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INFLUENCE OF SURFACE PHENOMENA ON THE GROWTH OF AEROSOL PARTICLES IN A BUFFER (ADMIXTURE) GAS

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The influence of a buffer (admixture) gas on the deposition of molecules of a vapor on particles of an aerosol system is investigated.

It is known that the processes related to the formation and growth of aerosol particles occur, as a rule, in the presence of a buffer gas, the pressure of which greatly exceeds the vapor pressure of a condensing component [1]. These processes can include numerous processes of particle formation by homogeneous or heterogeneous condensation both under actual conditions (formation of particles in the atmosphere) and during the study of the physics of the process itself, for example, with the use of a diffusion chamber. At present, considerable efforts are being made toward obtaining nanoparticles by chemical decomposition of a certain starting gaseous substance (precursor) into the components, one of which is condensing under these thermodynamic conditions, in ordinary heating or by the action of laser radiation [2, 3]. This process is also realized in a buffer gas (for example, in nitrogen). Besides a buffer gas, different admixture components are usually present in the system. The adsorption of the molecules of a buffer (admixture) gas at the phase-transition boundary can substantially change the regularities of deposition of a substance from the gas phase. We note that in the classical theory of nucleation the parameters of a buffer gas do not enter explicitly into the expression describing the nucleation rate. On the other hand, the dependence of the rate of homogeneous nucleation on the buffer-gas pressure has been revealed in a number of experimental works on investigation of this process (review of both theoretical and experimental works related to the influence of a buffer gas on the nucleation process can be found, for example, in [4, 5]). Here, in most cases, a decrease in the nucleation rate with increase in the buffer-gas pressure was observed. However, experimental data are known in which an inverse dependence occurred (increase in the nucleation rate with increase in the buffer-gas pressure) [5]. It should be noted that at present there are a sufficiently great number of theoretical works where individual aspects of the influence of a buffer gas on the homogeneous-nucleation rate are discussed on the basis of different physical models. These theoretical works on the influence of a buffer gas on the deposition process can be subdivided conditionally into two groups. The first group includes investigations in which the effects leading to a deviation of the nucleation rate from the classical theory (in particular, the influence of the difference in properties of a vapor-buffer gas mixture from the regularities describing an ideal gas) are studied on the basis of thermodynamic, statistical, or kinetic approaches regardless of the concrete device where the process considered is studied. The second group includes works in which the influence of heat- and mass-transfer processes on deposition (nucleation) in concrete devices (for example, in a diffusion chamber) is analyzed. Clearly, as this takes place, a dependence of transfer processes on the system's geometry is manifested, which affects the distribution of thermodynamic parameters in this device, including the overall pressure in it

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that is determined mainly by the buffer-gas pressure. We note that in the works of the two groups mentioned insufficient attention is given to the influence of surface processes on the resultant flux of vapor molecules into a growing particle.

We will assume in analysis of the effects associated with the processes which are realized on the surface of aerosol particles that the radius of the latter is substantially smaller than the mean free path of both the vapor and buffer-gas molecules (the free-molecular regime of flow). For simplicity, we will disregard the effects related to the occurrence of resistance to the supply of vapor molecules to the particle surface in the presence of the buffer gas [6, 7] and the influence of the buffer gas on the potential of interaction of the vapor molecules with the particle [8] (it should be noted that the factors mentioned lead to a decrease in the deposition rate with increase in the buffer-gas pressure). The condensation coefficient for molecules impinging on the particle surface which is free from adsorbed molecules is assumed to be independent of the particle size and equal to the evaporation coefficient. In [5], the influence of the adsorbed molecules of a buffer gas on the surface tension (its decrease) is considered for interpretation of the results of experiments on the rise in the homogeneous-nucleation rate with increase in the buffer-gas pressure. This effect, in turn, leads to a decrease in the re-evaporation of molecules from small particles (clusters) and accordingly to an increase in the deposition (condensation) rate. However, in [5], no account is taken of the effect of blockage of the phase-transition surface by buffer-gas molecules (this effect leads to a decrease in the rate of deposition of the substance). In the general case, clearly, both of the above effects related to the adsorption of buffer-gas molecules on the particle (cluster) surface will manifest themselves. As will be shown below, joint manifestation of the factors mentioned can lead to the appearance of a maximum in the dependence of the flux of deposited molecules on the coverage of the surface with adsorbed molecules and accordingly on the pressure of the buffer (admixture) gas.

Taking account of the above, we can write the following expression for the density of the molecular flux of the condensing component into a particle I_1 in the free-molecular regime of flow and under the assumption that a vapor molecule is elastically reflected when it arrives at the part of the surface occupied by adsorbed molecules:

$$I_1 = \frac{\alpha_1 (1-\theta) P_1}{(2\pi m_1 kT)^{1/2}} \left[1 - \frac{1}{S} \exp\left\{ \frac{4\sigma(\theta) V_{\mathrm{m}}}{dkT} \right\} \right], \tag{1}$$

where α_1 is the condensation coefficient of vapor molecules upon their arrival at the part of the surface free from the adsorbed molecules of the buffer gas and θ is the coverage of the surface with the adsorbed molecules of the buffer (admixture) gas.

In [5], the following expression has been obtained for the dependence of the surface-tension coefficient on the buffer-gas pressure P_2 with allowance for the Langmuir adsorption isotherm:

$$\sigma(P_2) = \sigma(0) - n_0 kT \ln\left(\frac{P_2 + P_{\mathrm{L}}}{P_{\mathrm{L}}} \right). \tag{2}$$

The quantity P_{L} can be represented as

$$P_{\mathrm{L}} = \frac{n_0 (2\pi m_2 kT)^{1/2}}{\alpha_2 \tau},$$

where τ is the adsorption time of the buffer (admixture) gas and α_2 is the coefficient of sticking of the molecules of the buffer (admixture) gas to the part of the surface free from the adsorbed molecules of the given gas.

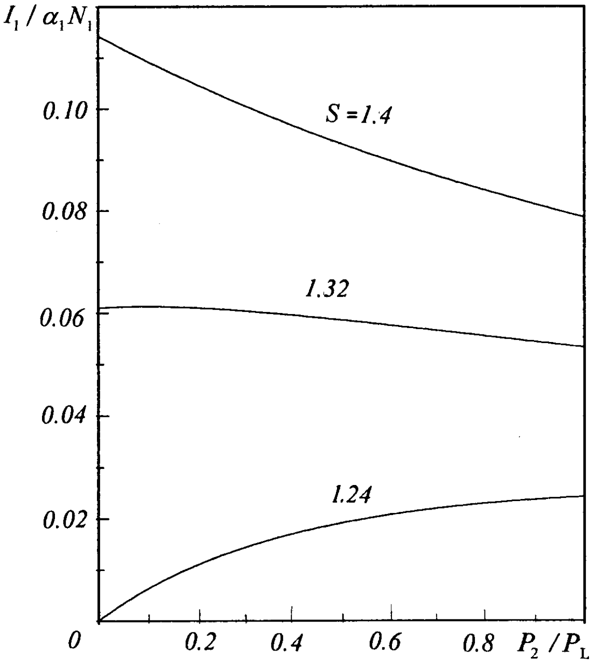

Fig. 1. Dependence of the dimensionless resultant flux of vapor molecules into a water droplet of diameter $d = 10^{-6}$ cm at 293 K on the dimensionless pressure of a buffer (admixture) gas with different values of the parameter S.

With account for (2) and the expression $\theta = P_2/(P_2 + P_L)$, we have for the value of I_1

$$I_1 = \alpha_1 N_1 \left[\frac{P_L}{P_2 + P_L} - \frac{1}{S} \exp\left\{ \frac{4\sigma(0)\, V_m}{dkT} \right\} \left(\frac{P_L}{P_2 + P_L} \right)^{G+1} \right], \tag{3}$$

where

$$N_1 = \frac{P_1}{(2\pi m_1 kT)^{1/2}}\,; \quad G = \frac{4V_m n_0}{d}\,.$$

It follows from (3) that the dependence $I_1(P_2)$ (and accordingly the rate of particle growth) can be characterized by the maximum for the fixed values of the parameters.

The value $P_2' = P_2/P_L$ for which the function $I_1(P_2')$ reaches the maximum has the form

$$P_{2\max}' = \left[\frac{1}{S} \exp\left\{ \frac{4\sigma(0)\, V_m}{dkT} \right\} (G + 1) \right]^{1/G} - 1\,. \tag{4}$$

Figure 1 shows the dependence of the dimensionless flux $I_1' = I_1/\alpha_1 N_1$ on the quantity P_2' for a water droplet of diameter $d = 10^{-6}$ cm at 293 K. The value of n_0 is taken to be equal to $6 \cdot 10^{14}$ cm^{-2} (such a value of n_0 was used in [5] for the case where the buffer gas was nitrogen). It follows from the calculations performed that the function $I_1'(P_2')$ can be decreasing and having a maximum or increasing, depending on the value of the quantity S, in the set range of pressure of the buffer (admixture) gas.

We take account of the fact that only the part of the impinging molecules that is assumed be equal to $\alpha_1(1 - \theta)$, just as in the above-described case of deposition on an individual particle, can condense on the cluster surface. It should be noted that the following expression may be written for the rate of homogeneous nucleation using [1]:

$$J = \frac{\alpha_1 (1-\theta) P_1}{(2\pi m_1 kT)^{1/2}} \frac{2\sigma^{1/2} V_\mathrm{m}}{(kT)^{1/2}} \frac{n_1}{S} \exp\left\{-\frac{16\pi\sigma^3 V_\mathrm{m}^2}{3\,(kT)^3\,(\ln S)^2}\right\}, \tag{5}$$

where n_1 is the concentration of monomers of the condensing component.

The change in the nucleation rate (its increase) with decrease in the surface tension owing to the adsorption of buffer-gas molecules on the cluster surface was discussed in [5]. However, the presence of the multiplier $(1-\theta)$ in expression (5) can lead to regularitites analogous to the above ones in analysis of the process of deposition on an individual particle. In this case, we also have factors affecting the nucleation rate in opposite directions, which in principle can result in the appearance of a maximum in the dependence of the nucleation rate on the buffer-gas pressure.

NOTATION

d, diameter of a particle; P_1, pressure of the vapor; $P_{1\mathrm{e}}$, pressure of the saturated vapor for a flat surface; $S = P_1/P_{1\mathrm{e}}$; P_2, pressure of the buffer (admixture) gas; T, temperature; σ, surface tension; V_m, volume per molecule in a particle; n_0, number of buffer (admixture) gas molecules in the filled monolayer; k, Boltzmann constant; m_1, mass of the molecule of the deposited component; m_2, mass of the molecule of the buffer (admixture) gas. Subscripts: 1, deposited component; 2, buffer (admixture) gas; e, saturated vapor.

REFERENCES

1. J. H. Seinfeld and S. N. Pandis, *Atmosphere Chemistry and Physics: From Air Pollution to Climate Change*, N. Y. (1998).
2. K. Okuyama, Y. Kousaka, N. Tohge, S. Yamamoto, J. J. Wu, R. C. Flagan, and J. H. Seinfeld, *AIChE J.*, **32**, 2010–2019 (1986).
3. P. Moravec, J. Smolík. V. Dřínek, and V. V. Levdanskii (Levdansky), *J. Aerosol. Sci.*, **27**, Suppl. 1, 157–158 (1996).
4. D. Kashchiev, *J. Chem. Phys.*, **104**, 8671–8677 (1996).
5. C. C. M. Luijten, K. J. Bosschaart, and M. E. H. van Dongen, *J. Chem. Phys.*, **106**, 8116–8123 (1997).
6. V. V. Levdanskii, J. Smolík, P. Moravec, and V. Ždímal, in: *Heat and Mass Transfer-97* [in Russian], Minsk (1997), pp. 41–45.
7. A. L. Itkin, *Chem. Phys.*, **238**, 273–284 (1998).
8. V. M. Novikov, O. V. Vasil'ev, and H. Reiss, *Phys. Rev. E*, **55**, 5743–5749 (1997).