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Abstract

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On the Possible Influence of the Diffusive Flux of Reaction Products from the Flame on the Decomposition of the Condensed Phase

(Presented by Academician Ya. B. Zel' dovich, 23 VIII 1963)

In the problem of the burning rate of powder, the question of the effect of the reaction in the gas phase (the flame) on the decomposition of the condensed phase, which occurs in the heated layer adjacent to the surface of the powder and has a temperature close to the temperature at the powder surface T_p, is of substantial interest.

It is generally recognized that the g-phase (gas phase) acts on the decomposition of the k-phase (condensed phase) by supplying to it a heat flux that maintains in the decomposing k-phase the temperature T_p at which the required mass rate of decomposition is ensured.

The decomposition reaction of powder during combustion is exothermic, and therefore the heat flux from the g-phase must supply to the k-phase not the entire amount of heat needed to heat the k-phase from the initial temperature T_0 to T_p, but only a part of it, equal to K. The fraction K may be small (0.1 or less). For details, see works ([1–3]).

The purpose of the present work is to draw the attention of researchers to the possibility of another mechanism by which the g-phase acts on the rate of decomposition of the k-phase, namely, through catalysis of the decomposition reaction in the k-phase by combustion products (including active molecules) diffusing from the flame to the surface of the k-phase.

The point is that the presence of a heat flux from the flame to the k-phase automatically also means the presence of a diffusive flux of reaction products from the flame to the powder surface. It is natural to allow for the possibility of a catalytic action of this flux of molecules, or of part of this flux, consisting of active molecules, radicals, intermediate products, etc.

In work ([4]), as it seems to us, the necessity of such catalysis was demonstrated in the case of ammonium perchlorate combustion: the temperature at the surface of perchlorate burning at a rate of 3 mm/sec turned out to be 270°. The known kinetics of the thermal decomposition of perchlorate cannot ensure such a high decomposition rate at 270°; therefore it is necessary to assume that the

decomposition of perchlorate during its combustion is under the strong catalytic influence of the flame located near the surface, i.e., that the flame supplies not only heat for heating the perchlorate, but also chemical products that accelerate the decomposition of perchlorate.

We do not know whether the chemical action on the k-phase of the diffusive flux is a general phenomenon in the decomposition of the k-phase, or whether this is a specificity of the combustion only of ammonium perchlorate. The above-mentioned data on the low temperature at the surface of perchlorate are so surprising that they require the most diverse verification. But regardless of the results of this verification, the idea of a catalytic action in the k-phase of reaction products from the g-phase seems possible to us. To judge the reality of this idea, it is necessary to determine the kinetics of thermal decomposition of the k-phase at temperatures close to T_{p} (in the absence of ignition) and at elevated P, and to compare it with the kinetics of decomposition of the k-phase during combustion at the same P. However, for most substances, information on the kinetics of thermal decomposition of the k-phase near T_{p} and at elevated pressure is absent or

insufficiently reliable. Concerning the mechanism of decomposition of the c-phase during combustion, suggestions have often been made that a reaction (“en route”) of the gasification products of the c-phase with the c-phase may occur. Considerations regarding the action of combustion products diffusing toward the surface, so far as we know, have not previously been expressed.

Let us estimate the magnitudes of the concentration of combustion products in the g-phase near the powder surface and of the diffusion flux of combustion products from the flame to the powder surface. In doing so we shall proceed from the simplest assumption, namely that the state of the mixture (the number of active centers) is uniquely related to the amount of heat evolved and to the temperature. In reality, cases are possible in which the concentration of active centers is not related to the gas temperature; it may be greatest where the temperature is not maximal, etc. Another simplification of the calculation is the neglect of dispersion of the solid phase.

Let us denote by: T_{g}, T_{p}, T_0 the temperatures of combustion and of the powder surface and the initial temperature of the powder; c, c_p the specific heats of the powder and the g-phase $\left(\frac{\text{Mcal}}{\text{g}\cdot\text{deg}}\right)$ ($c \simeq c_p$); r, p, v the gas constant per 1 g, pressure, and specific volume of the gases; a_{g}, $a_{\text{g}i}$, a_{p} the concentrations (in g/g of gas mixture) of all combustion products, of the i-th combustion product, and of the decomposition products of the powder; q the chemical energy of the products of decomposition of the powder at the powder surface (in Mcal/g); ρu the mass burning rate of the powder, or the motion of the gases ($\text{g/cm}^2 \cdot \text{s}$); I_D, I_Q the diffusion (in $\text{g/cm}^2 \cdot \text{s}$) and heat (in $\text{Mcal/cm}^2 \cdot \text{s}$) fluxes to the powder surface; K the fraction of heat supplied from the g-phase in the total amount of energy required to heat the powder to T_{p}.

Ya. B. Zel’ dovich ([1]) showed that, under the condition of equality of the coef-

ficients of thermal conductivity and diffusion of the gas mixture (and equality of the diffusion coefficients of the different components of the gas mixture), the concentrations of combustion products and decomposition products at the powder surface are equal to:

$$a_{\mathrm{g}} = \frac{T_{\mathrm{p}} - T_0}{T_{\mathrm{g}} - T_0}, \qquad a_{\mathrm{p}} = \frac{T_{\mathrm{g}} - T_{\mathrm{p}}}{T_{\mathrm{g}} - T_0}. \tag{1}$$

Since, in deriving these formulas, the then-unknown fact of the considerable exothermicity of the powder decomposition reaction was not taken into account, a correction to formula (1) is introduced below which accounts for the exothermicity of powder decomposition.

From the theory of Ya. B. Zel' dovich it follows that, under the condition of equality of the coefficients of thermal conductivity and diffusion along the coordinate along which transfer occurs, the value of the enthalpy remains constant. Equating the enthalpy values of the gas mixture at the powder surface and in the combustion zone,

$$a_{\mathrm{p}} q + c_p T_{\mathrm{p}} = c_p T_{\mathrm{g}}.$$

Then

$$a_{\mathrm{p}} = \frac{c_p \left(T_{\mathrm{g}} - T_{\mathrm{p}}\right)}{q}, \qquad a_{\mathrm{g}} = 1 - a_{\mathrm{p}} = \frac{q - c_p \left(T_{\mathrm{g}} - T_{\mathrm{p}}\right)}{q}. \tag{2}$$

The chemical energy of the gasification products q is expended on heating the gases from T_{p} to T_{g} and on the k-th part of the heating of the powder from T_0 to T_{p} (the remaining part is covered by the heat of the exothermic reactions during decomposition of the powder):

$$q = c_p \left(T_{\mathrm{g}} - T_{\mathrm{p}}\right) + Kc \left(T_{\mathrm{p}} - T_0\right). \tag{3}$$

Substituting (3) into (2), we obtain

$$a_{\mathrm{p}} = \frac{c_p \left(T_{\mathrm{g}} - T_{\mathrm{p}}\right)}{c_p \left(T_{\mathrm{g}} - T_{\mathrm{p}}\right) + Kc \left(T_{\mathrm{p}} - T_0\right)}, \qquad a_{\mathrm{g}} = \frac{Kc \left(T_{\mathrm{p}} - T_0\right)}{c_p \left(T_{\mathrm{g}} - T_{\mathrm{p}}\right) + Kc \left(T_{\mathrm{p}} - T_0\right)}. \tag{4}$$

For $k = 1$ and $c = c_p$, formula (4) reduces to formula (1).

Experimentally observed values of K may be small, for example, $K = 0.1$.

For such small K that the quantity $Kc(T - T_0)$ may be neglected in comparison with $c_p(T - T_0)$,

$$a_p \simeq 1, \qquad a = \frac{Kc(T - T_0)}{c_p(T - T)}. \tag{4'}$$

The concentration of the i-th component of the combustion products is determined by substituting $a_i = a\,\nu_i$.

For judging the catalytic action of the combustion products, estimates of the ratios a/a_p or $I_D/\rho u$ are of interest.

From (4) we obtain

$$\frac{a}{a_p} = \frac{Kc(T - T_0)}{c_p(T - T)} \simeq \frac{K(T - T_0)}{T - T}; \tag{5}$$

$$\frac{I_D}{\rho u} = \frac{a\,\rho u}{\rho u} = \frac{Kc(T - T_0)}{c_p(T - T) + Kc(T - T_0)} \simeq \frac{K(T - T_0)}{(T - T) + K(T - T_0)}. \tag{6}$$

If the active centers are absorbed by the surface so vigorously that their concentration at the surface may be set equal to zero ($a = 0$), then from the condition $I_Q = qI_D$ and $I_Q = Kc(T - T_0)\rho u$ we obtain

$$\frac{I_D}{\rho u} = \frac{Kc(T - T_0)}{c_p(T - T) + Kc(T - T_0)},$$

i.e., formula (6) remains valid.

For $K = 1$ (for example, nitroglycol)

$$\frac{I_D}{\rho u} = \frac{T - T_0}{T - T_0}. \tag{6'}$$

For small K (gunpowder)

$$\frac{I_D}{\rho u} = K\frac{T - T_0}{T - T}. \tag{6"}$$

Let us estimate a/a_p and $I_D/\rho u$ for gunpowder and nitroglycol.

Gunpowder (formulas (5), (6″)):

$$\frac{a}{a_p} \simeq \frac{0.1(350 - 20)}{1200 - 350} = 3.9 \cdot 10^{-2}, \qquad \frac{I_D}{\rho u} \simeq 3.9 \cdot 10^{-2}.$$

Nitroglycol (formulas (5), (6′)):

$$\frac{a}{a_p} \simeq \frac{1(200-20)}{1200-200} = 18 \cdot 10^{-2}, \qquad \frac{I_D}{\rho u} \simeq \frac{200-20}{1200-20} \simeq 15 \cdot 10^{-2}.$$

It is evident from these estimates that the amount of combustion products at the surface of burning gunpowder is not negligibly small and does not contradict the idea of their catalytic action.

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