

EFFECT OF ZONE OF CHEMICAL TRANSFORMATION
ON COMBUSTION RATE OF A CONDENSED SYSTEM

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The problem of determining in practice the effect of a zone of chemical transformation on the combustion rate is discussed. Working relations are presented and their effectiveness is demonstrated on specific examples.

While the combustion of gunpowder and explosives has been treated in a number of works [1-10], the reactions involved have been most completely treated in a theoretical scheme. Practical solutions of the problem of the effect of individual zones of chemical transformation on the combustion rate in the system have been limited to estimates of the thermal contributions of various phases - the gas phase and the condensed phase.

The present paper adopts a somewhat different approach to this problem, by means of which, for a known heat-liberation function, it is possible to determine not only the effects of the gas and condensed phases, but also, in general, the effect of any zone of transformation of given extent.

We consider the case of a steady-state exothermic reaction in a homogeneous medium. Assuming the front corresponding to the onset of reaction to be plane, we introduce a system of coordinates (axis Ox) such that the point $x = 0$ serves as the projection of the front. This case corresponds to a steady distribution in space of the values of the volume rate of heat liberation, given by some function $\Phi(x)$.

We will calculate the desired heat-flux distribution function $q(x)$ in the region $x \geq 0$. Then the heat-conduction equation can be written in the form

$$\frac{d}{dx} q(x) - \frac{c\rho u}{\lambda} q(x) + \Phi(x) = 0 \quad (1)$$

with boundary condition $x = \infty, q = 0$.

We solve Eq. (1) to give

$$q(x) = \int_x^{\infty} \exp \left[\frac{c\rho u}{\lambda} (x - \xi) \right] \Phi(\xi) d\xi. \quad (2)$$

Here we assume weak variations in c/λ [11].

In particular, at the point $x = 0$, i.e., at the front corresponding to onset of the exothermic reaction, the heat flux is

$$q(0) = \int_0^{\infty} \exp \left[\frac{c\rho u}{\lambda} (-\xi) \right] \Phi(\xi) d\xi. \quad (3)$$

This heat flux leads to an increase in temperature of the starting material in the region $x < 0$ from an initial value T_1 to some critical value T_0 at which a self-promoting exothermic reaction begins; i.e., it is consumed preliminarily by the chemical transformation proceeding at constant rate u of a layer of the starting material. Hence

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$$q(0) = c\rho u (T_0 - T_1). \quad (4)$$

Equating the expressions for $q(0)$ in Eqs. (3) and (4), we obtain

$$u = \frac{\int_0^{\infty} \exp \left[-\frac{c\rho u}{\lambda} x \right] \Phi(x) dx}{c\rho (T_0 - T_1)}, \quad (5)$$

and hence, if the thermophysical properties of the medium and the function $\Phi(x)$ are known, the combustion rate can be determined by successive approximation.

The exponential expression under the integral sign is a Green's function and can be called the influence function. This term gives a sufficiently accurate idea of its physical meaning. In fact, its value at each point determines that fraction of the heat liberated which is consumed in the preliminary heating of the starting material that ensures the onset of combustion. In other words, the numerical value at each point x is the characteristic efficiency of the reactive layer dx . This function is unity at $x = 0$ and falls steadily as x increases. This means that, as the zones of chemical transformation become ever more distant from the exothermic-reaction front, they become progressively less "useful" for propagating the flame. The rate of decrease of the influence function is larger if the rate of combustion of the k -system is higher; with increase in the heat-conduction of the medium it decreases, since heat transfer at the point $x = 0$ from more distant regions of the flame becomes possible. Some distance from the exothermic-reaction front the heat liberation has virtually no effect on the rate of combustion, since the derivative of the function $\exp[-(c\rho u/\lambda)x] \Phi(x)$ is close to zero. We denote this derivative by $F(x)$. The region inside which $F(x)$ is nonzero can be called the influence zone, following [7].

If the area of heat liberation is divided into subregions of arbitrary extent, the thermal contribution made by each subregion in preparing the starting material for reaction may be determined, i.e., the effect of the subregion on the combustion rate may be found. If the subregions are of equal extent Δx , then the subregion that has the greatest effect on the combustion rate will evidently be that in which the integral of $F(x)$ over the interval Δx has the largest value.

In the particular case of heat liberation concentrated in a narrow zone, as in Ya. B. Zel'dovich's model, the value of the exponent in the limits of the heat-liberation subregions is very close to unity, and the combustion rate is determined by the maximum heat liberation $\Phi(x)$. In fact, setting the influence function equal to unity in Eq. (5) and transforming as in [12], we obtain

$$u = \frac{\int_0^{\infty} \Phi(x) dx}{c\rho (T_0 - T_1)} \simeq \frac{\Phi_{\max} \Delta x_{\text{eff}}}{c\rho (T_0 - T_1)} = \frac{\Phi_{\max} \lambda (RT_c^2/E)}{c^2 \rho^2 u (T_0 - T_1) (T_c - T_1)}, \quad (6)$$

where Δx_{eff} is the effective width of the reaction zone; T_c is the combustion temperature; E is the activation energy. Assuming further that $T_0 - T_1 = T_c - T_1$ (this assumption holds for the case of a narrow combustion zone), we obtain Zel'dovich's expression for the combustion rate, differing from the usually quoted form by a factor $\sqrt{2}$:

$$u = \sqrt{\frac{\lambda \Phi_{\max} R T_c^2}{[c\rho (T_c - T_1)]^2 E}}.$$

It is interesting to note that the influence function is of the same form as the exponent determining the temperature profile in the preliminary-heating zone $x < 0$,

$$T(x) = T_1 + (T_0 - T_1) \exp \left[\frac{c\rho u}{\lambda} x \right]. \quad (7)$$

This agreement is not a matter of chance, but has a physical explanation. Whereas the first function expresses the efficiency of the various heat sources in the region $x > 0$ with respect to a fixed point $x = 0$, the second expresses the efficiency of a fixed source at the point $x = 0$ for various points in the region $x < 0$.

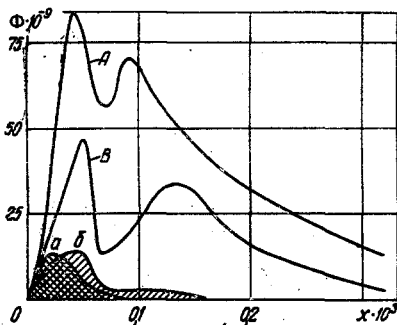


Fig. 1

Fig. 1. Distribution of total (A, B) and "useful" (a, b, respectively) heat liberation in combustion zone of nitroglycerine powder for initial temperatures +120°C (curve A) and 0°C (curve B) and pressure $19.6 \cdot 10^5 \text{ N/m}^2$, $x \cdot 10^3, \text{ m}$; $\Phi \cdot 10^{-9}, \text{ J/m}^3 \cdot \text{sec}$.

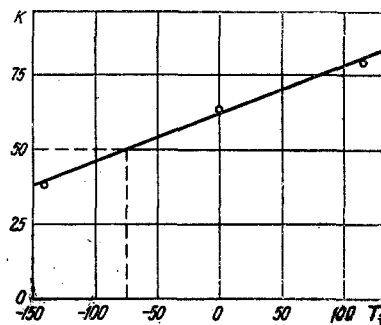


Fig. 2

Fig. 2. Effect of initial temperature on the fractional participation of the k-phase in the formation of a preheated layer in the combustion of nitroglycerine powder at a pressure of $19.6 \cdot 10^5 \text{ N/m}^2$. $T, \text{ }^\circ\text{C}$; $K, \%$.

Taking account of Eq. (7), we can write Eq. (5) in the form

$$u = \frac{\int_0^\infty [T(-x) - T_i] \Phi(x) dx}{cp(T_0 - T_i)^2} \quad (8)$$

This relation may prove useful in practice, since at present finding the function $\Phi(x)$ involves obtaining the temperature profile $T(x)$, knowledge of which in the form of an oscillogram, for example, allows the influence zone to be determined without the need to calculate values of the exponent at a large number of points.

To illustrate the practical use of Eqs. (5) or (8), we shall analyze, as an example, experimental results [13] obtained for nitroglycerine powder burning at a pressure of $19.6 \cdot 10^5 \text{ N/m}^2$ and initial temperatures of -140°C , 0°C , and $+120^\circ\text{C}$. Effective exothermic reaction is assumed to begin at a temperature $T_0 = +150^\circ\text{C}$ [14].*

In Fig. 1, graphs of the function $\Phi(x)$ are shown for two initial temperatures: $T_i = +120^\circ\text{C}$ (curve A) and $T_i = 0^\circ\text{C}$ (curve B). The graphs of $F(x)$ at the same temperatures are also shown (curves a and b, respectively). The area bounded by curves a and b (shaded) corresponds to the part of the heat consumed in the preliminary heating of the starting material. As seen from Fig. 1, "useful" heat accounts for only a small fraction of the total heat liberation (corresponding to the area bounded by the curves A and B). Direct calculation shows that the useful portion amounts to 29% for $T_i = -140^\circ\text{C}$, 8% for $T_i = 0^\circ\text{C}$, and only 1% for $T_i = +120^\circ\text{C}$.

It is also evident that the second maximum of heat liberation shows some influence on the combustion rate at $T_i = 0^\circ\text{C}$, but at $T_i = 120^\circ\text{C}$ its influence is negligible.

The extent of the influence zone is sufficiently clear in Fig. 1; $h = 0.16 \text{ mm}$ for $T_i = 0^\circ\text{C}$; $h = 0.08 \text{ mm}$ for $T_i = +120^\circ\text{C}$. For comparison, it is appropriate to give the magnitude of the influence zone determined experimentally in [7] for combustion at pressure $29.4 \cdot 10^5 \text{ N/m}^2$ in a special laminar system. The influence zone was 0.20 mm .

In Fig. 2, estimated values of the thermal contribution of the k-phase for different initial temperatures of the nitroglycerine are shown. The fractional contribution of the k-phase is denoted by K and expressed in percent. It is evident from Fig. 2 that, as the initial temperature rises, the k-phase supplies an ever larger fraction of the necessary heat. From the graph, the value of the initial temperature at which the contribution of the k-phase begins to predominate was found to be -75°C , which is in satisfactory agreement with the results of

*In [14] it was reported that, beginning at $+120^\circ\text{C}$; there was a change in state of the nitroglycerine (gas bubbles were released, the volume increased, and on cooling a porous mass was obtained), but vigorous liberation of nitrogen began only on heating to $150\text{--}160^\circ\text{C}$.

[15]. In [15] the temperature at which a discontinuity appeared in the curve of the temperature coefficient of combustion rate against the initial temperature of the material was taken as the point at which the k-phase began to predominate.

It should be noted that, according to our analysis, only two phases have an effect on the combustion rate: the condensed phase and the smoky-gas phase. The gas phase plays a negligible role, which confirms direct experiments showing little change in the powder combustion rate when the gas-phase reactions were profoundly inhibited [16].

NOTATION

c, specific heat, J/kg · deg; E, activation energy, J/mole; q, heat flux, W/m²; R, universal gas constant, J/deg · mole; T, temperature, °C; u, combustion rate, m/sec; x, coordinate, m; λ, coefficient of thermal conductivity of the medium, W/m · deg; ξ, variable of integration, m; ρ, density, kg/m³; φ, rate of volume heat liberation, J/m³ · sec. Indices: c, combustion; i, initial value; 0, critical value; eff, effective value; max, maximum value.

LITERATURE CITED

1. Ya. B. Zel'dovich, *Zh. Fiz. Khim.*, **22**, No. 1 (1948).
2. K. K. Andreev, *Thermal Decomposition and Combustion of Explosives* [in Russian], Gosénergoizdat, Moscow-Leningrad (1957).
3. A. D. Margolin, *Dokl. Akad. Nauk SSSR*, **141**, No. 5 (1961).
4. N. N. Bakhman and Yu. A. Kondrashkov, *Zh. Fiz. Khim.*, **37**, No. 1 (1963).
5. A. D. Margolin, *Zh. Fiz. Khim.*, **38**, No. 6 (1964).
6. N. N. Bakhman, *Fiz. Goreniya Vzryva*, No. 3 (1965).
7. N. N. Bakhman and A. F. Belyaev, *Combustion of Heterogeneous Condensed Systems* [in Russian], Nauka, Moscow (1967), p. 115.
8. S. S. Novikov, P. F. Pokhil, and Yu. S. Ryazantsev, *Fiz. Goreniya Vzryva*, No. 4 (1968).
9. P. F. Pokhil, *Fiz. Goreniya Vzryva*, No. 3 (1969).
10. A. K. Filonenko, *Author's Abstract of Candidate's Dissertation*, Chernogolovka (1970).
11. A. Miessner, *Heat Conduction of Solids, Liquids, Gases, and Composite Systems* [Russian translation], Mir, Moscow (1968).
12. Ya. B. Zel'dovich, *Zh. Éksp. Teor. Fiz.*, **12**, Nos. 11-12, (1942).
13. A. A. Zelin and O. I. Nefedova, *Fiz. Goreniya, Vzryva*, No. 1 (1968).
14. A. I. Korotkov and O. I. Leipunskii, in: *Physics of Explosions* [in Russian], No. 2 (1953).
15. P. F. Pokhil, O. I. Nefedova, and A. D. Margolin, *Dokl. Akad. Nauk SSSR*, **145**, No. 4 (1962).
16. A. G. Merzhanov and A. K. Filonenko, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, No. 3 (1963).