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The Thermal Theory of the Ignition of Reacting Condensed Substances

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The processes involved in the solid-phase ignition of reacting condensed substances, taking place in the absence of mass diffusion due to temperature or concentration gradients, have been examined using a single asymptotic method. An analytical criterion for the ignition of a substance has been formulated, and a basis obtained for a universal linearisation method, which makes it possible to express experimental results statistically in the form of a linear relationship in a special system of coordinates. The question of the range of existence of non-degenerate ignition conditions has been discussed in detail. Experimental data confirming the reliability of the thermal of ignition have been given.
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I. INTRODUCTION

The study of the processes involved in the ignition of reacting condensed substances has developed extensively throughout the world in recent decades, because of their practical importance. The development of the theory of ignition originates in classical studies of the theory of thermal explosion,[1-3] summarised in a monograph.[4] The simplest model of the surface ignition of a condensed substance was first studied in Refs.5–8, where numerical integration using a computer was used to solve the non-stationary problems of the heating of the surface of a substance with an exothermic reaction taking place in the solid phase and with the Arrhenius dependence of the reaction rate on temperature.

The non-stationary thermal model of ignition adopted in these studies provided a basis for subsequent theoretical and experimental work, which has been reviewed in Refs.9 and 10 and in a recent monograph.[11] Since then, a large number of studies have been carried out, and a new asymptotic method in the theory of ignition has been developed, leading to the further development of the thermal theory and its experimental justification. It has therefore become necessary to summarise the theoretical principles of the thermal theory of ignition from a single asymptotic viewpoint. Present-day asymptotic procedures, which provide a powerful analytical method for solving boundary problems for differential equations with partial and complete derivatives, are most fully described in Refs.12–16. In the solution of problems of mathematical physics of this type, represented by the problems of the thermal theory of ignition, the asymptotic method provides a well-founded and convenient instrument of study, since the numerical values of the activation energy E and the heat Q for the chemical reactions of the ignition and combustion of known substances are fairly large.

To solve these problems, extensive use is made of approximate methods, which can be divided into four groups: 1) the critical condition method,[17-21] 2) the method of breakdown into stages,[22-25] 3) the method of successive approximations,[26,27] and 4) the method of integral relationships.[28] All these approximate methods are based on physical and mathematical simplifying assumptions about the course of the process, and not on the rigorous analytical solution of the non-linear problems of the thermal theory of ignition. At the same time it should be noted that all approximate methods are based on the same general view that the ignition process takes place in two stages: inert warm-up of the substance and progressive chemical spontaneous warm-up, ending in a "temperature explosion" at the surface at the moment of ignition. These ignition conditions have been called non-degenerate,[10] in contrast to degenerate conditions, in which the ignition process cannot develop in the warm-up and spontaneous warm-up stages. Degenerate ignition conditions can obviously lead either to "superficial burning" of the substance, at high thermal fluxes from an external source, or to the production of transition conditions intermediate between ignition and spontaneous ignition, at extremely low thermal fluxes.

None of the studies mentioned above, carried out using approximate methods, gives an answer to the problem of the range of existence of non-degenerate ignition conditions. Moreover, up to the present there has been no single definition of the criterion of ignition. Since the experimental determination and the calculation of the ignition delay time depend on the choice of ignition criterion, the arbitrary nature of this choice naturally also influences the conclusions about the agreement between theory and experiment. The moment of ignition is determined experimentally by measuring either the temperature at the surface of the substance, or the intensity of radiation, or the pressure in the system, and also by recording the behaviour of the specimen after the external heat supply is stopped. Reliable ignition takes place when the total quantity of heat liberated in the chemical reactions is greater than the heat loss. It is usually assumed that ignition does not take place if stationary combustion conditions are not established after the abrupt removal of the external heat source.[3] It has been shown,[10] however, that the calculation of pulse ignition conditions using this criterion is not a rigorously justified procedure, since this criterion was obtained by solving the particular problem of the unsymmetrical combustion of a thin slab of the reacting substance.

It should also be noted that the principle of linear universalism, which makes it possible, within the ignition model adopted, to "plot" the experimental results statistically on a straight line in a special system of coordinates, and when necessary to solve the inverse problem of determining the thermokinetic constants, has not yet been sufficiently developed.

Before proceeding to the presentation of the asymptotic thermal theory of ignition, it may be noted that in the literature[9] there are three main groups of ignition model, differing in their representation of the place where the main chemical reactions take place: 1) the model of gas-phase ignition, 2) the model of heterogeneous ignition, and 3) the model of solid-phase ignition.

In the first group of models it is assumed that ignition takes place as a result of a chemical reaction between a gaseous oxidant and a fuel vapour. This reaction is a self-maintaining heat source. Studies of the gas-phase model of the ignition of solid rocket fuels have been reviewed.[9,29] A method for calculating the ignition delay time for the case where the warm-up time of the substance is greater than the excitation time of the chemical reaction in the gas phase has been described.[30,31]

In the heterogeneous ignition model, the reaction at the phase boundary between a solid fuel and a gaseous oxidant is regarded as decisive. In the analysis of the heterogeneous ignition process it is necessary to take account of diffusion and hydrodynamic phenomena. In the particular case when the rate of the process is determined by the kinetics of the heterogeneous reaction, however, a purely thermal approach is possible.[22,23,32-37]

The solid-phase (or thermal) theory of ignition is based on the simplest (from the physical viewpoint) model of the phenomenon, in which only the processes of heat liberation and propagation in the substance are taken into account, and diffusion factors and possible phase transformations are not considered. The characteristic features of this model have been formulated,[9,10] and it is now widely used in the analysis of the processes involved in the ignition of non-volatile systems and systems difficult to volatilise.

In the present review, only the solid-phase models of ignition are analysed, for different initiation conditions.

II. THE ASYMPTOTIC ASPECT OF THE THERMAL THEORY OF IGNITION AND THE INFLUENCE OF THE MECHANISM OF HEATING ON THE BASIC REGULAR FEATURES OF THE IGNITION PROCESS

The dimensionless numerical parameters $\varepsilon = RT_0/E$, $\gamma = cRT_0^2/QE$, where T_0 is the initial temperature of the substance, c the heat capatity, and R the universal gas constant, appear in the mathematical description of the thermal model of ignition;[38-40] when $\varepsilon = 0$, because of the Arrhenius temperature dependence of the reaction rate, the chemical sources of heat become degenerate, and when $\gamma = 0$ there is no combustion of the substance in the ignition delay period, which corresponds to a zeroth-order reaction.

A natural element of the asymptotic analysis of the problems of the thermal theory of ignition is the construction of a non-stationary space–time temperature field in the substance as $\varepsilon \to 0$ ($\varepsilon \neq 0$). For this purpose, use is made of a compound asymptotic expansion, which gives a uniform approximation to the exact solution of the ignition problems both in and outside the boundary layer. Since in this case non-linear equations of a parabolic type with an exponential source are being analysed, it follows that in cases where the highest temperature is reached at the surface of the substance there is a "temperature explosion" at the surface at the moment of ignition t_*, that is there exists only a local solution of the boundary problems in the range $0 < t < t_*$. For the specific thermal model of ignition, the relationship between the rates of supply of heat from an external source of energy and from chemical reactions at the moment of ignition is calculated unambiguously. This relationship, which can be taken as a criterion of ignition, is generally easily transformed into a linear equation in a special system of coordinates and can be used to calculate the thermokinetic constants of the reaction from experimental data. In contrast to the ignition criterion, which assumes that the rates of supply of heat from the reaction and from an external source of energy are equal at the moment of ignition,[10,18,19,26,41] the asymptotic criterion in principle does not specify this equality. Other criteria, adopted in Refs. 28 and 42–47, are not sufficiently well-founded, since they were not obtained from a rigorous analysis of the corresponding boundary problems of the thermal theory of ignition. They are applicable only in a restricted range of conditions of combustion initiation.

The asymptotic analysis, together with the ignition criterion, leads to two definite inequalities, fulfilment of which determines the range of existence of the asymptote or, in other words, the range of existence of non-degenerate ignition conditions. This question has not previously been discussed in the literature, although information on the range of existence of non-degenerate ignition conditions is very necessary for experimental workers in the correct organisation of experiments and choice of initial parameters and appropriate recording apparatus. The analytical apparatus of the method of compound asymptotic expansion exists in differential[40] and integral[48] versions. The influence of the mechanism of heating of a substance on the basic regular features of the ignition process is examined below for the case of the solution of the specific problems in the thermal theory of ignition, and simple equations are given for calculating the characteristics of ignition.

1. Dynamic Conditions of Ignition of a Non-transparent Condensed Substance

For a semi-infinite solid slab and a one-dimensional thermal flux, the mathematical formulation of the ignition problem has the form:[49]

$$\left.\begin{aligned} &T_t = \varkappa T_{xx} + Qk_0c^{-1}(1-\eta)\exp[-E/RT],\\ &\eta_t = k_0(1-\eta)\exp[-E/RT]\\ &t=0: T=T_0,\ \eta=0;\ x=\infty: T=T_0 \end{aligned}\right\} \quad (1)$$

$$x=0: -\lambda T_x = q(t);\ q>0 \quad (2)$$

Here, T is the current temperature of the substance, t the time, x the spatial coordinate, η the degree of transformation, q the density of the thermal flux from the external source, ρ, λ, and $\varkappa$ the density, coefficient of thermal conductivity, and temperature conductivity of the substance respectively, and k_0 the pre-exponential factor. The other symbols were given above.

The asymptotic study of the general problem (1) and (2) has been carried out.[48,49] The chief characteristics of the ignition for the particular case $q = At^n$, $A > 0$, $n > -0.5$ are calculated using the equations:[50]

$$t_* = \left[\left(\frac{\lambda T_0}{A}\right)^2 \frac{u_*}{\varkappa}\right]^{\frac{1}{2n+1}},\quad T_* = T_0\theta_*,\quad T_i = T_*\left(1 + \frac{\theta_*}{2}\varepsilon\ln(1/\varepsilon)\right),$$
$$Q_* = \frac{At_*^{n+1}}{n+1},\quad \eta_* = 1.48\gamma\varepsilon^{-1/2}\theta_*\left(\frac{d\theta_*}{du_*}\right)^{-1/2} \quad (3)$$

Here, the dimensionless ignition delay time u_* is determined from the transcendental equation

$$A=\left[\frac{\varkappa}{u_*(\lambda T_0)^2}\right]^n\cdot\left[1.5385\,\varepsilon^{1/2}Q\rho k_0\lambda T_0\theta_*\left(\frac{d\theta_*}{du_*}\right)^{-1/2}\exp\left(-\frac{1}{e\theta_*}\right)\right]^{n+1/2} \quad (4)$$

and $\theta_* = \theta_*(u_*)$ is calculated from the equations

$$\theta_*=1+\frac{u_*^{1/2}}{\delta_n},\quad \delta_n=\frac{\Gamma(1.5+n)}{\Gamma(1+n)} \quad (5)$$

In Eqns.(3), T_* is the scale temperature, T_i the ignition temperature, Q_* the minimum energy required for ignition, and η_* the extent of the combustion in the ignition delay period. The tabulated Euler gamma-function $\Gamma(z)$ is used in Eqns.(5). Eqn.(4) gives the relationship between the rates of supply of heat from the external source and from the chemical reactions at the moment of ignition. It can be written in the form

$$At_*^n=\sigma_n\left\{\lambda\rho Qk_0\frac{RT_*^2}{E}\exp\left(-\frac{E}{RT_*}\right)\right\}^{1/2} \quad (6)$$

where

$$\sigma_n=\theta_0^{1/4}[2.1757\,\delta_n]^{1/2},\quad \theta_0=E(T_*-T_0)/RT_*^2$$

For $n = 0$ (constant thermal flux), the expression for σ_0 has the form $\sigma_0 = 1.39\,\theta_0^{1/4}$, and with increase in the parameter n the function σ_n increases, that is $\sigma_n > \sigma_0 \cong 2.9$–$3.1$. Eqn.(6) can be used as a criterion of ignition. At the same time, in Refs.10, 18, 41, and 51, the value of σ_n is assumed to be 1. The range of existence of non-degenerate ignition conditions is determined by the inequalities [50,52]

$$A^-(n,\,T_0)\leqslant A\leqslant A^+(n,\,T_0) \quad (7)$$

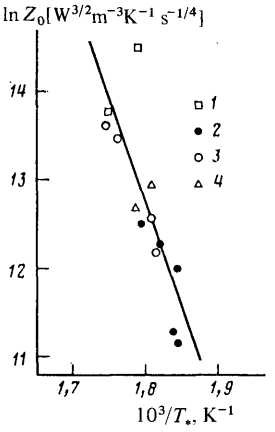


Figure 1. Determination of the thermokinetic constants of the ignition of nitrocellulose from experimental data;[50] continuous line—calculated by the least-squares method; the experimental points were obtained for the following values of n: *1*) 0.6; *2*) 1.0; *3*) 1.39; *4*) 2.8.

Eqn.(4) is readily transformed to the special form

$$\ln Z_0=\ln[2.1757\,\rho Qk_0\varkappa^{1/4}(R\lambda/E)^{1/2}]-\frac{E}{RT_*} \quad (8)$$

where Z_0 and the scale temperature T_* are determined from the measured values of T_0, A, n, and t_* using the equations

$$Z_0=A^{1/2}T_*^{-1}t_*^{(6n-1)/4}\delta_n^{-1/2},\quad T_*=T_0+At_*^{n+1/2}\cdot\delta_n^{-1}(c\rho\lambda)^{-1/2} \quad (9)$$

Eqn.(8) is described graphically by a straight line in the coordinates $\{\ln Z_0,\ 10^3/T_*\}$. It is universal for any values of $\{A, n, T_0\}$ in the range of existence of non-degenerate conditions. By treating the experimental results by the least-squares method in the system of coordinates indicated, it is possible readily to calculate the thermokinetic constants E and Qk_0. Fig.1 gives experimental data on the ignition of nitrocellulose under dynamic conditions in a special light apparatus.[50] The least-squares method gave the values

$$\ln Z_0=56.3458-24.25\frac{10^3}{T_*},\ E=201\,760\ \text{J mole}^{-1},\ Qk_0=2.4932\times10^{25}\ \text{W kg}^{-1},$$

in good agreement with published data.[10]

To illustrate the effectiveness of the asymptotic method of calculating the characteristics of ignition, Table 1 compares the experimental[50] values of the ignition delay time of nitrocellulose at $T_0 = 300$ K with the values calculated using Eqns.(3). The agreement between these values of t_* is good. Finally, it may be noted that the influence of the relative uncertainty of the determination of σ_n on the accuracy of the estimation of t_* has been studied,[53] and it was concluded that this influence decreases with increase in n.

Table 1. Principal characteristics of the ignition of nitrocellulose by a variable thermal flux.

Experiment (Ref.50)		Calculated from Eqns.(3)–(6)				
$10^5 A$, W m^{-2}s^{-n}	t_*^e, s	t_*^c, s	T_i, K	Q_*, kJ m^{-2}	$10^4\eta_*$	σ_n
			$n=0.6$			
18.813	0.105	0.107	608.6	33.1529	1.8429	3.3894
41.146	0.0495	0.054	919.6	24.4484	1.9079	3.3902
			$n=1.0$			
0.9218	1.442	1.453	571.5	97.2854	1.8470	3.6029
1.0685	1.310	1.321	572.8	93.2294	1.8557	3.6033
3.1257	0.640	0.662	582.8	68.4039	1.9209	3.6063
4.6509	0.500	0.512	586.6	60.9925	1.9457	3.6072
6.4526	0.410	0.415	589.7	55.4927	1.9664	3.6079
			$n=1.39$			
4.7515	0.602	0.611	585.4	61.3179	2.1398	3.7900
9.8465	0.411	0.420	591.0	51.8317	2.1805	3.7913
50.28	0.179	0.181	603.9	35.5799	2.2749	3.7937
67.166	0.155	0.156	606.2	33.2798	2.2922	3.7940
			$n=2.8$			
25.308	0.492	0.494	592.3	45.6457	2.8152	4.2986
61.731	0.372	0.379	596.4	40.5171	2.8531	4.2995

2. The Ignition of a Transparent Substance by a Constant Thermal Flux ($n = 0$, $A = q$)

This problem requires special consideration because of its considerable methodological importance, since in this case it is possible to compare results obtained by different authors. Eqns.(3)–(6) for $n = 0$ lead to calculation equations for determining the characteristics of ignition, and also ignition criteria, differing considerably from those adopted in the literature. This difference is illustrated by data on the value of σ_0 used in approximate methods (Table 2).

This variety of ignition criteria obtained is related to the fact that rigorous allowance was not made for the explosive character of the change in temperature at the surface of the

substance at the moment of ignition. Only the method of compound asymptotic expansions[50,54] has made it possible to obtain a well-justified ratio of the rates of supply of heat from the reaction and from the external source at the moment of ignition, and also to find the relationship $\tau_* = (t_*/t_0) = 0.4065\ \theta_0^{3/2}$, where t_0 is the adiabatic induction period of the thermal explosion at a temperature T_*.

Table 2. Comparison of different criteria for the ignition of condensed substances by a constant thermal flux.

σ_0^2	Refs.
$1.39^2 \cdot \theta_0^{1/2}$	[5, 4]
2	[43]
1	[18, 19, 28, 55]
17.64	[46]
$0.1 \cdot \pi\theta_0$	[7]
$0.5 \cdot \pi\theta_0$	[19]
$0.5 \cdot \pi^{1/2}\theta_0$	[47]
$\{[(1+0.2\theta_0^{-1})-2.67\theta_0^{-1}\lg\theta_0]+1.0424\theta_0^{-0.845}\}^{-1}$	[24]*
$[2\theta_0^2-2\theta_0+1]/1.76(2\theta_0-1)$	[25]
$\exp\{\theta_0[(1.71+38\theta_0^{-2})^{1/2}-1]-3.13\}$	[10, 46]
$0.25 \cdot \pi[1+\theta_0^{-1}\ln 2\theta_0]^{-2}$	[28]*
$0.25 \cdot \pi\theta_0^2(1+0.5\theta_0)^{-1}$ (adiabatic method)	[44]*
$0.137^2 \cdot \theta_0^{1/2}$	[21]*

*Relationship obtained by the present authors using Eqn. (18) from Ref.10.

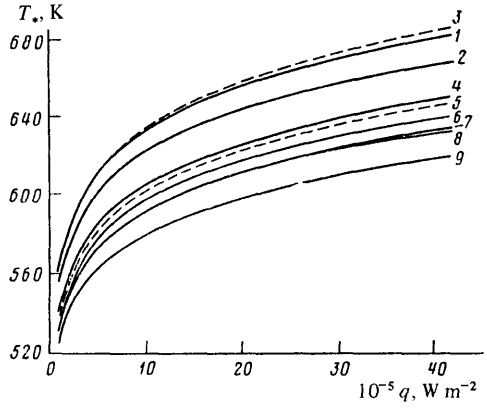


Figure 2. Dependence of the ignition temperature of nitrocellulose on q, calculated from various data: *1*) Refs.18, 19, 55, *2*) Ref.45, *3*) from Eqn.(3), *4*) Ref.7, *5*) from Eqn.(3), *6*) Ref.25, *7*) Ref.46, *8*) Ref.47, *9*) Refs.10 and 46.

To illustrate the influence of the value of σ_0 on the scale temperature T_*, calculated on the basis of the combustion criterion (6) for $n = 0$, Fig.2 gives the $T_*(q)$ relationships obtained from the data of different authors for $T_0 = 303$ K for nitrocellulose; the thermophysical and kinetic constants required for the calculation were taken from Ref.10. Since all the authors assume that $T_* = T_i$, Fig.2 gives the curve for the ignition temperature T_i (curve *3*), calculated using Eqn.(3). Curve 5, obtained by the asymptotic method, is extremely close to curve *4*, obtained by numerical integration using a computer,[7] and curve *3* agrees fairly well with curve 1.[18,19,55] On the whole, the discrepancy in the values of T_* obtained by different authors increases with increase in the density of the thermal flux, reaching 10%. A comparison of the values of t_* and T_* calculated by the asymptotic method with the results of the numerical solution of the problem using a computer[7] can be carried out for nitrocellulose at $T_0 = 303$ K on the basis of the data in Table 3. Good quantitative agreement is observed.

Table 3. Comparison of the results of the asymptotic and numerical solutions of the problems of ignition by a constant thermal flux.

$10^{-4}q$, W m^{-2}	8,38	41,9	83,8	209,5	419
T_*, K (Ref.7)	542	582	601	628	650
t_*, s (Ref.7)	1.564	0.0852	0.0243	0.00463	0.00132
T_*, K (Ref.54)	539	578	597	623	645
t_*, s (Ref.54)	1.522	0.0828	0.0236	0.00449	0.00128

Note. The values of T_* and t_* were obtained by numerical integration using a computer in Ref.7, and by the asymptotic method in Ref.54.

The results of the calculation of the ignition delay time using the asymptotic equations (3)–(5) and the equations obtained in Refs.28 and 56 can be compared. In Ref.56, the value of t_* was calculated using the interpolation equation

$$t_* = 0.699\ \frac{\lambda\rho c}{q^2}(T_* - T_0)^2,\quad T_* = \frac{E}{2R}\left[D - \ln D + \frac{\ln D}{D}\right]^{-1},$$
$$D = \frac{1}{2}\ln\left(\frac{\lambda\rho Q k_0 E}{2Rq^2}\right) \qquad (10)$$

In Ref.28, an equation obtained by the method of integral relationships

$$t_* = \frac{c\rho\lambda\,(T_* - T_0)^2}{q^2}[1 + \theta_0^{-1}\ln(2\theta_0)]^2,\quad \theta_0 = \frac{E\,(T_* - T_0)}{RT_*^2} \qquad (11)$$

was used; the ignition criterion (6) with $\sigma_0 = 1$ was used to determine T_*.

Table 4 compares the values of t_* for nitrocellulose, calculated by the three methods indicated for different values of q and T_0. The appreciable difference between the results indicates that the approximate methods[28,56] are insufficiently rigorous. The range of existence of non-degenerate ignition conditions for a substance for q = const is given by Eqn.(7) with $n = 0$. Using the relationships which follow from Eqn.(9) for $n = 0$,

$$Z_0 = q^{3/2}t_*^{-1/4}T_*^{-3}\delta_0^{1/2},\quad T_* = T_0 + 2q\,[t_*(\pi\lambda\rho c)^{-1}]^{1/2}$$

Eqn.(8) can be transformed to

$$\ln\left[\frac{(T_* - T_0)^{3/2}}{T_* t_*}\right] = 2\ln[2.78(\pi c)^{-1/4}\cdot(Qk_0)^{1/4}\cdot(R/E)^{1/4}] - \frac{E}{RT_*} \qquad (12)$$

and can be used to determine the thermokinetic constants from experimental data. Fig.3 gives the results of experiments on the ignition of "N" powder,[57] which lie on a straight line on the coordinates of Eqn.(12). The use of the thermophysical constants from Ref.42 and Eqn.(12) gives the values $E = 147.8$ kJ mole^{-1}, $Qk_0 = 4.97 \times 10^{20}$ W kg^{-1}.

Although the asymptotic approach developed in Ref.44 does not make it possible to establish the range of existence of non-degenerate ignition conditions, to determine the values of σ_0, T_i, and η_*, or to obtain a universal straight line (12), it nevertheless gives good agreement between the calculated principal characteristics of the ignition of a substance by a constant thermal flux, and the results obtained by numerical integration using a computer. This indicates the advantage of using asymptotic analysis to study the ignition process.

Table 4. Delay time for the ignition of nitrocellulose by a constant thermal flux.

$\lg t_*^0$ [s] for T_0, K			Method of calculation	Refs.
220	300	340		
$q = 10^4$ W m^{-2}				
1.9562	1.8475	1.5781	I	[54]
2.1558	1.8740	1.6892	II	[56]
2.4517	2.2065	2.0499	III	[28]
$q = 10^6$ W m^{-2}				
−2.0438	−2.1525	−2.4219	I	[54]
−1.5545	−1.7467	−1.8616	II	[56]
−1.2509	−1.4178	−1.5158	III	[28]

Note. I—calculation using the asymptotic equations (3)–(5); II—calculation using the interpolation equation (10); III—calculation by the method of integral relationships (Eqn. (11)).

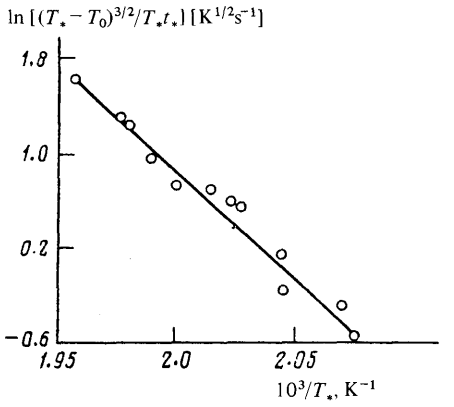


Figure 3. Determination of the thermokinetic constants of "N" powder from experimental data;[57] continuous line—calculation by the least-squares method, points—experiment.

3. The Ignition of Non-transparent Condensed Substances

The simplest case of the ignition of a substance by a stream of hot gas having a constant temperature T_c ($T_c > T_0$) can be considered. In this case, the heat exchange at the surface of the substance ($x = 0$) can be described using Newton's law

$$-\lambda T_x = \alpha [T_c - T(0, t)] \qquad (13)$$

where α is the coefficient of heat transfer from the gas to the substance (a constant quantity). This problem was previously analysed using the methods of the critical condition,[7,10,18,46,51] breakdown into stages,[24] and integral relationships.[28] These approximate methods do not give sufficient accuracy, however, since they do not use the analytical procedure of the method of compound asymptotic approximations.[40,48,58] As shown below, the latter makes it possible to establish the ignition criterion and the range of existence of non-degenerate ignition conditions, and also to calculate the principal characteristics of ignition and to construct a universal straight line for calculating the kinetic constants from experimental data.

The ignition criterion in this case has a form analogous to that of Eqn.(6)

$$\alpha (T_c - T_*) = \sigma \left\{ \lambda \rho Q k_0 \frac{RT_*^2}{E} \exp\left(-\frac{E}{RT_*}\right) \right\}^{1/4} \qquad (14)$$

where

$$\sigma = \frac{\theta_0^{1/4}}{(0.65)^{1/2}} \left(\frac{T_c - T_*}{T_* - T_0}\right)^{1/4} F^{1/4}(x_0), \quad x_0 = \varphi(y), \quad y = \frac{T_c - T_*}{T_c - T_0},$$

$$F(x_0) = \frac{y(x_0)}{(\pi x_0)^{-1/2} - y(x_0)}, \quad y = \exp(x_0)\,\mathrm{erfc}\,[x_0^{1/2}]$$

The value of σ obtained differs considerably from other published values: $\sigma = 1$,[10,51] 4.2,[46] and $(0.1\,\pi\theta_0)^{1/2}$.[7] Eqn.(14) can be used to find the scale temperature T_* and then to calculate the quantity $x_0 = \phi(y)$ and the ignition delay time:

$$t_* = c\rho\lambda\alpha^{-2}x_0 \qquad (15)$$

The ignition temperature T_i and the minimum energy of ignition Q_* are calculated using the equations:

$$T_i = T_* \left[1 + 0.5\frac{T_*}{T_0}\,\varepsilon \ln(1/\varepsilon)\right]$$

$$Q_* = c\rho\,(\lambda/\alpha)\,(T_c - T_0)\,[2\,(x_0/\pi)^{1/2} + \exp(x_0)\,\mathrm{erfc}\,[x_0^{1/2}] - 1]$$

Eqns.(14) and (15) can be used to compare the results of the calculation of the ignition delay time t_* by the asymptotic method and by the method used in Refs.10 and 51 (for $\sigma = 1$). Fig.4*a* compares the dependence of t_* on α for nitrocellulose, calculated for $T_0 = 303$ K, with the experimental data.[59] The relationship has the form $t_* \sim \alpha^{-m}$ noted earlier.[46] Fig.4*b* shows that the function $m = m(T_c)$ obtained by the asymptotic method practically coincides with the curve obtained by numerical integration using a computer and interpolation, with the form:[46]

$$m = 1.79 - 44\left[\frac{RT_0T_c}{E\,(T_c - T_0)}\right]^{1.67} \qquad (16)$$

The experimental value $m = 1.64$ for $T_c = 573$ K[60] also lies satisfactorily on the calculated curve. The curves obtained by the method of Refs.10 and 51 differ considerably from the asymptotic relationships, indicating that the use of the ignition criterion with $\sigma = 1$ is not sufficiently correct.

The asymptotic approach also makes it possible to determine the kinetic parameters E and Qk_0 from experimental data on the ignition of a substance in a stream of hot gas. No accurate relationships for calculating E and Qk_0 have been published, and the method used in Refs.51 and 57, based on the use of the ignition criterion (14) with $\sigma = 1$, as noted above, leads to errors. The method proposed in Ref.60 also is not universal, although it enabled the authors of Ref.59 to carry out the treatment of experimental data on the ignition of a number of substances. The best-justified method for determining the kinetic constants from experimental data is that described in Ref.58. If in the experiment the conditions of heat exchange (T_c, α) are recorded, and the initial temperature of the substance T_0 and the ignition delay

time t_* measured, then Eqns.(14) and (15) in the coordinates $\{\ln Z_0,\ 10^3/T_*\}$ can be used to obtain the equation of a universal straight line for determining the kinetic parameters

$$\ln Z_0 = \ln[(0.65)^{-1}\lambda\rho Q k_0 (R/E)^{1/2}] - \frac{E}{RT_*} \qquad (17)$$

where

$$Z_0 = \alpha^2 T_*^{-1}(T_c - T_*)(T_e - T_0)^{1/2}[(\pi x_0)^{-1/2} - y]^{1/2},$$
$$T_* = T_c - (T_c - T_0)\exp\left[\frac{\alpha^2 t_*}{c\rho\lambda}\right]\operatorname{erfc}\left[\left(\frac{\alpha^2 t_*}{c\rho\lambda}\right)^{1/2}\right]$$

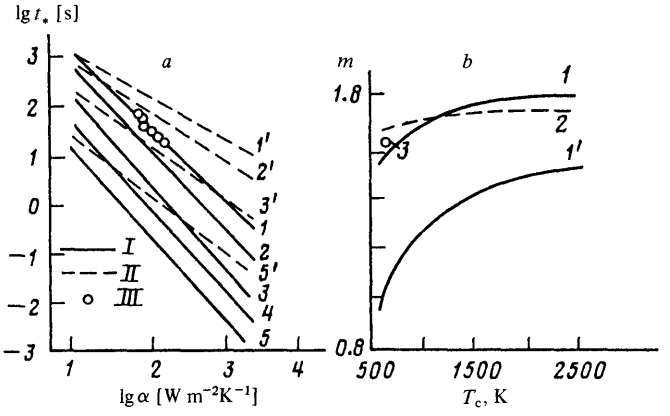


Figure 4. *a*) Dependence of the ignition delay time of nitrocellulose on the thermal properties of the external medium for T_c, K: *1*, *1'*) 600; *2*, *2'*) 700; *3*, *3'*) 1000; *4*) 1800; *5*, *5'*) 2500 (*I*—calculation using Eqns.(14) and (15); *II*—calculation by the method of Refs.10 and 51; *III*—experiment[59]); *b*) dependence of the parameter *m* on the temperature T_c: *1*) calculation using Eqns.(14) and (15), *1'*) calculation by the methods of Refs.10 and 51, *2*) calculation using Eqn.(16), *3*) experiment.[60]

As an illustration, E and Qk_0 can be calculated for nitrocellulose using published experimental data[60] for T_0 = 298 K and T_c = 573 K. The least-squares method and treatment of the experimental data on coordinates $\{\ln Z_0,\ 10^3/T_*\}$ gives the linear equation

$$\ln Z_0 = 61.7386 - 24.1843\,\frac{10^3}{T_*}$$

With allowance for Eqn.(17) this gives

$$E = 2.012 \times 10^5 \text{ J mole}^{-1};\quad Qk_0 = 3.475 \times 10^{26} \text{ W kg}^{-1}$$

The value of Qk_0 obtained is 19.5 times that previously calculated by other methods.[10] This is apparently due to the inadequacy of the mathematical model adopted for the calculations, and of the physical experiment,[60] where in addition to convective heat exchange between nitrocellulose and the gas stream, radiant heat exchange from the walls of the vessel also took place. According to the authors' estimates it amounted to ~30% of the total heat exchange.

The asymptotic approach also makes it possible to find the range of existence of non-degenerate ignition conditions

$$\alpha^-(T_0, T_c) \leqslant \alpha \leqslant \alpha^+(T_0, T_c) \qquad (18)$$

The corresponding data are given in Fig.5. The thermophysical and thermokinetic characteristics were taken from Ref.10. It can be seen that with increase in T_0 and decrease in the temperature of the hot gas T_c, the range of existence of non-degenerate ignition conditions becomes much narrower. This important feature must be taken into account when carrying out experiments.

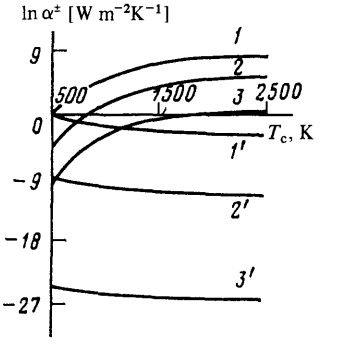


Figure 5. Ranges of existence of non-degnerate ignition conditions for nitrocellulose at T_0, K: *1*, *1'*) 383, *2*, *2'*) 303; *3*, *3'*) 223; α^+—curves *1*, *2*, and *3*; α^-—curves *1'*, *2'*, and *3'*.

The approximate equation $t_* \cong C\exp(E/RT_*)$ given in Ref.10, under the conditions of convective heating, makes it possible to calculate with an accuracy reaching 10% only the activation energy from the experimental values of t_*, T_c, α, and T_0, but gives no answer to the question of the magnitude of Qk_0. Calculations carried out by the asymptotic method for octogen, hexogen, nitrocellulose, and "N" powder confirmed this important conclusion and demonstrated again the practical applicability of Eqn.(17).

4. The Ignition of Non-transparent Condensed Substances Using a Heated Block

The simplest thermal model for the ignition of non-volatile condensed systems by a heated block assuming that a zeroth-order reaction takes place has been examined by many workers using various approximate analytical and numerical methods.[8,26–28,44,45,61–65] The lack of agreement between the results obtained, however, indicates that the approximate methods used are insufficiently accurate. Allowance for the combustion of the substance during the ignition delay time was made only in Ref.63, but the equation proposed in this study for calculating the conditional degeneration boundary gives results which are too high.

The present section gives the results of applying the asymptotic theory of the ignition of reacting substances; the examination is carried out for a boundary condition of the first kind without allowance for phase transformations and the large number of kinetic and physical stages, and also without allowance for the dispersal of the substance by the expanding gaseous reaction products. For ideal heat exchange between the substance and the heated block, the system of equations (1) is examined, and the conditions at the surface are written in the form $T(0,t) = T_b$, where T_b is the temperature of the heated block. In Refs.66 and 67, a complete asymptotic analysis of the problem was

carried out, and its analytical solution given (in dimensionless units)

$$\left.\begin{aligned}\tau_* &= \frac{\theta_0^2}{2\pi}[1 + 2\theta_0^{-1}\ln\theta_0],\ \tau_i = \frac{\theta_0^2}{2\pi}[1 + 2\theta_0^{-1}\ln\theta_0 + 7.545\theta_0^{-1}]\end{aligned}\right\} \quad (19)$$

$$\left.\begin{aligned}&\Delta H = 2^{1/4}\pi^{-1}H_0\theta_0^2[1 + \theta_0^{-1}\ln\theta_0],\ H_0 = cp(\varkappa t_0)^{1/4}\cdot(RT_b^2/E),\\ &\Delta Q = 2^{-1/4}\pi^{-1}H_0\theta_0^2\{[\theta_0^{-1}(1+\theta_0^{-1})]^{1/4} + 0.5(\arcsin(-1+2\theta_0^{-1}) - 0.5\pi]\},\\ &\Delta R = \Delta H - \Delta Q,\ (\Delta R/H_0) = 0.297 - 0.372 \text{ for } \theta_0 = 10-30,\\ &\eta_* = 1 - \exp(-\gamma\tau_*),\ \eta_i = 1 - \exp(-\gamma\tau_i)\end{aligned}\right\} \quad (20)$$

where

$$\tau = t/t_0,\ t_0 = \frac{cRT_b^2}{EQk_0}\exp\left(\frac{E}{RT_b}\right),\ \gamma = \frac{cRT_b^2}{QE} \quad (21)$$

Here, t is the current time, t_0 the adiabatic induction period of the thermal explosion at T_b, τ_* the dimensionless warm-up time of the specimen, τ_i the dimensionless ignition delay time, θ_0 the temperature head of the heating block ($\theta_0 \gg 1$), η_* the depth of combustion in the warm-up time, η_i the depth of combustion in the ignition delay time, and ΔH, ΔQ, and ΔR the stored energy, the energy supplied from outside, and the energy liberated in the reaction respectively.

Eqns.(19) and (20) were obtained neglecting the quantity $\beta = RT_b/E$ and with the condition that the warm-up of the substance is complete at the moment t_* when the temperature gradient at the surface becomes zero, and the ignition of the substance takes place at the moment t_i when the temperature gradient at the surface becomes infinite. For sufficiently small values of $\gamma\theta_0^2$, the equations for η_* and η_i are simplified and take the form

$$\eta_* = \gamma\tau_*,\ \eta_i = \gamma\tau_i \quad (22)$$

The conditional boundary of degeneration of normal ignition conditions can be determined from the inequalities $\eta_* \leqslant a$, $\eta_i \leq a$, where $a = 0.1-0.2$.[66] Eqn.(20) is then used to find the equation for calculating the limiting value of the parameter γ characterising the conditional boundary of degeneration

$$\gamma \leqslant \gamma_0 = \tau_i^{-1}\cdot\ln[1/(1-a)] \quad (23)$$

The equation proposed in Ref.63 has the form $\gamma_0 = 0.5\,\theta_0^{-1}$ and gives results which are 1–2 times higher than those given by Eqn.(23).

The accuracy of the asymptotic equations for calculating the basic characteristics of ignition is extremely high, as indicated by comparing with the results of numerical integration using a computer (Table 5). Fig.6 compares the results of the calculation of the warm-up periods of a reacting substance τ_* for $\beta = 0$ with the approximate equations used by a number of authors and also with Eqn.(19). The results of the calculation using Eqn.(19) practically coincide with those obtained[61] by computer calculation. Curves *2* and *3*, calculated using the data of Refs.27 and 63, are close to one another. The results obtained in Ref.26 (curve *1*) and in Ref.64 (curve *7*) are extremely far from the true values of the warm-up period. Most authors have tried to obtain simplified equations for calculating the warm-up time in the form of functions $\tau_* = A\theta_0^2$; the coefficient A has been assigned the values 0.21,[68] 0.207,[65] 0.25,[27,28] and 0.159.[45,62] This simplification, however, leads to marked deviations from the results obtained using Eqn.(19).

The asymptotic method has been used[44] to obtain more rigorous values of τ_*. Although the authors[44] did not use this method in complete form to solve the problem of the ignition of a substance by a heated block, they were able to estimate the lower and upper values of τ_* (denoted τ_*^- and τ_*^+ respectively). Table 6 gives the values of τ_*^- and τ_*^+ from Ref.44, and also compares the values of τ_* calculated using Eqn.(19) and obtained by numerical integration using a computer.[61] Good quantitative agreement is observed. As $\theta_0 \to \infty$, Eqns.(19) are simplified, and in the limit give the values obtained in Refs.45 and 62. This limit, however, is only the zeroth asymptotic approximation to the actual value of the warm-up period of the substance; this approximation does not give the required accuracy.

Table 5. Dimensionless characteristics of the ignition of a condensed substance by a heated block.

Ignition characteristic	θ_0					Method of calculation	Refs.
	10	15	20	25	30		
τ_*	25.7 23.2	51.6 48.7	86.2 82.7	129.5 125.1	181.5 175.7	I II	[61] [66, 67]
τ_i	37.3 35.2	67.7 66.7	106.2 106.7	152.9 155.1	207.7 211.7	I II	[61] [66, 67]
$\Delta Q/H_0$	40.0 35.5	84.75 79.7	146.0 141.4	223.8 220.8	318.0 315.8	I II	[61] [66, 67]

Note. I—numerical integration using a computer; II—calculation using the asymptotic equations (19) and (20).

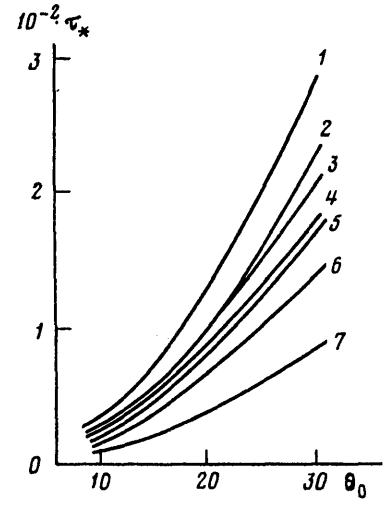


Figure 6. Dependence of the dimensionless warm-up time of a reacting substance τ_* on the parameter θ_0, calculated from various data: *1*) Ref.26, *2*) Ref.27, *3*) Ref.63, *4*) Ref.61, *5*) from Eqn.(19), *6*) Ref.45, *7*) Ref.64.

Fig.7 gives the results of the calculation, using Eqns.(20) and (22) for η_*, of the boundary conditions of the degeneration of the normal ignition conditions of nitrocellulose. Non-generate ignition conditions are produced at temperatures lying below the corresponding curves *1–3*, each of which corresponds to a definite value of the parameter a. Using Eqn.(21), Eqns.(19) can be represented in a form convenient for determining the kinetic constants, that is they can be

linearised. For example, the following expression is obtained for the warm-up time

$$\ln\left[\frac{t_*}{T_b-T_0}\right]=\frac{E}{RT_b}+\ln\left\{\frac{c}{2\pi Qk_0}\left[\frac{E(T_b-T_0)}{RT_b^2}+2\ln\left(\frac{E(T_b-T_0)}{RT_b^2}\right)\right]\right\} \quad (24)$$

Table 6. Comparison of ignition delay times calculated by different methods.

Ignition characteristic	θ_0			Method of calculation	Refs.
	10	20	30		
τ_*	25.7	86.2	181.5	I	[61]
τ_*	23.2	82.7	175.7	II	[66, 67]
τ_*^-	20.9	74.6	160.7	III	[44]
τ_*^+	28.7	97.4	203.3	III	[44]

Note: I—numerical integration using a computer; II—calculation using the asymptotic equation (19); III—calculation by the asymptotic method.

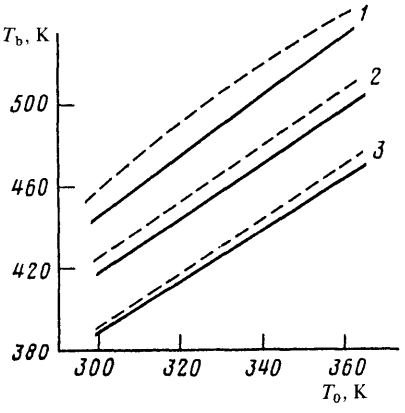


Figure 7. Conditional boundaries of the degeneration of the normal ignition conditions of nitrocellulose for values of the parameter a: *1*) 0.2; *2*) 0.15; *3*) 0.1; continuous lines—calculation using Eqn.(20), broken line—calculation using Eqn.(22).

The results of an experimental study of the ignition of nitrocellulose by a heated block with a temperature T_b = 485–515 K at a temperature of the specimens T_0 = 293–298 K have been published.[69] Fig.8 gives these results, treated by the least-squares method on the coordinates of Eqn.(24). In the treatment of the experimental data, allowance was made for the fact that under the conditions of the experiment, the quantity $(T_b-T_0)/T_b^2$ varied within a range of 5%. Assuming that the average value of this quantity is 0.816×10^{-3} K^{-1}, treatment of the experimental data[69] using Eqn.(24) gives E = 200 kJ mole^{-1} and $Qk_0 = 1.08\times10^{26}$ W kg^{-1}. Treatment of the data of the same experiment using the equation for the delay time τ_i gives the value $Qk_0 = 7.45\times10^{26}$ W kg^{-1}.

Thus the ignition criterion in the problem with boundary conditions of the first kind is the "explosion" of the temperature gradient on the surface of the substance at the moment of ignition, whereas in problems with boundary conditions of the second and third kind the criterion is the "explosion" of the actual temperature at the surface of the substance.

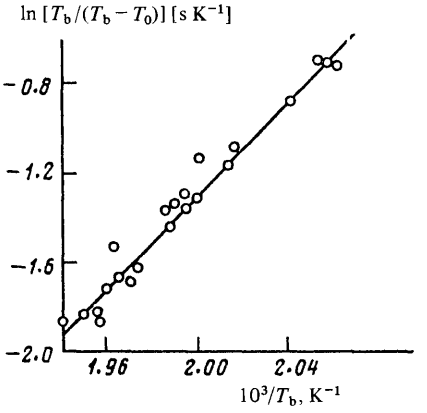


Figure 8. Determination of the thermokinetic parameters of the ignition of nitrocellulose from experimental data:[69] continuous line—calculation by the least-squares method, points—experiment.

5. The Ignition of a Semi-transparent Substance by a Beam of Radiant Energy

In the last ten years, studies of the combustibility of condensed systems using a CO_2 laser (wavelength 10.6 μm) have found extensive application in various branches of science and technology. They make it possible to carry out experiments at appreciable thermal flux densities and to take correct account of the bulk character of the absorption of light by the substance. The problem of the ignition of a semi-transparent substance by a beam of radiant energy has been studied by numerical and approximate analytical methods by many authors.[10,18,21,24,39,42,44,56,70,71] The works cited, however, give no single expression for the ignition criterion, do not indicate the ranges of existence of non-degenerate ignition conditions, and do not contain universal linear equations making it possible to solve the inverse problem of calculating the thermokinetic parameters from experimental data on the ignition of a substance by a beam of radiant energy.

The mathematical formulation of the problem with the notation given above has the form:[72]

$$T_t=\varkappa T_{xx}+Qk_0c^{-1}(1-\eta)\exp(-E/RT)+q\nu(c\rho)^{-1}\exp(-\nu x),$$
$$\eta_t=k_0(1-\eta)\exp(-E/RT);\ t=0:\ T=T_0,\ \eta=0;$$
$$x=0:\ T_x=0;\ x=\infty:\ T=T_0 \quad (25)$$

Here, q is the density of the beam of radiant energy, and ν the coefficient of bulk absorption of energy at a given wavelength.

The principal results obtained using the asymptotic theory of ignition described in Refs.72 and 73 will be given. The parameter $\nu_1 = \nu\lambda T_0 q^{-1}$ is introduced, representing the ratio of the thickness of the heated layer to the thickness of the absorption zone. In the case where $\nu_1 \gg 1$, the ignition

criterion has a form analogous to that of Eqn.(6):

$$q=\sigma\left\{\lambda\rho Q k_0\frac{RT_*^2}{E}\exp\left(-\frac{E}{RT_*}\right)\right\}^{1/2},\quad \sigma=\left[\frac{\Phi(\alpha)}{0.65}\right]^{1/2}\theta_0^{1/4}\left[(\theta_*-1)\frac{d\theta_*}{du_*}\right]^{-1/4} \quad (26)$$

where

$$\alpha=\nu_1\varepsilon\theta_*^2,\ \Phi(\alpha)=(\alpha)^{1/\alpha-1}\cdot\gamma\left(\frac{1}{\alpha},\frac{1}{\alpha}\right)\exp\left(\frac{1}{\alpha}\right),$$
$$\theta_*=1+2(u_*/\pi)^{1/2}-\frac{1}{\nu_1}+\frac{1}{\nu_1}\exp(\nu_1^2u_*)\operatorname{erfc}[(\nu_1^2u_*)^{1/2}], \quad (27)$$
$$\gamma(n,m)=\int_0^m t^{n-1}\exp(-t)\,dt$$

Eqn.(26), with allowance for Eqn.(27), can be used to calculate the dimensionless ignition delay time u_*, and hence the values of θ_* and $d\theta_*/du_*$. The dimensional characteristics of the ignition are calculated from the equations

$$t_*=\left(\frac{\lambda T_0}{q}\right)^2\frac{u_*}{\varkappa},\ T_*=T_0\theta_*,\ T_i=T_*[1+0.5\theta_*\varepsilon\ln(1/\varepsilon)],$$
$$\eta_*=1.48\gamma\varepsilon^{-1/2}\cdot\theta_*\left(\frac{d\theta_*}{du_*}\right)^{-1/2}\cdot[\Phi(\alpha)]^{-1} \quad (28)$$

As $\nu_1\to\infty$, Eqns.(26) and (27) lead to the familiar result given in the section on the ignition of a non-transparent substance: $\sigma_0=1.39\,\theta_0^{1/4}$.

Eqn.(26) and the function θ_* are readily transformed to

$$\ln Z_0=\ln\left[\frac{\rho Q k_0}{0.65}\left(\frac{R\lambda}{E}\right)^{1/2}\right]-\frac{E}{RT_*} \quad (29)$$

$$Z_0=\frac{q^{3/2}[\nu y(t_*)]^{1/2}}{T_*\Phi(\alpha)},\ T_*=T_0+\frac{q}{\nu\lambda}\left[y(t_*)+2\left(\frac{\varkappa\nu^2t_*}{\pi}\right)^{1/2}-1\right],$$
$$y(t_*)=\exp[\varkappa\nu^2t_*]\operatorname{erfc}[(\varkappa\nu^2t_*)^{1/2}] \quad (30)$$

If the quantities T_0, q, ν, and t_* are measured experimentally Eqn.(30) can be used to calculate T_*, y, and Z_0, and, having expressed the experimentally obtained relationships on coordinates $\{\ln Z_0,\ 10^3/T_*\}$, Eqn.(29) can be used to calculate the thermokinetic constants E and Qk_0. The ignition characteristics of nitrocellulose t_* and T_* calculated from Eqns.(28) for $T_0=293$ K show good quantitative agreement with the same quantities obtained by the method used in Refs.10, 21, and 56.

For the case where $\nu_1=0$ (1), when the thicknesses of the heated layer and the absorption zone are commensurate, the function σ in the expression for the ignition criterion (26) has the form:

$$\sigma=\theta_0^{1/2}\left[(\theta_*-1)\frac{d\theta_*}{du_*}\right]^{-1/2}\exp\left[-\frac{C}{2}\bar{x}^m\right] \quad (31)$$

where

$$\bar{x}=\nu_1^2u_*=\varkappa\nu^2t_* \quad (32)$$

and the values of the constants C and m are given in Ref.72.

Eqn.(26) can be used to calculate the dimensionless delay time $\bar{x}$, and hence θ_* and $d\theta_*/du_*$ from Eqns.(27) and t_* from Eqn.(32). The temperatures T_* and T_i are then determined:

$$T_*=T_0\theta_*,\ T_i=T_*[1+0.75\,\theta_*\varepsilon\ln(1/\varepsilon)] \quad (33)$$

Eqn.(26), in which σ is given by Eqn.(31), can also be represented in the form of the universal linear equation:

$$\ln[\nu q\exp(C\bar{x}^m+\bar{x})\operatorname{erfc}(\bar{x}^{1/2})]=\ln(\rho Q k_0)-\frac{E}{RT_*} \quad (34)$$

The value of T_* is calculated from the experimental values of $\{T_0,\ q,\ \nu,\ t_*\}$ using Eqn.(30), and the left-hand side of Eqn.(34) is calculated from the value of $\bar{x}$ using Eqn.(32). By treating the experimental results by the least-squares method and using Eqn.(34) it is possible to calculate E and Qk_0. Fig.9 gives experimental data[56] on the ignition of nitrocellulose ($\nu=3\times10^4$ m^{-1}) and nitrocellulose containing 1% carbon ($\nu=6\times10^4$ m^{-1}) for $T_0=293$ K. Treatment of these data on coordinates $\{\ln Z_0,\ 10^3/T_*\}$, where $\ln Z_0$ is the left-hand side of Eqn.(34), makes it possible to calculate the thermokinetic parameters

$$E=192767\text{ J mole}^{-1},\ Qk_0=2.1\times10^{25}\text{ W kg}^{-1}$$

in good agreement with the values given in Ref.10.

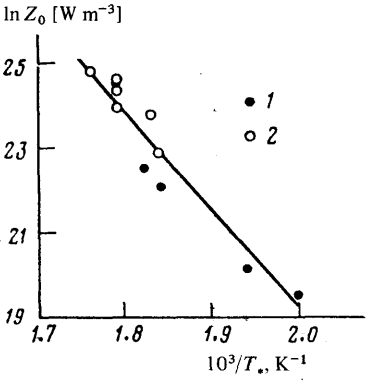


Figure 9. Determination of the thermokinetic constants of the ignition of nitrocellulose from experimental data;[56] continuous line—calculation by the least-squares method; *1, 2*) experimental points obtained for the following values of ν, m^{-1}: *1*) 3×10^4, *2*) 6×10^4.

Comparison of the results of the calculation of the ignition characteristics t_* and T_* by the asymptotic method (31)–(33) with the results in Refs.10, 21, and 56 on the whole shows good quantitative agreement and, which is particularly important, indicates that the "asymptotic" values practically coincide with the values obtained by numerical integration using a computer.[21] An exception is the method of Ref.56, where in the estimation of the scale temperature T_* no account is taken of the change in the value of ν, so that the values obtained are too high.

If the thickness of the heated layer is much less than the thickness of the absorption zone, that is for $\nu_1\ll1$, the absorption of energy in the zone of the chemical reaction is slight, and the substance heats up slowly. In this case the ignition process becomes degenerate and resembles the conditions of thermal explosion. The principal characteristics of ignition can be calculated using the equations

$$T_*=\frac{E}{R}\left[\ln\left(\frac{\rho Q k_0}{q\nu}\right)\right]^{-1},\ t_*=\frac{c\rho}{\nu q}(T_*-T_0),\ \theta_*=\frac{T_*}{T_0},$$
$$T_i=T_*[1+\theta_*\varepsilon\ln(1/\varepsilon)],\ \eta_*=\gamma\theta_*^2\ln(1/\varepsilon) \quad (35)$$

with the condition that

$$q>q_m=\rho Q k_0\nu^{-1}\exp(-E/RT_0)$$

Eqn.(35) readily gives the universal straight-line equation

$$\ln(q\nu/\rho)=\ln(Qk_0)-E/RT_*,\ T_*=T_0+\nu q t_*/c\rho \quad (36)$$

which makes it possible to treat experimental data in the range $\nu_1\ll1$ and to calculate the thermokinetic parameters for the values of T_0, q, ν, and t_* recorded in the experiment. Comparison of the results of the calculations using

Eqns.(35) and the methods of Refs.10, 21, and 56 shows that none of these methods gives satisfactory results in the range of variation in the parameter ν_1 examined. This is revealed by the excessively high value of T_*[10,21] and by the fact that T_* is completely insensitive to change in ν.[56] Only the asymptotic method[35] gives acceptable results in the range $0.009 \leq \nu_1 \leq 0.1$, confirming again the usefulness of its practical application.

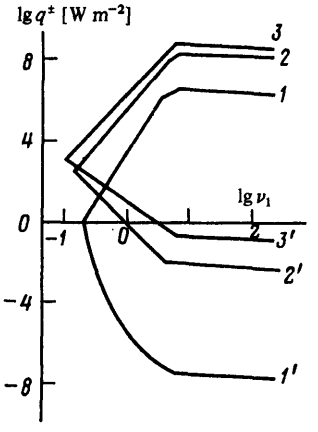


Figure 10. Ranges of existence of non-degenerate conditions for the ignition of nitrocellulose by laser radiation for T_0, K: 1,1') 223; 2,2') 293; 3,3') 323; curves 1–3 correspond to q^+, and curves 1'–3' correspond to q^-.

Fig.10 gives the ranges of existence of non-degenerate ignition conditions for nitrocellulose, calculated with allowance for the thermophysical and thermokinetic constants from Ref.10, for three values of the initial temperature T_0 for the cases $\nu_1 = 0$ (1) and $\nu_1 \gg 1$, when the thickness of the heated layer is much greater than or commensurate with the thickness of the absorption zone.[73] The ignition conditions are non-degenerate if the following condition is satisfied:

$$q^-(T_0, \nu_1) \leqslant q \leqslant q^+(T_0, \nu_1) \qquad (37)$$

For $q \gg q^+$, the thickness of the heated layer is small, and "superficial burning" of the substance is observed, and for $q \ll q^-$, the thickness of the heated layer is appreciable and ignition does not take place. In neither case does the ignition process take place in two stages, since the warm-up of the substance is accompanied by spontaneous chemical heating with an appreciable energy contribution from the chemical reaction.

III. THE IGNITION OF NON-TRANSPARENT CONDENSED SYSTEMS ON THE PULSED INTRODUCTION OF HEAT, WITH HEAT LOSSES, AND ON UNSYMMETRICAL HEATING

1. Pulse Ignition Conditions

The development of a self-accelerating reaction in a reacting substance and the formation of a sufficiently wide heated layer requires the definite action of an external energy source on the substance. If the external source acts for a limited time, then under certain conditions, ignition of the substance may not take place. Pulse ignition conditions have been studied[7,9,10,17,43,68,74] by numerical and analytical methods using the Zel'dovich criterion,[3] applicable only to the problem of the unsymmetrical ignition of a thin slab of substance by a heated block. The aim of the works cited was to determine the critical ignition conditions. A more general problem, however, is the determination of the ranges of existence of non-degenerate ignition conditions, examined above for the problems of the thermal theory, in which the continuous supply of heat from the source is assumed.

The problem of the ignition of a substance with stepwise change in the density of the thermal flux at its surface ($x = 0$) is examined below:

$$-\lambda T_x = \begin{cases} q_1, & 0 < t < t_0 \\ q_2, & t > t_0 \end{cases}$$
$$q_1 > q_2 > 0 \qquad (38)$$

This problem has been studied[75] by the method of compound asymptotic expansions[68] without introducing any of the additional conditions used in Refs.10 and 74. The ignition criterion for the pulsed introduction of heat is given by the expression:

$$q_1 q_2 = 1.5385 \varepsilon^{1/2} Q \rho k_0 \lambda T_0 \theta_* \left(\frac{d\theta_*}{du_*}\right)^{-1/2} \exp(-1/\varepsilon\theta_*) \qquad (39)$$

where

$$\theta_* = 1 = 2\pi^{-1/2}[u_*^{1/2} - A_0(u_* - u_0)^{1/2}], \quad A_0 = 1 - q_2/q_1, \quad u_0 = \varkappa t_0 (\lambda T_0/q_1)^{-2},$$
$$u_* = \varkappa t_* (\lambda T_0/q_1)^{-2}, \quad u_* > u_0 \qquad (40)$$

The calculation of the dimensionless quantity u_* and hence the calculation of the quantities θ_* and $d\theta_*/du_*$ is carried out using Eqn.(39), and the dimensional characteristics of the ignition are calculated using the equations

$$t_* = \frac{u_*}{\varkappa}\left(\frac{\lambda T_0}{q_1}\right)^2, \quad T_* = T_0\theta_*, \quad T_i = T_*[1 + 0.5\theta_*\varepsilon \ln(1/\varepsilon)],$$

$$\eta_* = 1.48\gamma\varepsilon^{-1/2}\frac{q_2}{q_1}\theta_*\left(\frac{d\theta_*}{du_*}\right)^{-1/2}, \quad Q_* = \frac{c\rho\lambda T_0^2}{q_1}\left[u_0 + \frac{q_2}{q_1}(u_* - u_0)\right] \qquad (41)$$

In the limiting particular case $A_0 = 0$, $q_2 = q_1$, Eqns.(39)–(41) can be used to calculate all the characteristics of ignition for the continuous action of a source with a flux density q_1.

Eqn.(39) can be represented on coordinates $\{\ln Z_0, 10^3/T_*\}$ in the form of the universal straight-line equation

$$\ln Z_0 = \ln\{1.5385 Q\rho k_0 (\pi\varkappa)^{1/4}(R\lambda/E)^{1/2}\} - \frac{E}{RT_*} \qquad (42)$$

where

$$Z_0 = \frac{q_1^{1/2} q_2 [(t_* - t_0)^{1/2} - A_0 t_*^{1/2}]^{1/2}}{T_* [t_* (t_* - t_0)]^{1/4}}, \quad T_* = T_0 + \frac{2q_1[t_*^{1/2} - A_0(t_* - t_0)^{1/2}]}{(\pi c\rho\lambda)^{1/2}} \qquad (43)$$

If the quantities T_0, t_0, t_*, q_1, q_2 are recorded experimentally, it is possible using the least-squares method in the coordinates indicated to carry out the treatment of the experimental data and to calculate the parameters E and Qk_0. In the particular case $A_0 = 0$, $q_2 = q_1$, Eqns.(43) become

$$Z_0 = q_1^{1/2} T_*^{-1} t_*^{-1/4}, \quad T_* = T_0 + 2q_1(t_*/\pi c\rho\lambda)^{1/2}$$

The range of existence of non-degenerate pulse ignition conditions is given by the inequalities[75]

$$t_0^-(q_1, q_2, T_0) < t_0 < t_0^+(q_1, q_2, T_0) \qquad (44)$$

and the switch-over time t_0 is shorter than the ignition delay time $t_*(q_1)$ with continuous action of a source with an energy flux density q_1. Fig.11 illustrates the change in the ranges of the non-degenerate ignition conditions of nitrocellulose

for $T = 300$ K in the range of values $q_1 = 10^4-5\times10^6$ W m^{-2}, $A_0 = 0.1-0.9$ [75] (the values of the constants from Ref.10 were used).

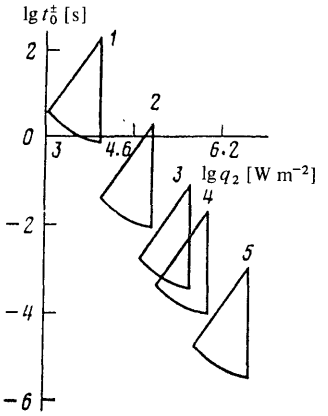


Figure 11. Ranges of existence of non-degenerate conditions for the pulse ignition of nitrocellulose for q_1, W m^{-2}: *1*) 10^4, *2*) 10^5, *3*) 5×10^5, *4*) 10^6, *5*) 5×10^6.

Analysis of the results of the calculation using Eqns.(39)–(41) shows that with decrease in the values of q_2 and t_0 from the range of existence of non-degenerate ignition conditions at a fixed value of the thermal flux density, the ignition delay time increases sharply. This corresponds to the physical picture of pulse ignition conditions.

2. The Ignition of Condensed Systems with Heat Loss from the Lateral Surface of the Specimen

The critical conditions for the ignition of non-transparent condensed substances have been studied by the thermal explosion and integral relationships methods, and approximate equations have been obtained for calculating the ignition delay time for a cylindrical specimen with heat loss from the lateral surface and boundary conditions of the second kind at the ends.[28,56,76] As shown below, however, the methods used[28,56,76] do not ensure sufficient accuracy of the determination of the ignition delay time, do not make it possible to formulate rigorously the ignition criterion, and leave open the questions of the range of existence of non-degenerate ignition conditions and the conversion of the experimental curves to straight lines in a special system of coordinates.

To solve these problems of the thermal theory of ignition, it is possible to examine the "two-dimensional" problem of the ignition of a semi-infinite cylindrical specimen of radius r_0 with heat loss into the surrounding medium, given by Newton's law

$$T_t = \varkappa[T_{xx} + r^{-1}(rT_r)_r^{\cdot}] + Qk_0c^{-1}(1-\eta)\exp(-E/RT),$$
$$\eta_t = k_0(1-\eta)\exp(-E/RT);\ t=0\colon T=T_0,\ \eta=0;$$
$$x=\infty\colon T=T_0;\ x=0\colon -\lambda T_x = q;\ r=r_0\colon -\lambda T_r = \alpha(T-T_0) \quad (45)$$

Here, x and r are the longitudinal and radial coordinates respectively, and α the coefficient of heat transfer (a constant quantity) from the lateral surface of the specimen to a surrounding medium with temperature T_0. The problem (45) was solved by averaging[77] with respect to the variable r, and the similarity criterion σ_α determined[78]

$$\sigma_\alpha = \beta\mu_0(\mathrm{Bi}),\ \beta = (\lambda T_0/qr_0)^2,\ \mathrm{Bi} = \alpha r_0/\lambda \quad (46)$$

where $\mu_0(\mathrm{Bi})$ is the function of the Biot criterion, defined and tabulated by Lykov.[79] The ignition criterion according to Ref.78 has the form

$$q = \{1.5385\varepsilon^{1/4}\rho Qk_0\lambda T_0\theta_*(d\theta_*/d\,u_*)^{-1/4}\exp(-1/\varepsilon\theta_*)\}^{1/4} \quad (47)$$

where

$$\theta_* = 1 + (\sigma_\alpha)^{-1/4}\,\mathrm{erf}\,[\tilde{x}^{1/4}],\ \frac{d\theta_*}{d\,u_*} = \left(\frac{\sigma_\alpha}{\pi\tilde{x}}\right)^{1/4}\exp(-\tilde{x}) \quad (48)$$

Solving Eqn.(47) gives the dimensionless ignition delay time $\tilde{x}$, and hence the quantities of Eqn.(48) at the moment of ignition. The dimensional characteristics of the ignition of the substance are calculated from the equations

$$T_* = T_0\theta_*,\ T_i = T_*[1 + 0.5\theta_*\varepsilon\ln(1/\varepsilon)],\ t_* = \frac{\tilde{x}}{\varkappa\sigma_\alpha}\left(\frac{\lambda T_0}{q}\right)^2,$$
$$\eta_* = 1.48\gamma\varepsilon^{-1/4}\theta_*\left(\frac{d\theta_*}{d\,u_*}\right)^{-1/4},\ Q_* = qt_* \quad (49)$$

Eqn.(47) can also be written in the form

$$\ln Z_0 = \ln\left[\frac{\rho Qk_0}{0.65}\left(\frac{R\lambda}{E}\right)^{1/4}(\pi\varkappa)^{1/4}\right] - \frac{E}{RT_*} \quad (50)$$

where

$$\tilde{x} = \varkappa t_* r_0^{-2}\mu_0(\mathrm{Bi}),\ Z_0 = q^{1/4}(T_*t_*^{1/4})^{-1}\exp(-x/2),$$
$$T_* = T_0 + qr_0[\lambda\mu_0^{1/4}(\mathrm{Bi})]^{-1}\,\mathrm{erf}\,[\tilde{x}^{1/4}] \quad (51)$$

For $\alpha = 0$, the particular case of ignition without heat loss, examined in section II, is obtained. If the values of T_0, q, α, t_*, and r_0 are recorded experimentally, Eqns.(51) can be used to calculate the values of $\tilde{x}$, T_*, and Z_0, and the least squares method in the coordinates $\{\ln Z_0,\ 10^3/T_*\}$ can be used to determine the coefficients of the linear equation (50), and then the thermokinetic parameters E and Qk_0.

The range of existence of non-degenerate ignition conditions is given by the inequalities[52]

$$\theta_*\left(\frac{d\theta_*}{d\,u_*}\right)^{-1/4} \leqslant \frac{1}{3}\varepsilon^{-1/4},\quad \theta_*\left(\frac{d\theta_*}{d\,u_*}\right)^{1/4} \leqslant \frac{1}{3}\varepsilon^{-1/4}$$

Introducing the ignition criterion (47) gives:[78]

$$q^-(T_0, \sigma_\alpha) \leqslant q \leqslant q^+(T_0, \sigma_\alpha) \quad (52)$$

The ranges of existence of the non-degenerate conditions (52) for the ignition of nitrocellulose are given in Fig.12, and Fig.13 makes it possible to compare the results of the calculation of the ignition delay time t_* from Eqns.(47)–(49) and by the methods of Refs.28 and 76 for $T_0 = 300$ K, $q = 10^4$ W m^{-2}, and $0 < \sigma_\alpha < 2$.

The delay time with heat loss can be calculated using the equation[76]

$$t_* = t_*^0[1 - 1.78t_*^0/d]^{-1},\ d = c\rho\lambda T_0^2/q^2\sigma_\alpha \quad (53)$$

where t_*^0 (without allowance for heat loss) is given by Eqns.(10). In Ref.28 the time t_* was calculated from the equation

$$t_* = d\ln[(1 - t_*^0/d)(1 - 2t_*^0/d)^{-1}] \quad (54)$$

and t_*^0 was determined from Eqns.(11). Fig.13 shows that the methods of Refs.28 and 76 give an unjustifiably high value for the ignition delay time, compared with the asymptotic method (47)–(49). This is due to the insufficient accuracy of the determination of the quantity t_*^0 (see Table 4) and the critical conditions for ignition of the substance.

The problem (45) is readily generalised to the case where there is additional heat loss due to flow over the surface being ignited in the case of conductive and convective heat exchange mechanisms.

Thus the rigorous asymptotic approach also has an appreciable advantage over published approximate methods in the analysis of the ignition of substances with heat loss.

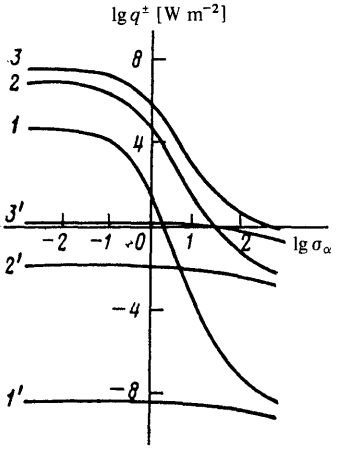


Figure 12. Ranges of existence of non-degenerate conditions for the ignition of nitrocellulose with heat loss for T_0, K: *1, 1'*) 220; *2, 2'*) 300; *3, 3'*) 340; curves *1–3* and *1'–3'* correspond to q^+ and q^- respectively.

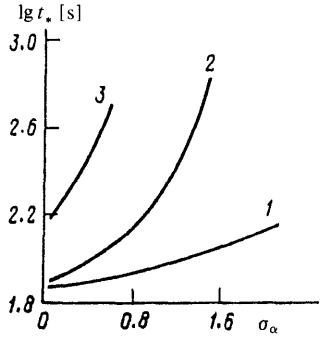


Figure 13. Calculated dependence of the ignition delay time of nitrocellulose on the parameter σ_α: *1*) calculation using Eqn.(49), *2*) calculation using the method of Ref.76, *3*) calculation using the method of Ref.28.

3. The Ignition of Substances with Unsymmetrical Heating

The theory of the ignition of a thin slab of condensed substance with thickness h, for which a constant high temperature T_1 is continuously maintained at one surface, and a low temperature T_2 at the other, has been examined.[3,61,80–82] In Refs.3 and 80, a stationary theory of ignition was developed, and an equation obtained for calculating the heat removed from the reaction zone under critical conditions. It was shown that if the heat removed is lower than a critical value, the slab ignites; otherwise, stationary heat liberation conditions are established. In Ref.61, numerical integration using a computer was used to study the dependence of the warm-up time and the ignition delay time on the parameters of the problem, and also the critical conditions of ignition. In Ref.82, the zeroth approximation of the asymptotic method was used to determine the warm-up time of a substance and to find the critical conditions for ignition. An asymptotic non-stationary theory of unsymmetrical ignition of a substance was developed in Ref.83, where the method of compound expansions was used to obtain equations for calculating the ignition delay time and the energy supplied to and stored by the substance in the warm-up period, and the critical conditions for ignition were found.

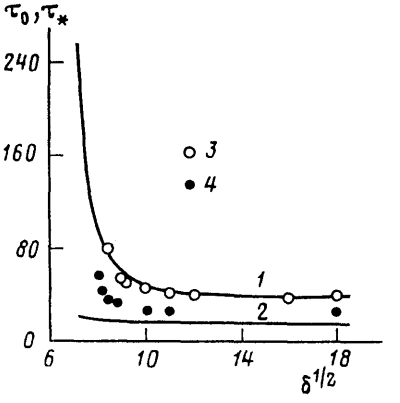


Figure 14. Calculated dependence of the dimensionless ignition delay time τ_* and the warm-up time τ_0 of a reacting substance on $\delta^{1/2}$ for unsymmetrical heating: *1*) τ_* calculated from Eqn.(55), *2*) τ_0 calculated by the method of Ref. 82; the open and black circles give the values of τ_* and τ_0 respectively, obtained by numerical integration.[61]

Fig.14 for $\varepsilon_0 = 0.1$ compares the results of the calculation of the dimensionless ignition delay time τ_* obtained in Refs. 61 and 82 with the results from Ref.83:

$$\tau_* = \delta \sum_{k=0}^{5} \varepsilon_0^{k/4} u_k(\mu),\ \mu = \varepsilon_0 \delta^{1/4},\ u_1 \equiv 0,$$
$$\varepsilon_0 = \frac{RT_1^2}{E(T_1 - T_2)},\quad \delta = \frac{E}{RT_1^2}\frac{\rho Q k_0 h^2}{\lambda}\exp(-E/RT_1) \qquad (55)$$

Curve *1*, calculated using Eqn.(55), shows good agreement with the results of the numerical integration.[61] At the same time, the values of τ_0, which were also found by numerical integration,[61] do not lie on curve *2*, obtained by the method of Ref.82. Non-degenerate ignition conditions are produced if the following condition is satisfied:[3,61,80,82,83]

$$h > h_* = \left[\frac{E}{2R}\left(\frac{T_1 - T_2}{T_1}\right)^2 \frac{\lambda}{\rho Q k_0}\exp\left(\frac{E}{RT_1}\right)\right]^{1/4} \qquad (56)$$

which with allowance for stationary heat removal from the reaction zone gives the critical value of the density of the thermal flux

$$q_* = 2^{1/4}\left[\lambda\rho Q k_0 \frac{RT_1^2}{E}\exp\left(-\frac{E}{RT_1}\right)\right]^{1/2} \qquad (57)$$

In the stationary case for $q < q_*$ the slab ignites, and when $q \geq q_*$, ignition does not take place.

The coefficient $\sigma_0 = 2^{1/2}$ from Eqn.(57) has been used[43] to find a criterion for the ignition of a semi-infinite slab by constant thermal flux. This approximation is not rigorous, as noted above (section II).

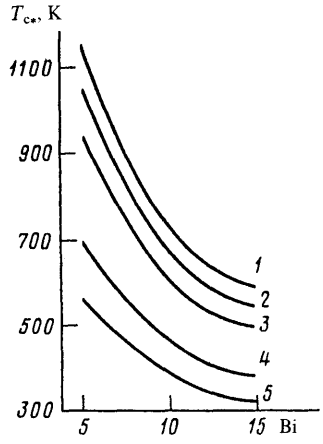


Figure 15. Ranges of existence of non-degenerate conditions for the ignition of spherical nitrocellulose particles in a stream of hot gas for T_0, K: *1*) 340, *2*) 320, *3*) 300, *4*) 250, *5*) 220.

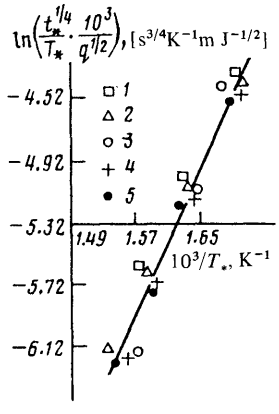


Figure 16. Determination of the thermokinetic constants for the ignition of a composite fuel from experimental data;[32] continuous straight line—calculation by the least-squares method;[87] the experimental points were obtained for T_0, K: *1*) 213, *2*) 243, *3*) 273, *4*) 303, *5*) 333.

V. THE IGNITION OF NON-TRANSPARENT SUBSTANCES IN SYMMETRICAL HEATING, AND WHEN HETEROGENEOUS REACTIONS AND MULTI-STAGE CHEMICAL REACTIONS TAKE PLACE

The asymptotic method of compound expansions makes it possible to solve the important applied problem of the ignition of lamellar, cylindrical, and spherical specimens of a substance in a stream of hot gas, to establish the ignition criterion and the range of existence of non-degenerate conditions, and to construct a universal straight line in a special system of coordinates.[84,85] Fig.15 gives the dependence of the critical temperature of the medium T_{c*} on the Biot criterion and the initial temperature of the substance T_0 for spherical particles of nitrocellulose. Ignition takes place in the regions lying above the curves with fixed values of T_0, when the temperature of the hot gas T_c is higher than the critical temperature T_{c*}(Bi). For $T_c < T_{c*}$, intermediate conditions between ignition and spontaneous ignition are produced.

An asymptotic solution has been described[86,87] for the problem of the heterogeneous-exchange ignition of a substance when a heterogeneous reaction of zeroth order takes place, and the results of studies[10,22,23,32-37] in which various approximate methods were used have been summarised. Experimental data[32] on the purely heterogeneous ignition of a composite fuel are given in Fig.16 in linearised form. The constants E and Qk_0 obtained differ considerably from those found in Ref.32.

The solution of the problem of the ignition of a substance when successive and parallel reactions take place in it is also of undoubted interest. The examination of this problem extends the theory of the influence of multi-stage chemical reactions on the regular features of the ignition process. An asymptotic analysis and analytical solution of these problems have been given.[88-90] The thermal theory of ignition has also been used to analyse the ignition of gas systems. In Ref.91, numerical integration using a computer was used to study the regular features of the ignition of gases by a heated surface when a single-stage reaction takes place and with allowance for diffusion and hydrodynamic phenomena. An asymptotic analysis made it possible to study this problem without allowance for hydrodynamic factors.[92] The most general asymptotic solution of the problem of the ignition of gases by a heated surface without allowance for hydrodynamic factors when successive two-stage and parallel N-stage reactions take place was obtained in Ref.93, which generalises the results of Ref.92 to the case of multi-stage reactions.

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The aspects of the thermal theory of ignition examined in the present review do not exhaust existing problems of the ignition of condensed systems, particularly for the case of the diffusion and hydrodynamic phenomena accompanying a multi-stage chemical reaction. The actual ignition of solid fuels is generally extremely complex, and cannot be described within a single theory of gas-phase, heterogeneous, or solid-phase ignition. Attempts are therefore now being made to develop a single theory taking account of reactions in the gas and solid phases, and also at the surface of a solid fuel.[94,95] The constructive ideas of the intermediate asymptote of a non-stationary ignition process, described in Ref. 96, may prove extremely useful in the study of these questions.

The thermal theory of ignition, in which no account is taken of the gas phase, generally does not make it possible to predict the influence of the surrounding medium. In the ranges of existence of non-degenerate conditions and at low thermal flux densities and high concentrations of oxidant in the surrounding medium, however, the inert warm-up is appreciably greater than the time of diffusion and chemical reaction, so that good quantitative agreement is obtained between the ignition delay times determined experimentally and calculated from the thermal theory.[97] The method of compound asymptotic expansions has been used successfully for the practical solution of problems of the thermal theory

of ignition. This makes possible an optimistic approach to the study of the more complex and promising problems of the ignition of condensed and gaseous reacting systems.

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