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Laser Ignition of Propellants and Explosives

by Leonid Strakovskiy, Arthur Cohen, Robert Fifer,
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Abstract

Laser and radiative ignition of 24 solid propellants and explosives was analyzed. The effect of ignition criterion used to calculate ignition delays from models was evaluated. Values for the optical parameters reflection, R_λ and absorption, k_λ coefficients at wavelengths 0.36–1, 1.06 and 10.6 μm were summarized. Effects of in-depth absorption and vaporization were considered. Methods for determining the relation of ignition delays for conductive heating ($R_\lambda = 1$, $k_\lambda = \text{infinity}$) and radiative heating at various wavelengths are presented. Methods for deriving kinetic parameters for the ignition and vaporization mechanisms for RDX-based materials were developed. Changes in the ignition mechanism at high radiative flux levels are discussed. A summary of the minimum flux levels needed for ignition and the Arrhenius kinetic parameters determined from ignition delay measurements with several energetic materials is presented.

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1. Introduction

Ignition is the initial stage of a self-sustaining wave process in which thermal and mechanical energy are produced by chemical reactions of energetic materials. The conditions that lead to ignition are important in determining the characteristics of the self-sustaining wave. The study and understanding of ignition are of interest from the standpoint of improving combustion and explosion theory as well as solving practical problems. Among the latter are those related to sensitivity and safety of energetic materials and development of advanced weapons.

There are several experimental methods of ignition study, for instance, ignition by hot bodies (conductive), compressed gases (shock), or disperse flows (convective) [1]. Radiative heating has unquestionable advantages in comparison with other methods: (1) known (fixed) heat exchange boundary conditions and (2) possibility of independently varying external pressure, composition of surrounding gases, initial temperature, and igniting heat flux [2-7]. Therefore, radiative ignition techniques have been widely used for energetic materials research and testing. Different sources of radiation were implemented: arc image furnace [2, 4-6], powerful gas-discharge tubes [3], and solar energy [7].

Application of laser techniques [8-12] offers several additional advantages. The most significant are (1) energy flux to the sample can be measured, controlled, and reproduced with high accuracy; (2) laser beam intensity can reach a very high level to simulate the broad range of heat fluxes in propulsive devices; and (3) the volumetric absorption of radiant energy (q) can be correctly described by Bouguer's law $q(x) = q_0 \exp(-kx)$ using measured values for the absorption coefficient, k .

Investigation of laser radiation action upon propellants and explosives has several specific practical aspects, for instance, development of a laser weapon and design of safe, effective, and reliable laser igniters and detonators. One of the objectives of the U.S. Army Research Laboratory Laser Ignition in Guns, Howitzers, and Tanks (LIGHT) program, for example, is to determine the feasibility of replacing gun igniter systems with lasers.

Data on laser ignition of propellants and especially explosives are fragmentary. There is a significant difference in the results of different studies. The main objective of this report is to analyze and summarize the following aspects related to laser and radiative ignition: (1) theoretical description of the process, ignition criteria; (2) optical characteristics of propellants and explosives, evaluation of results and experimental methods; (3) effect of wavelength and volumetric radiation absorption, and converting the experimental results to the cases of surface absorption; (4) role of vaporization in the ignition process, laser method of determining vaporization kinetic parameters; (5) laser ignition delays as a function of absorbed radiation flux; and (6) high-temperature kinetic parameters derived from radiative ignition experiments.

There are several excellent surveys based mostly on the results of U.S. Army studies, which in more or less detail summarize some of these topics [13, 14]. This report covers mainly Soviet studies in the area, including comparing some data with the U.S. Army researchers' results. Because of time limits, space ignition transients and combustion instability have not been considered.

2. Theoretical Approach, Ignition Criteria

Several ignition models are available for evaluating experimental results [12–14]. They are classified according to the phase in which the exothermic reaction governing the process takes place. Gas and heterogeneous models are rather complex, and calculation of ignition parameters, as a rule, requires numerical solution of the heat balance equations for both gas and condensed phases. For condensed-phase models, it is possible to neglect gas-phase contributions, and the heat balance equation can be written as

$$\rho c \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left[\lambda \frac{\partial T}{\partial x} - q \right] + w, \quad (0)$$

T , t , x , ρ , c , and λ are temperature, time, distance (from surface), density, heat capacity, and thermal conductivity, respectively; q is given by Bouguer's law; and w is the volumetric energy production

rate due to chemical reaction. Analytic solutions to equation (0) do not exist when the rate is given in its usual Arrhenius form, $w = rQz \exp(-E/RT)$, where R , Qz , and E are the universal gas constant, first order preexponential factor, and activation energy, respectively. Phenomenological condensed-phase models consider the ignition mechanism to be a two-stage process, an inert induction period followed by an adiabatic thermal explosion. These are sometimes referred to as "thermal explosion" models. The corresponding heat balance equations usually have analytic solutions that lead to algebraic formulas for predicting ignition delays and the effects of flux level on the ignition process. This approach has been widely used in the Former Soviet Union (FSU) for describing the ignition of propellants and explosives. The methods for obtaining these solutions vary with the boundary conditions and the ignition criterion of the problem. Some of these methods are described in Vilyunov and Zarko [1]; Vilyunov, Kuznetsov, and Skorik [3]; Marzhanov and Averson [12]; Kulkarni, Kumar, and Kuo [13]; Strakovskiy [15]; and Cohen and Beyer [16].

The validity of the model is determined in part by its ability to predict the ignition delays of volatile and nonvolatile materials. Many models define ignition as a rapid increase in temperature. The simplest and the most widely used method for obtaining ignition delays is based on measuring emission delays and assuming that emission is due to the rapid increase in temperature accompanying initiation of exothermic reactions [1]. For comparison with condensed-phase models, another method—thermocouple measurement of surface temperature—has also been used [2].

A simplified condensed-phase theory has been used to predict radiative ignition of volatile materials at low flux levels. This needs some justification since the initial emission (flame) appears to be located in the gas phase near the surface. At typical preignition temperatures, 500–550 K vaporization rates of explosives and volatile components of double-base propellants (nitroglycerin [NG] and dinitrotoluene [DNT]) are 2–6 orders greater than the rates of condensed-phase thermal decomposition [17]. However, counterflow of vaporized molecules and the inverse exothermic process of condensation [18] lead to an equilibrium state near the surface in which a thin layer of vapor is formed and the heat loss due to vaporization can be neglected [15].

Vapor absorption of radiation by vapor is very low [15]. Assuming the absence of heterogeneous exothermic reactions, flame appearance near the surface is evidence of a gas-phase reaction in the equilibrium vapor layer. Condensed-phase reactions are the only source of heating for ignition in the cold, ambient atmosphere. Thus, the light emission near the surface may be considered as the consequence of the self-acceleration of a condensed-phase reaction, and ignition delay is determined by the time required to heat the surface to the ignition temperature [14, 15].

Even within the framework of the thermal ignition model, there are several ignition criteria [1] used to calculate ignition delays (t_i) and ignition temperatures (T_i). In this report, the two criteria most widely used for calculating ignition delays and deriving thermokinetic parameters will be analyzed:

(1) achievement of the equality between the rates of heat release (per unit area) due to the chemical reaction, $Q_*(x_*) = Q_{pzx_*} \exp(-E/RT_i)$, and conduction heat losses from reaction zone, $Q(x_*) = \lambda(\partial T/\partial x)|_{x_*}$, [1, 19]

$$Q_* = Q, \quad (1)$$

x_* is the width of the chemical reaction zone and is determined from the condition $Q_*(x_*) = Q_*(x_0)/e$ where

$$x_0 = \sqrt{\frac{\lambda}{\rho c}} t_0, \quad t_0 = \frac{CRT_i^2}{EQ\rho Z} e^{E/RT_i};$$

(2) equality between Q_* and the radiant flux absorbed at the surface [12]

$$Q_* = q_0. \quad (2)$$

These criteria are almost equivalent for surface radiation absorption [19]. Under volumetric absorption conditions ($1/k_\lambda \gg (a t_i)^{1/2}$) and for $k_\lambda q \gg w$, the temperature distribution can be approximated by the expression [19]

$$T(x,t) = T_0 + (k_\lambda q_0 t / \rho c) \exp(-k_\lambda x), \quad (3)$$

and at ignition

$$Q_- = k_\lambda^2 a t_i \exp(-k_\lambda x_*) q_0 \approx \varphi_i^2 q << q_0, \quad (4)$$

where k_λ is the absorption coefficient, a is the thermal diffusivity, and $\varphi_i = k_\lambda (at_i)^{1/2}$ is a dimensionless parameter determining the relation between the characteristic dimension of the thermal wave at the ignition instant and the depth of radiation penetration. In accordance with (4), the value Q_- can be an order (or two) of magnitude less than radiation flux, and ignition parameters calculated on the basis of criteria (1) and (2) will differ considerably. For example, the value of laser flux q_L at which ignition temperature of RDX reaches the boiling point calculated on the basis of (1) is 520 W/cm²; using (2), we will obtain $q_L = 57$ W/cm² and the experimental value is 180 W/cm² [20].

On the basis of numerical analysis of equations describing radiative ignition within the framework of a condensed-phase (surface) theory, another ignition criterion was proposed. It effectively combines criteria (1) and (2) [15, 20]. In criterion formulation, ignition takes place when the rate of heat release from a chemical reaction becomes equal to a fraction (coefficient B) of heat input intensity. The value of this fraction depends both on the conditions of heat removal from the reaction zone and on the activation energy of the ignited substance:

$$Q_+ = B q_0, \quad (5)$$

where

$$B = 4.1 \varphi_i^{1/4} \theta_i^{-1} \quad (6)$$

for semitransparent substances, and

$$B = 9.2\theta_i^{-1} \quad (7)$$

for the case of surface radiation absorption (Bradley [21] used a similar approach to correlate approximated and numerical calculations for opaque materials). Parameter φ_i is an analog of the Fourier criterion that reflects the energy removal conditions from the reaction zone. As a rule, when $\varphi_i < 0.1$, we can neglect the heat removal factor, and if $\varphi_i > 10$, volumetric nature of absorption is insignificant (the more precise condition is $k_\lambda x_* > 1.2$ [10]). Parameter θ_i depends mostly on the activation energy and the initial temperature T_o of the material: $\theta_i = E(T_i - T_o)/RT_i^2$. It characterizes the relation between the chemical induction period and the total ignition time (the greater the activation energy, the shorter the self-acceleration period) and, as the consequence, the accuracy of the approximated parameter calculations.

Criterion (5) provides high accuracy (2% for T_i and 3% for t_i). Besides, it reflects some essential regularities of the process, for instance, dependence of ignition parameters on the initial temperature.

To calculate ignition parameters t_i and T_i , it is necessary to use, along with the ignition criteria, the solution of the “inert” thermal problem [22]:

$$T_i = T_o + (2/\pi^{1/2})q_o (t_i/\rho c \lambda)^{1/2} \quad (8)$$

for an opaque substance, and

$$T_i = T_o + (2/\pi^{1/2})q_o (t_i/\rho c \lambda)^{1/2} - (q_o/k_\lambda \lambda)[1 - \text{erfc}(\varphi_i) \exp(\varphi_i^2)] \quad (9)$$

for a substance with volumetric absorption ($k_\lambda < \infty$).

Combining (5), (7), and (8), we obtain a simple formula for the dependence of ignition delay on the temperature T_i :

$$t_i(s) = 66.4(RT_i^2/E) (c/Qz) \exp(E/RT_i). \quad (10)$$

As is evident from (10), ignition temperature at the given ignition delay does not depend on the T_o , a result consistent with the experimental results [1, 23]. At the same time, in accordance with (5) and (7), when the heat flux q is fixed, the value of T_i increases with increase of initial temperature because of the rise of coefficient B . This effect has a simple explanation. The increase in T_o leads to a considerable reduction of ignition delay t_i , which is accompanied by a decrease in thickness of the heated zone ($a t_i$)^{1/2}, an increase in the temperature gradient, and an increase in the rate of heat removal. To conserve the heat balance condition, it is necessary for the rate of chemical heat release (i.e., for the ignition temperature) to be increased. Such a result was also obtained in the experiments. The effect of T_o on HMX + 4% wax ignition by a CO₂ laser [15] is presented in Table 1. In this table, q is the absorbed laser flux and t_i is the measured ignition delay. The calculated ignition delay, t_{ic} , is for $T_o = 343$ K with (1) as the ignition criterion using kinetic parameters derived from experiments conducted at $T_o = 293$ K. The ignition temperatures, T_i , are calculated from (9) using $k_\lambda = 174 \text{ cm}^{-1}$.

Table 1. Effect of Initial Temperature on Ignition Delays in HMX + 4% Wax

	$T_o = 293 \text{ K}$			$T_o = 343 \text{ K}$		
$q, \text{ W/cm}^2$	45	76	170	45	76	170
$t_i, \text{ ms}$	206	99	36	167	78	31
$t_{ic}, \text{ ms}$				164	79	29
$T_i, \text{ K}$	550	565	595	568	575	614

The results in Table 1 suggest that the condensed-phase model is valid for HMX composites. Note that using ignition criterion (2) in place of (1) does not lead to the correct prediction of the initial temperature effect.

As can be judged from expressions (3) and (9), the effect of optical properties on the ignition parameters in the framework of the condensed-phase model is very strong. For instance, in accordance with (3), ignition delay varies almost as the reciprocal of the absorption coefficient

$t_i = \rho c(T_i - T_o)/k_\lambda q_o$. In order to make meaningful comparisons with radiant ignition model predictions, it is necessary to know the optical properties of materials.

3. Optical Characteristics of Explosives and Propellants

The principal methods of optical parameters determination are based on the measurements of (1) radiation transmittance by thin samples [10, 16, 24–25], (2) reflectance [3, 4, 15], and (3) the surface temperature of ignited samples [2–4]. Transmittance is measured by two techniques. Transmittance spectra are recorded using wide-range spectrometers [25, 16], and attenuation of laser radiation is measured [15, 16]. The most widely used equipment for reflectance determination is an integrating sphere [3]. The third method [2] compares measured temperature distributions in the solid with calculated values based on Bouguer's law for the volumetric radiation absorption.

The difference in values of the absorption coefficient (k_λ) for some explosives and propellants obtained by different authors and methods in the regions of weak spectral absorption may be very significant [3, 4]. The main reason is the complex nature of attenuation and reflection, which is due to the multiple radiation scattering from the crystal faces of the material [15]. This leads, in particular, to the significant deviation from Bouguer's law, especially for low-density (high porosity) systems [27].

A detailed investigation and description of the mechanism of radiation scattering, reflection, and absorption are the subject of a special study. Based on analysis of experimental results, it is possible to derive the following conclusions and restrictions, which will minimize the effect of absorptive capacity uncertainties.

(1) For most homogeneous propellants, cast explosives, and pressed explosives with porosity less than 10%, Bouguer's law is approximately valid if (a) the thickness of the sample $h > (3-5)/k_\lambda$ and (b) the direction of the incident beam is approximately normal to the surface. Significant deviations

from exponential radiation distribution may occur when the change of the beam diameter in the sample is comparable with the sample's radius (sharp focusing conditions).

(2) Experiments showed that optical parameters of double-base propellants and high explosives (HE) did not vary considerably during radiation heating for ignition delays (t_i) < 2 s [15, 25].

(3) Optical parameters should be measured using the samples with the same density and dispersity as those in the ignition experiments.

(4) The thickness h of the samples in the measurements of radiation attenuation should be at least two times greater than the value $1/k_\lambda$. In the case of reflectance measurements, to avoid the effect of the rear surface reflection and radiation losses, it is better to use specimens with $h > (3-5)/k_\lambda$ [15].

(5) The inner surface of the integrating sphere in the reflectance measurements should provide diffuse scattering conditions. At the wavelength $10.6 \mu\text{m}$, the surface should be subjected to additional treatment so that the characteristic size of inhomogeneity is comparable to the wavelength [10].

(6) It is impossible to provide a normal beam incidence in the reflectance experiments with an integrating sphere, but it is better that the angle not exceed 10° .

(7) To determine the absolute value of the reflection coefficient R_λ , it is recommended to use a calibration specimen with a known value of R_λ . The specular reflectance of this specimen should be small.

(8) To avoid radiation losses in transmittance measurements, it is recommended to place a focusing lens directly behind the sample, which would collect all the radiation on the detector's surface.

Table 2 presents experimental results on optical parameter measurements for some propellants. The composition of double-base propellant N is: 58% nitrocellulose (NC), 28% NG, and 12–14% DNT. Most double-base propellants have similar composition. Unfortunately, authors, as a rule, do not present exact composition and exact amount and kind of utilized catalyst (CT). Composition of N-5 is close to that of propellant N with several percent of catalyst. M9 consists of 58% NC and 40% NG.

Table 2 shows that for different broad band sources over similar spectral ranges the difference in the measured optical parameters may be very significant. At the same time, on the basis of data, it is possible to derive some important conclusions.

(1) The value of reflection coefficient at the wavelength $10.6\ \mu\text{m}$ is less than 10% for all propellants.

(2) The effect of different additives on the optical parameters at this wavelength is small. The value of k_λ is in the range of $500\text{--}600\ \text{cm}^{-1}$.

(3) Comparison of results for NC and double-base propellants shows that NG considerably decreases the value of k_λ in the region of weak spectral absorption and slightly increases it at the wavelength $10.6\ \mu\text{m}$.

(4) The order of k_λ and R_λ values for NC in the spectral range $1\text{--}1.1\ \mu\text{m}$, corresponding to neodymium (Nd) lasers, is $50\text{--}100\ \text{cm}^{-1}$ and 70–85%, respectively.

Recently, solid propellant researchers have focused much attention on the study of RDX-based energetic materials [11, 16, 30]. There are several studies on radiative ignition of RDX and RDX-based explosives that provide direct measurements of optical parameters [15, 20, 31–34].

Table 2. Optical Parameters for Nitrate-Ester Propellants

Propellant	ρ (g/cm ³)	λ (μ m)	Ref.	MM	R_λ (%)	k_λ (cm ⁻¹)
NC	1.45–1.50	0.36–1.0	[3]	3, 4	48–85	300
NC + 1% C					9.9–10.1	600
NC	1.5	0.4–1.1	[4]	3, 2	74	70
NC	1.48	10.6	[28]	3, 1	7.2	500
N	1.6	0.4–1	[2]	4, 4	14	15
N + 1% C					3	115
N	1.6	0.3–1 10.6	[24]	3, 1 1	5–10	≈ 12 >1000
N + 1% C	1.6	0.3–1 10.6	[24]	3, 1 1	4–7	≈ 400 >1000
N + CT	1.6	0.3–1 10.6	[24]	3, 1 1	7–15	≈ 40 >1000
N	1.6	10.6	[28]	3, 1	5	550
N + CT					4	560
N-5	1.6	10.6	[29]	3, 1	8	623
M9	1.6	10.6	[16]	3, 1	10	536
M9	1.6	1.06	[30]	1, 2	68	7.1

Notes: C - carbon, MM - measurement method (1 - transmittance spectra, 2 - direct attenuation measurements, 3 - integrating sphere, 4 - surface temperature registration).

Table 3 lists the optical parameters for RDX and RDX-based compositions. In the first column, third row, the C-1 in parentheses stands for composition 1, which, in addition to wax, contains 0.3% of dye used to increase absorption.

Table 4 presents experimental results on optical parameter measurements for other explosives and compositions. THAF consists of 60% HMX, 18% TNT, 17% Al, and 5% wax. NP is a special reacting additive. TG40 is 60% RDX and 40% TNT.

Table 3. Optical Parameters for RDX-Based Explosives^a

Composition	ρ g/cm ³	λ μm	Ref.	MM	R_λ (%)	k_λ (cm ⁻¹)
RDX	1.3–1.4	1.06	[31]	2, 2	78–85	18–22
RDX + 1% wax	1.64	1.06	[20]	3, 2	71	5.7
RDX + 5% wax (C1)	1.62	1.06	[15]	3, 2	70	19
RDX + 20% wax	1.56				60	11
RDX + 5% wax	1.62	10.6	[32]	3, 2	3.8	172
RDX + 20% wax	1.56				3.2	167
RDX + 3% KNO ₃	1.64	10.6	[15]	3, 2	3.7	180
C1 + 20% Al	1.78	10.6			22	$\rightarrow\infty$
		1.06			70	$\rightarrow\infty$
RDX	1.6	0.36–1.1	[33]	3	72	—
RDX + Al	1.93				56	—
RDX + 1% C	1.6	0.36–1.1	[34]	3, 4	7	600

^a See notes in Table 2.

Tables 2–4 show that introducing carbon black to propellants as well as to explosives decreases the reflectance up to 10 times and increases the value of k_λ up to 7 times in the regions of a weak spectral absorption and has no effect at the wavelength 10.6 μm .

Absorption coefficients determined on the basis of direct surface temperature measurements (method 4) seem to exceed the real values of k_λ .

On the basis of these results, we can also derive the following conclusions:

(1) Introducing 17% or more aluminum powder to the substance makes it opaque at the wavelength 10.6 μm as well as in the region of a weak spectral absorption. The effect of aluminum

Table 4. Optical Parameters for Various Explosives^a

Composition	ρ (g/cm ³)	λ (μ m)	Ref.	MM	R_λ (%)	k_λ (cm ⁻¹)
HMX		10.6	[15]	3, 2	9.8	180
HMX + 4% wax					9.6	174
HMX + 1% C					9.5	178
HMX + 5% NP					10.3	225
HMX	1.7	0.36–1.0	[35]	3	87–93	—
HMX + 1% C					11–12	—
HMX	1.73	0.36–1.1	[33]	3	77	—
Tetryl	1.6	1.06	[15]	3, 2	68	18.4
		10.6			5.7	163
TNT (cast)	1.5	1.06	[36]	3, 2	51	3.6
		10.6			6.2	198
TNT (pressed)	1.51	1.06	[15]	3, 2	60	12.6
		10.6			5.1	195
TG40 (cast)	1.67	1.06			59	4.3
		10.6			5.2	196
TNT + 20% Al (cast)	1.52	10.6	[15]	3, 2	35	$\rightarrow\infty$
THAF	1.8	10.6			13	$\rightarrow\infty$
PETN	1.6	1.06	[27]	3, 1	96	3
	1.5–1.6	0.69	[37]	2	80	0.4

^a See notes in Table 2.

on reflectance is different at wavelengths 10.6 and 1.06 μ m. It considerably increases (up to five times) the value of R_λ in the first case and has a weak influence for Nd laser radiation.

(2) Such inert additive as wax has a significant effect on the optical parameters (especially on the value of k_λ) in the spectral range 0.36–1.1 μ m. For CO₂ laser radiation, this effect is very small.

At the same time, some additives may have a very strong effect (for instance, NP) because of resonance character of absorption.

(3) The cast samples, as a rule, are more homogeneous than pressed samples. Therefore, their reflectance in the region of weak spectral absorption is considerably less and transmittance is up to three times greater.

4. Converting Ignition Delays to the Cases of Surface Energy Absorption and Radiation at Different Wavelengths

The next questions that arise are (1) how to eliminate the effect of volumetric radiation absorption to derive kinetic parameters or to estimate ignition delays due to heat flux on the basis of laser experiments and (2) how to predict delays of radiative ignition at different wavelengths.

Based on a comparison of calculated and measured ignition delays, a simple formula was offered [3] to calculate ignition delays for a semitransparent substance [$t_i(k_\lambda)$] on the basis of appropriate value $t_i(k \rightarrow \infty)$ for the opaque material:

$$t_i(k_\lambda) = t_i(k \rightarrow \infty) (1 + 1.65/\varphi_i)^{0.945 - 1.7/\theta_i}, \quad (11)$$

where dimensionless parameters φ_i and θ_i were defined earlier. This formula is very useful when we know the ignition delay due to convection or conduction from hot gases and want to calculate it under radiative ignition conditions.

Often it is necessary to solve the inverse problem. The graphs shown in Figure 1 together with expressions (5–9) can be used for this purpose. These graphs have been calculated for tetryl [10], a typical HE. Tetryl was chosen because its thermophysical and kinetic parameters were thoroughly measured in the several studies [38, 39] from which it was determined that $E = 38.4$ kcal/mole, $\log(z) = 15.4$, $Q = 1,430$ J/g, and $a = 1.1E-3$ cm²/s.

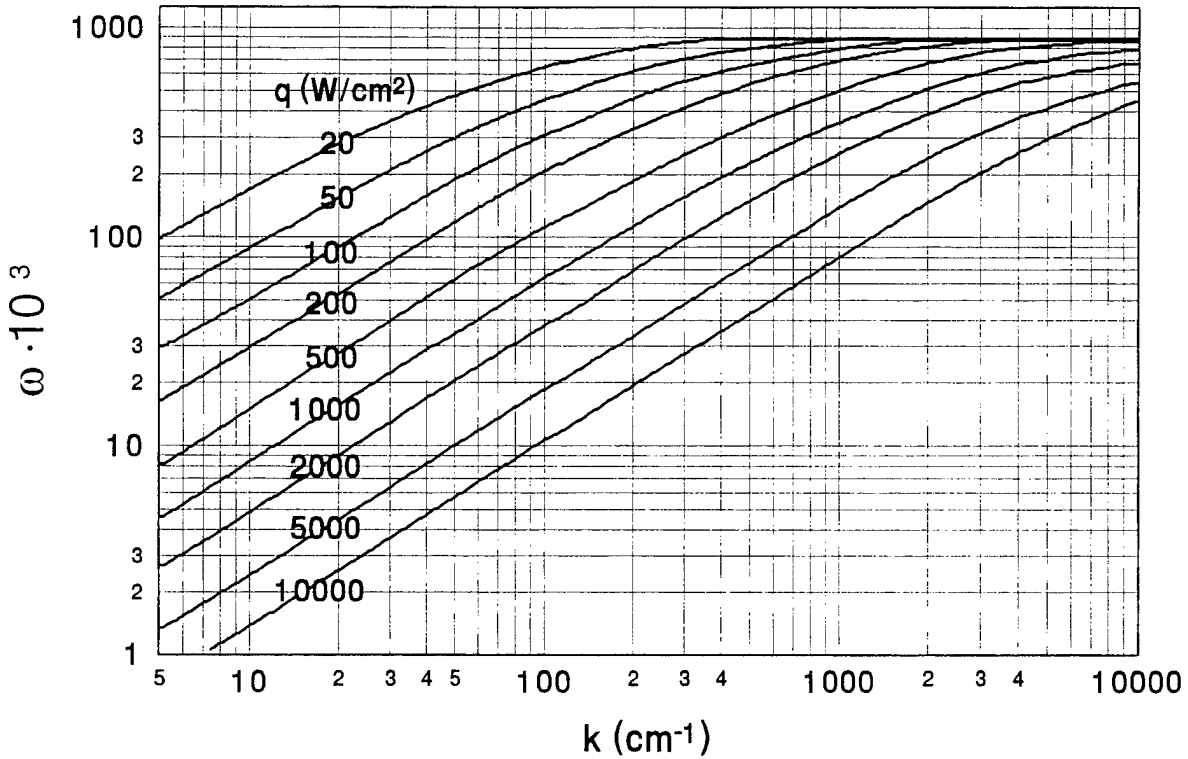


Figure 1. Graphs for Converting Delays of Laser Ignition to the Case of the Surface Absorption (RDX Explosives and Propellants).

The value ω shown, along the vertical axis, indicates the relationship between ignition delays due to a heat flux $t_i(q, k \rightarrow \infty)$ and those due to a laser pulse with a wavelength at which the absorption coefficient is equal to a value k , shown along horizontal axis: $\omega = t_i(q, k \rightarrow \infty)/t_i(q, k)$. To convert an experimental value $t_i(q_i, k_\lambda)$, we should multiply it by the conversion coefficient $\omega(q_i, k_\lambda)$, found from the graphs in Figure 1:

$$t_i(q_i, k \rightarrow \infty) = \omega(q_i, k_\lambda) t_i(q_i, k_\lambda). \quad (12)$$

Similarly, to convert experimental delays to the case of radiative ignition at a different wavelength λ_1 , we can use the following formula:

$$t_i(q_i, k_{\lambda_1}) = t_i(q_i, k_\lambda) \omega(q_i, k_\lambda) / \omega(q_i, k_{\lambda_1}), \quad (13)$$

where $k_{\lambda 1}$ = absorption coefficient at the wavelength λ_1 .

The difference in values of the conversion coefficients $\omega(q_i)$, calculated for several secondary explosives (RDX, HMX, and RDX+wax), is less than 10%. So, besides tetryl, the graphs in Figure 1 can be used for almost all explosives and RDX-based propellants. Ignition delays of NC and double-base solid propellants at the same values of q_i and k_λ are, as a rule, considerably less than for HE. Therefore, the values of parameter φ_i and, as a consequence, coefficients $\omega(q_i)$ are 15–20% less. To make an application of the described method for NC-based propellants convenient, the author calculated the appropriate graphs, which are presented in Figure 2.

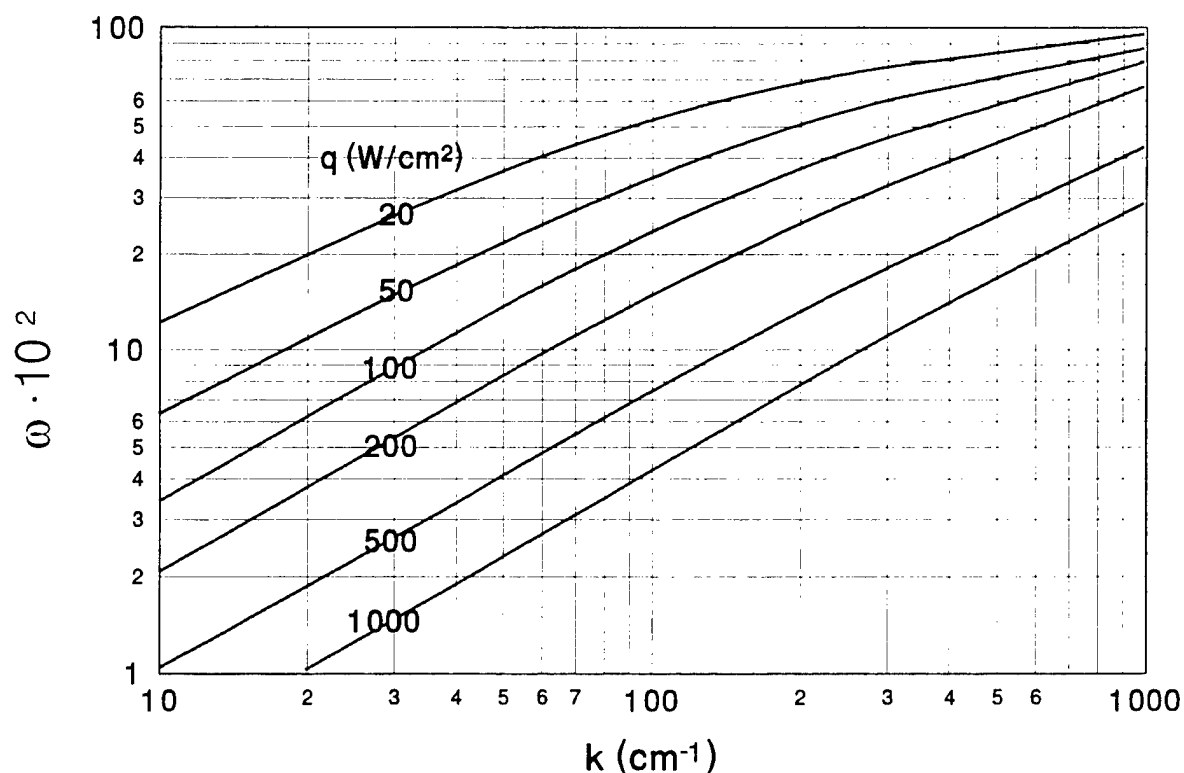


Figure 2. Graphs for Converting Laser Ignition Delays (Double-Base Propellants).

The more general method for calculating conversion coefficients $\omega(q_i, k_\lambda)$ is based on its dependence on the dimensionless parameter $k_\lambda x_*$. This parameter is the analog of the Frank-Kamenetsky parameter (σ) and represents the relation between the width of chemical reaction zone x_* and the depth of radiation penetration $1/k_\lambda$.

Calculations were performed for five substances over a wide range of parameters: $E = 27\text{--}52$ kcal/mole, $\phi_i = 0.07\text{--}9.9$, $k_\lambda x_* = 0.09\text{--}1.3$. The results are presented in Figure 3. As can be seen, the relationship $\omega(k_\lambda x_*)$ is actually universal: the difference in ω (at the same value of $k_\lambda x_*$) for five energetic materials is less than 8%. So to convert ignition delays $[t_i(q_i, k \rightarrow \infty)]$ to the case of the surface absorption $[t_i(q_i, k_\lambda)]$, we should just calculate the value x_* , find the coefficient ω from Figure 3, and use formula (12).

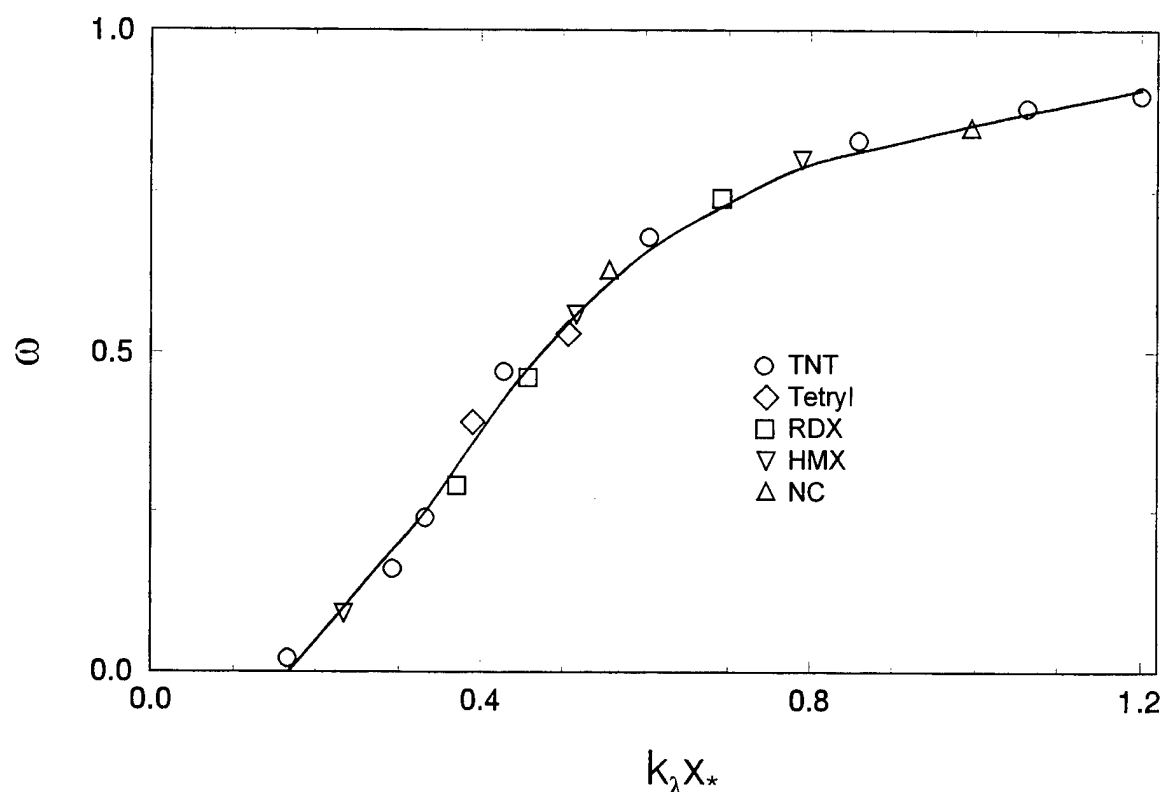


Figure 3. Universal Relationship for Converting Laser Ignition Delays.

Figure 3 shows, in particular, that when $k_\lambda x_* > 1.2$ the difference between radiative ignition delays for volumetric (in-depth) and surface absorption becomes less than 10%. The validity of assuming surface absorption is determined by the condition that the depth of radiation penetration ($1/k_\lambda$) should be less than the width of the chemical reaction zone (x_*).

As is evident from Figures 2–3, the effect of volumetric absorption increases with flux. Values for the absorption coefficient k_0 at which the ignited substance may be regarded as opaque within flux range $q < q_u$ has been determined by numerical calculations of ignition delays. These results are presented in Table 5.

Table 5. Minimum Absorption Coefficient, k_0 , cm^{-1} , for Which Materials Can Be Considered Opaque

q_u (W/cm^2)	20	50	100	200	500
Tetryl	650	1,400	2,500	4,500	11,000
RDX	560	1,300	2,500	4,700	12,000
HMX	580	1,370	2,700	5,200	12,500
NC	980	2,100	3,700	6,800	15,800

5. Thermophysical Properties

The effect of thermophysical properties on the results of ignition temperature and delay calculations is very significant. So prior to comparing the experimental results with the model prediction, it is necessary to present all values of these parameters that were used in the calculations. Table 6 presents the most reliable average values (in the indicated temperature intervals ΔT) obtained primarily from Soviet literature.

Thermophysical parameters for explosives and propellants were taken from Belyaev [17], Andreev [40], Andreev and Belyaev [41], and Mikheev [2], respectively. A small amount (<5%) of such additives as wax or carbon black has no effect on the thermal diffusivity or specific heat capacity. T_m in the table denotes melting point.

Table 6. Thermophysical Properties of Various Energetic Materials

Substance	ρ (g/cm ³)	c (J/g K)	a (cm ² /s)	ΔT (° C)	T_m (° C)
RDX	1.64	0.98	1.04E-3	15–180	201
RDX + 20% Al	1.78	1.05	4.22E-3	20–150	201
TH 40	1.67	0.89	1.08E-3	15–80	81–201
HMX	1.74	0.99	1.69E-3	15–200	280
TNT	1.51	0.92	1.1E-3	20–80	81
Tetryl	1.60	1.09	1.1E-3	15–125	131
NC	1.50	1.22	7.9E-4	20–250	—
N	1.60	1.46	0.99E-3	–75–220	—

6. Principal Experimental Results

It is difficult (if possible at all) to generalize experimental results on radiative ignition because of the tremendous variety of conditions employed. Sources with different spatial and temporal energy distributions have been used, and authors often did not indicate this factor at all. Here we will mainly consider ignition delays (transient conditions) which, as a rule, are the first limiting stage of ignition. Several experimental ignition criteria were used. The most common are changes in emission intensity and surface temperature and evidence of flamespreading (go - no-go).

The thermal model indicates that the dependence of ignition delay on the flux has the form $t_i = A/q^m$. For the ignition criterion T_i constant, $m = 2$ for opaque materials (see formula [8]). For semitransparent materials, the values of m vary from $m = 2$ at low flux levels to $m < 1$ at very high flux levels. For the latter condition, the clearly expressed volumetric absorption condition ($1/k_\lambda \gg (a t_i)^{1/2}$) is realized (see formula [3]). So the (negative) slope of logarithmic plot t_i vs. q for semitransparent explosives and propellants should decrease with an increase in flux.

Figure 4 shows experimental results obtained for RDX and two RDX-based composites using a cw CO₂ laser with an average power of 40 W and spatial nonuniformity of radiation energy less than 15% [15, 29]. Ignition delays were measured in the air at 1 and 5 atm pressure using the sharp increase in emission intensity (flame appearance) criterion.

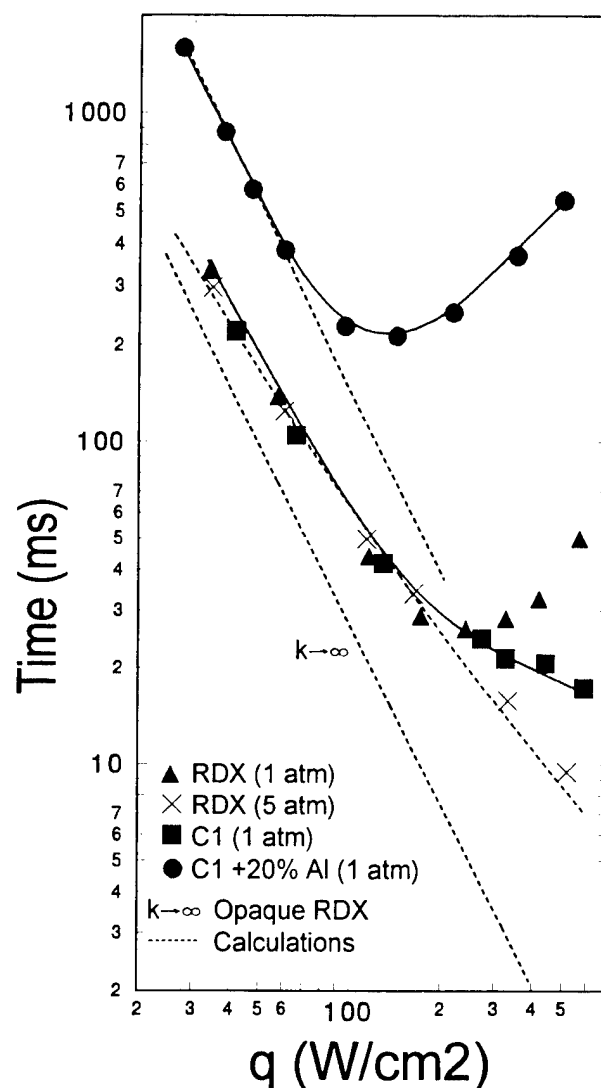


Figure 4. Dependence of the Ignition Delay on the Absorbed Laser Flux.

Calculations were made on the basis of RDX kinetic parameters $E = 41$ kcal/mole, $z = 2.88 \times 10^{15}$ s, and $Q = 2,100$ J/g [40, 41], employing optical and thermophysical properties listed in Tables 3 and 6.

Good agreement can be noted between predicted and measured results for neat RDX at 5 atm for all flux values. In the case of atmospheric pressure, beginning with $q = q_L = 200 \text{ W/cm}^2$ for RDX and composition C1 and $q_L = 70 \text{ W/cm}^2$ for C1 + 20% Al, a considerable deviation of experimental points from calculated values is observed. Note that for flux values $q > q_L$, the ignition mechanism changes. The irradiation leads to the appearance of a jet of gasification products. The flame is formed in the gas phase at a significant distance from the surface. At low fluxes, where good agreement between predictions and measurements is observed, the flame appears directly on the surface.

The same U-shaped curve $t_i(q)$ was obtained for tetryl [10], and a strong effect of ambient atmosphere composition was established: in the case of ignition in nitrogen at $q > 300 \text{ W/cm}^2$, there was no flame at all. Experiments on TH 40 ignition [42] showed that in the flux range where process is preceded by intensive evaporation/gasification, additional heat flux was generated by preignition reactions of gaseous products. Under these conditions, the heat flux generated in air is three times greater than in nitrogen. Similar effects were observed for double-base propellant N-5 [29]. All of these results indicate that at high flux levels the effects of gas-phase reactions cannot be neglected.

Observed deviations from condensed-phase model predictions are explained by ignition occurring near the boiling point temperature (i.e., $T_i = T_b$) [10, 15, 20, 42, 43]. The time at which gasification begins was determined from motion-picture records. Figure 5 shows calculated RDX ignition temperatures T_i (equation 9) for $k_\lambda (\text{cm}^{-1}) = 5, 175$, and ∞ ($k_\lambda = 175 \text{ cm}^{-1}$ at $10.6 \mu\text{m}$) and ignition criterion $Q_* = B q_0$ (equation 5). T_i is equal to T_b (at atmospheric pressure, $T_b = 613 \text{ K}$ [16]) at flux $q_L = 170 \text{ W/cm}^2$, which is close to the experimental value $q_L = 200 \text{ W/cm}^2$. At 5 atm is $T_b = 663 \text{ K}$ [17]. The corresponding value of $q_L = 1,400 \text{ W/cm}^2$, which is greater than the upper limit of the flux range studied. That is why at 5-atm pressure we observe a good agreement with a condensed-phase model in the whole flux range studied.

For composition C1 + 20% Al ($k_\lambda = \infty$), the ignition temperature reaches the boiling point at a considerably lower flux value ($q_L = 50 \text{ W/cm}^2$). This is also in a good correspondence with

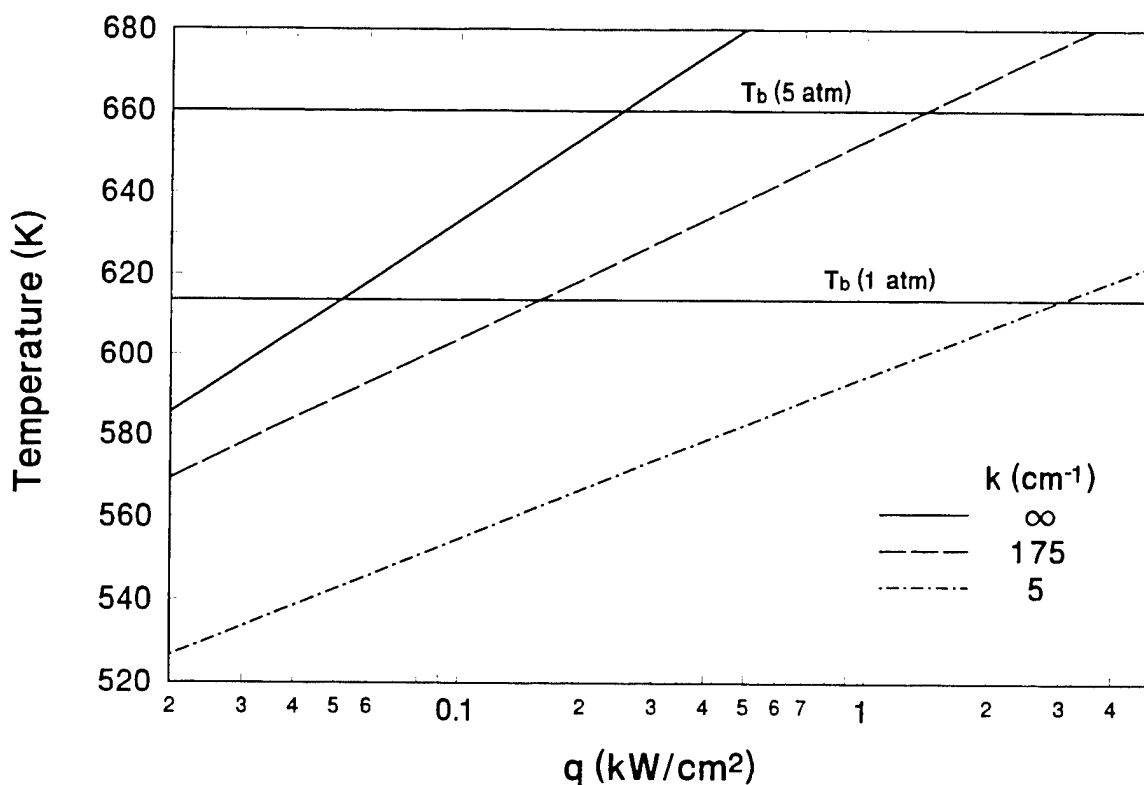


Figure 5. Effect of the Absorption Coefficient on Calculated Ignition Temperatures of RDX.

experimental value $q_L = 70 \text{ W/cm}^2$. Similar results were obtained for tetryl, where the corresponding (calculated) “inert” surface temperature is very close to the boiling point [10, 42].

Thus, although vaporization takes place also at low temperatures, its effect on ignition delays changes near the boiling point. The vaporization process becomes irreversible, and we can no longer neglect its effect on the ignition parameters.

Additional evidence of condensed-phase model validity at $q < q_L$ is the relation between ignition delays t_{i1} for C1 ($k_\lambda = 19 \text{ cm}^{-1}$), converted to the case $k \rightarrow \infty$, and t_{i2} for C1 + Al. In this case, the only expected difference in t_i for these explosives is due to differences in their thermophysical parameters. In accordance with the model, equation (8), $t_{i2}/t_{i1} = (\rho c \lambda)_2 / (\rho c \lambda)_1 = 5.1$. The experimental value of t_{i2}/t_{i1} at $q = 50 \text{ W/cm}^2$ is 5.02.

Table 7 presents the calculated effect of pressure p on the RDX boiling point and the flux q_L , where $\log p = 9.272 - 5683/T_b$.

Table 7. Effect of Pressure on RDX Boiling Point

p (atm)	T_b (K)	$q_L (k \rightarrow \infty)$ (kW/cm ²)	$q_L (k_\lambda = 175 \text{ cm}^{-1})$ (kW/cm ²)
1	613	0.048	0.17
5	663	0.19	1.6
10	687	0.34	4.85
20	713	0.60	13.8
50	750	1.29	55
100	781	2.3	157

On the basis of these results, we can derive three important conclusions:

- (1) Ignition of volatile secondary explosives over a sufficiently wide flux range is well described by the simplified condensed-phase model.
- (2) The limits of the model's applicability are determined by the condition that for a given external pressure the ignition temperature of the explosive should be less than the boiling point.
- (3) As the pressure increases, these limits are considerably expanded.

It is necessary to point out that the boiling point is not an upper limit of the surface temperature in the laser ignition experiments. For highly volatile materials or under sufficiently intense flux, the rapid vaporization leads to a large mass flux, which disrupts the phase equilibrium: the vapor pressure becomes higher than atmospheric pressure, and the surface temperature $T_v > T_b$ [43]. The increase in pressure at the surface due to the outflowing vapor causes an additional increase of T_v .

This effect of the surface overheating was found to be significant in the process of TNT ignition by a CO₂ laser [36]. Because of the high volatility and low thermal decomposition rate of the explosive, even at low fluxes $q_0 \approx 20 \text{ W/cm}^2$, its ignition temperature becomes greater than the boiling point. So vaporization has a strong effect on the ignition delay. But this effect decreases with increasing flux, and at $q \approx 350 \text{ W/cm}^2$, the observed deviation of t_i from the condensed-phase model prediction is less than 20%. A possible explanation for the observed behavior (based on equation 5) is as follows: At low flux, $T_i > T_v \approx T_b$, and the surface temperature is determined by vaporization, which has a strong effect on the process. But as the flux is increased, the value of T_v rises more rapidly than T_i because the latent heat of vaporization is significantly less than the activation energy of the condensed-phase reaction. Therefore, at some flux q_{l2} , the reverse condition $T_v > T_i$ is realized (i.e., the surface temperature increases sufficiently, leading to self-acceleration of the condensed-phase reaction prior to occurrence of appreciable vaporization). Such an approach was qualitatively corroborated by the numerical solution of the ignition problem with moving surface and energy consumption due to vaporization [15, 36].

An important question that should be taken into account while considering the effect of vaporization (gasification) is absorption of radiation by gaseous products. The measurements and calculations performed for explosives showed that the vapor absorption coefficient at the wavelength $10.6 \mu\text{m}$ is of order $.1 \text{ cm}^{-1}$ [15]. At high fluxes, when the length of vaporization products jet is several centimeters, the radiation attenuation by the gas phase is very significant.

Observations of the ignition of semitransparent explosives at the wavelength $1.06 \mu\text{m}$ in a region of a weak spectral absorption are quite different. A Nd glass laser (energy $< 1 \text{ kJ}$) with peak-free mode and high spatial homogeneity was used for ignition study [15, 26]. Experiments were conducted with tetryl in the flux range $1\text{--}5 \text{ kW/cm}^2$. Measured ignition delays were 2–10 times less than calculated results. The temperature of the explosives surface prior to ignition is just $25\text{--}65^\circ \text{ C}$. A motion-picture recording of the process shows that ignition develops at one or several hot spots, although the whole surface is subjected to irradiation. The dimensions of these hot spots increase very slowly. The stage of self-acceleration, leading to practically instantaneous flame formation in normal ignition condition, does not occur. It was shown that the gasification/emission process is

determined by absorption and subsequent heating of inclusions of soot particles (dimensions about 10 μm). When the flux magnitude exceeds 10 kW/cm^2 , the heating of such inclusions at ignition reaches the critical temperature $T_c \approx 0.7(T_o + Q/c)$. The critical temperature concept (discussed in Merzhanov and Averson [12]) is based on an analysis of the effects of reactant consumption on the ignition process. The response of energetic materials under these conditions is the direct initiation of flamespreading without the rapid increase in reaction rates associated with the ignition stage. The increase of measured ignition delays with increasing flux for tetryl and HMX at $q > 10\text{--}20 \text{ kW}/\text{cm}^2$ [15] is also consistent with Merzhanov and Averson [12].

At the same time, measured in the flux range 1–6 kW/cm^2 , ignition delays for opaque explosive C1 + 20% Al were in good agreement with calculated results. In accordance with Aleksandrov and Voznyuk [44], for short enough laser pulses, the mechanism of ignition at local sites (inclusions) is important for materials with high transparency (there should be sufficient sites in the characteristic volume of the material absorbing the radiation). Estimates show that for $k_\lambda > 100 \text{ cm}^{-1}$ and $t_l > 5 \text{ ms}$, the effect of absorbing inclusions should not be important. For instance, it was not observed in the laser ignition experiments at the wavelength 10.6 μm .

There are a lot of studies on NC radiative ignition [2–4, 28, 30]. All experiments indicate good agreement with the condensed-phase model. A detailed study [3] performed in the flux range 5–230 W/cm^2 , in air, nitrogen, and helium, at pressures 1–31 atm, shows that even effects of pressure and composition of ambient gas (heat losses at high pressure) can be described in terms of this model. Table 8 presents comparison of some experimental results with calculation on the basis of kinetic parameters: $E = 41.6 \text{ kcal/mole}$, $Q_z = 1.98 \text{ E}20 \text{ W/g}$ [2].

Good agreement of light emission delays with calculations on the basis of kinetic parameters, determined from shock tube experiments, was obtained for double-base propellant M-9 [16]. At the same time, for RDX composite propellant XM39, a considerable effect of O_2 in the ambient gas at high flux values ($\approx 150 \text{ W}/\text{cm}^2$) was observed. This is consistent with the results presented earlier for RDX.

Table 8. Condensed-Phase Model Ignition Delay, t_i (ms), Predictions for NC Compared With Measurements

Parameter	Flux (q) (W/cm ²)	Ignition Delay (t_i)	
		Experiment (ms)	Calculation (ms)
$\lambda = .36\text{--}1.0\ \mu\text{m}$ $k_\lambda = 300\ \text{cm}^{-1}$ Ref. [3]	30	191	227
	51	101	103
	85	56	51
	152	27	24
	240	—	—
$\lambda = 10.6\ \mu\text{m}$ $k_\lambda = 500\ \text{cm}^{-1}$ Ref. [28]	30	205	199
	51	90	87
	85	42	41
	152	17	18
	240	9.1	9.7

Observations of double-base propellant N ignition by low fluxes ($q < 30\ \text{W/cm}^2$) are in good agreement with condensed-phase model predictions [2, 23, 45]. The model describes the effect of pressure (1–30 atm), presence of O_2 in the ambient atmosphere (no effect), and initial temperature ($-75\text{--}100^\circ\ \text{C}$). Special diagnostic experiments were conducted to establish the actual site of the initial exothermic reaction [45]. Intense flow of nitrogen (up to 40 m/s) was produced over the surface of ignited samples to prevent the accumulation of gaseous decomposition products (development of gas-phase reaction). But the only effect of the flow was an increase of the ignition pulse (qt_i) in accordance with increase of the heat transfer coefficient. Measured ignition temperature ($200\text{--}250^\circ\ \text{C}$) at the fixed t_i did not depend on the flow speed and, within the range of experimental scatter, was the same as in the experiments in the air without nitrogen flow. This result confirms the small effect of gas-phase reactions on the ignition parameters.

For arc-image fluxes below 40 W/cm², ignition delays of double-base propellants M2 and JPN can also be fit well with the condensed-phase theory [46]. But the strong pressure dependence of the ignition time found at higher fluxes is inconsistent with the model. The authors described all results obtained in the range 1–200 W/cm² in terms of gas-phase theory, taking a “good-fit” value $k_\lambda = 150 \text{ cm}^{-1}$ and considering vaporization of NG with temperature dependence of saturated vapor pressure $p(\text{atm}) = 7\text{E}9 \exp(-24,000/RT)$ and activation energy of gas-phase reaction $E_g = 45 \text{ kcal/mole}$. As noted in Vilyunov and Zarko [1], the observed decrease of the $t_i(q)$ curve slope can also be described by a condensed-phase model using $k_\lambda = 500\text{--}570 \text{ cm}^{-1}$, which is the range of the measurements for noncatalyzed double-base propellants.

It may be assumed that the validity at high flux levels of condensed-phase model for double-base propellants is limited by achievement of the NG boiling point $T_b = 548 \text{ K}$ [17]. This value is close to the surface temperature of propellant N burning at atmospheric pressure [2]. However, experiments conducted using continuous CO₂ laser [28] show that for double-base propellant the question is not as simple as for the secondary explosives. Table 9 presents results for propellant N: t_i - experimental ignition delays (average value of 5–7 measurements), T_i - calculated “inert” surface temperature corresponding to t_i , t_{ic} - calculation on the basis of kinetic parameters $E = 33 \text{ kcal/mole}$, $Q_z = 5\text{E}13 \text{ W/g}$ [2].

Table 9. Comparison of Condensed-Phase Model Predictions of Ignition Delays for Propellant N With Measurements

q (W/cm ²)	33	42	54	79	160	250
t_{ic} , ms	330	229	152	83	29	15.4
t_i , ms	362	251	167	90	39	44
T_i , K	570	579	585	599	—	—

As can be seen, even at the lowest flux value, the surface temperature at the ignition instant is considerably higher than the boiling point. Nevertheless, significant deviation from calculation takes

place only at $q_L \approx 150 \text{ W/cm}^2$. The effect of ambient oxidizer also becomes significant at $q > q_L$ (Table 9 presents ignition delays, measured in the nitrogen atmosphere). Ignition at high fluxes is preceded by gasification distinguishable in the motion-pictures, although appearance of the flame takes place both directly on the surface and at a considerable distance from it.

Table 10 presents similar results for catalyzed propellant N+2% PbO. In the case of catalyzed propellant, the influence of vaporization begins at a flux level of $q_L \approx 60 \text{ W/cm}^2$, although the surface temperature $T_i(q_L)$ is less than the boiling point (the difference exceeds the calculation accuracy). This result is probably the consequence of the catalyst effect. In accordance with Dolgoplatev and Ioffe [47], a small amount of additives may significantly facilitate vaporization.

Table 10. Comparison of Condensed-Phase Model Predictions of Ignition Delays With Measurements for Propellant N Catalyzed With 2% PbO

q (W/cm^2)	33	42	54	79	160	250
t_{ic}, ms	330	229	152	83	29	15.4
t_i, ms	261	174	117	107	87	95
T_i, K	521	528	533	—	—	—

Although the condition $T_i(q) = T_b$ does not define the limit of condensed-phase model applicability, the general trends of double-base propellant ignition by high radiant flux are similar to those of explosives.

7. Experimental Determination of High-Temperature Kinetic Parameters for Thermal Decomposition and Vaporization of Explosives

Most available data on thermal decomposition kinetics of explosives and, especially, vaporization were obtained at relatively low temperatures using, for instance, the isothermal

calorimetry method [40]. Because of strong temperature dependence, extrapolation of these value-to-ignition conditions is questionable. As a result of new experimental methods and theory development, several approaches for deriving thermokinetic parameters from ignition experiments [2, 12, 48, 49] became available. This part of the report presents results obtained using laser techniques. Some aspects of the question peculiar to the radiative ignition are also discussed. All methods are based on the analysis of ignition delays t_i and temperatures T_i in terms of an assumed ignition criterion. The most widely used criteria for this purpose are Vilyunov and Zarko [1] and Mikheev [2].

A detailed study of the method for deriving thermokinetic parameters was performed in Mikheev [2]. Radiative ignition experiments were conducted on pyroxylin (NC) powder samples pressed to a density of 1.49–1.50 g/cm³. Radiation from heated graphite was used to provide the flux range 2.5–17.8 W/cm². To avoid the influence of volumetric light absorption, the samples were blackened with a thin (approximately 18 μm) layer of a lamp soot. Direct measurement of the surface temperature by microthermocouples (5–6-μm thick and 60-μm wide) showed that the layer does not introduce distortion into the thermal picture of the process. The ignition delay corresponded to the beginning of the sharp temperature rise in the surface heating oscillogram. The ignition temperature corresponded to the thermocouple temperature at this time.

The thermophysical parameters of the samples were also determined on the basis of thermocouple measurements: $c = 1.22$ J/g K, $a = 7.92E-4$ cm²/s. This allowed calculation of the “inert” ignition temperature corresponding to the ignition time.

To obtain thermokinetic parameters, the authors used ignition criterion (1) in the form [1]:

$$\ln \left[\frac{t_i}{(T_i - T_o) (1 + \chi H (at_i)^{1/2})} \right] = \frac{E}{RT_i} + \ln \left[\frac{F_o c}{Qz} \right], \quad (14)$$

where F_0 and χ are coefficients shown in Figure 6, the term $(1 + \chi H (at_i)^{1/2})$ represents the heat losses to the ambient atmosphere, $H = \epsilon/\lambda$, and ϵ is the heat transfer coefficient. Equation (14) is a straight line $y = Ax + B$ in the coordinates $1/T_i = x$, $\ln[t_i/(T_i - T_0) (1 + \chi H (at_i)^{1/2})] = y$. Having determined the coefficients A and B on the basis of several experimental points (t_i , T_i at different fluxes), we could obtain kinetic parameters: $E = AR$ and $Qz = F_0 c / \exp(B)$.

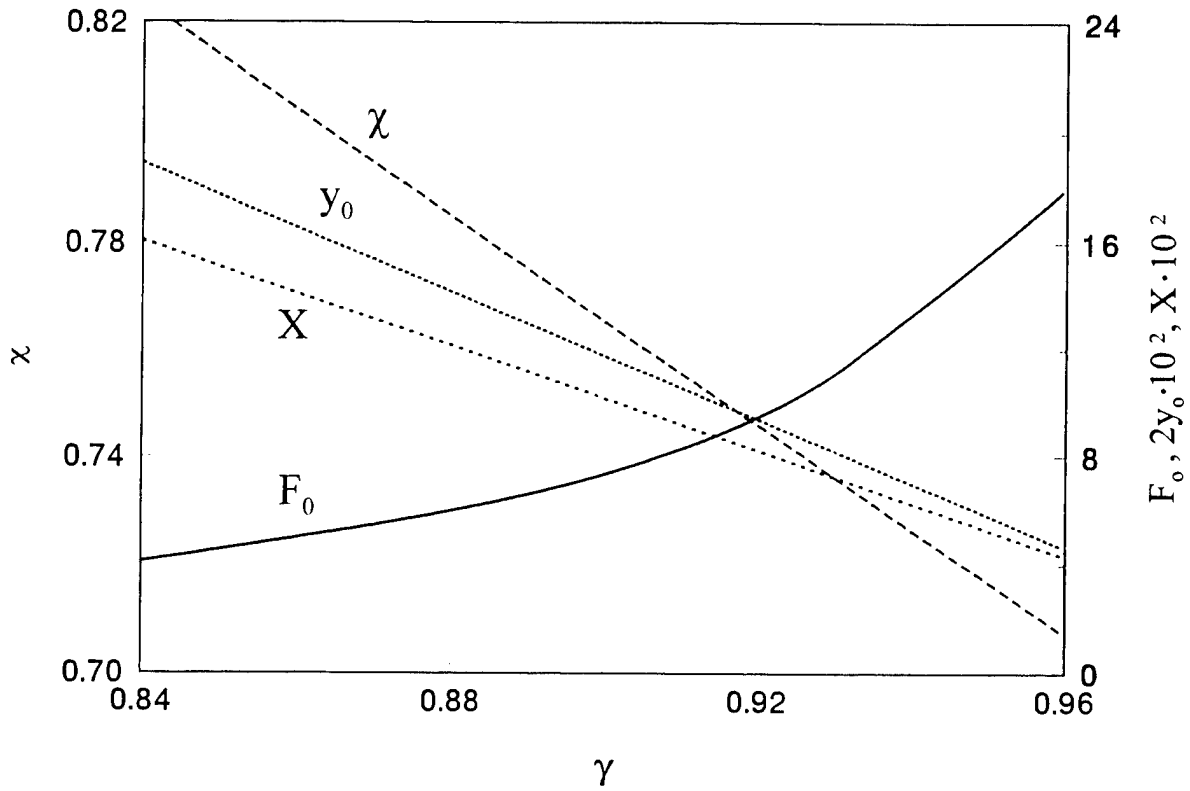


Figure 6. Parameters F_0 , X , Y_0 , and χ as Functions of Gamma (γ).

When analyzing equation (14), the authors used both the “inert” temperature calculated on the basis of the measured ignition time t_i :

$$T_i = T_{in} = T_0 + q/\lambda H [1 - \exp(aH^2 t_i) \operatorname{erfc}(H(at_i)^{1/2})], \quad (15)$$

where $(\operatorname{erfc}(z) = 2/(\pi)^{1/2} \int_z^{\infty} \exp(-x^2) dx)$ and directly measured value T_i . In the first case, kinetic parameters derived from (14) were:

$$E = 50.4 \text{ kcal/mole}, Q_z = 3.2 \times 10^{24} \text{ W/g.} \quad (16)$$

In the second case,

$$E = 41.6 \text{ kcal/mole}, Q_z = 2 \times 10^{20} \text{ W/g.} \quad (17)$$

The difference in parameters is significant, and calculated on the basis of (17) rates of heat release at characteristic temperatures, 530–560 K is 3–5 times less than those computed from (16).

The large difference between kinetic parameters (16) and (17) may be due to the authors using as an “inert” value the temperature related to the beginning of a sharp temperature rise (at t_{i1}). It was 6–18° less than the measured one. The more common approach [12] is to use “inert” temperatures corresponding to the time t_{i2} at which deviations from inert behavior (temperature) are observed. According to Belyaev [17] and Strakovskiy [18], at $E = 40 \text{ kcal/mole}$, the relative duration of the self-acceleration period is $(t_{i2} - t_{i1})/t_{i2} 11\%$, and the corresponding difference in “inert” ignition temperature is 12°. Using this correction will result in kinetic parameters closer to (17):

$$E = 44 \text{ kcal/mole}, Q_z = 2.5 \times 10^{21} \text{ W/g.}$$

(1) Nonuniformity of the surface temperature (i.e., individual parts of the surface [sources] may have a temperature considerably higher than that registered by the thermocouple, and these sources will actually govern the ignition process) [50].

(2) At the beginning of sample gasification, either a complete or partial detachment of the thermocouple takes place, and the observed effect of a sharp temperature rise may occur before real ignition due to the thermocouple overheating by the radiation flux [1].

(3) The stepwise increase of the signal at the ignition can also be partly due to the heating by flame rather than by evolution of the chemical reaction in the condensed phase [1]. Thus, to obtain objective information, it is better to use nonintrusive (optical) methods.

Employing an “inert” temperature in the method is the easiest way, but it requires accurate values of thermophysical characteristics. The possible errors in the thermal diffusivity or heat capacity will result in the errors of derived values E and Qz . However, as long as we continue to use these values for ignition parameters calculation together with the same thermophysical characteristics, the resulting errors will be minimal [12, 20]. This approach seems to be reasonable.

One of the principal problems in the method is elimination of the volumetric absorption effect. Coating the surface with an absorbing layer is not the best way. First, this layer (or film) may be completely or partly removed by the gasification products before ignition [8]. The thermal distortions introduced by the layer increase as the igniting flux increases. It was a significant achievement in Mikheev [2] to obtain such a thin (18 μm) homogeneous layer of carbon black because the common size of lamp soot particles is 10 μm [51]. Nevertheless, even such a thin layer will considerably distort the temperature field in the sample at fluxes $q > 30 \text{ W/cm}^2$. Finally, it is impossible to completely eliminate the catalytic effect of introduced carbon [8].

In Strakovskiy [15] and Strakovskiy, Ulyakov, and Frolov [20], thermokinetic parameters were derived using ignition delays, converted to the case of the surface absorption described earlier. Ignition delays calculated from formula (12) can be regarded as a zeroth approximation $t_i^0(q_i, k \rightarrow \infty)$. On the basis of this dependence, we can determine the kinetic parameters E^0 and $(Qz)^0$ using expressions (5), (7), and (8). Then we calculate new conversion coefficients $\omega_1(q_i, k_\lambda)$ on the basis of E^0 and $(Qz)^0$. Using $\omega_1(q_i, k_\lambda)$ in (12), we obtain the dependence of ignition time on the flux for the surface absorption in the first approximation $t_i^1(q_i, k \rightarrow \infty) = \omega_1(q_i, k_\lambda) t_i(q_i, k_\lambda)$.

Let us consider this procedure using an example with composition HMX + 5% wax. The thermophysical parameters of explosive are the same as for HMX: $\rho = 1.74 \text{ g/cm}^3$, $a = 1.72\text{E-}3\text{cm}^2/\text{s}$, and $c = 0.98 \text{ J/g K}$ (Table 6). The volumetric absorptive capacity of the substance is 174 cm^{-1} (Table 4).

Kinetic parameters are derived on the basis of ignition criterion (5), (7), and the solution of the "inert" thermal problem (8). Using formula for $Q_*(x_*)$, ($x_* = ([RT_i^2/E] (\rho\lambda Q_z) \exp(E/RT_i))^{1/2}$) and taking the logarithm of (5), we obtain the following expression:

$$2\log (Bq/T_i) = \log(Q_z \rho\lambda R/E) - E/4575T_i \quad (18)$$

that presents an equation of a straight line $y = C - Dx$ in the coordinates $y = 2\log(Bq/T_i)$, $x = 1,000/T_i$. Coefficient $D = E/4.575$ ($4.575 = R \ln 10$) determines the activation energy in kcal/mole, C - preexponent Q_z . C also depends on the E , but it is justified to neglect this factor because of the logarithmic character of the dependence. So we can use any reasonable literature value of E to calculate the initial values of B and C .

Table 11 presents the procedure of converting the laser ignition data to the case of the surface absorption and derivation of the kinetic parameters. For convenience (to obtain a positive value of $\log$), we used erg instead of J in (18). On the basis of experimental results (rows 1 and 2), using nomogram (Figure 1) and formula (12), we obtain ignition delays for the case of the surface absorption in zeroth approximation (row 3). Ignition temperatures (row 4) in this approximation, calculated from (7) were substituted into (18). As a result, the line 2 (in Figure 7) was obtained with coefficients $D = 8.35$ and $C = 25.45$, which define the kinetic parameters in the zeroth approximation:

$$E^0 = 38.2 \text{ kcal/mole}, (Q_z)^0 = 1.07\text{E}18 \text{ W/g.}$$

On the basis of these parameters, calculations of converting coefficients $\omega_1(q_i, k_\lambda)$ have been performed (row 8) using equations (5–9). The largest difference between ω_0 and ω_1 is 14%, which

Table 11. Procedure for Deriving Kinetic Parameters by Modifying Measured Ignition Delays for Conditions of Surface Absorption

1	q_i , W/cm ²	32	52	100	170	320
2	$t_i(q_i)$, ms	358	177	71.6	35	16
3	$\omega(q_i)$	0.78	0.66	0.53	0.42	0.306
4	$t_i^0(q_i, k \rightarrow \infty)$, ms	281	117	37.9	14.8	4.9
5	T_i^0 , K	565	585	610	621	658
6	$1,000/T_i^0$, K ⁻¹	1.77	1.71	1.64	1.61	1.52
7	$2\log(Bq_i/T_i^0)$	10.77	11.15	11.68	12.14	12.63
8	$\omega_i(q_i)$	0.796	0.69	0.544	0.44	0.317
9	$t_i^1(q_i, k \rightarrow \infty)$, ms	285	122	39	15.4	5.08
10	T_i^1 , K	568	588	614	629	662
11	$1,000/T_i^1$, K ⁻¹	1.76	1.70	1.63	1.59	1.51
12	$2\log(Bq_i/T_i^1)$	11.03	11.42	11.96	12.4	12.9

is about five times greater than calculation error. The procedure was repeated in the next approximation with new values of ignition delays and temperatures (rows 9–12). The line 1 (in Figure 7) was obtained, and kinetic parameters were derived:

$$E^1 = (35 \pm 3) \text{ kcal/mole}, (Qz)^1 = (1.1 \pm 0.5)E17 \text{ W/g}. \quad (19)$$

The errors shown in (19) include both calculation errors and scatter of experimental results. It is not expedient to perform the next approximation step, because the parameters' change will be considerably less than the indicated error of the method.

Knowledge of vaporization kinetics for explosives and volatile propellants is important not only from the standpoint of a quantitative description of their ignition but also for development of a combustion model, since for HE and some propellants, surface temperature under steady-state

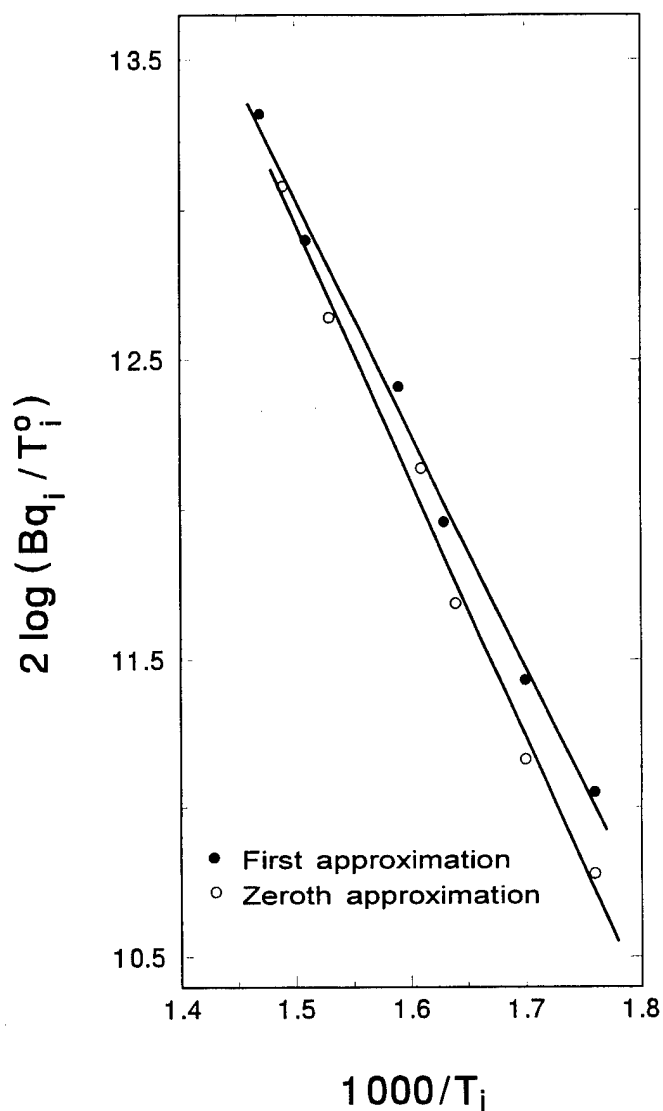


Figure 7. Derivation of Kinetic Parameters.

steady-state combustion is very close to the boiling point and a fresh layer is formed by vaporization (combustion and vaporization rates are equal) [17, 40]. Besides, on the basis of vaporization kinetics, it may be possible to evaluate pressurization rates in the gun chamber, which is important for the LIGHT program [16, 30].

Most studies of vaporization kinetics were conducted at relatively low temperatures where the effect of thermal decomposition can be neglected (i.e., times required for vaporization measurements $\ll$ ignition/explosion delay) [17, 39]. Extrapolation of these results to combustion or ignition

temperature range can lead to mistakes: calculation of RDX and tetryl vaporization rates at the boiling point (atmospheric pressure) on the basis of kinetics [17] gives values from 5 to 10 cm/s, which are more than 100 times the real combustion speed [40].

High temperatures corresponding to combustion regimes can be obtained by irradiating materials with short high-power laser pulses. By operating under vacuum conditions, decomposition is minimized [40]. Such a method of evaporation kinetics determination was discussed in Strakovskiy [18]. Surface temperatures at different laser fluxes were evaluated on the basis of recoil pulse measurements.

The value of recoil pressure on evaporated surfaces is given by the formula $p = \rho c(T) u(T)$, where ρ = density, $c(T) = (\gamma RT/M)^{1/2}$ = sonic speed, γ = specific heat capacity ratio of the vapor, and $u(T)$ = vaporization rate. Expressing $u(T)$ in accordance with the energy-conservation law, we obtain relation between specific recoil pulse value and surface temperature:

$$I/E_r = \rho c(T) (1 - R_\lambda)/Q_v, \quad (20)$$

where I = recoil pulse, E_r = total radiation energy, and Q_v = the heat consumption for evaporation of the substance unit volume:

$$Q_v = \rho [L + \gamma RT/2 + c_v(T) (T - T_0)], \quad (21)$$

where L = latent heat of vaporization and $c_v(T)$ = specific heat capacity for the vapor.

The principle of the method is in the measurement of specific recoil pulses at different laser fluxes $I/E_r(q_i)$. Using these values and measured reflection coefficient R_λ , we can evaluate the surface temperature from (20) and (21):

$$T(q_i, L) = \frac{\gamma R/M + 2(c_v T_0 - L)c_v [I/E(q_i) (1 - R_\lambda)^{-1}]^2}{c_v^2 [I/E(q_i) (1 - R_\lambda)^{-1}]^2}, \quad (22)$$

Now, expressing the vaporization rate in accordance with Arrhenius and the energy-conservation laws and using values $T_i = T(q_i, L)$, we obtain final expression for evaluation of kinetic parameters and L :

$$z(M/\rho N_O)^{1/3} \exp(-L/RT_i) = \frac{q_i}{\rho[L + \gamma RT_i/2 + c_v(T_i)(T_i - T_O)]} \quad (23)$$

that has to be analyzed in the semilogarithmic coordinates $\log [q_i/Q_v(T_i)]$ vs. $1/T_i$ using published values for the zeroth approximation of L .

The limits of applicability of this method (ranges of laser fluxes and temperature interval) are determined by the condition of steady-state vaporization:

$$\rho c(T) T(q)/k_\lambda q \ll t_o, \quad (24)$$

where t_o = duration of a laser pulse and k_λ = absorption coefficient. The greater the value t_o (at sufficiently high flux level), the wider the temperature interval. However, the pulse duration should be short enough to eliminate the considerable sample destruction, which may have an effect on the measured recoil pulses.

Experiments conducted for TNT and tetryl using a Nd-glass laser with a spherical confocal resonator allowed a peak-free generation mode to be obtained, characterized by a uniform distribution of the pulse energy over both time and space. A rotating disk-shutter was used to provide pulse duration within interval 0.5–0.8 ms at which, as a rule, no evidence of ignition was observed. Total energy (J) in the pulse was 120–350.

Cylindrical specimens of pressed TNT and tetryl were used with diameters of 5–10 mm. Explosives specific heat capacities c_v have been calculated on the basis of data [52]: $c_v(\text{J/gK}) = 0.43 + 1.4\text{E-}3T + 2.2\text{E-}7T^2$ for tetryl and $0.38 + 1.7\text{E-}3T - 3.6\text{E-}7T^2$ for TNT.

A long focus lens was used to direct the laser beam into the vacuum chamber. The diameter of the irradiated zone was varied from 4 to 7 mm. The samples were placed on the holder of the ballistic pendulum. Recoil pulse value was fixed on the basis of pendulum deviation in the range $(4-60) \cdot 10^{-4}$ Ns with accuracy greater than 5%. Samples were weighed before and after laser action, which allowed evaluation of the average vaporization rates.

The measured recoil pulses are shown in Figure 8. The experimental points were constructed on the basis of 5-6 measurement results. It is important to point out that specific pulses in vacuum are 3-4 times greater than appropriate values at atmospheric pressure. This is evidence of a significant counterflow of molecules and a nonelastic character of their interaction with the irradiated surface [53]. In vacuum, the counterflow is negligible. In this case, neglecting the exothermic condensation process is justified.

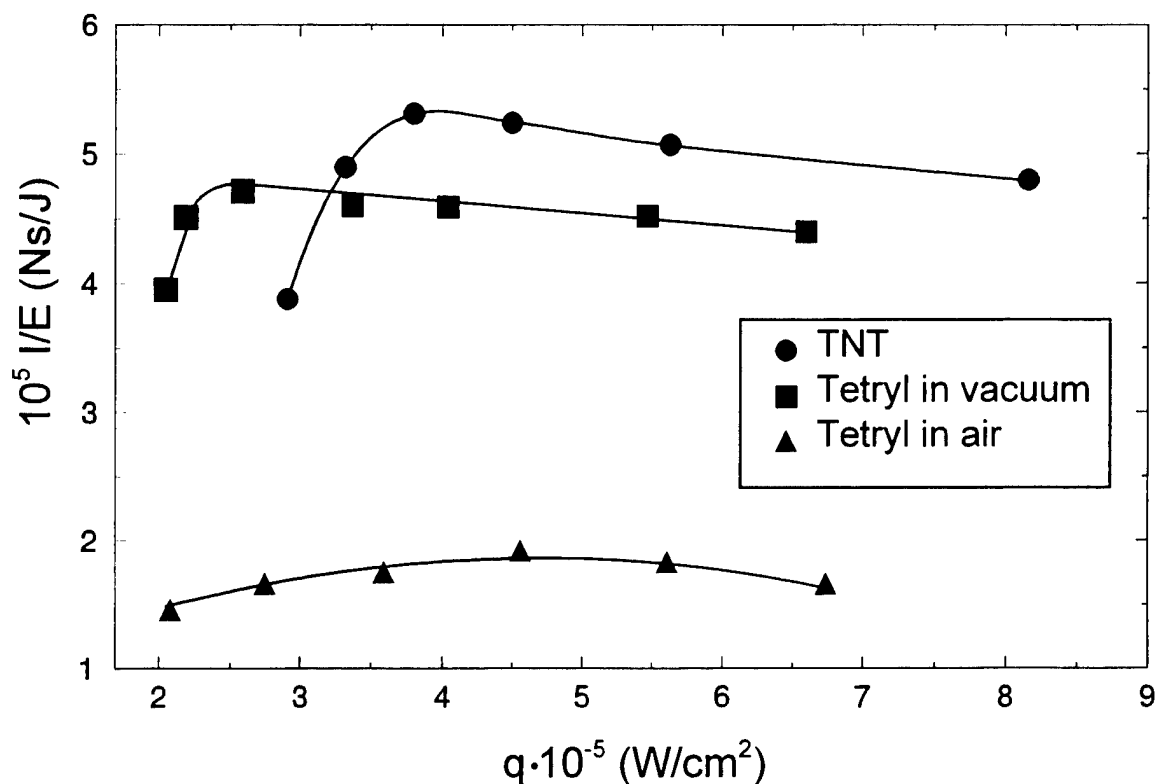


Figure 8. Recoil Pulses of Gaseous Products of TNT and Tetryl in Vacuum and Air.

High-speed motion-picture recording of the process showed an appearance of the luminescent zone as a result of laser action at atmospheric pressure. The flame disappeared several milliseconds after radiation removal. In vacuum, light emission was not observed.

Figure 8 shows that in atmospheric air as laser flux is decreased, beginning with value $2.5E5 \text{ W/cm}^2$ for tetryl and $3.5E5$ for TNT, a sharp reduction in the recoil pulses occurs. This is due to disruption of the steady-state vaporization conditions: at these fluxes, the energies required for the heating of the surface layer and vaporization become comparable. Thus, the lower limit of the method's applicability is determined directly from the experimental curve $I/E(q)$.

As flux is increased, a certain decrease of pulses is observed that is consistent with formulas (20–21). Figure 9 presents the result of experimental data analysis for tetryl in accordance with expression (23).

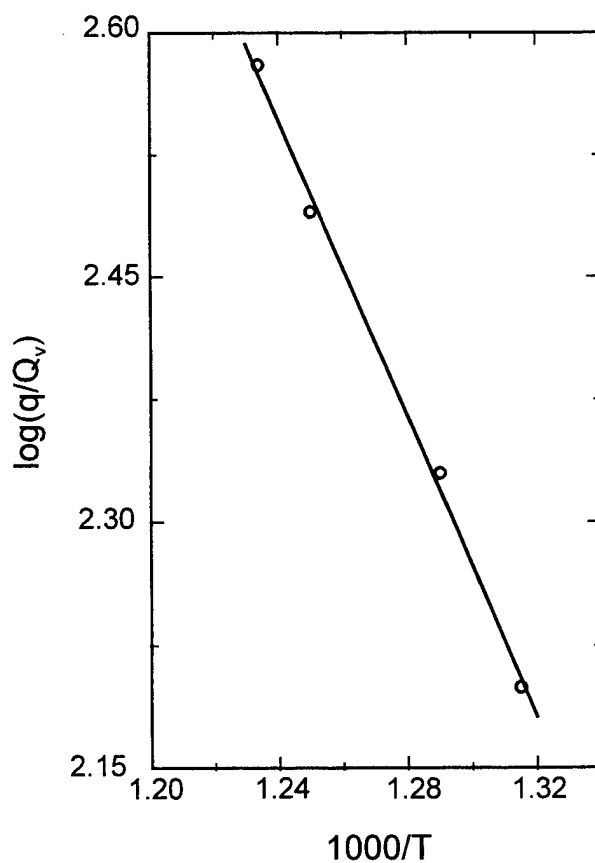


Figure 9. Dependence of Vaporization Rate on the Surface Temperature.

The slope of the line (2.3 L/1000R) in the figure determines the value of latent heat $L = 24$ kcal/mole with accuracy about 12%. The second coefficient in the line equation $-\log[z(M/\rho N_0)^{1/3}]$ determines the value of preexponent: $z = 2E16 \text{ s}^{-1}$ with accuracy ~60%. These kinetic parameters correspond to the temperature interval 760–810 K.

The results of the analysis of the experimental data for TNT are:

$$L = 18 \pm 2.5 \text{ kcal/mole},$$

$$z = (2.4 \pm 1.4) E13 \text{ s}^{-1}. \quad (25)$$

Measured values of the average vaporization rates are about 20 times less than results calculated on the basis of low-temperature (373–423 K) experiments [17]. This is evidence of the significant temperature effect on the vaporization kinetic parameters. The temperature range of L and z parameters determined by this method may be considerably expanded. For instance, application of a pulse CO_2 laser with the same E and t_0 parameters instead of Nd laser allows reduction of the low-temperature limit by 100° . At the same time, there may be a significant effect of radiation absorption by gasification products at the wavelength $10.6 \mu\text{m}$ and high flux level. An increase of the upper limit is easy to accomplish using a more powerful laser.

On the basis of measured kinetic parameters, expressions for vaporization rate temperature dependence were obtained:

$$u \text{ (cm/s)} = 5E10 (T)^{-1/2} \exp(-12318/T) \text{ for tetryl}$$

$$u \text{ (cm/s)} = 4E7 (T)^{-1/2} \exp(-8807/T) \text{ for TNT}. \quad (26)$$

For composition, TH 40 vaporization rate at low fluxes ($q = 26\text{--}84 \text{ W/cm}^2$) was directly measured [42]:

$$u \text{ (cm/s)} = 2E4 \exp(-7533/T).$$

These expressions allow us to evaluate preignition pressurization rates.

8. Summary of Laser Ignition Thresholds and Kinetic Parameters Derived From Experiments

It is sometimes desirable to calculate radiative ignition delays corresponding to the case of surface absorption [$t_i(q, k \rightarrow \infty)$] from measurements (finite k). This allows direct comparison of ignitability for substances with different absorption coefficients and evaluation of results obtained by different authors at different wavelengths. It also allows for easy conversion of experimental $t_i(q, k \rightarrow \infty)$ values to ignition delays at any wavelength using the graphs in Figures 1 and 2 and formulas (15–16).

As was indicated above, the dependence of ignition delay $t_i(k \rightarrow \infty)$ on the flux has the following form:

$$t_i(k \rightarrow \infty) = A/q^m. \quad (27)$$

The dependence of ignition temperature on the flux increases as the activation energy of the condensed-phase reaction decreases. This leads to a decrease in the value of m .

The values of coefficients A and m are shown in Tables 12 and 13. The kinetic parameters derived from ignition experiments and heat flux $q_{0.1}$ that ignite the substance with delay 0.1 s are also shown. Temperature interval ΔT corresponds to the range in which the parameters were derived. The lowest temperature is either a calculated “inert” temperature at ignition $t_i(q_{\min}, k_\lambda)$, where $q_{\min}$ is the lowest radiative flux in the experiments or a measured value $T_i(q_{\min})$. The upper boundary of ΔT corresponds either to the boiling point or to the ignition temperature at the highest radiative flux.

Table 12. Values for A and m for Various Propellants

Propellant	Ref.	A (W ^m /cm ²)	m	E (kcal/mole)	log(Qz) (W/g)	ΔT (K)	q _{0.1} (W/cm ²)
NC	[2]	72	1.79	41.6	20.3	506–559	39.5
		68.7	1.825	50.4	24.5	500–541	35.9
	[3]	69	1.76	—	—	—	41
	[28]	74	1.80	43	20.8	540–610	39
N	[2]	127	1.74	33	16.7	475–520	61.2
	[28]	155	1.758	36	17.4	570–600	65.3
N + 1% C	[1]	148	1.736	32.8	16.1	^a	67.1
N + 1% PbO		115	1.67	26	13.7	^a	68
N + CT	[4]	137	1.75	35	^a	^a	62
N + CT	[28]	140	1.787	41	20.05	521–535	57.7

^a Authors did not derive kinetic parameters or specify the temperature range.

It is pertinent to point out that as the ignition delay is decreased the dependence of ignition temperature on the flux becomes stronger and the values of coefficients A and m may significantly change [54, 55]. The values presented in Tables 12–13 correspond to the interval $t_i = 0.001 - 5$ s.

Errors of derived kinetic parameters dE and $d(Qz)$ are related to the total error of measured ignition delays dt_i including experimental spread. In accordance with ignition criteria (1), (2), and (5), $dE/E \approx dt_i/t_i$, $d(Qz)/Qz \approx \theta/2 dt_i/t_i$. The average value of dt_i/t_i is 5–10%. Therefore, the error of presented results for preexponential factor Qz is very significant ≈ 30 –80%.

Table 13 presents the similar results for secondary explosives, which are placed in the order of their ignitability. Coefficients A and m for HMX + 1% C were calculated assuming that the absorption coefficient of the substance is equal to the appropriate value of RDX + 1% C ($k_\lambda = 600 \text{ cm}^{-1}$) [34].

Table 13. Values for A and m for Various Explosives

Explosive	Ref.	A (W ^m /cm ²)	m	E (kcal/mole)	log(Qz) (W/g)	ΔT (K)	q _{0.1} (W/cm ²)
RDX	[15]	110	1.84	56	24.5	595–613	45
C1		124	1.83	53	22.7	593–613	49
Tetryl		110	1.79	43	20.1	555–583	50
RDX + 1% C	[34]	123	1.80	^a	^a	^a	53
TH 40	[15]	111	1.76	38.5	16.3	680–710	53.7
RDX + 20% wax	[32]	113	1.76	39	^a	^a	54.3
HMX + 4% wax	[15]	123	1.75	35	17	550–620	58.3
HMX + 5% NP		147	1.79	43	19.8	575–612	58.8
HMX		172	1.82	51	22.8	550–590	60
HMX + 1% C	[35]	190	1.78	^a	^a	^a	69
C1 + 20% Al	[15]	610	1.82	50.7	21.3	600–620	120
THAF		664	1.82	49	17.4	590–620	126
TNT		670	1.74	35	14	790–830	158
TNT + 20% Al		670	1.74	35	—	—	158

^a Authors did not derive kinetic parameters or specify the temperature range.

It is pertinent to note that the order of ignitability (thermal sensitivity) corresponds to a relatively narrow range of flux (ignition time). Places of some explosives in the row change, as the value of t_i is decreased. For instance, flux that ignites HMX with a delay of 1 ms is less (750 W/cm²) than the appropriate value for HMX + 4% wax (810 W/cm²). Generally, there is a reduction in the difference of the energy parameters characterizing explosives ignition with a decrease of t_i (i.e., the difference in the thermal sensitivities of the explosives gradually disappears) [54]. This circumstance, in particular, reflects the fact that the ignition process becomes degenerate due to reactant consumption [12] with sufficiently intensive external loading [26].

On the basis of data presented in Table 12, we can derive several conclusions: (1) the ignitability of NC is significantly greater (up to 1.8 times greater than the corresponding values for double-base propellants); (2) although there are considerable differences in the values of the kinetic parameters of NC obtained by different authors, the effect of these differences on calculated heat release rates is small; and (3) the effect of different additives including catalysts on the ignitability of double-base propellants is low.

The data in Table 13 indicate that a small amount of a low-melting additives (such as wax) have a significant effect on kinetic parameters for RDX and HMX. The partial solubility of the explosives solution in wax may be a possible explanation. The activation energy for RDX and HMX thermal decomposition in solution is less than in the molten state [40, 56], although the decomposition rates at typical ignition temperatures are approximately equal. The increase of wax content facilitates the solution of the explosives and may make this effect more significant.

RDX also dissolves in TNT. Therefore, the activation energies and ignitability of TH40 (40% TNT 60% RDX) and RDX + 20% wax almost coincide. It is interesting to point out that in the case of sufficiently long ignition delays (0.01–1 s) the ignitability of TH40 is close to that of RDX and is close to TNT at short ignition times. It appears that the short times are not sufficient for RDX to dissolve [54].

Introducing 20% of aluminum into explosive makes it opaque. On the other hand, it significantly increases thermal diffusivity and conductivity, which lead to a considerable decrease of RDX ignitability. At the same time, aluminum has no effect on the thermal sensitivity of TNT because its thermal diffusivity and conductivity in the molten state are sufficiently high and the effect of the additive is small [40].

A small amount of carbon black, as a rule, has a strong accelerating effect on the radiative ignition delays of explosives in the region of a weak spectral absorption. But when the modification creates an opaque surface, there may be a reverse influence: carbon slightly increases ignition delays

of RDX and HMX. Such an effect was observed also for PETN initiation at the wavelength 0.69 μm [56]. Introducing 0.5–3% of carbon black increased ignition delays by 17%.

Interesting results were obtained for the initiation of explosive mixtures with ammonium and potassium perchlorate by a 50-ns duration Nd laser pulse [57]. The effect of additives decreases as external pressure and explosive sensitivity increase. At sufficiently high pressure (about 1 GPa), the energy threshold does not depend on the amount of perchlorate (up to 80%) and is determined by the characteristics of the HE (PETN, RDX, and TNT).

An important practical question is determination of an optimal flux range in which the ignition pulse $u_i = qt_i$ is a minimum. According to Baranovskii [27], in the case of surface absorption, the ignition pulse monotonically decreases as flux is increased. However, there are several factors that lead to the increase of u_i with flux in the real case of radiative ignition and, as a consequence, to the occurrence of a minimum u_i value. Even in the framework of a condensed-phase model for volumetric absorption, the ignition pulse is determined by the formula $u_i = \rho c(T_i - T_o)/k_\lambda$ (equation 3). Therefore, increase of ignition temperature T_i with flux leads to an increase in u_i . Calculated values of flux q_m for tetryl, which correspond to the minimum ignition pulse, are presented in Table 14 [15].

Table 14. Values of the Minimum Ignition Energy Pulse for Tetryl

$k_\lambda, \text{cm}^{-1}$	5	10	18.4	50	100
$q_m, \text{W/cm}^2$	63	120	225	650	1,800

Such factors as vaporization or gasification, mechanism of radiation absorption, external pressure and percentage of introduced additives are more significant. Taking into account all of these effects is very complicated. For each material, the amount of additive and operating wavelength required for the optimal flux range may be obtained only by experiment. For instance, the optimal percentage of aluminum for explosive ignition (initiation) by a short (15 ns) laser pulse at the wavelength

1.06 μm was found by Ioffe [58]. These results are presented in the Table 15, where α = % aluminum (by weight).

Table 15. Optimal Percent Al Additive for Radiative Initiation of Explosions at 1.06 μm

Explosive	PETN	RDX	HMX	Ammonium Nitrate
α (%)	1.5-5	3	5	5

9. Conclusions

Ignition of 24 propellants and explosives by laser and radiative flux has been considered. Over a given flux range, the initial stage of the process is well described by the simplified condensed-phase model. Limits of the model's applicability are determined by the condition that at a given pressure the ignition temperature should be less than the boiling point or steady-state vaporization value.

Optical parameters of about 20 propellants and explosives at wavelengths 0.36–1.0, 1.06, and 10.6 μm have been summarized. There are very significant differences in the results of different studies. The most widely used experimental methods for determining absorption coefficients were analyzed and techniques and restrictions for minimizing uncertainties in their values were derived. The effect of different additives on the optical properties has been considered.

The quantitative effect of volumetric radiation absorption has been analyzed, and methods of determining the effects of surface absorption and changes in wavelength on ignition delays have been developed.

At high laser flux values, it was possible to observe new features of the ignition process: (1) anomalous dependence of ignition delay on the flux (U-shaped $t_i(q)$ curves for several explosives and propellants), (2) hot spot type ignition and degeneration of the self-propagation process at

wavelength $1.06\text{ }\mu\text{m}$ ($q > 10\text{ kW/cm}^2$), (3) disruption of the phase equilibrium and effect of the surface overheating, and (4) decrease of the difference in energetic materials ignitability, which gradually disappears with an increase in flux.

Methods to derive thermokinetic parameters from radiative ignition experiments have been analyzed. It is expedient to use the "inert" temperature approach and then to use the same thermophysical properties for further calculations.

The method of vaporization kinetics determination based on the measurements of recoil pulses of explosives gaseous products was developed. Experiments indicated the importance of counterflowing vaporized molecules and the exothermic process of condensation.

Ignition thresholds and derived kinetic parameters for 20 explosives and propellants have been summarized. The global Arrhenius kinetics do not reflect the real processes but make it possible to calculate ignition parameters for different practical cases. The order of explosives sensitivity was obtained, and the effect of inert and active additives was summarized.

From the point of optimal ignition (i.e., ignition with minimal energy consumption), there is a certain flux range, which is primarily determined by (1) laser wavelength (optical parameters), (2) material volatility, and (3) external pressure. Introducing a small amount of additives can reduce the energy thresholds by a factor of 20. The higher a material's ignitability, the smaller the effect of chemically active additives.

In the last 15 years, a new branch of research has been developed in Russia: laser thermochemistry, for instance [59–61]. It deals mostly with controlling rates of oxidation reactions by means of the thermal action of a laser radiation. The main idea is to take advantage of the significant differences in the optical properties of reactants and products. This may be useful for laser ignition studies.

Additional analysis and summary should be performed for the following aspects: (1) ignition of particles and crystals, effect of geometry and shape of solids, and (2) ignition stability and dynamic events.

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List of Symbols

q_o	external radiation flux absorbed at surface
k_λ	absorption coefficient at wavelength λ
R_λ	reflection coefficient at wavelength λ
λ	thermal conductivity or wavelength
ρ	density
a	thermal diffusivity
c	specific heat capacity
R	universal gas constant
E	activation energy
z	first-order Arrhenius parameter
Q	specific heat of reaction
Q_+	heat release due to the chemical reaction
Q_-	conduction heat losses from reaction zone
x_*	width of chemical reaction zone
t_i	ignition delay
T_i	ignition temperature
T_o	initial temperature
$\phi_i = k_\lambda(at_i)^{1/2}$	ratio of the characteristic thermal wave thickness ignition to the absorption length
$\theta_i = E(T_i - T_o)/RT_i^2$	dimensionless temperature change at ignition that characterizes the relation between the chemical induction period and the total ignition delay
B	ratio of chemical heat release to external heat input at ignition

$\omega(q, k_\lambda)$	ratio of ignition delays calculated assuming surface and in-depth absorption
k_0	absorption coefficient at which ignited substance may be regarded as opaque
T_m	melting point
T_b	boiling point
q_L	flux at which ignition temperature reaches boiling point
T_v	vaporization temperature
T_c	critical temperature (at $T_i > T_c$, reactant consumption is significant)
$c(T) = (\gamma RT/M)^{1/2}$	sonic speed
γ	adiabatic index of vapor
$u(T)$	vaporization rate
I	recoil pulse
E_r	total radiation energy
L	latent heat of vaporization
$c_v(T)$	specific heat capacity of a vapor
Q_v	volumetric heat of vaporization
M	molecular weight
N_0	Avogadro constant
t_0	laser pulse
A and M	coefficients in the dependence of ignition delay on the flux $t_i(k \rightarrow \infty) = A/q^m$
ΔT	temperature interval that indicates the range to which derived kinetic parameters correspond
u_i	ignition pulse
q_m	flux that corresponds to ignition pulse minimum

α amount of Al (by weight) in the ignited substance

ε heat transfer coefficient

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