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CHEMICAL DEPOSITION ON AEROSOL PARTICLES

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Problems on the growth of aerosol particles in chemical deposition with allowance for the influence of a buffer (impurity) gas have been investigated theoretically.

It is well known that the deposition of molecules on a surface can occur both through ordinary condensation (physical deposition) and in a heterogeneous chemical reaction of gas molecules with the production of molecules (atoms) from which the condensed (in particular, solid) phase is formed and of the fragments of the initial molecules desorbing back into the gas phase [1, 2]. Moreover, the initial gas molecule can transform into a chemisorbed state as the whole. The processes of chemical deposition play a decisive role both for the physics and chemistry of the atmosphere and in production of nanoparticles. We note that in the latter case first we have the chemical reaction of decomposition of the initial substance (precursor) in the gas phase [3], as a result of which a component appears whose molecules in turn are capable of participating in the process of nucleation and growth of the clusters that arise. Particles (clusters) can grow both owing to the ordinary condensation of the molecules of the deposited component that are incident on them and due to the heterogeneous chemical reaction on the particle surface.

In what follows, we will consider chemical deposition on the already existing aerosol particles (for example, in deposition of a thin layer of a certain substance on the particles as a protective coating or to improve the catalytic capacity of the particles).

To describe the processes mentioned above it is necessary to know the probability of transition of a gas molecule (or of part of it) to a bound state as a result of the collision of a reactant molecule with the particle. Subsequently, we will denote it as γ. The quantity γ is equal to the ratio of the number of effective collisions of the initial molecules with a unit surface in a unit time upon realization of the heterogeneous chemical reaction to the flux density of the initial molecules incident on the surface.

Let us consider the following simple scheme of chemical deposition analogously to [1]. In our opinion, the molecules of the reactant gas AB_χ collide with the particle surface and the reaction occurs, resulting in the transition of one of its products to a bound state (c) (condensed phase or the state of chemical adsorption) and the formation of gas molecules (g) desorbing from the surface:

$$AB_\chi\,(g) \rightarrow A\,(c) + \chi\,B\,(g)\;. \tag{1}$$

We analyze the case where a reaction of the type described by (1) occurs in adsorption of the reactant molecules on the particle surface (the Langmuir–Hinshelwood mechanism). The molecules, i.e., reaction products of the B type, are assumed to be of very low desorption energy, so that their being in the adsorbed state can be neglected. The following relations can be written within the framework of the Langmuir theory of adsorption and the heterogeneous chemical reaction of first order in the steady state:

$$\gamma N = \beta N \left(1 - \frac{n_a}{n_0} - \frac{n_b}{n_0}\right) - k_d n_a\;, \tag{2}$$

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$$\gamma N = k_r n_a \,. \tag{3}$$

Here N is the flux density of initial molecules (of the AB_χ type in scheme (1)) incident on the particle surface (with the Maxwell velocity distribution function for incident molecules N has the form $N = n(R)v/4$, where $n(R)$ is the number concentration of the initial molecules at the particle surface and v is the mean thermal velocity of these molecules), n_a and n_b are the number concentrations of the molecules of the reactant and the buffer (impurity) gas in the adsorbed layer respectively, and k_r and k_d are the rate constants of the heterogeneous chemical reaction and the desorption respectively, which have the form

$$k_r = k_{r0} \exp\left\{- Q_r/R_g T\right\} , \tag{4}$$

$$k_d = k_{d0} \exp\left\{- Q_d/R_g T\right\} . \tag{5}$$

When the adsorption of the molecules of the buffer (impurity) gas can be neglected, we have for γ from (2) and (3)

$$\gamma = \frac{\beta}{1 + \dfrac{k_d}{k_r} + \dfrac{\beta N}{k_r n_0}} \,. \tag{6}$$

It is evident from (6) that in the general case the quantity γ depends on the flux density of molecules incident on the particle surface. When $\beta N/n_0 << k_d$ Eq. (6) yields the expression of [2] for γ:

$$\gamma = \frac{\beta}{1 + \dfrac{k_d}{k_r}} = \frac{\beta}{1 + \dfrac{k_{d0}}{k_{r0}} \exp\left\{- (Q_d - Q_r)/R_g T\right\}} \,. \tag{7}$$

At $k_r << k_d$ when the unity in the denominator of (5) can be neglected γ takes the form

$$\gamma = \gamma_0 \exp\left\{- (Q_r - Q_d)/R_g T\right\} , \tag{8}$$

where $\gamma_0 = k_{r0}/k_{d0}$.

It can be noted that in the simplest case of the single-stage approximation (without regard for the molecule being in the adsorbed state) with the reaction of first order and the Maxwell velocity distribution function of the molecules incident on the particle surface we have for γ [4]

$$\gamma = \frac{4}{v} k'_r = \frac{4}{v} k'_{r0} \exp\left\{- Q/R_g T\right\} = \gamma'_0 \exp\left\{- Q/R_g T\right\} , \tag{9}$$

where k'_r is the reaction-rate constant in the single-stage approximation and Q is the effective activation energy of the chemical reaction.

For the case where the molecules of a buffer (impurity) gas are adsorbed on the surface and the concentration of the adsorbed molecules of the reactant is rather low, so that the term n_a/n_0 on the right-hand side of (2) can be neglected, with account for the expression $\theta_b = P_b/(P_b + P_L)$ we obtain for γ

$$\gamma = \frac{\beta}{1 + k_d/k_r} \frac{P_L}{P_b + P_L} , \tag{10}$$

where P_L is the quantity entering into the expression for the Langmuir adsorption isotherm and having the forms

$$P_L = \frac{n_0 \,(2\pi m_b kT)^{1/2} \exp\left\{- Q_b/R_g T\right\}}{\beta_b \tau_0} \,. \tag{11}$$

Knowledge of the quantity γ enables one to formulate, at the kinetic level, the problems of mass transfer with heterogeneous chemical reactions on the surface of an aerosol particle when this particle is used as a catalyst and the resultant mass flux into the particle is equal to zero (the particle radius remains constant), as well as the problems of gas-phase deposition of a substance on the particle, which leads to its growth. Next we assume that the concentration of the buffer gas is considerably higher than the concentration of all the other components participating in the process (which is usually realized in practice).

It is well known that the processes of transfer in the gas–aerosol particle system (in particular, determination of the quantity N for an arbitrary size of the particle and realization of phase transitions or chemical reactions on its surface) can accurately be described only by solution of the kinetic Boltzmann equation [5–7]. However, mathematical difficulties associated with the solution of the given equation lead to the necessity of obtaining rather simple expressions for the mass and energy fluxes either on the basis of an approximate solution of the Boltzmann equation or with the use of simpler models. In particular, in the literature wide use is made of the "boundary sphere" model [5–7]. Here the entire flow range is subdivided into zones in which free-molecular and continuous flow regimes respectively are realized. The first zone is located between the particle surface and the spherical surface which is at a distance of the order of the mean free path of gas molecules from the particle surface. It is assumed that beyond this spherical surface the continuous regime of gas flow is realized and the mass transfer can be described by a diffusion equation. Matching is carried out at the dividing boundary between the indicated zones. It should be noted that the exact value of the coefficient of proportionality δ between the distance at which the indicated "boundary sphere" is located and the mean free path of the gas molecules is generally unknown and different values (including the zero value) are used for this coefficient in different works [5–7]. At the same time, as is noted in [5], when it is considered that the diffusion equation describes the concentration distribution of the gas up to the particle surface, the expression obtained on its basis for the resultant molecular flux into the particle in its growth or evaporation gives correct results for the limit cases at $\mathrm{Kn} \to 0$ and $\mathrm{Kn} \to \infty$. It is noteworthy that the zero value of the above-mentioned coefficient δ actually means that the diffusion equation is assumed to hold true up to the particle surface. The possibility of using the diffusion equation in the problems of growth of aerosol particles with assignment of a boundary condition on the surface of a particle whose size is smaller than the mean free path of the molecules has been discussed in [8]. With allowance for what has been stated above we will describe the problem of mass transfer in the system gas–particle by the diffusion equation

$$\frac{\partial n}{\partial t} = D \frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial n}{\partial r} \right) \tag{12}$$

with the boundary conditions assigned for $r = R$ and $r \to \infty$.

We consider the process of particle growth using the production of nanoparticles through gas-phase chemical deposition as an example. Under the action of high temperature or laser radiation, the initial molecules (precursor molecules) can decompose into components in the gas phase with the formation of molecules participating in the heterogeneous chemical reaction which leads to the deposition of a substance and accordingly the growth of a particle (molecules AB_χ in scheme (1)). These molecules diffuse to the growing particle and react on its surface with the formation of molecules (atoms) of the A type and molecules B_χ. The A molecules (atoms) embedding into the condensed phase can, in principle, evaporate again from the particle. Thus, to determine the growth rate of the particle one must solve the diffusion equation with the corresponding boundary conditions for both the component AB_χ and the component A (this component will further be marked by the subscript A).

At $r \to \infty$ we set the concentrations of the components AB_χ and A as

$$n = n_\infty , \quad n_\mathrm{A} = 0 . \tag{13}$$

At $r \to R$ for the given components with allowance for the possible blocking of the phase transition surface by the adsorbed molecules of the buffer (impurity) gas and using the Langmuir adsorption mechanism we can write the following boundary conditions:

$$D \left. \frac{dn}{dr} \right|_{r=R} = \gamma \frac{n\,(R)\,v}{4} , \tag{14}$$

$$D_{\mathrm{A}} \frac{dn_{\mathrm{A}}}{dr}\bigg|_{r=R} = \alpha_{\mathrm{A}} (1-\theta_{\mathrm{b}}) \left(\frac{n_{\mathrm{A}}(R)\, v_{\mathrm{A}}}{4} - \frac{n_{\mathrm{Ae}}\, v_{\mathrm{A}} \exp\{2\sigma V_{\mathrm{A}}/RkT\}}{4} \right), \tag{15}$$

where α_{A} is the condensation coefficient of the molecules (atoms) of the component A on the particle surface free of the adsorbed molecules of the buffer (impurity) gas (this coefficient is assumed to be independent of the particle radius and equal to the evaporation coefficient) and D_{A} and D are the diffusivities of the components A and AB_{χ}, respectively, in the buffer gas.

When the value of γ is independent of the reactant molecular flux incident on the particle surface, we can write the expression for the quasi-steady rate v_{p} of growth of the particle with account for (10)–(15):

$$v_{\mathrm{p}} = V_{\mathrm{A}} \left(\frac{P_{\mathrm{L}}}{P_{\mathrm{b}} + P_{\mathrm{L}}} \right) \left[\frac{\beta (1 + k_{\mathrm{d}}/k_{\mathrm{r}})^{-1} n_{\infty} v/4}{1 + \frac{\beta (1 + k_{\mathrm{d}}/k_{\mathrm{r}})^{-1} R v}{4D} \frac{P_{\mathrm{L}}}{P_{\mathrm{b}} + P_{\mathrm{L}}}} - \frac{(\alpha_{\mathrm{A}} n_{\mathrm{Ae}} v_{\mathrm{A}}/4) \exp\{2\sigma V_{\mathrm{A}}/RkT\}}{1 + \frac{\alpha_{\mathrm{A}} R v_{\mathrm{A}}}{4D_{\mathrm{A}}} \frac{P_{\mathrm{L}}}{P_{\mathrm{b}} + P_{\mathrm{L}}}} \right]. \tag{16}$$

In the general case, the concentration n_{∞} must be determined based on consideration of the processes in the reactor. Some problems related to the influence of the processes occurring in the reactor and of resonance radiation on the particle growth have been discussed in [9].

In the case where the evaporation of the component A from the particle can be neglected, the simple expression for the effective value of the coefficient γ_{p} for the particle as a whole follows from (7) and (16) with allowance for the diffusion resistance and blocking of the particle surface by the adsorbed molecules of the nonreacting gas:

$$\gamma_{\mathrm{p}} = J_{\mathrm{A}} \left(\frac{n_{\infty} v}{4} \right)^{-1} = \frac{v_{\mathrm{p}}}{V_{\mathrm{A}}} \left(\frac{n_{\infty} v}{4} \right)^{-1} = \frac{1}{\left(1 + \frac{P_{\mathrm{b}}}{P_{\mathrm{L}}}\right)\left(1 + \frac{k_{\mathrm{d}}}{k_{\mathrm{r}}}\right)\beta^{-1} + \frac{3}{4\,\mathrm{Kn}}}, \tag{17}$$

where the Knudsen number is $\mathrm{Kn} = \lambda/R$; λ is the mean free path of the reactant molecules. It is seen from (17) that the lower the quantity β and the higher the quantity $k_{\mathrm{d}}/k_{\mathrm{r}}$, the lower the value of the Knudsen number for which the second term in the denominator of (17) that describes the diffusion resistance to the supply of deposited molecules to the particle surface can be neglected.

We note that, as is evident from (17), the quantity γ_{p} (and accordingly v_{p}) will decrease with increase in the pressure of the adsorbing nonreacting gas in all the flow regimes, including the free-molecular one ($\mathrm{Kn} \gg 1$). In the last case, the quantity v_{p} is proportional to the factor $1/(1 + P_{\mathrm{b}}/P_{\mathrm{L}})$.

In the case of the absence of the adsorbed molecules of the buffer (impurity) gas on the particle surface ($P_{\mathrm{b}}/P_{\mathrm{L}} = 0$), Eq. (17) yields an expression for the growth rate of a particle that coincides with the expression given in [10].

When $Q_{\mathrm{r}} > Q_{\mathrm{d}}$, from (11) and (17) it is seen that γ_{p} will increase with increase in the temperature. The reason is that the rate of the heterogeneous reaction increases, as well as the area of the particle surface free of the adsorbed molecules of the buffer (impurity) gas. The analogous dependence is realized for the case of calculation of γ_{p} using formula (9) at $Q > 0$. However, the situation can occur where the inequality $Q_{\mathrm{d}} > Q_{\mathrm{r}}$ is fulfilled [2]. Here the value of γ_{p} can change in a nonmonotonic manner with increase in the temperature due to the different character of the temperature dependence for the cofactors in the first term in the denominator of expression (17). To illustrate the nonmonotonic dependence $\gamma_{\mathrm{p}}(T)$ we consider the following model example. We use the parameters given in [2] for the initial stage of the reaction of decomposition of the $\mathrm{SiH_2Cl_2}$ molecules on the Si surface that leads to the chemisorption of the formed SiCl molecules: $Q_{\mathrm{d}} - Q_{\mathrm{r}} = 3.8$ kcal/mol, $k_{\mathrm{d0}}/k_{\mathrm{r0}} = 600$, and $\beta = 0.36$. The value of $Q_{\mathrm{b}} = 7$ kcal/mol is taken for the adsorbed nonreacting molecules. We assume that the buffer (impurity)-gas pressure is kept constant and that the value of $P_{\mathrm{b}}/P_{\mathrm{L}}$ is equal to 1/2 at a temperature of 300 K. For the indicated values of the parameters the dependence $\gamma_{\mathrm{p}}(T)$ has the form shown in Fig. 1. As follows from the given dependence, the function $\gamma_{\mathrm{p}}(T)$ has a maximum. With decrease in the Kn number this maximum becomes less pronounced.

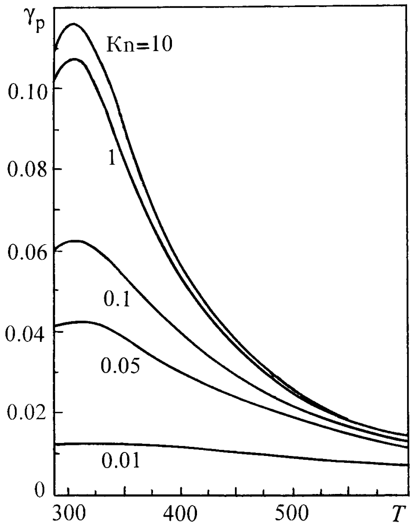

Fig. 1. Dependence of the coefficient γ_p on the particle temperature for different Kn numbers, $Q_d - Q_r = 3.8$ kcal/mol, $Q_b = 7$ kcal/mol, $k_{d0}/k_{r0} = 600$, $\beta = 0.36$ and, $P_b/P_L = 1/2$ at $T = 300$ K.

Thus, the presence of the adsorbed molecules of a foreign nonreacting gas on the particle surface can significantly affect the course of a heterogeneous chemical reaction on the particles (in particular, particle growth through chemical deposition). Some questions on the influence of the adsorbed molecules of a buffer (impurity) gas on the resultant flux of vapor molecules into aerosol particles (and accordingly on the rate of their growth) in physical deposition have been considered in [11].

We emphasize that when expression (6) is used for γ in complete form, the flux density of the molecules reacting on the particle surface will depend nonlinearly on the flux density of the reactant molecules incident on the particle.

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NOTATION

R, particle radius; r, radial coordinate reckoned from the particle center; T, temperature; V_A, volume per molecule (atom) of the component A in a particle; n_0, number of adsorption centers per unit surface (assumed to be a constant); k, Boltzmann constant; m_b, molecular mass of the buffer (impurity) gas; k_{d0} and k_{r0}, preexponential factors for the constants of desorption and heterogeneous chemical reaction; Q_d and Q_r, heat of desorption of the reactant molecules and of the heterogeneous chemical reaction respectively; Q_b, desorption energy of the buffer (impurity)-gas molecules; τ_0, quantity characterizing the period of oscillation of an adsorbed molecule in the direction perpendicular to the surface; β and β_b, coefficients of sticking of the reactant molecules and buffer (impurity)-gas molecules, respectively, to the portion of the surface not occupied by the adsorbed molecules; P_b, pressure of the buffer (impurity) gas; J_A, resultant flux of the molecules (atoms) of component A into the particle; σ, surface tension; n, number concentration of the reactant molecules; n_{Ae}, number concentration of the saturated vapor of component A above a flat surface; θ_b, surface coverage by the adsorbed molecules of the buffer (impurity) gas; D and D_A, diffusivities of the molecules of the reactant and of component A, respectively, in the buffer gas; R_g, universal gas constant. Subscripts: d, desorption; r, reaction; b, buffer; e, saturated vapor; p, particle; g, gas.

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