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INFLUENCE OF FOREIGN ADSORBABLE GASES ON THE FORMATION OF CLUSTERS IN VAPOR–GAS SYSTEMS

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The influence of a foreign adsorbable gas on homogeneous and heterogeneous nucleation is investigated theoretically.

Keywords: *adsorbable gas, phase transitions, nucleation.*

Introduction. The study of phase transitions in aerosol systems is of great current interest for a number of new technologies connected with obtaining nanoparticles [1] as well as for the processes occurring in the Earth's atmosphere [2]. The formation and growth of nanosized aerosol particles occur generally in the presence of a buffer gas whose pressure noticeably exceeds the pressure of the vapor of a condensing component. It should be noted that in the majority of cases adsorption of the buffer gas molecules on the surface of phase transition is realized, with the concentration of adsorbed molecules being determined by the buffer gas pressure and their adsorption energy. In what follows we consider some questions of the influence of the adsorption of the buffer gas molecules on the processes of homogeneous and heterogeneous nucleation. In the classical theory of nucleation, the buffer gas parameters do not enter explicitly into the expression describing the nucleation rate. On the other hand, in a number of experimental works on the study of homogeneous nucleation both a decrease and an increase in the nucleation rate with the buffer gas pressure were observed, and in some experiments the dependence of the nucleation rate on this pressure was not detected at all. A review of theoretical and experimental works, where the influence of a buffer gas on the nucleation process was studied, can be found, for example, in [3–5]. Various mechanisms of a possible influence of a buffer gas on the nucleation rate were considered to explain the experimental data. In particular, the authors of [3] attribute the increase in the nucleation rate with the buffer gas pressure to the decrease in the surface tension on adsorption of the buffer gas molecules on the surface of clusters which leads to the lowering of the rate of evaporation of molecules from the clusters. In [5], the different behavior of the nucleation rate on increase in the buffer gas pressure in gas–clusters systems with various values of parameters is explained by the presence of two factors that oppositely influence the nucleation rate (by their competition). One of them is related to the increase in the rate of the removal of the heat released in condensation of vapor molecules on a cluster with the buffer gas pressure, which leads to a rise in the nucleation rate. The second factor, according to the authors of that work, is the increase in the free energy of cluster formation with the buffer gas pressure, which results in the nucleation rate reduction. The problem of phase transformations in aerosol systems involving nanoparticles with allowance made for the size effect, the presence of adsorbable foreign (buffer) gas in the system, and the influence of resonance radiation was studied in [6–9].

Influence of an Adsorbable Buffer Gas on Trapping of Vapor Molecules by Clusters in Homogeneous Nucleation. It is known that the nucleation rate depends on the free energy of formation of a critical cluster and the frequency of incorporation of molecules into the cluster [10–13]. Within the framework of the classical theory of nucleation, the expression for the rate of homogeneous nucleation in a gas phase can be written as [11, 12]

$$J_{\text{hom}} = k_{\text{Z}} \omega S_{\text{cr}} N_{\text{cr}} = k_{\text{Z}} \alpha_1 \frac{n_1 v_1}{4} \pi d_{\text{cr}}^2 n_1 \exp\left(-\frac{\Delta G_{\text{hom}}}{kT}\right) = A_{\text{hom}} \exp\left(-\frac{\Delta G_{\text{hom}}}{kT}\right), \tag{1}$$

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where $\omega = \alpha_1 \dfrac{n_1 v_1}{4}$ is the so-called frequency factor [11]; α_1 is the coefficient of condensation of vapor molecules on a clean cluster surface (without taking account of adsorbed foreign gas molecules), which is defined as the probability that the vapor molecule that falls on the particle surface is not reflected elastically back into the gas phase. The free energy of formation of the critical cluster ΔG_{hom} in the classical theory of homogeneous nucleation is expressed as $\Delta G_{\mathrm{hom}} = \pi\sigma d_{\mathrm{cr}}^2/3$.

A buffer adsorbable gas exerts a twofold effect on the rate of homogeneous nucleation in adsorption of its molecules at the phase transition front. First, there is the effect of blocking of the phase transition surface by adsorbed molecules of the foreign gas, which, with the use of the Langmuir model of adsorption, leads to the appearance of the additional multiplier $1 - \theta_2$ in (1). Naturally, this effect will decrease the rate of homogeneous nucleation. Moreover, adsorption of the foreign gas molecules on the cluster surface can result in a decrease in the surface tension coefficient, manifested as an increase in the nucleation rate [3].

It should be noted that the frequency factor ω in (1) with the above-given determination of the coefficient α_1 characterizes the flux density of vapor molecules sticking to the surface of the critical cluster.

We will consider the problem on the coefficient of trapping of vapor molecules by a particle (cluster) β_1, which is defined as the ratio of the resulting flux density of vapor molecules into the particle to the flux density of vapor molecules incident on the particle surface.

In the case of a free-molecular regime of gas flow, we can write an expression for the density of the resulting flux of vapor molecules into a spherical particle (next an isothermal case will be considered)

$$J_1 = \frac{v_1}{4}(1-\theta_2)\left[\alpha_1 n_1 - \alpha_{\mathrm{e}} n_{\mathrm{e}} \exp\left\{\frac{4\sigma(\theta_2) V_{\mathrm{m}}}{dkT}\right\}\right] = \beta_1 \frac{n_1 v_1}{4}. \tag{2}$$

Here for the quantity β_1 we have

$$\beta_1 = \alpha_1 (1-\theta_2)\left[1 - \frac{\alpha_{\mathrm{e}}}{\alpha_1 S} \exp\left\{\frac{4\sigma(\theta_2) V_{\mathrm{m}}}{dkT}\right\}\right]. \tag{3}$$

In [3], the dependence of the surface tension coefficient on the buffer gas pressure P_2 obtained taking account of the Langmuir adsorption isotherm is given:

$$\sigma(P_2) = \sigma(0) - n_0 kT \ln\left(\frac{P_2 + P_{20}}{P_{20}}\right). \tag{4}$$

where the quantity P_{20} can be represented as

$$P_{20} = \frac{n_0 (2\pi m_2 kT)^{1/2}}{\alpha_2 \tau_2}. \tag{5}$$

In view of Eq. (3) and the expression for the surface coverage by the adsorbed buffer (admixture) gas molecules $\theta_2 = \dfrac{P_2}{P_2 + P_{20}}$, for β_1 we have

$$\beta_1 = \alpha_1 \frac{P_{20}}{P_2 + P_{20}}\left[1 - \frac{\alpha_{\mathrm{e}}}{\alpha_1 S}\left(\frac{P_{20}}{P_2 + P_{20}}\right)^G \exp\left\{\frac{4\sigma(0) V_{\mathrm{m}}}{dkT}\right\}\right], \tag{6}$$

where $G = \dfrac{4V_{\mathrm{m}} n_0}{d}$.

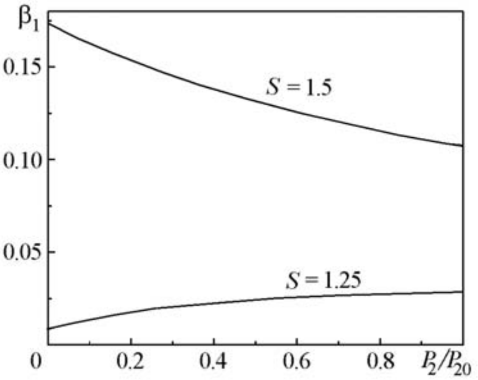

Fig. 1. Dependence $\beta_1(P'_{20})$ for a water drop of diameter $d = 10^{-6}$ cm at $\alpha_1 = \alpha_e = 1$, $T = 293$ K.

Figure 1 presents the dependence of β_1 on $P'_2 = P_2/P_{20}$ for a water drop at $\alpha_1 = \alpha_e = 1$. It is seen from the figure that the function $\beta_1(P'_2)$ can be both decreasing and increasing depending on the value of the quantity S. If the surface coverage by adsorbed foreign gas molecules θ_2 is rather small (i.e., the quantity $1 - \theta_2 = P_{20}/(P_2 + P_{20})$ is close to unity) and, moreover, the second term in brackets in (6) can be neglected, then $\beta_1 \approx \alpha_1$.

The critical diameter of a neutral particle governing the quantity ΔG_{hom} in (1), with allowance for the influence of adsorbed molecules on the surface tension coefficient and for the difference between the condensation and evaporation coefficients, can be presented [9] as

$$d_{\text{cr}} = \frac{\dfrac{4\sigma(0)\,V_{\text{m}}}{kT} + 4V_{\text{m}}n_0 \ln \dfrac{P_{20}}{P_2 + P_{20}}}{\ln S + \ln\left(\dfrac{\alpha_1}{\alpha_{\text{e}}}\right)}. \tag{7}$$

We note that previously it was assumed for simplicity that the foreign gas molecules were only adsorbed on the surface of clusters not entering them. Generally generation of clusters in vapor–gas systems can be interpreted as binary nucleation [4].

Influence of an Adsorbable Foreign Gas on Heterogeneous Nucleation. We will consider the question of the influence of adsorbable foreign gases on the process of heterogeneous nucleation occurring on a flat surface or on small particles. The expression for the rate of heterogeneous nucleation J_{het} can be presented in the form analogous to the case of homogeneous nucleation [14]:

$$J_{\text{het}} = A_{\text{het}} \exp\left(-\frac{\Delta G_{\text{het}}}{kT}\right). \tag{8}$$

In [14], a relation for the free energy of formation of a critical cluster on a spherical particle is presented, which in the limiting case goes over into the expression for the free energy of formation of a critical cluster on a flat surface. The pre-exponential factor in (8), just as in the case of homogeneous nucleation, is proportional to the quantity characterizing the frequency of incorporation of vapor molecules into a critical cluster. In the case of heterogeneous nucleation the latter quantity is determined both by the mechanism of direct penetration of molecules from a gas phase into the cluster and by a mechanism related to the surface diffusion of molecules on the substrate to the boundary line between the gas, cluster, and substrate. Here, as noted in [15], the influence of the surface diffusion of absorbed molecules can considerably increase the nucleation rate. The influence of adsorption of foreign gases on direct incorporation of molecules from a gas phase into a cluster in heterogeneous nucleation is analogous to the above-considered case of homogeneous nucleation. In [16], the influence both of the surface diffusion of vapor molecules and of the line tension that appears on the boundary line between the gas, cluster, and substrate was considered. A more substantial influence of surface diffusion in comparison with the effect of line tension is noted. In what follows the influence of an adsorbable foreign gas on incorporation of molecules into a cluster by surface diffusion is considered. The mechanism of the surface diffusion is assumed to be of activation character. The foreign gas molecules can be adsorbed on the substrate and cluster surfaces, as well as on the boundary line between the gas, cluster, and substrate. It should be noted that the presence of the adsorbable foreign gas molecules in a gas phase decreases the concentration of condensable phase molecules adsorbed on the substrate. This leads to a smaller flux of molecules incorporating into the cluster on the mentioned boundary line by surface diffusion of adsorbed molecules, of which the cluster is composed. The surface coverage of the substrate by such molecules with the Langmuir adsorption kinetics can be written, according to [17], as

$$\theta_1 = \frac{P_1}{P_1 + P_{10} + \dfrac{P_{10}}{P_{20}} P_2}, \tag{9}$$

where $P_{i0} = \dfrac{n_0 (2\pi m_i kT)^{1/2}}{\alpha_i \tau_i}$, $i = 1, 2$.

The surface coverage for the adsorbed molecules of a foreign gas θ_2 is determined analogously to Eq. (9) (where the subscripts 1 and 2 should be interchanged).

Adsorption of the foreign gas molecules on the boundary line between the gas, cluster, and substrate leads to blocking the transition of vapor molecules into the cluster by surface diffusion. Further, for simplicity we will consider the influence of the surface diffusion of molecules of both a vapor and foreign gas on the incorporation of vapor molecules into a cluster only on the substrate surface. The surface diffusion of molecules on the surface of the cluster itself will affect the process of incorporation of molecules into the cluster in a like manner. The frequency of jumps of adsorbed vapor molecules (atoms), of which the cluster is composed, per unit length of the boundary line can be estimated [15] as

$$j_1 = \frac{n_{a1}\delta}{4} \nu_0 \exp\left(-\frac{E_{d1}}{kT}\right) = \frac{n_{a1} D_{s1}}{\delta} = \frac{n_0 \theta_1 D_{s1}}{\delta}, \tag{10}$$

where $D_{s1} = \dfrac{1}{4}\delta^2 \nu_0 \exp\left(-\dfrac{E_{d1}}{kT}\right)$ is the coefficient of surface diffusion of adsorbed vapor molecules; δ is the mean length of a jump of an adsorbed vapor molecule which, for simplicity will be assumed, just as the mean length of a jump of an adsorbed molecule of a foreign gas, to be equal to the lattice parameter; ν_0 is the oscillation frequency of an adsorbed particle (which is considered to be the same for adsorbed particles of a vapor and foreign gas). It should be noted that in (10) the concentration of molecules adsorbed on the surface was considered, for simplicity, constant as far as the boundary line between the gas, cluster, and substrate. A closer analysis requires the solution of the diffusion equation for the concentration of adsorbed molecules under corresponding boundary conditions on the above-mentioned boundary line and at an infinite distance from it.

If we allow for the blocking influence of the molecules adsorbed on the boundary line between the gas, cluster, and substrate and assume that the adsorbed molecules can be incorporated into the condensed phase only when they fall on the free part of the boundary line mentioned, then for the frequency of jumps of molecules leading to their "condensation" on a unit length of the boundary line (further the sticking coefficients of adsorbed molecules of both the vapor and foreign gas on the part free of adsorbed foreign gas molecules are assumed to be equal to unity), we have

$$j_1' = (1 - \theta_{L2})\, j_1 . \tag{11}$$

For simplicity, we ignore the transition of molecules on the boundary line between the gas, cluster, and substrate from the cluster to the adsorption position on the substrate, i.e., the two-dimensional evaporation of molecules.

The expression analogous to (10) can be written also for the frequency of jumps of adsorbed foreign gas moleculs (atoms) per unit length of the boundary line:

$$j_2 = \frac{n_{a2}\delta}{4}\nu_0 \exp\left(-\frac{E_{d2}}{kT}\right) = \frac{n_{a2}D_{s2}}{\delta} = \frac{n_0\theta_2 D_{s2}}{\delta}, \quad (12)$$

where $D_{s2} = \frac{1}{4}\delta^2\nu_0 \exp\left(-\frac{E_{d2}}{kT}\right)$ is the surface diffusion coefficient of adsorbed foreign gas molecules.

With the use of the Langmuir adsorption kinetics, the expression for the coverage θ_{L2} of the boundary line between the gas, cluster, and substrate by adsorbed foreign gas molecules has the form

$$\theta_{L2} = \frac{\theta_2 A}{1 + \theta_2 A}, \quad (13)$$

where $A = \frac{D_{s2}n_0\tau_{L2}}{n_0'\delta}$.

Provided the inequality $A\theta_2 >> 1$ is fulfilled, the value of θ_{L2} can be close to unity even at sufficiently small surface coverage by these molecules θ_2. This means that the boundary line will be actually blocked for transition of the adsorbed vapor molecules from the substrate to this line. For $n_0 = 6 \cdot 10^{14}$ cm^{-2} [3], $D_{s2} = 10^{-6}$ cm$^2 \cdot$s^{-1}, $\tau_{L2} = 10^{-5}$ s, and $n_0' = \delta^{-1}$, we obtain $A = 6 \cdot 10^3$. Here the quantity θ_{L2} will be close to unity even at a sufficiently small surface coverage by adsorbed molecules (for example, at $\theta_2 = 0.01$).

Conclusions. The influence of a foreign gas on the processes of homogeneous and heterogeneous nucleation has been considered. The expression for the coefficient of trapping of vapor molecules by a small aerosol particle (cluster) with allowance made for an adsorbable foreign gas has been obtained. The pre-exponential factor, as well as the exponent power in the expression for the rate of homogeneous nucleation, were shown to depend generally on the foreign gas pressure. The influence of a foreign gas on heterogeneous nucleation has been considered. It is shown that even a low enough pressure of a foreign adsorbable gas leading to a small surface coverage by adsorbed molecules can result in a coverage of the boundary line between the gas, cluster, and substrate close to unity. This leads to the blockage of the attachment of vapor molecules to a cluster on the boundary line in the case of their surface diffusion.

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NOTATION

d, particle (cluster) diameter; d_{cr}, diameter of a critical cluster; E_{d1} and E_{d2}, activation energy of the surface diffusion of vapor and foreign gas molecules, respectively; ΔG_{hom} and ΔG_{het}, free energy of the formation of a critical cluster in homogeneous and heterogeneous nucleation; j, frequency of jumps of adsorbed molecules per unit length of the boundary line between the gas, cluster, and substrate; k, Boltzmann constant; k_Z, Zel'dovich factor; m_1 and m_2, mass of vapor and foreign gas molecules; N_{cr}, number density of critical clusters; n_1, number density of vapor molecules in a gas phase; n_{e1}, number density of saturated vapor molecules for a flat surface; n_{a1}, number density of adsorbed vapor molecules; n_0, number of adsorption centers per unit surface; n_0', number of adsorption centers per unit length of the boundary line between the gas, cluster, and substrate; P_1 and P_2, pressure of a vapor and foreign gas; P_e, saturated vapor pressure above a flat surface; $S = P_1/P_e$, vapor saturation ratio; $S_{cr} = \pi d_{cr}^2$, surface area of critical cluster; T, temperature; v_1, mean velocity of vapor molecules; V_m, volume per molecule in a particle; α_1, condensation coefficient of vapor molecules on a clean surface; α_2, sticking coefficient of molecules of a foreign gas; α_e, evaporation coefficient; β_1, coefficient of trapping of vapor molecules by a particle (cluster); δ, lattice parameter; θ_1 and θ_2, surface coverage for adsorbed molecules of a vapor and foreign gas; θ_{L2}, fraction of the boundary line occupied by adsorbed foreign gas molecules; ν_0, oscillation frequency of an adsorbed particle; σ, surface tension coefficient; $\sigma(0)$, surface tension coefficient for a clean surface (without adsorbed molecules); τ_1 and τ_2, time of adsorption of vapor and foreign gas molecules on the surface; τ_{L2}, time of adsorption of a foreign gas atom (molecule) on the boundary line between the gas, cluster, and substrate. Subscripts: cr, critical; hom, homogeneous nucleation; het, heterogeneous nucleation; L, boundary line; m, molecule; d, diffusion; e, evaporation; s, surface; 1, vapor; 2, foreign gas.

REFERENCES

1. M. T. Swihart, Vapor-phase synthesis of nanoparticles, *Current Opinion in Colloid and Interface Science*, **8**, 127–133 (2003).
2. J. H. Seinfeld and S. N. Pandis, *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, John Wiley & Sons, New York (1998).
3. C. C. M. Luijten, K. J. Bosschaart, and M. E. H. van Dongen, High pressure nucleation in water/nitrogen systems, *J. Chem. Phys.*, **106**, 8116–8123 (1997).
4. M. P. Anisimov, E. G. Fominykh, S. V. Akimov, and P. K. Hopke, Vapor–gas/liquid nucleation experiments: A review of the challenges, *J. Aerosol Sci.*, **40**, 733–746 (2009).
5. J. Wedekind, A. P. Hyvarinen, D. Brus, and D. Requera, Unraveling the "pressure effect" in nucleation, *Phys. Rev. Lett.*, **101**, 125703-1–125703-4 (2008).
6. V. V. Levdanskii, Dependence of the condensation (sticking) coefficient on the radius of small aerosol particles, *Inzh.-Fiz. Zh.*, **75**, No. 4, 18–22 (2002).
7. V. V. Levdansky, J. Smolik, and P. Moravec, Influence of size effect and foreign gases on formation of nanoparticles, *Int. Commun. Heat Mass Transfer*, **33**, 56–60 (2006).
8. V. V. Levdansky, J. Smolik, and P. Moravec, Critical size of aerosol particles in the resonance radiation field, *Int. Commun. Heat Mass Transfer*, **32**, 116–122 (2005).
9. V. V. Levdansky, J. Smolik, and P. Moravec, Influence of size effect, resonance radiation and surface processes on critical diameter of aerosol particles, in: *Proc. 18th Int. Conf. "Nucleation and Atmospheric Aerosols,"* 10–14 August, 2009, Prague, Czech Republic (2009), pp. 630–633.
10. J. W. P. Schmelzer, Kinetic and thermodynamic theories of nucleation, *Mater. Phys. Mech.*, **6**, 21–33 (2003).
11. J. P. Hirth and G. M. Pound, *Condensation and Evaporation. Nucleation and Growth Kinetics*, *Progress in Material Science*, Pergamon Press, Vol. 11, Oxford (1963).
12. B. Helfgen, P. Hils, Ch. Holzknecht, M. Turk, and K. Schaber, Simulation of particle formation during the rapid expansion of supercritical solution, *J. Aerosol Sci.*, **32**, 295–319 (2001).
13. T. A. Ring, Nano-sized cluster nucleation, *Adv. Colloid Interface Sci.*, **91**, 473–499 (2001).
14. N. H. Fletcher, Size effect in heterogeneous nucleation, *J. Chem. Phys.*, **29**, 572–576 (1958).
15. G. M. Pound, M. T. Simnad, and L. Yang, Heterogeneous nucleation of crystals from vapor, *J. Chem. Phys.*, **22**, 1215–1219 (1954).
16. M. Lazaridis, The effects of surface diffusion and line tension on the mechanism of heterogeneous nucleation, *J. Colloid Interface Sci.*, **155**, 386–391 (1993).
17. D. A. Frank-Kamenetskii, *Diffusion and Heat Transport in Chemical Kinetics* [in Russian], Nauka, Moscow (1987).