Full Articles

A kinetic model for formation of nanodisperse matter in the gas phase

I. V. Melikhov,[a] N. B. Mikheev,[b] S. A. Kulyukhin,[b] A. N. Kamenskaya,[b] E. D. Kozlovskaya,[a] and A. V. Gopin[a]*

[a]Department of Chemistry, M. V. Lomonosov Moscow State University,
Bldg. 3, 1 Leninskie Gory, 119991 Moscow, Russian Federation.
Fax: +7 (495) 932 8846. E-mail: melikhov@radio.chem.msu.ru
[b]A. N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences,
Bldg. 4, 31 Leninsky prosp, 119991 Moscow, Russian Federation.
Fax: +7 (495) 429 9200. E-mail: mikheev@ipc.rssi.ru

Taking CsI aerosol as an example, it was shown that growth of primary aerosol particles can be described in terms of both discrete and continuum models. This conclusion is based on the results of experiments carried out using a method that makes it possible to distinguish primary particles against the background of their aggregates, to provide a complete transfer of the primary particles from aerosol bulk to a collector, and to determine the particle sizes by transmission electron microscopy. Under the conditions studied, the size distribution of the primary particles is described by a Fokker—Planck type equation.

Key words: aerosols, primary particles, aggregates.

Many nanodisperse substances necessary for nanotechnology and nanomedicine are obtained by condensation of vapors.[1] In this connection, elaboration of a theoretical model for condensation suitable for quantitative prediction of the kinetics of the process is topical. Such a model should predict which set of factors ($\vec{Z}$) should act on a system under examination in such a manner that the set of properties ($\vec{Y}$) of the medium in which the particles are formed provide the desired properties $\vec{X} = \{x_1 \ldots x_i \ldots x_p\}$ of the particles. The model should describe the functional

$$\varphi(\vec{X},t) = \varphi\{\vec{X}[\vec{Y}(\vec{Z})]\}$$

and the rate of the process

$$\frac{\mathrm{d}\bar{x}_i}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t}\int_V N_0^{-1}\mathrm{d}V\int_{\vec{x}} x_i\varphi(\vec{X},t)\mathrm{d}\vec{X}. \qquad (1)$$

Here $\varphi(\vec{X},t)$ is the distribution function of particles over states at the instant t; $\vec{X}(\vec{Y})$ and $\vec{Y}(\vec{Z})$ are the functions to be determined; $\bar{x}_i$ is the parameter x_i averaged over all particles in the system; N_0 is the number of particles in the system; and V is the volume of the system.

The model, in its general form, is still under construction. Information on the functions $\vec{Y}(\vec{Z})$ is collected in studies of gas flows,[2,3] the functions $\bar{x}_i(\vec{Y})$ and $\varphi(x_i,t)$ are

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1445—1449, August, 2010.
1066-5285/10/5908-1477

determined in the studies of aerosols[4,5] and optimum conditions for desublimation of various substances.[6] From expression (1) it follows that the key problem is to determine the form of the kinetic equation for condensation:

$$\partial\varphi(\vec{X},t)/\partial t = F\{\vec{X}[\vec{Y}(\vec{Z})]\}. \quad (2)$$

Since the general form of the functional $F[\vec{X}(\vec{Y})]$ is unknown, experimental data are generalized under some assumptions that have no substantiation by independent experiment. In particular, it is assumed that Eq. (2) may have the form of the Liouville, Zeldovich, Farkas equations or other modifications of the Fokker—Planck equation.[7—9] Because of this, a special research on the determination of the actual form of the function $F[\vec{X}(\vec{Y})]$ for nanodisperse substances becomes appropriate.

Studies in this field are difficult because they should be carried out in a wide range of supersaturations of the medium including those at which investigations of condensation are complicated. This can be avoided using the phenomenon of "morphological memory" of aerosols, which consists in that at the end of condensation the function $\varphi(\vec{X},t)$ retains, for some time, information on the kinetics of the early stages of the process; this information can be extracted in some way.[10] In the present work, we report the results of such "extraction", which was completed by the determination of the form of the kinetic equation for condensation of CsI vapor.

Experiments were designed taking account of the following considerations:

1. Condensation may begin with the formation of small molecular clusters; correspondingly, investigations of such systems should be the first step of research.

2. In the course of condensation, the state of each particle changes in a discrete manner upon the addition or removal of single molecules or clusters; therefore, the distribution $\varphi(\vec{X},t)$ is discrete in character. This requires special investigations on the conditions for passage from a discrete to continuum description.

3. Since nucleation, growth, and aggregation of particles in supersaturated vapor may occur simultaneously, the methods of investigation to be used should allow one to distinguish individual particles against the background of aggregates. In this case, methods of *in situ* observation are of very limited use. On the other hand, methods of *ex situ* observation may change the properties of particles when they are removed from vapor.

4. Particles can be characterized by different values of experimentally determined morphological parameters; therefore, one has

$$\varphi(\vec{X},t) = \varphi(l,t)f(x_2)_l..f(x_p)_l, \quad (3)$$

where $\varphi(l,t)$ is the distribution function of particles over the size l in electron micrograph and $f(x_i)_l$ is the distribution density of particles of size l over the parameter x_i.

Here we present the methodology and some results obtained in the experiments performed taking account of the aforesaid.

Experimental

We studied an aerosol formed after pulsed heating of a layer of CsI microcrystals in a reactor filled with cooled argon. Preliminary experiments revealed the formation of aerosol near the surface of the layer a short time after the heating began. CsI vapor saturated at the temperature of microcrystals was transferred to this zone from the surface of the layer of microcrystals. Within the zone, the vapor cooled and thus became supersaturated with respect to CsI. This was accompanied by the formation of CsI particles that left the zone with convective flow of argon in the form of a plume of smoke. In the experiments, a number of cooled, small plate-like collectors were introduced into the reactor and arranged along the plume of smoke. Particles deposited on the collector were then studied with an electron microscope. In particular experiments, prior to melt formation the reactor was filled with NH_4Br aerosol whose particles could hold CsI particles.[11,12]

This procedure made it possible to obtain information on the behavior of $(CsI)_n$ clusters at $n > 5$ and to determine the discrete and continuous size distribution functions of primary particles and aggregates whose size was larger than 2 nm. These functions were determined using the set of properties $\vec{X} = \{l,\chi,H\}$ and the set of factors $\vec{Z} = \{T_g,T_z,\bar{v}\}$, where $l = S^{1/2}$, S is the surface area of the particle in the electron micrograph, χ is the length of the perimeter of the particle image, H is the distance between the particle and the source of vapor, T_g and T_z are the temperatures of argon and microcrystals, respectively, and $\bar{v}$ is the argon flow rate.

Results and Discussion

Three types of CsI particles (Fig. 1) were found on collectors at $T_g = 300$—450 K, $T_z = 1300$ K, and distances between the melt surface and the collectors in the range $H = 5$—40 cm (vertically). The particle sizes were $l = 1$—10 (type 1) and 8—20 nm (type 2), and 0.1—10 μm (type 3). The particle sizes and shapes suggest that the type-1 particles ($j = 1$) are primary aerosol particles, the type-2 particles ($j = 2$) are ordered aggregates of primary particles (first-generation aggregates, or G-1 aggregates), and the type-3 particles ($j = 3$) are aggregates of aggregates (second-generation aggregates, or G-2 aggregates). The dimensions of the images of the type-1 and type-2 particles in the electron micrographs were determined with an accuracy of ±2 nm, while the size of the type-3 particles was determined with an accuracy of ±0.1 μm. With these accuracies, no discrete groups of particles of a particular size l were found among particles on the surface of collectors. Particles are characterized by continuous size distribution functions in the whole range of sizes studied. The measured distribution functions are independent of the conditions under which the collectors were removed

Fig. 1. Electron micrographs of CsI particles and aggregates deposited on a collector; T_g = 313 K, t = 10 s, H = 5 cm, a JEM-100B electron microscope.

from the reactor and of the operating mode of the microscope. This fact was considered as a proof that the measurements introduced no distortion into the desired distributions. The size distributions of the primary particles deposited on the collector surface individually and the primary particles-constituents of G-1 aggregates were identical. The size distribution of the G-1 aggregates arranged on the collector surface individually and the G-1 aggregates-constituents of G-2 aggregates were also almost indistinguishable. The size distributions of the primary particles deposited on collectors in the presence and in the absence of NH_4Br aerosol are similar (Fig. 2), although in the former case the CsI particles were transferred to the collector along with NH_4Br microcrystals rather than individually. These facts were treated as an indication that the sampling procedure for aerosol particles had no effect on the results of measurements, so that the integrated distribution functions $\theta(l)$ shown in Figs 2 and 3 characterize not only the aerosol particles deposited on the collector, but also the aerosol arrived at the collector at the instant t.

The size distribution density $\psi_j(l,t)$ of the primary aerosol particles and G-1 aggregates in the time interval $t = 10—10^4$ s is given by

$$\psi_j(l,t) \equiv \frac{1}{N_{j0}}\frac{\partial N_{jl}}{\partial l} = \frac{\lambda_j}{l_j}\exp\left[-\lambda_j\left(\frac{l}{l_j}-1\right)\right], j = 1, 2, \quad (4)$$

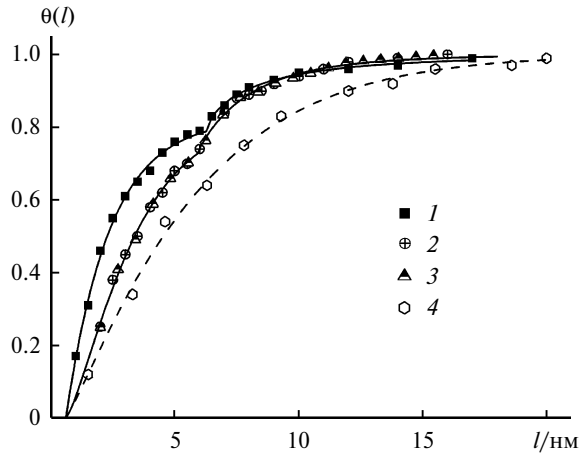

Fig. 2. Integrated size distributions of CsI particles: free particles, t = 10 s, H = 5 cm (*1*); free particles, t = 3600 s, H = 20 cm (*2*); particles within aggregates, t = 3600 s, H = 20 cm (*3*); particles on NH_4Br microcrystals, t = 3600 s, H = 20 cm, T_g = 313 K, l = 1—20 nm (*4*); solid lines denote the results of calculations using expression (4) with the parameters λ_j and l_j listed in Table 1.

and the corresponding size distribution density of the G-2 aggregates has the form

$$\psi_3(l,t) = (\pi Ap)^{-1/2}\exp(-X_-^2) - (2p)^{-1}\exp(l/p)\mathrm{erfc}(X_+), \quad (5)$$

where N_{jl} is the number of measured particles of the jth type whose size is smaller than l, N_{j0} is the total number of the measured particles of the jth type,

$$X_\pm = (l \pm A)/(4\pi A)^{1/2},$$

$$\mathrm{erfc}(X_+) = \frac{2}{\sqrt{\pi}}\int_{X_+}^{\infty}\exp(-x^2)\mathrm{d}x,$$

and λ_j, l_j, $A = 0.30\pm0.01$ μm, and $p = 70\pm4$ nm are empirical parameters.

The parameters λ_j and l_j increase as H increases (Table 1) while the parameters A and p are independent of H and t. This suggests that the primary particles and aggregates were formed in the zone of aerosol formation. In the bulk of the plume of smoke, the size of the primary particles remained almost unchanged and the G-1 aggregates contained no large particles which seemingly transferred to G-2 aggregates.

The images of the smallest primary particles detected (l_1 = 0.6 nm) were comparable in size with the $(CsI)_2$ cluster. This suggests that the role of the seeds of the

Table 1. Parameters of the size distribution of CsI particles

H/cm	t/s	λ_1	λ_2	l_1	l_2
				nm	
5.0	10	0.34±0.08	1.7±0.1	0.6±0.1	5.7±0.1
20.0	3600	0.34±0.09	3.0±0.3	1.0±0.1	5.7±0.1

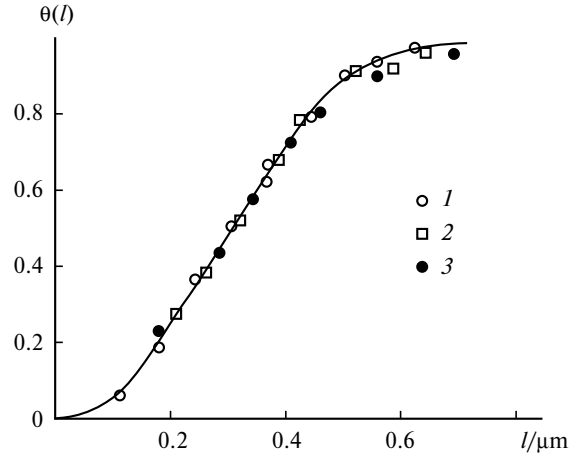

Fig. 3. Integrated size distributions of G-2 aggregates: experimental data for individual particles (*1*) and particles within G-3 aggregates (*2*) and results of calculations performed by integrating Eq. (5) at A = 0.3 μm and p = 70 nm; T_g = 426 K, l = 0.1—1.0 μm (*3*).

primary particles was played by the dimers $(CsI)_2$, which grew by adding individual molecules. However, already at l = 1.5 nm their growth can be described using a continuum model, as indicated by the smooth character of the function

$$\theta_1(l) = \int_0^l \psi_1(l,t)\mathrm{d}l$$

(see Fig. 2) at $l > 1$ nm. In this case, we failed to accurately determine the functions $f(x)_l$ and $f(H)_l$ and had to reduce ourselves to the function

$$\varphi_1(l,t) \equiv N_1\psi_1(l,t) = (N_1\lambda_1/l_1)\exp[-\lambda_1(l/l_1 - 1)], \qquad (6)$$

where N_1 is the number of primary particles in the unit volume of aerosol, l_1 is the size of the seed, and λ_1 characterizes the rate of the process. The fact that the process is independent of H (see Table 1) indicates that the formation of primary particles takes less than 10 s to complete.

According to expression (4), by analogy with relation (6), one gets

$$\varphi_2(l,t) = N_2 p^{-1}\exp[-(l - l_2)/p], \qquad (7)$$

where $p = l_2/\lambda_2$; l_2 = 5.7 nm is the size of the smallest G-1 aggregate detected on collectors. From Eq. (5) it follows that the G-2 aggregates are described by

$$\varphi_3(l,t) = (N_3/p)\{[p/(\pi A)]^{0.5}\exp(-X_-^2) - 0.5\exp(l/p)\mathrm{erfc}(X_+)\}, \qquad (8)$$

where N_3 is the number of the G-2 aggregates in the unit volume. The parameters A and p are independent of time at $t > 10$ s, which indicates that aggregation is completed prior to the instant at which these regions of aerosol arrive at the surface of the collector.

Relations (6)—(8) are particular solutions to the equation of balance of the number of molecules, derived with allowance for discrete character of elementary acts of changes in size and represented, by analogy with the equation of connective diffusion,[8,13,14] in the form:

$$-\frac{\partial\varphi_j}{\partial t} = \frac{\partial}{\partial l}\left[G_j\varphi_j - \frac{\partial}{\partial l}(D_j\varphi_j)\right] + \Omega_j \qquad (9)$$

at

$$G_j = \alpha_j a_j - \beta_j b_j,\ D_j = 0.5(\alpha_j a_j^2 + \beta_j b_j^2).$$

Here α_j and β_j are the occurrence frequencies of the events leading to an increase and a decrease in l; a_j and b_j are the corresponding characteristic changes in l upon the occurrence of such events; and Ω_j is the intensity of transformation of the given-type particles to other types of particles.

At $\Omega_j = 0$, $\alpha_j = \alpha_{j0}F(t)$, $\beta_j = \beta_{j0}F(t)$ and assuming that G_j and D_j are independent of l, Eq. (9) is transformed to expressions (6)—(8) and the relationships

$$\lambda_j = l_j/p,\ p = a_j(1 + zb_j/a_j)/[2(1 - z)],$$

$$A = \alpha_{j0}a_j(1 - z)\int_0^t F(t)\mathrm{d}t,$$

where $z = (\beta_{j0}b_j)/(\alpha_{j0}a_j)$ and $F(t)$ is the function, which characterizes the changes in the supersaturation and the concentration of particles in the medium.

This suggests that the primary particles either had time to grow before aggregation or continued to grow within G-1 aggregates (being constituents of G-1 aggregates); as a result, one has $\Omega_1 = 0$. The G-1 aggregates either grew much faster than became constituents of G-2 aggregates or continued their growth within the G-2 aggregates by adding the primary particles trapped by the G-2 aggregates, so that $\Omega_2 \to 0$.

Equation (9) represents the condition for balance of the number of particles when they move in the space of sizes. It can be derived by going from the discrete to a continuous form of the condition for balance of the number of molecules and subsequent expansion of the particle addition and removal frequencies in the Taylor series and followed by truncation of all terms except the first three ones. This equation includes no parameters of the critical seed and other values inaccessible to direct experimental determination and differs from other forms of the currently used kinetic equations[15–17] in that the search for the functional (2) is reduced to the determination of the frequencies $\alpha_j\{\vec{Y}[\vec{Z}]\}$ and $\beta_j\{\vec{Y}[\vec{Z}]\}$.

Our experimental study of the properties of an aerosol formed on cooling vapor over molten CsI revealed that the rate of changes in the size distribution functions of primary aerosol particles and aggregates can be described

by a Fokker—Planck type equation which takes into account a continuous exchange of molecules between particles and the medium. This equation is basic to the kinetic model for phase formation formulated using the frequencies of the addition and removal of molecules from particles of the newly formed phase. The model has no arbitrary admissions and includes some frequency functions that can be determined experimentally.

References

1. *Handbook of Nanostructured Materials and Nanotechnology. Five-Volume Set (Hardcover)*, Ed. H. S. Nalwa, Academic Press, San Diego, 2000, 3583 p.
2. G. A. Bird, *Molecular Gas Dynamics and the Direct Simulation of Gas Flows*, Clarendon Press, Oxford, 1994, 458 p.
3. S. C. Garrick, K. E. J. Lehtinen, M. R. Zachariah, *J. Aerosol Sci.*, 2006, **37**, 555.
4. S. K. Friedlander, *Smoke, Dust and Haze. Fundamentals of Aerosol Dynamics*, Oxford University Press, New York, 2000, 432 p.
5. S. H. Park, K. W. Lee, M. Shimada, K. Okuyama, *J. Aerosol Sci.*, 2002, **33**, 1297.
6. M-Y. Yi, J-W. Lee, *J. Aerosol Sci.*, 2007, **38**, 764.
7. N. N. Tunitskii, V. A. Kaminskii, S. F. Timashev, *Metody fiziko-khimicheskoi kinetiki* [*Methods of Physicochemical Kinetics*], Khimiya, Moscow, 1972, 196 pp. (in Russian).
8. I. V. Melikhov, *Fiziko-khimicheskaya evolyutsiya tverdogo veshchestva* [*Physicochemical Evoluton of Solid Matter*], Binom, Moscow, 2006, 309 pp. (in Russian).
9. A. A. Lushnikov, V. A. Zachainov, V. E. Agranovskii, Yu. S. Lyubovtseva, *Zh. Fiz. Khim.*, 2008, **82**, 1950 [*Russ. J. Phys. Chem.* (*Engl. Transl.*), 2008, **82**].
10. I. V. Melikhov, N. B. Mikheev, S. A. Kulyukhin, E. D. Kozlovskaya, *Kolloid. Zh.*, 2001, **63**, 808 [*Colloid. J.* (*Engl. Transl.*), 2001, **63**].
11. I. V. Melikhov, E. N. Kitova, A. N. Kamenskaya, E. D. Kozlovskaya, N. B. Mikheev, S. A. Kulyukhin, *Kolloid. Zh.*, 1997, **59**, 780 [*Colloid. J.* (*Engl. Transl.*), 1997, **59**].
12. N. B. Mikheev, I. V. Melikhov, A. N. Kamenskaya, E. N. Kitova, E. D. Kozlovskaya, E. L. Novichenko, *Radiokhimiya*, 1997, **39**, 523 [*Sov. Radiochem.* (*Engl. Transl.*), 1997, **39**].
13. I. V. Melikhov, I. E. Mikheeva, V. N. Rudin, *Kristallografiya*, 1989, **34**, 1272 [*Crystallogr. Repts* (*Engl. Transl.*), 1989, **34**].
14. N. B. Mikheev, I. V. Melikhov, E. N. Kitova, A. N. Kamenskaya, E. D. Kozlovskaya, V. L. Novichenko, *Kolloid. Zh.*, 1997, **59**, 774 [*Colloid J.* (*Engl. Transl.*), 1997, **59**].
15. S. E. Pratsinis, *J. Colloid. Interface Sci.*, 1988, **124**, 416.
16. I. J. Ford, *Phys. Rev. E*, 1997, **56**, 5615.
17. T. Hawa, M. R. Zachariah, *J. Aerosol Sci.*, 2006, **37**, 1.

Recieved November 13, 2009;
in revised form April 5, 2010