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# Physical Chemistry

G. B. Manelis, A. G. Merzhanov, and F. I. Dubovitskii

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**Abstract**

**Full Text**

## Physical Chemistry

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### On the Mechanism of Combustion of Powders

*(Presented by Academician V. N. Kondrat'ev, March 2, 1960)*

In the experiments of P. F. Pokhil<sup>1</sup> it was shown that, during combustion, a considerable part of the initial powder is dispersed and is carried away by the gas stream in the form of smoke. In the smoke-gas mixture thus formed, in P. F. Pokhil's opinion, heterogeneous-homogeneous reactions take place, and these determine the burning rate.

For the theory of combustion, it is undoubtedly of interest to clarify the question of where and how the dispersed particles burn—whether they burn in the hot-flame zone at a temperature close to the maximum, or whether they manage to decompose according to the usual laws of reaction in the condensed phase at the surface of the powder, without reaching the flame.

An exact solution of the problem of the thermal decomposition of dispersed particles in space and time can be obtained on the basis of knowledge of the laws of motion of the particles and the laws of heat exchange between the particles and the surrounding gas. However, to answer the question posed it proved quite sufficient to carry out an isothermal estimate of the lifetime of a particle. In the isothermal estimate we assume that the particle decomposes at the temperature  $T_p$ , equal to the temperature at the surface of the burning powder. The values of  $T_p$  may be calculated from the formula obtained in our work<sup>2</sup>, taking dispersion into account:

$$u^2 = \frac{1}{1 - \eta_d} a k_0 e^{-E/RT_p} \frac{RT_p^2/E}{T_p - T_0 - \frac{1}{2}Q(1 - \eta_d)/c},$$

where  $Q$  is the heat effect of decomposition of the powder;  $C$  is the specific heat of the powder;  $a$  is the thermal diffusivity;  $T_0$  is the temperature of the powder far from the surface;  $E$  and  $k_0$  are the activation energy and the pre-exponential factor of the rate constant for decomposition of the powder;  $\eta_d$  is the depth of dispersion.

The lifetime of a particle is

$$t = \frac{1}{k_0 e^{-E/RT_p}},$$

and the distance that it has time to fly is

$$x_d = u_g t,$$

where  $u_g = \frac{\rho}{\rho_g} u$  is the velocity of motion of the gases (the maximum possible velocity of the particle);  $u$  is the burning rate;  $\rho$  is the density of the powder;  $\rho_g$  is the density of the gases.

Thus, from the experimental values of the burning rate  $u$ ,  $T_p$ ,  $t$ , and  $x_d$  are calculated, and the calculated quantities  $x_d$  are compared with the experimental values of the width of the preflame (dark) zone  $x_g$ .

A specific numerical calculation was carried out for pyroxylin powder. The initial data for the calculation were:  $a = 1 \cdot 10^{-3}$  cm<sup>2</sup>/sec;  $c = 0.35$  cal/g · deg;

$$\rho = 1.6 \text{ g/cm}^3; \quad Q = 270 \text{ cal/g (1)}; \quad k_0 = 10^{17.8} \text{ s}^{-1}; \quad E = 44600 \text{ cal/mol (3)};$$

$$T_0 = 20^\circ\text{C}; \quad \rho_g = 5 \cdot 10^{-4} p \text{ g/cm}^3 \text{ (} p \text{ is the pressure in kgf/cm}^2\text{)}; \quad \eta_d = 0.7$$

The results of the calculation, as well as the experimental data on the width of the preflame zone  $x_g$ , are given in Table 1.

It should be emphasized that the calculated values of  $x_d$  represent an upper estimate. Taking account of autocatalysis in the decomposition process, of heating due to self-heating, of heating due to the heat flux from the flame, and also of the fact that the particles may move at velocities lower than the gas velocity, will lead to a decrease in the calculated value of  $x_d$ .

**Table 1**

$p$ , kgf/cm <sup>2</sup>	$u$ , cm/s	$T_p$ , °C	$t$ , s	$x_d$ , cm	$x_g$ exp., cm
20	0.6	385	$1 \cdot 10^{-3}$	0.1	1.3
30	0.9	400	$4 \cdot 10^{-4}$	0.04	0.5
40	1.1	410	$2.5 \cdot 10^{-4}$	0.025	0.3
50	1.2	415	$2 \cdot 10^{-4}$	0.016	0.2

Thus, even the upper estimate shows that the particles do not enter the flame zone, but have time to decompose near the surface of the powder. This result leads to the establishment of a decomposition zone for the dispersed particles of the initial powder. The existence of this zone is confirmed by experimental data on the transparency of the smoke-gas phase <sup>(4)</sup> and on the temperature distribution in burning powder <sup>(5,6)</sup> (a sharp increase in the temperature gradient and the presence of a maximum of heat release near the powder surface).

Consequently, the combustion of pyroxylin-based powder can at present be regarded as follows. In the condensed phase there proceeds a substantially exothermic decomposition reaction, accompanied by the dispersion of a considerable amount of the initial powder. In the zone closely adjacent to the surface of the burning powder, the decomposition reaction of particles of the dispersed powder takes place; moreover, in the condensed phase and in the particle-decomposition zone, from 300 cal/g and more is released. In the third zone (the zone of maximum temperature), a reaction occurs with the formation of final products and the release of the remaining heat.

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

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