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Abstract

Full Text

Physical Chemistry

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ON THE LEADING STAGE OF COMBUSTION

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According to modern views, the combustion of powders and explosives proceeds in several spatial stages ($^{1-6}$). In the general case the combustion rate of a system depends on the interaction of all stages of combustion. But in a number of cases some one stage of combustion determines the rate of flame propagation throughout the system, while the remaining stages "adjust themselves" to the leading one. Identifying the leading stage is one of the fundamental problems of combustion theory. Because of the complexity of the combustion process it is expedient to consider a simplified scheme which, however, takes into account the main features of the real process.

According to the Belyaev–Zel' dovich model (^{1,2}), evaporation or gasification occurs at the surface of the burning secondary explosive, and the vapors formed burn to final products in the gas phase. The leading stage determining the combustion rate is combustion in the gas phase. The process of powder combustion is more complex. As P. F. Pokhil showed (^{3}), in the reaction layer at the surface of the condensed phase of the powder, overall exothermic reactions take place, accompanied by dispersion of a considerable part of the substance; near the powder surface there is a "cold" flame, in which the smoke-gas mixture burns to intermediate products that burn out in a second, luminous flame.

Fig. 1. Scheme of the dependence of the surface temperature of the condensed phase of the powder and the combustion temperature T_g on the initial powder temperature T_0

It will be shown here that, for different values of the parameters affecting the combustion process, the leading stage of combustion may be either combustion of the smoke-gas mixture or combustion in the reaction layer of the condensed phase; moreover, the stage of combustion in the reaction layer of the condensed phase can become leading only if reactions with heat release take place there.

For simplicity we shall consider a two-stage scheme of combustion. First let us trace how the process of combustion is affected by a change in the initial temperature. The line CED (Fig. 1) is the surface temperature of the condensed phase when the leading stage is in the gas phase. The line MEN is the temperature to which the surface of the condensed phase is heated owing to the release of heat q in the reaction layer of the condensed phase,

$$T_{MEN} = T_0 + \frac{q}{c_p}. \tag{1}$$

If combustion proceeds according to a three-stage scheme: condensed sta-

stage, the smoke-gas stage, luminous flame, then T_{g} will be the temperature attained in the combustion of the smoke-gas mixture in the second stage of burning.

The surface of the condensed phase of the powder is heated in the combustion process by the heat released in the condensed phase q, and by the heat arriving from the gas phase Δq $\left(T_{\mathrm{p}} = T_0 + \frac{q}{c_p} + \frac{\Delta q}{c_p}\right)$. The rate of combustion of the condensed phase increases sharply with an increase in the surface temperature T_{p}. In the range of initial temperatures $0 < T_0 < T_{0E}$, the leading stage of combustion is combustion in the smoke-gas phase. Regulation of the combustion rate of the condensed phase is accomplished by the heat Δq. For $T_0 > T_{0E}$ we have $\Delta q = 0$, if heat release occurs in the gas phase. The surface temperature T_{p} in the first approximation grows along the curve CEN as T_0 increases. For $T_0 > T_{0E}$, the leading stage is combustion in the reaction layer of the condensed phase. The rate of combustion of the condensed phase ($T_0 > T_{0E}$) exceeds the combustion rate of the smoke-gas mixture of the given composition; therefore either the combustion front in the gas phase will move away from the surface until it is extinguished, or the combustion process will pass into an afterburning process, whose (mass) rate is determined only by the rate of supply of the combustion products of the preceding stage.

The initial temperature T_{0E}, at which the transition of the leading role from one stage of combustion to another takes place, is determined as follows:

$$T_{0E} = T_{\mathrm{p}E} - \frac{q}{c_p}. \tag{2}$$

In the general case, at the point of intersection it may be that

$$\left(\frac{\partial T_{CED}}{\partial T_0}\right)_E \gtreqless \left(\frac{\partial T_{MEN}}{\partial T_0}\right)_E. \tag{3}$$

The leading role passes from the gas phase to the condensed phase as the initial temperature is raised if

$$\left(\frac{\partial T_{CED}}{\partial T_0}\right)_E < \left(\frac{\partial T_{MEN}}{\partial T_0}\right)_E .$$

This case was considered above (see Fig. 1). The leading role passes from the condensed stage to the gas stage at $T_0 > T_{0E}$, if

$$\left(\frac{\partial T_{CED}}{\partial T_0}\right)_E > \left(\frac{\partial T_{MEN}}{\partial T_0}\right)_E .$$

The character of the intersection of the curves CED and MEN determines the relation between the temperature coefficients of the combustion rate $\beta = (\partial \ln u / \partial T_0)_p$ at $T_0 > T_{0E}$ (index $+$) and below the point of intersection (index $-$):

$$\left(\frac{\partial u_+}{\partial T_0}\right)_E \gtreqless \left(\frac{\partial u_-}{\partial T_0}\right)_E ; \qquad \beta_+ \gtreqless \beta_- ;$$

$$\left(\frac{\partial \ln u_+}{\partial \ln T_0}\right)_E \gtreqless \left(\frac{\partial \ln u_-}{\partial \ln T_0}\right)_E \quad \text{when} \quad \left(\frac{\partial T_{CED}}{\partial T_0}\right)_E \gtreqless \left(\frac{\partial T_{MEN}}{\partial T_0}\right)_E . \qquad (4)$$

If the overall kinetics of the chemical reactions in the gas phase and in the reaction layer of the condensed phase are described by the Arrhenius law with activation energies E_g and E_p, respectively, then approximately (for $E/RT \gg 1$) formula (3) is equivalent to the expression

$$\frac{E_\mathrm{g}}{T_\mathrm{g}^2} \gtreqless \frac{E_\mathrm{p}}{T_\mathrm{p}^2}\left(1 + \frac{\partial}{\partial T_0}\frac{q}{c_p}\right) . \qquad (5)$$

Let us apply the considerations set forth to some problems in the theory of combustion. Raising T_0 of a powder above a certain level leads to a substantial increase in β [7-9]. Thus, O. I. Leipunskii and A. I. Korotkov

showed (^{9}) that raising the initial temperature of nitroglycerin powder H above $\sim 40^\circ$C leads to an increase in β by approximately a factor of 7 at atmospheric pressure. On the basis of what has been said above, one may suppose that this dependence $\beta(T_0)$ is explained by the transition, for $T_0 > T_{0E}$, of the leading role from combustion in the smoke-gas phase to combustion in the reaction layer of the condensed phase of the powder. Let us estimate the value T_{0E} from formula (2). P. F. Pokhil (^{3}) experimentally carried out flameless combustion of powder in a vacuum, which propagates steadily only due to heat release in the condensed phase, and showed that $q = 80$ cal/g, $c_p = 0.3$–0.4 cal/g $\cdot$ deg;

$T_{\mathrm{p}} \approx 300^{\circ}$. Calculation gives $T_{0E} \simeq 30$—100°, which is in qualitative agreement with the data of work (9). Assuming that for $T_0 > T_{0E}$ the leading stage of combustion is combustion in the condensed phase, we were able to find the effective activation energy of the reactions in the reaction layer of the condensed phase of the powder, equal to 25 kcal/mol, from the experimental dependence of the burning rate on T_0 (9) and formula (1). The value T_{0E} was taken from work (9), while $T_{\mathrm{p}E}$ was taken equal to 300° ($q/c_p = \mathrm{const}$).

By experimentally determining the point T_{0E} at which the curve $\beta(T_0)$ bends, at constant pressure and $T_{\mathrm{p}E}$, one can in principle find q at any pressure:

$$q = c_p(T_{\mathrm{p}E} - T_{0E}). \tag{6}$$

The theory of Ya. B. Zel' dovich (2) predicts that raising the initial temperature of a condensed explosive or of powder at constant pressure can increase the burning rate by no more than a factor of e (2.7). It is known (9) that in reality the burning rate can increase by more than a factor of 10 when the powder temperature is raised. We believe that Zel' dovich' s conclusion can be applied only below the temperature T_{0E}, when the leading combustion stage is in the gas phase. Indeed, below the point T_{0E} at which the curve $\beta(T_0)$ bends, the burning rate changes by less than a factor of e (9). The burning rate of nitroglycol changes by no more than a factor of e when the initial temperature is varied at constant pressure (7), which is consistent with what was set out above, since for nitroglycol the value of q is small, and therefore the leading combustion stage lies in the gas phase over the entire possible range of initial temperatures.

It is known that the burning rate of powder at any temperature depends on pressure. This dependence, when the leading stage is combustion in the reaction layer of the condensed phase, can probably be explained as follows. The value q and, consequently, T_{MEN} may depend on pressure; in addition, the reaction layer of the condensed phase contains gaseous products (3–5), which may also lead to a pressure dependence of the burning rate determined by processes in the reaction layer of the condensed phase,

$$u \sim p^{\nu_1} e^{-E_{\mathrm{p}}/2RT_{\mathrm{p}}(p)}, \tag{7}$$

whence we have the following expression for $\nu_{\mathrm{p}} = d\ln u/d\ln p$, when the leading stage is combustion of the condensed phase:

$$\nu_{\mathrm{p}} = \frac{p}{u}\frac{\partial u}{\partial p} + \frac{p}{u}\frac{\partial u}{\partial T_{\mathrm{p}}}\frac{dT_{\mathrm{p}}}{dp} = \nu_1 + p\frac{E_{\mathrm{p}}}{4RT_{\mathrm{p}}^2}\frac{dT_{\mathrm{p}}}{dp}, \tag{8}$$

where

$$\frac{dT_{\text{p}}}{dp} = \frac{1}{c_p}\frac{dq}{dp}.$$

The influence of pressure on the transition of the leading role from one combustion stage to another can be analyzed in the same way as the influence of temperature.

In particular, formula (4) remains valid if T_0 is everywhere replaced by p. The physical meaning of the lines CED and MEN remains the same ($T_{MEN} = T_0 + q/c_p$).

With an increase in pressure, the leading stage of combustion shifts from the gas phase to the condensed phase if $(v_{\text{p}}/v)_E > 1$ $((\partial T_{MEN}/\partial p)_E > (\partial T_{CED}/\partial p)_E)$, and from the condensed phase to the gas phase if $(v_{\text{p}}/v)_E < 1$ $((\partial T_{MEN}/\partial p)_E < (\partial T_{CED}/\partial p)_E)$.

P. F. Pokhil and V. M. Mal' tsev have shown experimentally that the specific weight of the heat released in the reaction layer of the condensed phase of nitroglycerin powder increases with increasing pressure, i.e., there is indeed a tendency for the leading role to pass to reactions in the reaction layer of the condensed phase; that is, the case $(v_{\text{p}}/v)_E > 1$ is realized; v refers to the gas phase.

The dependence of the surface temperature T_{p} on pressure, when the leading stage is in the gas phase, is approximately described (for $E/RT \gg 1$) by the formula

$$\frac{dT_{\text{p}}}{dp} = \frac{v - v_1}{p}\frac{4RT_{\text{p}}^2}{E_{\text{p}}}. \tag{9}$$

The work presented is in full agreement with the physical foundations of the theory of powder combustion formulated by P. F. Pokhil (^{3}).

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Note: Figure translations are in progress. See original paper for figures.

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