FORMATION OF A CONDENSATION AEROSOL AT HIGH SUPERSATURATIONS

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ABSTRACT: A description is given of condensation aerosol formation at high supersaturations; this takes account of simultaneous nucleation, growth by condensation, and coalescence. The free energy of formation of a nucleus is calculated via a model for pair interaction of the molecules. A calculation is performed for silver vapor in a hot argon jet emerging into cold air at rest. The results agree satisfactorily with experiment. The size distribution at high supersaturations is governed by the tendency of the particles to coalesce.

Various technical processes involve a highly supersaturated vapor that condenses spontaneously, e.g., powder production by the plasma method, rocketry, hypersonic wind tunnels, etc. However, theoretical calculation is made difficult because the ordinary theory of spontaneous nucleation is imperfect and also because nucleation is accompanied by growth and coalescence. Sometimes it is necessary to take into account the kinetics of the process producing the supersaturation, e.g., mixing of a hot vapor with a cold gas, or a reaction accompanying nucleation.

Doubt has often been cast on the applicability of the usual theory [1] even in describing condensation at low supersaturations, on account of difficulty in expressing the free energy of nucleation in terms of the physical properties of macroscopic volumes of liquid. There has recently [2,3] been extensive discussion of the contribution to the free energy from the external degrees of freedom of a nucleus. The size of the critical nucleus bears an inverse relation to the supersaturation, so the above difficulties increase for condensation at very high supersaturations, where a critical nucleus consists of only a few molecules.

1. General. The discussion of condensation at very high supersaturations is facilitated by the following features.

1) The free energy of formation for a cluster of a few molecules can be calculated by the methods of statistical physics without making assumptions about the density and surface tension.

2) The concentration of groups less than the critical size is close to the equilibrium value at all times.

3) The nucleation time is about 100 times the interval Δt between successive collisions of molecules with a critical nucleus.

The concentration of precritical groups may be considered as the equilibrium one (corresponding to the existing temperature and concentration). The nucleation rate can be determined via the frequencies of collision between molecules and critical or precritical groups in successive intervals Δt via

$$\Delta f_{g^*+1} / \Delta t = \sum_{j+k=g^*+1} K_{jk} c_j c_k -$$
$$- \sum_{i=1}^{\infty} K_{ig} f_{g^*+1} c_i - \beta_{g^*+1} f_{g^*+1} + \beta_{g^*+2} f_{g^*+2}. \quad (1.1)$$

Here f_{g^*+1} is the concentration of groups containing $g^* + 1$ molecules, g^* is the number of molecules in a critical nucleus, c is the equilibrium concentration of precritical groups, K_{jk} is the constant for collisions between groups containing j and k molecules, $j + k = g^* + 1$, and β_{g^*+1} is the probability of evaporation of a molecule from a group containing $g^* + 1$ molecules. The number of intervals Δt into which it is necessary to divide the nucleation is only moderately large at high supersaturations, and so no excessive volume of calculation is needed to solve the equations of the type of (1.1), whose number equals the number of intervals Δt.

The growth and coalescence rates for $g > g^*$ can be calculated via expressions of the type of (1.1), but without the terms that take account of the evaporation probability, since this rapidly decreases

as the droplet enlarges. This scheme can be modified to include chemical reactions accompanying nucleation.

Calculations show [3] that the time needed to reach a steady concentration is proportional to g and so is very small when g is small. The number of nuclei was calculated on the assumption that T and the concentration are constant within a given Δt but change stepwise at the boundaries between intervals. Published calculations [4] and ours imply that, in some cases, allowance for the external degrees of freedom causes the free energy of formation to have a minimum at very small g as well as a maximum at g^*. This means that it is possible to have $c_g > c_{g-1}$ and $c_g > c_{g+1}$, so c_g cannot be close to equilibrium during nucleation, since it cannot exceed c_{g-1}, and an equation like (1.1) has to be solved in order to determine this concentration.

Reed [5] was the first to use the chemical potential μ to determine the equilibrium c_g for g up to 8, this being determined via the sum over states of the groups, which were considered as polyatomic molecules. Reed made the following assumptions in calculating these sums. A group has only the interaction described by the Lennard-Jones equation between nearest neighbors. The molecules in a group retain their rotational degrees of freedom. Each group exists in its most stable spatial configuration.

Strictly speaking, the equilibrium c_g should be calculated via cluster integrals, as in the Mayer-Born-Fuchs theory of the equation of state [6]. Recently a method has been developed [7] for calculating these integrals up to g = 10 that requires relatively little computation, though much more than Reed's method [5].

The particle size distribution can therefore be calculated as follows. Relations of the form

$$\mu_g = g\mu_1, \qquad c_1 + 2c_2 + \ldots + g c_g = \text{const}$$

are used, where μ_1 is the chemical potential of a molecule and μ_g is that of a group; these give the c_g at the start of condensation. The group with the least μ_g is considered as the critical group. Then kinetic arguments are applied to determine the Δt for a critical group to collide with a molecule or smaller group. It is assumed that T and the concentration remain constant during this interval. If the probability of coalescence on collision is unity, all critical nuclei become postcritical in this interval. Then Δt is determined again and the c_g for $g < g^*$, with allowance for the vapor used up in producing $g > g^*$. From this time on, allowance is made for the loss of vapor by group growth, and the changing particle sizes are followed. The collisional frequencies are derived via formulas for the collisions of gas molecules, the groups and nuclei being considered as spheres whose density equals that of the corresponding liquid.

Coalescence occurs because the number of particles with $g > g^*$ increases. It is not possible, even with the fastest computers, to calculate exactly the particle-size distribution in such an aerosol when some of the particles are thousands of times larger than the primary ones. Rosinski and Snow [8] described a scheme for coalescence of polydisperse droplets that coalesce upon collision; the continuous distribution function is replaced by discrete function, the aerosol being considered to consist of particles each containing 2^i molecules, in which i is an integer. Two particles of class 2^i produce a particle of class 2^{i+1}. It is also assumed that collision of particles of classes 2^i and 2^{i+1} also produces particles of class 2^{i+1}, but in an amount equal to $(2^i + 2^{i+1})/2^{i+1} = 0.75$ of the primary particles involved in the collisions. If classes 2^i and 2^{i-j} (j > 1) collide, the sizes do not increase, but the number increases by a factor $(2^i + 2^{i-j})/2^i$. The first of these assumptions increases the rate of transfer of mass along the particle-size axis, while the second reduces it, and so the errors balance out.

Stockham [9] used this scheme for the coalescence of a silver aerosol, and his results agree well with experiment.

Calculations on nucleation and condensation growth can provide a nearly continuous size distribution (almost, since particles cannot differ in mass by less than the mass of one molecule), but the Rosinski-Snow method requires a discrete distribution, so the following method is used. First we calculate the coalescence during time Δt of the particles that have formed up to that instant, and then the condensation growth in this interval. Independently we determine the number of new particles with $g > g^*$. Then we make a conversion, in which N particles each containing g molecules are replaced by $Ng/2^i$ particles containing 2^i molecules (the 2^i closest to g). This conversion is done for each Δt. The vapor concentration and T can cause wide variations in the balance between the rates of coalescence and formation of new particles, so Δt may be less or greater than the time for which the concentration of coalescing particles may be considered as constant. The condensation can be considered as coalescence of single molecules with growing particles when the concentration of vapor molecules becomes comparable with the concentration of nuclei, and so the Rosinski-Snow scheme can be applied.

The error due to these assumptions was estimated via an exact calculation of the production of the particle distribution up to the time when there is an appreciable c_{64}. The Rosinski-Snow method was applied simultaneously. The two gave the same number of particles and the same width for the size distribution within the error of the calculations.

The above scheme neglects particle heating by the latent heat of condensation. If the partial pressure of the vapor does not exceed about 1 mm Hg, a nucleus collides with at least 10^3 molecules of inert gas in the time between collisions with vapor molecules, which serves to remove the heat.

This scheme takes account of the transient nature of the process, of the contribution from the external degrees of freedom, and of particle coalescence, while being free from various assumptions made in the classical theory. It can be improved by taking account of the heating of nuclei at high vapor concentrations, the effects of molecular forces on coalescence and condensation, etc. The discussions, and some of the conclusions in the second part, involve not very reliable assumptions, but the problem could not be solved at all without them.

2. Condensation in a turbulent jet. Division of the condensation into time intervals causes no difficulty in discussing, for example, the condensation in a closed chamber or in a one-dimensional adiabatic flow in a wind tunnel. The problem is much more complicated in turbulent mixing of flows differing in T, since T and c are functions of two or three variables. We consider the condensation in a hot axially symmetric turbulent gas jet entering cold air at rest.

Amelin [10] examined condensation in a free turbulent jet in order to test the theory of spontaneous nucleation; he expressed the supersaturation as

$$S = \frac{p_0}{p_T} \frac{1}{n+1}.$$ (2.1)

Here P_0 is the partial pressure of the vapor at the nozzle exit, p_T is the saturation pressure at the T prevailing at that point, and n is the time-average of the ratio by weight of the amounts of cold and hot gas at this point in the mixing zone.

At a certain n $S(n)$ has a maximum because of the opposing effects of dilution and cooling. In Amelin's experiments [10] S exceeded the critical value only in a very narrow range in n, so it could be assumed that nucleation occurs at the maximum S attained in the mixing zone. Higuchi and O'Conski [11] improved the method and expressed the number of nuclei formed in unit time in the mixing zone as

$$N = \int_0^\infty I(n) \frac{dV(n)}{dn}\, dn.$$ (2.2)

Here I is nucleation rate and $V(n)$ is the volume of the mixing zone bounded by $n = $ const.

Clearly, T and p at any point in the mixing zone can be expressed as functions of n alone. Higuchi and O'Conski used in the expressions

for $V(n)$ and $I(n)$ equations [12,13] that use Reichardt's model of turbulence to describe the time-averages of the concentration, excess temperature θ, and axial velocity component u of the jet in the mixing zone:

$$\gamma_m \frac{\rho u^2}{\rho_0 u_0^2} = \frac{d^2}{4C_m^2 x^2} \exp \frac{-r^2}{C_m^2 x^2},$$ (2.3)

$$\gamma_\chi \frac{\rho \chi u}{\rho_0 \chi_0 u_0} = \frac{d^2}{4C_\chi^2 x^2} \exp \frac{-r^2}{C_\chi^2 x^2}, \qquad \chi = \frac{1}{n+1},$$ (2.4)

$$\gamma_\theta \frac{\rho \theta u}{\rho_0 \theta_0 u_0} = \frac{d^2}{4C_\theta^2 x^2} \exp \frac{-r^2}{C_\theta^2 x^2}, \qquad \theta = T - T_a.$$ (2.5)

Here x and r are the axial and radial coordinates, while ρ is the time-averaged density of the gas mixture, χ is the weight proportion of the hot gas, T_a is the temperature of the cold gas, and C_m, C_χ, and C_θ are constants. Baron [13] found from the extensive experimental evidence that $C_\chi = C_\theta = 0.855$ and $C_m = 0.075$. The coefficients γ_m, γ_χ, and γ_θ are introduced because the mean of a product is not equal to the product of the means. In the first and second approximations, respectively,

$$\gamma_m = \gamma_\chi = \gamma_\theta, \qquad \gamma_\theta / \sqrt{\gamma_m} = \gamma_\chi / \sqrt{\gamma_m} = 1.$$

Surfaces of constant T and c are naturally used as the step boundaries in stepwise calculation of the aerosol formation (as $C_\theta = C_\chi$, these boundaries coincide), while the time intervals are those required for the mixture to pass across the space between two such surfaces.

We find the equation for a surface $n = $ const by taking the square root of both sides in (2.3) and dividing (2.4) into the result. We substitute for the constants and convert to polar coordinates R and φ (the latter is the angle between the radius vector R and the plane containing the end of the nozzle); as $\chi_0 = 1$, we have

$$\chi = 5.14\ (\rho_0 / \rho)^{1/2}\ d\ /\ R\ \sin \varphi \exp (-48\ \mathrm{ctg}^2 \varphi).$$ (2.6)

Consider the mean time spent by an elementary gas volume between surfaces with $n = $ const. Assuming that the gas moves along R, which has its origin at the pole of the jet, we get the path in which the dilution changes from n_1 to n_2 as

$$\Delta R\ (\varphi) = R\ (n_2,\ \varphi) - R\ (n_1,\ \varphi)$$ (2.7)

and the time needed as

$$\Delta t\ (\varphi) = \int_{R_1}^{R_2} \frac{\sin \varphi dR}{n},$$ (2.8)

which can be expressed from (2.6). Consider $u(n)$. We divide (2.3) by (2.4) to get

$$\frac{\gamma_m u^2 u_0}{\gamma_\chi u u_0^2} = \frac{C_\chi^2}{C_m^2} \exp \left[-\frac{r^2}{x^2} \left(\frac{1}{C_m^2} - \frac{1}{C_\chi^2} \right) \right].$$ (2.9)

If we assume that

$$\frac{\gamma_m}{\gamma_\chi} \frac{u^2 u_0}{u u_0^2} = \frac{u}{u_0}, \qquad u = 1.3 u_0 \chi \exp (-41\ \mathrm{ctg}^2 \varphi).$$ (2.10)

A more exact expression for u can be derived from Abramovich's empirical relation [14], which gives for the axis of a jet in which T changes that

$$\theta / \theta_0 = 0.73 u/u_0.$$ (2.11)

We assume that this applies everywhere in the main part of the mixing zone (not merely at the axis) to get

$$\frac{\gamma_m}{\gamma_\chi} \frac{\bar{u}^2 u_0}{u u_0^2} = 0.97 \frac{u}{u_0} \qquad u = 1.34 u_0 \chi \exp (-41\ \mathrm{ctg}^2 \varphi).$$ (2.12)

It follows from (2.11) that $0.73\ u_0 > u_0$ for $1 > \theta/\theta_0$, which is impossible, because (2.3)-(2.5) and (2.11) are not applicable to processes

near the start of the jet. The results of this treatment therefore cannot be used to calculate the condensation near the boundary of the main part.

We substitute the $u(n)$ and $R(n)$ of (2.6) and (2.10) into (2.8) to get

$$\Delta t(\varphi) =$$

$$= 1.89 \frac{d}{u_0} \left(\frac{\rho_0}{\rho}\right)^{1/2} \left[\frac{(n_2+1)^2}{2} - \frac{(n_1+1)^2}{2}\right] \exp(-7 \operatorname{ctg}^2 \varphi). \quad (2.13)$$

We average Δt over all φ as

$$\triangle t_{av} = \left(\int_0^{1/2 \pi} \Delta t(\varphi) \, m(\varphi) \, d\varphi\right)\left(\int_0^{1/2 \pi} m(\varphi) \, d\varphi\right)^{-1}. \quad (2.14)$$

Here $m(\varphi)$ is the mass of hot gas flowing through a ring between φ and $\varphi + d\varphi$ in the surface $n = \text{const}$ in unit time and is

$$(p \chi \, u \, / \sin \varphi)_{n=n_i} \cos \alpha ds,$$

in which α is the angle between the direction of the velocity and the tangent to the surface $n = \text{const}$, while ds is the area of the ring. Elementary geometry gives

$$\operatorname{tg} \alpha = \frac{1}{R} \frac{dR}{d\varphi} \qquad \cos \alpha = \frac{1}{\sqrt{1 + (dR/Rd\varphi)^2}}. \quad (2.15)$$

The area of the body of rotation in polar coordinates is

$$s = 2\pi \int_0^{1/2 \pi} R \cos \varphi \sqrt{(dR/d\varphi)^2 + R^2} d\varphi, \quad (2.16)$$

so

$$\cos \alpha ds = 2\pi R^2 \cos \varphi \, d\varphi. \quad (2.17)$$

We substitute into (2.14) for $\Delta t(\varphi)$ and $m(\varphi)$ to get

$$\Delta t^* = 1.89 \frac{d_0}{u_0} \left(\frac{\rho_0}{\rho}\right)^{1/2} [(n_2+1)^2 - (n_1+1)^2]. \quad (2.18)$$

If $n_2 - n_1$ is small, (ρ_0/ρ) may be taken as constant and may be averaged by linear interpolation. Although $\Delta t(\varphi)$ is very much dependent on φ, the function $\exp(-41 \operatorname{ctg}^2 \varphi)$ in the expression for $m(\varphi)$ becomes virtually zero at φ such that Δt is about 0.6 of the Δt at the jet axis. Therefore, only a minute fraction of the material is in this volume for a time very different from Δt^*, and the averaging is permissible.

Higuchi and O'Conski [11] concluded that the Baron-Alexander equations are applicable to mixing in a turbulent jet if the Reynolds number is greater than 3000 and the pressure drop in the nozzle is not too great. These conditions are required because Reichardt's theory of turbulence takes no account of terms containing the molecular viscosity and the pressure gradient. Huguchi and O'Conski concluded that, if the highest S is not too greatly in excess of the critical S, the turbulent fluctuations will produce not more than 8% local increase in S, which they considered as unimportant even at S close to the critical value. The derivative dI/dS decreases rapidly, so the effects of turbulent fluctuations should be even less at high S.

Expression (2.18) provides some general conclusions about the effects of the various parameters on aerosol formation. The cooling rate in-
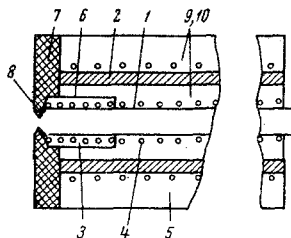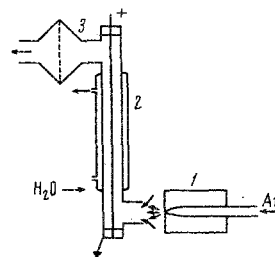
creases with the efflux velocity but decreases as the nozzle diameter increases, so a slow jet from a wide nozzle should show more effect from coalescence, while the nucleation rate should rise more slowly as cooling proceeds. We thus expect that the size spread in the aerosol should increase with the speed but decrease as the nozzle diameter increases for a given concentration of condensing vapor.

3. Experiments on jets. The tests were done on silver vapor in an argon jet emerging into cold air at rest. Silver was chosen as the working substance because it is chemically inert and because silver particles are convenient for electron microscopy. Our apparatus was somewhat similar to Higuchi and O'Conski's [11] but had some marked differences due to the operation at high temperatures.

Figure 1 shows the design, where 1 and 2 are alundum tubes, 3-5 are molybdenum heater windings, 6 is an alundum sleeve, 7 is a sintered corundum ring, 8 is the nozzle, and 9 and 10 are the insulating parts. The alundum boat containing the silver is placed in tube 1, which carries a stream of pure argon which passes also through the joints in the insulation to protect the heaters from oxidation. The voltages on the winding can be adjusted to vary the temperature of the silver while keeping the exit temperature constant.

The hot jet enters the air of the laboratory. As in Higuchi and O'Conski's study [11], care was needed to prevent the air from being heated by the oven, although the air and jet temperatures had no great effect on the particle concentration and size. For instance, ±50% change in the temperature at the nozzle exit did not affect the size.

The size was measured via the specific surface of the powder as deduced by the BET method (adsorption of krypton at $78°$ K) on material deposited in an electrical precipitator whose intake was 80 mm in diameter and 80 mm from the nozzle. Behind the precipitator was an analytical aerosol filter to monitor for the degree of deposition. The air was drawn through the filter at about 60 liters/min. The precipitator intake was seen by eye to disturb the mixing only for $n > 10$. Figure 2 shows how the aerosol was collected, in which 1 is the device for producing the aerosol, 2 is the precipitator, and 3 is the filter. The aerosol concentration was determined by weighing the material collected in a set time.

It has been reported [15] that finely divided metal powders change in specific surface F on storage, but we found that, for $F = 27$ m^2/g, there was no change on storing the powder at room temperature for a week.

Figure 3 shows $F(\text{m}^2/\text{g})$ as a function of c in the jet (molecules/ /cm^3). The tests were done with a nozzle 0.08 cm in diameter with the argon flowing at 40 m/sec and a temperature in the exit cross section of $1663°$ K.
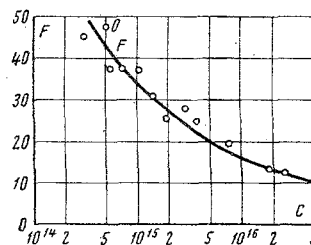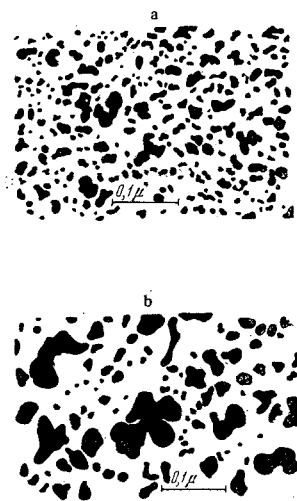
Fig. 2

Fig. 1

Fig. 3

Fig. 4

The value of F gives the mean particle size d on the assumption that the particles do not fuse or sinter together on contact; but coalescence at elevated temperatures can cause this. Large solid particles can sinter together if T exceeds the Tamman point (about 0.6 of the melting point on the absolute scale), but there are statements that small particles sinter at much lower T. We related the sintering temperature T_s to d via the change in F on heating at a pressure of $5 \cdot 10^{-6}$ mm Hg for an hour, and also by electron microscopy of aerosol samples taken at various points in the mixing zone. The following are some results on the effect of T on F:

$T^\circ C =$	20	60	115	160	200		
$F(m^2/g) =$	25.7	28.8	23.6	12.4	8.5	(spec	1)
$F(m^2/g) =$	34.2	38.5	24.7	13.2	8.7	(spec	2)

The rise in F at 60° is due to desorption of contaminants. There was no further change in F on heating for more than 1 h. The largest F (for an evacuated specimen at 60°) was 108 m^2/g. If the fall in F is ascribed to sintering, it would seem that particles of radius less than 100 Å can sinter at T > 150° C.

The aerosol was sampled onto electron-microscope grids as follows. A brass grid carrying a collodion film was attached to a scalpel blade, which was cooled to 77° K and quickly inserted in the mixing zone near the axis of the jet. Thermophoresis deposited particles on the grid. The precooling prevented the film from being overheated. Figure 4 shows tracings of pictures of particles taken from zones at about 400 and 530° K (a and b, respectively). In each case the clumps contain few primary particles (about the same number in each), although a substantial degree of coalescence would be expected during the motion between the two sampling points according to the calculation. The particle size is appreciably larger in the second case, which can only be due to coalescence, since calculations indicate that the vapor phase was exhausted at higher T. These pictures thus show that particles of radius less than or equal to 100 Å (and perhaps larger) fuse together, which undoubtedly takes a certain time, and the process is halted by deposition on the cold grid. X-ray examination showed that the silver powder did not contain silver oxides.

An apparatus of this type was used not only to examine spontaneous condensation but also to produce a few grams of powders with F up to 200 m^2/g from a variety of substances. Salts and metal oxides distilled at 600–900°, e.g., MoO_3, gave much larger F than did silver, although higher supersaturations should be attained with silver vapor.

Clearly, F is dependent on the tendency of the particles to sinter together, especially since MoO_3 powder with d ≈ 100 Å did not change in F on heating to 350° under vacuum. Silver itself gave F 2–3 times larger when He replaced A_r, all the other conditions being the same.

The results were compared with calculations by the above method for silver in argon issuing from a 0.08-cm jet at 410 m/sec and 1663° K,

the air being at 301° K. Three concentrations were used: A) $5.01 \cdot 10^{14}$, B) $5.01 \cdot 10^{15}$, C) $5.01 \cdot 10^{16}$ molecules/cm³ at the exit cross section. Sokolov [16] indicates that the Lennard-Jones parameters for silver atoms are $\varepsilon = 9.96 \cdot 10^{-13}$ erg and $\sigma = 1.67 \cdot 10^{-8}$ cm. It has been shown [17] that the coalescence constant can be expressed via the formula for the collisional frequency of gas molecules with a correction for the intermolecular forces if the particle size is much less than the apparent mean free path, and this correction is not dependent on the particle size. Sokolov's data [16] give the correction factor as 2.20, with the assumption that these forces have equal effects on the collision probability for particles equal or unequal in size. In case B we also made the same calculation without allowance for the effects of the molecular forces.

We took as the start of condensation the time at which the nucleation rate reached 10^4 per cm³ during the period spent in one stage. The size of the critical nucleus in case A was 6 molecules at the start of condensation, but it then fell and was only 2 throughout much of the process. In cases B and C the critical number was initially 6, falling to 5. The number of stages for the Δt used were, respectively, 28, 49, and 195 in cases A, B, and C.

Figure 5 shows the concentration C (molecules/cm³) for sizes as follows:

curve =	0	1	2	3	4	5	6	7	8
g =	1	2^3	2^5	2^7	2^9	2^{11}	2^{13}	2^{15}	2^{16}

The set of curves for the 2^i allows us to construct a size histogram for any instant.

The production of the aerosol can be divided into six stages: 1) formation and growth of nuclei, 2) formation of nuclei, growth by condensation, and coalescence with fusion, 3) condensation growth and coalescence with fusion, 4) coalescence with fusion, 5) coalescence with fusion of small particles and sintering of large ones, 6) coalescence without fusion and sintering (this does not affect F).

Figure 5 shows that nucleation and condensation growth very soon come to an end (in not more than 200 μsec); then there is only coalescence with fusion, which determines F. The stage size in the coalescence calculations was chosen such that there was not more than 5% reduction in the concentration of particles in any class. The dilution in each stage was allowed for before the coalescence calculation. The calculations were carried up to n = 10, since the flow pattern for higher n was affected by the filter. For cases A and B it was assumed that fusion occurred on collision of particles of any size, while in case C we neglected coalescence for particles in the last group ($2^{18} = 2.65 \cdot 10^5$ atoms in a particle), whether colliding with one another or with smaller
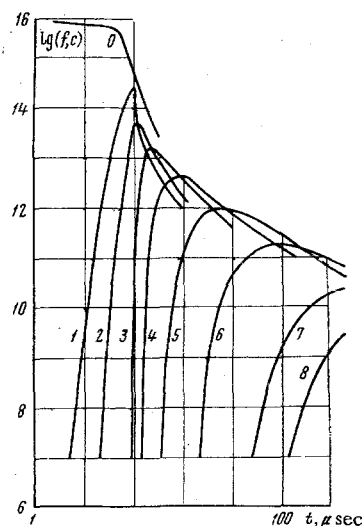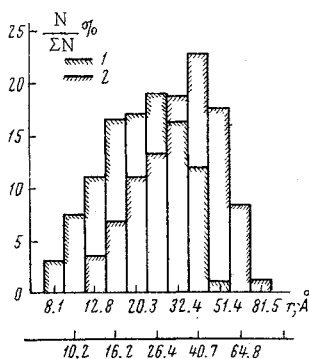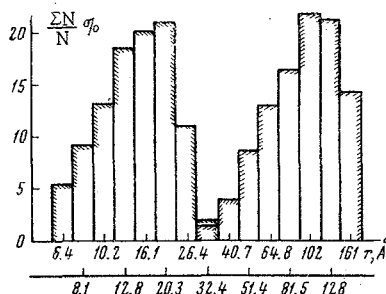

Fig. 5

Fig. 6

Fig. 7

The asymptotic nature of coalescence means that the particle/cm^3 result should be only slightly dependent on the vapor concentration C, and so the particle size should be dependent on C somewhat more strongly than on C$^{1/2}$ (the coalescence constant increases with the particle size in the gas-kinetic state). Firgue 3 shows that the observed results are fitted satisfactorily by F $\propto$ 1/c$^{1/3}$. Evidently the increase in the coalescence constant with size is balanced by the slighter tendency of large particles to fuse or sinter together.

particles. Figure 6 shows calculated size histograms for cases A and C, while Fig. 7 shows the results for case B, in which histogram 1 was derived neglecting the molecular forces while 2 was derived incorporating them.

These aerosols should have given F of 174, 64, and 31.5 m^2/g (case B without the molecular forces gave 92.5 m^2/g). Figure 3 shows that the measured F in the first two cases are 44 and 20 m^2/g, while extrapolation for case C gave about 11 m^2/g.

The mean particle sizes are inversely proportional to F, and the actual values exceed the calculated ones by a factor 4 (case A) or 3 (cases B and C), while the concentrations are wrong by factors of about 70 and 30. The discrepancy in case A is larger because here nucleation starts later and goes on much longer. Much of the discrepancy occurs because coalescence does not cease at n = 10 and can continue in the electrical precipitator; also, some fusion and sintering may occur after deposition. Some part must be due also to the assumptions, especially those concerning coalescence, since that process determines the final result. However, the calculation correctly reflects the general relation of particle size to vapor concentration.

The most important conclusion from calcuation and experiment is that coalescence dominates the formation of the aerosol, so error in the nucleation calculation should not substantially affect the final result.

REFERENCES

1. Ya. I. Frenkel, The Kinetic Theory of Liquids [in Russian], ch. 6, Izd-vo AN SSSR, Moscow, 1945.

2. L. Hearse and H. Pound, Evaporation and Condensation [Russian translation], ch. 2, Izd-vo Metallurgiya, Moscow, 1966.

3. Ya. B. Zel'dovich, "Theory of formation of a new phase: cavitation," ZhETF, **12**, no. 11-12, 525, 1942.

4. R. A. Oriani and B. E. Sundquist, "Emendations to nucleation theory and the homogeneous nucleation of water from the vapor," J. Chem. Phys., vol. 38, no. 9, p. 2082, 1963.

5. S. Reed, "On the early stages of condensation of rare-gas type molecules," J. Chem. Phys., vol. 20, no. 2, p. 208, 1952.

6. J. Mayer and M. Goeppert-Mayer, Statistical Mechanics [Russian translation], Izd-vo inostr. lit., Moscow, 1952.

7. J. E. Kilpatrick and S. Katsura, "Irreducible cluster integrals of hard-sphere gases," J. Chem. Phys., vol. 45, no. 6, p. 1866, 1966.

8. R. Rosinski and J. Snow, "Secondary particulate matter from meteor vapors," J. Meteorol., vol. 18, no. 6, p. 736, 1961.

9. J. Stockham, "Coagulation of millimicron-sized silver aerosol particles," Microscope, vol. 15, no. 3, p. 106, 1966.

10. A. G. Amelin, "Formation of a supersaturated vapor and an aerosol on mixing gases at different temperatures containing vapor," Koll. zh., **10**, no. 3, 169, 1948.

11. W. Higuchi and C. O'Conski, "A test of the Becker-Doring theory of nucleation kinetics," J. Coll. Sci., vol. 15, no. 1, p. 19, 1960.

12. T. Baron and L. Alexander, "Momentum mass and heat transfer in free jets," Chem. Engng. Progr., vol. 47, no. 4, p. 181, 1951.

13. T. Baron, "Reactions in turbulent free jets—the turbulent diffusion flame," Chem. Engng. Progr., vol. 50, no. 2, p. 73, 1954.

14. G. N. Abramovich, Turbulent Free Jets of Liquids and Gases [in Russian], Gosenergoizdat, Moscow-Leningrad, p. 237, 1948.

15. T. Selover, "Properties of nickel fume generated in a plasma jet," AIChE J., vol. 10, no. 1, p. 79, 1964.

16. N. D. Sokolov, "Chemical bond and gas characteristics of interacting systems," Acta Physicochimica URSS, vol. 19, nos. 2-3, 1944.

17. N. A. Fuks and A. G. Sutugin, "The coalescence constant for finely divided aerosols," Koll. zh., **28**, no. 1, 1966.