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## Abstract

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# THE KINETIC REGIME OF COMBUSTION OF CONDENSED MIXTURES

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The combustion rate of condensed mixtures in the general case is determined by the rates of three processes: mixing of the components, the chemical reaction between them, and heat transfer from the reaction zone to the fresh mixture.* However, in certain cases the mixing processes do not affect the combustion rate, and the latter proceeds in the kinetic regime.

One such case was briefly considered in work ($^1$). Its essence is that the mixing processes will not affect the combustion rate if they have time to be fully completed within the preparatory zone, between the fresh substance and the reaction zone (we neglect the influence of mixing on the thermal constants of the mixture). Obviously, in this case the combustion rate is in general independent of the particle size of the components (so long as they are not too large) and is equal to the combustion rate of a homogeneous system of the same chemical composition.

1. Let us consider this case in more detail. For the described regime to exist, two conditions must be fulfilled, the first of which is that the mutual solubility of the components at the temperatures existing in the preparatory zone must be sufficiently high.

Consider a mixture of two solid components, for which the degree of heterogeneity** is proportional to the particle size $d$ of one component. In the preparatory zone each of the components may either remain in the solid phase or melt or gasify. The following variants are then possible:

1) solid + solid; 2) solid + liquid; 3) solid + gas; 4) liquid + liquid; 5) liquid + gas; 6) gas + gas.

Complete mixing of the components within the preparatory zone is obviously possible in case 6) and practically excluded in cases 3) and 5), since the weight quantity of gas that can dissolve in, or be sorbed by, one gram of condensed component is, as a rule, much smaller than the usual ratio of components in condensed mixtures. The gaseous component can be consumed only in the reaction zone. In cases

1), 2) and 4), the possibility of complete mixing of the components can be estimated only for each particular mixture.

2. The regime under consideration can be observed only for sufficiently small $d$ (for $d \leqslant d_{\min}$). The quantity $d_{\min}$ increases with increasing diffusion rate and is bounded from below, since in any case it must exceed the effective size of the molecules:

$$d_{\min} > 10^{-8} \div 10^{-7}\ \text{cm}. \tag{1}$$

Consequently, the second condition for the existence of the regime under consideration is that the rate of mutual diffusion of the components not be too small –such that condition (1) is satisfied.

Starting from the considerations given in [1], we shall trace the mutual diffusion of the components in a certain cross section ($x = 0$) of the charge. During the time $dt$, the boundary of the mixing zone will shift in the transverse direction by an amount of the order

$$d(y^2) \sim D\,dt, \tag{2}$$

where $D$ cm$^2$/sec is the diffusion coefficient. Assuming that the combustion front moves relative to the given cross section with constant velocity $v$, we may write $x = x' - vt$, where $x'$ is measured from the combustion front. Using the well-known expression for the profile of the heating wave ahead of the combustion front,

$$x' = \frac{a}{v} \ln \frac{T - T_0}{T_m - T_0}, \tag{3}$$

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* For a thermal combustion mechanism.

** The degree of heterogeneity may be defined as a quantity proportional to

$$\frac{1}{N} \sum_{i=1}^{N} x_i,$$

where $\sum_{i=1}^{\nu} x_i$ is the path that the molecules of the substances constituting the given mixture (initial substances or those formed as a result of destruction, if such precedes mixing) must traverse in order to obtain a completely homogeneous mixture (on the molecular scale). In certain important special cases (see ([2])) the degree of heterogeneity is proportional to the particle size of one of the components.

where $a$ cm$^2$/sec is the thermal diffusivity and the temperatures $T_0$ and $T_m$ refer, respectively, to the cold mixture and the reaction zone, after substituting $dt = dx'/v$ into (2) and integrating we obtain that, to order of magnitude, $d_{\min}$ is equal to

$$d_{\min} \sim \frac{1}{m}\sqrt{\frac{\bar{\lambda}}{\bar{c}}}\left[\int_{T_1}^{T_m} \frac{\rho D}{T - T_0}\, dT\right]^{1/2}, \tag{4}$$

where $m$ g/cm$^2 \cdot$ sec is the mass burning rate (for $d \leqslant d_{\min}$), $\rho$ g/cm$^3$ is the density; for the quantities $\bar{\lambda}$ cal/cm $\cdot$ sec $\cdot$ deg and $\bar{c}$ cal/g $\cdot$ deg, values averaged over the preparatory zone are taken. If phase transitions occur in the latter, it is divided into several subzones, and the integration in (4) is carried out successively over each of them. For brevity, suppose that mixing occurs mainly in one subzone lying in the interval from $T_1$ to $T_m$ (where $T_0 < T_1 < T_m$). For the mutual diffusion of gases it is usually assumed that $D = D_0(T/T_0)^n$, where $n = 1.75$–$2$. For $n = 2$, from (4) we obtain

$$d_{\min} \sim \frac{1}{m}\sqrt{\frac{\bar{\lambda}}{\bar{c}}\rho_0 D}\sqrt{\frac{T_m - T_1}{T_0} + \ln\frac{T_m - T_0}{T_1 - T_0}}. \tag{5}$$

For diffusion in the solid and liquid phases, $D = D_0 e^{-Q/RT}$, and then from (4) it follows that

$$d_{\min} \sim \frac{1}{m}\sqrt{\frac{\bar{\lambda}\rho}{\bar{c}}} \times$$

$$\times\sqrt{D_0\left\{\operatorname{li}\left(e^{-Q/RT_1}\right) - \operatorname{li}\left(e^{-Q/RT_m}\right) + e^{-Q/RT_0}\left[\operatorname{li}\left(e^{Q/RT_0}e^{-Q/RT_m}\right) - \operatorname{li}\left(e^{Q/RT_0}e^{-Q/RT_1}\right)\right]\right\}}. \tag{6}$$

The values of $\operatorname{li} z$ are taken from tables; however, for $Q \gg RT$ (approximately, for $e^{-Q/RT} < 10^{-4}$ and $e^{Q/RT_0}e^{-Q/RT} > 10^4$) one may, with an error of no more than 10-12%, use the approximation $\operatorname{li} z \sim z/\ln z$. If, moreover, the following is satisfied:

$e^{-Q/RT_m} \gg e^{-Q/RT_1}$, then from (6) we obtain:

$$d_{\min} \sim \frac{1}{m}\sqrt{\frac{\bar{\lambda}\rho}{c}}\sqrt{D_0\frac{RT_m}{Q}e^{-Q/RT_m}}. \tag{7}$$

Formulas (5), (6), and (7) in principle make it possible to estimate $d_{\min}$ for each particular system.

3. It is of interest to estimate the interval within which the quantity $d_{\text{min}}$ may lie for a given type of system. This can be done well for the variant g + g. The point is that the value of the complex $\vartheta = \sqrt{\frac{\lambda}{c}\rho_0 D_0}$ for all gases that may be products of the gasification of various condensed mixtures and for which tabulated data are available varies within comparatively narrow limits: thus, for example, all ordinary diatomic and triatomic gases, various gaseous hydrocarbons, including very heavy ones, vapors of many organic liquids, etc. fall within the interval $\vartheta = 10^{-4} \div 10^{-3}$ g/cm · sec (at temperatures from ∼ 200–300°C; $T_0 = 273$°K is adopted). In addition, if the dependence $m(p, T)$, which is specified experimentally, is not considered, then the right-hand side of (5) is independent of pressure and depends comparatively weakly on the choice, within reasonable limits, of the temperatures $T_m$, $T_1$, and $T_0$. Assuming, for example, that the temperatures $T_m$ and $T_1$ can vary independently in the intervals $1500 \div 3000$°K and 600—1000°K, respectively, we obtain from (5) the following interval of values of $d_{\text{min}}$:

$$d_{\text{min}} \sim \frac{1.5 \div 35}{m}\ \mu. \tag{8}$$

In work (2) the experimental value of $d_{\text{min}}$ for a stoichiometric mixture $KClO_4$+ bitumen at $m \simeq 0.2$ g/cm$^2$ · sec was ∼ 70 $\mu$, which lies within the limits of estimate (8).*

The situation is much worse for the variants l + l, s + l, and especially s + s, since there are no data whatever on diffusion in the systems metal + salt, resins + salt, etc. Indirect data (diffusion of metals in metals and slags, mutual diffusion of salts, etc.) show that for the s + s system the diffusion coefficient depends extremely strongly on the nature of the components, and this rules out the possibility of any estimates of $d_{\text{min}}$ from indirect data. For diffusion in the liquid phase the dependence on the nature of the components is considerably weaker; however, the interval of values of $d_{\text{min}}$ given by the indirect data, when substituted into (6) (under reasonable assumptions regarding the range of variation of $T_1$ and $T_m$), is still about 4 orders of magnitude. Such a broad estimate is of no practical interest.

4. There exists at least one more case in which combustion of condensed mixtures can proceed in the kinetic regime. It will be observed if the reaction takes place on the surface of particles of one component, while the rate of supply of the second component does not limit the rate of the overall process. For this it is necessary that the degree of heterogeneity and the value of $T_m$ not be too large and that $D_1 \ll D_2$, where $D_1$ and $D_2$ are, respectively, the diffusion coefficients of the first (the one forming the particles) and second components in the reaction products. This case is clearest for the variant s + g, where it is possible to use data on the combustion of carbon in air or oxygen. Combustion of condensed mixtures

in whose reaction zone this variant is realized is considered in works (${}^{3,4}$). At the same time, in contrast to the case considered above in points 1—3, in the present

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* In work (${}^{2}$), in deriving the expression for $d_{\min}$, both molecular and turbulent diffusion were considered. However, the considerations expressed in (${}^{5}$) and estimate (8) show that near $d_{\min}$, apparently, only molecular diffusion should be considered.

in this case the burning rate $u$ depends on the particle size (in (4) it was obtained that $u \sim d^{-1/3}$) and, consequently, the heterogeneous system here is not equivalent to a homogeneous one. In addition to the s + g variant, such a regime can in principle be observed for the s + l variants and (less probably) l + l.

5. In conclusion, we note that the kinetic regime of combustion, associated with mixing of the components in the preparatory zone, is of fundamental importance for the concept of the normal burning rate $u_n$ of condensed mixtures. The latter must satisfy the condition of stationarity and be reproduced unambiguously. Meanwhile, for $d > d_{\min}$ the burning rate undergoes oscillations with a period $\sim d/u$ and may be considered constant only for sufficiently long charges. Moreover, it is practically impossible to prepare a mixture completely identical with the reference one, since for this it is necessary to select particles not only with the same size distribution, but also with the same shape, etc. Of course, errors due to the nonstationarity of combustion and the nonidentity of mixtures may be made very small, but it is fundamentally important to note that for $d \ll d_{\min}$ they disappear completely, and the burning rate acquires the meaning of a physicochemical constant ($u = u_n$).

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