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EXTINCTION THRESHOLD IN RANDOM HETEROGENEOUS CONDENSED MIXTURES WITH AN EXTREMELY SMALL AMOUNT OF A COMBUSTIBLE

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A mathematical model describing the process of combustion of heterogeneous condensed mixtures with account for the randomness of the distribution of combustible particles over the system is proposed. The step dependence of the reaction rate on the temperature is used as a model of chemical kinetics. The case where the concentration of the particles is extremely low but the heat energy released in their combustion is high has been investigated. It is shown that for an adiabatic system there exists a concentration limit of combustion. The relation of this combustion limit to the geometric phase transition occurring in a heterogeneous condensed mixture with rare combustion inclusions has been demonstrated. An analytical approach to the evaluation of the threshold concentration of the combustible in such systems, based on the continual theory of percolation, is proposed.

In the present work, we consider the combustion of heterogeneous condensed mixtures in which the concentration of combustible particles is extremely low but the heat energy released in their combustion is high. As is known, in systems where the rate of chemical transformation is described by the Arrhenius dependence the concentration limit of combustion can arise only at a certain level of heat loss. However, for many heterogeneous condensed mixtures the step dependence of the reaction rate on the temperature is a more adequate model of chemical kinetics [1, 2]. This points to the fact that in heterogeneous condensed mixtures the reaction rate abruptly increases (by several orders of magnitude) in the case of melting of one component. It should be noted that a concentration limit of combustion arises in heterogeneous condensed mixtures with such chemical kinetics even in the case where the combustible is uniformly distributed over all the particles of the mixture and the system is heat-insulated. It turns out that this limit changes if the factor of randomness in the distribution of the combustible particles over the space is taken into account. It is shown in the present work that the existence of the limit of combustion of heterogeneous condensed mixtures with a low concentration of the combustible is directly related to the existence of the geometric phase transition (called more often the percolation transition) in such systems. It is also demonstrated that the combustion of the system considered can be described within the framework of the continual theory of percolation.

The starting point of the present investigation was the experimental work [3], where the combustion of a low-exothermic mixture of sodium chlorate $NaClO_3$ (more than 90 wt.%) with a small addition of tin Sn (0.5–15 wt.%) was investigated. Such a system is used for emergency generation of oxygen in spacecraft, airplanes, submarines, coal mines, etc. [4–6]. When a combustion wave propagates in the above mixture, sodium chlorate breaks down into NaCl and oxygen. A portion of the oxygen reacts with tin and the propagation of the combustion wave is sustained due to the large thermal effect of this reaction. Since the density of Sn is equal to 7.29 g/cm^3 and the density of sodium chlorate is 2.49 g/cm^3, the volume fraction of tin in such a system accounts for only 1–5% (depending on the porosity). Nonetheless, this small amount of the combustible (tin) is sufficient for propagation of the combustion wave.

Formulation of the Problem. In the idealized model of the indicated system, proposed below, it is assumed that heat is released only as a result of combustion of combustible particles whose concentration is low. In this case, primary attention was given to the study of the influence of the randomness factor in their distribution over the system on the combustion process. For this purpose, we used the two-dimensional model of a heterogeneous condensed mixture (Fig. 1) whose basic element is a unit cell. It includes both a solid phase (an effective particle) and chemically

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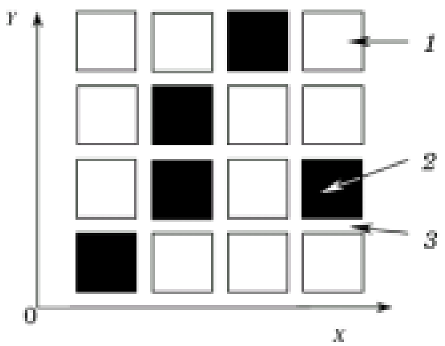

Fig. 1. Geometric scheme of a two-dimensional heterogeneous reacting medium: 1) combustible particles; 2) inert particles; 3) interparticle gaseous interlayers.

inert gaseous interlayers. Unit cells are positioned at the points of a two-dimensional square grid. All the cells of the system possess the same physical (thermal conductivity, density, etc.) and geometric (shape and size) properties and differ only by the initial chemical composition of the solid phase: a particle can contain either a combustible or an inert component. The local chemical composition of the cell, characterized by the degree of conversion η, changes in the process of reaction. The initial chemical composition of the cell is determined in a random manner: the cell contains a combustible with a given probability p, and it is inert with a probability $(1-p)$. We note that in this case the quantity p is equal to the volume and, simultaneously, the number concentrations of the combustible particles in the system. The model selected takes no account of the effects that arise as a result of the spreading of the melted components, the energy release resulting from the breakdown of sodium chlorate, and the limitations on the transport of oxygen to the metal (it is assumed that the oxidizer is present in excess).

One distinguishing feature of the model proposed is that the unit cell is considered not as a point but as an object having an internal distribution of the temperature and the degree of conversion. In this case, the heat transfer inside the particle is determined by the conduction mechanism with a certain thermal-conductivity coefficient.

The model is described by the following system of dimensionless equations:

$$\frac{\partial}{\partial \tau}\left[\Theta_{ij}(x, y, \tau)\right] = S\left(\frac{\partial^2 \Theta_{ij}}{\partial x^2} + \frac{\partial^2 \Theta_{ij}}{\partial y^2}\right) + c_{ij}^{(0)} W(\Theta_{ij}, \eta_{ij}) , \tag{1}$$

$$\frac{d}{d\tau}\left[\eta_{ij}(x, y, \tau)\right] = W(\Theta_{ij}, \eta_{ij}) , \tag{2}$$

$$W(\Theta_{ij}, \eta_{ij}) = \begin{cases} 0 , & \Theta_{ij} < \Theta_{\text{ig}} , \\ 1 , & \Theta_{ij} \ge \Theta_{\text{ig}} , \quad \eta_{ij} < 1 , \\ 0 , & \Theta_{ij} \ge \Theta_{\text{ig}} , \quad \eta_{ij} = 1 . \end{cases} \tag{3}$$

Here $i = 1, ..., L$, $j = 1, ..., L$, and $\Theta = (T - T_0)/\Delta T_{\text{ad}}$. The energy equation (1) involves the dimensionless number S that is determined as $S = at_{\text{rc}}/d^2$ and has the meaning of an effective dimensionless thermal diffusivity; its appearance in the system of equations is due to the specific character of the process of combustion in a heterogeneous medium. It should be noted that the width of the cell in dimensionless variables is equal to unity.

As has been noted above, the model of chemical kinetics is most adequate for the physicochemical system considered. According to this model, the reaction between the two components begins when one of them melts, i.e., when the ignition temperature Θ_{ig} is attained (3).

The heat fluxes at the boundaries of the cells are determined by the temperature difference and the Biot criterion

$$\mathrm{Bi}\,(\Theta_{ij}\,|_{\mathrm{lf}} - \Theta_{i-1,j}\,|_{\mathrm{r}}) = -\left.\frac{\partial\Theta_{ij}}{\partial x}\right|_{\mathrm{lf}}, \quad \mathrm{Bi}\,(\Theta_{i+1,j}\,|_{\mathrm{lf}} - \Theta_{ij}\,|_{\mathrm{r}}) = \left.\frac{\partial\Theta_{ij}}{\partial x}\right|_{\mathrm{lf}},$$
$$\mathrm{Bi}\,(\Theta_{ij}\,|_{\mathrm{d}} - \Theta_{i,j-1}\,|_{\mathrm{u}}) = -\left.\frac{\partial\Theta_{ij}}{\partial y}\right|_{\mathrm{d}}, \quad \mathrm{Bi}\,(\Theta_{i,j+1}\,|_{\mathrm{d}} - \Theta_{ij}\,|_{\mathrm{u}}) = \left.\frac{\partial\Theta_{ij}}{\partial y}\right|_{\mathrm{d}}. \tag{4}$$

In this case, the Biot criterion has the form $\mathrm{Bi} = \alpha_{\mathrm{eff}} d/\lambda_{\mathrm{s}}$. The value of α_{eff} is determined by the conduction transfer in interparticle contacts and gaseous interlayers and by the radiation heat exchange through these interlayers. According to [7], in the case of a fairly close-packed arrangement of the gaseous interlayers between the particle, the relative effective thickness of these interlayers δ/d is independent of the particle size d and is 0.03–0.06. The estimates show that for particles with a size of the order of 100 μm the contribution of the radiative transfer through these thin gaseous interlayers to the interparticle heat exchange is small in comparison with the contribution of the thermal conductivity. In this case, the Biot criterion was estimated at $\mathrm{Bi} = \lambda_{\mathrm{g}} d/(\lambda_{\mathrm{s}}\delta) \approx 0.02$–$0.1$. However, the role of radiative heat exchange can be more significant in the system with pores having dimensions of the order of the particle size. In this work, we investigated the systems in which Bi = 0.5. As a result of the analogous evaluations, we selected the value of the parameter $S = 0.1$ for numerical modeling of the process.

The adiabatic boundary conditions were set at the upper, lower, and right boundaries of the system. Combustion was initiated by setting a fairly high temperature at the left boundary of the system:

$$\Theta_{1j}\,|_{x=0} = \Theta_{\mathrm{in}} = 0.5\,. \tag{5}$$

When the ignition of the system was completed, namely, when several first layers burned out, condition (5) was replaced by the adiabatic condition

$$\left.\frac{\partial\Theta_{1j}}{\partial x}\right|_{x=0} = 0\,. \tag{6}$$

To avoid confusion, we emphasize that the ignition temperature Θ_{ig} at which the chemical reaction begins in accordance with the equation of chemical kinetics (3) differs from the initiation temperature Θ_{in} that enters into boundary condition (5).

Procedure of Numerical Solution. The system of equations (1)–(6) was solved numerically using the explicit finite-difference scheme. The number of grid points in the cell in each direction was equal to seven for all the variants of the calculation, which was sufficient in accuracy for $S \geq 0.1$. The initial concentration of the combustible in each cell was set in a random manner: a) the pseudorandom number ξ distributed uniformly in the interval [0, 1] was generated; b) it was assumed that a combustible particle is found in the cell ($c_{ij}^{(0)} = 1$) if $\xi \leq p$; if $\xi > p$, the particle found in this cell was assumed to be inert ($c_{ij}^{(0)} = 0$). We processed 100 to 200 cases of the combustion-wave propagation in the system for each combination of the parameters $\{\Theta_{\mathrm{ig}}, p\}$. Calculations were carried out on a Pentium III two-processor personal computer with a clock frequency of 800 MHz. In this case, more than 3000 h of processor time was expended in modeling.

Numerical Experiment. The results of the modeling of the combustion of a random heterogeneous system at low concentrations of the combustible and low ignition temperatures point to the existence of a concentration limit of combustion of a random system even in the adiabatic case. Figure 2 illustrates the critical behavior of the mean degree of conversion when the concentration of the combustible changes in the system.

The dimension of the system modeled was 50 × 50 cells. For systems with larger dimensions, on the plot of the degree of conversion versus the concentration of the combustible there must be a more abrupt transition from the mixtures practically noncombustible under these conditions to completely combustible mixtures. In the limit of an infinitely large system, there will take place a threshold transition. To determine the threshold concentration in a system of finite dimension we interpolated the data of the numerical experiment by a dependence of the form $\eta(p) = A + (B - A)/(1 + \exp\,[(p - p_0)/\Delta p])$. The inflection point of the interpolation function, which coincides with the parameter p_0, was identified with the threshold concentration p_{c}. For example, for $\Theta_{\mathrm{ig}} = 0.025$ and $\Theta_{\mathrm{ig}} = 0.05$ we have ob-

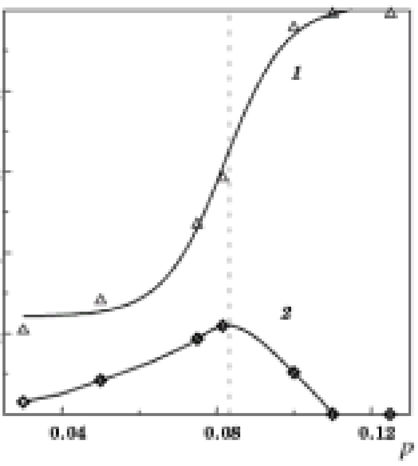

Fig. 2. Dependence of the mean degree of conversion $\langle \eta \rangle$ on the concentration p of combustible particles (1) and root-mean-square deviation for the degree of conversion (2). $\Theta_{ig} = 0.05$, $p_c = 0.081$ (vertical dashed line).

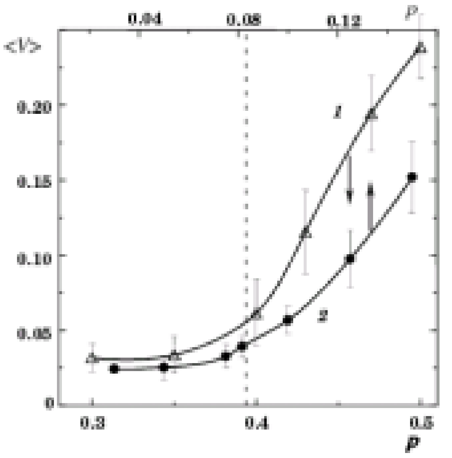

Fig. 3. Dependence of the mean velocity of propagation of the combustion wave on the concentration of combustible particles for $\Theta_{ig} = 0.25$ (1) and 0.05 (2). The critical concentration is denoted by the vertical dashed line.

tained $p_c = 0.042$ and $p_c = 0.081$ respectively. It is significant that in the neighborhood of the threshold concentration shown in Fig. 2 by the vertical dashed line the fluctuations of the degree of conversion increase markedly (by approximately a factor of 10^2 in our experiment). This circumstance is a direct indication of the existence of a phase transition in the system. As is known, the fluctuations of the order parameter increase abruptly in the neighborhood of the point of phase transition [8, 9]. In the problem considered, this parameter is the mean degree of conversion of the combustible particles; in this case, the ordered state of the system corresponds to the complete combustion of the particles ($\eta \to 1$), and the disordered state corresponds to the impossibility of propagation of the combustion process over the system ($\eta \to 0$). It will be shown below that in this case we are dealing with the geometric phase (percolation) transition. The physical interpretation of this phenomenon is as follows: for given thermophysical properties of the system its internal organization can facilitate the propagation of the combustion process or hinder it.

Figure 3 shows the dependence of the mean velocity of propagation of the combustion process over the system on the concentration of combustible particles for two different ignition temperatures. This velocity was determined in each case as the ratio of the distance from the last burned-out layer to the left boundary of the system and the time of its complete extinction. In the figure, the critical concentrations obtained from the analysis of the mean degree of conversion for these cases are brought into coincidence. As is seen from the figure, the system in the disordered state behaves in such a manner that the combustion process propagates in it with a small velocity that is practically independent of the ignition temperature. In this case, only several first layers of particles burn out. When the concentration exceeds the threshold value, the velocity of the wave begins to increase abruptly; it increases more rapidly in the system with a higher critical concentration.

Approximation of the Continual Theory of Percolation. Along with the direct numerical modeling of the phenomenon considered, the model of continual percolation can be used for evaluation of the threshold concentration of the combustible.

We now consider the formulation of the problem of the continual theory of percolation. Let there be a system of points chaotically distributed over the space with a number concentration n. Two points are considered to be connected with each other if the distance between them does not exceed R. This condition causes the separation of the system of points into clusters, i.e., bound aggregates of points. If two points are connected directly or with the help of pairwise connected points, they belong to one cluster. When the concentration n or the distance R is small, the dimensions of the clusters are limited and they occupy only a small part of the space. At the same time, at large n and (or) R the entire space will be occupied by one large cluster that is called the percolation cluster. It is necessary to find the minimum value of the parameters n and R at which a percolation cluster appears in the system for the first

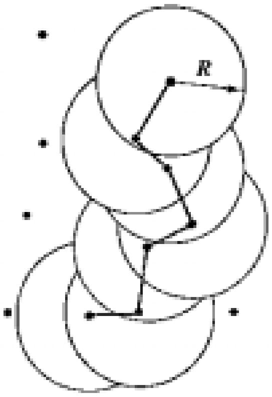

Fig. 4. Example of percolation on the enveloping circles. The bound points are connected by the straight lines.

time, i.e., at which a geometric phase transition occurs. The geometric interpretation of this problem is as follows: at a given n it is necessary to find the least value of $R = R_c$ at which there exists an infinite chain of points where each subsequent point lies inside the circle constructed around the previous point. We note that it is common practice to call this problem the percolation on the enveloping circles (Fig. 4).

It follows from the dimensional theory that all the dimensionless characteristics of such a system are determined by the unique dimensionless number $\alpha = \pi R^2 n$ (for the two-dimensional case). The number π was added for the sake of convenience. This number is related to the part of the space ϕ occupied by the circles by the following relation [10, 11]:

$$\phi = 1 - \exp(-\alpha) . \tag{7}$$

The parameter ϕ is an approximate invariant in the percolation threshold. It depends only on the dimension of the space d_t and is independent of the local properties of the grid. The most exact result of its calculation for the two-dimensional systems [12], known to us, is

$$\phi_c = 0.676339 \pm 0.000004 , \tag{8}$$

in the case $\alpha_c \approx 1.128$.

The process of ignition of a combustible particle by an analogous neighboring particle, which gives rise to the combustion-wave propagating in a random medium, can be described in terms of the formulated percolation problem. In this connection, we consider a simple model in which heat propagates in a homogeneous medium characterized by the effective dimensionless thermal conductivity S. Let the quantity of heat Q ($Q = 1$ in dimensionless variables) be instantaneously released at the instant of time $\tau = 0$ at the point $r = 0$. It is necessary to find the dimension of the region that will be able to be heated to the temperature $\Theta \ge \Theta_{ig}$ in this case (the thermophysical properties of the medium are assumed to be given). Evidently, the sought region will have finite dimensions. The dimensionless equation of thermal conductivity for this two-dimensional problem has the form

$$\frac{\partial \Theta(r, \tau)}{\partial \tau} = S \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \Theta}{\partial r} \right) . \tag{9}$$

In the case where the initial source has the form of a δ function, the solution of (9) is as follows:

$$\Theta(r, \tau) = \frac{1}{4\pi S \tau} \exp\left[-\frac{r^2}{4S\tau} \right] . \tag{10}$$

From the condition determining the boundary of the ignition region $\Theta_{ig} = \Theta(r, \tau)$ we find

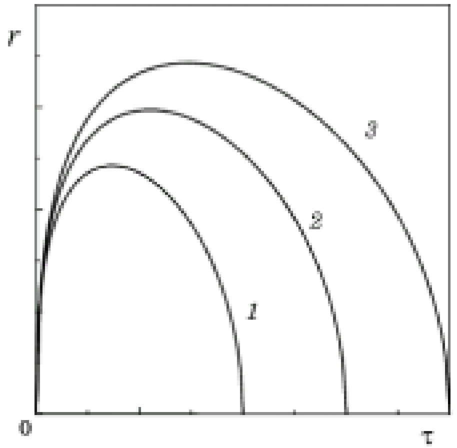

Fig. 5. Evolution of the position of the isotherms corresponding to different ignition temperatures: 1) $\Theta_{ig}^{(1)}$; 2) $\Theta_{ig}^{(2)}$; 3) $\Theta_{ig}^{(3)}$ ($\Theta_{ig}^{(1)} > \Theta_{ig}^{(2)} > \Theta_{ig}^{(3)}$).

$$r\,(\Theta_{ig}, \tau) = \sqrt{-\,4S\tau \ln\,(4\pi S\tau\Theta_{ig})}\ . \tag{11}$$

The maximum dimension of the region heated to the temperature Θ_{ig} is determined by the extremum of the function $r(\Theta_{ig}, \tau)$ (Fig. 5). Then, from (11) we have

$$R_{\max} = \frac{1}{\sqrt{\pi e \Theta_{ig}}}\ . \tag{12}$$

Now we can describe the process of propagation of combustion in a random system with rare inclusions of the combustible components in the following way. Let combustion be initiated in one combustible particle. Having burned out, this particle will heat a certain region of radius $R_{\max}$ to the ignition temperature Θ_{ig}. If in this region there is at least one unreacted combustible particle, a reaction is also initiated in it and it in turn heats a new region to Θ_{ig}. In such a way the combustion process propagates over the specimen. It is seen that in this formulation the problem in question is equivalent to the problem of percolation on the enveloping circles (Fig. 4). The combustion process will propagate over the entire specimen if in it there is a percolation cluster of circles with a radius $R_{\max}$ around the combustible particles. Then, from (7), (8), and (12), one can evaluate the number concentration of the combustible particle, at which a percolation cluster is formed and accordingly the propagation of the combustion process over the system is possible:

$$n_c \approx -\frac{\ln\,[1 - \phi_c]}{\pi R_{\max}^2} \approx 3.06\ \Theta_{ig}\ . \tag{13}$$

Thus, for Θ_{ig} = 0.025 from (13) we obtain $n_c \approx 0.076$. In reality, relation (13) is only the upper bound of the threshold for the combustion problem in question. The fact is that when the reaction is initiated in the next particle, a part of the space around it is already heated to a fairly high temperature; therefore, this particle can heat to Θ_{ig} a region somewhat larger than the above-mentioned circle of radius $R_{\max}$. This will be especially pronounced at those sites of the system where there are conglomerates of several particles. Because of this, the threshold concentration will be decreased in the problem studied in comparison with estimate (13).

We must offer the following explanation. On the one hand, the model of a heterogeneous condensed mixture used in this work is in fact a grid since all the particles are located at the points of the square grid. On the other hand, the process of propagation of combustion over the system with rare combustible inclusions has been described above in terms of the continual percolation. The continual approach can be used for investigation of grid problems if the parameter R is much larger than the distance between the neighboring grid points or, which is equivalent, the area of the circle is much larger than the area of the conglomerate found at the center of this circle [13]. Because of this,

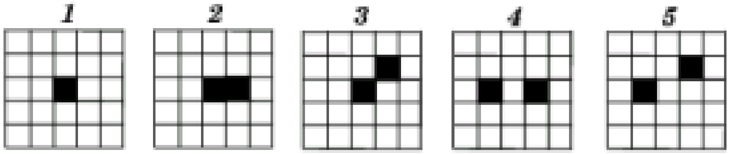

Fig. 6. Conglomerates of particles (1–5) used in evaluating the threshold concentration of combustible particles for the process of combustion in the heterogeneous condensed system.

the scheme of further calculations is as follows. The critical value of the number α of the continual problem will be used for evaluation of the threshold concentration. Since conglomerates of different numbers of particles are present in the system, the problem of continual percolation must be considered with regard for the distribution of circles over the radii, and the expression for the number α must be generalized correspondingly. In this case, the grid model will be used for calculating the concentration of conglomerates having different spatial configurations.

Let us consider the approximation that will allow us to take into account the influence of conglomerates consisting of several particles. The number α for the percolation problem in which the circles have a distribution over the radii (rather than one fixed dimension) is determined through averaging with the use of the distribution function [14]: $\alpha = \int \pi R^2 N(R)\, dR$ ($n \equiv p$ in the problem considered). In this case, the centers of the circles are uniformly distributed over the plane, and $n(R)dRdA$ is the probability that the center of a certain circle is within a small region dA and this region itself has a radius lying in the interval $(R, R + dR)$. An analogous relation can also be used in the case where more complex geometric figures overlap and not the circles. In this case, the critical value of the number remains unchanged (unless the radii of the regions differ by an order of magnitude). In our case, there is a discrete set of overlapping regions; therefore, the number α takes the form $\alpha = \Sigma p_k \Omega_k$. All the conglomerates of one or two particles that will be considered are presented in Fig. 6. Thus, for example, the probability of the appearance of conglomerate 3 (Fig. 6) is equal to $2p^2$, where 2 is the number of different spatial orientations in such disposition of two particles on the square grid and p^2 is the probability that the two particles are combustible.

Next we consider the solution of (9) on condition that the quantity of heat mQ is released at the initial instant of time (i.e., m particles burn out and not one). It can be shown that the maximum radius of the region heated to Θ_{ig} will be determined as

$$R_{\max}(\Theta_{\text{ig}}, m) = \sqrt{\frac{m}{\pi e \Theta_{\text{ig}}}} . \tag{14}$$

In this case, it is assumed that all m particles are positioned at the same point. This corresponds to the above-discussed condition of the applicability of the continual approach to grid problems. Taking into account the fact that the area of one particle in dimensionless variables is equal to unity, we can now write this condition, in view of (14), as $\pi R^2_{\max}(\Theta_{\text{ig}}, m) >> m$; whence it follows that

$$\Theta_{\text{ig}} << \frac{1}{e} \approx 0.367 . \tag{15}$$

The analytical estimates of the threshold concentrations of the combustible in the system, presented below, will be true at these temperatures.

Thus, to find the indicated concentrations, it is necessary to solve the following algebraic equation:

$$a_{\text{c}} = \sum_k p_k \Omega_k , \tag{16}$$

which, in this case, is conveniently represented as

TABLE 1. Critical Concentrations of the Combustible p_c (%) Obtained on the Basis of the Continual Theory of Percolation and the Numerical Experiment

Θ_{ig}	p_c	
	theory	numerical experiment
0.025	4.2	4.2
0.05	7.9	8.1
0.10	14.3	16.1
0.25	33.0	39.4

$$\alpha_c = \sum_{m=1}^{2} \left[\pi R^2_{\max} (\Theta_{ig}, m) \sum_k p_k \right] . \tag{17}$$

Here, the sum in square brackets is taken only over conglomerates consisting of m particles, since it is assumed that they correspond to the same radius $R_{\max}(\Theta_{ig}, m)$. The number of spatial orientations for conglomerates containing one or two particles will be equal to 1, 2, 2, 2, and 4 for the conglomerates with the serial numbers 1, 2, 3, 4, and 5 respectively (Fig. 6). Here, mention should be made of the circumstance associated with the calculation of $\Sigma\, p_k$, which will be illustrated by the following example. In conglomerate 5 (Fig. 6), one particle cannot ignite another particle even at $\Theta_{ig} \geq 0.5$; therefore, it should not be included in the indicated sum at such ignition temperatures. This means that care must always be exercised to see fulfillment of the following condition: if a conglomerate of m particles consists of two spatially separated parts of m_1 and m_2 particles ($m_1 + m_2 = m$, $m_1 \geq m_2$), the distance l between these parts must be $l < R_{\max}$ (Θ_{ig}, m_1). Then from (17), in view of (14), we have

$$\Theta_{ig} = 0.025\,, \quad p + 20p^2 - \alpha_c e \Theta_{ig} = 0\,; \tag{18.1}$$

$$\Theta_{ig} = 0.05\,, \quad p + 12p^2 - \alpha_c e \Theta_{ig} = 0\,; \tag{18.2}$$

$$\Theta_{ig} = 0.10\,, \quad p + 8p^2 - \alpha_c e \Theta_{ig} = 0\,; \tag{18.3}$$

$$\Theta_{ig} = 0.25\,, \quad p + 4p^2 - \alpha_c e \Theta_{ig} = 0\,. \tag{18.4}$$

The roots of these equations in the interval [0, 1], which represent the estimate of the threshold concentrations for the corresponding ignition temperatures, are given in Table 1 along with the results of the direct numerical modeling. As is seen, there is a good correspondence between the theory and the numerical experiment for low ignition temperatures down to Θ_{ig} = 0.10. We note that it is precisely these combustible concentrations that are used in a large number of practical applications [4–6]. At higher ignition temperatures, a significant discrepancy between the theoretical and experimental data is observed. One reason for this is the violation of condition (15). On the other hand, our expansion is limited only by the conglomerates of two particles. If the concentration of the combustible exceeds 10%, in the system there are a large number of conglomerates of three, four, or a larger number of combustible particles. The fact that these large conglomerates were not taken into account in the consideration is another reason for the indicated discrepancy. However, in the case where conglomerates, for example, of three particles are used in the expansion, the regions heated by them will be several times larger than the region heated by one particle. This means that in this case we do not have the right to use the value of α_c = 1.128 in Eq. (16)–(18). This critical value of the number α has been obtained for the problem of percolation on the enveloping circles of the *same* radius. In [14], this problem has been investigated for the case where there are spheres of two different radii R_1 and R_2. It has been shown in this work that the critical value of the number α has a minimum at R_1/R_2 = 1 and increases when the ratio $R_1/R_2 \to 0$ or, which is equivalent, $R_1/R_2 \to \infty$. Analysis of the solutions of Eq. (18) shows that when the coefficients of powers

p are fixed, an increase in the free term, i.e., in α_c, leads to an increase in the real root of these equations in the interval [0, 1]. This means that at large Θ_{ig} the discrepancy between the theory and the experiment will decrease if a more exact value of α_c is used for the system of circles having different radii. However, to obtain a more exact estimate for the critical concentration at high ignition temperatures in the problem considered it is necessary to investigate the pure problem of percolation on the enveloping circles having a radial distribution, which is beyond the scope of the present work.

Thus, the results of the numerical modeling point to the fact that a random heterogeneous system in which a reaction is initiated as a result of the melting of one component has a concentration limit of combustion even in the case of its heat insulation. It has been shown that this limit exists due to the existence of a geometric phase transition in the system; to put it otherwise, it is due to the formation of a percolation cluster consisting of the regions of ignition of individual combustible particles and their conglomerates. We have proposed an analytical approach to the description of this problem, which is based on the continual theory of percolation. The results of the numerical experiment and the analytical (percolation) approach are in good agreement at the dimensionless temperature of ignition $\Theta_{ig} \leq 0.1$. The discrepancy between the analytical theory and the numerical experiment at higher ignition temperatures can be explained by the errors in the analytical (percolation) solution because of the neglect of the contribution of the conglomerates with a large number of particles and the restrictions imposed on the use of the continual percolation approach at such ignition temperatures.

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NOTATION

ΔT_{ad}, adiabatic heating of the system as a result of the reaction, K; T_0, initial temperature of the system, K; T, running temperature, K; Θ, dimensionless temperature; η, degree of conversion of the combustible particles; $\langle\eta\rangle$, mean degree of conversion; $\langle V\rangle$, mean velocity of the combustion wave; p, number fraction of the combustible particles in the mixture; p_c, threshold fraction of the combustible particles in the mixture; L, dimension of the system (number of cells in one directions); $c_{ij}^{(0)}$, initial concentration of the combustible in the particle; S, effective dimensionless thermal diffusivity; a, thermal-diffusivity coefficient of a particle, m^2/sec; t_{rc}, characteristic time of the reaction, sec; d, dimension of a unit cell, m; τ, dimensionless time; W, chemical-reaction rate; Bi, Biot criterion; α_{eff}, effective coefficient of heat exchange between particles, W/(m^2·K); λ, thermal-conductivity coefficient, W/(m·K); δ, effective thickness of the gaseous interlayers between the particles, m; A, B, p_0, and Δp, dimensionless parameters of the interpolation function; ξ, pseudorandom number; n, number concentration of points chaotically distributed over the space, 1/m^2; R, radius of the circle in the problem of continual percolation, m; α, dimensional number of the continual theory of percolation; ϕ, part of the space occupied by the spheres; d_t, topological dimensionality of the space; Q, quantity of heat, J; R_{max}, maximum radius of the region heated to the ignition temperature; Ω_k, area of the region which can be heated to the ignition temperature by the kth combination of particles; p_k, probability of the appearance of the kth combination of particles; m, number of particles in the conglomerate; l, distance between the parts of the conglomerate; r, modulus of the radius vector; X, Y, coordinate axes; x, y, spatial coordinates; e, base of natural logarithm. Subscripts: lf, r, u, and d, left, right, upper, and lower boundaries of the cell respectively; s, solid body; g, gas; i and j, serial numbers of the particle along the X and Y axes, respectively; k, serial number of the conglomerate of particles in accordance with Fig. 6; c, critical; ad, adiabatic; t, topological; 0, initial; ig, ignition; in, initiation; rc, reaction; eff, effective; max, maximum.

REFERENCES

1. A. S. Rogachev and A. G. Merzhanov, *Dokl. Ross. Akad. Nauk*, **365**, No. 6, 788–791 (1999).
2. A. Varma, A. S. Mukasyan, and S. Hwang, *Chem. Eng. Sci.*, **56**, 1459–1466 (2001).
3. E. Shafirovich, A. S. Mukasyan, A. and Varma, *Combust. Flame*, **128**, No. 1/2, 133–144 (2002).
4. G. S. Kshirsagar, J. C. Cannon, and Yu. Zhang, U.S. Patent No. 6030583 (2000).
5. Yu. Zhang and J. C. Cannon, U.S. Patent No. 6231816 B1 (2001).

6. Yu. Zhang and J. C. Cannon, U.S. Patent No. 6352652 B2 (2002).
7. D. Kunii J. M. and Smith, *AIChE J.*, **6**, No. 1, 71–78 (1960).
8. L. D. Landau and E. M. Lifshits, *Statistical Physics* [in Russian], Pt. 1, Moscow (1976).
9. R. Balescu, *Equilibrium and Nonequilibrium Statistical Mechanics*, Vol. 1, New York (1978).
10. L. I. Kheifets and A. V. Neimark, *Multiphase Processes in Porous Media* [in Russian], Moscow (1982).
11. B. I. Shklovskii and A. L. Efros, *Electronic Properties of Doped Semiconductors*, Berlin (1984).
12. J. Quintanilla, S. Torquato, and R. M. Ziff, *J. Phys. A*, **33**, No. 42, L399–L407 (2000).
13. B. I. Shklovskii and A. L. Efros, *Usp. Fiz. Nauk*, **117**, No. 3, 401–435 (1975).
14. M. K. Phani and D. Dhar, *J. Phys. A*, **17**, No. 12, L645–L649 (1984).