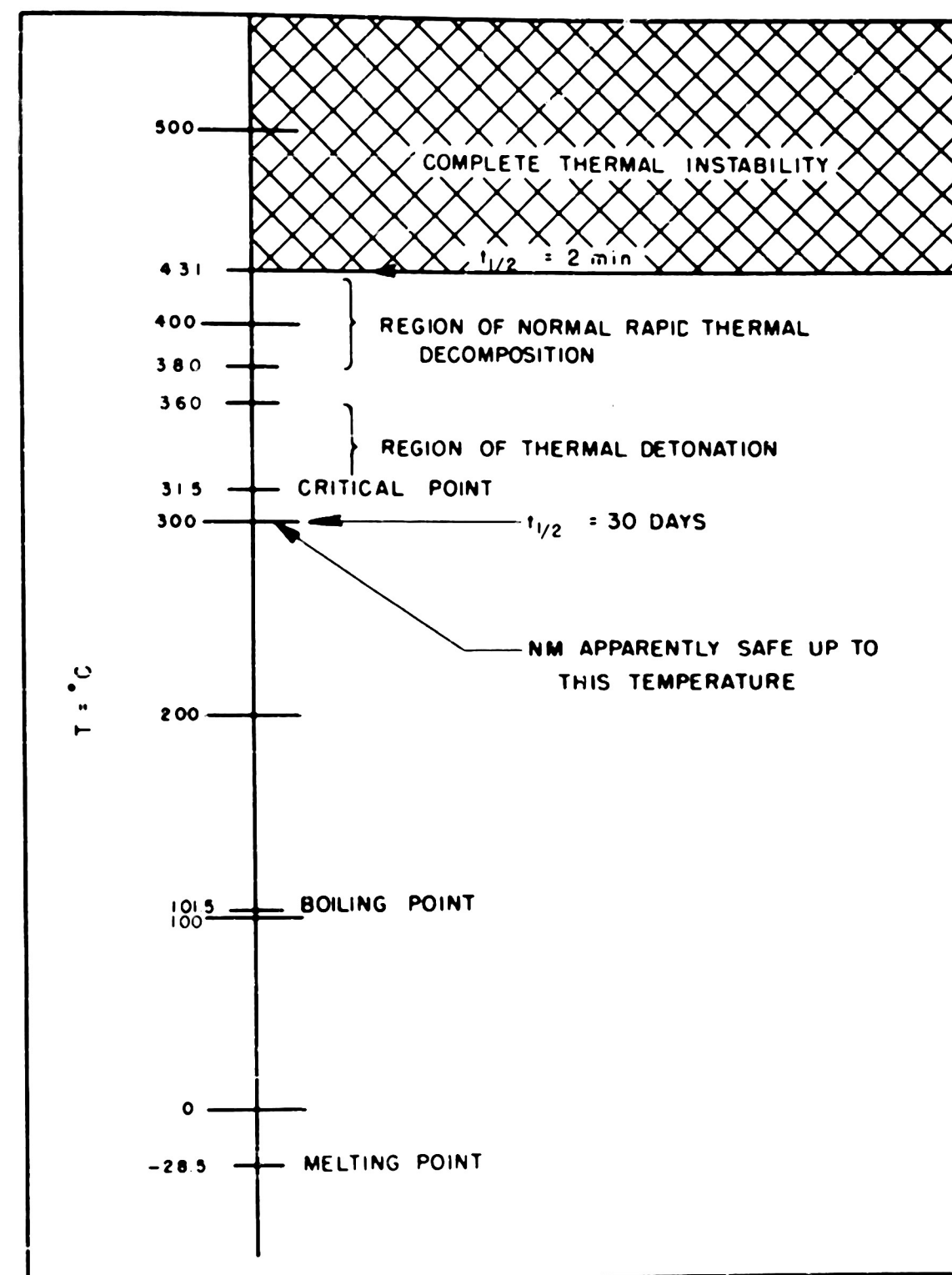


Figure 15. Temperature Scale of Nitromethane

REFERENCES

1. Kaplan, N., et al, *Thermal and Shock Sensitivity of Nitromethane*, Progress Report No. 1-35. Pasadena: Jet Propulsion Laboratory, December 26, 1945 (Restricted).
2. Laurence, E. A., *Rapid Thermal Decomposition of Nitromethane*, Aerojet Technical Memorandum No. RTM-18. Azusa (California): Aerojet Engineering Corporation, February 28, 1946.
3. McKittrick, D. S., et al, "Nitromethane Potential Hazards in Use," *Industrial and Engineering Chemistry*, anal. ed., 10:630, November 15, 1938.
4. Taylor, H. A., and Vesselovsky, V.V., "The Thermal Decomposition of Nitromethane," *Journal of Physical Chemistry*, 39(No. 8):1095-1101, November 1935.
5. Griffin, D. N., *The Critical Point of Nitromethane*, Memorandum No. 9-11. Pasadena: Jet Propulsion Laboratory, April 16, 1948.

RESTRICTED

THIS REPORT HAS BEEN DISTRIBUTED ACCORDING TO
JOINT ARMY-NAVY SOLID PROPELLANT DISTRIBUTION
LIST DATED 17 DECEMBER 1948

RESTRICTED