ON THE NONSTEADY-STATE THEORY OF THERMAL AUTOIGNITION

S. A. Kaganov

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Numerous investigations [1-7], etc. have been devoted to the phenomenon of thermal explosion, mainly to the steady-state theory: the basic problem consists in determining the critical value of the parameter.* Essentially, the steady-state theory gives an estimate of the explosion parameters if it is known beforehand that an explosion can take place. However, this theory can not take into account the effect of very important factors associated with the development of the process in time. Only the nonstationary theory can do this.

The nonsteady-state problem was first investigated by O. Todes [4] (see also [2]). In this theory the temperature at all points of the reaction vessel was assumed to be the same, and only one form of the temperature dependence (exponential) of the reaction rate was considered.

In the nonsteady-state theory proposed below, just as in [6], the functions $\varphi(T)$ (characterizing the reaction rate) are taken in a very general form (cf. [5]), and the temperature distribution in the space of the reaction vessel is taken into account. Furthermore, we go on to show how the change of concentration of the reactant in the course of the reaction may be taken into account, and some qualitative conclusions are drawn relative to the parameters that characterize explosives. These parameters can be accurately evaluated by numerical integration of the corresponding equation for a specific relation φ (T).

The exact theory of exothermic chemical reactions must take into account both the change in concentration $n(x,t)$ and the change in temperature $T(x,t)$ in space and time, where $x = \{x_1, x_2, x_3\}$. For determining T and n we have the system

$$\frac{\partial T}{\partial t} = a_1^2 \Delta T + \varphi_1(n, T), \qquad \frac{\partial n}{\partial t} = a_2^2 \Delta n + \varphi_2(n, T), \tag{1}$$

with the appropriate boundary and initial conditions. Here φ_1 (n, T) is a function characterizing the heat release, and φ_2 (n, T) is the absorption (release) of matter; φ_2 (n, T) ≤ 0 if the concentration falls and φ_2 (n, T) > 0 if it increases (for example, in the case of a chain reaction).

System (1) is extremely difficult to investigate. We can simplify the problem by assuming the concentration to be constant $\varphi_1(n, T) = \lambda\varphi(T)$; here λ is a constant characterizing the heat release [3]. Thus, the problem considered may be written:

$$\frac{\partial T}{\partial t} = a^2 \Delta T + \lambda\varphi(T) \qquad T|_{t=0} = 0, \qquad T|_{\Gamma} = 0, \tag{2}$$

where Γ is the surface bounding the vessel, which occupies the region G. The function $\varphi(T) > 0$ also increases in the interval $[0, +\infty)$. Note that if we assume that $\varphi_2(n, T) = \lambda^* \varphi^*(n)$, then Eq. (1) for n can be investigated in exactly the same way. Thus, problem (2), where n is considered in place of T, describes the development in time of a chain reaction with a single multiplying substance.

Three possibilities for the development of the reaction with time can be conceived a priori:

A. The temperature at any instant of time and at any point is finite and bounded as $t \to \infty$.

B. The temperature at any instant and at any point is finite, but increases without limit as $t \to \infty$.

C. There exists a value $t = t_\infty$ such that as $t \to t_\infty$ the temperature increases without limit in a certain part of the vessel.

Obviously, a reaction of type C corresponds to an explosion. The nature of a type B reaction is considered separately. Note, however, that as yet the steady-state theory does not distinguish between type B and type C reactions.

We shall consider instead of Eq. (2) the integral equation:

$$T(x, t) = \lambda \int_0^t dt \int_G K_G(x, \xi, t - \tau)\, \varphi[T(\xi, \tau)]\, d\xi, \tag{3}$$

* Note that in [8] an equation slightly different from the equation of the stationary theory was investigated for the first time for an arbitrary function φ (T). In this paper the conditions for the existence of a critical value of the parameter of the problem were obtained and corresponding estimates given.

where $K_G(x, \xi, t)$ is the Green function for the region G [9]. We construct the sequence of functions:

$$T_k(x, t) = \lambda \int_0^t d\tau \int_G K_G(x, \xi, t-\tau)\, \varphi[T_{k-1}(\xi, \tau)]\, d\xi$$
$$(T_0 = 0,\ k = 0, 1, 2\ldots). \tag{4}$$

It is easy to show that if Eq. (3) has a solution, then sequence (4) converges as $k \to \infty$, and vice versa. Using the ordinary method of successive approximations, it is easy to show that if the region G is sufficiently small, or λ is small, then Eq. (5) has a solution that is bounded over the entire interval of variation of time. This implies that in vessels of small diameter, and also for small values of λ, the reaction is of type A, i.e., in these cases an explosion does not occur. Taking into account the decrease in concentration only strengthens this statement. This result may also be derived from the steady-state theory.

We shall now consider regions (vessels) of sufficiently large dimensions or large values of λ. It is not difficult to show that for any M, however large, regions G and $G' \subset G$ (or a value of λ) and a value of $t = t_1$ can be chosen such that the inequalities

$$\lambda \int_0^t d\tau \int_{G'} K_G(x, \xi, t-\tau)\, \varphi(0)\, d\xi > M \qquad (x \in G',\ t > t_1) \tag{5}$$

$$\lambda \int_{G'} K_G(x, \xi, \tau)\, d\xi > \alpha, \qquad t_1 \alpha > M \qquad (x \in G',\ \tau < t_1) \tag{6}$$

are satisfied.

For fixed values of G and G' it is possible to fulfil these inequalities by means of a sufficient increase in λ. For the case of large regions, these inequalities can be demonstrated, in view of the fact that the problem of a large region and a fixed value of λ can be reduced, by a change of scale (a change of variables of the form $y = x/l$), to the problem of some fixed region and a large value of λ (it is easy to see that λ increases as l^2). If inequalities (5), (6) are fulfilled by making λ large, then t_1 can be made very small.

We now have

$$T_1(x, t) = \lambda \int_0^t dt \int_G K_G(x, \xi, \tau)\, \varphi(0)\, d\xi > \lambda \int_0^t d\tau \int_{G'} K_G(x, \xi, \tau)\, \varphi(0)\, d\xi > M \tag{7}$$
$$(x \in G',\ t > t_1).$$

We put $t_2 = t_1[1 + 1/\varphi(2)]$; then for $t > t_2$, $x \in G'$

$$T_2(x, t) = \lambda \int_0^t d\tau \int_G K_G(x, \xi, t-\tau)\, \varphi[T_1(\xi, \tau)]\, d\xi >$$
$$> \lambda \int_{t_1}^t d\tau \int_{G'} K_G(x, \xi, \tau)\, \varphi(M)\, d\xi > \varphi(M)\, \lambda \int_0^{t-t_1} d\tau \int_{G'} K_G(x, \xi, \tau)\, d\xi >$$
$$> \varphi(M)\, \frac{\alpha t_1}{\varphi(2)} > \frac{M\varphi(M)}{\varphi(2)}. \tag{8}$$

If it is assumed that $\varphi(M)/\varphi(2) > M$, then from (8) we obtain

$$T(x, t) > M^2 \qquad (x \in G',\ t > t_2).$$

We put

$$t_3 = t_2 + \frac{t_1}{\varphi(3)} = t_1\left[1 + \frac{1}{\varphi(2)} + \frac{1}{\varphi(3)}\right].$$

By similar reasoning and assuming that $\varphi(M^2)/\varphi(3) > M^2$, we obtain

$$T_3(x, t) > M^3 \qquad (x \in G',\ t > t_3) \text{ etc.}$$

Assuming that

$$t_n = t_1\left[1 + \frac{1}{\varphi(2)} + \frac{1}{\varphi(3)} + \ldots + \frac{1}{\varphi(n)}\right]$$

we have

$$T_n(x, t) > M^n \quad (x \in G' \; t > t_n) \quad \text{for} \quad \varphi(M^{n-1})/\varphi(n) > M^{n-1}.$$

We shall assume that the integral $J = \int_1^\infty dT/\varphi(T)$ is convergent; then the series

$$1 + \frac{1}{\varphi(2)} + \frac{1}{\varphi(3)} + \ldots + \frac{1}{\varphi(n)} + \ldots$$

is convergent. We put

$$t_\infty^* = t_1\left[1 + \frac{1}{\varphi(2)} + \frac{1}{\varphi(3)} + \ldots + \frac{1}{\varphi(n)} + \ldots\right]. \tag{9}$$

Now it is easy to show, taking M > 1, that $T_n(x,t) \to \infty$ for $n \to \infty$, $t \to t_\infty^*$, and $x \in G'$. This implies that there exists a value $t = t_\infty$ such that the solution of equation (4) $T(x,t) \to \infty$ when $t \to t_\infty$, $x \in G'$. Thus, if

$$J < \infty, \qquad \frac{\varphi(M^{n-1})}{\varphi(n)} > M^{n-1}, \tag{10}$$

the latter for all values of n (or beginning with a certain value of n) and beginning with a certain value of M, in a vessel occupying a region G, for which (5) and (6) are fulfilled for the stated value of M, the reaction will be of type C. Note that the conditions (10) are fulfilled even for the function

$$\varphi(T) \sim T^{1+\varepsilon}, \quad \varphi(T) \sim T\,(\ln T)^{1+\varepsilon} \quad \text{etc.}, \qquad (\varepsilon > 0).$$

We shall now show that if the integral J is divergent, then the reaction cannot be of type C.

In fact, assuming for simplicity that the vessel is symmetrical, we find that the temperature will be a maximum at its center. At the point of maximum T, $\Delta T < 0$; then from (2) we have

$$\frac{\partial T}{\partial t} < \lambda\varphi(T), \qquad \frac{dT}{\lambda\varphi(T)} < dt, \qquad J_1(t) = \int_0^T \frac{dT}{\lambda\varphi(T)} < t.$$

Then $J(T) \to \infty$ as $T \to \infty$, and therefore $t \to \infty$. Thus, if J is divergent, then for large vessels the reaction cannot be of type C. For a function $\varphi(T) \sim T$, $\varphi(T) \sim T \ln T$, etc., the reaction cannot be of type C. If $\lim T^{-1}\varphi(T) = 0$ as $T \to \infty$, then in any case the reaction is of type A. If $\lim T^{-1}\varphi(T) > 0$ as $T \to \infty$ (including $\lim T^{-1}\varphi(T) = \infty$, $T \to \infty$) and J is divergent, then for large vessels or large values of λ the reaction is of type B.

According to the steady-state theory, for the case $\lim T^{-1}\varphi(T) > 0$ as $T \to \infty$ in vessels of large dimensions (or for large values of λ) an explosion must occur irrespective of the convergence or divergence of the integral J.

This difference is very important. Only in the case of a type C reaction can we naturally introduce the concept of an induction period and an explosion period [3, 5]. The term induction period may be applied to the interval during which the system heats up relatively slowly. The term explosion period may be applied to the interval during which the temperature increases very rapidly up to enormous values. A value t_n can be chosen somewhat conditionally for the induction period, and for the explosion period a value

$$\theta_n = t_1\left[\frac{1}{\varphi(n+1)} + \frac{1}{\varphi(n+2)} + \ldots + \right],$$

the value of n being determined by the actual conditions of the problem.

It is important to note that the induction period is determined by t_1 and by the rate of increase of the function $\varphi(T)$ at small T. As mentioned above, if λ is large, then t_1 is small and the induction period is small. Even if λ is small, an explosion can be ensured by increasing the dimensions of the vessel, but in this case t_1 is large, and the induction period may prove to be large. Thus, for a small heat release in a large vessel, an explosion may occur if the induction period is large (see [10], p. 201). It is possible that such processes actually occur: for example, development of a benign tumor into a malignant tumor [concentration interpretation of equation (2)].

The explosion period is determined from the expression

$$\frac{1}{\varphi(n+1)} + \frac{1}{\varphi(n+2)} + \ldots + \ldots,$$

i.e., by the rate of increase of the function $\varphi(T)$ at large values of T.

In the case of a type B reaction we cannot naturally introduce the above-mentioned periods characteristic of the explosion process, which gives us reason to suppose that only reactions of type C should be considered explosive. As mentioned above, steady-state theory does not distinguish between reactions of types B and C.

Below we consider the variation in the concentration n of an explosive in accordance with Eqs. (1). However, it is already worth drawing attention to the importance of the behavior of the function $\varphi(T)$ at small and large values of T in connection with the study of explosions. If φ (T) increases rapidly at small values of T, then the substance may react completely during the induction period. If φ (T) does not increase rapidly enough at large values of T, then there will not be the sharp rise in temperature in a very short period of time characteristic of an explosion.

As mentioned above, the study of chain explosions is linked with the investigation of a problem of the form (2), in which the unknown function is the concentration. It is usual to consider the case in which $\varphi(n)$ is a linear function [11, 12], etc. One of the chief problems is to find the critical size of the reactor. The corresponding result can be fomulated as follows: at supercritical reactor dimensions the reaction develops with time according to the law exp(kt) (k > 0), i.e., according to type B. Thus, the linear theory does not permit the introduction of the concept of an induction and an explosion period needed to characterize the explosive nature of the process. It is natural to suppose that in studying a chain (neutron) explosion the function $\varphi(n)$ should be assumed to satisfy conditions (10) and the above results applied. The actual form of the function $\varphi(n)$ is determined by the nature of the process.

We shall now attempt to take into account the effect of the change in concentration in the course of the reaction. For this purpose we shall consider system (1), neglecting diffusion (it can be assumed that if the concentration decreases the diffusion is insignificant).

With these assumptions, and taking a first-order reaction, we obtain

$$\frac{\partial T}{\partial t} = a^2 \Delta T + \lambda n \varphi(T), \qquad \frac{\partial n}{\partial t} = -\nu \varphi(T) n \tag{11}$$
$$T|_{t=0} = 0, \quad T|_{\Gamma} = 0, \quad n|_{t=0} = n_0 .$$

From the second equation we have

$$n = n_0 \exp\left(-\nu \int_0^t \varphi(T)\, dt\right)$$

and, substituting in the first,

$$\frac{\partial T}{\partial t} = a^2 \Delta T + \lambda n_0 \left[\exp\left(-\nu \int_0^t \varphi(T)\, dt\right]\varphi(T)\right. \tag{12}$$
$$T|_{\Gamma} = 0, \qquad T|_{t=0} = 0 .$$

This problem can be solved numerically.

Without going into a detailed investigation of Eq. (12), let us dwell, at the "physical" level, on certain properties of its solutions, using the results obtained above. As a first step in adapting the theory to the actual explosion process, we shall assume that in the second equation of the system the value of $\varphi(T)$ is constant and equal to φ (0); then $n = n_0 \exp(-\nu \varphi(0)t)$; we substitute the value of n in the first of equations (11):

$$\frac{\partial T}{\partial t} = a^2 \Delta T + \lambda n_0 \exp(-\nu \varphi(0)\, t)\, \varphi(T)$$
$$T|_{t=0} = 0, \qquad T|_{\Gamma} = 0 .$$

Hence it follows that with small initial concentrations no explosion occurs. Nor will an explosion occur if ν is large. If, however, the concentration is sufficiently large and ν is small, in a large vessel an explosion will occur, since the product $\lambda n_0 \exp(-\nu\varphi(0)t)$ up to a certain moment, sufficient for a powerful increase in temperature, will be large (it is sufficient for this, for example, that $n_0 \exp[-\nu\varphi(0)t_\infty] \approx 1$, where t_∞ is obtained from the theory without allowance for the fall in concentration).

In another extreme case the temperature T can be postulated as the parameter in the second of equations (11), then

$$n = n_0 \exp[-\nu \varphi(T)\, t]$$
$$\frac{\partial T}{\partial t} = a^2 \Delta T + \lambda n_0 \exp[-\nu \varphi(T)\, t]\, \varphi(T)$$
$$T|_{t=0} = 0, \qquad T|_{\Gamma} = 0 .$$

Similar reasoning can be followed. Very small values of ν are necessary for an explosion. The difference from the previous case consists in that the temperature cannot tend to infinity, but reaches a maximum and then falls to zero. The last equation more accurately describes the development of the real process. If the solution of this equation has a sharp and large maximum, then an explosion will actually take place. The solution of system (11) is, in a certain sense, intermediate between these extremes.

In considering problem (12), note that at small values of n_0 no explosion occurs. This follows from the results obtained above (the product $\lambda_1 = \lambda n_0 \exp\left[-\nu \int_0^t \varphi(T)\, dt\right]$ is small). It is obvious that even at large values of ν no explosion will occur.

Thus, we get the known [3] property of an explosive — the reaction rate must be very small at low temperatures.

Above we obtained the characteristic properties of explosives: large heat release, slow increase of the function $\varphi(T)$ at small values of T, very rapid increase at high values of T, low value of the number ν. This is confirmed by the experimental data [5]. It is worth noting that for explosives the ratio λ/ν must be large.

Finally, note that by combining different behaviors of $\varphi(T)$, different values of λ, and different values of ν it is possible to describe different types of exothermic processes.

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REFERENCES

1. K. K. Andreev and A. F. Belyaev, The Theory of Explosives [in Russian], Gostekhizdat, 1960.
2. F. P. Bowden and A. D. Ioffe, Fast Reactions in Solids, 1958.
3. N. N. Semenov, Certain Problems of Chemical Kinetics and Reactivity [in Russian], Izd-vo AN SSSR, 1958.
4. D. A. Frank-Kamenetskii, Diffusion and Heat Transfer in Chemical Kinetics [in Russian], Izd-vo AN SSSR, 1947.
5. I. M. Gel'fand, "Some problems in the theory of quasilinear equations," §16, Uspekhi matem. nauk, vol. 14, no. 2, 1959.
6. S. A. Kaganov, "On the steady-state theory of thermal autoignition," PMTF, no. 1, 1963.
7. S. I. Khudyaev, "Solvability criteria of Dirichlet's problem for elliptic equations," DAN SSSR, vol. 148, no. 1, 1963.
8. S. A. Kaganov, "Concerning the steady-state flow of a liquid," PMTF, no. 3, 1962.
9. A. M. Il'in, A. S. Kalashnikov, and O. A. Oleinik, "Linear equations of the parabolic type," Uspekhi matem. nauk, vol. 17, no. 3, 1962.
10. Ya. B. Zel'dovich and A. S. Kompaneets, Theory of Detonation [in Russian], Gostekhizdat, 1955.
11. A. N. Tikhonov and A. A. Samarskii, Equations of Mathematical Physics [in Russian], Gostekhizdat, Leningrad, 1951.
12. B. Davison, Neutron Transport Theory [Russian translation], Atomizdat, 1960.

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Saratov