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DEPENDENCE OF THE CONDENSATION (STICKING) COEFFICIENT ON THE RADIUS OF SMALL AEROSOL PARTICLES

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The processes of condensation-evaporation and adsorption-desorption of molecules on small aerosol particles are investigated theoretically with account for the dependence of the condensation (sticking) coefficient on the particle size.

In recent years, problems related to the distinctive features of the processes of formation and growth of small particles (clusters) and of adsorption of molecules on such particles have attracted the increasing attention of researchers. Among them are problems of the physicochemistry of the atmosphere [1], problems of obtaining nanoparticles of different kind in the course of chemical deposition [2], and heterogeneous chemical reactions on small particles [3]. Here the dimensional effect influencing the processes mentioned above is usually related to the Knudsen number, determined as the ratio of the free path of gas molecules to the radius of a particle, and to the effect of increase in the vapor pressure above a spherical surface of phase transition that is described by the Kelvin formula. It should be noted that the dimensional effect will also occur in collision of a gas (vapor) molecule with the particle, which will appear as the dependence of the sticking (condensation) coefficient on the particle radius.

Let us explain the aforesaid using Fig. 1, which shows the spherical particle 1 with an incident gas (vapor) molecule *a* and an adsorbed molecule *b*. It is clear from the figure that both in escape from the particle surface (evaporation or desorption of molecules) and on collision of the incident molecule with the particle the gas molecule interacts with the smaller number of molecules of the condensed phase than in the case of its escape from or collision with a flat surface of the condensed phase of the same substance of which the particle consists. The difference lies in the fact that for the particle calculation of the forces acting on the gas molecule on the source side of the particle eliminates the molecules of the condensed phase located in region *2* beneath the surface S_c, i.e., all the molecules of the condensed phase beneath the surface S_c except for those located in region *1* (in the particle).

In [4], consideration has been given to the problem of evaporation of a droplet with account for the dependence of the condensation coefficient on the droplet size (radius). In obtaining the expression for the dependence of the condensation coefficient (which, in [4], was assumed to be equal to the evaporation coefficient) on the droplet dimension, Okuyama and Zung [4] proceeded from the following. It was assumed that condensation on the flat surface of a massive specimen was a non-activation process. However in condensation on a droplet a molecule must overcome the activation barrier due to the surface curvature. In [4], this activation energy is assumed to be equal to the surface energy divided by the number of molecules in the droplet. The following expression is given for the condensation coefficient α_c [4]:

$$\alpha_c = \alpha_{c\infty} \exp\left\{-\frac{3\sigma V_m}{RkT}\right\}, \tag{1}$$

where $\alpha_{c\infty}$ is the condensation coefficient for the flat surface of the massive specimen.

Let us consider the condensation growth of an aerosol particle in the atmosphere of a buffer gas. The system is assumed to be isothermal. The concentration of the vapor is considered to be much lower than the con-

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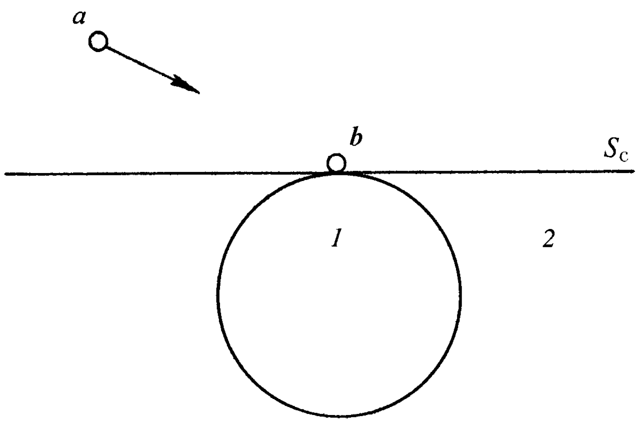

Fig. 1. Scheme of interaction of gas (vapor) molecules with a small aerosol particle.

centration of the buffer gas, and the adsorption of the buffer-gas molecules on the particle surface as well as their absorption will thereafter be neglected.

It is known that an exact description of the transfer processes in a gas–aerosol particle system with an arbitrary size of the particle and phase transitions on its surface can be performed only by solution of the Boltzmann kinetic equation [1, 5, 6]. However, the arising mathematical difficulties lead to the necessity of obtaining rather simple expressions for the resultant molecular flux into the particle either on the basis of an approximate solution of the Boltzmann equation or with the use of simpler models. As is noted in [5], when it is considered that the diffusion equation describes the distribution of the vapor concentration in a gas–particle system up to the surface of the particle and the boundary condition is assigned on its surface, the expression for the resultant flux of vapor molecules into the particle will give correct limiting cases for free-molecular and continuous flow regimes. In [7], the possibility of assigning the boundary condition on the particle surface when the particle radius is less than the free path of the gas molecules is discussed.

Without dwelling on the numerous theoretical approaches available in the literature that enable one to obtain expressions for the resultant flux of vapor molecules into the particle with a certain degree of accuracy (a review of these works can be found, for example, in [1, 5, 6]), we will describe, in view of what has been said above, the problem of mass transfer in a gas–particle system by a diffusion equation with the boundary conditions assigned for $r = R$ and $r \to \infty$. The distribution of the vapor concentration in the vicinity of the spherical particle in a quasisteady approximation has the form [1]

$$n = A - \frac{B}{r}\,, \tag{2}$$

where A and B are the integration constants determined from the boundary conditions.

For $r \to \infty$ we set $n = n_0$, whence it follows that

$$A = n_0\,. \tag{3}$$

Based on the assumptions made, the second boundary condition with the Maxwell velocity-distribution function for incident vapor molecules can be written as

$$D\left.\frac{dn}{dr}\right|_{r=R} = \left(\frac{kT}{2\pi m}\right)^{1/2}\left[\alpha_c n\,(R) - \alpha_e n_e \exp\left\{\frac{2\sigma V_m}{RkT}\right\}\right]. \tag{4}$$

In what follows, for simplicity we set the condensation coefficient for a flat surface and the evaporation coefficient equal to unity. With account for (1)–(4) for the density of the resultant flux of vapor molecules into the particle we obtain

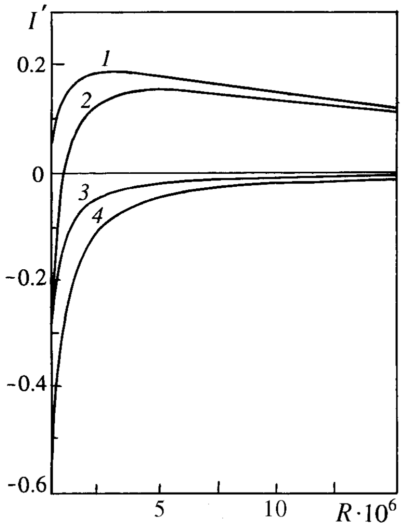

Fig. 2. Dimensionless density of the resultant flux of vapor molecules into the water drop vs. radius of the drop ($T = 273$ K): 1, 3) $\alpha_c = 1$; 2, 4) $\alpha_c = f(R)$; 1, 2) $S = 1.35$; 3, 4) $S = 1$. R, cm.

$$I = \frac{N\left[\exp\left\{-\dfrac{3\sigma V_m}{RkT}\right\} - \dfrac{1}{S}\exp\left\{\dfrac{2\sigma V_m}{RkT}\right\}\right]}{1 + \exp\left\{-\dfrac{3\sigma V_m}{RkT}\right\}\dfrac{vR}{4D}}, \tag{5}$$

where $S = \dfrac{n_0}{n_e}$, $N = n_0\left(\dfrac{kT}{2\pi m}\right)^{1/2}$, and $\dfrac{vR}{4D} = \dfrac{3}{4\mathrm{Kn}}$.

It follows from (5) that the critical (equilibrium) drop radius, which is determined from the condition of equality of the expression in square brackets of (5) to zero, shifts toward larger values in the case of the dependence of the condensation coefficient on the dimension of the drop. The value of the critical radius R^* is equal to $R^* = 5\sigma V_m/(kT \ln S)$, whereas the critical radius is $R^* = 2\sigma V_m/(kT \ln S)$ for the condensation coefficient independent of the dimension of the drop.

Figure 2 shows the dependence of the dimensionless density of the molecular flux $I' = I/N$ on the radius of a water drop at 273 K and the diffusivity of water molecules in a buffer gas $D = 0.219\ \mathrm{cm}^2/\mathrm{sec}$ (such a value of D has been given for water vapor in air in [8]) with account for the dependence of the condensation coefficient on the particle size and at a constant value of this coefficient equal to unity. The values of the parameter S were taken to be equal to 1.35 and 1. It follows from Fig. 2 that the growth of the drop is retarded and the evaporation rate increases with account for the dependence of the condensation coefficient on the dimension of the drop. It should be noted that Okuyama and Zung [4] mistakenly inferred that there can be a maximum in the dependence of the evaporation rate on the dimension of the drop. The reason is that in [4] the incorrect dependence of the ratio of the fluxes of condensing and evaporating molecules on the drop dimension was used. When the drop dimension increases, the density of the resultant flux of molecules evaporating from the drop will decrease due to both the Kelvin effect and the increase in the density of the flux of condensing molecules because of the increase in the condensation coefficient in accordance with (1). Thus, the density of the resultant flux of the molecules evaporating from the drop with increase in its dimension will do nothing but decrease owing to the effects mentioned above and because of the diffusive resistance hindering the removal of vapor molecules from the drop. It is clear from Fig. 2 that the maximum in the dependence of the density of the resultant molecular flux on the dimension of the drop appears in its condensation growth. This is attributed to two factors affecting the rate of growth in opposite directions. For rather small drops when the curvature correction for the density of the resultant molecular flux into the drop is substantial the increase in the drop radius leads to an increase in the density of the indicated flux. On the other hand, the diffusive resistance to the supply of vapor molecules to the drop which is characterized by the second term in the denominator of expression (5) begins to increase with increase in the drop radius, which, naturally, decreases the density of the resultant molecular flux into the drop (and correspondingly the rate of its growth).

It should be noted that dimensional effects analogous to those considered above can also occur in the processes of adsorption and desorption of molecules on small particles. Here, similarly to the case of evaporation of small particles, the probability of desorption of a gas molecule from a particle will be higher than that from a flat surface. As follows from Fig. 1, determination of the adsorption energy of a molecule on a small particle necessitates summation of the forces affecting the adsorbed molecule on the source side of the particle. We note that with the particle radius approaching infinity the adsorption energy must tend to such on the flat surface; otherwise, when there is a single molecule of the adsorbate substance, the "adsorption" energy is actually equal to the energy E_{12} of breaking of the bond of two molecules, one of which is a gas molecule and the other of which is an adsorbate molecule. On this basis, in the general case we can write the following approximate interpolation formula for the energy required for the escape of a gas molecule from the spherical particle (cluster) which gives the limiting cases for the energy of adsorption of a molecule on a flat surface and the energy of breaking of the bond E_{12} for the molecules indicated above:

$$E_{\mathrm{a}} = E_{\mathrm{a}\infty} - (E_{\mathrm{a}\infty} - E_{12})\left(\frac{\delta}{l}\right)^{\varphi}, \tag{6}$$

where δ is the sum of the radii of the gas molecule and the molecule of the particle substance, l is the distance between the centers of the particle and the molecule adsorbed on it (in the limiting case of two molecules $l = \delta$), $E_{\mathrm{a}\infty}$ is the energy of adsorption of the molecule on the flat adsorbate surface, and φ is the parameter accounting for the properties of the potential of interaction between the gas molecule and the molecules of the particle.

It should be noted that a formula analogous to (6) can also be written for the energy of evaporation of a molecule from the small particle.

As follows from (6), when $E_{12} < E_{\mathrm{a}\infty}$ the energy of adsorption on the small spherical particle will be less than the energy of adsorption on the flat surface. The smaller values of the adsorption energy generally correspond to a better reflection of molecules from the surface [9] (i.e., to smaller values of the sticking coefficient).

For the sticking coefficient we can write the expression [10, 11]

$$\beta = 1 - \exp\left\{-\frac{E_{\mathrm{s}}}{kT}\right\}. \tag{7}$$

The value of E_{s} depends on the adsorption energy [10, 11]. For example, in the simplest case of approximation considering the collision of a molecule with a surface atom as the impact of free particles and with fulfillment of the inequality $m_{\mathrm{g}}/M << 1$, where m is the mass of the impinging gas molecule and M is the mass of the atom of the adsorbent lattice, it follows for E_{s} [10, 11] that

$$E_{\mathrm{s}} \approx 4\frac{m_{\mathrm{g}}}{M}E_{\mathrm{a}}. \tag{8}$$

It is seen from (6)–(8) that with decrease in the particle radius (and correspondingly in the adsorption energy) the coefficient of sticking of the gas molecule to the particle surface will also decrease.

We note that when adsorbed molecules move over a curved surface the centrifugal force f will affect the molecule [12, 13]. In the case of an aerosol particle the considered effect promotes the detachment of the molecule adsorbed from the particle. In modeling the molecules adsorbed by a two-dimensional gas, the value of the centrifugal force can be estimated as $f = m_{\mathrm{a}}\overline{v_{\mathrm{a}}^2}/R$, where m_{a} is the mass of the adsorbed molecule and $\overline{v_{\mathrm{a}}^2}$ is the mean square of the velocity of two-dimensional motion along the surface [12]. It follows from the expression for f that the smaller the particle radius, the larger the quantity f. The effect considered will lead to an increase in the probability of desorption (evaporation) of the molecules from the surface of the small particle.

A decrease in the energy of adsorption of the molecules on the surface of small particles and a decrease in the coefficient of sticking of the gas molecules to such particles can also result in a change in the course of heterogeneous chemical reactions on the small particles.

We disregard the effect of blocking of the surface by the adsorbed molecules in the two-stage approximation which allows for the reactant molecule that is in the intermediate state of physical adsorption. For the coefficient γ characterizing the probability of a heterogeneous chemical reaction of first order on collision of the molecule with the surface we can write the following expression:

$$\gamma = \frac{\beta}{1 + (k_{\mathrm{r}}\tau)^{-1}} = \frac{\beta}{1 + (k_{\mathrm{r}0}\tau_0)^{-1} \exp\left\{(E_{\mathrm{r}} - E_{\mathrm{a}})/(kT)\right\}} . \qquad (9)$$

As has been noted above, for small particles the values of β and E_{a} can be lower than for a massive specimen of condensed phase. This in turn can also result in a decrease in the coefficient γ.

Let us consider the question of the influence of a decrease in the evaporation (desorption) energy and the sticking coefficient with decrease in the particle radius on the arrival of impurity molecules at small (nano) particles during their condensation growth. For the relative concentration c_{i} of the impurity molecules in the particle in the free-molecular regime of flow we have [14]

$$c_{\mathrm{i}} = \frac{\beta_{\mathrm{i}} N_{\mathrm{i}}}{I + F_{\mathrm{i}}} , \qquad (10)$$

where β_{i} is the coefficient of sticking of the impurity molecules to the particle surface and N_{i} is the flux density of the impurity molecules impinging on the particle,

$$F_{\mathrm{i}} = n_{\mathrm{s}} \left(\frac{kT}{2\pi m_{\mathrm{i}}}\right)^{1/2} \exp\left\{-\frac{Q_{\mathrm{i}}}{kT}\right\} . \qquad (11)$$

Here n_{s} is the number of molecules per unit volume of the condensed phase (assumed to be a constant), m_{i} is the mass of the impurity molecule, and Q_{i} is the energy of evaporation of the impurity molecules from the particle.

On this basis in the case $F_{\mathrm{i}} >> I$ it follows from (10) that the smaller the particle, the lower the concentration of the impurity in it. This is caused by the decrease in both the sticking coefficient of the impurity molecules and the evaporation energy of these molecules with decrease in the particle size.

The considered regularities associated with the decrease in the condensation (sticking) coefficient with decrease in the particle size will, naturally, manifest themselves in the problems of homogeneous nucleation as well. We note that, in analyzing nucleation processes, the condensation and evaporation coefficients are assumed to be equal to unity in a number of cases. It follows from what has been said above that for rather small particles (clusters) the condensation coefficient for vapor molecules will be less than unity.

The critical (equilibrium) radius R^* of the particle (cluster) is generally determined by the expression

$$R^* = \frac{2\sigma V_{\mathrm{m}}}{kT \ln\left(S \dfrac{\alpha_{\mathrm{c}}}{\alpha_{\mathrm{e}}}\right)} . \qquad (12)$$

It follows from (12) that the decrease in the condensation coefficient at constant values of the other parameters leads to an increase in the critical radius. The quantity α_{c} can decrease both with decrease in the particle radius and as a result of external actions (for example, of resonance laser radiation).

Thus, in the problems of growth (evaporation) of small particles as well as in the problems of adsorption (desorption) and heterogeneous chemical reactions on small particles, taking account of the dependence of both the condensation (sticking) coefficient and the adsorption energy on the particle size results in the peculiarities attributed to this dimensional effect. In particular, under the conditions where the dependence of the condensation coefficient on the particle size is substantial, the assumption of equality of the condensation and evaporation coefficients (this assumption is often used in analyzing problems of heat and mass transfer with allowance for phase transitions) fails. This can lead to incorrect results in calculating the flux of vapor molecules into the particle. The decrease in the condensation coefficient for small particles (clusters) and the difference in the condensation and evaporation coefficients should also be taken into account in investigating the problem of homogeneous nucleation.

NOTATION

R, particle (drop) radius; r, radial coordinate reckoned from the particle center; T, temperature; V_m, volume per molecule in the particle; k, Boltzmann constant; k_r, rate constant of the heterogeneous chemical reaction; τ, adsorption time of the reactant molecules; k_{r0} and τ_0, preexponential factors for the rate constant of the heterogeneous chemical reaction and the adsorption time; D, diffusivity of the vapor molecules in the buffer gas; m, mass of a vapor molecule; α_c, condensation coefficient; α_e, evaporation coefficient; β, sticking coefficient; I, density of the resultant flux of the vapor molecules into the particle; σ, surface tension; n, number concentration of the vapor molecules; n_e, number concentration of the molecules of a saturated vapor above the flat surface; c_i, relative concentration of the impurity molecules in the particle; Kn, Knudsen number; E_a, adsorption energy; E_r, activation energy of the heterogeneous chemical reaction; E_s, specific energy of interaction of a molecule with a wall. Subscripts: a, adsorption; r, reaction; m, molecule; c, condensation; e, evaporation; i, impurity; g, gas.

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