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A METHOD OF DETERMINING INFLAMMABILITY
OF EXPLOSIVES

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ABSTRACT: The article deals with various thermodynamic parameters during combustion of igniters, pyroxline and ammonium nitrate, used in small manometric and calorimeter bombs. Parameters for heat, pressure, condensation and water evaporation resulting from combustion are presented in theoretical and experimental form. The critical amounts of igniter and use of different explosive mixtures are discussed.

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Several years ago K. K. Andreyev and V. M. Rogozhnikov suggested characterizing the inflammability of explosives by the minimum amount of igniter exciting the smooth burning of a small explosive charge in a manometric bomb. The igniter used was a mixture (1:1) of No. 1 pyroxyline with finely-crushed ammonium nitrate (average particle size approximately $20 \mu m$), as opposed to black powder, the igniter normally used, since it did not allow for the complete combustion of substances capable of catalyzing the combustion of explosives or interact intensely with them. This method was successfully used when investigating and improving permissible explosives for the coal mining industry (in particular, modifications allowing for the simulation of the most dangerous conditions of explosive burning in blast holes) and was undoubtedly useful. It is interesting to examine combustion in a manometric bomb which is rather more detailed than by calculating the critical amount of igniter, estimating the amount of heat into the explosive charge during ignition, and to compare the results of experiments with theory.

The manometric bomb. Tests were carried out on a manometric bomb (bomb core diameter 3 cm, thickness of the wall 2.9 cm) with tensometric time recording of pressure. The ullage of the bomb core was 102 cm³, the explosive charge volume with the stand on which it was mounted was 6 cm³. The lower cap of the bomb was a water-filled channel 6 mm in diameter, leading to the tensometric sensor. (Special tests established that the presence of water in the channel did not affect the cooling process of the combustion products.)

The tensometric sensor was connected on a full-wave circuit to the TU-4M tensometric amplifier (carrier frequency 6 KHz) or to the UTS-12K tensometric station. The MPO-2 magneto-electric oscillograph (type IV oscillator with a natural oscillation frequency of 3 KHz) recorded the pressure over time. This allows recording to be done without distortions lasting more than 1 msec. The accuracy of pressure measurement is approximately 3%. An igniter in a cigarette paper sleeve was attached to the electrical inputs of the upper cap. The density of the substance in the sleeve was approximately 0.5 g/cm³, the weight of the paper was approximately 2% of the weight of the igniter. Air was not removed from the bomb, the initial pressure was atmospheric.

The thermodynamics of igniter combustion products. The amount of heat during combustion of the igniter was determined by using a calorimeter bomb with a volume of 280 ml in air atmosphere. The charging density m/V (the ratio of igniter weight to the volume of the bomb) was used as a parameter for showing the ratio between the

amount of air and the weight of the igniter, the mean pressure during combustion, and, consequently, the volume of the latter. The dependence of heat of the explosion on m/V in the interval from 2 to 1.4 g/cm^3 is shown in Figure 1.

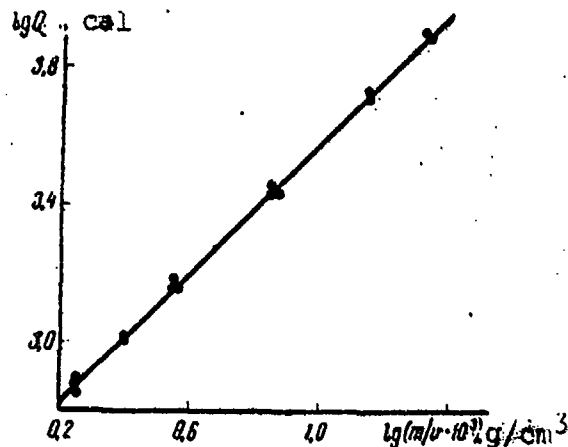


Figure 1
The heat of an explosion of a mixture (1:1) of No. 1 pyroxyline with finely-crushed ammonium nitrate in a calorimeter bomb with a volume of 280 ml.

It is expressed by the ratio

$$Q_{\text{liq}} = 1,01 \cdot 10^3 \left(\frac{m}{V} \right)^{-0,06}, \text{ cal/g} \quad (1)$$

* Hence, it follows that the heat of explosion noticeably increases with a reduction of m/V , in spite of the incomplete combustion (when $m/V = 3.6 \text{ mg/cm}^3$ nitrogen oxides remain in the calorimeter bomb). Probably, this is linked with the fact that the combustion of pyroxyline and paper in the air's oxygen gives off greater heat than interaction with the nitrate.

The heat of the explosion when there is water in a bomb with a volume of 96 ml

$$Q_{\text{liqu}} = 1,33 \cdot 10^3 m^{-0,06}, \text{ cal/g} \quad (2)$$

Comparison of the results of these tests with calculations according to data [1] is given in Table 1. The same table shows the calculated quantities of gaseous explosion products (in gram molecules for 1 kg of gas), the explosion temperature is T_{exp} , and the mean molecular weight of gas and their mean thermal capacity with a constant volume (in the interval 1000-3000°K). Furthermore, Figure 3 (curve 4) shows the dependence of the amount of igniter on value,

(a)

$$Q'_{\text{max}} = p'_{\text{max}} / p'_0$$

where p'_{max} is the calculated maximum pressure, developed in the bomb during the explosion temperature;

p'_0 - is the pressure of explosion products at room (293°K) temperature (H_2O - steam).

TABLE 1

m, g	Q_{liqu} , cal/g (calculated)	Q_{liqu} , cal/g (experimental)	V_0 , l/kg	T_{exp} , °K	\bar{M}_{mean}	c_v , cal/degrees 1000-3000°K	Composition of gases at $T = 1900^\circ \text{K}$, g-mol /kg				
							CO_2	CO	H_2O	H_2	N_2
0.6	1425	1370	829	3414	27.0	0.340	8.20	1.30	15.50	0.57	11.54
1.0	1343	1330	830	3419	26.6	0.341	8.16	1.63	16.16	0.75	10.41
1.4	1339	1300	845	3418	26.5	0.348	8.30	1.93	16.73	0.91	9.66
2.0	1314	1275	852	3423	26.2	0.350	8.24	2.24	17.0	1.08	9.52

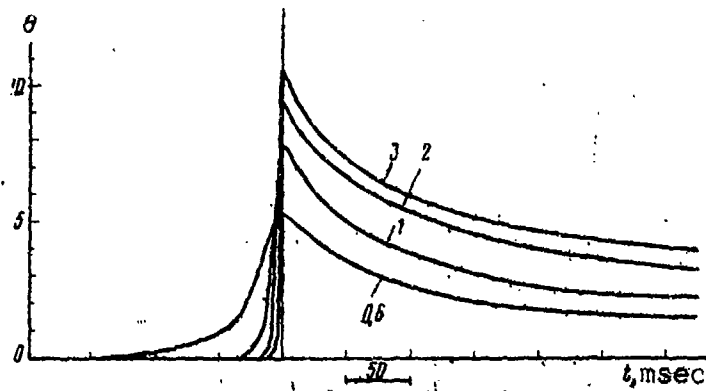


Figure 2

The change of pressure over time during combustion of igniters in a manometric bomb with a volume of 96 ml; 0.6; 1; 2; 3 - amount of igniter, gm.

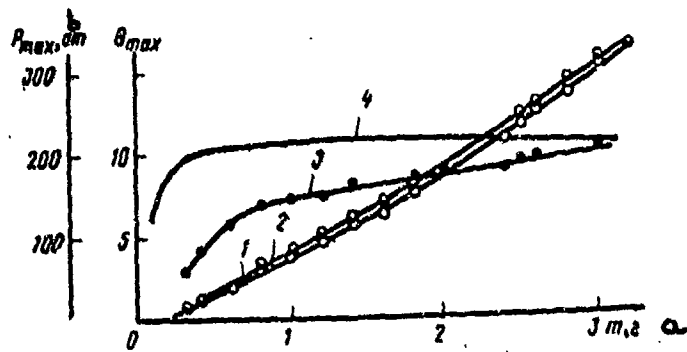


Figure 3

Maximum pressure developed in a manometric bomb during igniter combustion in it:

- 1 - P_{max} in a bomb without explosives;
- 2 - P_{max} in a bomb with an explosive charge (during failures)
- 3 - $\theta_{max} = P_m/P'_0$ (according to curve 1);
- 4 - θ_{max} (calculated value of P_{max}/P'_0 without allowance for dissociation and heat loss).

Key: a - g.
b - atm.

Igniter combustion. The change of pressure over time during combustion of igniters of different weights in a manometric bomb is shown in Figure 2. Value $\theta = p/p'_0$, characterizing (when there is no condensation) the temperature of gas in the bomb ($\theta = T/T_0$), is placed along the Y-axis. The curve of $\theta(t)$ is divided by the maximum into two sections, on the first of which there is a predominance of heat-evolution and gassing, and on the second, heat-dissipation. Apparently, the combustion of an igniter ends when it reaches the maximum. During combustion the mean pressure is lower, and the combustion time and relative heat losses during the combustion period are higher when there is a smaller amount of igniter. The amount of heat loss during the combustion period can be characterized by the difference between the maximum values of θ'_{max} and θ_{max} , obtained by calculation and experimentally from known values of Q_{liqu} . The dependence of $\theta_{max}(m)$ is shown in Figure 3 (curve 3). Here each point is the mean of 3-10 tests. This also shows the dependence of maximum pressure p_{max} on m during combustion of igniters of various weights when there is no explosive charge (curve 1) and when there is an explosive charge (curve 2) during failures.

The effective heat transfer coefficient λ_{eff} on combustion products by the cold walls of the bomb can be obtained from experimental data according to a formula obtained if one assumes that Newton's law of cooling is correct when the temperature of the walls is $T_{wall} = T_0 = \text{const}$:

(3)

$$\alpha_{\text{eff}} = -\frac{c_p m r}{S} \cdot \frac{d \ln(\Theta - 1)}{dt},$$

Where S - the wall surface of the bomb;
t - the cooling time.

Calculation shows that the warming up of the walls does not exceed 10% of the mean temperature of gases. Figure 4 shows the view of function $\alpha_{\text{eff}}(\Theta)$.

The heat transfer coefficient α_{eff} during the combustion of the igniter can be estimated by the combustion time and in the heat loss during combustion, characterized by the difference between Θ'_{max} and Θ_{max} (curves 4 and 3 in Figure 3). Here, the most reliable are values α_{eff} , obtained when the amount of igniter was approximately 1 g. When m is smaller, the increase of pressure during combustion occurs too slowly, and it is more difficult to determine the combustion time, when there are greater ones dissociation is possible, and the temperature of gas Θ'_{max} become rather indeterminate. Finding t and Θ according to figures 2 and 3 for m = 1 gm, we obtain $\alpha_{\text{eff}} = 4 \cdot 10^{-2}$ cal/cm²·sec·deg (when m = 1.4 g, $\alpha_{\text{eff}} = 6 \cdot 10^{-2}$ cal/cm² x sec·deg).

The value of α_{eff} is the result of heat transfer by convection and radiation, and also the result of heat losses during condensation of water on the walls of the bomb, and possibly, during its subsequent evaporation. Therefore, $\alpha_{\text{eff}} = \alpha_{\text{con}} + \alpha_{\text{rad}} + \alpha_{\text{cond}} + \alpha_{\text{eva}}$. The value of α_{con} and α_{rad} can be calculated in a similar fashion for that of a model rocket chamber [17]. We shall accept the mean

temperature of gases as equaling 1900°K. The averaged composition of gases at this temperature is g-mol/kg: CO₂ - 8.8; CO - 1.7; H₂O - 17.8; H₂ - 1.1; N₂ - 8.6.

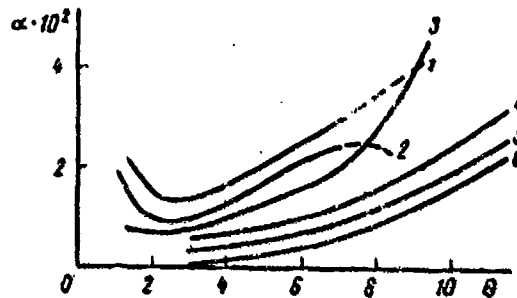


Figure 4

The change of heat transfer coefficient (cal/cm²·sec·deg) during cooling of combustion products of a mixture of No. 1 pyroxyline with NH₄NO₃ and pure No. 1 pyroxyline:
 1 - α_{eff} when $m = 2\text{g}$; 2 - α_{eff} when $m = 1\text{g}$;
 3 - α_{eff} during combustion of 1 g of No. 1 pyroxyline;
 4 - $\alpha_{\text{rad}} + \alpha_{\text{con}}$ for 2 g of the mixture (calculation);
 5 - $\alpha_{\text{rad}} + \alpha_{\text{con}}$ for 1 g of the mixture (calculation);
 6 - α_{rad} for 1 g of the mixture (calculation);

The heat transfer coefficient by convection during free convection can be found by ratio,

$$\alpha_{\text{con}} = \frac{\text{Nu} \bar{\lambda}}{d}, \quad (5)$$

where Nu - the Nusselt number;

$\bar{\lambda}$ - the mean integral value of the coefficient of thermal conductivity of gas between the temperature in the volume and the temperature of the internal surface of the walls ($1.7 \cdot 10^{-4}$ cal/cm x sec·deg);

d - the equivalent diameter of the bomb, equal to 5 cm.

According to work [2]

$$Nu = \sqrt[4]{\frac{\mu \Delta T}{\eta v_b^2 T}} \sqrt{m_g} \quad (c)$$

where $\Delta T/T$ - the ratio of difference of temperatures between gas and the wall to the mean temperature of gas

$$\left(\sqrt[4]{\frac{\Delta T}{T}} \approx 0.96 \right); \quad (d)$$

- m_g - the amount of gas in the bomb; $m_g = m + 0.12$ g;
- η - the dynamic viscosity of the gas, equal to $7.1 \cdot 10^{-4}$ pieze;
- v_b - the free volume of the bomb, equal to 96 ml.

Calculation according to the data shown gives $\alpha_{con} = 3 \cdot 10^{-3} \sqrt{m_g}$, cal/cm²·sec·deg.

The heat transfer coefficient by radiation can be calculated by the formula

$$\alpha_{rad} = \frac{q_{rad}}{T - T_{deg}} = \frac{\epsilon \cdot 4.96 \left[\left(\frac{T}{100} \right)^4 - \left(\frac{T_{deg}}{100} \right)^4 \right]}{3.6 \cdot 10^8 (T - T_{deg})} \text{ cal/cm}^2 \cdot \text{sec} \cdot \text{deg} \quad (e)$$

where q_{rad} - the heat flow transmitted to the wall by radiation;

ϵ - the effective degree of gas blackness; $T_{deg} \approx T_0 \approx 300^\circ K$.

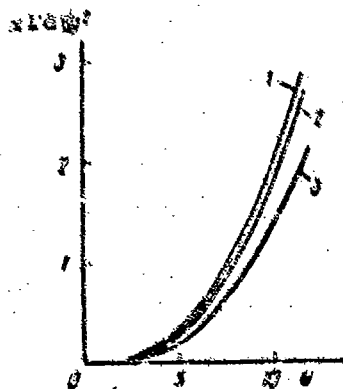
Water vapor and carbonic acid result from gaseous products produced during igniter combustion. The degree of blackness of H₂O and CO₂ depends significantly on the temperature and pressure in the bomb.

The value $\epsilon(\theta, m)$ can only be calculated very approximately by using extrapolation of experimental data published in literature. Values of

$\epsilon m = 0.6-2$ and $\theta = 12-2$ vary in the interval 0.55-0.58; ϵ increases with the increase of m .

Values for $\alpha_{\text{rad}}(\theta)$ for the amount of igniter 0.6; 1.4 and 2 g are shown in Figure 5. When $\theta > 5$, $\alpha_{\text{rad}} > \alpha_{\text{con}}$, the difference also increases between them rapidly during the increase of θ , so that when $\theta > 10$, α_{rad} is several times greater than α_{con} . The effect of the amount of igniter on one or the other heat transfer coefficient is small. On Figure 4, together with $\alpha_{\text{eff}}(\theta)$ is shown the dependence of value $\alpha' = \alpha_{\text{con}} + \alpha_{\text{rad}}$ for amounts of 1 and 2 grams on θ . Figure 4 shows that α' is significantly smaller than α_{eff} . In the large interval of θ , the ratio $\alpha'/\alpha_{\text{eff}} \approx 0.4$. Consequently, a large amount of heat is transmitted to the walls of the bomb as a result of condensation in them of water vapors from combustion products.

Figure 5
The heat transfer coefficient by radiation from combustion products of a mixture of pyroxyline with $\text{NH}_4\text{NO}_3(1:1)$ in a monoometric bomb with a volume of 96 ml (calculation). With an amount of igniter 1-2 g; 2-1.4 g; 3-0.6 g; θ - ratio of gas temperature to room temperature (293°K); α_{rad} , cal/cm²·sec·deg



Calculation of condensation water evaporation. The differential equation of heat emission allowing for condensation and evaporation has the form

$$-\frac{dQ}{dt} = \sigma S(T - T_{\text{amb}}) + c_0 \frac{dmc}{dt} + q_0 \frac{dmc}{dt} \quad (1)$$

where dm_c/dt and dm_e/dt - the rate of condensation and water evaporation;
 q_c and q_e - the amount of heat lost by the gas during
condensation and evaporation of 1 g of water.

One can accept approximately that $q_c = q_e = c_v H_2O (T - T_{sat}) =$
 $c_v (T - T_{deg}) = c_v (T - T_0)$.

By designating

$$\Theta = \frac{p}{p_0} \mu = 1 - \frac{m_c}{m_0} + \frac{m_e}{m_0}, \quad (g)$$

we obtain

$$T = \frac{\Theta}{\mu} T_{oi}; \quad \frac{dQ}{dt} = m_0 c_p \frac{dT}{dt} \quad (h)$$

and

$$\frac{d \ln(\Theta - \mu)}{dt} = \frac{1}{\mu} \frac{S}{c_p m_r} \left(\alpha' + 2 \frac{c_v}{S} \frac{dm_e}{dt} \right). \quad (4)$$

The mean value of $\mu = 0.8$. If we accept that on the left side of
the equation (4) $\mu = 1$, and compare (3) and (4), we can obtain

$$\alpha_{eff} = \frac{\alpha'}{\mu} + \frac{2}{\mu} \frac{c_v}{S} \frac{dm_e}{dt} \quad (5)$$

From Figure 4 and correlation (5) it follows that the condensation
rate depends little on the amount of igniter and, on an average, is
 ~ 3 g/sec. At this rate, if there were no evaporation, all the
water contained in combustion products of an igniter weighing, for example,
1 g, would be condensed in 0.1 sec., after which α_{eff} would sharply
(3 times) decrease. Since this does not occur, and furthermore since
 α_{eff} decreases by approximately the same amount as α' it is possible

that during cooling condensation, to a considerable degree, is compensated by evaporation. By assuming that the process is stationary and $\mu \approx \text{const}$, we can introduce a correction into the value of the heat transfer coefficient by radiation. When $\mu = 0.9-0.8$, $\alpha_{\text{rad}} (\theta)$ increases by 1.5-2 times. Correspondingly, the ratio $\alpha' / \alpha_{\text{eff}}$ increases up to 0.5. We shall use this value during subsequent calculations. Such a significant role of water condensation on the walls is connected with the large (up to 40%) content in the igniter's combustion products. This assumption was confirmed by tests with No. 1 pyroxyline (13.42% N), used in a pure form without ammonium nitrate. The water content in combustion products is $\sim 24\%$. The curve of $\alpha_{\text{eff}} (\theta)$ (Figure 4, curve 3) is noticeably lower than for a mixture with nitrate, although it is higher than $\alpha' (\theta)$.¹

Calculating the critical amount of igniter. . Before calculating the critical amount of igniter, we shall estimate the correlation between the heat flux occurring on 1 cm^2 of the surface face of the explosive charge. The latter depends, mainly, on the temperature difference of gas T and the surface of the explosive T_s and, consequently, on the rate of temperature increase of the surface and its maximum value. Since the coefficient of thermal conductivity of an explosive

1. Probably the excess actual heat losses above those calculated earlier in the model rocket chamber, which in test conditions [2] were about 30%, are linked with condensation and water evaporation on the walls.

is smaller by a factor of 2 than steel, the temperature increase of the charge surface will occur much quicker than the walls of the bomb. The calculation will give the time required for the increase of T_s to 300-400°C in the order of 20 msec. On one hand, this temperature is close to the critical for water, and on the other hand when this temperature is reached, intensive gasification of the explosive occurs. Correspondingly, the condensation of water vapors on the surface of the explosive will quickly become impossible and, apparently, no attention should be paid to it. In this case, the heat transfer coefficient to the charge surface of the explosive can be accepted as equalling

$$\alpha = \alpha' = \alpha_{\text{conv}} + \alpha_{\text{rad}} \approx 0,5\alpha_{\text{eff}} \quad (\text{i})$$

The amount of heat obtained on 1 cm^2 of the explosive charge surface q_v is a known amount of all heat lost by gas due to heat exchange to the walls of the bomb q_w during ignition time t_i :

$$q_w = \frac{mQ_v - Q_i}{S} \approx \frac{m\epsilon_p T_0}{S} (\theta'_{\text{max}} - \theta_i), \text{ cal/cm}^2, \quad (\text{j})$$

where Q_v - the explosive heat of the igniter;

Q_i - the amount of heat contained in combustion products of the igniter during ignition when $t = t_i$ and $\theta = \theta_i$.

If $q_v / q_w = k = \alpha' / \alpha_{\text{eff}}$, then

$$q_v = kq_w = \frac{km\epsilon_p T_0}{S} (\theta'_{\text{max}} - \theta_i). \quad (\text{k})$$

We shall accept in accordance with [3], that the amount of heat required for ignition (q'_v) equals

$$q'_v = \frac{\lambda_v}{u_i} (T_c - T_0), \quad (1)$$

where λ_v - the heat conduction of the explosive;

u_i - its combustion rate at a pressure of p_i ;

T_c - the temperature of the explosive surface during stable combustion.

By accepting $u_i = Bp_i$, we obtain

$$q'_v = \frac{\lambda_v T_0}{B p_i \theta_i} (\theta_c - 1), \quad (m)$$

where $\theta_c = T_c/T_0$.

At the moment of ignition $q_v = q'_v$.

By designating

$$\frac{k m_g c_p B p_i}{3 \lambda_v (\theta_c - 1)} = a, \quad (n)$$

we obtain

$$a (\theta_{\max} - \theta_i) = \frac{1}{\theta_i}. \quad (o)$$

In coordinates $\theta - y_{1,2}$, where $y_{1,2} = a (\theta_{\max} - \theta_i)$, and $y_2 = 1/\theta_i$, the right part of this equation is an equilateral hyperbola, the left, a family of straight lines $y_1 = A - B \theta$, in which the segment cut off at the Y-axis, and the inclination to the axis of X increases, as the value of m_g increases.

It is obvious that with sufficiently small values of m_g , the straight lines and the curve will not have one general point - combustion will not occur. With large values of m_g there will be two intersection points, of which the upper one is normally realized (over time it is reached first), but the lower one cannot be deliberately excluded (due to its smaller value $|dp/dt|$ combustion at this point will be more stable). Hence, the larger the value of θ_i (as the smaller the difference of $\theta_{\max} - \theta_i$), the greater m_g . Finally, there is a value of m_g , during which the straight line touches the curve. This value will also be critical for a given explosive. At the critical point (critical values will be shown with an asterisk):

$$y_1^* = y_2^* \text{ and } \left(\frac{dy_1}{d\theta}\right)^* = \left(\frac{dy_2}{d\theta}\right)^* \quad (p)$$

from where

$$\theta_i^* = \frac{\theta_{\max}^*}{2} \text{ and } m^*/m_{\max} = 2/\sqrt{a^*} \quad (q)$$

The first relation shows that when $m = m^*$ at the moment of combustion the pressure is half of the possible maximum, and combustion products contain half of the heat they contained initially. ¹

1. Knowing $\theta(t)$, one can find from the first ratio the value of the critical induction. From Figure 2 (we shall disregard the combustion time of the igniter), for example, we obtain for $m = 1g$, $t_i = 0.1$ sec.

The second ratio makes it possible to determine m^* , since both the right and left parts of it are known functions of m .¹

For the bomb and igniters which we use: $k = 0.5$; $m_g = m + 0.12 \text{ g}$;
 $c_v = 0.34 \text{ cal/g} \cdot \text{deg}$; $P_0 = 9.4 \text{ m}_g$; $S = 144 \text{ cm}^2$.

By accepting that $\lambda_v = 4 \cdot 10^{-4} \text{ cal/cm sec} \cdot \text{deg}$ and $\alpha_c \approx 2$, we obtain

$$f(m) = m_r^* \theta'_{\max} = \frac{0.43}{\sqrt{B}} \quad (r)$$

Function $f(m)$, calculated according to the relation $\theta'_{\max}(m)$ is shown in Figure 6.

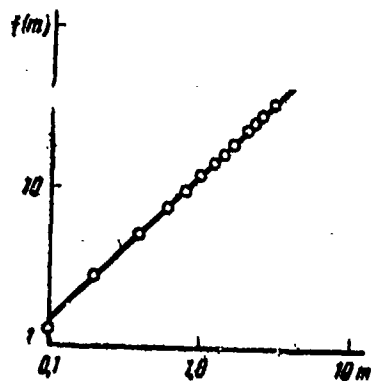


Figure 6
 The form of function $f(m)$ for calculating the critical amount of the igniter.

The value of m^* is obtained from this figure, as the point on the X axis, , the point which corresponds to the straight line with ordinate

1. An approximate value of m^* can be calculated according to $m^* = \frac{0.03}{\sqrt{B}}$

(t)

$$0.43 / \sqrt{B}$$

values of m^* and B obtained by calculation according to the relation μ (p) at pressures close to p_i , for some individual investigated secondary explosives and explosive mixtures are shown in Table 2

TABLE II

Explosive	Value of Coefficient B, cm/sec x cm ² /kg	Critical amount of igniters, g	
		theoretical	experimental
Tetryl	0.18	0.2	0.2
Trotyl	0.0045	0.4	0.5
Trinitrobenzene	0.0045	0.4	0.5
No. 6 Ammonite	0.003	0.3	1.4
No. 6 ZhV Ammonite	0.0036	0.5	1.1
PZhV-20	0.0046	0.4	0.9
No. 6 Ammonite + 20% NaCl	0.0046	0.4	1.0
+20% Na ₂ SO ₄	0.0033	0.5	1.0
+20% LiF	0.0022	0.6	2.1
+5% Black I*	0.0038	0.5	0.9
+5% Black II*	0.0042	0.4	0.6

* various specimens of black

It can be easily seen that for tetryl, trotyl, trinitrobenzene and a mixture of amatol with 5% black II the critical amount of igniter, obtained by calculation is close to that determined experimentally. The considerable difference obtained for other ammonium nitrate explosives requires special interpretation.

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