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THERMAL EXPLOSION UNDER CONDITIONS OF INCREASED HYDROSTATIC PRESSURE

by
L. A. Shipitsin

USSR

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13. ABSTRACT

An experimental study was performed of the effects of high hydrostatic pressure and temperature on thermal explosion of explosives. The pressure range covered was up to 1,000 atm. The results produced are important for the use of thermal explosives in deep boreholes.

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ENGLISH TITLE: Thermal Explosion Under Conditions of Increased Hydrostatic Pressure

FOREIGN TITLE: Teplovoy Vzryv v Usloviyakh Vozdeystviya Povyshennogo Gidrostaticheskogo Davleniya

AUTHOR: L. A. Shipitsin

SOURCE: Termostoykiye Vzryvchatyye Veshchestva i ikh Deystviye v Glubokikh Skvazhinakh [Thermostable Explosives and Their Effects in Deep Boreholes], Moscow, 1969, pp 5-24.

Translated for FSTC by Albert L. Peabody
Leo Kanner Associates

NOTICE

The performance of shooting and explosive operations in boreholes has required the development and study of a number of explosives which retain their properties under conditions of high temperatures and liquid pressures.

Table 1 presents values of critical and limiting diameters (d_{cr}, d_1) and detonation velocities (D) of explosives with the operating charge densities ρ_{ex} and diameters exceeding the limiting values.

EXPLOSIVE CHARACTERISTICS OF THERMOSTABLE EXPLOSIVES. TABLE 1.

Explosive	Density, g/cm^3	Critical Diameter, mm	Limiting Diameter, mm	Detonation Velocity, m/sec
TNT	1.58	3.0	8.0	6,950
GFG-2	1.65	1.0-2.0	5.2	7,800
GFG-2	1.0	3.0	-	-
GNDS	1.66	1.8	3.0	7,150
LT-4	1.60	2.0	10.0	7,500
V-5	1.62	2.5	7.5	7,200
V-5	0.7	15.9	-	-
P-90	1.80	3.0	12.0	6,600
NTFA	1.62	1.5-2.0	8.0	7,200
NTFA	0.95	6.3	-	-
Dodenite	1.55	-	12.0	6,400
Dodenite	0.80	15.3	-	-

The limiting diameter is determined by measuring the detonation velocity of charges of thermostable explosives of various diameters using a Type SFR high speed photorecorder. With a charge diameter greater than the limiting diameter, the detonation velocity remains constant.

Measurements performed also allowed determination of the heat of the explosion (Q) and specific volume (V_0) of explosion products (Table 2).

TABLE 2.
HEAT OF EXPLOSION AND SPECIFIC VOLUME OF EXPLOSION PRODUCTS OF THERMOSTABLE EXPLOSIVES.

Explosive	Density, g/cm^3	Heat of Explosion, kcal/kg	Specific Volume, 1/kg
GFG-2	1.68	1,380	565
GNDS	1.72	1,120	580
LT-4	1.52	1,010	585
V-5	1.55	980	525
P-90	1.68	875	450
NTFA	1.46	1,010	585

Specifics of Thermal Explosion at Low Pressures

The basis for a complete and proper understanding of the processes of thermal ignition occurring under high temperature conditions is the theory of the thermal explosion [67, 72, 73].

The theory of the thermal explosion allows us to establish the quantitative relationship between the critical self-ignition temperature T_{cr}, separating the explosive and nonexplosive course of the reaction, and the charge diameter as a function of kinetic characteristics of explosive decomposition and heat transfer conditions.

Few works have been dedicated to investigation of thermal ignition under conditions of elevated or high pressure, although this problem is of significant interest, for example in connection with the problem of initiating an explosion by shockwaves and mechanical impact.

Yu. N. Ryabinin [62] determined the influence of high pressure (25,000 33,000 atmospheres) on the flashpoint of barium azide, fulminate of mercury, TNRS and PETN and found that the flash point changes slightly (usually by 5-10°). F. P. Bouden, etal [23] studied the same problem for cyanurtriazide, lead azide and PETN at pressures up to 20-22,000 atmospheres and noted a slight increase in flash point with increasing pressure. However, the results of these works, performed under thermal flash conditions (supercritical mode) at constant charge temperature with slight quantities of explosive, do not give us a sufficiently full conception of the process of thermal explosion under high pressure conditions. The reasons for the phenomena observed remained unexplained.

In the work of A. G. Merzhanov and F. I. Dubovitskiy [57], we find information on the specifics of thermal explosion of condensed explosives at low pressures (up to 50 atm). It is noted in this work that with increasing pressure, the critical temperature drops (by approximately 30°), this decrease stopping at pressures over 20 atm. The decrease in critical temperatures explained by the fact that as pressure increases, elimination of gaseous decomposition products from the reaction zone becomes more difficult and the catalytic effect of these gases on the process of thermal decomposition taking place increases.

The constancy of critical temperature at higher pressures is explained, according to these researchers, by the fact that the corresponding gaseous products are converted to the condensed state are not removed from the reaction zone.

Our studies have shown that generally under high pressure conditions (400-1,000 atmospheres), the threshold of thermal stability[1] drops by 20-30°C.

Thus, thermal explosion under increased hydrostatic pressure has not yet been studied in the theoretical aspect, and has been only incompletely studied experimentally. The only exception is the area of low pressures.

During our preliminary investigations, we detected certain qualitative differences in the course of thermal explosions at pressures of not over 20-50 atmospheres and at higher pressures. We found that at low pressures, the critical self-ignition temperature (T_{cr}) and corresponding induction period (t_{cr}) decrease significantly (up to a certain limit), which agrees with the data of A. G. Merzhanov and F. I. Dubovitskiy [57]. In connection with this, we performed studies of the specifics of thermal explosions under these conditions.

Experimental Method

The experiments were performed using an installation diagramed on Figure 1.

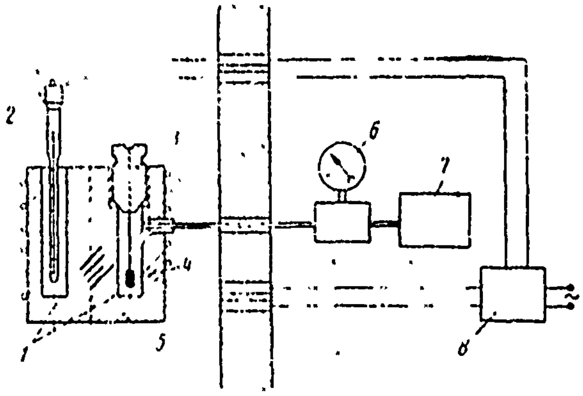

Figure 1. Diagram of Installation for Study of Thermal Explosion at up to 1,000 atm.

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[1] The threshold of thermal stability is the maximum permissible temperature which the explosive can withstand under practical utilization conditions in a borehole for 6 hours without a noticeable change in its explosive characteristics.

A pressed charge of explosive 4, contained by plug 3, was placed in Wood's alloy 1 or any inert fluid (for example, organosilicon fluid No 5), heated to the required temperature in thermostat 5. The temperature of the Wood's alloy was maintained constant with an accuracy of ±1°C using contact thermometer 2, placed in Wood's alloy and connected to the electrical circuit heating the thermostat 8.

Sealing of the working volume of the thermostat was performed by the contact between the conical surface of the plug and the cylindrical surface of the hole; the remaining joints were sealed using flat copper inserts. The working pressure was created using a Type NZhR pump 7 and recorded by Type MTI manometer 6. The decomposition mode (explosive or nonexplosive) was generally determined by the increase in pressure in the working volume of the thermostat caused by decomposition of the explosive (Figure 2).

The critical self-ignition temperature was determined by the "sighting" method with an accuracy of ±1°C, the corresponding induction period -- with an accuracy of ±10%.

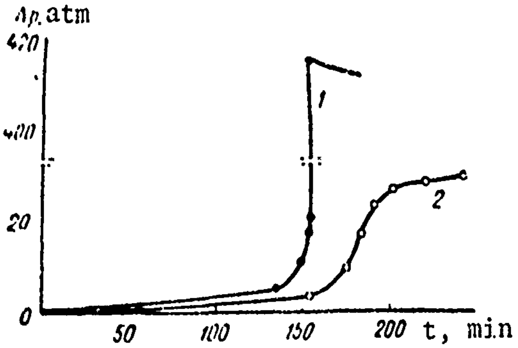

Figure 2. Increase in Pressure (Δp) as a Function of Time (t).
1, explosive mode; 2, nonexplosive mode.

The experiments were performed with cylindrical charges, diameter equal to height.

Comparison of the heat conductivity factors (λ) of the explosive charges ($\lambda \approx 3 \cdot 10^{-4}$ cal/cm•sec•degree) and Wood's alloy ($\lambda \approx 4 \cdot 10^{-2}$ cal/cm•sec•degree) indicates that first order boundary conditions are realized on the charge surface. A similar conclusion was drawn in the work of E. I. Maksimov, A. G. Merzhanov and V. M. Shkiro [52]. The observations showed that Wood's alloy does not penetrate into the pores of the explosive and has no influence on the process of thermal decomposition of the explosives studied within the limits of error of the experiments.

Results of Experiments

Octogene. Experiments were performed with charges 3.8 to 15.0 mm in diameter in the 168-22[illegible] temperature interval and 1-800 atm pressure interval. Charge density was 1.63 g/cm^3.

The experimental data on the critical parameters of the thermal explosive at normal pressure, necessary at high pressure:

d, mm	T_{cr}, °C	t_{cr}, min
3.8	223	150
6.0	215	300
7.0	209	510
8.0	207	560
9.2	205	700
15.0	193	3,000

The experimental data for determination of the dependence of critical temperature (T_{cr}) on pressure (p) are presented on Figure 3.

As we can see from Table 3, at a certain, comparatively low pressure (about 20 atm), "saturation" occurs and the critical temperature remains unchanged within the limits of error of the experiments as pressure increases to 800 atm.

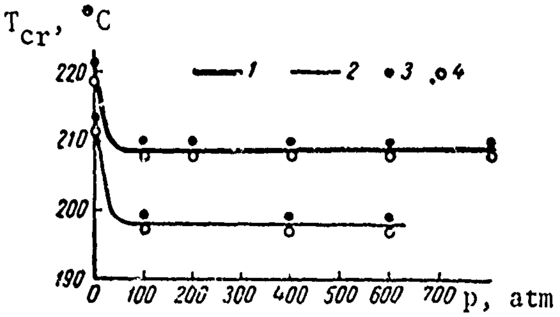

Figure 3. Critical Temperature (T_{cr}) as a Function of Pressure (p) for Octogene.
1, for 3.8 mm diameter charge; 2, for 6.0 mm diameter charge; 3, explosive mode; 4, nonexplosive mode.

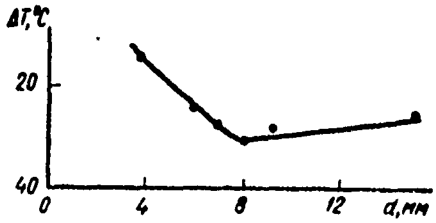

Figure 4. Maximum Critical Temperature Drop (ΔT) as a Function of Charge Diameter (d) for Octogene.

TABLE 3.

RESULTS OF DETERMINATION OF DEPENDENCE OF INDUCTION PERIOD (min) IN SUPERCRITICAL AND CRITICAL MODES OF DECOMPOSITION ON PRESSURE WITH CHARGE DIAMETER 3.8 mm.

Experimental Temperature, °C	Pressure, atm			
	20	200	600	800
226	20	16	16	16
223	-	23	20	24
220	-	-	27	-
218	-	38	45	40
216	-	40	-	-
212	-	45	56	59
208	111*	80*	78*	85*

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* Time (min) of attainment of maximum decomposition rate in subcritical mode.

The maximum drop in critical temperature $\Delta T = T_{cr} - T^{s}_{cr}$ (where T^{s}_{cr} is the critical temperature in the "saturation" area) depends on charge diameter. Since in the saturation area the pressure can be selected rather arbitrarily, all experiments were performed only at 200 atmospheres. The results of experiments for determination of ΔT as a function of charge diameter are presented on Figure 4.

The values of the period of induction were:

d, mm	T_{cr}, °C	t_{cr}, min
3.8	209	70
6.0	192	200
7.0	181	380
8.0	176	510
9.2	178	500
15.0	168	1,200

Substance LT-4. Experiments were performed with a charge from 6.0 to 15.0 mm in diameter at 170-234°C and 1-600 atm. Charge density was 160 g/cm^3.

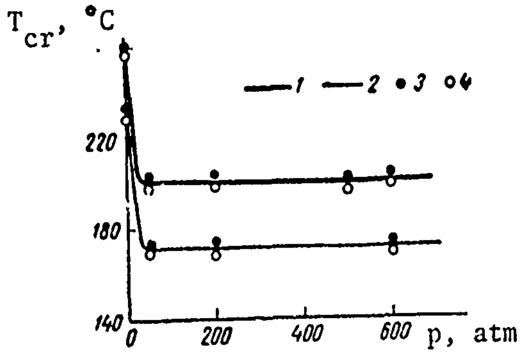

Figure 5. Critical Temperature (T_{cr}) as a Function of Pressure (p) for LT-4.
1, for 6.0 mm diameter charge; 2, for 15 mm diameter charge; 3, explosive mode; 4, nonexplosive mode.

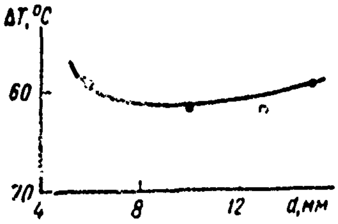

Figure 6. Maximum Critical Temperature Drop (ΔT) as a Function of Charge Diameter (d) for LT-4.

The critical parameters of thermal explosion at atmospheric pressure are:

d, mm	T_{cr}, °C	t_{cr}, min
6.0	261	300
8.0	252	400
10.0	245	610
12.0	240	820
15.0	232	1,200

Table 4 presents the values of induction period at 200 atm. The dependence of T_{cr} on pressure and ΔT on charge diameter at 200 atm is shown on Figures 5 and 6.

NTFA. Experiments were performed with a charge from 5.8 to 15.0 mm in diameter at 260-300°C and 1-600 atm. Charge density was 1.54 g/cm^3.

The critical parameters of thermal explosion of atmospheric pressure are:

d, mm	T_{cr}, °C	t_{cr}, min
5.8	295	180
7.5	293	330
9.8	289	720
11.8	285	1,050
15.0	279	1,470

TABLE 4.

INDUCTION PERIOD (min) AS A FUNCTION OF TEMPERATURE AT 200 ATM FOR LT-4.

Experimental Temperature, °C	Charge Diameter, mm	
	6.0	15.0
230	-	14
223	105	-
210	270	47
204	330	-
200	360*	68
190	-	350
180	-	650
174	-	2,100
170	-	2,600*

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* Time (min) of achievement of maximum decomposition rate in subcritical mode.

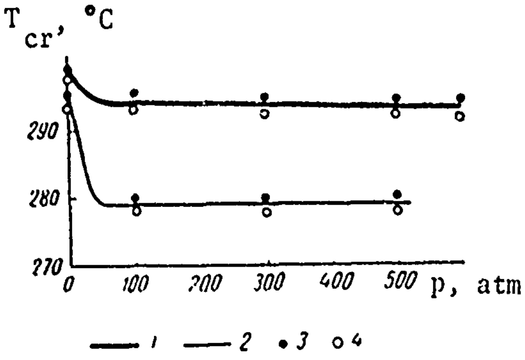

Figure 7. Critical Temperature (T_{cr}) as a Function of Pressure (p) for NTFA. 1, for 5.8 mm diameter charge; 2, for 7.1 mm diameter charge; 3, explosive mode; 4, nonexplosive mode.

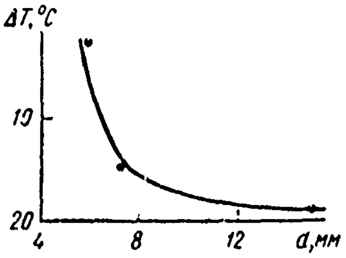

Figure 8. Maximum Critical Temperature Drop (ΔT) as a Function of Charge Diameter (d) for NTFA.

The dependence of the induction period on pressure is shown in Table 5. Figure 7 shows the dependence of T_{cr} on pressure, while Figure 8 shows the dependence of ΔT on charge diameter at 200 atm.

Hexogene, LT-5, thermol, TNT. Thermal explosion of these explosives under conditions of high hydrostatic pressure were studied less completely (Table 6).

As a result of the study of the thermal explosion of a number of explosives, certain general regularities were established.

1. The critical temperature and critical induction period decrease significantly with increasing applied pressure up to 20-30 atm.

At higher pressures (up to 800 atm), the values of T_{cr}, t_{cr} remain practically unchanged.

2. The time of maximum drop in the critical temperature ($\Delta T = T_{cr} - T^{s}_{cr}$) in the saturation area depends in a complex manner on charge diameter, reaching its greatest value with d_0 equal to 5-10 mm. Where $d < d_0$, the value of ΔT decreases significantly with decreasing d, where $d > d_0$ it does not increase.

TABLE 5.

INDUCTION PERIOD (min) AS A FUNCTION OF PRESSURE FOR NTFA.

Pressure, atm	Temperature, °C				
	298	204	280	270	290
	Charge diameter, mm				
	5.8	7.1			8.0
1	207	240	--	--	300
50	194	201	-	—	210
100	98	180	400	460*	160
200	85	106		—	119
300	62	90	270	360*	108
400	58	83	—	—	--
500	- -	—	130	150*	—
600	32	—	--	—	-

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*Time (min) of attainment of maximum decomposition rates.

CRITICAL PARAMETERS OF THERMAL EXPLOSION OF EXPLOSIVES. TABLE 6.

Explosive	Diameter, mm	Density, g/cm^3	Critical Temperature, °C (p = 1 atm)	Induction Period, min (p = 1 atm)	Critical Temperature in Saturation Area, °C	Induction Period in Saturation Area, min
Hexogene	7.5	1.54	-	-	179	190
	6.5	1.60	296	60	-	-
LT-5	8.0	1.60	292	240	-	-
	10.0	1.60	289	400	-	-
	15.0	1.60	274	1,400	258	1,700
Thermol	10	1.60	304	360	-	-
	15	1.60	292	1,200	281	700
	20	1.60	285	1,800	-	-
TNT (liquid)	17.6	-	214	330	180	800

3. The values of ΔT for the explosives studied has a tendency toward decreasing with increasing thermol stability. We present below the results of experiments for a charge 15 mm in diameter:

Explosive	T^{s}_{cr}, °C	ΔT, °C
Octogene	168	30
LT-4	170	60
TNT	180	25
LT-5	258	16
Thermol	281	11

Our experiments confirmed the existence for many explosives of an area of saturation over a broad range of pressures, the beginning of which was detected earlier [57].

In correspondence with the primary statements of the theory of thermal explosion, the possible causes of the observed regularities might be changing conditions of heat transfer or rate of heat liberation.

Our studies showed that the change in the heat physical properties of inert materials [24], similar in physical properties to pressed explosive charges, is not great (≈1%). Apparently, we should ignore also the slight worsening of heat transfer conditions resulting from cessation of removal of gaseous decomposition products from the reaction zone, since under the conditions of our experiments the first order boundary conditions remain correct over rather broad limits.

Thus, a change in heat transfer conditions does not lead to a significant effect.

Studying the changes in heat liberation conditions, we must note that the possible change in the thermal effect of the reaction resulting from more complete development of intermediate oxidation-reduction reactions with the participation of oxides of nitrogen does not agree with the experimental data. Actually, using the Frank-Kamenetskiy critical conditions, we can show that, for example, as the heat of reaction doubles the maximum drop in critical temperature is about 7°C, i.e., significantly less than the observed values of ΔT.

Generalizing the explanation of the regularities observed presented in the work of A. G. Merzhanov and F. I. Dubovitskiy [57], we can assume that the decrease in critical temperature and critical induction period with increasing pressure results primarily from the effects of the gaseous decomposition products, which accelerate the process of decomposition of the material, the removal of which from the reaction zone is greatly hindered at increased pressures (conditions of mechanical equilibrium). Apparently, adsorption of the gaseous decomposition products on the surface of the crystals of the material occurs. At a certain limiting pressure, equal to the saturated liquid vapor pressure ($p = p_s$), depending on temperature, volumetric condensation of vapors occurs and the crystals are completely covered with a layer of liquid. In this case, the further process of decomposition of the material is independent of the applied pressure.

In the simplest case, when the concentration of adsorbed decomposition products on the surfaces of material crystals is determined by the Langmuir isotherm, it follows from the Frank-Kamenetskiy critical conditions that the value ΔT for d = const is determined by the expression

$$\Delta T = \frac{RT_{cr}^2}{E} \ln \frac{p_s}{p_1}, \qquad (1)$$

where p_s is the saturated vapor pressure; p_1 = 1 atm; E is the activation energy; R is the universal gas constant.

Equation (1) where p = 20 atm and $E \approx 50$ kcal/mol properly reflects the order of experimental values of ΔT. It follows from this equation that for LT-4, which corresponds to a value of $E \approx 30$ kcal/mol, the value of ΔT is anomalously high, which has also been confirmed experimentally.

We must note that in the 200-250°C temperature interval the saturated water vapor pressure is 15-40 atm, which is similar to the values of p_s determined in our experiments.

The decrease in ΔT with increasing charge diameter $d > d_0$ (see Figures 4, 6) also follows from equation (1) and results from the dependence of p_s on T_{cr} (according to the Clapeyron-Clausius equation).

In order to explain the decrease in ΔT where $d > d_0$, we must study the course of the process of material decomposition in greater detail. As was assumed in concluding equation (1), pressure p_s is reached no later than attainment of the maximum decomposition rate, i.e., where $\eta \leq \eta_{max}$ (η being the depth of conversion). If the natural pressure of the gaseous decomposition products where $\eta = \eta_{max}$ is $p_{max} < p_s$, equation (1) gives elevated values of ΔT and we should replace p_s by p_{max}. The decrease in ΔT where $d < d_0$ is apparently explained by the dependence of p_{max} on experimental temperature.

. The experimental data are also correct for the case when charges are placed in a sealed, strong shell, preventing removal of gaseous decomposition products but not transmitting external pressure to the charge. This conclusion was confirmed experimentally for octogene and LT-4 in the case when the natural pressure of gaseous decomposition products exceeded the value of p_s.

Thermal Explosion at Elevated Pressure (up to 8,000 atm).

The results of experiments showed that the critical temperature of self-ignition at 20-800 atm remains practically constant. To determine the nature of further changes in the value of T_{cr} with increasing pressure, experiments were performed studying thermal explosion of pressures up to 8,000 atm.

Experimental Method

Studies were performed using two installations, differing in the maximum permissible working pressure due to design specifics.

In the installation for studies of thermal explosions at up to 4,000 atm (Figure 9), explosive charge 5, pressed directly into a depression in plug 4, was placed in a special thermostat 2, the temperature of which was maintained constant with an accuracy of ±1°C using contact thermometer 3, installed in a depression in the body of the thermostat and connected to heating circuit 8. To produce high pressures, a multiplication type installation was used with relative piston area selected so that liquid 6 was under pressure of about 150 atm, created by hand pump 9, generating a maximum pressure on the order of 4,000 atm in the small cylinder, which was recorded by type SV manometer 7 with an accuracy of ±1% of the assigned pressure. The maximum pressure was determined by the sealing method used (rubber rings) 1. The method and accuracy of determination of critical thermal explosion conditions as well as charge shape remained as before.

In the installation for studying thermal explosions at pressures up to 8,000 atm (Figure 10), explosive charge 5 and sealing inserts 4 were placed in cylinder 2, into which tightly fitted pistons 3 were inserted at each end. Cylinder 2 was heated using a double-walled vessel, between each heat transfer medium 6 (fluid No 5) was circulated, after being heated in TS-15 thermostat 7 to the required experimental temperature. The temperature was maintained constant with an accuracy of ±0.5°C. The high pressure was created using press 1 and hand pump 8. The maximum pressure was determined by the strength characteristics of pistons 3, which were made of high quality steel and heat treated. The decomposition mode was established on the basis of phenomena in companying ignition of the explosive charge in the closed volume (sharp sound effect, deformation of pistons, etc.). At the beginning of each experiment at various pressures, the explosive charge was preliminarily compressed to the maximum pressure of $8\cdot10^3$ atm in order to produce comparable results.

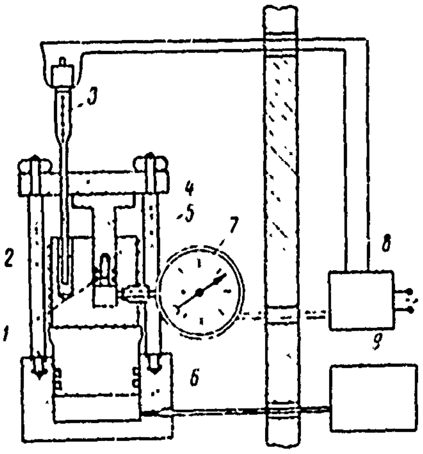

Figure 9. Diagram of Installation for Study of Thermal Explosion of Explosives at up to 4,000 atm.

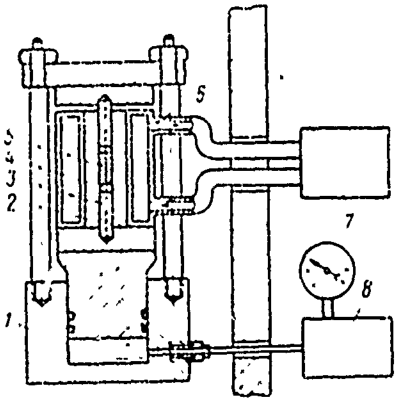

Figure 10. Diagram of Installation for Study of Thermal Explosion of Explosives at up to 8,000 atm.

The pressure acting on the specimen was determined by the known ratio of areas of pistons and press and indications of the standard manometer installed on the hand press. The error arising in this case in the pressure interval studied [65] is not over a few percent.

Results of Experiments

Octogene. Experiments were performed with charges 5.0 mm in diameter at 198-214°C and $(1\text{-}8)\cdot10^3$ atm. The primary results of the experiments determining the changes in critical temperature $\Delta T_1 = T_{cr} - T_{cr}^{(0)}$ with increasing pressure are shown on Figure 11 ($T_{cr}^{(0)}$ is the critical temperature at low pressures).

Figure 12 shows the experimental data of the dependence of induction period in the supercritical mode on pressure (T = 230°C) in semilogarithmic coordinates ln t, p. The critical period is 130-160 min.

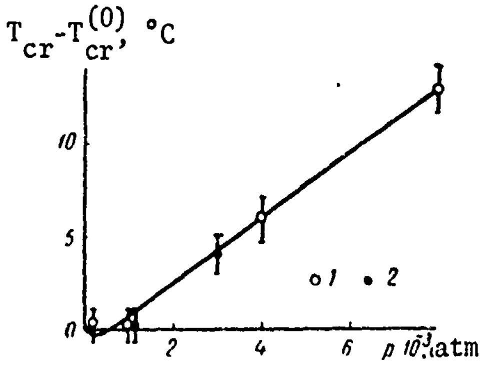

Figure 11. Changes in Critical Self-Ignition Temperature $(T_{cr} - T_{cr}^{(0)})$ as Functions of Pressure (p) for Octogene. 1, on installation operating at up to 8,000 atm; 2, on installation operating at up to 4,000 atm.

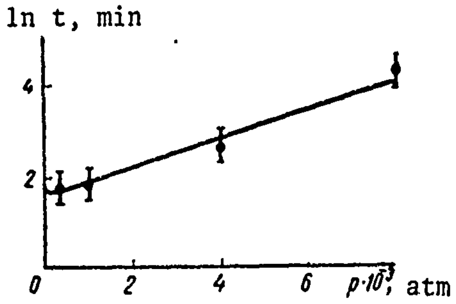

Figure 12. Induction.Period as a Function of Pressure (T = 230°C) for Octogene.

Material LT-4. The diameter of the charges was 5.0 mm, the temperature 200-206°C, pressure $(1\text{-}3)\cdot10^3$ atm (see Figure 13). The induction period under critical conditions is independent of pressure within the limits of the experimental area and equals 100-120 minutes.

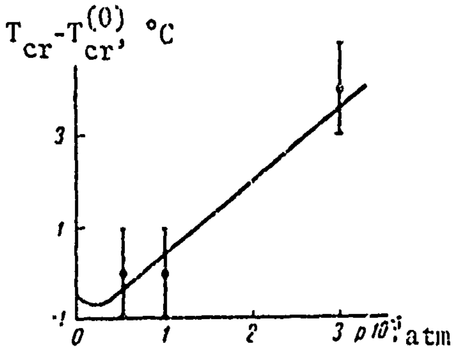

Figure 13. Change in Critical Self-Ignition Temperature $(T_{cr} - T_{cr}^{(0)})$ as a Function of Pressure (p) for LT-4.

As we can see from the data presented, the influence of pressure on critical self-ignition temperature does exist in this pressure interval, but is so slight that it could not be detected at lower pressures (up to 800 atm).

According to M. Evans, the dependence of reaction rate constants (K) on pressure is approximately defined by the formula

$$\frac{\partial \ln K}{\partial p} = -\frac{\Delta V_a}{RT}, \tag{2}$$

where ΔV_a is the activation volume (cm^3/mol).

Equation (2), as experiments have shown [21, 31], is well confirmed for reactions occurring in the liquid and solid phases. For reactions in solutions, the value of $\Delta V_a/RT$ is generally 10^3 atm, while the change in pressure may influence the reaction rate only when it exceeds 10^3 atm [21]. According to A. Stern, etal, for reactions in the solid phase the value of $\Delta V_a/RT$ is still lower.

In the case ΔV_a = const in the interval of temperatures and pressures studied, it follows from equation (2) that

$$K \sim \exp\left(-\frac{E \pm p\Delta V_a}{RT}\right). \tag{3}$$

If equation (3) is also correct for decomposition of explosives at temperatures corresponding to thermal explosion, the following relationships should obtain for a charge of fixed diameter under critical conditions:

$$\frac{E \pm p\Delta V_a}{RT_{cr}} \approx \frac{E}{RT_{cr}^{(0)}}; \tag{4}$$

$$t_{cr} = B\exp\left(\frac{E \pm p\Delta V_a}{RT_{cr}}\right). \tag{5}$$

Using equation (4) and the experimental data produced, we found the effective values of activation volume ΔV_a. It was found that for octogene at T_{cr} = 472°K and E = 38,000 cal/mol, ΔV_a = 4 ± 1 cm^3/mol, while for LT-4 at T_{cr} = 472°K and E = 32,000 cal/mol, ΔV_a = 3 ± 1 cm^3/mol. The value of ΔV_a determined from the angle of inclination of the straight line ln t = f(p) (see Figure 12) is approximately 10 cm^3/mol. The increase in the value of ΔV_a is apparently explained by the fact that in the supercritical mode the experiments were actually performed at different distances from the critical mode due to the existence of dependence T_{cr} = f(p) (see Figure 11). Since as we move further away from the critical mode the induction period drops rapidly, these experiments show a certain summary picture, which results in elevated values of ΔV_a.

In processing the data produced by F. P. Bouden and A. D. Ioffe [23], we produce a dependence similar to that shown on Figure 11, 13. Calculations have showed that where $p > 100\text{-}200$ atm, the value of $\Delta V_a \simeq 10\ \text{cm}^3/\text{mol}$, which is similar to the values which we have produced.

In processes dependent on pressure, quantity ΔV_a plays a role similar to the role of activation energy in processes occurring with variable temperature; therefore, we should look upon the value of ΔV_a in equations (4) and (5) as the effective value of activation volume, depending on the change in explosive parameters (heat conductivity, etc.) with increasing applied pressure. In particular, the value of ΔV_a, as we will show below, may be significantly determined by state conversions in the material during the process of decomposition.

Thermal Explosion at Temperatures Near the Melting Point of the Explosive.

For certain explosives used in the performance of shooting operations in boreholes, the threshold of thermal stability of charges of comparatively small diameter is near the melting point of the explosive and the influence of pressure is felt in a specific manner. This problem is also of scientific interest.

The study of thermal explosions was performed using the installation we have already described (see Figure 1).

The dependence of induction period on pressure for PETN charges 6.0 mm in diameter with a density of 1.47 g/cm^3 at 136°C and for charges of hexogene 6.0 mm in diameter with a density of 1.56 g/cm^3 at 188°C is shown in Table 7.

TABLE 7.

DEPENDENCE OF INDUCTION PERIOD (t) ON PRESSURE (p) FOR PETN AND HEXOGENE.

PETN		Hexogene	
p, atm	t, min	p, atm	t, min
1	203	1	133
100	255	40	30
200	360	100	34
300	390	200	38
400	450	400	47
600	530	600	56
		800	67

When solid explosives decompose at temperatures near their melting point, the formation of liquid decomposition products plays a significant role. This phenomenon was observed during decomposition of PETN [71], EDNA [94] and certain other explosives. The study of the kinetic regularities of thermal decomposition of solid explosives under conditions of formation of liquid phase is the subject of a work by G. B. Manelis and F. I. Dubovitskiy, K. Boun [53]. A quasistable system of thermal explosion equations, considering the kinetic regularities detected, was produced by A. G. Merzhanov.

If we ignore the change in volume and heat conductivity of an explosive charge during the process of an experiment, the system of equations of a thermal explosion can be written as follows:

$$e^{\theta}\left(1+\frac{\sigma e^{\theta}}{1-\sigma e^{\theta\omega}}\frac{\eta}{\eta_0}\right)-\frac{\theta}{\varkappa}=0; \tag{6}$$

$$\frac{d\eta}{d\tau}=e^{\theta}\left(1+\frac{\sigma e^{\omega\theta}}{1-\sigma e^{\theta\omega}}\frac{\eta}{\eta_0}\right), \tag{7}$$

where $\theta = E/RT_0^2\ (T - T_0)$; $\tau = K_0 t \exp\ (- E/RT_0)$; $\eta_0 = K_s/K_1$; K_s, K_1 are the reaction rate constants in the solid and liquid phases respectively; $\sigma \approx e^{[-Q_m(T_m - T_0)/RT_mT_0]}$; Q_m, T_m are the heat and temperature of melting; T_0 is the experimental temperature; $\omega = Q_m/E\ T_0^2/T_m^2$.

Substituting the known dependence of melting point on pressure into equations (6) and (7)

$$T_m = T_m^{\circ} + \left(\frac{\partial T}{\partial p}\right)_0 p + \dots \tag{8}$$

and solving the system of these equations using the known plan of A. G. Merzhanov, we can find the dependence of induction period on pressure. However, the expression for $t = f(p)$ produced is so cumbersome that its comparison with experimental data is difficult.

Considering that, according to the experimental conditions $T_m - T_0/T_0 \ll$ $\ll 1$ and, generally, $Q_m/E \approx 1/5 \ll 1$, we can simplify the initial system of equations and find:

$$t = \mathrm{const}\exp\left(\frac{p\,\Delta V_s}{RT_0}\right), \tag{9}$$

where $\Delta V_a = Q_m(\partial T/\partial p)_0/T_m$ (cm^3/mol), and the value of const in the first approximation is independent of pressure.

The equation $\Delta V_a = Q_m(\partial T/\partial p)_0/T_m$ is the known Clapeyron-Clausius equation. Assuming that Q_m = 10 kcal/mol, $(\partial T/\partial p)_0$ = 0.025 degree/atm, $T_0 \approx 500°K$, we find ΔV_a = 20-30 cm^3/mol.

In correspondence with equation (9), the experimental data presented in Table 7 were represented in semilogarithmic coordinates ln t, p (Figures 14 and 15).

The values of ΔV_a determined from the angle of inclination of the straight lines are 30 cm^3/mol for PETN and 37 cm^3/mol for hexogene, which agrees with the theoretical estimate of ΔV_a if we assume Q_m = 14.5 kcal/mol for PETN and 12.5 kcal/mol for hexogene. The value of ΔV_a in this case has a precise physical sense -- the change in the specific volume of the material during a conversion of state (melting). The divergence between the experimental and calculated values of ΔV_a results apparently from distortions of the model.

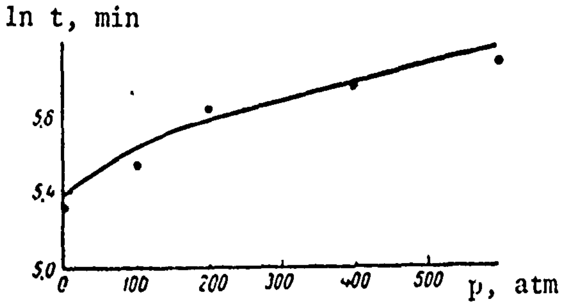

Figure 14. Induction Period (t) as a Function of Pressure (p) for PETN.

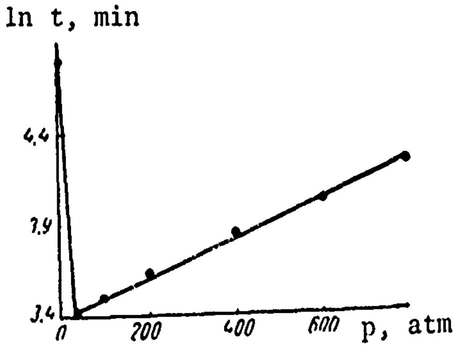

Figure 15. Induction Period (t) as as Function of Pressure (p) for Hexogene.

Thermal Explosion at Pressures on the Order of 10^5 atm.

We can conclude from the data presented above that at pressures exceeding p_s throughout the entire interval of pressures studied (up to 8,000 atm), the dependence of the reaction rate constant of thermal decomposition of the explosive on pressure is described well by equation (2). However, when the data produced are extrapolated into the area of pressures on the order of 10^5 atm where ΔV_a = 3-4 cm^3/mol, we produce elevated values of effective activation energy which, as we will indicate, contradict the available experimental data.

On the other hand, during calculations involved in the determination of critical conditions of initiation of detonation of secondary explosives by shockwaves, standard values of activation energy and pre-exponent are used, which also are not well founded.

We must consider, in our opinion, that at high pressures the energy of elastic compression ε of an explosive crystal will play an ever increasing role in the mechanism of activation of molecules.

As Ya. I. Frenkel' emphasized [74], establishment of closer contact between molecules must be accompanied by weakening of the coupling between the simpler particles forming the molecules (antagonism of internal and external bonds), which has been confirmed by many numerical experiments for inert materials. For example, the increasing dipole moment and decreasing frequency of intramolecular oscillations upon transitions in the gas-liquid-solid direction for polar molecules, the change in Raman spectra for nonpolar molecules upon transition from the gaseous to the solid state, the dissociation of one substance upon dissolution in another, phenomena of ionization, changes in valance under the influence of high pressure, etc.

Consideration of the influence of crystal compression energy on the rate of thermal decomposition of the explosive can be performed using quantum mechanical ideas; however, the solution of this problem brings up tremendous mathematical difficulties due to the large number of atoms in an explosive molecule.

The influence of compressibility on activation energy and the pre-exponent can be formally considered in the following form:

$$E = E_0 + p\Delta V_a - f(\varepsilon); \tag{10}$$

$$K = K_0\varphi(\varepsilon). \tag{11}$$

where f(ε) and φ(ε) are functions of compressive energy, which can be defined if we know the potential energy surface for the given reaction.

Let us expand f(ε) into a series with respect to powers of ε near the point ε = 0:

$$f(\varepsilon) = f(0) + \left(\frac{df}{d\varepsilon}\right)_0 \varepsilon + \frac{1}{2}\left(\frac{d^2 f}{d\varepsilon^2}\right)_0 \varepsilon^2 + \cdots \tag{12}$$

Assuming that where $\varepsilon = 0$ compressibility can be ignored, we find $f(0) = 0$. Further, considering that where $\varepsilon \sim E_0$ the value of $f(\varepsilon) \sim E_0$, we find $\left(\frac{\partial f}{\partial \varepsilon}\right)_0 = C_1 \approx 1$, $\left(\frac{\partial^2 f}{\partial \varepsilon^2}\right)_0 \approx C_2 \approx \frac{1}{E_0}$, ...

Then in the first approximation:

$$E = E_0 + p\Delta V_a - C_1\varepsilon \tag{13}$$

and equations (4) and (5) will look as follows:

$$\frac{E_0 + p\Delta V_a - C_1\varepsilon}{RT_{cr}} \approx \frac{E_0}{RT^0_{cr}}. \tag{14}$$

$$t_{cr} = B\exp\left(\frac{E_0 + p\Delta V_a - C_1\varepsilon}{RT_{cr}}\right). \tag{15}$$

With impact compression, which occurs during excitation of detonation by shockwaves, the internal energy and, consequently, its elastic component are determined by the Hugoniot equation

$$\varepsilon = \frac{p}{2}(V_0 - V) = \frac{p}{2}\Delta V_{com},$$

where V_0, V are the specific volumes of the charge at atmospheric pressure and pressure p.

The value of ΔV_{com} is an increasing function of pressure, therefore, equation (14) indicates that the curve T_{cr} (p) where $\Delta V_a > 0$ will have a maximum at a pressure determined by the condition

$$\frac{\partial}{\partial p}(p\Delta V_a - C_1\varepsilon) = 0.$$

Using data on the compressibility of explosives [27], we find that for PETN the bend point on the curve of T_{cr} (p) corresponds to a critical pressure on the order of $(30\text{-}40)\cdot 10^3$ atm.

At pressures higher than the critical pressure, the rate of the reaction of thermal decomposition of the explosives should increase markedly with increasing pressure, while the effective value of activation energy decreases. Similar considerations were set forth by E. Teller.

Ch Mader [99] showed experimentally that with increasing pressure the critical size of an explosion center decreases. Thus, a center at 1,400°K in nitromethane, not subjected to impact, is no smaller than 0.27 cm, while the size of a center in nitromethane subjected to explosive impact

($p = 95 \cdot 10^3$ atm) is 0.03-0.06 cm in diameter at the same temperature.

Approximate calculations using equation (13) and considering the compressibility of nitromethane at $p = 95 \cdot 10^3$ atm has shown that under these conditions there is a significant decrease in activation energy (on the order of 20 kcal/mol).

Thermal Explosion Under Conditions of Heating at Constant Rate.

In order to determine the capabilities of the material studied, it seemed interesting to study the process of thermal explosion under conditions of heating at constant rate, corresponding to the rate of increase in temperature in shooting apparatus lowered into a borehole at $W =$ $= 1$ to 2 degree/min.

The heating rate of an explosive in the installation (see Figure 1) was fixed by mechanical rotation of the head of the contact thermometer at the required frequency. The critical heating rate W_{cr} separating explosive from nonexplosive decomposition was determined by sighting.

Octogene. The experiments were performed at normal and elevated pressures with charges 9.0 and 15.0 mm in diameter, density 1.6 g/cm^3. Since the critical temperature of autoignition and the induction period under critical conditions are practically not influenced by pressure in the 20-800 atm range, the experiments were performed only at atmospheric pressure and 200 atm. The medium used to surround the charge was primarily Wood's alloy (Figure 16).

NTFA. Experiments were performed with charges 7.1 mm in diameter with a density of 1.54 g/cm^3. The medium surrounding the charge was Wood's alloy (Figure 17).

The regularities of thermal decomposition under conditions of heating (and cooling) at constant rates and normal atmospheric pressure have been discussed in many works [54, 69]. We note only one specific feature of thermal explosion under conditions of linear heating and atmospheric pressure, not described earlier.

At heating rates near the critical, T_{cr+} increases rather rapidly with increasing heating rate. However, where $W/W_{cr} >> 1$ (the area of practical application of the explosives), there is an area of "saturation," where T_{cr+} increases very slightly with increasing W/W_{cr}.

The temperature T_{cr+} in the area of saturation is several dozen degrees (50°C) higher than the static critical temperature T_{cr}.

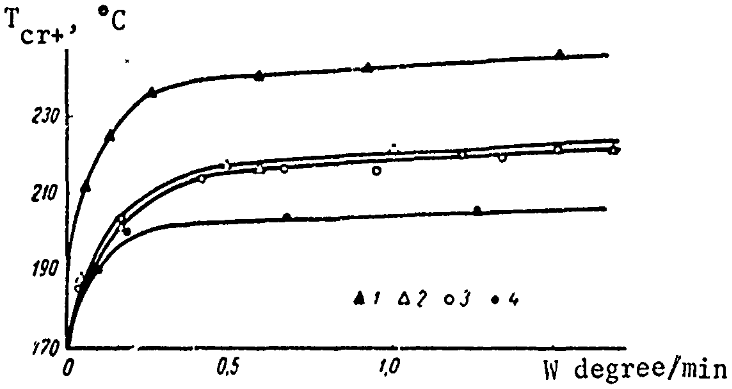

Figure 16. Autoignition Temperature (T_{cr+}) as a Function of Heating Rate (W). Surrounding Medium for Curve 4 -- Clay Solution.
1, d = 15 mm, p = 1 atm, $W_{cr} = 1.6 \cdot 10^{-2}$ degree/min; 2, d = = 15 mm, p = 200 atm, $W_{cr} = 0.5 \cdot 10^{-2}$ degree/min; 3, d = 9 mm, p = 200 atm, $W_{cr} = 2.5 \cdot 10^{-2}$ degree/min; 4, d = 9 mm, p = = 200 atm, $W_{cr} = 2.5 \cdot 10^{-2}$ degree/min.

As we can see from Figure 16, the change in autoignition temperature (T_{cr+}) upon transition from atmospheric pressure to elevated pressure is generally similar to the change in critical autoignition temperature (T_{cr}) under static conditions and the corresponding values of $\Delta T_+ = T_{cr+} - T^s_{cr+}$ and $\Delta T = T_{cr} - T^s_{cr}$ are numerically similar. However, the dynamic mode, allowing the thermal ignition process to develop in time, contains somewhat greater information than the static mode. In articular, the experiments performed allow us to find an explanation for the sharp decrease in critical induction period for NTFA with increasing pressure (see Table 5).

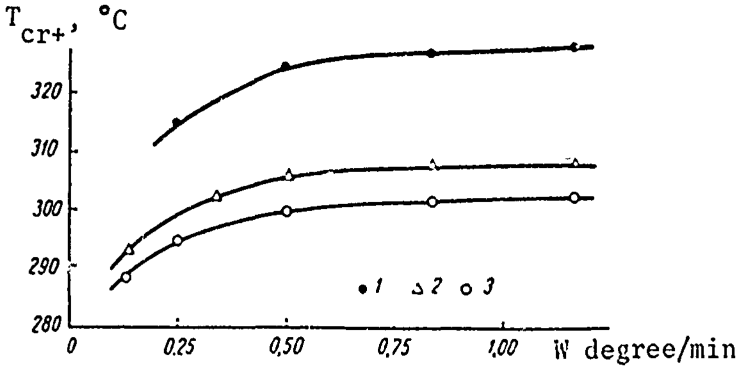

Figure 17. Autoignition Temperature (T_{cr+}) as a Function of Heating Rate (W).
1, d = 7.1 mm, p = 1 atm; 2, d = 7.1 mm, p = 100 atm; 3, d = 7.1 mm, p = 400 atm.

Comparing the experimental data (see Figure 17) with the results of calculation of the dependence $T_{cr+} = f(W/W_{cr})$ for the autocatalytic reaction [56], we can conclude that the value of η_0 (η_0 is the autocatalytic criterion) increases for NTFA upon transition from atmospheric pressure to elevated pressure throughout the entire pressure interval (for octogene, η_0 increases only upon transition from atmospheric pressure to pressures $p \leq p_s$). The results of this is a sharp decrease in T_{cr+} in the area of saturation with increasing pressure with fixed values of heating rate. However, the value of T_{cr} remains practically unchanged, since the critical Frank-Kamenetskiy conditions depend little on η_0 at comparatively low values.

The results of studies of thermal explosion of octogene, LT-4, LT-5, NTFA, hexogene and TNT under elevated hydrostatic pressure conditions, both in static and in dynamic modes, indicated the following.

1. In the area of low pressure ($p < p_s \approx 20$ atm), there is a significant reduction (to a certain limit) in critical autoignition temperature (T_{cr}) and induction period (t_{cr}).

The function $\Delta T = T_{cr} - T^s_{cr}$ depends on charge diameter in a complex manner.

The regularities observed are apparently primarily related to the accelerating influence of gaseous decomposition products adsorbed on the surface of the crystals of the material. The calculation values of ΔT produced on the basis of this assumption are similar to the experimental values.

2. At pressures exceeding p_s, right up to 8,000 atm, a slight increase in T_{cr} occurs, while the value of t_{cr} remains practically unchanged. It has been demonstrated that the data produced can be explained using the known kinetic equation $\partial \ln K/\partial p = -\Delta V/RT$, where the value of ΔV (effective activation volume) must be looked upon as the primary kinetic constant, the value and sign of which determine the nature and degree of the influence of pressure on the parameters of the thermal explosion.

3. Near the melting point for PETN and hexogene, the induction period increases with increasing pressure over a broad interval of pressures. Based on analysis of the system of equations from the quasistable theory of a thermal explosion, it has been shown that the value of ΔV in this case has a precise physical sense and is determined by the Clapeyron-Clausius equation: $\Delta V = (Q_m \, \partial T/\partial p)|T_m$.

4. The change in the ignition temperature T_{cr+} under conditions of linear heating occurs similarly to the change in T_{cr} under static conditions upon transition from atmospheric pressure to increased pressure.

The value of T_{cr+} at a heating rate near that encountered in boreholes is significantly greater (approximately 50°C) than the value of T_{cr}.