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NONISOTHERMAL EFFECTS IN THE GROWTH OF CARBON CLUSTERS IN THE GAS PHASE

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A numerical investigation of the nonisothermal effects occurring in the process of growth of carbon clusters in the gas phase in the temperature range 2000–3000 K has been carried out. It has been established that these effects are due to the phase-transition latent heat released as a result of the volume condensation of nonequilibrium carbon vapor as well as the convective and radiative cooling of the clusters. It is shown that, under the indicated conditions, the radiative cooling of carbon clusters is the dominant cooling mechanism. A mathematical simulation was carried out for the cases of optically thin and thick layers of a vapor-gas mixture embedded in cold walls. The dependence of the growth and temperature of the carbon clusters on their porosity, the supersaturation of the carbon vapor, and the temperature of the vapor-gas mixture was detected. It has been established that the temperature of the growing carbon clusters can be higher or lower than the temperature of the vapor-gas mixture and the deviation from this temperature can exceed 500 K. The data obtained were compared with the results of experiments on shock tubes.

Keywords: *radiative cooling, free-molecule regime of growth, porosity of a cluster.*

Introduction. The formation of carbon clusters in the gas phase as a result of different physicochemical transformations of hydrocarbons is of considerable scientific and technical interest [1, 2]. It is well known that such clusters are of great astrophysical interest because they play an important role in the formation of the interstellar dust [3]. Carbon clusters are also involved in many transfer processes occurring in the Earth's atmosphere and determining the ecological state of the environment [4, 5]; in particular, they contribute much to the rise in global temperature.

The aim of the present work is to simulate the nonisothermal effects that are due to the phase-transition latent heat released as a result of the volume condensation of nonequilibrium carbon vapor. We will consider the initial stage of the growth of a carbon cluster, where its initial radius is equal to 1 nm and the growth time does not exceed a millisecond.

Model of a Cluster. Clusters formed as a result of the volume condensation of vapor are frequently considered as liquid drops. However, this approximation does not apply in the case of carbon-vapor condensation in the temperature range 2000–3000 K. It has long been known [2] that carbon clusters are very different in geometrical structure. Therefore, to characterize a carbon cluster, in addition to the main parameter g, the number of carbon atoms, we will use the parameter ε defining its porosity and representing the ratio between the volume of the cluster and the volume of the sphere constructed about it. In this case, the radius of a cluster $R(g, \varepsilon)$ consisting of g atoms and having a porosity ε (the radius of the inclosing sphere in fact) is equal to

$$R\,(g, \varepsilon) = \left(\frac{3g\, v_{\mathrm{a}}}{4\pi\varepsilon}\right)^{1/3}, \tag{1}$$

where v_{a} is the volume per a carbon atom in the condensed phase. It is evident that the porosity is an integral representation of the cluster structure. Note that, at a temperature of 2000 K, the atomic volume $v_{\mathrm{a}} \approx 10^{-29}$ m^3. As follows from (1), small variations in the number of atoms in a cluster or in its porosity practically have no influence on the radius of the cluster. It will be assumed that the area of the surface of such a cluster is $4\pi R^2(g, \varepsilon)$, i.e., the area of

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the surface of a cluster having a porous structure is larger as compared to that of the cluster in the condensed phase. In the calculations, the porosity will be taken into account only parametrically. We will consider only the clusters, the porosity of which ε is close to unity.

The energy of the force interaction between the carbon atoms in a cluster will be calculated on the assumption that the thermal motion of atoms in the cluster is identical to the atomic motion in a potential well. The depth of the potential well U is equal to the evaporation energy per an atom.

The supersaturation of carbon vapor S is calculated as

$$S = \frac{n}{n_{\mathrm{s}}(T)}, \tag{2}$$

where n and $n_{\mathrm{s}}(T)$ are respectively the numerical densities of the carbon vapor and the saturated carbon vapor at a temperature T.

It is known that, for a definite supersaturation, there exists a critical cluster radius, so that clusters whose size is larger than the critical one are capable of further microscopic growth. The smaller clusters are thermodynamically unstable and break down. In our model, the critical radius R_{cr} of a carbon cluster is determined from the expression representing a simple generalization of the Gibbs formula [5]:

$$R_{\mathrm{cr}}(\varepsilon) = \frac{2\sigma v_{\mathrm{a}}}{\varepsilon kT \ln S}. \tag{3}$$

At $\varepsilon = 1$, formula (3) is transformed into the classical expression given in [6]. At $R = R_{\mathrm{cr}}$, the free energy of cluster formation reaches a maximum and all the thermodynamic forces become equal.

A characteristic feature of carbon is that, at a fairly high supersaturation of its vapor, the radius of a critical cluster becomes comparable to the size of an atom. In this case, the nucleation kinetics degenerates and we can simply consider the growth of a cluster in the supersaturated carbon vapor. In what follows the nonisothermal growth of carbon clusters of initial radius 1 nm having an initial temperature equal to the temperature of the vapor-gas mixture will be simulated.

Simulation of the Nonisothermal Growth of Clusters. Let us consider the growth of a carbon cluster from the standpoint of the kinetic theory of gases. Actually, at atmospheric pressure, the mean free path of the carbon atoms is much larger than the diameter of a carbon cluster, so that the nonisothermal growth of a cluster can be described with the use of the free-molecule approximation of the transfer processes in the gas phase.

The nonisothermal growth of a carbon cluster is defined by the system of two ordinary differential equations [7]. The equation for the change in the cluster radius with time has the form

$$\frac{dR}{dt} = \frac{m}{\rho_{\mathrm{c}}\varepsilon\sqrt{2\pi mk}}\left[\frac{nkT}{\sqrt{T}} - \frac{p_{\mathrm{s}}(T_{\mathrm{c}})}{\sqrt{T_{\mathrm{c}}}}\right], \tag{4}$$

where $p_{\mathrm{s}}(T)$ is the pressure of the saturated carbon vapor at a temperature T, ρ_{c} is the density of the cluster (~2000 $\mathrm{kg/m^3}$), and m is the mass of a carbon atom.

In the approximation of an optically thick gas layer around the cluster, its temperature T_{c} is determined from the expression

$$\frac{dT}{dt} = \frac{3}{Rc}\left[-(cT_{\mathrm{c}} - U)\frac{dR}{dt} + \frac{3\Pi v_{\mathrm{a}}}{\varepsilon} - \frac{\sigma_{\mathrm{S-B}}(T_{\mathrm{c}}^4 - T^4)\, v_{\mathrm{a}}}{\varepsilon}\right], \tag{5}$$

where c is the heat capacity per a carbon atom in the condenced phase, $\sigma_{\mathrm{S-B}}$ is the Stefan–Boltzmann coefficient, and Π defines the gas-energy flux propagating to the cluster:

$$\Pi = \frac{1}{\sqrt{2\pi mk}}\left[\frac{nkT\,(c_{\mathrm{car}}T + U + 0.5kT)}{\sqrt{T}} - \frac{p_{\mathrm{s}}(T_{\mathrm{c}})\,(c_{\mathrm{car}}T_{\mathrm{c}} + U + 0.5kT_{\mathrm{c}})}{\sqrt{T_{\mathrm{c}}}}\right] + \frac{kn_{\mathrm{car}}}{\sqrt{2\pi m_{\mathrm{car}}k}}\left[\frac{2kT^2}{\sqrt{T}} - \frac{2kT_{\mathrm{c}}^2}{\sqrt{T_{\mathrm{c}}}}\right]. \tag{6}$$

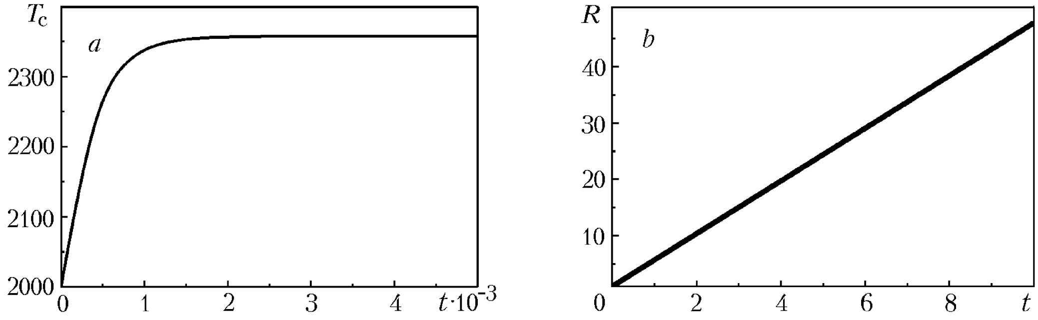

Fig. 1. Change in the temperature (a) and radius (b) of a cluster with time at $T = 2000$ K, $\varepsilon = 0.5$, and $S = 10^7$. T_c, K; R, nm; t, msec.

A phase-transition latent heat release causes the cluster temperature to increase. In the optically-thick-layer approximation, it is suffice to know the gas temperature for calculating the nonisothermal effects. In the approximation of an optically thin gas layer around the cluster, the temperature of the gas can differ from the temperature of the walls of a chamber (a shock tube). The possibility of use of the Stefan–Boltzmann law involved in Eq. (5) for description of the heat radiation of carbon nanoparticles will be considered below.

The numerical calculations were carried out with MathCad software. Figure 1 shows the change in the temperature of a cluster with time, determined in the optically-thick-layer approximation. It is seen that the temperature of the cluster increases by 350 K within several microseconds and, thereafter, remains constant, i.e., the processes of heating and cooling of the cluster balance each other. As our calculations have shown, the dominant mechanism of cooling of the cluster is radiative cooling [8, 9]. It is interesting to note that, according to (3), at a supersaturation $S = 10^7$ the critical cluster radius is smaller than the radius of a carbon atom.

As follows from Eq. (4), in the free-molecule regime, the radius of a carbon cluster increases with time by the linear law. Figure 1b shows the change in the radius of a cluster under these conditions. It is seen that, even at an enormous supersaturation, the rate of growth of the cluster is fairly small, which is explained by the low density of the saturated carbon vapor at the indicated temperature. Actually, as follows from Eq. (4), the rate of change in the cluster radius is

$$\frac{dR}{dt} \sim \frac{p_s(T)(S-1)}{\rho_c \varepsilon}.$$

Since the temperature dependence of the saturated-vapor pressure is exponential in character, the same rate of growth of a cluster with increasing mixture temperature is attained at a substantially lower supersaturation of the carbon vapor. A decrease in the parameter ε leads to a decrease in the effective density of the material of the cluster, with the result that the rate of its growth increases. At a supersaturation $S > 10^6$, the radius of the cluster increases by several nanometers for a growth time of the order of 1 msec; this time of growth of carbon clusters was detected in many experiments [1, 10].

Figure 2a shows the dependence of the difference between the stationary temperature of a cluster and the temperature of the gas mixture on the supersaturation of the carbon vapor S, determined in the optically-thick-layer approximation at temperatures of the vapor-gas mixture of 2000 and 2500 K. It is seen that, at a higher temperature of the gas mixture, the cluster is heated to a higher temperature (its stationary temperature increases). Note that, at $T =$ 2000 K and $S > 5 \cdot 10^7$, the temperature of the cluster does not reach a stationary value.

Figure 2b shows the influence of S on the relative radius of the cluster at a growth time $t = 1$ msec. As follows from the graphs, at $T = 2000$ K, the radius of the cluster increases by an order of magnitude only at $S > 10^6$; at lower supersaturations, the cluster grows very slowly with a characteristic growth time measured in astronomical scales. As the temperature of the vapor-gas mixture increases to $T = 2500$ K, the rate of growth of the cluster increases by almost several times at a lower supersaturation. The physical reason for the increase in the rate of cluster growth is the exponential dependence of the saturated-carbon-vapor pressure on the temperature.

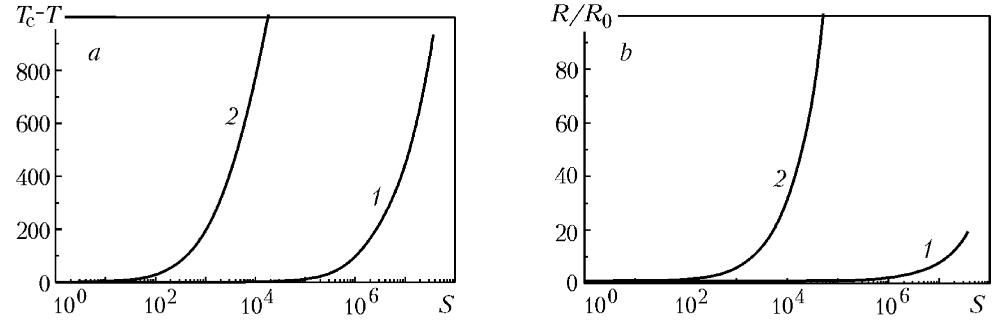

Fig. 2. Dependence of the difference between the stationary temperature of a cluster and the temperature of the gas mixture (a) and of the relative radius of the cluster (b) on the supersaturation at $\varepsilon = 0.5$: $T = 2000$ (1) and 2500 K (2). $T_c - T$, K.

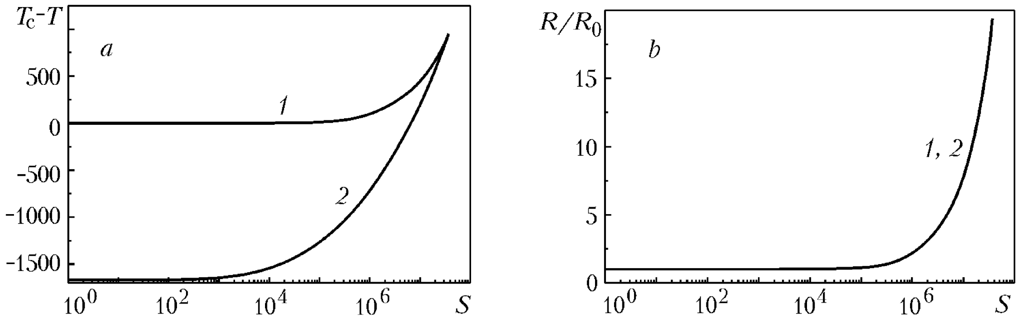

Fig. 3. Dependence of the difference between the stationary temperature of a cluster and the temperature of the gas mixture (a) and of the relative radius of the cluster (b) on the supersaturation at $\varepsilon = 0.5$, $T = 2000$ K, and a shock-tube wall temperature of 300 K: 1) optically thick layer; 2) optically thin layer. $T_c - T$, K.

Note that, in this work, the porosity of a cluster implies the ratio between the volume of the cluster and the volume of the sphere constructed about it. Our calculations have shown that, at $\varepsilon > 0.5$, the stationary temperature of a carbon cluster is low and the rate of its growth remains unchanged. This is explained by the fact that the mass of the cluster increases with increase in ε and, consequently, with increase in its heat capacity.

For consideration of the cooling of a carbon cluster in the optically-thin-layer approximation, the gas temperature in the last term of Eq. (5) should be changed for the temperature of the walls of a shock tube (approximately 300 K). The results of calculations performed for different values of the carbon-vapor supersaturation S are shown in Fig. 3. It is significant that, in the optically-thin-layer-approximation that holds for small concentrations of carbon clusters in the gas mixture, the stationary temperature of the clusters is much higher than the temperature of the shock-tube walls; however, it is lower than the gas temperature, and the difference between these temperatures can reach 1500 K. At fairly high supersaturations of the carbon vapor and, consequently, at large rates of growth of clusters, their temperature is higher than the gas temperature by almost 1000 K.

The question arises of whether the Stefan–Boltzmann law can be used for description of the radiating capacity and the absorptivity of carbon nanoparticles. The answer to this question depends on the size and temperature of these particles [8, 11]. Clearly, electromagnetic radiation with a wavelength much longer than the radius of a nanoparticle will interact with it weakly and, consequently, will be absorbed poorly. Thus, in our calculations, the role of the radiative cooling of carbon clusters is overstated because of the use of the Stefan–Boltzmann law in the mathematical model; the accuracy of the calculations increased with increase in the nanoparticle radius. However, in our opinion, the qualitative results obtained by us are valid. At a definite temperature, the criterion of applicability of the Stefan–Boltzmann law implies qualitatively that the maximum wavelength of the equilibrium heat radiation should be larger by an order of magnitude than the radius of a nanoparticle. At a temperature of 3000 K, clusters with a radius of

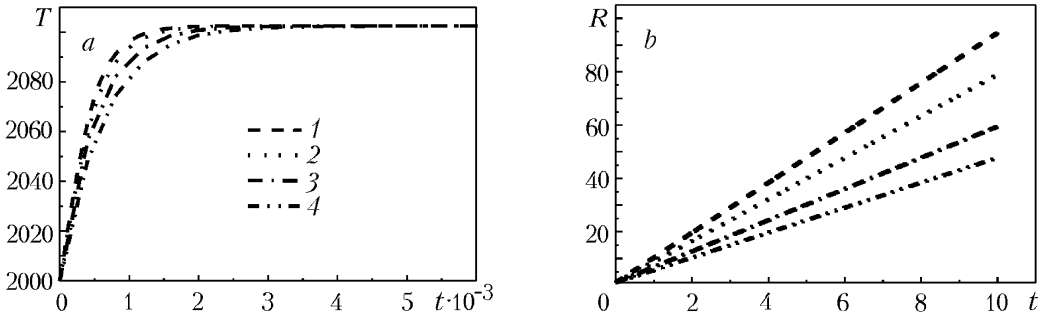

Fig. 4. Dynamics of the change in the temperature (a) and radius (b) of a cluster with time for different values of ε at T = 2000 K, a shock-tube wall temperature of 300 K, and $S = 10^7$: ε = 0.5 (1), 0.6 (2), 0.8 (3), and 1.0 (4). T, K; R, nm; t, msec.

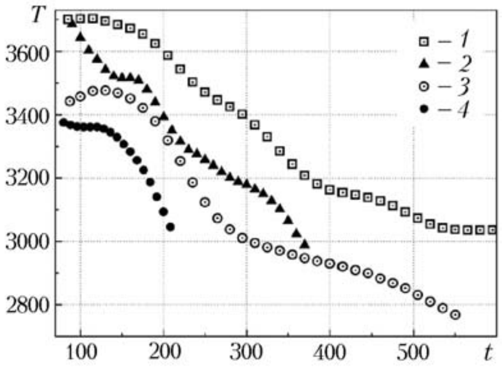

Fig. 5. Dynamics of the change in the temperature of the soot particles formed in the process of pyrolysis of the gas mixture 2% of C_2H_4 + 98% of Ar at a gas temperature behind the shock wave T = 2867 (1), 2810 (2), 2720 (3), and 2948°C (4). T, °C; t, μsec.

larger than 100 nm meet these condition. Despite the enormous difference between the clusters in temperature, they grow with an equal rate. The physical reason for this paradoxial result is that, at the temperatures being considered, the evaporation of carbon atoms from the clusters is practically absent, and the condensation process is determined by only the parameters of the gas medium.

It is significant that a change in the character of the radiative heat exchange between the clusters and the environment has no influence on the rate of their growth (the calculation curves coincide). In the case of an optically thin gas layer, at a relatively low supersaturation $S \le 5 \cdot 10^6$, the temperature of a cluster decreases rapidly to a stationary value that is much lower than the gas temperature. This is evidence of its rapid radiative cooling as a result of the interaction with the cold walls of the shock tube [12]. At $S > 5 \cdot 10^6$, the temperature of the cluster increases with increase in the rate of the heat release caused by the carbon-vapor condensation and, once again, exceeds the gas temperature.

The influence of the cold walls of the shock tube on the growth of a carbon cluster and its temperature, estimated in the optically-thin-layer approximation at different values of the cluster porosity, is shown in Fig. 4. Clearly the stationary temperature of the cluster is independent of its porosity because the energy fluxes falling on the cluster and emerging from it do not change with change in the cluster porosity. However, the rate of establishment of a stationary temperature increases with decrease in the value of ε, which is explained by the relative decrease in the heat capacity of the cluster. As the parameter ε increases, the rate of growth of the cluster substantially decreases, which is due to the denser packing of carbon atoms in it.

It is expected that the mathematical model proposed can be used for the qualitative description of the pyrolysis of hydrocarbon fuels in experiments on shock tubes [10, 12]. In [12], the dynamics of change in the temperature of the carbon soot formed in the pyrolysis of an ethylene-argon mixture behind the reflected shock wave (Fig. 5) at the cooling stage was investigated. It should be noted that the zones in Fig. 5 in which the temperature of the clusters is constant can be considered as the growth zones with a constant carbon-vapor supersaturation. Our calculations have shown that, if, at a temperature of 2000 K, ethylene with a partial pressure of 1 Pa is substituted for the carbon gas, the supersaturation of this gas will be equal to $6 \cdot 10^6$.

It has been established that the description of experimental data on the radiative cooling of soot particles with the use of the optically-thick-layer approximation [13] gives qualitatively correct results [11]. The hypotheses of an optically thick layer is associated with a large concentration of fairly large soot particles preventing radiative heat exchange between the clusters and the shock-tube walls. In particular, the optically thick layer approximation is true for carbon clusters of radius 10 nm with a numerical density of 10^{16} m^{-3}. Note that, for correct simulation of the results of this experimental investigation, including pyrolysis of ethylene (C_4H_4) with the use of the model proposed by us, the partial pressure of the carbon vapor should not exceed twice the partial pressure of the ethylene.

Conclusions. A mathematical model representing a system of two ordinary differential equations allowing one to calculate the nonisothermal effects during the growth of carbon clusters in a gas chamber with a constant temperature 2000–3000 K has been proposed. The nonisothermal growth of the clusters is caused by the phase-transition latent heat released as a result of the carbon-vapor condensation. The equations of our model also account for the radiative cooling of the carbon nanoparticles and the cooling of the clusters in their collisions with the carrier gas. In the calculations, argon was used as the carrier gas. The calculations were carried out for conditions under which the radius of carbon clusters increases to a value not smaller than 10 nm for a time not larger than 1 msec. The last-mentioned circumstance and the gas temperature actually determined the order of the carbon-vapor supersaturation.

The numerical calculations carried out in the optically-thick- and optically-thin-layer approximations have given radically different temperatures of the carbon clusters at low supersaturations of the carbon vapor. In this case, the calculations with the optically-thin-layer approximation were performed on the assumption that the temperature of the gas-chamber walls is equal to the room temperature.

It was shown that for a time of the order of 1 μsec the temperature of the carbon clusters reaches a stationary value that can differ substantially (by several hundreds of degrees) from the temperature of the surrounding gas. It is notable that, as our calculations have shown, at small values of the supersaturation S and a low temperature of the chamber walls, the temperature of the clusters, determined in the optically-thin-layer approximation, can be lower by a thousand degrees than the gas temperature; of course it is higher than the wall temperature. The dependences of the growth and stationary temperature of clusters on their porosity, determined in the optically-thick and optically-thin-layer approximations, are somewhat different. In the first case, an increase in the porosity of the clusters does not influence the rate of their growth but leads to an increase in their temperature. In the second case, carbon nanoclusters grow with a lower rate but have equal stationary temperatures.

It has been established that, in the temperature range 2000–3000 K, a cluster releases an energy in the process of carbon-vapor condensation mainly due to the radiative cooling. Clearly, this cooling mechanism will remain dominant when the temperature of the mixture increases.

In the free-molecular regime, carbon clusters grow with time by the linear law. In this case, the rate of growth of the clusters increases exponentially with increase in the temperature of the vapor-gas mixture. An increase in the temperature of this mixture leads to an increase in the stationary temperature of the clusters, and the same rate of growth is attained at substantially lower supersaturations of the carbon vapor.

A comparison of the data obtained with the available data of experiments on the radiative cooling of submicron carbon clusters in shock tubes has shown that the model developed qualitatively well describes the dynamics of cooling of carbon clusters in the optically-thick-layer approximation. This approximation is entirely warranted at a fairly high concentration of such carbon microparticles in a gas. It is significant that the characteristic time of cooling of a cluster is directly proportional to its radius and varies in inverse proportion to the gas temperature cubed. The calculations made on the basis of our model and the characteristic time of cooling determined allow the conclusion that, in some experiments [11], the radius of the carbon microparticles was no more than 0.3 μm (Fig. 5, curve 1). On curve 4 there is a region in which the temperature changes slowly evidently because of the change in the supersaturation; this region is followed by the region with a rapid relaxation of the temperature, caused by the radiative cooling. The calculation of the cooling of a carbon cluster on the basis of our model has shown that the radius of the clusters was about 80 nm in these experiments. There is a need to develop a more complex model that would allow one to take into account the dynamics of the change in the supersaturation of the vapor in an experimental setup. This work is being actively done at present. For the time being we compared the calculation results with experimental data without considering the kinetics of the pyrolysis of hydrocarbon gases; instead of these complex processes, a carbon vapor found near a cluster at a distance of the order of the mean free path was investigated. When the results of our calculations are compared with experimental data, one must bear in mind that the partial pressure of the carbon gases is always higher than the partial pressure of the carbon vapor at the same temperature. Thus, knowing the composition of a carbon gas mixture, one can estimate the maximum partial pressure of the carbon vapor.

Our calculations can undoubtedly be useful for the planning of new experiments on the formation of primary soot particles [1]. The theoretical investigation of the nonisothermal growth of carbon clusters will be continued.

NOTATION

c, heat capacity per an atom, J/K; g, number of atoms; k, Boltzmann coefficient, J/K; m, atomic mass, kg; n, numerical density of a gas, m^{-3}; p_s, pressure of the saturated carbon vapor, Pa; R, radius of a cluster, m; S, supersaturation of the carbon vapor; t, time, sec; T, temperature, K; U, latent heat of a phase transition per an atom, J; v_a, volume of a carbon atom in the condensed phase, m^3; ε, porosity; Π, energy flux from the gas to a cluster, J/(m^2·sec); ρ, carbon density, kg/m^3; σ, surface tension of the condensed carbon, N/m; σ_{S-B}, Stefan–Boltzmann coefficient, W/(m^2·K^4). Subscripts: a, atom; c, cluster; car, carrier gas; cr, critical; s, saturated.

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