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PRESENT STATE OF THE THEORY OF THERMAL EXPLOSIONS

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I. INTRODUCTION

Studies of scientific and practical problems associated with thermal explosions have attracted considerable interest in recent years. These investigations are highly relevant not only to the development of the physics of combustion and of explosions, which includes the theory of thermal explosions as one of its subdivisions, but also to fundamental branches of knowledge such as chemical kinetics and the theory of heat transfer. The phenomenon of thermal explosion is used in the laboratory as a method of physicochemical research. Thermal explosion is the simplest among the forms of transformation of matter considered in the physics of combustion and of explosion. Therefore the formalism of the theory of thermal explosions finds application in the study of more complicated phenomena, such as the initiation of explosion by external (non-thermal) effects (impact, friction, etc.), multistage combustion, and detonation. The practical interest in thermal explosion processes arises mainly from problems of industrial safety in some types of operation with explosive systems (processing, manufacture of articles, explosive operations in high-temperature boreholes, etc.). In many cases, safe conditions excluding the possibility of spontaneous explosion can in principle be predicted, on the basis of the theory of thermal explosions.

The first quantitative formulation of the theory of thermal explosions was published in 1928 by Semenov [1], who used the simplest ideas on the evolution and extraction of heat to calculate critical conditions leading to thermal explosion, and the heating effect preceding explosion. This paper by Semenov laid the foundations for the development of the theory of thermal explosions, and stimulated numerous investigations in the 1930's, notably those of Todes, Ricę, Frank-Kamenetskii and others [2-10]. A generalised treatment of these researches, which we shall call the classical theory of thermal explosions, was given in a review by Semenov [11] and in monographs by Frank-Kamenetskii [12] and by Semenov [13].

Since gas-phase reactions were studied intensively in the investigation of chemical kinetics in the 1930's, the classical theory of thermal explosion deals mainly with gases. In later years, in connection with the great interest taken in condensed matter, systematic studies of thermal explosions in condensed media were begun. These studies contributed to the development of the general principles of the theory as well as to some specific aspects characteristic of condensed phases.

No reviews dealing with the work done since the formulation of the classical theory of thermal explosions have appeared in the literature. A few papers have been discussed [14] from the standpoint of the thermophysical aspects of the theory of thermal explosions. Thus the present review is of definite interest, since it gives an account of the present state of the theory of thermal explosions and suggests probable lines along which further development can be expected.

II. GENERALISATION AND DEVELOPMENT OF THE CLASSICAL THEORY OF THERMAL EXPLOSIONS

In the classical theory, the problem of thermal explosion is formulated as follows: given a region (or vessel) containing the reactant, knowing the kinetic laws of the evolution of heat and the mechanism of heat transfer within the region, and given the initial and boundary conditions, we are required to determine the basic parameters of the phenomenon (the critical conditions and the induction period). The actual expressions for the evolution and extraction of heat used in the classical theory are based on the simplest model of these phenomena, applicable to gaseous systems.

Generalising and making more concrete some initial premises adopted by Semenov, Frank-Kamenetskii, and

Todes, we shall formulate the essential outlines of the classical model in the following way:

1. The reaction taking place in the region under study occurs in one stage and is irreversible.

2. Heat transfer in the reaction zone occurs by conduction. There is no motion of the reacting substance, and therefore no convective heat transfer.

3. The starting material and the reaction products are in the same state of aggregation, i.e. the reaction is not accompanied by any phase transition.

4. The boundary of the region is impermeable to matter. Heat exchange at the boundary obeys Newton's law.

5. The physical parameters of the material (thermal conductivity, specific heat, density), the characteristics of the chemical reaction (activation energy, pre-exponential factor, enthalpy), and the conditions under which the reaction proceeds (pressure, temperature of the surrounding medium, shape and size of the region, emissivity) remain constant throughout the reaction.

This model, the simplest possible, has been widely applied to the study of thermal explosions in condensed as well as in gaseous media.

A mathematical statement of the problem, which satisfies the above premises, leads to the familiar equations of the classical theory

$$c\rho\frac{\partial T}{\partial t} = Q\frac{\partial \eta}{\partial t} + \lambda\left(\frac{\partial^2 T}{\partial x^2} + \frac{n}{x}\frac{\partial T}{\partial x}\right),$$

$$\frac{\partial \eta}{\partial t} = k_0 e^{-\frac{E}{RT}}\varphi(\eta).$$

Boundary conditions:

$$x = 0, \frac{\partial T}{\partial x} = 0;\ x = r, -\lambda\frac{\partial T}{\partial x} = \alpha(T - T_0).$$

Initial conditions:

$$t = 0,\ T = T_{\text{init}},\ \eta = 0.$$

We shall deal with symmetrical regions, of plane-parallel ($n = 0$), cylindrical ($n = 1$), and spherical geometry ($n = 2$).

Symbols. The following symbols will be adopted:

T temperature in the reaction zone (°K);
T_0 temperature of the surrounding medium (°K);
T_{init} initial temperature of the substance (°K);
η extent of reaction;
x spatial coordinate (cm);
r the characteristic dimension of the region (radius of the vessel)(cm);
t time (s);
Q the exothermicity of the reaction (cal cm^{-3});
E activation energy (cal mole^{-1});
k_0 pre-exponential factor (s^{-1});
λ thermal conductivity of the material (cal cm^{-1} × × s^{-1} deg^{-1});
c specific heat (cal g^{-1} deg^{-1});
ρ density (g cm^{-3});
α thermal emissivity coefficient (cal cm^{-2} s^{-1} deg^{-1}).

The function $\varphi(\eta)$ expresses the law governing the reaction under isothermal conditions:

$\varphi(\eta) \equiv 1$ for a zero-order reaction;
$\varphi(\eta) = (1 - \eta)^m$ for a reaction of order m;
$\varphi(\eta) = (\eta + \eta_0)(1 - \eta)$ for a first-order autocatalytic reaction;
η_0 the criterion for autocatalysis (ratio of initial reaction rate to autocatalytic constant).

This system of equations, when reduced to dimensionless quantities as suggested by Frank-Kamenetskii, takes the form

$$\frac{\partial\theta}{\partial\tau} = \varphi(\eta)\exp\frac{\theta}{1+\beta\theta} + \frac{1}{\delta}\left(\frac{\partial^2\theta}{\partial\xi^2} + \frac{n}{\xi}\frac{\partial\theta}{\partial\xi}\right);\ \frac{\partial\eta}{\partial\tau} = \gamma\varphi(\eta)\exp\frac{\theta}{1+\beta\theta}. \quad (1)$$

Boundary conditions:

$$\xi = 0, \frac{\partial\theta}{\partial\xi} = 0;\ \xi = 1, \frac{\partial\theta}{\partial\xi} = -\text{Bi}\cdot\theta.$$

Initial conditions:

$$\tau = 0, \theta = -\theta_{\text{init}}, \eta = 0.$$

Dimensionless variables:

$$\theta = \frac{E}{RT_0^2}(T - T_0) \text{ initial heating up,}$$

$$\xi = \frac{x}{r} \text{ coordinate,}$$

$$\tau = t\cdot\frac{Q}{c\rho}\frac{E}{RT_0^2}k_0\exp\left(-\frac{E}{RT_0}\right) \text{ time.}$$

Dimensionless parameters:

$$\delta = \frac{Q}{\lambda}\frac{E}{RT_0^2}r^2k_0\exp\left(-\frac{E}{RT_0}\right),$$

is the Frank-Kamenetskii criterion, giving the relationship between the scale factors for the supply and the dissipation of heat (the fundamental parameter in the theory of thermal explosions).

$\text{Bi} = \alpha r/\lambda$ is the familiar Biot criterion of the theory of heat transfer, which characterises the relationship between external and internal heat transfer. The case of $\text{Bi} \to \infty$ corresponds to constant surface temperature, whereas $\text{Bi} \to 0$ denotes absence of temperature gradients in the vessel under consideration.

$$\theta_{\text{init}} = \frac{E}{RT_0^2}(T_0 - T_{\text{init}}),$$

is the initial temperature excess of the surroundings, which determines the role of the heating-up stage, and

$$\beta = \frac{RT_0}{E} \text{ and } \gamma = \frac{c\rho}{Q}\frac{RT_0^2}{E},$$

are parameters which characterise the "quality" of the thermal explosion as a limiting case of reaction under non-isothermal conditions. For normal, non-degenerate régimes, $\beta \ll 1$ and $\gamma \ll 1$, and the theory of thermal explosions usually deals with the limiting cases $\beta \to 0$ and $\gamma \to 0$.

Solution of the general system of equations (1) presents great mathematical difficulties. Therefore approximate ways of approaching the problem — known as the stationary and the non-stationary theory of thermal explosions — have been developed within the classical theory. Table 1 lists some concrete examples of solutions of the equations for thermal explosions, discussed in the classical theory

TABLE 1.

Cases considered						Type of solution*	Method**	Ref.
θ_{init}	n	Bi	β	γ	$\varphi(\eta)$			
—	—	→0	β	—	1	s	a	1
—	—	0	β	γ	1—η; (1—η)²	n	a	2
$\theta_{init} \leq 0$	—	→0	β	γ	1 ; 1—η; (η+η₀)(1—η)	n	n	4,5
—	0	∞	0	—	1	s	a	9
—	1; 2	∞	0	—	1	s	n	
0	—	→0	0	γ	$(1-\eta)^n$	n	a	
—	1; 2	∞	0	—	1	s	a	25
—	0; 1	Bi	0	—	1	s	a	29,30
—	2	Bi	0	—	1	s	n	
—	0; 1; 2	∞	β	—	1	s	n	36
0	—	→0	—	—	1	n	a	32
0	—	→0	—	γ	$(1-\eta)^n$	n	a	38
0	0; 1; 2	Bi	β	γ	1 ; 1—η; (η+η₀)(1—η)	n	n	42,45
0	—	→0	0	—	(η+η₀)(1—η)	q	a	44
0	1	∞	0	—	(η+η₀)(1—η)	q	a	46
$\theta_{init}>0$	0; 1; 2	∞	β	—	1	n	n	15
$\theta_{init}>0$	0; 1; 2	Bi	β	γ	1 ; 1—η; (η+η₀)(1—η)	n	n	16—19

* s = stationary; n = non-stationary; q = quasistationary.
** a = analytic; n = numerical integration.

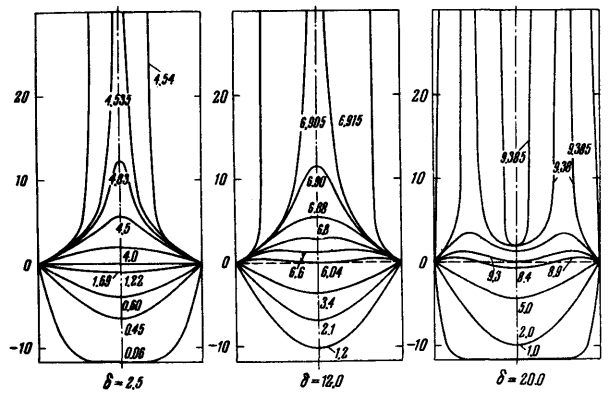


Fig. 1. Non-stationary temperature profiles during ignition with allowance for the heating-up stage [16]:
$n = 1$; $\theta_{init} = 11.7$; $\beta = 0.03$; $\gamma \to 0$. The numbers on the curves give the values of τ.

and also in more recent work. It is evident that generalisation and development of the classical theory have proceeded by making due allowance for the heating-up stage, considering the various modes of heat transfer at the surface, and elucidating the role of isothermal self-acceleration of the reaction (autocatalysis). Also, various approximate procedures have been developed within the framework of the stationary and the non-stationary theories.

We shall now briefly consider the main results of papers devoted to the generalisation and development of the classical theory.

1. Thermal Explosion as an Ignition Régime

Usually, a substance has to be heated to some definite temperature in order to achieve thermal explosion. The classical theory considers that the heating-up stage is unimportant and can be ignored.

Zinn and Mader [15] were the first to solve the thermal explosion equation with allowance for the heating-up stage, by numerical integration on an electronic computer for the case of a zero-order reaction, but they gave no general conclusions (either qualitative or quantitative). Abramov, Gontkovskaya, and one of us made some more detailed calculations [16-19], which revealed the specific effects which arise with a heating-up stage and explained the place of thermal explosions within the more general framework of ignition régimes. They also formulated the conditions under which conventional views on the role of the heating-up stage can be applied to thermal explosions.

The main conclusions of these investigations are based on an analysis of temperature distribution curves in space and time. (The most typical cases are illustrated in Fig. 1). Ignition in the presence of a heating-up stage proceeds in the following way.

In general, the heating-up of the system as a result of an exothermic reaction does not occur simultaneously throughout the volume. A temperature of T_0 is reached initially in the surface layers, and spreads to the inner layers. Temperature maxima appear close to the surface, and in time these grow and move towards the centre: in other words, a heat-evolution wave of increasing amplitude moves from the surface towards the centre of the vessel. The magnitude of the heating effect at the maximum increases faster than linearly with time, leading to ignition, which may occur either at the centre (when the heating-up wave reaches the centre, and the maxima coalesce) or at some distace from it.

This state of affairs is very sensitive to the parameter δ. At low values of δ this model degenerates, and heating-up proceeds practically simultaneously at all points in the reaction volume, so that there are no heating-up waves. As δ increases, the wave character of the heating-up stage becomes more and more distinct, and for very large values of δ the system does not heat up: ignition occurs when the central regions of the material are almost at the initial temperature.

The change in ignition régime as δ increases is conveniently observed from the change in position of the point corresponding to the onset of ignition, whose coordinate we shall denote $\xi_{expl}(\delta)$ (see Fig. 2). The plot of ξ_{expl} against δ shows two critical values of δ: (*a*) δ_{cr}, the lower limit of thermal explosion, is the value of δ which separates the ignition region from the region of non-explosive reaction (this quantity is known from the classical theory, and its value has been calculated by Frank-Kamenetskii); (*b*) δ'_{cr}, the upper limit of thermal explosion, is a value which separates two ignition régimes according to whether

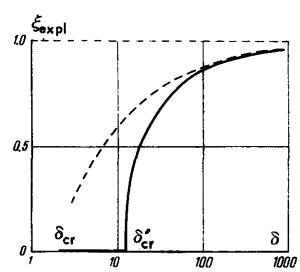


Fig. 2. Variation of ξ_{expl} with δ for the same values of the parameters as in Fig. 1. The broken line gives the limiting curve for ignition [16].

ignition sets in at the centre of not. This is essentially a new characteristic of thermal explosions, revealed by a consideration of the heating-up process — allowance for the parameter θ_{init} in the initial conditions of the system of equations (1) — and was not recognised until recently

Thus, according to the value of δ, we can distinguish the following régimes —

$\delta \ll \delta_{cr}$ the reaction proceeds isothermally (with very fast initial heating)
$\delta < \delta_{cr}$ the reaction proceeds non-isothermally, but non-explosively (with rapid heating-up and a heat-evolution stage)
$\delta_{cr} < \delta < \delta'_{cr}$ thermal explosion (self-ignition)
$\delta > \delta'_{cr}$ transition from thermal explosion to ignition
$\delta \gg \delta'_{cr}$ ignition.

We shall stress two important conclusions relating to this problem.

(*a*) Under the most favourable conditions (constant surface temperature and absence of isothermal autocatalysis) the region of thermal explosions is very narrow. It has been found[17] that the ratio δ'_{cr}/δ_{cr} is ~ 10 for a flat layer, ~ 6 for an infinite cylinder, and ~ 4 for a sphere. This corresponds to a range of about 1–2 critical diameters or a few tens of degrees. Decrease in the coefficient of heat transfer from the surface to the surrounding medium[18] and the appearance of isothermal autocatalysis[19] lead to a wider region of thermal explosion. When $Bi \to 0$, $\delta'_{cr} \to \infty$: obviously, if the system does not contain temperature gradients, ignition can occur only under the thermal explosion régime.

(*b*) Over the whole range $\delta_{cr} < \delta < \delta'_{cr}$ the overall time lag of the ignition τ_{expl} can be separated into a heating-up time τ_{heat} and an induction period τ_{ind}:

$$\tau_{expl} = \tau_{heat} + \tau_{ind},$$

the quantity τ_{ind} being almost independent of θ_{init}, i.e. of whether or not a heating-up stage is present. This separation was found to be possible even when $\tau_{heat} > \tau_{ind}$.

Thus, the framework of classical theory, which assumes $T_{init} = T_0$ ($\theta_{init} = 0$), can also be used when a heating-up stage is present, but only over a certain range of values of δ.

It is interesting to note that the formulation of the problem of thermal explosions with allowance for the heating-up stage is essentially equivalent to a general formulation of the problem in the theory of combustion, and that the equations considered in the thermal theory of ignition[20–23] for a semi-infinite space represent a limiting case of the system of equations (1) when $\delta \to \infty$. An analysis of the phenomenon close to the limiting region $\delta \to \infty$ has been made by Zel'dovich[24]. Problems in the general theory of combustion are being intensively studied at the moment by numerical integration of Eqns. (1) with the help of an electronic computer. This approach has revealed the main features of the phenomenon, and has enabled some quantitative generalisations to be made, but we still lack an approximate mathematical theory for the transition region (and in particular for calculating the value of δ'_{cr}).

2. Steady-State Theory of Thermal Explosions

The steady-state theory of thermal explosions is an approximate method for calculating the critical conditions (the δ_{cr} values) and the temperature distributions. It consists in solving the equation

$$\frac{d^2\theta}{d\xi^2} + \frac{n}{\xi}\frac{d\theta}{d\xi} = -\delta \exp\frac{\theta}{1+\beta\theta}, \qquad (2)$$

with the boundary conditions

$$\xi = 0, \ \frac{d\theta}{d\xi} = 0; \ \xi = 1, \ \frac{d\theta}{d\xi} = -Bi \cdot \theta.$$

Explosion is treated as the absence of a solution for the steady-state equation (2). The approximation arises mainly from neglect of the combustion of material which occurs during the induction period: in other words, the reaction is assumed to be of zero order.

In the classical theory, Eqn. (2) is solved in two limiting cases —

$Bi \to 0$, β arbitrary (Semenov's theory)
$Bi \to \infty$, $\beta \to 0$ (Frank-Kamenetskii's theory)

The steady-state theory has been developed further in recent years[25–31]. The most interesting achievement is the generalisation of the classical theory[29,30] for the case of an arbitrary value of the Bi parameter, which is particularly relevant to the discussion of thermal explosions in condensed media. The régime $Bi \to \infty$ (constant temperature of the walls of the vessel) usually applies to gases; condensed phases, on the other hand, can have any value of Bi, including both limiting cases and the transition region. The variation of δ_{cr} with Bi for $\beta = 0$ has been obtained in the form of a transcendental equation for the case of planar geometry, in explicit analytical form for cylindrical geometry, and by numerical integration of Eqn. (2) for spherical geometry. It has been shown[29] that for the symmetrical geometries under discussion the variation of δ_{cr} with Bi can be approximated (to an accuracy equal to or better than 10%) in the form

$$\delta_{cr} \simeq \delta_n \varphi(Bi),$$

where δ_{cr} is the critical value of the parameter δ for $Bi = \infty$, which depends on the form of the function (according to Frank-Kamenetskii's theory, $\delta_0 = 0.88$, $\delta_1 = 2.00$, $\delta_2 = 3.32$), and

$$\varphi(Bi) = \frac{Bi}{2}\left(\sqrt{Bi^2+4} - Bi\right)\exp\frac{\sqrt{Bi^2+4} - Bi - 2}{Bi}, \qquad (3)$$

is a universal parameter, independent of the form of the function.

The significance of recent researches[29,30] lies in the fact firstly that they provide means for calculating critical thermal explosion conditions in many practical cases, and secondly that they are able to unify the theories of Semenov and Frank-Kamenetskii by eliminating the apparent contradiction between their respective models of the temperature distribution in the system. This work has allowed a re-evaluation of the original and simplest theory of thermal explosions.

The rules applying to the transition from the Semenov to the Frank-Kamenetskii régime are illustrated in Figs. 3 and 4. The latter diagram is reproduced from a paper by Gray and Harper[32].

Many workers[29,31,33,34] have discussed various approximate methods for calculating the variation of δ_{cr} with Bi. The simplest of these[29] is based on Frank-Kamenetskii's

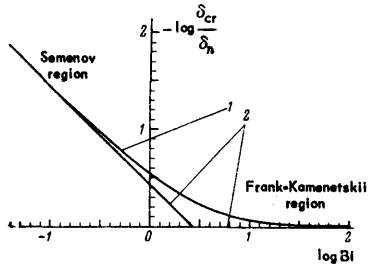


Fig. 3. 1) General form of the function φ(Bi); 2) asymptotes according to Semenov and Frank-Kamenetskii [29].

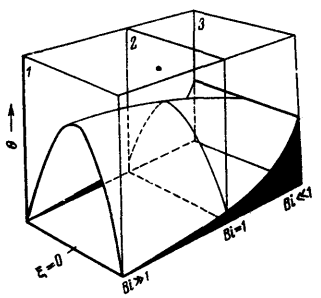


Fig. 4. Steady-state temperature distribution at the thermal explosion limit [32].

concept of an effective internal heat transmission coefficient, and on his rule for combining thermal resistances. The resulting formula

$$\frac{1}{\delta_{cr}}=\frac{1}{\delta_n}+\frac{e}{(1+n)\,\mathrm{Bi}},$$

is very convenient and gives tolerably accurate results (~ 15% in the most unfavourable case).

One of the main problems of the steady-state theory is the calculation of δ_{cr} for bodies of complicated geometrical form (the so-called geometrical problems of the theory of thermal explosions). The mathematical difficulties of the calculation, especially for three dimensional regions, are obvious. Starting from various physical and mathematical considerations, a simpler procedure for approximately calculating the critical conditions has been obtained [12,31,34]: according to this, $\delta_{cr}\simeq\mu_1^2/e$, where μ_1^2 is the first eigenvalue of the homogeneous linear equation of thermal conduction

$$\Delta\theta+\mu^2\theta=0,$$

for the region under consideration, with the appropriate boundary conditions. This method has been used [12,35] to calculate δ_{cr} for a hollow cylinder, a cylinder of finite length, a cylindrical sector, and a cube. The results have been shown to agree satisfactorily with the numerical integration of the original equation of thermal explosion. It is not yet clear, however, whether the method can be applied to the calculation of critical conditions for complicated, unsymmetrical shapes.

Analytical solutions of Eqn. (2) have been obtained for the limiting cases of $\beta\to 0$. The possibility of considering this case followed from Semenov's theory, and was put on a physical basis by Frank-Kamenetskii (the so-called Frank-Kamenetskii exponential transformation). Using Semenov's theory, and the numerical calculations of Parks [36], we can introduce corrections for the quantity β:

$$\delta_{cr}(\beta)\simeq\delta_{cr}(0)(1+\beta),\quad\theta_{cr}(\beta)\simeq\theta_{cr}(0)(1+2\beta),$$

where θ_{cr} is the initial heating preceding explosion. Hence we can estimate the error of the formulae obtained in the steady-state theory for $\beta = 0$:

$$\Delta_1=\frac{\delta_{cr}(\beta)-\delta_{cr}(0)}{\delta_{cr}(0)}\simeq\beta;\ \Delta_2=\frac{\theta_{cr}(\beta)-\theta_{cr}(0)}{\theta_{cr}(0)}\simeq 2\beta.$$

For the commonly encountered values of β, the error in the calculation of δ_{cr} is 1–5%, whilst the error in θ_{cr} is 2–10%.

3. Non-Stationary Theory of Thermal Explosions

In its classical form, the non-stationary theory of thermal explosions studies the variation with time in the heating-up of the system and in the extent of chemical reaction by analysing equations set up in terms of quantities which are averaged over the entire volume (or on the assumption that there is no temperature distribution within the reaction zone). The initial temperature is assumed equal to the temperature of the surroundings. Thus

$$\frac{d\theta}{d\tau}=\varphi(\eta)\exp\frac{\theta}{1+\beta\theta}-\frac{1}{\varkappa}\theta,$$

$$\frac{d\eta}{d\tau}=\gamma\varphi(\eta)\exp\frac{\theta}{1+\beta\theta},\qquad(4)$$

$$\tau=0,\ \theta=0,\ \eta=0,$$

where

$$\varkappa=\frac{Q}{\alpha\dfrac{S}{V}}\frac{E}{RT_0^2}k_0\exp\left(-\frac{E}{RT_0}\right),$$

is Semenov's parameter, V being the volume occupied by the reacting substance, and S the area of the heat-emitting surface.

In the non-stationary theory, explosion conditions are identified with a progressive increase in heating up. The main objective of the non-stationary theory is to study simple reactions which are not autocatalytic under isothermal conditions.

The classical non-stationary theory was developed in papers by Todes and his coworkers [2,4,5]. It gives an analytical solution of the simplest non-stationary problem (the adiabatic explosion), as well as results of the numerical integration of a set of equations of type (4), whence it is possible to analyse the development of heating-up preceding the explosion and to draw important conclusions concerning the kinetic features of the phenomenon. However, the authors used laborious manual computation and inconvenient dimensionless parameters, and were therefore unable to arrive at a satisfactory quantitative generalisation of their results.

The hope of obtaining formulae for calculating the induction period has led to a number of investigation [32,37-39], aimed mainly at an analytical solution of simplified non-stationary equations. A common feature of all these researches is the attempt to express the Arrhenius exponent in terms of a power series. In our opinion, none of these investigations has produced a computational procedure applicable to the non-stationary theory, although

several useful results have been obtained with the help of Gray and Harper's quadratic approximation.

One of the problems which concern the non-stationary theory is the displacement of the thermal explosion limit caused by the combustion of material during the induction period, i.e. the variation of δ_{cr} with γ. For normal, non-degenerate thermal explosion régimes ($\gamma < 10^{-2}$), this variation merely introduces a correction, but it becomes very significant for large values of γ (systems with a relatively small heat of reaction). The variation of δ_{cr} with γ was first calculated by Frank-Kamenetskii, who discussed the non-stationary explosion system close to the limit and showed that

$$\delta_{cr} \simeq \delta_n [1 + 1.39 (m\gamma)^{\frac{2}{3}}].$$

This formula has enjoyed wide popularity, but it has recently been pointed out [40,41] that the value of 1.39 given for the coefficient is erroneous. The correct value of this coefficient in Frank-Kamenetskii's solution is 2.7. A comparison of various reported variations of δ_{cr} as a function of γ is made in Gray and Lee's note [41].

Practically all the papers mentioned above have considered a set of equations in which the temperature distribution in the reaction zone is ignored. A detailed analysis of non-stationary solutions to the general system of equations (1) for thermal explosion régimes ($\theta_{init} = 0$) has been carried out [42] by numerical integration on an electronic computer. This work involved many calculations over a wide range of values of all the parameters, and produced results of relatively high accuracy. This enabled the authors to discuss a number of "fine effects" in the non-stationary model of thermal explosions which had not been given due prominence in the classical theory, and to put forward a quantitative generalisation of the calculated critical conditions and induction periods. Basing ourselves on that paper [42] and on earlier work, we shall note the basic features of the phenomenon revealed by an analysis of the non-stationary equations.

The theory of thermal explosions deals with two clearly distinguishable régimes, comprising reactions occurring under non-isothermal conditions with relatively little heating-up, and reactions undergoing progressive autocatalysis leading to explosion. In the model for a zero-order reaction, $\gamma \to 0$ or $\varphi(\eta) \equiv 1$, the transition from one régime to the other occurs abruptly at $\delta = \delta_{cr}$, and a maximum value of the steady-state heating-up θ_{cr} exists. When combustion of the reactant occurs, the mathematical discontinuity separating these two régimes disappears. The transition from one régime to the other becomes continuous. Continuity of the transition is conveniently demonstrated by the plot of the maximum (with respect to time) heating-up at the centre of the system θm against the parameter δ (Fig. 5).

Thus, analysis of the non-stationary equations leads to the conclusion that there are no critical conditions in the mathematical sense. Likewise, there is no heating-up preceding explosion, a characteristic introduced in the steady-state theory. It is evident from Fig. 5 that some régimes can have $\theta m > \theta_{cr}$ and yet not qualify as explosions. The width of the transition region in terms of δ depends on the value of γ: the larger γ, the wider is the transition region. By the very nature of the phenomenon, thermal explosion corresponds to a narrow transition region (usually $\gamma = 10^{-2}$–10^{-3}), and the critical conditions have a clear physical significance. At high values of γ

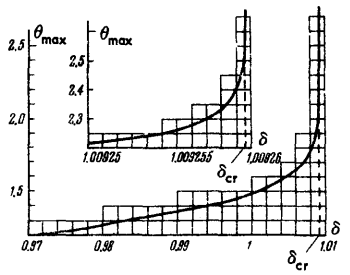


Fig. 5. Variation of the maximum heating-up of the system with the parameter δ when $n = 1$, $\theta_{init} = 0$, Bi = 2, $\beta = 0.03$, and $\gamma = 0.005$ for a first-order reaction [42]. The values of δ_{cr} and θ_m calculated from the steady-state theory are 0.95 and 1.35 respectively.

the phenomenon of thermal explosion becomes degenerate, and critical conditions become meaningless in the physical as well as in the mathematical sense. The transition from normal to degenerate régimes of thermal explosion is also continuous. If we definite the conditions for normal régimes as

$$\delta_*(\gamma) - \delta_{cr}(0) \ll \delta_{cr}(0),$$

where $d^2\theta_m(\delta_*)/d\delta^2 = 0$, we can take the quantity δ_* to be the critical value of the parameter δ in the presence of combustion.

We shall now consider the problem of determining the induction period τ_{Ind}, which has been defined [4,11,43] as the time for completion of the heating-up preceding explosion θ_{cr}. It was assumed that the time of reaction $\theta > \theta_{cr}$ is much shorter than the induction period. This definition is inaccurate, since firstly there is no pre-explosion heating-up as such, and therefore the time needed to reach θ_{cr} is not a characteristic quantity, and secondly the time during which the reaction proceeds at $\theta > \theta_{cr}$ cannot be neglected. Even in the most favourable case (under adiabatic conditions) this time amounts to ~ 30% of the total time lag [42]. As the limit is approached, this value increases rapidly and becomes greater than the time of the heating-up preceding explosion.

Surprisingly, this definition of the induction period originated from a curious error made by Todes. When analysing his calculated θ–τ curve (Fig. 5 of Ref. 4, p. 874), Todes stated in the text that the increase in heating-up from the value corresponding to θ_{cr} to the highest value ($\theta m \simeq 1/\gamma$ in our symbols) "occurs at almost constant time, i.e. practically instantaneously". This conclusion is based on a misunderstanding, and certainly does not follow from the published curve. This erroneous statement then found its way into Semenov's review [11], where it forms the basis of the definition of induction period: "The time elapsing between the beginning of the reaction and the heating-up preceding explosion is called the induction period. It is practically identical with the time between the beginning of the reaction and the explosion" (Ref. 11, p. 275). This error by Todes was pointed out to the present writers by Barzykin.

It would seem more correct to identify the induction period with the time needed to reach the maximum rate of a non-isothermal reaction [42]. This definition of the induction period gives a more accurate impression of the

time needed for the onset of explosion, and gives an insight into the transition region in terms of the time characteristic. The function $\tau_{ind}(\delta)$ has a maximum at the value of δ corresponding to δ_{cr}. As $\delta \to \delta_{cr}$ (from either side) τ_{ind} rises steeply towards its maximum value τ_{cr}.

The following empirical formulae have been derived[42] for calculating δ_{cr} and τ_{ind} for a first-order reaction, which quantitatively reflect the basic features of thermal explosions: (*a*) the critical condition

$$\delta_{cr} = \delta_n \varphi(\mathrm{Bi})(1 + 2.4\,\gamma^{1/2})(1 + \beta),$$

where $\varphi(\mathrm{Bi})$ has the form of Eqn. (3); (*b*) the induction period ($1.1 < \Delta < 10$)

$$\tau_{ind} = \tau_{av}(1 - K),$$

where

$$\tau_{av} = \left[1 + 0.62\,\frac{1 - 4\Delta^{-2}\sqrt{\gamma}}{(\Delta - 0.95)^{0.9}}\right](1 + 2\beta),$$

$$K = \frac{[1 + 1.5(1 - 0.1\,\Delta)n]\,\mathrm{Bi}}{16(1 + \mathrm{Bi})},$$

and $\Delta = \delta/\delta_{cr}$ is the relative departure from the thermal explosion limit.

The function τ_{av}, obtained by solving the system of equations (4), which disregards the temperature distribution in the reaction zone, expresses the basic variation of the induction period with Δ for different values of β and γ. The function K describes the variation in induction period resulting from geometrical shape and from heat exchange, i.e. the extra information obtained by considering the system of equations (1) in comparison with (4). The quantity K expresses the error involved in calculating the induction period from the averaged set of equations, and is essentially a criterion of the accuracy of the non-stationary theory in the classical treatment. The largest error occurs with $n = 2$, $\mathrm{Bi} = \infty$, and $\Delta \to 1$: under these conditions $K \simeq 0.23$. A small value of K (which makes averaging possible) is obtained when the heating-up of the system in the pre-explosion period is not too large. We should stress that the averaging can lead to significantly large errors when degenerate régimes are considered (β and γ relatively large) or when $\theta_{init} \neq 0$.

4. Quasistationary Theory of Thermal Explosions

The non-stationary theory is essentially the most general theory of thermal explosions, because its methods (based mainly on numerical integration) give a comprehensive picture of the phenomenon and allow calculation of all the characteristics for different reactions under different conditions. The critical conditions for thermal explosion is simple, non-autocatalytic reactions can also be determined using the approach of the steady-state theory. Thermal explosions in reactions showing isothermal autocatalysis are considered in the quasistationary theory.

The quasistationary procedure for calculating the characteristics was unknown in the classical theory. Todes and Melent'ev discussed the thermal explosion of autocatalytic reactions on the basis of numerical integration of the equations, and showed in particular that the critical condition is of the same form as for a zero-order reaction provided that the rate constant is replaced by the maximum reaction velocity under isothermal conditions. Semenov[11] suggested isothermal computation for calculating the induction period.

The quasistationary theory of thermal explosions has been developed by the present writers[44]; it is based on the specific features of autocatalytic reactions occurring under non-isothermal conditions. The quasistationary theory deals also with régimes under which the initial reaction rate does not satisfy explosion conditions. It is well known that in these circumstances an explosion can develop at high degrees of conversion. The course of the process preceding explosion in autocatalytic reactions can be envisaged[44] as involving in the initial stages on essentially non-stationary thermal régime, which continues until the initial rate of heat evolution is balanced by the heat losses. The resulting equilibrium situation then begins to be displaced by isothermal autocatalysis of the reaction, leading to an increase in the temperature of the system: thus, the higher the rate of heat evolution, the greater is the steady-state heating-up. Under this régime practically the whole of the heat evolved by the reaction is lost to the surrounding medium, the rate at which heat accumulates in the system is small compared with the rate of evolution of heat, and the heating-up increases slowly (quasi-stationarily). When the reaction rate reaches a value which satisfies the condition for explosion, the quasi-stationary régime is disturbed, and gradual autocatalysis of the reaction sets in, leading to an explosion. If, however, the maximum rate of the isothermal reaction does not satisfy the explosion condition, the reaction goes to completion under a quasistationary régime. The induction period in systems showing appreciable isothermal self-acceleration is practically equal to the time of the quasistationary stage of the reaction, and can be calculated by means of the quasistationary model.

A procedure for calculating all the basic characteristics of the thermal explosion in self-accelerating reactions has been proposed[44] involving solution of the system of equations (4) in the quasistationary approximation (in which the term $d\theta/d\tau$ is assumed to vanish), for the case of an autocatalytic first-order reaction $\varphi(\eta) = (\eta + \eta_0)(1 - \eta)$. The conditions under which a quasistationary régime can arise are also discussed, a criterion for a quasistationary reaction being obtained. The region of existence of the quasistationary régime (and therefore the applicability of the quasistationary theory) is illustrated by the $\kappa - 1/\eta_0$ diagram (Fig. 6). The boundary of the quasistationary region (the quantity κ_{qs}) is arbitrary, because the quasi-stationary régime becomes gradually degenerate as we depart from the thermal explosion limit. The value of κ_{qs} depends on γ: the smaller γ, the greater is κ_{qs}, and the wider is the region of quasistationary pre-explosion régime.

The general system of equations (1) has been integrated numerically[45] on an electronic computer for $\varphi(\eta) = (\eta + \eta_0) \cdot (1 - \eta)$ and $\theta_{init} = 0$. It is found that the "fine effects" observed in the non-stationary theory for simple reactions (continuous variation of θ_m with δ, presence of a maximum induction period close to δ_{cr}) occur also in autocatalytic reactions, but are not so clearly developed. Fig. 7 shows the non-stationary "surge" of the induction period, superimposed on the general quasistationary tendency for τ_{ind} to decrease. Since this effect is relatively small, the quantity τ_* calculated by the quasistationary theory can be identified with the induction period at the thermal explosion limit. Calculation shows that τ_{ind} at constant Δ is very insensitive to n and Bi, so that the error involved in applying the averaged system of equations (4) to autocatalytic reactions is insignificant (much less than the quantity K as calculated in the non-stationary theory). Therefore the formula obtained by Khudyaev[46] for the particular case of

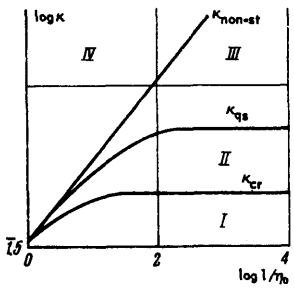


Fig. 6. Different thermal explosion régimes for an autocatalytic reaction, $\varphi(\eta) = (\eta + \eta_0)(1 - \eta)$: I) quasistationary régime below the thermal explosion limit; II) quasistationary régime below the thermal explosion limit; III) degenerate quasistationary régime; IV) effectively non-stationary reaction.

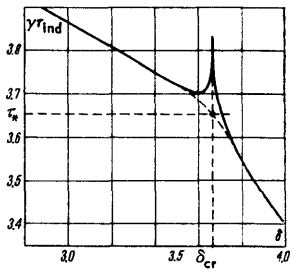


Fig. 7. Variation with δ of the induction period near the limit for $\varphi(\eta) = (\eta + \eta_0)$. $(1 - \eta)$, $n = 1$, $\eta_0 = 0.01$, $\gamma = 0.005$, $\beta = 0$, and Bi = 2.[45]

$n = 1$, Bi $\to \infty$, can be recommended for calculating the induction period of an autocatalytic first-order reaction:

$$\tau_{ind} = \frac{1}{\gamma(1+\eta_0)}\left\{\ln\frac{\sqrt{\tau_1}}{\eta_0} + \frac{1}{2}\ln\frac{(1-\eta_0)\tau_2 + \tau_3}{2} + \tau_4 - \sqrt{\Delta}\ln\frac{\sqrt{\Delta}(1-\eta_0)+\tau_2}{1+\eta_0} - \Delta\left(\frac{1}{1+\eta_0} + \frac{1}{1+\tau_1}\right)\right\}$$

$$\tau_1 = 1 \text{ for } \Delta \leqslant 1$$

$$\tau_1 = 2[\Delta - \sqrt{\Delta(\Delta-1)}] - 1 \text{ for } \Delta \geqslant 1; \quad \tau_2 = \sqrt{(1+\eta_0)^2 - 4\Delta\eta_0},$$

$$\tau_3 = (1+\eta_0)^2 - 2(\Delta+1)\eta_0; \quad \tau_4 = \frac{1}{2}\left|\sqrt{\Delta} - 1\right|\ln\left|\Delta - 1\right|.$$

At the thermal explosion limit the formula takes the simple form

$$\tau_{cr} = \frac{1}{\gamma(1+\eta_0)}\left[\ln\frac{1+\eta_0}{2\eta_0} - \frac{1-\eta_0}{2(1+\eta_0)}\right].$$

It is interesting to note that, in a simpler case than that considered by Khudyaev, not taking account of the temperature distribution in the reaction zone, τ_{ind} is expressed by a definite integral which cannot be resolved into elementary functions.

The quasistationary theory is now widely used in experimental studies of thermal explosions in condensed phases.

III. THERMAL EXPLOSION RÉGIMES NOT DESCRIBED BY THE CLASSICAL THEORY

In this Section we shall consider some thermal explosion processes whose description does not fall within the scope of the classical theory based on the simple model formulated at the beginning of this Review. These include thermal explosion régimes with applied heating or cooling, in the presence of external heat exchange by conduction, with local application of a heat pulse, etc.

1. Dynamic Thermal Explosion Régimes in the Presence of Heating and Cooling

We shall call thermal explosion régimes involving variation in the temperature T_0 of the surroundings according to a given time law "dynamic régimes", to distinguish them from the static régimes (T_0 = const) considered in the classical theory. The study of dynamic régimes is of considerable interest from many points of view, since it allows us: (1) to develop and generalise the quasistationary theory of thermal explosions, and to supplement it with an analysis of constrained quasistationary régimes involving a shift in the position of balance between the supply and the removal of heat resulting from variation in T_0; (2) to propose dynamic methods for the experimental measurement of thermal explosion characteristics (including rapid, approximate methods), which are sometimes more satisfactory than the static methods; and (3) to solve some applied problems of possible explosion under actual conditions of variation in T_0, which arise in the practical employment of explosive systems (e.g. in the application of explosives for "torpedoing" and for drilling oil-wells[47]).

A theory of thermal explosions under conditions of linearly varying T_0 (both heating and cooling) has been developed[48-51] on the basis of solving the systems of equations (1) and (4) in conjuction with the time law for the change in temperature of the surroundings

$$T_0 = T_{init} + wt,$$

(where w is the rate of change of the temperature). Two cases of particular interest were examined —

$$T_{init} \ll T_{0,cr}, \; w > 0 \text{ — heating},$$
$$T_{init} > T_{0,cr}, \; w < 0 \text{ — cooling},$$

where $T_{0,cr}$ is the critical temperature for thermal explosion under static conditions (a quantity known from the classical theory).

Under the dynamic régimes T_0 is not a constant, and it cannot therefore appear among the dimensionless parameters of the problem. The quantity $T_{0,cr}$ was found to be a convenient scale factor for the temperature. The fundamental parameter of the dynamic problem

$$\left(\omega = w\frac{E}{RT_{0,cr}^2}\frac{1}{k_0}\exp\right)\frac{E}{RT_{0,cr}},$$

is the ratio of the scale factors for reaction time and for temperature change.

This is, essentially, the dynamic analogue of the parameters proposed by Semenov and by Frank-Kamenetskii. The basic dynamic characteristic is the temperature of the surroundings at which explosion occurs (analogous to the induction period).

Let us briefly examine, on the basis of recent results[48-51], the development of explosions under conditions of heating and of cooling.

On heating, provided that $T_{init} \ll T_{0,cr}$, the system behaves at first as an inert substance, and the temperature in it develops a steady-state lag with respect to T_0. On further heating, the reaction begins to evolve heat, the lag disappears, and the temperature within the system rises above that of the surroundings. For a zero-order reaction this temperature rise in the system leads to explosion. In real systems, there is always a critical rate of heating ω_{cr}, such that when $\omega < \omega_{cr}$ the reaction goes smoothly to completion without excessive overheating, whereas when $\omega > \omega_{cr}$ an explosion occurs.

We should stress that the appearance of critical conditions on heating is fundamentally due to burning off of the material, whereas under the static régime burning off merely introduces a correction. In the neighbourhood of ω_{cr} various types of reaction show a region of quasi-stationary reaction characterised by a considerable extent of pre-explosion transformation (as with autocatalytic reactions in the static case). At large values of ω we find a transition from thermal explosion to ignition (with a clearly defined value of ω'_{cr}), which is in a qualitative sense entirely analogous to the static régime [51]. An approximate analytical procedure, based on quasistationary concepts, has been developed for the calculation of ω_{cr} and other characteristics in the neighbourhood of the limit [48,49].

The pattern of thermal explosion on cooling (when $T_{init} > T_{0,cr}$ always) depends essentially on whether the thermal self-acceleration régime at T_{init} is quasistationary or non-stationary under static conditions. If the former, the initial reaction velocity at T_{init} does not satisfy the explosion condition, and this condition may result from competition between two opposing factors — isothermal self-acceleration of the reaction and the decrease in reaction rate caused by the fall in temperature — in which conditions the extent of the pre-explosion reaction η_{expl} is always less than the extent of reaction corresponding to the maximum rate under isothermal conditions (in other words, the burning-off of material actually does not play a major part). In the second case the explosion condition is satisfied from the beginning, and the thermal balance is predetermined by the competition between the fast development of the pre-explosion process and the decrease in reaction velocity due to the fall in temperature. At high values of T_{init} an explosion invariably occurs, however high the cooling rate. A quasistationary calculation of the characteristics and a numerical integration of the system of equations (4), have been made [50] for the case of $\varphi(\eta) = (\eta + \eta_0)(1 - \eta)$. Studies under a cooling régime are very interesting from the point of view of technique, because heating the substance above the critical temperature followed by cooling allows the critical conditions for thermal explosion to be investigated with a much shorter induction period.

At the moment, the framework of the dynamic theory still lacks the unified and definitive form which characterises the classical thoey. In particular, it needs more mathematical work on the general dynamic set of equations for thermal explosion, based on explicit functions of time both in the equations themselves and in the boundary conditions. The principles needed to develop dynamic methods for studying thermal explosions, which will allow experimental investigations to be completed in a much shorter time (thus overcoming the difficulties arising from long induction periods), have not yet been formulated.

2. Thermal Explosions under Conditions of Conductive Heat Transfer in the Surrounding Medium

The solution of the problem in the classical formulation ignores heat-transfer processes in the external medium. The role of the surroundings is characterised uniquely by the boundary conditions. Yet, there are many thermal explosion régimes under which it is essential to consider the transfer of heat in the external medium. This is particularly true of systems surrounded by non-mobile media (a condensed phase in a solid block, a gas or a liquid in a thick-walled vessel, fine particles of a condensed substance in a gas or a liquid, a localised explosive impurity, etc.). To describe thermal explosions in systems of this type we must consider the equation for heat conduction in the surrounding medium as well as the system of equations for the internal region — of type (1) or of type (4) — in other words, we must solve the conjugate problem.

Grigor'ev and coworkers [52] have discussed this problem by considering the ignition of spherical particles in a hot gas, and have also made a more general study [53] of the critical thermal explosion conditions. They show, in particular, that the conjugate problem is equivalent to a boundary problem in which the conditions at the boundary of the inner region are expressed by integro-differential relations in the form of a Duhamel integral. Critical conditions have been calculated for $n = 0$, 1, and 2, and $\varphi(\eta) = 1 - \eta$, by numerical integration on an electronic computer.

Thermal explosions involving heat loss to the surroundings by conduction are shown [53] to have a number of specific features, summarised as follows:

1. The quantitative aspects of the phenomenon depend essentially on the geometry of the system. Of the three shapes which were considered, only the spherical case leads (under certain conditions) to a steady-state régime, thus allowing the approach of steady-state theory to be used. In the planar and the cylindrical geometries (excluding the limiting case of constant surface temperature) the critical conditions are determined mainly by the burning-off of the material (as in the case of linearly rising temperature).

2. The relationship between internal and external heat transfer is independent of the geometrical size of the system. It follows that the transition from the limiting case of constant temperature at the surface of the reacting substance to the limiting case of absence of temperature gradients in the reaction zone is also unaffected by the size of the system.

3. A reaction which is not autocatalytic under isothermal conditions can occur under a quasistationary régime close to the self-ignition limit during the pre-explosion period: this arises from the decrease in the effective coefficient of heat transfer from the surface of the reactant into the external medium. Hence it is possible, in principle, to develop a quasistationary theory of the phenomenon which deals with régimes under which the position of balance between heat supply and heat losses is a slowly varying function of some parameter. In autocatalytic reactions the shift in equilibrium is caused by an isothermal increase in reaction rate; under dynamic (heating) régimes it is caused by the increase in temperature of the surrounding medium; and the present case it is caused by a decrease in the effective heat-transfer coefficient. In consequence

of the quasistationary régime we find, as usual, extensive pre-explosion reaction, which is a characteristic of the present case.

Studies of thermal explosion in the present of conductive heat transfer in the external medium are still in their early stages: it is not surprising, therefore, that many of the problems have not been satisfactorily solved.

3. Localised Thermal Explosion Régimes

If, owing to special circumstances, the initial reaction in an explosive system does not proceed uniformly throughout the volume, the onset of thermal explosion can show a localised character. In the problems of explosion with a localised focus we can again distinguish (though arbitrarily) between an internal and an external region, and discuss the course of the chemical reaction in the two regions. The localised problem includes two aspects — the explosion of the local centre itself and the focal excitation of a self-propagating reaction in the medium — the former aspect being proper to the theory of explosions. We shall consider two types of focus —

1. A chemical focus, when the temperature of the focus is initially the same as that of the medium, but the kinetic parameters of the reaction are different.

2. A thermal focus, at which the temperature is higher than that of the medium, while the kinetic parameters of the reaction are the same.

The first type of focus includes cases of localised impurities of one explosive substance in another. The second type arises from external (non-thermal) influences on explosive systems.

The cases of localised explosion discussed in the literature [54-58] deal exclusively with the thermal type of focus, considered on the simplest model of a Π-shaped focus. Some workers [54,56,57] have attempted an approximate analytical calculation of the critical conditions: others [55,58] give the results of numerical solution of the equations, generalised to a dimensionless form. The basic parameters of the problem are

$$\delta = \frac{Q}{\lambda}\frac{E}{RT_0^2} r^2 k_0 \exp\left(-\frac{E}{RT_0}\right)$$ Frank-Kamenetskii's parameter,

$$\theta_0 = \frac{E}{RT_0^2}(T_0 - T_1)$$ initial temperature differential of the focus,

where T_0 is the initial temperature of the focus and T_1 is the temperature of the substance.

The critical explosion condition for the focus is of the form $\delta_{cr} = f_n(\theta_0)$. Merzhanov [58] has reviewed the work devoted to the evaluation of this function. As Table 2 shows, the approximate theories of Zinn [54], Friedman [56], and Boddington [57] lead to an incorrect form of the function $\delta_n^{init}(\theta_0)$, because they do not take into account the most essential feature of thermal explosion with a thermal focus, which is the presence of large temperature gradients in the focus. We have as yet no satisfactory approximate theory of this phenomenon.

The problem of thermal explosion of a thermal focus is of great importance to the theory, now being developed, of the sensitivity of explosive systems to external (non-thermal) influences. The expressions obtained for $\delta_{cr}(\theta_0)$ are adequate for the present level of development of the sensitivity theory and are widely used in tentative calculations of the critical size (or temperature) of the focus.

TABLE 2.

Reference		54	56	57	55, 58
General form of function $f_n(\theta_0)$		a_n	$b_n\,\theta_0$	$c_n\,\theta_0^2$	$d_n\,(\ln\theta_0)^m$
Values of the constants	$n=0$	$a_0=8$	$b_0=1$	$c_0=0.159$	$d_0=2.66$, $m_0=1.3$
	$n=1$	—	—	$c_1=0.637$	$d_1=7.39$, $m_1=0.83$
	$n=2$	$a_2=25$	—	$c_2=1.433$	$d_2=12.1$, $m_2=0.6$

4. Hydrodynamic Problems of Thermal Explosion Theory

Hydrodynamic problems arise in the discussion of thermal explosion régimes under which the reactant is in a state of motion. The two most interesting aspects of the problem are the forced flow of viscous liquids and convection in low-viscosity liquids. In the former case the main interest lies in the dissipation of the energy of motion, and two types of heat source — chemical and mechanical — have to be considered in the analysis of the thermal explosion. Nothing has yet been published on the theory of thermal explosions with mechanical sources of heat. However, a recent series of papers [59-62] has a bearing on the problem, since it deals with the so-called hydrodynamic thermal explosion. From a theoretical analysis of the flow of a chemically inert, viscous liquid under the influence of a pressure difference it is shown that under certain conditions the heat evolved by internal friction is unable to pass into the surrounding medium, and causes the temperature to rise at an increasing rate: the analogy with thermal explosions is evident. Bostandzhiyan and his coworkers [60] have calculated the critical conditions for hydrodynamic explosion, and discussed the analogy with thermal explosions of chemical origin. It is interesting to note that a hydrodynamic explosion can occur only under forced flow conditions, whereas in free flow there are always steady-state régimes with different amounts of heating-up [59,61]. The ideas and methods of the theory of hydrodynamic explosion can be useful in the analysis of the flow of a chemically reacting liquid, because in this case the basic characteristics of the phenomenon — the critical condition and the induction period — may be independent of the kinetics of the chemical reaction, being determined by hydrodynamic factors.

The second aspect of the hydrodynamic problem is concerned with the convection mechanism of heat transfer in a reacting liquid. This question has been discussed in the literature for many years, but a satisfactory solution is still lacking because serious difficulties arise in describing the process. The simplest problem (in essence not a hydrodynamic one) involving convective heat transport — that of thermal explosion in a gas stream — has been discussed by Merzhanov and Filonenko [63], and the results have been applied in the theory of the combustion of condensed phases.

IV. METHODS OF EXPERIMENTAL INVESTIGATION AND TESTS OF THE THEORY

The basic requirement of methods for the experimental study of thermal explosion processes is that the main parameters which determine the course of the reaction should be clearly defined and reproducible in successive experiments. These include the temperature of the surrounding medium, the shape and size of the vessel (or specimen), the conditions of heat exchange with the surroundings, the pressure, and the density (with condensed phases).

With gaseous systems the most commonly used methods are admission to a heated vessel and adiabatic compression. Frank-Kamenetskii's monograph[12] discusses the problems arising during experimental tests of the classical theory of thermal explosion in various gaseous mixtures.

The present writers, in collaboration with Abramov[64], proposed the use of thermal analysis for the study of thermal explosions in condensed substances, and have subsequently developed the method further[65-67]. The method consists essentially in placing the experimental substance in a cylindrical reaction vessel, heated by a thermostatically controlled heat-transfer agent, the coefficient of heat transfer to which is measured in preliminary experiments. The limiting cases of constant temperature at the inner surface of the vessel and of absence of temperature gradients in the material can be realised in various ways. Heat evolution in the material is recorded by a differential thermocouple. The results are analysed from plots of the heating effect against time, which give information on the critical conditions, subexplosive heating, induction periods, and heating times of the system. If the substance does not contain temperature gradients, the kinetic characteristics of the heat evolution can be calculated from the differential thermograms[68]. Different variants of the method have been developed (for different ranges of temperature and size, for different conditions of heat exchange with the surroundings, for static and dynamic régimes, for high pressures of an inert gas).

The thermographic method has been used in an extensive series of experimental investigations. We shall consider some of the results obtained in experimental tests of the theory in the specific case of the thermal explosion of DINA and tetryl in the liquid phase. The experimental conditions were chosen so that temperature gradients in the reaction zone were negligible[65,66]. The results of the experiment, and those of an absolute calculation based on independent kinetic[69,70] and thermophysical data, presented in Tables 3–5, illustrate the great precision of the theoretical description of the phenomenon. It is interesting to note that the critical conditions for DINA were calculated by Semenov's theory, because the experimental conditions agreed with the model assumed by Senemov. Thus, the simplest model of the thermal explosion phenomenon, proposed by Semenov and still lacking a rigid quantitative basis for the case of gases (owing to the presence of temperature distributions in the reaction volume), was first realised in a thermal decomposition in the liquid phase.

Another method[52,71] for the experimental study of thermal explosions in condensed phases uses a spherical particle of the material in a heated gas. The experiments are carried out at low Reynolds and Grashof numbers, and therefore the heat exchange between particle and gas can be characterised by the heat-transfer coefficient $\alpha = \lambda_g/r$,

TABLE 3.

d, mm	$a\frac{S}{V}$, cal cm^{-3} × × s^{-1} deg^{-1}	l/d	$T_{0,cr}$, °C		Pre-explosion heating ΔT_{cr}, deg		Experimental conditions
			calc.	expt.	calc.	expt.	
6.2	$1.4\cdot10^{-2}$	2	157	158	8.3	11	weak heat exchange with surrounding medium
8.5	$7\cdot10^{-3}$	2	152	152.5	7.95	8	
10.3	$3.1\cdot10^{-3}$	2	145	145.5	7.7	9	
10.3	$4.7\cdot10^{-3}$	1	147.5	148.5	7.8	9	
12.7	$3.5\cdot10^{-3}$	1	146	147.5	7.75	6	
32	$1.35\cdot10^{-2}$	2	160	162	8.25	9	artificial stirring of the material
36.5	$1.15\cdot10^{-2}$	2	157	159	8.15	10	
37.5	$1.05\cdot10^{-2}$	2	156	158	8.10	8	
49	$1.20\cdot10^{-2}$	2	154	153	8.05	8	
62	$1.15\cdot10^{-2}$	1	152	152	7.95	9	

TABLE 4.

d, mm	$a\frac{S}{V}$, cal cm^{-3} × × s^{-1} deg^{-1}	l/d	$T_{0,cr}$, °C		ΔT_{cr}, deg	
			calc.	expt.	calc.	expt.
6.1	$1.4\cdot10^{-2}$	2	155	151.5	9.5	8
8.4	$7.1\cdot10^{-3}$	2	149	148.5	9.4	12
8.7	$3\cdot10^{-3}$	2	140	139.5	8.9	10
11.7	$2.7\cdot10^{-3}$	2	139	139.5	8.9	9

TABLE 5.

d, mm	$T_{0,cr}$, °C	t_{cr}, min		d, mm	$T_{0,cr}$, °C	t_{cr}, min	
		calc.	expt.			calc.	expt.
6.1	151.5	70	60	8.5	143.5	170	160
8.4	148.5	100	100	11	141	225	240
9.8	148.5	100	95	8.7	139.5	275	280
8.1	148	115	110	11.7	139.5	275	300

where λ_g is the thermal conductivity of the gas and r is the radius of the particle. Under these conditions, calculation shows that temperature gradients within the particle are negligible. The thermal explosion of the particle is detected by an optical method, using the incandescence of the explosion products. The critical conditions and the total time lag before the explosion (including the heating-up stage) can be determined from these experiments. The theory of the method[52] allows adequate analysis of the experimental results. It is important to remember that flameless detonation, which cannot be observed, may occur near the limit. However, the presence of this régime can be discovered by a series of determinations of the critical conditions in different gases. The preparation of the material in the form of spherical particles often presents special problems.

We shall examine the results of a study[52], by this method, of the thermal explosion of pyroxylin. Fig. 8 shows the variation of the critical temperature as a function of particle size in air and in argon, and Fig. 9 shows the variation of the time lag with particle size and with gas temperature, expressed in dimensionless quantities.

From the critical condition the kinetic constants were evaluated, and from these the time lag was calculated. The agreement between calculated and experimental results is satisfactory.

The method based on the thermal explosion of a particle in a heated gas is of interest from the point of view of the study of ignition mechanisms at high temperatures, and of the measurement of effective kinetic parameters for rapid decompositions in condensed phases.

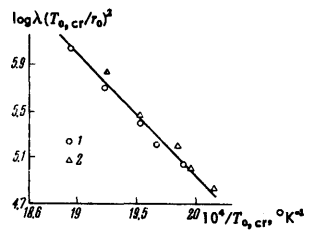


Fig.8. Critical thermal explosion condition for spherical particles of pyroxylin in a heated gas [52]: 1) air; 2) argon.

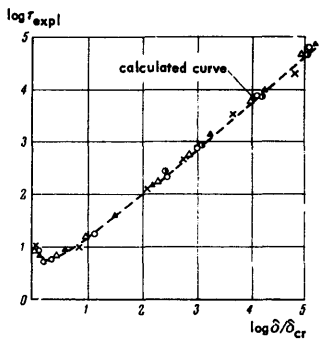


Fig. 9. Comparison of calculated (broken curve) and experimental values (points) of the time lag for the ignition of spherical particles of pyroxylin in a hot gas [52].

We shall not dwell on the other methods for the study of thermal explosions reported in the literature, because they lack proper theoretical foundations.

V. MECHANISM OF THERMAL EXPLOSION IN CONDENSED MEDIA

The very simple model of thermal explosion used as a basis for the classical theory can often be successfully applied to condensed systems. This is shown by the results of experimental investigations, some of which were discussed in the previous Section. However, thermal explosion in condensed media is, in general, a complex physicochemical reaction involving various phase transitions and associated effects in addition to chemical reaction.

We shall now briefly consider these physicochemical aspects of the mechanism of thermal explosions, and discuss the role of bulk gas evolution during thermal decomposition of a condensed material, of evaporation, of the formation of eutectics in the condensed phase, and of polymorphic transformations.

1. Effect of Bulk Gas Evolution during Decomposition on the Course of Thermal Explosion Processes

The role of bulk gas evolution depends on whether the process occurs in a solid or a liquid phase, whether it is fast or slow, and whether autocatalysis by gaseous decomposition products is possible.

One of the most interesting effects associated with gas evolution is convective heat transfer in liquid systems, resulting from the mixing effect of the bubbles of gaseous products on the reactant, and closely bound up with the rate of the chemical reaction.

The experimental work of Abramov and the present authors [64] on the critical thermal explosion conditions for molten tetryl has focussed attention on the specific features of thermal explosions in liquid media and on their relationship to the mechanism of stirring by gas bubbles. It was pointed out that:

1. The critical temperature $T_{0,cr}$ is strongly dependent on the material of the walls of the vessel: $T_{0,cr}$ is higher in a metal vessel than in a glass vessel.

2. The effective (overall) heat-transfer coefficient, calculated from the formula for the critical condition, increases with rise in temperature.

3. Pre-explosion heating-up is 3–5 times greater than the Semenov value:

$$\Delta T_{cr} = (3-5)\frac{RT_0^2}{E}.$$

4. The induction period at the thermal explosion limit is a much more sensitive function of temperature than the kinetic data suggest.

It should be stressed that this behaviour is shown by other liquids as well. In solids and gases, and also in liquids under conditions of rate limitation by external heat transfer, these observations do not apply. Merzhanov and coworkers [64] have given a qualitative explanation of these peculiarities in terms of stirring by bubbles.

Studies of the temperature field in a reacting liquid system at constant wall temperature are of considerable interest. The experimental results obtained by Barzykin and the present writers [75] indicate that in high-viscosity liquid systems the temperature profile does not differ appreciably from that in a solid (maximum heating-up at the centre and practically no heating-up close to the surface). In low-viscosity liquids a constant-temperature core appears in the reaction zone, and practically the whole of the thermal resistance of the system is concentrated in a thin boundary layer.

There is as yet no quantitative theory of thermal explosion in liquids which takes account of mixing effects, and the experimental results obtained under such conditions cannot be subjected to strict quantitative analysis. The most promising field for further studies is to acquire a fund of experimental data and to generalise it by simi-similarity methods, as is often done in the thoery of heat transfer.

Gaseous reaction products are frequently active, and capable of catalysing the reaction in progress. Under these conditions all the characteristics of the thermal explosion are strongly dependent on the conditions of removal of the gaseous products.

This dependence can be observed experimentally by controlling the escape of gaseous products through the pressure of the surrounding medium (constant-pressure bomb experiments). The most typical variation of the critical temperature $T_{0,cr}$ with pressure p is shown in Fig. 10 for a model mixture based on ammonium perchlorate (from

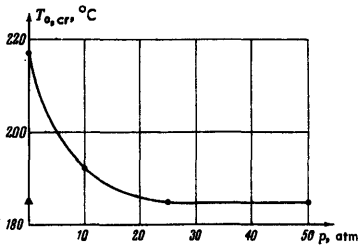


Fig. 10. Variation of critical temperature with pressure of inert gas. The solid triangle gives critical temperature in a sealed vessel without any free volume.

results obtained by Samoilenko, Abramov, and the present authors[75]). It is evident from the diagram that, as the pressure is increased, the critical temperature falls by ~ 30 deg, and thereafter stays constant. This lowering of the critical temperature occurs because the escape of gaseous reaction products is hindered by an increase in pressure, and this increases the catalytic effect of the products on the course of the reaction. The constancy of $T_{0,cr}$ at high pressures is probably due to the fact that at these pressures the gaseous products responsible for autocatalysis pass into the condensed state and cannot leave the reaction zone. It is significant that the value of $T_{0,cr}$ in the region of the plateau is the same as the value observed in a sealed vessel of the same diameter without any free volume. The gaseous reaction products cannot escape from the reaction zone in a sealed vessel, and the resulting complications are thus avoided. This is the simplest model for thermal explosions in a condensed phase: it will probably be widely applied in actual cases.

When discussing the thermal explosion of liquid explosives in open vessels, it is important to remember that the escape of gaseous reaction products produces a decrease in the reaction volume and alters its shape; this, in turn, affects both the formal kinetics of the thermal decomposition and the conditions of heat exchange between the reaction volume and the surroundings. The critical characteristics are altered because the volume occupied by the reacting system decreases a result of the escape of gaseous products, so that the concentration of the starting material and of the condensed products becomes higher than if the volume had remained unchanged. Thus, reaction velocities increase under conditions of changing volume. The conditions of heat exchange between the reaction volume and the external heat-transfer agent change because the ratio of the heat-emitting surface S to the volume of the condensed phase V is affected by the escape of gaseous products. We can distinguish two types of distortion of the model, simple shrinkage and frothing of the material. In the former case the behaviour of the system can be described mathematically[72], and expressions for the critical conditions and for the induction period of reactions of a specified type can be obtained. (These expressions are quite different from the corresponding expressions for the constant-volume case[44]). When frothing occurs the course of the reaction becomes more intermediate, and is fairly difficult to describe mathematically.

2. Thermal Explosion of Volatile Substances

The thermal explosion of substances which can evaporate has received very little attention. The literature of the 1930's and 1940's describes some experiments on the detonation of volatile substances, but the information given is inadequate for understanding the mechanism and developing a theory of the thermal explosion of volatile substances.

When analysing this phenomenon, it is important to remember that evaporation (or sublimation) in the presence of a chemical reaction in the bulk of the condensed phase, with evolution of gaseous products, follows quite a different course from evaporation in inert systems. Normally evaporation occurs from the surface of the material, and its rate is determined by the rate of diffusion of vapour in the gas phase above the surface and by the rate of supply of heat to the surface. In the case of a reacting system the rate of evaporation increases with the rate of gas evolution, because vapour is "entrained" by the mass flow of reaction products. Evaporation now becomes, as it were, a bulk process. Thus, when thermal decomposition and evaporation occur at the same time, an increase in the rate of the former process produces an increase in the rate of the latter. On the other hand, evaporation decreases the rate of the reaction, because: (1) evaporation consumes some of the starting material; (2) evaporation, being an endothermic process, absorbs a definite amount of heat. Evaporation occurring at the same time as thermal decomposition can therefore increase the induction period of the explosion and the critical temperature.

It should be noted that a given substance can behave, according to conditions, either as a volatile or as a non-volatile material. According to Belyaev[73], the determining factor is the relation between the temperature T_0, which characterises the reaction, and the boiling point T_b. If $T_0 > T_b$ or $T_0 \simeq T_b$, the evaporation is considerable, but if $T_0 \ll T_b$ the material behaves as though it were non-volatile. When $T_0 > T_b$ explosion cannot occur in the liquid phase, and the critical conditions are determined by reactions in a gas–vapour mixture.

3. Thermal Explosion of Organic Solids

Many solid organic explosives give rise to condensed decomposition products which form eutectic mixtures with the starting material. Eutectic formation, by converting some of the reactant into the liquid state, causes the reaction rate to increase, since the rate of decomposition of substances in the liquid state is higher than in the solid state.

A characteristic feature of these systems is autocatalysis of the reaction under isothermal conditions, arising from progressive dissolution of the starting material in the condensed reaction products. Solid-phase reaction is appreciable only in the initial stages of the decomposition; thereafter, the reaction occurs predominantly in the liquid phase.

On the assumption that the limiting step is associated with the kinetics of decomposition (and not with the kinetics of eutectic formation), i.e. that a state of quasi-equilibrium exists between the solid and the liquid phase, the kinetic features of the process can be put in mathematical form[74]. Unfortunately, the thermal explosion of

these materials (e.g. Hexogen and tetryl with T_0 below their melting points) has not been investigated experimentally, and there are no published data which illustrate the effects arising from eutectic formation.

4. Thermal Explosion in the Presence of Polymorphic Transformations

Polymorphic transformation (and, in general, any phase transition) affects the characteristics of thermal explosions in two ways: firstly, the transition to a new modification affects the laws governing the thermal decomposition and the thermophysical properties of the material, and secondly a definite quantity of heat is adsorbed (or evolved).

From the experimental results obtained by Abramov, Samoilenko, and the writers[75] for the thermal explosion of ammonium perchlorate, the development of thermal explosion in the presence of a polymorphic transformation shows the following pattern as a fuction of the relation between the experimental temperature T_0 and the phase transition temperature T_*:

1. $T_* < T_0$. The phase transition occurs during the heating-up stage, and its influence of the characteristics of the thermal explosion is not large.

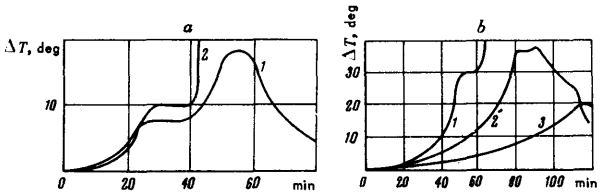


Fig. 11. Heating curves of ammonium perchlorate for different values of r (cm) and T_0:
a) 1) 1, 232°; 2) 1.25, 230°;
b) 1) 1.5, 212°; 2) 1.5, 206°; 3) 1.5, 202°.

2. $T_* - T_0 < RT_0^2/E$. The phase transition occurs during the pre-explosion period. The heat evolved in the reaction initially heats the material to T_*, and then is adsorbed by the phase transition. The critical conditions are determined, ultimately, by the reaction in the new phase (Fig. 11*a*).

3. $T_* - T_0 > RT_0^2/E$. The phase transition temperature is now reached during the substantially non-stationary régime; in this case the critical conditions are determined by the reaction in the old phase. It can happen, however, that the phase transition may halt the development of explosion: in this case the critical conditions are affected by the parameters of the phase transition (Fig. 11*b*), and the process is characterised by abnormally high pre-explosion heating-up.

A description of a process involving simultaneous chemical reaction and phase transition is of great theoretical interest, because the evolution of heat in the old phase makes methods of calculation based on Stefan's problem inapplicable.

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The theory of thermal explosions has undergone very important modification since it was first put forward. Present-day theory deals with a wide range of problems, differing in their physical content and practical importance. The development of the theory has been influenced by the overwhelming practical interest in condensed materials, which not only generated a number of specific problems but also brought about the solution of more general problems. Recent advances in computational techniques have contributed very significantly to the development of the theory. The solutions of the basic equations of thermal explosion in their general form, using numerical integration on fast electronic computers, has not only extended the computational equipment of the theory but also contributed to our understanding of the mechanism of the phenomenon. The theory of thermal explosions in its classical formulation has now been worked out in detail in its main aspects, and has been given a definitive form. More complicated thermal explosion régimes, particularly in the presence of physicochemical and hydrodynamic processes accompanying the chemical reaction, have not been adequately investigated, and their study is of the greatest interest in the further development of the theory of thermal explosions.

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FREE RADICALS AND CHEMILUMINESCENCE

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