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PARTICLE GROWTH IN CHEMICAL DEPOSITION FROM THE GAS PHASE

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The effect of the physicochemical processes occurring in an evaporator and a reactor on the growth of aerosol particles is investigated.

In a number of fields of modern chemical technology (creation of new materials with unique properties, manufacture of highly efficient catalysts, etc.) the problem of obtaining nanosized aerosol particles arises. This can be achieved in the process of chemical deposition from the gas phase [1-3]. A schematic of the laboratory setup used to obtain nanoparticles in experiments conducted at the Institute of Chemical Processes (ICP) of the Academy of Sciences of the Czech Republic (Prague) is depicted in Fig. 1. The initial substance (precursor) in the liquid phase is placed in an evaporator, where it passes into the gas phase. The gas formed is then deluted with a neutral gas (usually nitrogen), and the diluted mixture enters a reactor, where it is subjected to heating. As a result, a chemical reaction is initiated to yield molecules capable of forming aerosol particles. The kinetics of the actual reaction can be rather complicated and involve many stages (not all of the latter are known). Therefore, for an analysis of the processes occurring use is often made of some simplified model. Thus, in [1] the reaction of decomposition of the molecules of the initial substance in a reactor is assumed to be a first-order reaction of the form

$$A \to F + C . \tag{1}$$

Here A is the initial substance; F is the substance whose molecules are capable of condensing with formation of aerosol particles; C is a reaction product. From the reactor the gas mixture with the particles formed, also preliminarily diluted with the neutral gas, is brought to a DMPS (differential mobility particle sizer) aerosol analyzer, with the aid of which the amount and mean diameter of the particles formed and their size distribution can be determined. In the scheme described, particles are mainly formed in the reactor and this process depends, naturally, on the temperature in it and the delay time of the gas in it. These dependences were investigated experimentally using $Si(OC_2H_5)_4$ – tetraethylorthosilicate (TEOS) – as the precursor [2]. Here, with increase in the temperature in the tubular reactor the volume of the condensed phase V_p and the mean particle diameter D_p increased. Figure 2 shows V_p and D_p as a function of the reactor temperature T_R for different TEOS concentrations (mole/liter). A bulk flow of 600 cm^3/min passed through the reactor, and the delay time in the latter varied from 20.5 to 22.2 sec.

The simple scheme described above is, naturally, not always implemented. For instance, in experiments conducted at the ICP of the Academy of Sciences of the Czech Republic using $Al(OC_4H_9)_3$ – aluminum trisec-butoxide (ATBO) – as the precursor, the above parameters demonstrated a rather weak dependence on both the reactor temperature and the delay time of the gas in the reactor. Figure 3 presents dependences of the volume of the condensate formed and the mean particle diameter on the reactor temperature. Curve 1 pertains to data obtained for a constant bulk flow of 1000 cm^3/min through the reactor (the delay time varied within the limits of 14.5–34.4

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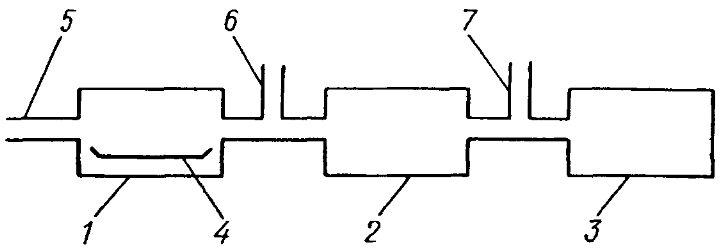

Fig. 1. Schematic of the setup used to obtain nanosized particles: 1) evaporator, 2) reactor, 3) aerosol analyzer, 4) initial substance, 5, 6, 7) means of communication by which the neutral gas is supplied to transport the gas mixture and the aerosol particles and to dilute the gas mixture.

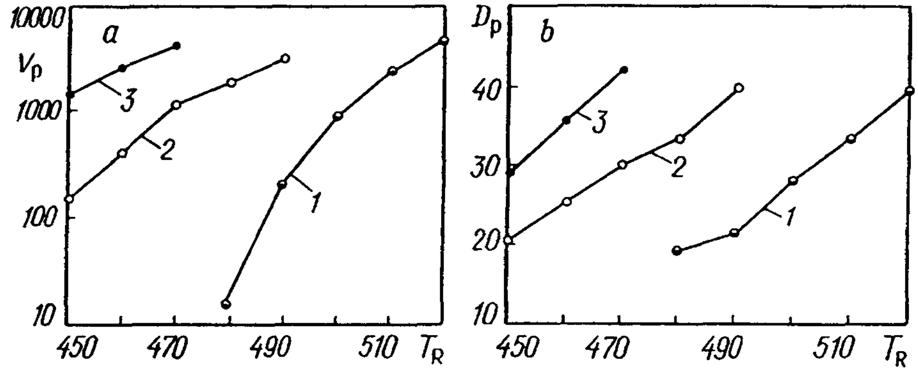

Fig. 2. Volume V_p (a) and mean diameter D_p (b) of the formed particles as a function of the reactor temperature T_R with $Si(OC_2H_5)_4$ used as the precursor: 1) TEOS $2.3 \cdot 10^7$, 2) $4.7 \cdot 10^7$, 3) $7.0 \cdot 10^7$. V_p, $\mu m^3/cm^3$; D_p, mm. T_R, °C.

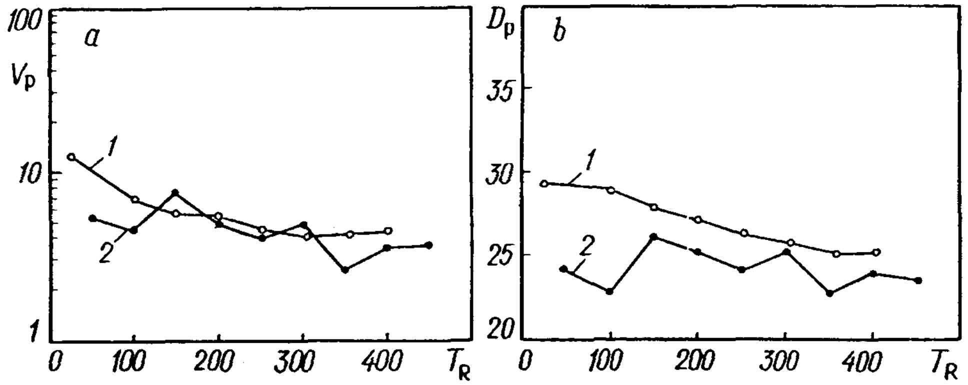

Fig. 3. Volume V_p (a) and mean diameter D_p (b) of the formed particles as a function of the reactor temperature T_R with $Al(OC_4H_9)_3$ used as the precursor: 1) ATBO $7.1 \cdot 10^9$, 2) $7.8 \cdot 10^9$.

sec), while curve 2 pertains to data with a constant delay time equal to 15 sec (the bulk flow through the reactor varied within 2080–840 cm^3/min).

The reported results allow us to suggest that formation of particles occurs already in the evaporator itself. Here, the following scheme of the process under consideration can be implemented. The initial substance (A) in the evaporator is capable of immediate decomposition into components B and C, passing into the gas phase [4]. Subsequently, molecules of the component formed (B) can react with molecules of component D, which are present in the carrier gas (for instance, molecules of water or oxygen), to form component F, whose molecules are already capable of condensing and forming aerosol particles:

$$B + D \rightarrow F. \qquad (2)$$

The reaction can be represented as

$$\frac{dn_{\mathrm{F}}}{dt} = kn_{\mathrm{B}}n_{\mathrm{D}}\,, \tag{3}$$

where n_{F}, n_{B}, n_{D} are the molecular densities of components F, B, and D, respectively; k is the reaction rate constant.

The passage of molecules of component F into the condensed phase can be implemented both through homogeneous nucleation and in deposition of the molecules onto a surface already available in the system (the surface of aerosol particles, the evaporator and reactor walls). Henceforth it will be considered that there is a sufficient amount of condensation centers in the system so that homogeneous condensation can be neglected. Deposition of molecules of component F is assumed to be chemical, and reevaporation of molecules from the condensate is neglected. For simplicity, the process of coagulation of particles available in the system is also not considered (a mathematical model taking into consideration these processes is described in [1]).

Now we will write the balance equations for the molecular densities of components B and F in the evaporator and the reactor under the assumption of ideal mixing of the mixture, physical parameters pertaining to the evaporator will be denoted by the superscript "e," and to the reactor, by "r." The temperatures in the evaporator and the reactor are assumed to be constant and maintained by external sources. Here under the assumption that only molecules of component F are deposited both on the surface of aerosol particles and on the evaporator and reactor walls we can write the following system of equations for the molecular densities n_{B}, n_{F} of components B and F:

$$\frac{dn_{\mathrm{B}}^{\mathrm{e}}}{dt} = (j^{+} - j^{-})\frac{S^{\mathrm{p}}}{V^{\mathrm{e}}} - \frac{n_{\mathrm{B}}^{\mathrm{e}}}{\tau^{\mathrm{e}}} - k^{\mathrm{e}}n_{\mathrm{B}}^{\mathrm{e}}n_{\mathrm{D}}^{\mathrm{e}}\,, \tag{4}$$

$$\frac{dn_{\mathrm{B}}^{\mathrm{r}}}{dt} = \frac{n_{\mathrm{B}}^{\mathrm{e}}}{\tau^{\mathrm{e}}} - \frac{n_{\mathrm{B}}^{\mathrm{r}}}{\tau^{\mathrm{r}}} - k^{\mathrm{r}}n_{\mathrm{B}}^{\mathrm{r}}n_{\mathrm{D}}^{\mathrm{r}}\,, \tag{5}$$

$$\frac{dn_{\mathrm{F}}^{\mathrm{e}}}{dt} = k^{\mathrm{e}}n_{\mathrm{B}}^{\mathrm{e}}n_{\mathrm{D}}^{\mathrm{e}} - G_{\mathrm{F}}^{\mathrm{e}}n_{\mathrm{F}}^{\mathrm{e}} - \frac{n_{\mathrm{F}}^{\mathrm{e}}}{\tau^{\mathrm{e}}}\,, \tag{6}$$

$$\frac{dn_{\mathrm{F}}^{\mathrm{r}}}{dt} = k^{\mathrm{r}}n_{\mathrm{B}}^{\mathrm{r}}n_{\mathrm{D}}^{\mathrm{r}} - G_{\mathrm{F}}^{\mathrm{r}}n_{\mathrm{F}}^{\mathrm{r}} + \frac{n_{\mathrm{F}}^{\mathrm{e}}}{\tau^{\mathrm{e}}} - \frac{n_{\mathrm{F}}^{\mathrm{r}}}{\tau^{\mathrm{r}}}\,, \tag{7}$$

where j_{B}^{+}, j_{B}^{-} are the densities of molecular flows escaping from the precursor surface and falling back to it, respectively (if the chemical reaction of decomposition yielding component B is irreversible, then j^{-} is equal to zero), S^{p} and V^{e} are the surface area of the precursor on which passage of molecules into the gas phase is implemented and the evaporator volume, respectively; τ^{e} and τ^{r} are the delay time of the gas in the evaporator and the reactor, respectively (the quantity τ^{r} depends, in particular, on the neutral-gas flow that is admitted to the reactor to dilute component B in the gas mixture). With use of the following expression for the density J_{F} of the molecular flow of component F to an aerosol particle growing due to chemical deposition, which yields the limiting transitions for the continuous and free-molecular regimes [5]:

$$J_{\mathrm{F}} = \frac{\alpha_{\mathrm{F}}v_{\mathrm{F}}n_{\mathrm{F}}/4}{1 + \alpha_{\mathrm{F}}v_{\mathrm{F}}R/4D_{\mathrm{F}}}\,, \tag{8}$$

for $G_{\mathrm{F}}^{\mathrm{e}}$ we have

$$G^e_F = \int_0^\infty \frac{\alpha^e_F v^e_F \pi R^2}{1 + \alpha^e_F v^e_F R/4D^e_F} f(R)\,dR + \frac{\alpha^e_F v^e_F/4}{1 + \alpha^e_F v^e_F/4\zeta^e_F} S^e/V^e . \tag{9}$$

In expression (9) the first term on the right describes deposition of molecules of component F on the surface of aerosol particles, and the second term, on the surface S^e of the evaporator. It is also assumed that complete mixing occurs in the gas-phase volume, while near the surfaces a boundary layer exists, and the mass transfer between component F and the surfaces is determined by the mass-transfer coefficient ζ^e_F, the coefficient α_F characterizes the probability of chemical deposition in collision of a molecule with a surface [6], v_F and D_F are the mean thermal velocity and the molecular diffusion coefficient of component F, respectively, and $f(R)$ is the size (radius) distribution function of the particles, which depends on the presence of condensation centers (ions and aerosol particles brought in from outside) in the system and on the process of homogeneous condensation. Some parameters (in particular, the size distribution of the particles brought in from outside) are, generally speaking, unknown. A mathematical model allowing evaluation of the influence of homogeneous condensation and coagulation on $f(R)$ is described in [1]. It should be noted that in the general case $f(R)$ depends on the molecular density of component F in the system, so that it must be determined by solving simultaneously Eqs. (4)-(7) and equations of the type given in [1], which make it possible to determine $f(R)$ as a function of the parameters of the system. For G^r_F an equation similar to (9) can be written with the only difference that all the parameters pertain to the reactor.

If precursor decomposition is considered to be a process of evaporation (condensation) of molecules of component B, and the distribution functions of the molecules escaping from the precursor surface and falling back to it and assumed to be of the Maxwell type, then for $j^+_B - j^-_B$ under the assumptions made above we have

$$j^+ - j^- = (n_{Be} - n^e_B) \frac{\alpha_B v_B/4}{1 + \alpha_B v_B/4\zeta^p_B} , \tag{10}$$

where ζ^p_B is the coefficient of mass transfer between component B and the precursor surface; α_B is the evaporation (condensation) coefficient of molecules of component B (for simplicity we will assume henceforth that the phase transitions of component B occur only on the precursor surface).

Here, Eq. (4) can be written in the form

$$\frac{dn^e_B}{dt} = \frac{(n_{Be} - n^p_B)}{\tau^p} - \frac{n^e_B}{\tau^e} - k^e n^e_B n^e_D , \tag{11}$$

where $1/\tau^p = [(\alpha^e_B v^e_B/4)/(1 + \alpha^e_B v^e_B/4\zeta^p_B)](S^p/V^e)$.

From (4)-(11) in the quasistationary approximation we have for n^e_B, n^r_B, n^e_F, n^r_F

$$n^e_B = \frac{n_{Be}}{\tau^p (1/\tau^e_0 + k^e n^e_D)} , \tag{12}$$

$$n^r_B = \frac{n_{Be}}{\tau^p (1/\tau^e_0 + k^e n^e_D)\, \tau^e (1/\tau^r + k^r n^r_D)} , \tag{13}$$

$$n^e_F = \frac{k^e n^e_D n_{Be}}{\tau^p (1/\tau^e_0 + k^e n^e_D)\,(G^e_F + 1/\tau^e)} , \tag{14}$$

$$n_{\mathrm{F}}^{\mathrm{r}} = \frac{n_{\mathrm{F}}^{\mathrm{e}}/\tau + k_{\mathrm{B}}^{\mathrm{r}} n_{\mathrm{D}}^{\mathrm{r}} n_{\mathrm{B}}^{\mathrm{r}}}{G_{\mathrm{F}}^{\mathrm{r}} + 1/\tau^{\mathrm{r}}}, \tag{15}$$

where $1/\tau_0^{\mathrm{e}} = 1/\tau^{\mathrm{e}} + 1/\tau^{\mathrm{p}}$.

The ratio $\gamma = n_{\mathrm{F}}^{\mathrm{r}}/n_{\mathrm{F}}^{\mathrm{e}}$ has the form

$$\gamma = \frac{1/\tau^{\mathrm{e}}}{G_{\mathrm{F}}^{\mathrm{r}} + 1/\tau^{\mathrm{r}}} \left[1 + \frac{k^{\mathrm{r}} n_{\mathrm{D}}^{\mathrm{r}}}{k^{\mathrm{e}} n_{\mathrm{D}}^{\mathrm{e}}} \frac{G_{\mathrm{F}}^{\mathrm{e}} + 1/\tau^{\mathrm{e}}}{k^{\mathrm{r}} n_{\mathrm{D}}^{\mathrm{r}} + 1/\tau^{\mathrm{r}}} \right]. \tag{16}$$

Note that in the case where molecular decomposition of the precursor does not occur and only its evaporation occurs followed by reaction of the evaporated molecules with molecules of type D, the above relations are still valid if by molecules of type B molecules of the initial substance A are understood.

Expressions (12)-(16) make it possible to evaluate the influence of the system parameters on the densities of the gas components in the evaporator and the reactor. Thus, for instance, from (12) it follows that the density of component B in the evaporator can be considered to be equal to that of the saturated vapor of the component n_{Be} provided only that the conditions

$$1/\tau_0^{\mathrm{e}} \gg k^{\mathrm{e}} n_{\mathrm{D}}^{\mathrm{e}}, \quad \tau^{\mathrm{p}} \ll \tau^{\mathrm{e}}. \tag{17}$$

are fulfilled.

Conditions (17) mean that the frequency of condensate–gas transitions of the molecules must be considerably larger than the frequency of exit of molecules from the evaporator caused by pumping of the system and the frequency of events of the chemical reaction. Here, it is pertinent to note that the parameters τ^{e} and τ^{p} in the general case are not independent since with increase in the pumping rate (i.e., decrease in τ^{e}) the mass-transfer coefficient $\zeta_{\mathrm{B}}^{\mathrm{p}}$ in (10) increases and the value of τ^{p} changes.

From the expression for γ it follows that the ratio of the molecular density of component B in the reactor to that of this component in the evaporator will decrease with increase in the pumping rate of the gas mixture through the reactor (decrease in τ^{r}) and decrease in the pumping rate through the evaporator (increase in τ^{e}). A value of γ also depends on the temperatures in the evaporator and the reactor (through the quantities k^{r} and k^{e}, $\alpha_{\mathrm{p}}^{\mathrm{r}}$, $\alpha_{\mathrm{p}}^{\mathrm{e}}$) and on the molecular densities of component D in the evaporator and the reactor. In the case $\gamma \ll 1$ particles will form and grow mainly in the evaporator while they are only transported through the reactor (depositing on its walls and on the walls of the pipelines connecting the evaporator to the reactor and the latter to the aerosol analyzer). From expression (8) the law of particle growth $R(t)$ can be derived:

$$R = \frac{[2\varphi g V_{\mathrm{m}} t + (1 + g R_0)^2]^{1/2} - 1}{g}, \tag{18}$$

where $g = \alpha_{\mathrm{F}} v_{\mathrm{F}}/4D_{\mathrm{F}}$; $\varphi = n_{\mathrm{F}} \alpha_{\mathrm{F}} v_{\mathrm{F}}/4$; R_0 is the particle radius at $t = 0$; V_{m} is the volume per molecule in a growing aerosol particle.

Note that in experiments with ATBO in some cases a decrease in the volume of the condensate formed and in the particle size with increase in the reactor temperature was observed. Now we will consider some factors that can be responsible for this decrease. In [7] the case of a decrease in the coefficient α_{F} with temperature is investigated. In recrystallization of a substance V_{m} can change (in particular, decrease) with increase in temperature. Moreover, in the above model the possibility of reevaporation of molecules from the particles formed is neglected. Allowance for this factor leads to subtraction of a term exponentially increasing with temperature from φ, which also causes a decrease in R with increase in T.

Equation (18) can be written for both the evaporator and the reactor. Thus, for the ratio of the particle radii at the outlet of the evaporator and the reactor $R^{\mathrm{e}}/R^{\mathrm{r}}$, with their radii R_0 at the inlet of the evaporator and the reactor being the same, we have

$$\beta = \frac{R^{\mathrm{e}}}{R^{\mathrm{r}}} = \frac{\left\{[2\varphi^{\mathrm{e}} g^{\mathrm{e}} V_{\mathrm{m}} \tau^{\mathrm{e}} + (1 + g^{\mathrm{e}} R_0)^2]^{1/2} - 1\right\} g^{\mathrm{r}}}{\left\{[2\varphi^{\mathrm{r}} g^{\mathrm{r}} V_{\mathrm{m}} \tau^{\mathrm{r}} + (1 + g^{\mathrm{r}} R_0)^2]^{1/2} - 1\right\} g^{\mathrm{e}}}. \tag{19}$$

From (19) it follows that β increases with the ratio $n_{\mathrm{F}}^{\mathrm{e}}\tau^{\mathrm{e}}/n_{\mathrm{F}}^{\mathrm{r}}\tau^{\mathrm{r}}$. The larger this value, the larger the ratio of the radii of the particles at the moment when they leave the evaporator and the reactor and the smaller the influence of the reactor on the formation and growth of the aerosol particles. At sufficiently high values of this ratio the reactor can play only the role of an additional means of communication between the evaporator and the aerosol analyzer, on the walls of which both molecules of component F and the aerosol particles formed settle. Here, deposition of aerosol particles on the walls of the setup can increase due to a temperature drop in the system, which leads to thermophoresis of the particles formed.

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