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MASS TRANSFER AND TRAPPING OF THE IMPURITY COMPONENT IN DEPOSITION FROM THE GAS PHASE

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The problem of removal of an impurity from a volume in the case of trapping of the impurity molecules by aerosol particles is investigated theoretically.

The problem of purification of different volumes of the impurity component is urgent for many areas of modern technology (in vacuum engineering, creation of the so-called clean rooms for production of microelectronics elements, removal of toxic molecules from volumes, and so on). The process of such a purification can be performed by introducing aerosol particles into a volume and realizing physical (conventional condensation) or chemical deposition of impurity molecules on the particles. At first, we consider the case of purification of a volume of a noncondensable component by deposition of the vapor of an easily condensable substance on aerosol particles introduced into the purified volume simultaneously with the vapor. It is known that in deposition of an easily condensable substance, the molecules of a noncondensable (for given thermodynamic parameters) component can be trapped by a growing layer of condensate. Cryocondensation pumps for pumping of noncondensable substances have been created on the basis of this principle [1]. It should be noted that trapping of the impurity molecules with growth in the condensate layer (or in the aerosol particle) in the process of deposition of the vapor of an easily condensable component can also occur at ordinary temperatures. Some questions related to the description of such processes have been considered in [2–5].

The impurity molecules can initially be present in the volume considered, can arrive at it from the outside through microleakages of different type, and can appear in the volume as a result of chemical reaction. Thus, for example, when nanoparticles are produced by chemical deposition, in the reactor there arise both molecules whose deposition results in the formation and growth of nanoparticles and reaction-product molecules that can find themselves in the growing nanoparticles. In what follows, we investigate the problem of purification of a volume with impurity molecules in their trapping by aerosol particles (with subsequent removal of the latter from the volume considered) and some questions related to the composition of the resulting particles. For the sake of simplicity, we assume that the gas–particles system is isothermal.

At first, we consider the case of a free-molecular flow regime where the particle size is much smaller than the mean free path of the molecules. For the number density of the impurity molecules n in the volume V and using the model of ideal mixing and the assumption of the Maxwell velocity-distribution function for the molecules incident on the particle surface, we can write the following expression:

$$V\frac{dn}{dt} = V\frac{n' - n}{t'} - \frac{nv}{4}G\,(S_{\text{p}} + S_{\text{w}}) + VQ_{\text{v}} + S_{\text{p}}Q_{\text{p}} + S_{\text{w}}Q_{\text{w}}\ , \tag{1}$$

where G is the trapping coefficient of the impurity molecules, determined by the ratio of the density of the resultant flux of the impurity molecules into the condensed phase J to the flux density of the impurity molecules incident on the surface of the condensed phase. In condensation growth of the aerosol particle (physical desorption), this coefficient can be written as [2]

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$$G = \frac{\beta J_c}{J_c + F}\,, \tag{2}$$

where β is the sticking coefficient of the impurity molecules and J_c is the density of the resultant flux of the condensable component molecules into the particle; the quantity F has the form

$$F = n_c' \left(\frac{R_g T}{2\pi M}\right)^{1/2} \exp\left\{-\frac{E}{R_g T}\right\}. \tag{3}$$

Next the values of β, F, and the condensation coefficient of vapor molecules α (which is assumed to be equal to the evaporation coefficient) are taken as being independent of the particle diameter. Based on the assumptions made above and the Kelvin correction for the density of the saturated vapor, expression (2) can be written as

$$G = \frac{\beta}{1 + \dfrac{4F}{\alpha n_c v_c}\left(1 - s^{-1}\exp\left\{\dfrac{4\sigma V_m}{d_p R_g T}\right\}\right)^{-1}}\,. \tag{4}$$

It is seen from (2) and (4) that the value of G differs from zero when the values of β and J_c are more than zero. The quantity S_p in (1) is found from the expression

$$S_p = \pi \int_0^\infty d_p^2 f(d_p)\, dd_p\,. \tag{5}$$

The diameter-distribution function of the particles $f(d_p)$ is determined by both the growth and coagulation of the particles and their deposition, in particular, under gravity. In what follows we will restrict our consideration to the system characterized by the mean particle diameter $\overline{d}_p$. Here the quantity S_p becomes

$$S_p = \pi \overline{d}_p^{\,2} N_p\,, \tag{6}$$

where N_p is the number of particles per unit volume.

At first we consider the case where the first member on the right-hand side of Eq. (1), along with the members with factors Q_p, Q_w, and S_w, can be neglected. The solution of Eq. (1) for the dimensionless number density $\overline{n} = n/n_0$ (n_0 is the value of the number density of the impurity molecules at $t = 0$) in the approximation, for which the mean size of the particles (drops) and the vapor pressure are assumed constant, may be written as follows:

$$\overline{n} = \left(1 - \frac{Q_v}{n_0\,\varphi}\right)\exp\{-\varphi t\} + \frac{Q_v}{n_0\,\varphi}\,, \tag{7}$$

where $\varphi = vGS_p/(4V)$.

As is clear from (7), the character of the dependence $\overline{n}(t)$ substantially depends on the dimensionless parameter $\phi = Q_v/(n_0\varphi)$. For $d\overline{n}/dt$ from (7) we have

$$\frac{d\overline{n}}{dt} = -\,\varphi\,(1 - \phi)\exp\{-\varphi t\}\,, \tag{8}$$

whence it follows that the concentration of impurity molecules in the volume will increase with time for $\phi > 1$ and will decrease for $\phi < 1$.

The parameter φ in (7) is in proportion to the particle surface area, which in turn depends on the number of particles and their diameter. It should be noted that different disperse systems (i.e., systems of particles of different number density and diameter) can be prepared of the same amount of a substance. For the sake of simplicity we con-

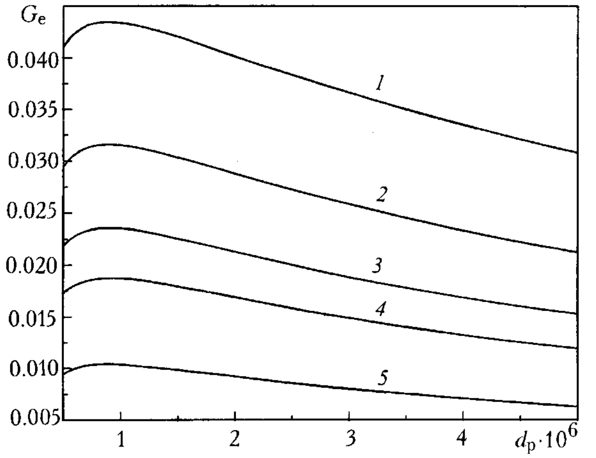

Fig. 1. Dependence of the trapping coefficient G_e on the diameter of a growing water drop (T = 273 K, $\alpha = \beta = 0.1$, $\lambda = \lambda_c = 6.5 \cdot 10^{-6}$ cm, s = 3): 1) $4F/(\alpha n_{c\infty} v_c)$ = 30; 2) 50; 3) 75; 4) 100; 5) 200. d_p, cm.

sider a monodisperse system of particles with a constant volume V_0 of the initial sprayed substance; the value of S_p can be represented as

$$S_p = \frac{6V_0}{d_p}\,. \tag{9}$$

Thus, the parameter φ in (7) and (8) governing the rate of purification of the volume of the impurity will increase with decrease in the particle size and increase in the value of the trapping coefficient G.

In the general case, when all the members in Eq. (1) are taken into account, the value of φ is equal to φ', where

$$\varphi' = \frac{vG\,(S_p + S_w)}{4V} + \frac{1}{t'}\,, \tag{10}$$

and the member $Q_v/(n_0\varphi)$ is replaced by the quantity

$$\phi' = \frac{Q_v + S_p Q_p/V + S_w Q_w/V + n'/t'}{n_0 \varphi'}\,. \tag{11}$$

For a rather large size of the growing aerosol particles, the probability of the impurity molecule trapping by a particle will depend on the diffusion resistance of a buffer gas relative to both the impurity molecules and the vapor molecules. In the case where the concentrations of the molecules of these components are much lower than the concentration of the molecules of a buffer gas, we can obtain, analogously to [3], the expression for the effective coefficient G_e of trapping of the impurity molecule by a particle:

$$G_e = J\left(\frac{n_\infty v}{4}\right)^{-1} = \frac{\beta}{1 + \dfrac{4F}{\alpha n_{c\infty} v_c}\left(1 + \dfrac{3\alpha d_p}{8\lambda_c}\right)\left(1 - s^{-1}\exp\left\{\dfrac{4\sigma V_m}{d_p R_g T}\right\}\right)^{-1} + \dfrac{3\beta d_p}{8\lambda}}\,. \tag{12}$$

Figure 1 gives the dependence of the quantity G_e on the diameter of a growing water drop at a temperature of 273 K. We assume for the sake of simplicity that $\alpha = \beta = 0.1$. From the figure it follows that the dependence $G_e(d_p)$ can be characterized by a maximum. The reason is that, under the indicated conditions, the resultant flux of vapor molecules into a drop will increase with the diameter of the drop for a sufficiently small size of the latter due to the Kelvin effect. On further increase in the drop diameter, the contribution of the Kelvin effect to the resultant molecular flux decreases, whereas the contribution of the diffusion resistance relative to both the impurity component and the condensable component increases.

Purification of a volume of impurity (in particular, toxic) molecules can also be realized in their bonding as the result of chemical reaction on aerosol particles introduced into the volume considered with subsequent removal of the aerosol particles from the volume. Moreover, when the impurity (reactant) molecules interact with the aerosol particles, dissociation of the initial molecules (i.e., their "disappearance" as such) can occur. In specific cases the component arising in the reaction can be embedded in the condensed phase, which leads to a growth in the condensate layer, and in the case of the aerosol particles this results in a growth in the latter [6–8]. Purification efficiency associated with the above-noted mechanisms can be described by the coefficient G_r determined analogously to the coefficient G_e in (12): $G_r = J_r/(n_{r\infty}v_r/4)$, where J_r is the flux density of the reactant molecules which have reacted on the particle surface, $n_{r\infty}$ is the number density of the reactant molecules at an infinite distance from the particle, and v_r is the mean velocity of these molecules. With a two-stage scheme taking account of the possibility of the reactant molecule staying in the intermediate stage of physical adsorption and for rather low concentrations of the adsorbed molecules (when their blocking effect may be neglected) in the quasistationary approximation with consideration for [6] we can write the expression for G_r:

$$G_r = J_r\left(\frac{n_{r\infty}v_r}{4}\right)^{-1} = \frac{1}{\left(1+\dfrac{k_d}{k_r}\right)\beta_r^{-1} + \dfrac{3}{4\mathrm{Kn}_r}} \,. \tag{13}$$

Here Kn_r is the Knudsen number for the reactant molecules ($\mathrm{Kn}_r = 2\lambda_r/d_p$), J_r is the flux density of the molecules subjected to the heterogeneous chemical reaction, β_r is the sticking coefficient of the reactant molecules, and k_r and k_d are the rate constants of respectively the chemical reaction and the desorption that have the form

$$k_r = k_{r0}\exp\left\{-E_r/R_gT\right\} , \tag{14}$$

$$k_d = k_{d0}\exp\left\{-E_d/R_gT\right\} . \tag{15}$$

It follows from (13)–(15) that the coefficient G_r diminishes as the Knudsen number decreases and that, depending on the relation between the quantities E_d and E_r, the particle temperature should at times be raised and at other times be lowered to increase the rate of chemical deposition of molecules on the aerosol particles. We emphasize that one can heat the aerosol particles and thus control the rate of the heterogeneous chemical reaction on their surface by the action of electromagnetic radiation on the system. In the field of resonance (in particular, laser) radiation, there are also nonthermal effects associated with excitation of reactant molecules. This leads to a change in the parameters α, β, E, E_r, and E_d, which in turn exerts an influence on both G_e and G_r.

In a number of cases (for example, in manufacture of multicomponent nanoparticles by chemical deposition from the gas phase) it is of interest to determine the concentration of the components in a particle in chemical deposition of several substances simultaneously. We assume that the embedding of the mixture molecules in the particle is described by an equation of the type of (13) for each component. Expressing the concentration of the ith component in the particle by the densities of the resultant molecular fluxes into the particle J_{ri}

$$c_i = \frac{J_{ri}}{\sum\limits_k J_{rk}} , \tag{16}$$

we can calculate the concentrations of individual components in the particle with account for (13). Thus, for example, when we have chemical deposition of two components whose parameters will be denoted further by subscripts 1 and

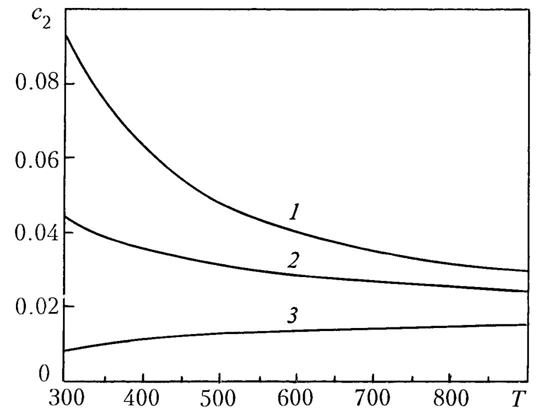

Fig. 2. Temperature dependence of the concentration of impurity molecules c_2 in the case of particle growth by chemical deposition in the free-molecular flow regime $(n_{r1}v_{r1}/(n_{r2}v_{r2}) = 50$, $\beta_{r1}/\beta_{r2} = k_{d01}/k_{r01} = k_{d02}/k_{r02} = 1$: 1) $\Delta E_1 = 3$ and $\Delta E_2 = 2$; 2) 3.5 and 3; 3) 3 kcal/mole and 3.5 kcal/mole respectively. T, K.

2 we obtain the expression for the concentration of the component with subscript 2 (it is assumed to be impurity) under the above assumptions and the conditions of a free-molecular flow regime:

$$c_2 = \left[1 + \frac{\beta_{r1} n_{r1} v_{r1} \left(1 + (k_{d02}/k_{r02}) \exp\left\{(E_{r2} - E_{d2})/R_g T\right\}\right)}{\beta_{r2} n_{r2} v_{r2} \left(1 + (k_{d01}/k_{r01}) \exp\left\{(E_{r1} - E_{d1})/R_g T\right\}\right)} \right]^{-1} . \tag{17}$$

Figure 2 shows the temperature dependence of c_2 for different values of $\Delta E_1 = E_{r1} - E_{d1}$ and $\Delta E_2 = E_{r2} - E_{d2}$. As follows from the figure, the value of c_2 can both increase and decrease with increase in the temperature depending on the quantities ΔE_1 and ΔE_2. This should be taken into account when it is necessary to produce fairly pure nanoparticles and nanoparticles with a given concentration of impurity molecules whose presence changes the physicochemical properties of the nanoparticles. We emphasize that the concentration of impurity molecules in the particle that is growing by vapor condensation on its surface in the presence of impurity molecules in the system can be calculated on the basis of expressions (12) and (16).

The foregoing shows that it is possible to purify a certain volume of the impurity molecules by introduction into it of aerosol particles on whose surface we have the deposition of an easily condensable component or a heterogeneous chemical reaction resulting in the dissociation of the initial molecules or their bonding on the particle surface. The process of purification is most efficient with rather small particles when the free-molecular flow regime is realized. The influence of the temperature on the concentration of the components in the aerosol particle growing in chemical deposition of the latter on its surface substantially depends on the relation between the energy of chemical reaction and the energy of desorption of the initial molecules from the particle surface.

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NOTATION

t, time; n and n', number density of the impurity molecules in the volume and outside it; t', residence time of the gas in the volume; v, mean velocity of a impurity molecules; Q_v, source of the impurity molecules arising per unit volume in a unit time as a result of the homogeneous chemical reaction; Q_p and Q_w, sources of the impurity molecules that are caused by their appearance per unit surface in a unit time due to the heterogeneous chemical reaction on the surface of the aerosol particles and on the walls of the considered volume (reactor) respectively; S_p and S_w, total area of the surface of the aerosol particles and area of the volume walls; R_g, gas constant; T, temperature; M, molecular weight of the impurity component; n'_c, number density of molecules in the condensed phase (assumed to be a constant); n_c, number density of molecules of the condensable substance in the gas phase; k_{d0}, k_{d0i} and k_{r0}, k_{r0i}, preexponential factors for the rate constants of desorption and heterogeneous chemical reaction; E, energy of evaporation of the impurity molecules from the particle; E_d and E_r, energy of desorption of the reactant molecules from the state of physical adsorption and activation energy of the heterogeneous chemical reaction; v_c, mean velocity of the molecules of the vapor of the condensable substance; d_p, particle diameter; α, condensation (evaporation) coefficient of the condensable component; s, saturation ratio; V_m, molar volume; σ, surface tension; $n_{c\infty}$, number density of vapor molecules at an infinite distance from the particle; λ and λ_c, mean free paths of the molecules of the impurity and condensable components; J, density of the resultant flux of the impurity molecules into the particle in its condensation growth. Subscripts: d, desorption; r, reaction; c, condensable; p, particle; v, volume; w, wall; e, effective; g, gas; m, molar; i, component; k, subscript of summation.

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